Synthesis and optical properties of heteroaromatic small molecules and oligomers for light-emitting devices

Hughes, Gregory

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SYNTHESIS AND OPTICAL PROPERTIES OF HETEROAROMATIC SMALL MOLECULES AND Oligomers for Light-Emitting Devices

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UNIVERSITY OF DURHAM

A Thesis submitted for the degree of Doctor of Philosophy at the University of Durham

June 2004
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DECLARATION

The work described in this thesis was carried out in the Department of Chemistry at the University of Durham, between October 2000 and September 2003. All the work was carried out by the author unless otherwise stated, and has not previously been submitted for a degree at this or any other university.
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New π-electron deficient heteroaromatic oligomers 175 and 225 have been synthesised by Suzuki cross-coupling methodology and incorporated into OLEDs. Using 175 as the emissive layer in the device configuration ITO/PEDOT/175/Ca/Al: blue-green light $\lambda_{\text{max}}$ 500 nm, most likely emanating primarily from excimer states is emitted at a high turn-on voltage. Blue electroluminescence, $\lambda_{\text{max}}$ 444 nm, (onset 6.5V) is observed for the device structure ITO/PEDOT/225/Ca/ with no long-wavelength emission from π-aggregates or exciton states.

New 2,5-diphenyl-1,3,4-oxadiazoles and 2-phenyl-5-(2-thienyl)-1,3,4-oxadiazoles heteroaryl-functionalised derivatives have been prepared under standard Sonogashira cross-coupling conditions. UV-Vis absorption and photoluminescence spectra establish that the substitution of a phenyl ring in the 2,5-diphenyl-1,3,4-oxadiazole derivative 232d $\lambda_{\text{max}}$ (PL) 380 nm, by a thienyl ring 239d $\lambda_{\text{max}}$ (PL) 415 nm, leads to a red shift in the lowest energy band. The absorption and emission spectra of 240 $\lambda_{\text{max}}$ (PL) 480 nm, is further red-shifted compared to 239f $\lambda_{\text{max}}$ (PL) 425 nm, which is consistent with the extended π-conjugation of the central bis(ethynylthiophene) unit of 240.
I would like to express my grateful thanks to several people whose assistance and support have been invaluable during my Ph.D, and as a result eased the preparation of this work.

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Finally, the deepest debt of gratitude must lie with my parents; my father who died during the final year of this study, and my mother who continues to be “there” when ever needed.
The intellect of man is forced to choose
Perfection, of the life, or of the work

The Choice
W. B. Yeats
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
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<tbody>
<tr>
<td>Alq3</td>
<td>tris-(8-hydroxyquinoline)aluminium 2</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammetry</td>
</tr>
<tr>
<td>DCM</td>
<td>Dichloromethane</td>
</tr>
<tr>
<td>ECHB</td>
<td>Electron-conducting / hole-blocking</td>
</tr>
<tr>
<td>EI</td>
<td>Electron Impact</td>
</tr>
<tr>
<td>EL</td>
<td>Electroluminescence</td>
</tr>
<tr>
<td>EQE</td>
<td>External quantum efficiency</td>
</tr>
<tr>
<td>ES</td>
<td>Electrospray</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium tin oxide</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>MEH-PPV</td>
<td>poly[2-(2'-ethylhexyloxy)-5-methoxy-1,4-phenylenevinylene] 11</td>
</tr>
<tr>
<td>mp</td>
<td>Melting point</td>
</tr>
<tr>
<td>NEt3</td>
<td>Triethylamine</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>OLEDs</td>
<td>Organic light-emitting devices</td>
</tr>
<tr>
<td>PBD</td>
<td>5-(4-biphenyl)-2-(4-tert-butylphenyl)-1,3,4-oxadiazole 25</td>
</tr>
<tr>
<td>PEDOT</td>
<td>poly(ethylenedioxy-thiophene)</td>
</tr>
<tr>
<td>PET</td>
<td>poly(ethyleneterphthalate)</td>
</tr>
<tr>
<td>PL</td>
<td>Photoluminescence</td>
</tr>
<tr>
<td>PLQY</td>
<td>Photoluminescence quantum yield</td>
</tr>
<tr>
<td>PPV</td>
<td>poly(p-phenylenevinylene) 8</td>
</tr>
<tr>
<td>PPY</td>
<td>poly(pyridine-2,5-diyl) 67</td>
</tr>
<tr>
<td>PPym</td>
<td>poly(pyrimidine-2,5-diyl) 86</td>
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<tr>
<td>PVK</td>
<td>poly(vinylcarbazole) 32</td>
</tr>
<tr>
<td>TIPD</td>
<td>2,2',2''-(1,3,5-benzenetriyl)tris(1-phenyl)-1H-benzimidazole 33</td>
</tr>
<tr>
<td>Tg</td>
<td>Glass transition temperature</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>TLC</td>
<td>Thin layer chromatography</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>Vis</td>
<td>Visible</td>
</tr>
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</table>
1 MATERIALS FOR ORGANIC LIGHT-EMITTING DEVICES

Since the serendipitous discovery of polymer organic light-emitting devices (OLEDs) in 1989 by Ph.D. student Jeremy Burroughes, in Richard Friend’s laboratory at Cambridge University OLEDs have attracted considerable interest and are now viewed as an important competitor with liquid crystal displays (LCDs) for a wide variety of display applications. Current research focuses on the use of small molecule and polymer materials to make organic electroluminescent (EL) displays with both passive and active matrix technologies.¹

1.1 ORGANIC ELECTROLUMINESCENCE

Organic electroluminescence (EL), or the generation of light by the electrical excitation of an organic molecule, was first reported in 1963 by applying *ca.* 400 V across single crystals of anthracene immersed in an electrochemical cell.² The cell contained an electrolytic solution of negatively charged anthracene ions, prepared from a solution of anthracene and sodium in THF next to the cathode and a solution of positively charged anthracene ions, prepared from a solution of anthracene and aluminium trichloride in nitromethane, next to the anode. The two liquid electrolytic solutions responsible for charge transport were physically separated from each other by the solid anthracene crystal. EL was witnessed in the part of the anthracene crystal next to the hole-injecting anode, which suggests an imbalance of charge-carrier injection and transport.³ In 1982 Vincett *et al.* reported the next development in organic EL using organic thin films. Approximately 0.6 μm vacuum-deposited anthracene films were prepared and when subjected to lower drive voltages, *e.g.* 30 V exhibited strong blue EL.⁴ However, the quantum efficiencies (defined as photons emitted/electrons injected) and the lifetimes of these devices were considerably lower than those based on inorganic systems which continued to be the focus of attention. It was the seminal work of Tang and VanSlyke with bilayers of low molecular weight organic molecules, reported in 1987, which initiated worldwide interest in the development of organic light-emitting devices (OLEDs).⁵ The device structure was conceptually simple, comprising evaporated thin layers of organic compounds, which were chosen for their ability to act as fluorophores and to transport charge carriers, sandwiched between two electrodes one of which was transparent. The device was fabricated by vacuum deposition, which ensured that both layers were smooth and continuous. In addition, the two-layer structure minimises the probability of overlapping pinholes within
the thin-film. Green EL was observed with devices comprising the bis(triarylamine) 1 as the hole-transporting layer and tris(8-hydroxyquinoline)aluminium (Alq3) 2 as the emitter and electron-transporting layer in the configuration ITO/1/2/Mg:Ag. A brightness of > 1000 cd m\(^{-2}\) at an operating voltage of < 10 V was achieved. Devices with photon/electron quantum efficiencies of 1% could now be realised. This discovery significantly enhanced the prospects for producing large area, inexpensive, flat panel displays that could rival cathode ray tubes (CRT).\(^6\)

![Scheme 1: Molecular structures of diamine 1 and Alq3 2 used by Tang and VanSlyke in the first two-layer sublimed molecular film device.\(^5\)](image)

The next fundamental breakthrough was reported by Friend \textit{et al.} in 1990, who demonstrated that the highly fluorescent conjugated polymer poly(\textit{p}-phenylenevinylene) (PPV) 8 could serve as the active material emitting yellow-green light in a single-layer OLED of configuration ITO/PPV/Al.\(^7\) The introduction of substituents into the PPV skeleton provides derivatives which are soluble in organic solvents and induces a lower glass transition temperature (\(T_g\)) compared to that of PPV. This removes the necessity of carrying out chemistry and thermal processing of the substrate.\(^3\) In 1991 Braun and Heeger reported a red-orange emitting OLED based on poly[2-methoxy-5-(2-ethylhexyloxy)-\textit{p}-phenylenevinylene] (MEH-PPV) 11 in the configuration ITO/MEH-PPV/Ca with an external quantum efficiency of 1%.\(^8\) These discoveries have led to intense worldwide interest in new materials for incorporation into OLEDs for practical applications, notably full-colour flat-panel displays. The world market for display devices using OLEDs is expected to grow to > $2500m by 2007.\(^9\) The study of organic electroluminescence is a multi-disciplinary field, which crosses the traditional boundaries of synthetic chemistry, applied and theoretical physics, materials science and device engineering.
There are three principle categories of organic EL material: small molecules, oligomers and light-emitting polymers. Each classification should exhibit a high $T_g$ in order to form a stable amorphous glassy state thereby inhibiting crystallisation during the lifetime of the device. Small molecules and oligomers must be capable of being deposited as a pure, uniform, thin solid film by vapour deposition under high vacuum. They are of considerable interest to organic material scientists due to their monodisperse character, flexibility of synthesis and good processability as thin solid films. An additional advantage is the improved properties observed due to the propensity of certain classes of these organic materials to self-organise in a supramolecular structure on the desired substrate surface. A distinct disadvantage of small molecules and to lesser extent oligomers is the tendency to form defects and traps at crystal grain boundaries over time. Polymers are made up of a large number of building blocks linked in a repetitive fashion (macromolecular structure), oligomers constitute their lower homologs, since they will contain only one or a few of these units. Small molecules and oligomers have to be deposited by sublimation or vapour deposition under high vacuum. This is an expensive process consequently not ideally suited for mass production of display technologies. In contrast, uniform thin films of conjugated light-emitting polymers can be deposited from dilute organic solutions by spin-coating. A further advantage is the reproducibility of polymer production. Without the incorporation of solubising substituents into the polymer framework the alternating configuration of single and double bonds results in a rigid, linear, and planar molecular confirmation. This results in very high melting points and severely limited solubility in organic solvents.

For this research project we chose substituted small molecules and oligomers because they are ideally suited to small-scale laboratory synthesis by Suzuki coupling reactions. Our primary objective was the preparation of glassy materials allowing formation of amorphous solid thin films in the fabrication of efficient OLEDs.

1.2 SYNTHESIS OF POLY($p$-PHENYLENEVINYLENE) AND ITS DERIVATIVES

PPV 8 is a bright yellow, fluorescent polymer. Its emission maxima at $\lambda\, 551$ nm (2.25 eV) and 520 nm (2.4 eV) are in the yellow-green region of the visible spectrum. PPV is a robust, intractable, insoluble polymer when produced directly from its monomer starting material. However, the physical and processability limitations of PPV have been overcome.
by the introduction of a solution processible sulfonium precursor route devised by Wessling and Zimmerman.\textsuperscript{12,13}

Treatment of 1,4-bis(dichloromethyl)benzene 3 with tetrahydrothiophene affords the bis-sulfonium salt 4. Polymerisation of a methanolic solution of monomer 4 is induced by the addition of slightly less than 1 mol equivalent of aqueous sodium hydroxide at 0-5 °C. It has been suggested that the \textit{p}-quinodimethane intermediate 5 undergoes radical polymerisation, although anionic propagation cannot be completely excluded. The almost completely colourless solution of the precursor polymer 6 is dialyzed against distilled water to remove impurities with low molecular weight. Treatment with refluxing methanol gives the neutral polymer 7 which by gel-permeation chromatography shows a number average molar mass \( M_n \) of >100,000 gmol\textsuperscript{-1}. The precursor polymer 6 is converted into PPV 8 by thermal evaporation. Under these conditions by-products of the elimination (tetrahydrothiophene and hydrogen chloride) escape easily.\textsuperscript{11}

Scheme 2: Synthesis of PPV 8: i) tetrahydrothiophene, MeOH, 65 °C; ii) NaOH, MeOH/H\textsubscript{2}O or Bu\textsubscript{4}NOH, MeOH, 0°C; iii) neutralisation (HCl); iv) dialysis (water); v) MeOH, 50 °C; vi) 220 °C, HCl (g)/Ar, 22 h; vii) 180-300 °C, vacuum, 12 h.
Alternative methods for the preparation of PPV suitable for OLEDs involve chemical vapour deposition (CVD)\textsuperscript{14} and a ring-opening metathesis polymerisation (ROMP).\textsuperscript{15,16} The materials produced by these routes may differ from PPV prepared by the Wessling route in molar mass, molar mass distribution, film quality and resulting device efficiency.\textsuperscript{11}

Solution processible analogues of PPV allow direct deposition as components in OLEDs. This eliminates the need for thermal elimination treatment of the soluble precursor polymer 6, which is one of the disadvantages of the Wessling sulfonium precursor route. However, solution processible polymers tend to have lower glass transition temperatures ($T_g$). Dialkoxy-substituted derivatives of PPV such as poly[2-((2'-ethylhexyloxy)-5-methoxy-1,4-phenylenevinylene] MEH-PPV 11 are readily soluble in solvents such as chloroform, THF and xylene. The alkoxy side chains have a beneficial effect on the polymer's fluorescence and EL quantum yields as demonstrated by a red shifted emission maximum of 590 nm (2.1 eV) (i.e red-orange) for MEH-PPV compared to 551 nm (2.25 eV) and 520 nm (2.4 eV) for PPV.

![Scheme 3: Synthesis of MEH PPV 11: i) 3-(bromomethyl)heptane, KOH, EtOH, reflux, 16 h; ii) HCHO, concd, HCl, dioxane, 20 °C, 18 h, reflux, 4 h; iii) KOTBu, THF, 20 °C, 24 h.](image)

The importance of PPV as a material for OLEDs is reflected in the number of analogous compounds that have been synthesized and fabricated into devices since its discovery. Examples include cyano-dialkoxyPPV 12,\textsuperscript{17,18} dimethyloctylsilyl-PPV 13,\textsuperscript{19} and 2-phenylated and 2,3-diphenylated PPVs 14 with solubilizing side chains.\textsuperscript{20}
Scheme 4: Examples of soluble, dialkoxy-substituted PPV derivatives.

This group of polymers showed very good photoluminescence (PL) efficiencies up to 65% in the solid state with blue shifted emission, PL $\lambda_{\text{max}}$ 490 nm, for a fully conjugated PPV system. PPV and its derivatives still command substantial research showing huge promise as materials for commercial display technologies. It is, however, difficult to achieve blue light with this class of conjugated polymer and, in addition, there are fears regarding the susceptibility of the vinyl linkages to oxidative degradation.

1.3 Simple Organic Electroluminescent Devices Based on PPV

The device pioneered by Tang and VanSlyke\(^5\) in 1987 comprising an aromatic diamine and Alq$_3$ sandwiched between two electrodes provided the foundation for EL devices using PPV as the emissive layer. Organic EL devices are made up of a sandwich-like structure. PPV as the light-emitting polymer is spin-coated onto an indium-tin oxide (ITO) glass or polymer substrate that is semitransparent, then a low work function metal cathode such as Al, Ca or Mg is positioned directly onto the polymer surface. Such a device structure is denoted as ITO/polymer/metal. Poly(ethyleneterphthalate) (PET) is often used as the polymer substrate.
Figure 1: a) Schematic drawing of a single-layer electroluminescent device. b) Schematic energy level diagram of a generalised monolayer OLED (Redrawn from reference 3).

Light emission is a consequence of radiative decay of excitons generated by the combination of electrons and holes. Organic EL devices operate by the injection of electrons and holes
from positive and negative electrodes, respectively. The mechanism for light emission can be summarised as follows: electrons are injected into the LUMO forming radical anions and holes are injected into the HOMO forming radical cations of the EL polymer material. Charge migration along the polymer chain occurs under the influence of an applied electric field. When a radical anion and radical cation combine on a single conjugated polymer segment, singlet and triplet states are formed of which the singlet states can emit light.\(^\text{11}\) The external quantum efficiency (EQE), \(\eta_{\text{ext}}\), of monolayer OLEDs, \(i.e.\) the number of photons actually seen by the observer, is related to the number of photons emitted per electrons injected. In the case of PPV this value is low 0.05%.\(^\text{7}\) The observed EQE, \(\eta_{\text{ext}}\), is much lower than the internal efficiency, \(\eta_{\text{int}}\), as given by the following relationship.\(^\text{3}\)

\[
\eta_{\text{ext}} = \eta_{\text{int}} / 2n^2
\]

\text{Equation 1: External quantum efficiency (EQE), } \eta_{\text{ext}}, \text{ where } n \text{ is the refractive index of the organic material.}

1.3.1 Additional Charge Transport Layers

Since most common organic semiconductors are predominately hole transporting (p-dopable), electrons and holes usually combine in the vicinity of the cathode. As a consequence, the lifetimes and efficiencies of the corresponding diodes are limited.\(^\text{21}\) The inclusion of an additional organic layer between the emissive material and the cathode metal can promote the passage of electrons through the EL material and, at the same time, inhibit the passage of holes. Such a layer is called an electron-conducting/hole-blocking (ECHB) layer. The ECHB material enhances the flow of electrons but resists oxidation. Electrons and holes accumulate near the PPV/ECHB interface. Charge recombination and photon generation occurs within the PPV segment and away from the cathode.\(^\text{11}\) The overall effect of such charge transport layers is to reduce the operating voltage, increase the quantum efficiency and the device stability. One of the earliest examples of an ECHB material is Alq\(_3\)\(^\text{2}\).

Electron-transport materials need to have a high electron affinity, \(i.e.\) be electron deficient. The most widely applied electron-transport materials are \(\pi\)-electron-deficient heterocycleics carrying imine nitrogens in the aromatic ring. The polarisation of the \(\text{C}^\delta^+\text{-N}^\delta^-\) bond due to the electron-withdrawing nitrogen atom lowers the energy of the LUMO and HOMO levels. This increases the electron affinity and promotes electron injection from the cathode.\(^\text{3}\)
Figure 2: a) Schematic drawing of a bilayer OLED with an extra ECHB layer adjacent to the metal cathode. b) Schematic energy level diagram of a generalised bilayer OLED. Illustrating the accumulation of charge carriers at the interface of the hole-transport and electron-transport layers (Redrawn from reference 3).
Materials for Organic Light-Emitting Devices

π-Electron-deficient heterocycles have been widely used as ECHB layers, such as 1,3,4-oxadiazoles, 1,3-oxazoles, 1,2,4-triazoles, pyridines, pyrimidines, pyrazines, 1,3,4-triazines, quinolines, quinoxalines and pyrazoloquinoline derivatives. The remainder of this chapter will review the application of these classes of low-molecular-weight and polymeric materials as ECHB layers as well as emissive materials in EL devices.

![Molecular structures of π-electron deficient heterocyclics with imine nitrogen atoms which have been incorporated into low molecular weight compounds and polymeric materials for use as ECHB materials.](image)

Scheme 5: Molecular structures of π-electron deficient heterocyclics with imine nitrogen atoms which have been incorporated into low molecular weight compounds and polymeric materials for use as ECHB materials.

1.4 1,3,4-OXADIAZOLEs

2,5-Diaryl-substituted 1,3,4-oxadiazoles have received considerable attention as electron transporting materials in EL devices due to their electron-deficient nature and thermal stability. The majority of investigations have used 5-(4-biphenyl)-2-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD) 25 as the electron transporting material in sublimed thin films or spin-coated polymer blends.11

![Molecular structures of 5-(4-biphenyl)-2-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD) 25.](image)

Scheme 6: Molecular structures of 5-(4-biphenyl)-2-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD) 25.

There are two common methods for the synthesis of 2,5-diaryl-1,3,4-oxadiazoles 26. The first involves a ring closure dehydration reaction of bishydrazides 27 using reagents such as POCl₃.22 The second, which is considered a more efficient method, is the reaction of tetrazoles 28 with acid chlorides 29.23
1.4.1 Low Molecular Weight Oxadiazoles

Brown et al\textsuperscript{24} demonstrated that PBD was a suitable ECHB material by blending the material in a film-forming poly(methylmethacrylate) on top of a PPV layer. An 8-10 fold increase in the EL efficiency was achieved compared with a simple EL PPV device. Zhang et al dispersed PBD into an active semiconducting polymer: dramatic increases in quantum efficiencies were reported by doping the soluble green emitter poly(2-cholestanoxy-5-thexyldimethylsilyl-1,4-phenylenevinylene) (CS-PPV) \textsuperscript{30}.\textsuperscript{25}

Vaeth and Tang\textsuperscript{26} reported the fabrication of polymer LEDs based on the emission from the phosphorescent molecule tris(2-phenylpyridine)iridium [Ir(ppy)\textsubscript{3}] \textsuperscript{31} doped into a poly(vinylcarbazole) (PVK) \textsuperscript{32} host. To completely confine the emission zone to the Ir(ppy)\textsubscript{3}:PVK layer a trilayered device was assembled. By replacing 10% of the PVK with PBD \textsuperscript{25} and including the electron transporting materials 2,2',2''-(1,3,5-benzenetriyl)tris(1-phenyl)-1H-benzimidazole (TPBI) \textsuperscript{33} and Al\textsubscript{q3} \textsuperscript{2} an exceptionally high external quantum
efficiency of 8.5% was observed. The device configuration was as follows ITO/Ir(ppy)$_3$:PVK$_{0.9}$PBD$_{0.1}$/TPBII/Alq$_3$/Mg$_{0.9}$Ag$_{0.1}$. However, further increases in PBD percentage levels into the polymer layer were found to reduce device performance.

![Molecular structures of tris(2-phenylpyridine) iridium (Ir(ppy)$_3$) 31, poly(vinyl carbazole) (PVK) 32 and 2,2',2''-(1,3,5-benzenetriyl)tris(1-phenyl)-1H-benzimidazole (TPBI) 33.]

Bipolar materials with electron accepting and donating capabilities provide a real alternative to bilayer devices involving the use of ECHB layers. Chien et al$^{27}$ reported 9,9'-spirobifluorene-bridged bipolar systems containing 1,3,4-oxadiazole-conjugated oligoaryl and triarylamine moieties. In this bipolar molecule 34 the 1,3,4-oxadiazole-conjugated oligoaryl system acts as the electron acceptor, while the triarylamine moiety acts as the donor counterpart. Guan et al$^{28}$ fabricated a highly stable, high performance blue electroluminescent device. Electron transporting 1,3,4-oxadiazole and hole transporting carbazole moieties were combined to create 2-(4-biphenylyl)-5-(4-carbazole-9-yl)phenyl-1,3,4-oxadiazole 35. A three layered device with a configuration of ITO/TPD/CzOxa/Alq$_3$/Mg$_{0.9}$Ag$_{0.1}$/Ag exhibited blue emission at $\lambda_{\text{max}}$ 470 nm with a maximum luminance of 26200 cd m$^{-2}$ at a drive voltage of 15 V and a maximum luminous efficiency of 2.25 lm W$^{-1}$. 

![Molecular structures of 9,9'-spirobifluorene-bridge$^{27}$ 34 and 2-(4-biphenylyl)-5-(4-carbazole-9-yl)phenyl-1,3,4-oxadiazole$^{28}$ 35 bipolar materials.]

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Within our group C. Wang has synthesised a series of 1,3,4-oxadiazole-pyridine and 1,3,4-oxadiazole-pyrimidine hybrids. In addition, vinylene and phenylene analogues were also prepared and their ECHB properties investigated.\textsuperscript{29,30}

![Scheme 11: Series of 1,3,4-oxadiazole hybrids synthesised by Wang et al.\textsuperscript{29,30}]

Initial studies focused on the fabrication and comparison of four types of devices: a single-layer LED using MEH-PPV 11 as the emissive material, ITO as the anode, and aluminium as the cathode; and the three bilayer LEDs with the structure ITO/MEH-PPV/PDXDP/Al where PDXDP layer was \textit{36a}, \textit{36b}, or \textit{36d}. The three bilayer structures yielded almost identical current versus electric field data, suggesting similar electrical transport processes in the three devices. The turn-on electric field for EL was lower for the bilayer structures than for the single layer counterpart. The lowest value was observed for the LED with \textit{36d}. External quantum efficiencies (EQE) were as follows: for the MEH-PPV device 0.0059\%, for the bilayer device using \textit{36a} 0.011\%, for the \textit{36b} containing structure 0.042\%, and 0.24\% for the LED incorporating \textit{36d}. The EQE of the MEH-PPV single layer device was approximately doubled by using \textit{36a}, increased by 6 times with \textit{36b}, and increased by about 30 times with \textit{36d}. EL emission for the bilayer devices was characteristic of MEH-PPV emission and independent of the PDXDP electron transport layer, indicating that all light originates from the MEH-PPV layer.
Figure 3: Light output versus current density for the single-layer and bilayer LED devices of 1,3,4-oxadiazole hybrids prepared by Wang and co-workers. 29

The improved electron transporting performance of 36d over the two analogues 36a and 36b was due to increased electron deficiency arising from the more electronegative nitrogen atom in the pyridine moiety, and secondly that electron mobility is higher in crystalline 36d than the other two materials. 29 The X-ray crystal structure of 36d was obtained.

Figure 4: X-ray molecular structures of 36a (top) and 36d (bottom), showing the disorder of the tert-butyl groups. Primed atoms are generated by inversion centres. The pyridine N atom in 36d is disordered between positions 4, 4', 5, and 5'. 29

Continuing investigations in our laboratories demonstrated that OXD-7 31 36c and its para isomer 36b, had different electron-injecting abilities in bilayer LEDs using MEH-PPV as the emissive material. 32 In view of this observation and the success of 36d, geometrical isomers
36e-g were synthesised. The success of 36d was attributed to its increased electron deficiency compared to its vinylene and phenylene counterparts. Therefore 36h was prepared as an analogue of 36d with an additional nitrogen atom introduced into the central conjoining ring.

Devices were constructed using ITO as the anode, rubrene doped (20% by weight) MEH-PPV [MEH(Ru)] as the emissive material and Al as the cathode. A single layer rubrene doped MEH-PPV device was used as a reference. Bilayer devices were of the general configuration ITO/MEH(Ru)/compound 36/Al. In every case the inclusion of a 1,3,4-oxadiazole containing material as an ECHB layer increased electron injection. This was clearly reflected in the EQEs, which showed increases of 5 to 20 times greater than that of the rubrene doped reference. The EQE for reference ITO/MEH(Ru)/Al device was 0.07%. For 36d and 36e an EQE of 0.14% was achieved for both respective devices. The more electron deficient 36h achieved a lower figure of 0.12% which is comparable with that of 0.11% for 36b.

Further increases in EQEs for this series of materials have been achieved by optimising both the MEH(Ru) and ECHB layers. An EQE of 0.7% was achieved by ITO/MEH(Ru)(90 nm)/36d (55 nm)/Al structure.

Figure 5: A photograph of a bilayer LED ITO/MEH(Ru)(90 nm)/36d (55 nm)/Al working at a current density of ca. 100 mAcm⁻² under forward bias, without encapsulation. The peak external quantum efficiency of the LED was ca. 0.7% and the brightness was ca. 4,000 cd m⁻².³⁰

As with previous observations, EL of the bilayer LEDs had almost identical emission profiles as the single layer device, indicating that charge-combination and light emission took place exclusively in the MEH(Ru) layer.³⁰
Although such low molecular weight 1,3,4-oxadiazole materials can be easily prepared and purified, their amorphous films can suffer from a lack of stability since crystallisation occurs with time or increased device operation temperature. 1,3,4-Oxadiazole polymers (Section 1.4.2) can be prepared conveniently but effective purification can be difficult. In contrast, dendrimers are highly-branched well-defined compounds and, like polymers, they have the advantage of forming stable amorphous glasses.\[^{33}\]

![Scheme 12: Molecular structures of four-armed conjugated dendrimers containing 1,3,4-oxadiazole moieties.\[^{34}\]](image)

Cha and co workers\[^{34}\] successfully synthesised two, four-armed conjugated dendritic structures with a 9,10-bis(phenylethynyl)anthracene core and 1,3,4-oxadiazole rings incorporating peripheral alkyl tail groups. It was found that \(37b\) has a high glass transition temperature \(T_g: 211 \, ^\circ\text{C}\) and exhibits good solubility in organic solvents, which resulted in good quality thin films by spin coating. In contrast, its tert-butyl counterpart \(37a\) has poor solubility which gave inferior quality thin films. An EL device structure of ITO/PEDOT-PSS/\(37b\)/Li:Al emitted only red light with an EQE of 0.02%. The (phenylethynyl)anthracene core is the only red light emitting chromophore in the structure which indicated that the outer diphenyloxadiazole moieties act only as electron transporters.

The thermal and EL properties of tetraphenylmethane-based compounds has remained largely unexplored. Tetraphenylmethane is a useful structural unit for forming glassy films that can
be readily incorporated into light-emitting or charge-transporting materials by varying the peripheral substituents. Yeh et al.\textsuperscript{35} produced a series of compounds with this core structural unit, e.g. the amorphous bipolar blue fluorescent 38, which has a high $T_g$ of 150 °C.

![Chemical Structure](image)

Scheme 13: Amorphous bipolar blue fluorescent 38.\textsuperscript{35}

A single layer device of the structure ITO/38/Ca/Ag showed blue luminescence at low applied voltage that turned to bluish-white at elevated applied voltages. The device had a photometric efficiency of $\sim 0.7$ cd A at a current density of $\sim 10$ mA cm$^{-2}$. The device brightness reached a maximum of 1690 cd cm$^{-2}$ under a driving voltage of $\sim 14$ V. Since 38 functions as an electron transporting material, doping an emissive layer host material may provide a more efficient device. Doping of PVK with 38 in a 3:1 weight ratio for the device configuration ITO/38:PVK/Ca/Ag resulted in an enhanced photometric efficiency of 0.8 cd/A with a current density of less than 8 mA cm$^{-2}$. This demonstrated that the 4-fold symmetrical tetraphenylmethane is an effective skeleton for improving thermal properties, which are high melting temperature and stable glass phase.

Liang et al.\textsuperscript{36} reported the successful synthesis of the blue emitting hydroxyphenyloxadiazole lithium complex 39. To investigate its EL properties, OLEDs based on 39 as the emitting and electron injection/transport layers were constructed. 39 as the emitting layer displayed blue EL emission centred at $\lambda_{\text{max}}$ 468 nm for the configuration ITO/TPD/39/Al with a maximum
luminance of 2900 cd m$^{-2}$. A current efficiency of 3.9 cd A$^{-1}$, and power efficiency of 1.1 lm W$^{-1}$ was obtained. TPD was chosen for its hole-transporting qualities. The efficiency of an ITO/NPB/Alq$_3$/Al device increased considerably when 39 was inserted between Alq$_3$ and aluminium. The performance of 39 as an interface material is directly related to optimum thickness of the lithium complex. The device specification was as follows, ITO/NPB(40 nm)/Alq$_3$(60 nm)/ 39 (x nm)/Al where x = 2 nm gave the best performance with a maximum luminance of 18389 cd m$^{-2}$ at a turn-on voltage of 3.0 V. Furthermore, this device exhibited high current and power efficiencies with values of 5.21 cd A$^{-1}$ and 2.4 lm W$^{-1}$, respectively. The impressive EL efficiency may be attributed to i) the oxadiazole segment in 39 has excellent electron-transporting ability and ii) the lithium salt is favourable for electron injection.

![Scheme 14: Hydroxyphenyloxadiazole lithium complex 39.](image)

### 1.4.2 Polymeric Oxadiazoles

The synthesis of $\pi$-conjugated polyoxadiazoles has been achieved by direct analogy with their low-molecular-weight counterparts, that is by ring closure of polyhydrazides with reagents such as POCl$_3$ and polyphosphoric acid or, alternatively, reaction of bis(tetrazole)s with bis(acid chloride)s. In addition, poly(oxadiazole ether)s can be prepared by activated nucleophilic substitution polycondensation of oxadiazole difluorides with aromatic diols. The electron deficient oxadiazole ring is incorporated directly into the main chain of the polyaryl ether or by attaching it as a pendant group to the polymeric aryl backbone.

Zheng and co-workers$^{37}$ reported a series of alternating copolymers containing 1,3,4-oxadiazole groups in the conjugated chain, together with flexible spacer units, with the objective of raising electron-transport ability. The effects of chromophore substituents on the optical properties of the copolymers were investigated.
Blue-green light was observed for the copolymers as single-layer devices relative to that of the reference copolymer 40. The general device configuration was ITO/copolymer 40a-c/Ca/Al; EL maxima for devices based on 41a, 41b, 41c and the reference 40 were $\lambda_{\text{max}}$ 494, 509, 480 and 477 nm, respectively. EL for 41a and 41b were comparable with their corresponding PL $\lambda_{\text{max}}$ 475 and 458 nm, which indicated that EL and PL originate from the same excited state. However, EL for 41c was significantly red-shifted compared with its PL $\lambda_{\text{max}}$ 455 nm. The copolymers not only were used as blue-green EL materials, but also were effective as ECHB layers in polymer LEDs. For the double-layer OLED ITO/PPV/41c/Ca/Al no emission was observed from 41c indicating that the PPV serves as the emissive layer and 41c as the electron transport layer. The brightness and efficiency of its single-layer counterpart ITO/PPV/ Ca/Al was improved by more than a factor of $10^3$ with the introduction of 41c. The double-layer device had a brightness of 2400 cd m$^{-2}$ at 6.8 V with an EQE of 0.094%. This work demonstrates that the oxadiazole moiety in 41c moves the recombination zone away from the cathode interface and increases the probability of hole/electron recombination in the PPV emitting layer.

Bipolar polymeric materials have attracted great interest as researchers attempt to harness both hole and electron transporting properties. Zhang et al. published the synthesis of two bipolar transporting luminescent polymers containing hole-deficient triphenylamine and electron-deficient 1,3,4-oxadiazole units in the main chain.
UV-vis absorption spectra of thin films of the two polymers showed that the main absorption peak is red-shifted from $\lambda_{\text{max}}$ 470 to 495 nm due to the inclusion of the electron-deficient oxadiazole ring. A similar red-shift was also observed in the PL spectra, from $\lambda_{\text{max}}$ 545 to 555 nm. The introduction of the oxadiazole unit increases the conjugated length of the polymer, which results in the red shift. Devices of the configuration ITO/PEDOT/polymer 42 or 43/CsF/Al gave blue EL. The polymer with oxadiazole units 42 has a maximum brightness of 3600 cd m$^{-2}$ and a maximum EL efficiency of 0.65 cd A$^{-1}$ equal to an EQE of 0.3%. In contrast, the performance of polymer 43 has a significantly reduced maximum brightness of 248 cd m$^{-2}$ and lower EL efficiency of 0.042 cd A$^{-1}$. Devices constructed using 42 were 15 times brighter and 15 times more efficient than the corresponding polymer without oxadiazole moieties.

Another example of a bipolar polymeric material is 44 prepared by Meng et al.$^{39}$ 44 emits greenish-blue light at 475 nm. A preliminary device of the configuration ITO/44/Al was constructed and emitted blue light (observable in a dark room) at 8 V with a current density of 1.14 cd m$^{-2}$. Initial findings suggest that 44 could be a potential novel active material as it has a similar LUMO but higher HOMO energy level when compared to MEH-PPV 11. This implies that it has more balanced charge injection, which ultimately enhances EL EQEs.
Scheme 17: Polymeric structure of PCOPO 44.39

$p$-OXD 45 was used a ECHB material in PPV based devices and its electron–transporting capabilities evaluated against triazine ($p$-TRZ) and quinoxaline ($p$-QUX) counterparts. 40

Scheme 18: Structure of $p$-OXD 45 synthesised from the corresponding difluoroheterocyclic monomers with hexafluorobisphenol via a nucleophilic displacement reaction of fluorine atoms by intermediate phenolate anion. 40

Polymer 45 forms stable glasses with a $T_g$ of 220 °C measured by DSC; it also has high thermal stability with a decomposition temperature of 415 °C. Optical data showed no absorption in the visible region of the spectrum [$\lambda_{\text{max}}$ (abs) 347 nm] and a fluorescence $\lambda_{\text{max}}$ (emission) 433 nm. Polymer 45 is readily soluble in common organic solvents and possesses excellent film forming properties.

A bilayer device of configuration ITO/PPV/45/Al demonstrated that 45 possesses hole-blocking capabilities showing increased operational performance in comparison to the reference single layer device. A maximum brightness of 55 cd m$^{-2}$ at a current density of 155 mA cm$^{-2}$ was recorded at a onset voltage of 7.0 V, compared to the reference which gave a maximum brightness of 2 cd m$^{-2}$ at a current density of 436 mA cm$^{-2}$, although a lower onset voltage of 6.0 V was achieved.
Peng et al.\textsuperscript{41} reported polymers containing both electron-accepting oxadiazole and hole-accepting alkoxy-phenylenevinylene segments, as an alternative to bilayer/multilayer devices. Fabrication of multilayer devices is difficult, and stability can be a problem.

![Scheme 19: Structures of polymers 46, 47 and 48.](image)

UV-Vis absorption spectra of 47 and 48 in THF solution are very similar to 46, although the structures are very different with $\lambda_{\text{max}}$ ca. 450 nm, showing no observable effect of the oxadiazole ring. Compounds 47 and 48 have similar PL in THF solution with emission peaks at 505 nm and a shoulder around 540 nm, similar to that of 46. As solid films 47 and 48 have significantly different PL, 48 has emissions red-shifted by 50 nm due to aggregation. 47, however, showed a smaller red shift of 35 nm.

As single-layer devices using ITO and Al as the contacts, 47 and 48 showed good light-emitting device characteristics with enhanced brightness compared to 46. These results support the hypothesis that the oxadiazole units in the main chain improve electron acceptor ability and electron mobility in the device structure. The carbazole substituent in 48 had little effect, suggesting that the polymer backbone itself has sufficient hole-transporting ability.
Figure 6: Current-light-voltage characteristics for single layer devices of polymers 47 and 48. The insets show light vs current for the two respective devices.\textsuperscript{41}

PBD 25 has been extensively used as a small-molecule electron-transport material due to its known capabilities of dramatically improving the EQE in OLEDs. In our group Wang et al.\textsuperscript{42} prepared the alkoxyPBD 49 derivative and its dipyridyl analogue 50 using Suzuki coupling methodology. These were the first polymeric materials containing PBD as the repeating unit. The alkoxy substituents impart good solubility in organic solvents.

![Polymer structures](image)

**Scheme 20:** Polymeric alkoxyPBD 49 and its dipyridyl analogue 50 prepared by Wang et al.\textsuperscript{42}

Thermal gravimetric analysis established that polymers 49 and 50 are highly stable up to 370 °C and 334 °C, respectively. The two polymers are also amorphous with $T_g$ values of 196 °C for 49 and 113 °C for 50. PL spectra of films spun from chloroform solution showed strong blue PL with $\lambda_{\text{max}}$ 444 nm. Polymer 50 has a PL quantum yield (PLQY) of 27% measured as a thin film using an integrated sphere. The dipyridyl analogue displayed blue PL with $\lambda_{\text{max}}$ 475 nm, which is significantly red-shifted compared to the emission of 49. Attempts to measure the PLQY for 50 were hampered by film degradation; however, the authors estimate the value to be 6% with a large percentage error. A possible explanation for this degeneration of the film could be cleavage of the polymer chain, leading to instability of the sample and low PLQY. Device studies were not pursued further with 50 since questions had been raised.
over the material’s stability. Polymer 49 was investigated as an electron-transporting polymer in bilayer LEDs with MEH-PPV as the emissive layer onto which 49 was spun. For the device ITO/PEDOT/MEH-PPV/49/Al an EQE of 0.26% and brightness of 800 cd m$^{-2}$ was readily achieved. For comparison a similar device without 49 was fabricated i.e., with MEH-PPV as the only semiconducting polymer layer. An EQE of 0.01% and brightness of 15 cd m$^{-2}$ was realised. Orange emission was seen from both single and bilayer devices the spectra of which were identical to the EL from MEH-PPV.

![Figure 7: Current density-field (i) and light-output-field (ii) of an ITO/PEDOT/MEH-PPV/49/Al device.](image)

Two PPV-based polymers with pendant oxadiazole units were reported by Chen et al., with the intention of imitating PDB and utilising the EL abilities of both PPV and PDB. The copolymer 51 was completely soluble in organic solvents, which was in contrast to the insolubility of homopolymer 52.

Scheme 21: Structures of oxadiazole containing PPV polymers prepared by Chen et al.
Copolymer 51 is highly stable with an onset for degradation at 386 °C. A high \( T_\text{g} \) of 205 °C was also reported which is rarely the case for a PPV derivative such as MEH-PPV. When excited at 426 nm, PL spectra of copolymer 51 showed \( \lambda_{\text{max}} \) 560 nm, which corresponds to orange-yellow light.

Several other groups have reported attaching PDB as a pendant unit directly to the PPV backbone. Lee et al\(^4^4 \) reported two new PPV derivatives bearing PDB 53 and 54. The only structural difference between the two polymers is the presence of an additional 2-ethylhexyloxy side chain in 54.

![Scheme 22: Structures of PPV derivatives bearing PDB pendants prepared by Lee et al.\(^4^4 \)](image)

Excitation at 420 nm gave PL \( \lambda_{\text{max}} \) of 530 nm and 534 nm for polymers 53 and 54, respectively, which are comparable with 540 nm for PPV. EQEs for devices of 53 and 54 were, respectively, 16 and 56 times the value of their PPV analogue. In particular, the device of configuration ITO/PEDOT/54/Al:Li has a maximum brightness of 1090 cd m\(^{-2} \) with a EQE of 0.045%. Device investigations demonstrate that the incorporation of the 2-ethylhexyloxy substituent of 54 improves EL efficiency in comparison to 53, which does not bear that substituent. This is supported by earlier findings of Wudl et al that the presence of long or bulky substituents enhances the device efficiency by reducing the possibility of the formation of polaron pairs.\(^4^5 \) In addition, the bulk substitution with aromatic rings and electron-withdrawing oxadiazole containing side chains on the phenylene ring also has the potential advantage of dispersing the electron density on the vinylene segment so as to minimise oxidation.\(^4^3 \) Further increases in EQE for PPV related polymers have been achieved by incorporating additional oxadiazole units into both the main chain and pendant side chains.\(^4^6 \)
1.5 1,3-OXAZOLES

1,3-Oxazoles are less electron deficient than 1,3,4-oxadiazoles. Consequently there are far fewer examples of 1,3-oxazole OLED materials than their 1,3,4-oxadiazole counterparts. 2,5-Diaryl-1,3-oxazoles 56 are prepared by the cyclocondensation of the amides 55. In practice this dehydration can be carried out using a broad range of acids or acid anhydrides such as phosphoric acid, POCl₃, phosgene and thionyl chloride.⁴⁷

\[
\text{Scheme 23: Synthesis of 2,5-diaryl-1,3-oxazole 56: i) Phosphoric acid, POCl₃, phosgene or thionyl chloride.}^{47}
\]

1.5.1 Low Molecular Weight Oxazoles

Jordan et al.⁴⁸ reported the fabrication and characterisation of a white-light emitting OLED which has a maximum brightness of 4700 cd m⁻² and a luminescent efficiency of 0.5 lm W⁻¹. A thin layer of the blue emitting material 57 was inserted between, hole-transporting TAD 59 and electron-transporting Alq₃ 2 layers in the device configuration ITO/TAD/57/Alq₃/Al which produced white light emission. Compounds 57 and 58 were prepared as detailed in the literature reference ⁴⁹.

\[
\text{Scheme 24: Structures of compounds 57, 58 and TAD 59.}^{48}
\]

Compound 57 has a broad luminescence spectrum spanning the range 400-650 nm with a significant fraction of emission occurring at wavelengths where Alq₃ emits poorly. The
corresponding single layer device (without 57) emitted green light $\lambda_{\text{max}}$ 540 nm. More light was observed by increasing the thickness of the 57 layer. Charge recombination must occur in this vicinity, therefore, 57 may be considered primarily as an electron transport material. Substitution of 57 with 58, which does not emit light but possesses similar transport properties, produces EL emission typical of a TAD/Alq$_3$ device. This indicates that 57 is responsible for the blue spectral components of the white emission, and not TAD. The proportion of red and green wavelengths was tailored by incorporating low percentages of the reddish dye DCM 1 into the Alq$_3$ at the 57 interface.

1.6 1,2,4-TRIAZOLES

1,2,4-Triazoles are π-electron deficient thermostable heterocyclic materials similar to 1,3,4-oxadiazoles. Synthesis of 3,5-diaryl-1,2,4-triazoles 62 involves a ring closure dehydration reaction of bis(hydrazides) 60 with aryl amines 61 in the presence of strong acids or alternatively by reaction of 5-aryltetrazole 63 with imine chloride 64 in pyridine.$^{11}$

![Scheme 25: Synthesis of 3,5-diaryl-1,2,4-triazoles 62: i) Polyphosphoric acid (PPA); ii) Pyridine, $\Delta$.](image)

27
1.6.1 Low Molecular Weight Triazoles

The literature contains fewer examples of low molecular weight triazole compounds compared to their oxadiazole counterparts. The most commonly used is TAZ 65, which has been shown to be a superior hole-blocking material compared to PBD 25. Furthermore, the electron mobility in 65 is lower than that of Alq$_3$.\(^{50}\)

![Scheme 26: Structure of low molecular weight triazole TAZ 65.](image)

Kido et al\(^{51}\) demonstrated that 65 can be efficiently applied as a hole-blocking layer in a triple layer device ITO/PVK/65/Alq$_3$/Mg:Ag; blue light with a $\lambda_{\text{max}}$ of 410 nm was emitted. In this device PVK functions as the emitting material and Alq$_3$ acts as an electron transport layer. In the absence of 65 EL is red-shifted $\lambda_{\text{max}}$ of 530 nm with light emission originating from Alq$_3$. White light was also realised for the same device configuration by doping PVK with fluorescent dyes.\(^{52}\) Jiang and co-workers\(^{53}\) showed that white light could also be produced from the following device ITO/CuPc/NPB/65:rubrene/Alq$_3$/Mg:Ag, in which 65 is used as a hole-blocking layer doped with 1.5% rubrene. Compound 65 has also been used as a ECHB layer for devices in which PVK has been blended individually with two d$^{10}$ metal ion complexes gold (I) and copper (I) compounds.\(^{54}\)

1.6.2 Polymeric Triazoles

Burn et al\(^{55}\) reported a blue-emitting triazole-based conjugated polymer 66 which when used as an ECHB component achieved significant improvement in device performance.

![Scheme 27: Structure of triazole-based conjugated polymer 66.](image)
UV-Vis absorption of 66 as a thin film showed a strong $\pi-\pi^*$ transition at $\lambda_{\text{max}}$ 3.30 eV (375 nm). The absorption in solution is at 3.31 eV (376 nm), corresponding to a shift of only 0.01 eV (1.14 nm) with respect to the solid film. Solid-state PL emission at $\lambda_{\text{max}}$ 2.55 eV (486 nm), PL in solution was blue-shifted by 0.11 eV (19.3 nm) with respect to that of the solid state at $\lambda_{\text{max}}$ 2.66 eV (466 nm). The larger observed blue-shift in the emission, in comparison with the absorption was explained by efficient exciton migration and excimer formation in the thin film. A PLQY of 33% was calculated for 66.

Polymer 66 was studied in both single- and double-layer devices; blue light was emitted and EL reached a maximum at 2.5 eV (496 nm). A peak luminescence of 50 cd/m$^2$ was recorded at a driving voltage of 18 V at a current density of 100 mA/cm$^2$ for the single layer device ITO/66/Al which corresponds to an EQE of 0.02%. A second, single-layer device achieved a reduced EQE of 0.015% when aluminium was substituted for a gold cathode. Since single-layer device investigations indicated that electrons are the majority charge carriers in 66, bilayer devices incorporating PPV as the hole-transporting emissive layer were fabricated using ITO and aluminium as the respective contacts. Light emission originated from the PPV layer and a device EQE reached 0.08% at a luminescence of 250 cd m$^{-2}$ for a driving voltage of 14 V and a current density of 100 mA cm$^{-2}$. Polymer 66 has also been used in conjunction with MEH-PPV as the hole-transporting emissive layer with an internal quantum efficiency of 0.65%.

1.7 Pyridines

Compared to benzene, pyridine is $\pi$-electron-deficient, consequently, the derived polymers have increased electron affinity, improved electron-transporting properties, and the symmetry of poly(phenylene) systems is broken.

1.7.1 Poly(pyridine-2,5-diyl) (PPY)

Poly(pyridine-2,5-diyl) (PPY) 67 has a number of attractive features: it has excellent resistance to photochemical and electrochemical oxidation; it has a PLQY of up to 37%; and is solution processible from formic acid giving solvent orthogonality with most commonly
used materials so enabling the simple fabrication of OLEDs. However, the efficiency of 67 single layer OLEDs with ITO and aluminium contacts is very low with an EQE of 0.001%.\textsuperscript{57}

![PPY structure](image)

\textbf{Scheme 28: Structure of PPY 67 prepared by dehalogenation polycondensation of 2,5-dibromopyridine.}\textsuperscript{57}

Polymer 67 EL emission is broad and featureless peaking at $\lambda_{\text{max}}$ 590 nm and with poor device performance it is considered unsuitable as an emissive material in single layer devices. However, 67 has proved to be an excellent electron-transporting layer in PPV devices. Hwang \textit{et al.}\textsuperscript{58} reported the incorporation of a 67 layer provides improvement in the conversion efficiency of current density to brightness by a factor of 17, whereas Dailey and co-workers\textsuperscript{59} stated that the inclusion of 67 as an additional electron-transport layer in PPV based devices gave an EQE of 0.25% when using aluminium contacts, 10 times greater than similar devices without the electron-transporting layer.

In addition to PPV based devices, Halim \textit{et al.}\textsuperscript{57} have also demonstrated the use of 67 in conjunction with dendrimers containing a distyrylbenzene core and stilbene dendrons. Green light $\lambda_{\text{max}}$ 570 nm was observed which is characteristic of 67. This indicated that charge recombination and light emission occurs within the 67 layer. In this study the effect of the dendrimer is to act as a hole-transporting layer, and assist in the injection of holes into 67. An EQE of 0.01% at maximum brightness was achieved for this green emitting OLED which is ten times greater than the EQE for a single layer 67 device.

\subsection*{1.7.2 Polymeric Pyridines}

Ng \textit{et al.}\textsuperscript{60} synthesised a series of soluble blue-emissive alternating copolymers comprising $\pi$-deficient pyridine and $\pi$-rich dialkoxy-functionalised phenyl rings. All polymers exhibited an onset of degradation at $>$300 °C indicating high thermal stability which is essential for fabricating OLED devices.
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Scheme 29: Structure of donor/acceptor polymers synthesised using Suzuki-coupling reaction by Ng et al.\textsuperscript{60}

Polymer 68 has a PL $\lambda_{\text{max}}$ 434 nm in chloroform solution, and 440 nm in the solid state. For 69 and 70 the $\lambda_{\text{max}}$ were blue-shifted to 397 and 404 nm in solution and 422 and 414 nm in thin films, respectively. Single layer devices were fabricated using ITO as the anode and magnesium-indium alloy as the cathode and blue light was emitted. Emission peaks for 68, 69, and 70 were 444, 432 and 428 nm, respectively. Similarly as for PL, polymers with meta-linkages showed blue-shifted peak emission in comparison to 68, due to a reduction in the $\pi$-conjugation lengths arising from the meta linkages. EL and PL spectra were similar indicating that charge recombination was the same in both cases.

In our laboratory Wang et al.\textsuperscript{61} reported the synthesis and luminescence properties of new pyridine-containing conjugated polymers, two of which were successfully used as electron-transport layers in OLEDs.

Scheme 30: Structures of pyridine-containing polymers prepared by Wang et al.\textsuperscript{61} Synthesis involved Suzuki coupling reactions of 2,5-dibromo-4-hexylpyridine and 2,5-dibromopyridine with 1,4-benzenediboronic acid and 2,5-dimethoxy-1,4-benzenediboronic acid.

Polymer 71 shows an absorption at $\lambda_{\text{max}}$ 322 nm for a thin film, which is similar to that of poly(6-hexyl-2,5-pyridylene) (PHexPY) at 327 nm and poly(para-phenylene) (PPP) at 330 nm, but significantly blue-shifted from the first absorption band of PPY at 382 nm. Polymer 71 is a blue luminescent material with a solid state peak emission at 447 nm, which is blue-shifted with respect to the maximum emission of PPP, PHexPY and PPY. Absorption and PL
spectra of the phenyl-terminated polymers 72 and 74 were essentially very similar to their dibrominated precursors 71 and 73. Measurements of the PLQY of films of 71 and 72 afforded respective efficiencies of 15 ± 2 % and 13 ± 2 %, suggesting that non-radiative quenching of the excited polymers by terminal bromines was not a significant consideration for these two polymers. However, for films of 73 and 74, the corresponding PLQY values were 5 ± 1 % and 17 ± 2 %, respectively.

The effect of the methoxy groups was identified by comparison of the spectra of polymers 71 and 73. In the absorption spectra, the first absorption band at 332 nm was red-shifted to 348 nm for the film with the appearance of an additional band at 285 nm. PL emission was blue-shifted from 447 nm to 438 nm for thin films.

A comparison of the spectra of 73 and 75 revealed the considerable influence of the hexyl side chain on the photophysical properties of these two polymers. In both the absorption and emission profiles, a blue-shift was brought about by the presence of the hexyl group. This is particularly evident in the PL spectra where the shift is 103 nm to give $\lambda_{\text{max}}$ 531 nm. Two possible explanations account for the difference in the spectra of 73 and 75. Firstly the steric repulsion introduced by the hexyl group serves to substantially increase the inter-ring torsion within the polymer chain, thus reducing conjugation leading to a blueshift in the spectra. Alternatively, differences in the degree of intermolecular interaction could lead to the formation of excimers or aggregates, which would account for the substantial red-shift in the absorption and PL spectra of 75.

Polymers 71 and 73 were used as electron-transport materials in MEH-PPV based devices with the general architecture ITO/MEH-PPV/polymer 71 or 73/Al. Whereas the EQE for the single-layer device was 0.0026%, the bilayer device incorporating polymer 73 had an efficiency of 0.03%, an order of magnitude larger. Orange light was emitted which shows that light emission originates entirely from the MEH-PPV layer. Bilayer devices containing polymer 71 had a higher EQE of 0.06%, but only very low current densities and consequently brightness of only a few cd m$^{-2}$ could be obtained. The increases in EQE can be understood to arise from a better balance of electron and hole injection in the bilayer structure.
Figure 8: Light output of LEDs as a function of current density flowing through them for pyridine polymer 73 bilayer and single layer devices fabricated by Wang et al. The inset shows the EL spectrum of the bilayer device.

An alternating copolymer composed of fluorenedivinylene as the light-emitting unit and pyridine 76 was synthesised by Kim and co-workers. Polymer 76 has a $T_g$ of 100 °C; the copolymer has an onset decomposition temperature of 380 °C. Blue PL emission of 76 film cast from chlorobenzene has $\lambda_{\text{max}}$ 440 nm; however peak emission is significantly red-shifted to the green region with $\lambda_{\text{max}}$ of 540 nm when spun from formic acid. PFPV was used as an electron transport layer in an OLED fabricated with a blend of PVK and the fluorene-based copolymer P-3, where ITO and Al were used as the anode and cathode, respectively. Blue EL emission with $\lambda_{\text{max}}$ 475 nm was observed with an EQE of 0.1%.

Scheme 31: Structure of alternating copolymer 76 synthesised by Wittig reaction by Kim et al.
1.7.3 Protonation as a Method of Tuning Luminescence in Pyridine Conjugated Polymers

Following the success of pyridine conjugated polymers prepared by Wang et al\cite{Wang2001}, workers in our laboratory investigated protonation and subsequent intramolecular hydrogen bonding as a method to control chain structure and tune luminescence in these systems,\cite{our_laboratory} specifically focusing on the structural and spectroscopic properties of 1,4-dimethoxy-2,5-bis(2-pyridyl)benzene 77 and the related AB copolymer poly{2,5-pyridylene-co-1,4-[2,5-bis(2-ethylhexyloxy)]phenylene} 80.

Scheme 32: Structure and subsequent protonation of 1,4-dimethoxy-2,5-bis(2-pyridyl)benzene 77: i) HCO$_2$H, EtOAc. ii) HBF$_4$, MeOH. Synthesis by Suzuki Coupling reaction of 2-bromopyridine with 2,5-dimethoxy-1,4-benzenediboronic acid.\cite{63}

X-ray crystallographic analysis demonstrated that reaction of 77 with formic acid does not form an ionic pyridinium salt in the solid state, rather the product 1,4-dimethoxy-2,5-bis(2-pyridyl)benzene bis(formic acid) 78 is a molecular complex with strong hydrogen bonds between each nitrogen atom and the hydroxyl hydrogen in formic acid.
Figure 9: X-ray molecular structure of 1,4-dimethoxy-2,5-bis(2-pyridyl)benzene bis(formic acid) 78. Interaction with formic acid results in a structural twist about the horizontal axis. Pyridyl ring is now in an inverted position compared to the neutral structure.  

In contrast, reaction of 77 with tetrafluoroboric acid leads to the dication salt 1,4-dimethoxy-2,5-bis(2-pyridinium)benzene bis(tetrafluoroborate salt) 79 with significant intramolecular hydrogen bonding (N-H–O-Me) causing planarisation of the molecule. Optical absorption and emission spectra of 79 were significantly red-shifted in comparison to 77 and 78.

Figure 10: X-ray molecular structure of 2,5-bis(2-pyridinium)benzene bis(tetrafluoroborate salt) 79.
Polymer 80 also showed similar red-shifted absorption and PL spectra when treated with strong acids in neutral solution. For instance when protonated with camphorsulfonic acid (CSA) the PL band shifted from 2.55 eV to ca. 2.2 eV. This trend was also observed for thin films of 80 doped with strong acids. Excitation profiles showed that emission arises from both protonated and nonprotonated sites in the polymer backbone. Typically EL for the device structure ITO/PEDOT/80/Ca/Al mirrored PL spectra upon protonation, with the EL peak being red-shifted from 2.4 to 2.15 eV. An EQE of 0.02% was measured for this device.

Scheme 33: Structure of AB copolymer poly{2,5-pyridylene-co-1,4-[2,5-bis(2-ethylhexyloxy)]phenylene} 80. Synthesised by Suzuki Coupling reaction of 2,5-dibromopyridine with 2,5-bis(2-ethylhexyloxy)benzene-1,4-diboronic acid. 63

The protonation of the pyridine rings in polymer 80 accompanied by intramolecular hydrogen bonding to the oxygen of the adjacent solubilising alkoxy substituent (as shown in the X-ray molecular structure of 78 and 79), provides a novel mechanism for driving the polymer into a near-planar configuration, thereby extending the π-conjugation, and tuning the emission profiles.

Figure 11: Electroluminescence spectra of protonated (CSA) and neutral polymer 80. 63

Upon protonation of the red neutral poly[2,5-bis(3,4-ethylenedioxy-2-thienyl)pyridine] 81 Irvin et al. 64 observed a 70 nm red shift in the absorption spectra of thin films accompanied by
a colour change to blue-indigo for the protonated species 82. The protonated and neutral state can be reversibly switched by exposure to 1 M HCl followed by rinsing with deionised water.

Scheme 34: Protonation and subsequent colour change of 81.64

Bouachrine et al65 investigated protonation of the 2,2'-bipyridyl units in the main chain of the chelating conjugated copolymer 83. In chloroform solution 83 has $\lambda_{\text{max}} \text{(abs)}$ 425 nm. Thin films on glass formed by evaporation of a chloroform solution gave $\lambda_{\text{max}}$ 438 nm. The absorption spectrum of 83 changed on addition of acetic acid from $\lambda_{\text{max}}$ 425 nm to 492 nm. This is due to the more planar protonated bipyridyl unit leading to an increase in the conjugation length and the resulting red shift.

Scheme 35: Structure of chelating conjugated copolymer 83. Synthesis based on Stille coupling reaction between a dihalogeno aromatic substrate and bis(tributylstannyl) aromatic species in the presence of Pd(0) as the catalyst.65

1.8 PYRIMIDINES

Pyrimidine has been less exploited than pyridine although it has a number of attractive features: i) it is more electron-deficient than pyridine and ii) due to the lack of ortho-ortho
interactions of C-H hydrogens, 2-arylpyrimidine derivatives are more planar possessing increased \( \pi \)-conjugation in comparison with 2-arylpyridine or biphenyl analogues.

1.8.1 Low Molecular Weight Pyrimidines

Wong et al.\(^6\) reported conjugated oligomers with an alternating phenylene-pyrimidine structure. Oligomers \(84\text{a-c}\) exhibit high thermal stability; TG data revealed no weight loss below 380 °C. Oligomers \(84\text{a}\) and \(84\text{c}\) exhibited relatively low \(T_g\)'s of 27.7 and 31.5 °C, respectively. The low \(T_g\)'s are presumably due to the octyloxyl side chain on the central phenylene ring acting as a solubilising group.

\[\text{Scheme 36: Structures of phenylene-pyrimidine alternating oligomers } 84\text{a-c, synthesised by successive Suzuki coupling reactions starting from 2-ido-5-bromopyrimidine.}\]  

Oligomers \(84\text{a-c}\) exhibit strong blue fluorescence with emission centred at \(\lambda_{\text{max}}\) 419 nm irrespective of the terminal substituents. PLQY values were determined as 37, 54 and 37% for \(84\text{a-c}\), respectively. EL devices of the general configuration ITO/PEDT-PSS/NCB/\(84\text{b}\) or \(84\text{c}/\text{Mg:Al (10:1)}/\text{Ag}\) were fabricated. Oligomers \(84\text{b}\) and \(84\text{c}\) function as efficient blue emitters displaying EL spectra similar to their PL emission with EQEs of 1.3-1.8% and brightness over 2000 cd m\(^{-2}\).

Researchers from the same group reported the pyrimidine-containing spirobifluorene-cored oligoaryl, \(85\), as an emitter or a host for blue OLEDs.\(^6\) Thermal analysis of \(85\) revealed its high thermal stability with a decomposition temperature of 420 °C. DSC demonstrated a high \(T_g\) of 195 °C, as a consequence homogeneous and amorphous films could be formed by thermal evaporation allowing fabrication of LEDs.
Scheme 37: Structure of 85. 85 was synthesised by Suzuki coupling reaction of the 2,7-diboronic ester of 9,9'-spirobifluorene and 5-bromo-2-(4-tert-butylphenyl)pyrimidine in the presence of Pd(PPh₃)$_4$ and P′Bu$_3$ catalysts. 67

Compound 85 is a blue emitter with a PL $\lambda_{\text{max}}$ 430 nm with exceptionally high PLQY in both solution and thin films with values $\Phi_{\text{sol}}$ (in chloroform) and $\Phi_{\text{film}}$ of 100 and 80%, respectively. When 85 was used as a host material for perylene in a multilayer blue emitting device, a maximum brightness of $\sim$80000 cd m$^{-2}$ was achieved.

1.8.2 Poly(pyrimidine-2,5-diyl) (PPym)

Poly(pyrimidine-2,5-diyl) (PPym) 86 shows highly electron accepting properties which can be utilised in n-type semiconductors. 68

Scheme 38: Structure of poly(pyrimidine-2,5-diyl) (PPym) 86 prepared by dehalogenation polycondensation of 2,5-dibromopyrimidine with a zero-valent nickel complex. 68

The cyclic voltamogram (CV) of PPym as a film showed an n-doping peak at ca. $-1.75$ V vs Ag/Ag$^+$ and an undoping peak at $-1.65$ V. The colour of PPym changes from reddish-yellow to dark purple during reduction. PPym film was electrochemically inert in the oxidative region up $+1.0$ V vs Ag/Ag$^+$. The polymer film electrode was stable during repeated scanning, showing essentially the same CV and colour change. This reflects the n-doping properties of PPym and confirms that the introduction of two electron-withdrawing imine nitrogens in the main chain raises the electron accepting character of the poly(arylene).
1.9 PYRAZINES

Pyrazines, like pyrimidines are highly $\pi$-electron-deficient heterocycles. In the context of materials with improved electron-transport capabilities, prior to our work in chapter 3 diarylpyrazines remain essentially unexplored although there had been several reports concerning distrylpyrazines and the incorporation of pyrazine units into ladder polymers.

1.9.1 Distyrylpyrazines

Grimsdale and co-workers$^{69}$ demonstrated that the PL of distyrylpyrazines could be tuned from blue to red by varying the substituents. The dimethoxy compound 87 showed green emission with $\lambda_{\text{max}}$ 480 nm, whereas PL for the diacetoxy derivative 88 was blue-shifted with respect to 87 by 20 nm and thus emitted in the blue region. The di-$N$-oxide 89 displayed a significant red-shifted PL emission that was red-orange with a broad $\lambda_{\text{max}}$ at 540 nm.

\[
\begin{align*}
87 & \quad R^1 = \text{OMe}, R^2 = \text{H} \\
88 & \quad R^1 = \text{OAc}, R^2 = \text{H}
\end{align*}
\]

Scheme 39: Structures of distyrylpyrazines derivatives prepared by Grimsdale et al.$^{69}$

Liu et al.$^{70}$ reported a series of blue emitting pyrazine derivatives. Compounds 90 and 91 have a PL $\lambda_{\text{max}}$ of 438 and 434 nm, respectively. However PL emission peaks for 92 and 93 are red-shifted with values of $\lambda_{\text{max}}$ of 476 and 473 nm, respectively. The red shift of 93 was attributed to an increase in conjugation due to the two naphthyl groups. For 92 the ethoxy-substituted phenyl groups in the backbone and the central pyrazine ring act as electron donating and withdrawing groups, respectively. The red shift for 92 is assigned to imbalanced electron distribution. For 91 the cyano-substituted phenyl groups and the pyrazine ring are both electron withdrawing so there is no charge imbalance, therefore the PL spectrum resembles that of 90. Multilayer EL devices in conjunction with the hole-transport NPB and the host material TPBI gave bright blue emission, $\lambda_{\text{max}}$ 468 nm.
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90 $X = H$

91 $X = CN$

92 $X = OC_2H_5$

Scheme 40: Structures of blue emitting distyrylpyrazine derivatives prepared by Liu et al.$^{70}$

1.9.2 Polymeric Pyrazines

Wu et al.$^{71}$ fabricated EL devices consisting of fluorescent polyimides which have the 2,5-distyrylpyrazine as the active unit incorporated into the polymer backbone. Polyimide Langmuir-Blodgett (LB) films of 94 showed a UV-Vis absorption and PL $\lambda_{max}$ of 396 and 564 nm, respectively. A single-layer device of the LB film of 94 using ITO as the anode and Mg:Al as the cathode emitted orange-red luminescence. Almost identical EL and PL spectra were obtained.

Scheme 41: Structure of polyimide 94, synthesised by reaction of 2,5-bis(4-aminostyryl)pyrazine with aliphatic tetracarboxylic dianhydrides.$^{71}$

Peng and Galvin$^{72}$ reported a new pyrazine-containing PPV polymer 95, which incorporates one pyrazine ring for every three phenyl rings. Polymer 95 is a strongly fluorescent material with a PL $\lambda_{max}$ 530 nm in THF solution and 550 nm as a solid film. Orange emission was observed for a single layer device of 95 as the emissive layer using ITO and aluminium as the respective contacts. The EQE was calculated to be 0.012% at a current density of 1mA mm$^{-2}$. A PPV based bilayer device including 95 as an additional transport layer only showed a slightly higher EQE of 0.015%.
1.9.3 Pyrazine Ladder Polymers

Ladder polymers are uninterrupted sequences of fused rings and have been reviewed extensively within the literature. Tour et al. reported the synthesis of highly functionalised coplanar pyrazine ladder polymers due to the presence of non-covalent linkages between adjacent aromatic rings. Hydrogen bonds are utilised to planarise the polymer backbone due to the excellent hydrogen bond accepting capabilities of pyrazine. Thereby the polymeric framework can be organised into a near-planar conformation, thus extending π-conjugation and ultimately tuning the optical luminescence properties.

Delnoye et al. synthesised a range of soluble π-conjugated oligomers and co-polymers comprising of alternating pyrazine and acylated 1,4-phenylenediamine units. Self-assembled ladder like structures were obtained by the use of intramolecular hydrogen bonding.
Scheme 43: Structures of self-assembled pyrazine ladder oligomers and copolymers prepared by Delnoye et al. 76

Strong hydrogen bonding was evident in the $^1$H-NMR spectra, which showed resonances for the carbamate N-H protons of 96 and 97 at $\delta$ 11.7 and 12.56 ppm, respectively. For methyl substituted pyrazines 98 and 99 higher values of $\delta$ 8.7 and 8.6 ppm were observed, indicating weaker hydrogen bonding due to severe steric hindrance. UV-Vis absorption spectra showed that in the presence of TFA, 96 is protonated and the hydrogen bonds are broken resulting in a blue-shift in the neutral compound $\lambda_{\text{max}}$ from 446 to 369 nm. Pieterse and co-workers 77 demonstrated that the hydrogen bond strength, as well as the electron affinity of such pyrazine oligomers, can be increased by placing more electron withdrawing substituents on ortho amine bonding groups on the 1,4-phenylenediamine unit. However, no device studies utilising this concept were reported.

1.10 1,3,5-TRIAZINES

1,3,5-Triazines have high thermal stability. They are prepared by three synthetic methods; firstly symmetrically substituted 2,4,6-triaryl-1,3,5-triazines 101 are formed by cyclisation of aryl nitriles 100; secondly, unsymmetrical diaryl triazines 104 can be obtained by ring formation of N-cyanoamidines 102 and chloromethylidininium salt 103; and finally, the
synthesis of unsymmetrical triaryltriazines 108 involves reaction of benzamides 107 with benzoic acid anhydride 105 or Schiff bases 106.

Scheme 44: i) Synthesis of symmetrically substituted 2,4,6-triaryl-1,3,5-triazines 101 by cyclisation of aryl nitriles 100 in the presence of PCl₅; ii) Unsymmetrical 2,5-diaryl-1,3,5-triazines 104; iii) Unsymmetrical triaryl-1,3,5-triazines 108.

1.10.1 Low Molecular Weight Triazines

Pang et al.⁷⁸ reported the synthesis and electroluminescence of new blue luminescent star-shaped compounds based on di-2-pyridylamino derivatives of 1,3,5-triazines. 2,4,6-Tris(di-
pyridylamino)-1,3,5-triazine 109 and 2,4,6-tris[p-(di-pyridylamino)phenyl]-1,3,5-triazine 110 were prepared by classic Ullmann condensation reactions.

Compound 109 does not show glass formation, whereas its larger counterpart 110 has a $T_g$ of 121 °C. The two di-2-pyridylamino derivatives emit blue light when irradiated in the solid state and in solution. In the solid state, PL $\lambda_{\text{max}}$ values of 393 and 440 nm were recorded for 109 and 110 respectively, whilst in solution, PL $\lambda_{\text{max}}$ for 109 was significantly red-shifted to 433 nm, whereas the value for larger 110 is the same value as in the solid state 440 nm. The fluorescence efficiencies recorded in solution were 0.43 and 0.78, respectively, indicating that these molecules are fairly efficient blue emitters which have potential in OLEDs.

Electrochemical investigations of 109 and 110 showed that their HOMO energy levels were similar to, or slightly below that of, ITO (-5.1 eV). In contrast, LUMO levels were found to be above that of the Al cathode (-4.2 eV), therefore the electron-transporting material PBD was incorporated into the device between the cathode and the emissive material. In addition, on the anode copper phthalocyanine (CuPc) was used to facilitate hole injection while LiF was added to the cathode to increase electron injection. EL devices were fabricated using the same device architecture, namely ITO/CuPc/compound 109-110/PBD/LiF/Al. Both devices displayed blue emission with EL $\lambda_{\text{max}}$ of 396 and 444 nm for 109 and 110 respectively, which approximately match PL solid-state values. Both devices have a high turn-on voltage of 15 V. Inclusion of the hole-transporting material TPD between CuPc and the emitting layer resulted in a lower turn-on voltage of 6 V. However, a second peak at $\lambda_{\text{max}}$ 532 nm corresponding to green emission was observed. Since compound 110 shows no green emission this must arise from an exciplex state formed between the TPD and 110 layers. The
corresponding device using $^{109}$ was not stable and produced very weak blue emission at an intensity of 14.7 cd m$^{-2}$. Devices with Alq$_3$ were also constructed: instead of blue emission, green light was observed which indicated that Alq$_3$ was not a suitable electron transport material for triazine based systems.

Lupton et al$^{79}$ reported EL from a distyrylbenzene based triazine dendrimer 111. The distyrylbenzene core moiety is a known blue light-emitting material. Within this molecule the triazine ring system has two roles; first to act as the branch point of the dendrimer; and second to behave as an electron transport component. PL and EL properties of this 111 were subsequently investigated.

![Scheme 46: Structure of distyrylbenzene based triazine dendrimer 111 synthesised by Lupton et al.$^{79}$](image)

The film absorption spectra of 111 with $\lambda_{\text{max}}$ of 365 nm, is slightly red-shifted with respect to that of solution spectra $\lambda_{\text{max}}$ 360 nm. This is in contrast to PL spectra, which showed a significant red shift in the film, $\lambda_{\text{max}}$ 462 nm, with respect to the solution, $\lambda_{\text{max}}$ 395, 417 and 440 nm (shoulder). The PLQY of a thin film of 111 was 31%. The dendrimer was incorporated into a single-layer OLED of configuration ITO/111/Ca and was found to emit blue light with an EQE of 0.003%. Comparison of EL and PL $\lambda_{\text{max}}$ values showed that EL peak emission $\lambda_{\text{max}}$ 506 nm was red-shifted by 44 nm with respect to that of the PL. EL intensity was weak and the emitted light changed irreversibly from blue-white to blue. The poor stability of this material during device operation suggests that the phenoxy linkage to the distyrylbenzene core was a poor choice.

Fink and co-authors$^{80}$ reported a series of 1,3,5-triazine ethers with high $T_g$ and demonstrated their potential application as ECHB layers in OLEDs. Ethers 112a-b are crystalline materials
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with high melting points; they exhibit glass transition at 106 and 115 °C, respectively. Compounds 112c-e are amorphous and exhibit \( T_g \) at 139, 133 and 144 °C, respectively. Compound 112b was applied as a ECHB layer in two different types of devices; i) a polymer blend bilayer layer device, ITO/blend of PVK + TDAPB + Alq3 (4:1:1)/112b/Mg:Ag (10:1) and ii) a multilayer device, ITO/TDAPB/Alq3/112b/ Mg:Ag (10:1). Both device types exhibited green emission similar to the PL of Alq3. The onset of EL was increased by the use of the triazine layer and the EQE of the bilayer layer device was twice that of its single layer counterpart. The influence of 112b in the multilayer device was evident by a threefold increase in the EQE accompanied by an increase in EL intensity. No EQE values were reported.

![Scheme 47: Structures of 1,3,5-triazine ethers 112a-e synthesised by Fink et al.](image)

1.10.2 Polymeric Triazines

Poly(triazine ether)s are prepared via nucleophilic aromatic substitution reactions between triaryltriazine difluorides and various bisphenols in an aprotic solvent in the presence of base. Strukelj, however, reported a second synthetic approach involving the preparation of poly(aryl
ether benzil)s and then reacting them with (2-pyridyl)hydrazine to form poly(aryl ether pyridyltriazine)s.\textsuperscript{81}

Pösch and co-workers\textsuperscript{40} reported the synthesis of \( p \)-TRZ 113 which was utilised as an ECHB material in PPV based OLEDs.

![Structure of p-TRZ 113](image)

**Scheme 48:** Structure of \( p \)-TRZ 113 synthesised from the corresponding difluoroheterocyclic monomers with hexafluorobisphenol via a nucleophilic displacement reaction of fluorine atoms by intermediate phenolate anion.\textsuperscript{40}

DSC measurements showed that 113 has a high \( T_g \) of 241 °C, in addition TGA analysis confirmed that 113 is thermally stable with a decomposition temperature of 466 °C. Optical data showed a UV-Vis absorbance at \( \lambda_{\text{max}} \) 293 nm, whereas the fluorescence \( \lambda_{\text{max}} \) was recorded as not detectable. The authors also reported that it was difficult to obtain excellent quality films by spin coating from cyclohexanone solution. 113 was used in the following device configuration ITO/PPV/113/Al and compared against the corresponding single layer reference device ITO/PPV/Al. The bilayer device ITO/PPV/113/Al gave a maximum brightness of 15 cd m\(^{-2}\) at a current density of 43 mA cm\(^{-2}\) in comparison to the reference diode which had a maximum brightness of 2 cd m\(^{-2}\) at a current density of 436 mA cm\(^{-2}\). Whilst the bilayer device structure is more efficient than its single layer counterpart, the higher onset voltage of 8.5 V compared to 6.0 V for the reference demonstrates that 113 facilitates efficient hole blocking at the PPV/ECHB interface rather than electron injection.

### 1.11 QUINOLINES

As stated earlier (Alq\(_3\)) 2 was first used in by Tang and VanSlyke\textsuperscript{5} and is probably the most widely used quinoline based electron-transport material. The quinoline moieties in the ligands of this metal complex are \( \pi \)-electron deficient systems, which contribute towards the electron injection/transport property of this green light-emitting complex. In addition to its
use in low molecular weight vapour-deposited OLEDs Alq₃ has been extensively used as an electron-transport material in polymer OLED systems with considerable improvements in EQEs reported.

Polyquinolines are characterised by high thermal and oxidative stability, outstanding mechanical properties, and optically clear film-forming properties. As for quinolines, polyquinolines 116 are prepared by acid catalysed Friedländer condensation reaction between bis(o-aminoketone)s 114 and diacetylaryl compounds 115.

![Diagram of the Friedländer synthesis of polyquinolines]

Scheme 49: Friedländer synthesis of polyquinolines 116: i) m-cresol, Δ.

1.11.1 Polymeric Quinolines

Kim et al⁸² produced a series of polyquinolines containing the 9,9-di-n-hexylfluorene units in the main chain. Their optical absorption and luminescence properties vary with chain rigidity and conjugation length.

![Diagram of the series of polyquinoline copolymers]

Scheme 50: Series of polyquinoline copolymers prepared by Kim et al.⁸²
As the chain rigidity increases $T_g$ values for this series of copolymers increase, ranging from 195 to 243 °C. Thermal stability is clearly enhanced by the quinoline ring as the $T_g$ values are much higher compared to those of polyfluorene ~55 °C or MEH-PPV ~65 °C. These polyquinolines showed high thermal stabilities with initial decomposition temperatures of >388 °C.

Optical properties show longer wavelength blue emission with increasing chain rigidity and conjugation length, the PL emission in solution increases from 404 nm for 117a to 446 nm for 117b, and the PL emission of thin films shows the same tendency but is red-shifted, i.e. 414 nm (117a) to 494 nm (117d) with respect to solution emission. To investigate the electron-transporting/hole-blocking properties of this series of polyquinolines 117a, and 117c were fabricated into OLEDs using the emissive statistical copolymer 118.

Scheme 51: Structure of statistical copolymer 118 with fluorene as one unit and a mixture of $p$- and $m$-divinylbenzene (n:m= 3:7).

Bi- and tri-layer devices were constructed of the form ITO/P-3:PVK blend/117a/Al and ITO/PVK/118/117c/Al. For the bilayer device configurations both 117a and 117c showed improved charge transport with increased EQE values of 0.041 and 0.052% respectively, compared to the reference value (no polyquinoline layer) of 0.0045%. Whilst bilayer layer devices operated at the same turn-on voltage of 14 V, luminance output for 117a was slightly lower than the reference at 6.0 μW whereas a 2.7 fold increase was recorded for 117c at 16 μW. EL spectra for OLEDs with and without 117c demonstrated that both devices show blue emission, $\lambda_{\text{max}}$ 480 nm, which is very close to the peak emission of the reference $\lambda_{\text{max}}$ at 476 nm, indicating that the 118:PVK blend acts as the emitting layer in the bi-layer device, and no exciplex formation occurs. In the case of tri-layer devices, both the light intensity (3.4 and 8.2 times increased) and EQE (17.5 and 15.6 times increased) equivalent to values of 0.014 and 0.012% respectively, were obtained compared to the control device, comprising ITO/PVK/118/Al.
Liu and co-workers\textsuperscript{83} successfully synthesised two EL copolymers containing biquinolines and 2,2-diphenylhexafluoropropane 119 or pyridine moieties 120. Both 119 and 120 possess excellent thermal stability with decomposition temperatures greater than 500 °C, a \( T_g \) of 286 °C for 120 was also recorded.

![Scheme 52: Structures of biquinoline copolymers 119 and 120 prepared by Liu et al.\textsuperscript{83}](image)

UV-Vis absorption spectra of thin film and solution samples exhibit similar profiles with two peaks in solution (\( \lambda_{\text{max}} \) 283, 340 nm for 119; \( \lambda_{\text{max}} \) 267, 347 nm for 120) and as thin films (\( \lambda_{\text{max}} \) 283, 363 nm for 119; \( \lambda_{\text{max}} \) 263, 340 nm for 120). PL of 119 in chloroform solution showed a maximum at 408 nm with a well-defined vibronic feature at 424 nm and a weak shoulder at ca 495 nm, while the thin film has a maximum 528 nm with a well-defined vibronic feature at 450 nm. In both cases excitation was at 366 nm. The fluorescence quantum yield for 119 was calculated to be 38%. For 120 in chloroform the emission was at \( \lambda_{\text{max}} \) 398 nm. The thin film showed a very broad emission profile with peaks at 440, 500, and 536 nm. The weaker broad emission at 500 and 536 nm was assigned as excimer emission. Large differences between PL in solution and thin films indicate the presence of aggregates or excimer formation within the film.

Yellow-green light with \( \lambda_{\text{max}} \) 523 nm with a weak shoulder at around 440 nm was observed for the device configuration ITO/CuPc/119/Al. A significant observation for the single-layer device ITO/120/Al was that the turn-on voltages both for current and light were almost the same at 5.9 V, indicating balanced injection and transport of charge carriers, while for the bilayer device ITO/CuPc/120/Al the turn-on voltages for current and light were 9.7 and 8.1 V respectively, when CuPc was used as a hole transport/injection layer. This high electron affinity of 120 suggests that its single layer device has balanced charge injection and the hole-transporting CuPc was unnecessary. An EQE of 0.002% was recorded for the device ITO/120/Al which is compatible with single layer MEH-PPV devices. The inclusion of CuPc only slightly increased the EQE to 0.003%.
Liu et al.\textsuperscript{84} reported a copolymer of alternating biquinoline and dialkoxyphenylene vinylene units in the polymer main chain. \textbf{121} has excellent thermal stability with a decomposition temperature above 400 °C and a \( T_g \) of 147 °C and is readily soluble in organic solvents.

\begin{center}
\includegraphics[width=0.5\textwidth]{structure.png}
\end{center}

\textbf{Scheme 53: Structure of copolymer 121 prepared by Horner-Wadsworth-Emmons olefination.}\textsuperscript{84}

UV-Vis absorption spectra in chloroform solution and thin films showed almost identical profiles with \( \lambda_{\text{max}} \) 406 nm. It is evident from the spectra that substituent chains prevent aggregation. PL spectra of \textbf{121} thin films and EL spectra for the device configuration ITO/121/Al were almost identical. Green-yellow emission was centred at \( \lambda_{\text{max}} \) 550 nm, slightly red-shifted in comparison with solution PL. MEH-PPV emits orange light, therefore, light emission from \textbf{121} emanates from the entire polymer chain and not just from the MEH-PPV segment. An EQE of 0.06% at a turn-on voltage of 18 V was achieved for ITO/121/Al.

\subsection*{1.12 QUINOXALINES}

Polyquinoxalines are a family of polymers with quinoxaline units in the main chain. In general they possess good chemical and thermal stability and excellent solubility. Simple quinoxalines are prepared by cyclocondensation of an aromatic \( o \)-diamine and 1,2-dicarbonyl compounds. The synthesis of polyquinoxalines \textbf{124} and poly(phenylquinoxalines) \textbf{127} is carried out in a similar manner involving cyclocondensation reaction between bis(\( o \)-diamine)s \textbf{122} and \textbf{125} and aromatic bis(\( \alpha \)-dicarbonyl) compounds, bisglyoxals \textbf{123} and bis(phenyl-\( \alpha \)-diketones) respectively \textbf{126}. 

\[52\]
Scheme 54: Synthesis of polyquinoxalines 124 and poly(phenylquinoxalines) 127: i) m-cresol, 80 °C; ii) m-cresol, 40 °C.\textsuperscript{50}

Poly(phenylquinoxalines) 130 can also be prepared by an activated poly(arylether) synthesis from bis(fluorophenylquinoxalines) 128 and various bisphenols 129 in the presence of base.\textsuperscript{50}
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Scheme 55: Synthesis of poly(aryl ether phenylquinoxaline)s 130: i) NMP/Toluene, K₂CO₃.

1.12.1 Low Molecular Weight Quinoxalines

Wang and co-workers reported high EL from bilayer OLEDs composed of triphenylamine and quinoxaline dimer derivatives. Emission from the subsequent devices originated from exciplex formation at the interface between the two organic layers. Bilayer devices consisting of the hole-transporting materials (HT) TPD or PVK and quinoxaline derivatives (QX) or were fabricated in the general structure ITO/HT/QX/Mg;Ag.

Scheme 56: Structures of quinoxaline derivatives 131 and 132 prepared by Wang et al.

PL measurements for 131 and 132 show blue emission with \( \lambda_{\text{max}} \) values of 450 nm and 500 nm, respectively. Yellow-orange emission centred at \( \lambda_{\text{max}} \) 575 nm was observed for device A consisting of TPB/131 and red light was witnessed for B TPB/132 at \( \lambda_{\text{max}} \) 685 nm. The maximum luminances of the two devices were 600 cd m\(^{-2}\) and 70 cd m\(^{-2}\), and the EQEs were 0.65% and 0.045%, respectively. In contrast peak emissions of bilayer devices incorporating PVK as the hole-transporting layer were blue-shifted with respect to their TPB counterparts. Blue light at \( \lambda_{\text{max}} \) 505 nm was emitted for device C PVK/131 and red light for device D.
PVK/132 at $\lambda_{\text{max}}$ 600 nm. Device C had a reduced brightness of 200 cd m$^{-2}$ and EQE 0.4% when compared to its counterpart A. Device D, however, showed considerable performance improvement compared to device B, with a maximum brightness of 140 cd m$^{-2}$ and EQE of 0.2%.

Thomas et al$^{86,87}$ have prepared dipolar compounds containing both quinoxaline/pyridopyrazine acceptors and arylamine/carbazole donors. It was demonstrated that the emission colour of these dipolar compounds could be tuned by modifying the donor and quinoxaline units.

![Scheme 57: Structures of dipolar quinoxaline/pyridopyrazine compounds synthesised by Thomas et al.$^{87}$](image)

High $T_g$'s were realised for compounds 133a-f over a range of 134-162°C. Glasses formed easily on heating with no crystallisation process observed even if the material was heated above the $T_g$. The pyridopyrazine derivatives 133d-f possess slightly higher $T_g$ (162, 148, 154 °C, respectively), than their quinoxaline counterparts 133a-c (146, 134, 150 °C, respectively).
UV-Vis absorption spectra showed that compounds 133a-f are green emitters in toluene solutions; however, in dichloromethane the emission is red-shifted with a reduction in quantum yield. Bright green/yellow emission was realised for the single layer device ITO/133a/Mg:Ag with $\lambda_{\text{max}}$ 548 nm, operating at a maximum brightness of 10437 cd m$^{-2}$ and maximum luminance efficiency 0.6 lm W$^{-1}$. Whilst single layer device performance was reasonable, this was enhanced by the inclusion of the electron-transport material Alq$_3$. The bilayer device ITO/133a/Alq$_3$/Mg:Ag again emitted green/yellow light with $\lambda_{\text{max}}$ 544 nm and the maximum brightness and luminance efficiency were increased to 42942 cd m$^{-2}$ and 2.5 lm W$^{-1}$ respectively. Bilayer devices were fabricated for 133b-e. Due to its low volatility no device using 133f could be constructed. The maximum brightness for the four devices was 4144, 41167, 6853 and 22366 cd m$^{-2}$, and the maximum luminance efficiencies were 0.2, 2.4, 0.3 and 0.8 lm W$^{-1}$, respectively. As for the previous bilayer device of 133a all four devices showed green/yellow emission. The reduced performance of the more electron-deficient pyridopyrazine derivatives 133b and 133d, compared to 133a-c is reminiscent of the work in our group by Wang et al.$^{30,42}$ however, this work clearly demonstrates the efficient electron-transporting qualities of quinoxaline based materials.

Wang et al.$^{88}$ have studied the novel dihydroquinazolinone derivative 134. PL spectra of 134 as a thin film showed green emission with $\lambda_{\text{max}}$ 525 nm. A single layer device was fabricated with 134 as the emissive layer in the following configuration ITO/134/Al and greenish-yellow light was emitted with an EQE of 0.07%. A three-layered device with the structure ITO/TPD/134/Alq$_3$/Al was constructed. The Alq$_3$ layer included was to lower the energy barrier for electron injection and to improve electron transport, and conversely TPD was added to increase hole production within the organic material and enhance exciton formation. The EL maximum $\lambda_{\text{max}}$ of 538 nm was consistent with the single-layered counterpart, which indicated that the emission originates from the radiative recombination of singlet excitons within 134. The EQE increased by a factor of ten to 0.07% for the triple-layered device.

Scheme 58: Structure of dihydroquinazolinone derivative MAPQ 134.$^{88}$
1.12.2 Polymeric Quinoxalines

A blue light emitting conjugated copolymer based on fluorene with a quinoxaline moiety in the main chain was reported as a potential candidate for OLEDs. 89 135 has glass-forming character with a $T_g$ of 208 °C. The absorption spectrum of 135 as a film and in chloroform solution have $\lambda_{\text{max}}$ 402 nm and 404 nm, respectively. PL emission is in the blue region; in solution $\lambda_{\text{max}}$ 448 nm, as a film emission is red-shifted by 7 nm to $\lambda_{\text{max}}$ 455 nm. This small shift indicates that aggregation and excimer fluorescence is suppressed.

Scheme 59: Structure of 135 prepared by polycondensation of 2,7-bis(phenyloxoacetyl)-9,9-bis(2-ethylhexyl)fluorene and 3,3-diaminobenzidine in m-cresol. 92

Polyether 136 functions as an ECHB material by lowering the current flow and increasing the EQE of PPV multilayer devices. Prepared by Pösch et al. 40 136 is highly soluble and thermally stable with a $T_g$ and thermal decomposition of 269 °C and 484 °C, respectively. Optical data showed a UV-Vis absorbance at $\lambda_{\text{max}}$ 269 nm and a fluorescence $\lambda_{\text{max}}$ 431 nm.

Scheme 60: Structure of ECHB material 136. 40

The bilayer device ITO/PPV/136/Al gave a maximum brightness of 65 cd m$^{-2}$ at a current density of 243 mA cm$^{-2}$ in comparison to the reference diode that had a maximum brightness of 2 cd m$^{-2}$ at a current density of 436 mA cm$^{-2}$. A lower onset voltage of 4.5 V was achieved compared to 6.0 V for the single layer PPV reference. EL spectra of bilayer OLEDs were identical to those of PPV devices, confirming that PPV acts as hole-transporting and emissive layer. Device performance clearly demonstrated increased injection of electrons from 136 facilitating charge recombination and photon generation in the emissive PPV material.
Dailey et al.\(^9\) reported a quinoxaline substituted vinylic polymer 137, used as a homopolymer or as a copolymer with the hole-transporting material poly(4-vinyltriphenylamine) PVTPA. 137 is a charge-transport material with negligible emission properties, therefore, to evaluate its performance in emissive devices it was doped at a concentration of 0.5\% (by weight) with the pyromethane laser dye PM580.

![Scheme 61: Structure of 137 polymerised under free radical conditions using 2\% AIBN under nitrogen in benzene at 70 °C.\(^9\)](image)

OLEDs were made using PVTPA:137 random copolymer and a 1:1 blend of the corresponding homopolymers; both devices produced green-yellow emission from the PM580 dopant centred at \(\lambda_{\text{max}}\) 560 nm. For single-layer devices relatively high brightness was realised. Maximum brightness of 2290 cd m\(^{-2}\) for the blend and 1557 cd m\(^{-2}\) for the random copolymer at the same current were achieved. Overall EQEs of 0.114 and 0.073\% were recorded for the blend and copolymer, respectively.

### 1.13 Pyrazolo[3,4-b]quinolines

Pyrazolo[3,4-b]quinoline derivatives 140 and 143 have been used as efficient blue emitters in multilayer OLEDs. They are prepared by two synthetic methods; firstly by reaction of \(o\)-aminobenzaldehyde 138 and 1-methyl-3-phenylpyrazol-5-one 139; secondly substituted PAQ can be obtained by reaction of appropriately substituted aniline 141 with 5-chloro-4-formyl-1-methyl-3-phenylpyrazol 142.\(^9\)
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Scheme 62: Synthesis of pyrazoloquinolines: i) POCl₃, 100 °C, 2 h, sulfolane, 220 °C, 3 h; ii) Δ, 150-210 °C.⁹¹

1.13.1 Low Molecular Weight Pyrazolo[3,4-b]quinolines

Tao et al.⁹² synthesized a series of 1-methyl-3-phenyl-1H-pyrazolo[3,4-b]quinolines carrying various substituents at the 6- or 7-position which were studied as emitting materials in OLEDs.

Scheme 63: Series of substituted pyrazoloquinolines prepared by Tao et al.⁹²

The parent PAQ derivative 146 exhibits a \( T_g \) of 31.9 °C. With a substituent at the 6- or 7-position, the \( T_g \) further decreased or was undetected. UV-Vis absorption in ethyl acetate solution showed a similar absorption pattern between 300 and 450 nm for the variously substituted derivatives with the exception of 144 and 150. A small but definite substituent effect was observed for derivatives with electron-withdrawing groups 147, 148 and 149 are redshifted \( \lambda_{\text{max}} \) 398, 399 and 398 nm, respectively in comparison with the electron-donating...
tert-butyl derivative \( \text{145} \) \( \lambda_{\text{max}} \) 388 nm. In contrast \( \text{144} \) was redshifted and splitting of \( \lambda_{\text{max}} \) 412 nm was observed. \( \text{150} \) was substantially redshifted \( \lambda_{\text{max}} \) 451 nm. PL in ethyl acetate solution showed that PAQ materials \( \text{144-149} \) are intensely blue emitters with the exception of \( \text{150} \) which emits in the green region \( \lambda_{\text{max}} \) 521 nm. The same substituent effect was observed for PL spectra. PAQ derivatives with electron-withdrawing groups \( \text{147, 148 and 149} \) being redshifted \( \lambda_{\text{max}} \) 446, 462 and 468 nm, respectively in comparison with the electron-donating tert-butyl derivative \( \text{145} \) \( \lambda_{\text{max}} \) 434 nm. The parent derivative \( \text{146 and 144} \) were also redshifted with respect to \( \text{145} \) \( \lambda_{\text{max}} \) 438 and 442 nm, respectively. All PAQ derivatives have quantum yield greater than 0.5 with the exception of \( \text{150} \), which has a quantum, yield of 0.19.

Multilayer OLED of the structure ITO/NPB/CBP/TPBI:PAQ-\( \text{144-150} / \text{TPBI/Mg:Ag} \) were fabricated. The TPBI was chosen as the host material for PAQ devices because it has a wide band gap material and emits strongly at \( \lambda_{\text{max}} \) 376 nm where most of the PAQ derivatives have strong absorption. Two-layers of hole-transporting material NPB and CBP were used because CBP serves as to provide an intermediate HOMO level by which holes can pass into the TPBI layer.\(^93\) EL spectra of OLEDs with 2% (w/w) PAQ doped into TPBI are blue except for \( \text{150} \) which is green. The EQE for devices with electron-donating substituents \( \text{144 and 145} \) were 2.93 and 3.00%, respectively, which were higher than 2.46% recorded for the parent derivative \( \text{146} \). Devices with electron-withdrawing substituents \( \text{147, 148 and 149} \) have lower EQE than their electron-donating counterparts with values of 2.03, 0.49 and 1.53%, respectively. The green emitting \( \text{150} \) based device has a EQE of 2.12%. It is worth noting that the maximum brightness of this device was 1169 cd m\(^{-2} \) which is double the maximum brightness of 584 cd m\(^{-2} \) achieved for the highest blue emitting \( \text{144} \) based device.

Tao and co-workers continued this research by synthesizing a second series of 6-substituted-3-methyl-1-phenyl-4-(4-methoxyphenyl)-1\(H\)-pyrazolo[3,4-b]quinolines MeOPAQ.\(^{94}\)
Scheme 64: Series of 6-substituted-3-methyl-1-phenyl-4-(4-methoxyphenyl)-1H-pyrazolo[3,4-b]quinolines MeOPAQ-X prepared by Tao et al.\textsuperscript{94}

$T_g$s were recorded for derivatives 151-153, which were 62.6, 53.6 and 38.1 °C, respectively; no $T_g$ data was recorded for the other three derivatives. All MeOPAQ derivatives have similar UV-Vis absorption profiles with a major absorption peak being around 390-400 nm. PL spectra show that all derivatives are blue emitting $\lambda_{\text{max}}$ for 151-153 448, 452, 450 nm, respectively; halogen derivatives 154-156 are redshifted in comparison $\lambda_{\text{max}}$ 460, 459 and 460 nm, respectively.

Four MeOPAQ derivatives 151-154 were selected for OLED fabrication of general configuration ITO/NPB/CBP/TPBI:2%-151-154/TPBI/Mg:Ag. Bright blue EL $\lambda_{\text{max}}$ 442, 454, 454 and 458 nm, respectively, was observed for all four dopants tested with emission originating from the MeOPAQ derivatives. The luminance reaches as high as 13,500 cd m$^{-2}$ in the case of 153 with an EQE of 3.4%. Other substituents also have similar performance but are less bright than 153.

Tao et al have also reported very bright blue OLEDs using highly fluorescent dipyrazolopyridine derivatives 4-(4-substituted-phenyl)-1,7-diphenyl-3,5-dimethyl-1,7-dihydrodipyrazolo[3,4-b,4',3'-e]pyridine (PAP), as emitter by doping the dye in a electron-transport host (TPBI).\textsuperscript{93,95}
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Scheme 65: Dipyrazolopyridine derivatives prepared by Tao and co-workers. 95

PL in ethyl acetate solution showed blue emission for 157-159 with $\lambda_{\text{max}}$ 426, 440 and 463 nm, respectively. Thin film emission was slightly redshifted with respect to solution $\lambda_{\text{max}}$ 438, 443 and 466 nm, respectively. The electron-withdrawing cyano derivative 159 has the lowest relative quantum yield of 0.50 in comparison to 0.76 for 157 and 0.89 for 158.

OLEDs with a general configuration ITO/NPB/CBP/TPBI:2%-PAP-157-159/Mg:Ag showed blue emission. As the substituent changes from electron-donating to electron-withdrawing EL emission is redshifted $\lambda_{\text{max}}$ 440, 448 and 462 nm, respectively. The 159 based device is exceptionally good, with a brightness of 11,200 cd m$^{-2}$ at 14.2 V and EQE of 3.2%.

1.14 CONCLUSIONS

In conclusion, since the initial discovery that organic conjugated polymers such as PPV could be used as emissive materials in OLEDs 7 there has been a plethora of publications describing new light-emitting polymers. An important aspect of this work has been the emergence of $\pi$-electron deficient heterocycles carrying imine nitrogen atoms being used to improve electron injection/transport and hole-blocking properties. This chapter has reviewed and updated the literature regarding the use of low molecular weight, oligomeric and polymeric $\pi$-electron deficient heterocycles, as emissive and ECHB layers in OLEDs.
2 NEW PYRIMIDINE- AND FLUORENE-CONTAINING OLIGOARYLENEs

2.1 INTRODUCTION

It is surprising that pyrimidine units have been only very rarely incorporated into conjugated oligomer or polymer structures. For example, poly(pyrimidine-2,5-diyl) \( \mathbf{86} \) is an electron accepting material which can be doped with sodium to obtain an n-type semiconductor,\(^6^8\) a 1,3,4-oxadiazole–pyrimidine hybrid oligo(arylene) \( \mathbf{37h} \) has been shown to function as an electron conducting/hole blocking (ECHB) layer in bilayer LEDs using poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene-vinylene] (MEH-PPV) as the emissive material.\(^3^0\) In addition, the linear phenylene-pyrimidine penta-arylene systems \( \mathbf{84a-c} \) and the spirobifluorene–pyrimidine hybrid \( \mathbf{85} \) are blue emitters.\(^6^6,^6^7\)

Pyrimidine was attractive to us for two main reasons: (i) it has a higher electron affinity than pyridine;\(^9^6\) and (ii) due to the lack of ortho–ortho interactions of C–H hydrogens, 2-arylpyrimidine derivatives should be more planar (i.e. possess increased \( \pi \)–conjugation) compared with 2-arylpyridine (or biphenyl) analogues. Our initial aim, therefore, was to develop efficient syntheses of new and versatile functionalised pyrimidines, especially pyrimidine-containing oligo(arylene) systems. This chapter reports the synthesis of such compounds, namely \( \mathbf{166} \) and \( \mathbf{172–175} \), along with the X-ray crystal structures of \( \mathbf{165}, \mathbf{166} \) and \( \mathbf{174} \), \textit{ab initio} calculations, optical absorption and photoluminescence spectra, and OLED studies using compound \( \mathbf{175} \) as the emissive layer. The fluorenyl core of \( \mathbf{172–175} \) was chosen because of its known high stability and luminescence efficiency, with the alkyl chains at C(9) imparting good solubility in organic solvents.\(^9^7,^9^8\)

2.2 RESULTS AND DISCUSSION

2.2.1 Synthesis

Suzuki cross-coupling methodology is a very versatile route to oligo(arylene)s\(^9^9\) and for this purpose we required 2,5-dibromopyrimidine \( \mathbf{163} \) as a starting material. Compound \( \mathbf{163} \) was
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readily obtained in 29% yield from commercial 2-hydroxypyrimidine hydrochloride 160 using a procedure that proved to be considerably more convenient than the literature routes.100 Goodby et al.101 reported the synthesis of 163 direct from the starting material 160 using Br₂, water then reflux in POBr₃. However, no detailed experimental procedure of percentage yield was reported therefore this method was not pursued.

![Scheme 66: Synthesis of 2,5-dibromopyrimidine 163](image)

There are very few examples of Suzuki reactions on halopyrimidines,66,102 so as a test reaction, 163 was treated with benzeneboronic acid 164 (3.0 equivalents) in the presence of catalytic Pd(PPh₃)₄ in refluxing tetrahydrofuran (THF). Two products were obtained which were easily separated and identified as 2-phenyl-5-bromopyrimidine 165 (43% yield) and 2,5-diphenylpyrimidine 166 (32% yield), both of which had been obtained previously by different routes.103 This reaction is of fundamental interest in that it established that the bromine atom at C(2) of compound 166 is more labile under standard Suzuki conditions. Compound 166 was obtained in higher yield (62%) using benzeneboronic acid 164 (2.0 equivalents) and Pd₂(dba)₃ catalyst104 at 20 °C.

![Scheme 67: Synthesis of 165 and 166](image)

2,7-Dibromo-9,9-dihexylfluorene 168 was obtained in 85% yield from commercial dibromofluorene 167 by deprotonation with potassium t-butoxide followed by alkylation with bromohexane.105 This procedure seems more convenient than the two-step route from
fluorene (alkylation, then bromination) reported by several other groups.\textsuperscript{97b,98} 9,9-
Dihexylfluorene-2,7-diboronic acid 169, which is a key reagent for many fluorene-based
luminophores, was obtained in 86\% yield from 168 by reaction with \textit{n}-butyllithium and
triisopropylborate, followed by aqueous workup.\textsuperscript{106} All the data obtained for 168 and 169
confirm no detectable contamination with unwanted fluorenone by-products. Compound 169
is a shelf-stable solid, and its reaction with two equivalents of 2-bromopyrimidine 170, 5-
bromopyrimidine 171 and 2,5-dibromopyrimidine 163, as above, gave 172, 173 and 174 in
34, 32 and 23\% yields, respectively. A further two-fold Suzuki reaction of benzeneboronic
acid with compound 174 afforded the hexa(arylene) system 175 (35\% yield) bearing terminal
phenyl groups. The low yield of pure product from this capping reaction was primarily due to
difficulties in the purification of 174.

![Scheme 68: Synthesis of compounds 168-175](image)

Scheme 68: Synthesis of compounds 168-175: i) 1-bromohexane, \textit{t}-BuOK, THF, 0 °C \textrightharpoons 20 °C; ii) \textit{n}-BuLi,
THF, \textt{-78 °C}, triisopropylborate. \textt{-78 °C \textrightharpoons 20 °C}, then H\textsubscript{2}O; iii) 2-bromopyrimidine 170, THF, Pd(PPh\textsubscript{3})\textsubscript{4}, Na\textsubscript{2}CO\textsubscript{3}, \Delta; iv) 5-bromopyrimidine 171, THF, Pd(PPh\textsubscript{3})\textsubscript{4}, Na\textsubscript{2}CO\textsubscript{3}, \Delta; v) 2,5-dibromopyrimidine 163, THF,
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Pd(PPh₃)₃, Na₂CO₃, Δ; (vi) benzeneboronic acid 164, THF, Pd(PPh₃)₃, Na₂CO₃, Δ.

2.2.2 X-Ray Crystal Structures of Compounds 165, 166 and 174

Crystal structures were solved by Dr A. Batsanov. Molecule 165 (Figure 12) is twisted around the C(2)-C(11) bond by 18.3° which is smaller than that observed in biphenyl (see discussion below), thus confirming that nitrogen atoms facilitate planarisation of the system.

Figure 12: X-ray molecular structure of 165 (henceforth thermal ellipsoid are drawn at 50% probability level).

Molecule 166 (Figure 13) is located on a crystallographic twofold axis, normal to the long axis of the molecule. The central pyrimidine ring is disordered between two orientations, related via this axis and forming an interplanar angle of 14.8°. In each case, the pyrimidine ring is inclined by 19.8° and 34.6° to the phenyl groups in positions 2 and 5, respectively that reflects the same tendency of planarisation of the system via substitution of C–H by nitrogen atoms in oligophenylenes.

Figure 13: X-ray molecular structure of 166, showing the disorder of the pyrimidine ring. Atoms, symmetrically dependant via the twofold axis, are primed.

In molecule 174 the fluorene moiety is planar, while the pyrimidine rings bonded to C(4) and C(10) are inclined to its plane by 5.1° and 5.6°, respectively (Figure 14). These angles are much smaller that those observed for 165 and 166, which could be a result of better
New Pyrimidine- and Fluorene-containing Oligo(arylene) Conjugation of the Pyrimidine Rings with the Central Planar Fluorene Core in this Extended π-System. One n-hexyl chain entirely and the other one nearly [with the exception of the terminal C(33) atom], adopt an all-trans conformation and lie in one plane, perpendicular to the fluorene plane.

Figure 14: X-ray molecular structure of 174.

In an isolated molecule, the twist angle (ω) between two bonded aromatic rings depends on the balance between π conjugation (which favours planarity) and steric repulsion between H atoms (or substituents) in peri-positions. For the latter, heteroatoms and substituents in meta- and para-positions are largely irrelevant. Hence a 5-phenylpyrimidine (or 5,5'-bispyrimidine) moiety (type A link) can be expected to behave in the same way as the biphenyl molecule, which has potential barriers (albeit low, 2 to 2.5 kcal mol⁻¹) at both ω = 0 and ω = 90°,¹⁰⁷ and the stable conformation with an intermediate twist, as observed in the gas phase by electron diffraction (ω = 45°),¹⁰⁸ Raman (ω = 25°)¹⁰⁹ or electron spectroscopy (ω = 40°),¹⁰⁷d as well as in solutions and melts (ω=32 ± 2°).¹¹⁰ Although in the solid state the molecule lies at a crystallographic inversion centre (which implies planarity) there are indications of disorder, so that the actual conformation is probably a slightly twisted one,¹¹¹ as in fact is observed in the non-centrosymmetric low-temperature phase.¹⁰⁷a In any case, a 2-phenylpyrimidine moiety (type B link) lacks the main driving force for twisting, the pyrimidine having no peri-H atoms. Indeed, in eight previously studied structures with sterically unhindered 2-
phenylpyrimidine moiety,\(^{96,112}\) the dihedral angle between the phenyl and pyrimidine rings varies from 0 to 14.5°. Four of these contain simultaneously type A and B links, and present two different conformations. In 2-(4-\(n\)-propoxyphenyl)- and 2-(4-\(n\)-butoxyphenyl)-5-phenylpyrimidines\(^{112b}\) and 1,4-bis(5-phenyl-2-pyrimidinyl)-phenylene\(^{96}\) the B-link is twisted much more (35 – 39°) than the A-link (3 – 9°); while in 2-phenyl-5-(4-\(n\)-pent oxyphenyl)pyrimidine\(^{112d}\) both A and B-twists are small (6–9°) and the molecule is approximately planar.

### 2.2.3 Optical Absorption and Photoluminescence Properties

Solution UV-Vis absorption and photoluminescence (PL) spectra for 172–175 were recorded in DCM. There is a progressive red shift in the value of \(\lambda_{\text{max}}\) of the low energy band in the sequence 173 (328 nm), 172 (352.5 nm), 174 (365 nm) and 175 (371.5 nm) (Figure 15, Table 1). Estimated from the low-energy absorption edge, HOMO–LUMO energy gaps \((E_g)\) are 3.39, 3.47, 3.28 and 3.13 eV, for compounds 173, 172, 174 and 175, respectively. This order of \(E_g\) evolution is expected: twisting between pyrimidine and fluorene rings in compound 173 as compared to its planar isomer 172 (see calculation section below) hinders electron delocalisation and therefore results in an increase of \(E_g\), whereas \(\pi\)-extension of the system by attaching additional phenyl rings to 172 to give 175 leads to \(E_g\) contraction. This trend in HOMO–LUMO gap changes is well reproduced by \textit{ab initio} calculations (see Appendix 1).

<table>
<thead>
<tr>
<th>Compound</th>
<th>UV-Vis Absorption, (\lambda_{\text{max}}/\text{nm})</th>
<th>PL, (\lambda_{\text{max}}/\text{nm})</th>
</tr>
</thead>
<tbody>
<tr>
<td>172</td>
<td>317.0, 337.5, 352.5</td>
<td>366, 384</td>
</tr>
<tr>
<td>173</td>
<td>328.0</td>
<td>361, 378</td>
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<tr>
<td>174</td>
<td>348.0, 365.0</td>
<td>377, 396</td>
</tr>
<tr>
<td>175</td>
<td>365.5, 371.5</td>
<td>391, 412</td>
</tr>
</tbody>
</table>

Table 1: UV-Vis absorption and emission \(\lambda_{\text{max}}\) values for compounds 172-175 in dichloromethane, 20°C.
New Pyrimidine- and Fluorene-containing Oligo(arylene)s

Figure 15: Normalised UV–Vis absorption (dashed lines) and PL (solid lines) (excitation at 355 nm) spectra for compounds 172-175 in DCM, 20 °C.

The $\lambda_{\text{max}}$ values for the emission spectra obtained by excitation at 355 nm are also red shifted in the same sequence as the absorption spectra (Figure 15, Table 1). Absorption of light by the conjugated organic molecules 172-175 gives rise to an n-$\pi^*$ or $\pi-\pi^*$ transition and promotes an electron to the LUMO. The energy levels are broadened by vibration and rapid vibronic relaxation to the bottom of the LUMO, followed by radiative decay to the ground state. Hence, the UV–Vis absorption and PL emission spectra (Figure 15) are broad bands, with the latter red-shifted to longer wavelengths. The photoluminescence quantum yield (PLQY) for 174 and 175 in DCM solution were 25% and 85%, respectively. The high PLQY value obtained for 175 is consistent with that observed in other fluorene-containing oligomers, and, importantly, confirms that the presence of the pyrimidine units is not detrimental to the high luminescence efficiency of the fluorene moiety. It has been reported that when some heterocyclic segments, e.g. 2,1,3-benzothiadiazoles, are incorporated into poly(fluorene) chains the fluorene photoluminescence is completely quenched due to exciton confinement. The considerably lower PLQY value for 174 can be explained by quenching of the emission by the bromine substituents.

The PL spectra of solution and thin film of 175 (Figure 16) show well-structured emission bands with $\lambda_{\text{max}} = 414$ nm (toluene solution) and 418, 440 nm (film). We calculate a solid state PLQY of 21%, similar to that of many polyfluorenes.
New Pyrimidine- and Fluorene-containing Oligo(arylene)s

Figure 16: Photoluminescence spectra of 175 in toluene solution (thin line) and solid state (thick line). Excitation was at 350 nm.

2.2.4 Light-Emitting Device Studies

The light-emitting diodes comprising a thin film (300 nm) of compound 175, sandwiched between poly(ethylenedioxy-thiophene) (PEDOT)-coated ITO glass and Ca electrodes, ITO/PEDOT/175/Ca/Al, were fabricated by B. P. Lyons in collaboration with Prof A. Monkman’s group in the Department of Physics, University of Durham. These devices had turn-on voltages of 40 – 50 V, such that an electric field of ~1.5 MV/cm (typical for this class of material) was required to achieve electroluminescence (EL). This luminescence was blue-green (λ_{max} = 500 nm) and of low intensity < 10 cd m^{-2} (Figure 17). This low-energy emission is absent from the PL spectra of the solution, suggesting that it arises from aggregates in the film. To support this point, Figure 13 also shows the difference between the PL in solid state and in solution. This represents emission from dimeric states in the film that are not present in the solution. As the film absorption spectrum (not shown) shows no evidence of a corresponding ground state absorption to the red side of the π-π* absorption band, these states are most likely to be excimers, which are formed by strong coupling between excited and ground state molecules, and usually have very low quantum yields. Small molecules like 175 (as opposed to polymers) are renowned for excimer formation. We can discount the presence of defect sites (e.g. ketones which can be formed during the operation of polyfluorene-based LEDs) as the source of low EL intensity as related fluorene-based compounds synthesized in our laboratory have been shown not to possess these defects. There is a reasonable match between this excimer emission and the EL spectra, supporting our claim that EL emanates from these excimer states. The high turn-on
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voltage and low intensity of the emission will preclude practical device applications, so we have not explored 175 further in this context.

Figure 17: Electroluminescence spectra (thin line) and excimer emission (thick line) from 175. The excimer emission was calculated by first red-shifting the solution photoluminescence by 31 nm, such that the emission modes coincided with those in the solid state. The spectra were then normalised and the solution emission was subtracted from that of the thin film.

2.2.5 Electrochemical Properties

The electrochemical behaviour of compounds 172, 173, and 175 was studied by cyclic voltammetry (CV) in DCM solution at room temperature using Bu₄NPF₆ (0.2 M) as supporting electrolyte.

Figure 18: Cyclic voltammogram of compound 175 in 0.2 M Bu₄NPF₆ / DCM, scan rate 100 mVs⁻¹, 20 °C.

The CV of compound 175 (Figure 18) shows a quasi-reversible (ΔEpa-pc = 120 mV) oxidation peak at E½ = +1.36 V (vs. Ag/Ag⁺). Compared to compound 175, compound 172 is a poorer donor with an oxidation observed at higher potentials. Moreover, the oxidation process
becomes irreversible showing only an anodic peak at $E_{pa} = +1.50$ V (at 100 mV s$^{-1}$) [in addition, the adsorption of the material on the electrode surface occurs during the CV experiment, so the current on subsequent scans is decreased]. The observed difference in $E_{pa}$ values between 172 and 175 (1.50 − 1.42 = 0.08 V) is in good agreement with the difference in the energies of their HOMO orbitals calculated at both Hartree-Fock (HF) and density functional theory (DFT) levels of theory (0.11 − 0.12 eV). For compound 173 we were not able to measure an $E_{ox}$ potential which should lie at much more positive potentials. Thus, the calculated energy of the HOMO orbital (Table A Appendix 1) for 173 is 0.41–0.45 eV lower than that of 175, so its $E_{pa}$ value is estimated to be around +(1.91 − 1.96 V) which is out of the range of the electrochemical transparency of DCM.

The estimated HOMO–LUMO gaps for all compounds 172–175 from their optical spectra are higher than 3 eV, therefore, reduction is predicted to occur at potentials around −2 V, which is out of the window of electrochemical transparency of DCM, so it is not possible to experimentally determine the electrochemical band gap for these compounds (although $E_{red}$ values for some oligo/poly-fluorenes were measured in THF or acetonitrile. 120

2.2.6 Quantum Chemical Calculations

Ab initio calculations were performed by Dr I. F Perepichka in our group. The geometries and electronic structures at the Hartree-Fock (HF) and density functional theory (DFT) levels of theory were determined for compounds 172, 173 and 175 (with ethyl substituents replacing hexyl) and for their dipyrazinyl and bistetrazenyl analogues, 176, 177, 179 and 180. The heterocyclic nitrogen atoms of 172 and 175 facilitate planarisation of the system, compared to 173, which is in agreement with X-ray structural data obtained for 5-bromo-2-phenylpyrimidine 166, 2,5-diphenylpyrimidine 167 and compound 174. Bistetrazenyl derivative 180 is calculated to be a fully planar system. (For a more detailed discussion of Quantum Chemical Calculations see Appendix 1).
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Scheme 69: Structures of compounds 17E, 173E, 175E-180E studied by ab initio calculations.

2.3 CONCLUSIONS

A series of new pyrimidine-containing oligo(arylenes) has been synthesised by Suzuki cross-coupling methodology and shown to possess interesting X-ray structural intramolecular twisting torsion angles, photophysical and electronic properties. Theoretical calculations for pyrimidine, pyrazine and tetrazine derivatives establish that the nitrogen atoms decrease steric repulsion, which exists in biphenyl derivatives, resulting in planarisation of the system as could be predicted from molecular models additional trends in HOMO and LUMO levels have been determined. X-ray crystal structures of 166, 167 and 174 together with ab initio calculations demonstrate that the nitrogen atoms of the pyrimidine ring facilitate planarisation allowing efficient electron transport through this class of material. Compound 175 has been used as the emissive layer in an OLED: at a high turn-on voltage blue-green light (λ_{max} 500 nm) is emitted, which most likely emanates primarily from excimer states. Our synthetic methodology is versatile and further chemical modifications within this class of oligomers are underway to provide new materials with tunable optoelectronic and photophysical properties.121
3 NEW PYRAZINE CO-OLIGOMERS

3.1 INTRODUCTION

In the search for materials with improved electron transport and tailored luminescence properties, the incorporation of electron deficient-heterocycles, e.g. 1,3,4-oxadiazole, pyridine, pyrimidine, quinoline, quinoxaline and 1,3,5-triazine into conjugated backbones is being vigorously pursued, as discussed in Chapter 1. In this context the symmetry of 2,5-disubstituted pyrazines has obvious attractions, and although distyrylpyrazines have been reported by several groups, diarylpyrazines and related oligomers remain essentially unexplored. Hasegawa et al.\textsuperscript{122} reported that substituted distyrylpyrazines show green electro luminescence, and Grimsdale et al.\textsuperscript{69} demonstrated that the photoluminescence of these materials [including a pyrazine-di(N-oxide) derivative] can be tuned from blue to red by changing the substituents. In conjunction with a substituted 1,1'-biphenyl-4,4'-diamine derivative as a hole transport layer, blue emission has been observed from distyrylpyrazines.\textsuperscript{70} Peng and Galvin reported orange electroluminescence from a single-layer LED using a pyrazine-containing PPV derivative as the emissive layer.\textsuperscript{72} Katimoto et al. reported orange-red luminescence from thin films of polyimides containing distyrylpyrazine units in the backbone.\textsuperscript{71} A bilayer device using 2,3-dicyano-5-phenyl-6-[2-(4-formylphenyl)ethenyl]pyrazine gave low intensity electroluminescence ($\lambda_{\text{max}}$ not reported).\textsuperscript{123}

In a different context, intramolecular hydrogen bonding in 2,5-bis(2-aminophenyl)pyrazine derivatives has recently been exploited in the construction of ladder-like oligomers,\textsuperscript{76} and condensation polymerisations of functionalised pyrazine monomers have been reported.\textsuperscript{74}

For heteroatomic systems with a basic nitrogen atom, protonation can provide a means of tuning the optoelectronic properties. For example, upon protonation of poly[2,5-bis(3,4-ethylenedioxy-2-thienyl)pyridine] Reynolds et al. observed a 70 nm red shift in the absorption spectra,\textsuperscript{64} and work in our group in collaboration with Monkman et al. established a similar shift in the absorption and emission spectra of poly\{2,5-pyridylene-co-1,4-[2,5-bis(2-ethylhexyloxy)]phenylene\}.\textsuperscript{63} We recognised, therefore, that it would be of interest to explore the protonation of pyrazine systems, for which, unlike the aforementioned pyridine systems, diprotonation of the heterocycle might be achieved.
3.2 RESULTS AND DISCUSSION

3.2.1 Synthesis

3.2.1.1 Attempted Preparation of 2,5-Dibromopyrazine 191

Our initial target molecule was 2,5-dibromopyrazine 191 with the intention of utilising the hydrogen bonding capacity of the pyrazine ring in driving the resulting oligomers into a planar configuration, thus extending the π-conjugation and tuning the optoelectronic properties. A review of the literature showed that 191 would require a lengthy and time-consuming synthesis. The published synthesis of 2,5-dibromopyrazine 191 by Ellingson and Henry\textsuperscript{124} started from 2-aminopyrazinecarboxylic acid methyl ester 186, which at the time of this work was not commercially available. Compound 186 was subsequently prepared as described by Chen \textit{et al} (Scheme 70).\textsuperscript{125}

![Scheme 70: Synthesis of 3-aminopyrazinecarboxylic acid, methyl ester 186 by Chen \textit{et al}.\textsuperscript{125}: i) Ac\textsubscript{2}O, Δ; ii) CH\textsubscript{3}OH, 20 °C; iii) SOCl\textsubscript{2}, Δ; iv) NaN\textsubscript{3}, acetone, H\textsubscript{2}O, 0 °C; v) PhH, Δ.](image)

Reaction of commercially available 2,3-pyrazinedicarboxylic 181 with acetic anhydride gave 182 in 92% yield; the reaction with methanol gave the methyl ester 183 in 89% yield. Treatment of 183 with thionyl chloride gave the acid chloride 184, which was not isolated, and reaction of 184 with sodium azide gave the acyl azide 185, which without isolation smoothly underwent a Curtis rearrangement to give 186 in 33% yield: 10 g batches of 186 were conveniently prepared by this procedure.
Due to the presence of the *para* directing amine substituent, bromination of 186 occurs at C-5 of the pyrazine ring yielding 187 in 36%. Following the literature precedent$^{126}$, we initially brominated using Br$_2$ in glacial acetic acid 36% yield. However, we found it far more convenient using *N*-bromosuccinimide (NBS), which gave 187 in a significantly higher 86% yield. Hydrolysis of 187 with NaOH gave 2-amino-5-bromopyrazinoic acid 188 in 78% yield. Decarboxylation of 188 readily occurred in tetralin yielding 2-amino-5-bromopyrazine 189 in 67% yield (Scheme 71).

![Scheme 71: Synthesis of 2-amino-5-bromopyrazine 189](image)

Scheme 71: Synthesis of 2-amino-5-bromopyrazine 189: i) AcOH, Br$_2$ or alternatively, NBS, DMF; ii) 5% NaOH (aq), Δ, 48% HBr; iii) Tetralin, Δ.

Whilst this route could prepare sufficient quantities of 189, the overall synthesis was time-consuming. We, therefore, attempted the direct bromination of commercially available aminopyrazine 190 with NBS that had previously been successful in preparing 187. This reaction was successful which allowed us to prepare 189 in a one step synthesis in 36% yield in 5 g batches (Scheme 72).

![Scheme 72: One step synthesis of 2-amino-5-bromopyrazine 189](image)

Scheme 72: One step synthesis of 2-amino-5-bromopyrazine 189: i) NBS, DMF.

2,5-Dibromopyrazine 191 has been prepared from its amino precursor 189 by means of the Sandmeyer reaction involving diazotisation in the presence of 48% hydrobromic acid.$^{126,127}$ Our initial test reaction was successful in low yield (Scheme 73). However, subsequent attempts were unsuccessful and intractable mixtures were obtained even though the temperature was regulated carefully (-10 °C to 0 °C) and reaction time varied. Under these conditions, according to literature, 2-amino-5-bromopyridine cleanly afforded 2,5-dibromopyridine (30% not optimised).$^{128}$

![Scheme 73: Synthesis of 2,5-dibromopyrazine 191 via the Sandmeyer reaction](image)
New Pyrazine co-Oligomers

Since the conventional synthesis of 2,5-dibromopyrazine 191 had been unsuccessful we adopted a different strategy and attempted to prepare 2,5-dichloropyrazine 197 on which we could perform a halogen exchange reaction. A search of the literature revealed two possible synthetic routes to 197 (Schemes 74 and 75).

Scheme 74: Proposed synthesis of 2,5-dichloropyrazine 197: i) AcOH, H₂O, 41 °C → 0 °C, Cl₂ (g); ii) Sodium bisulfite, H₂O, 20 °C; iii) 5% NaOH (aq), Δ, conc HCl; iv) Tetralin, Δ; v) NaN₃ (aq); vi) POCl₃.

Chlorination¹²⁹ of 2-aminopyrazinecarboxylic acid methyl ester 186 via the chloramine 192 gave 2-amino-5-chloropyrazine carboxylic acid methyl ester 193 in 56% yield. Hydrolysis of 193 gave 2-amino-5-chloropyrazinoic acid 194 in 84% yield. Decarboxylation of 194 in refluxing tetralin afforded 2-amino-5-chloropyrazine 195 in 74% yield.¹³⁰ However, despite numerous efforts we were again thwarted in our attempt to convert 195 in to 2-hydroxy-5-chloropyrazine 196 by the Sandmeyer reaction. No product was isolated and starting material could not be recovered.

Scheme 75: Synthesis of 2,5-dichloropyrazine 197: i) AcOH, H₂O₂, 65-75 °C; ii) POCl₃, 80 °C.

3-Chloropyrazine-1-oxide 199 was prepared from commercially available chloropyrazine 198 in 50% yield in accordance with the literature method.¹³¹ As described in the literature we anticipated isolating 197 directly from the N-oxide intermediate. However, ¹H-NMR spectroscopy and GCMS showed that a complex mixture of dichloropyrazine isomers had
been obtained, presumably the 2,5-197, 2,3-200 and 2,6-isomer 201, which could not be
separated. We, therefore, abandoned 2,5-dichloropyrazine as a target compound.

3.2.1.2 Suzuki Cross-coupling Reactions of 2-Amino-5-bromopyrazine

Although our efforts in synthesising 2,5-dibromopyrazine 191 had been unsuccessful we
recognised that novel chemistry could be developed using 2-amino-5-bromopyrazine 189 in
palladium-catalysed Suzuki cross-coupling reactions. The resulting heteroaromatics bearing a
primary amine group would also be potential candidates for Sandmeyer reactions.

![Scheme 76: Suzuki cross-coupling of 2-amino-5-bromopyrazine 189: i) benzeneboronic acid 164, THF,
Pd(PPh3)4, Na2CO3, Δ; ii) 2-methoxy-benzeneboronic acid 203, THF, Pd(PPh3)4, Na2CO3, Δ; iii) 4-
methoxy-benzeneboronic acid 205, THF, Pd(PPh3)4, Na2CO3, Δ.](image)

Reaction of 189 with benzeneboronic acid 164 (3.0 equivalents) in the presence of catalytic
Pd(PPh3)4 in refluxing THF gave 2-amino-5-phenylpyrazine 202 (59% yield) (Scheme 76).
This was a key result as it demonstrated that the primary amine group could survive
palladium-catalysed Suzuki cross-coupling conditions in spite of literature claims that the
amine group usually needs to be protected for successful Suzuki reactions.132,133 Our second
objective of performing the Sandmeyer reaction on 202 was, however, unsuccessful. The
reasoning behind the synthesis of 204 and 206 (35 and 23% yields, respectively) was to
modify the electronic structure of the pyrazine ring in the diarylamine system in the hope that
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Sandmeyer reactions would be successful. However yet again our efforts were in vain. Two-fold reactions of 189 with the diboronic acids 2,5-dimethoxy-1,4-diboronic acid\textsuperscript{61} 207 and 9,9-dihexylfluorene-2,7-diboronic acid 169, respectively yielded products 208 and 209 (56 and 51% yields) (Scheme 77). The oligo(arylene) systems 208 and 209 were not considered as suitable candidates for electron-transporting molecules in optoelectronic devices. This was due to the enormous potential for hydrogen bonding between the terminal amine group of adjacent molecules, which would cause crystallisation and ultimately degrade the device thin film. In addition the physical properties of 208 high melting point (> 300 °C) and unprocessability severely limit this compound as an electron-transport material.

![Scheme 77: Two-fold Suzuki cross-coupling of 2-amino-5-bromopyrazine 189: i) 2,5-dimethoxy-1,4-diboronic acid 207, THF, Pd(PPh\textsubscript{3})\textsubscript{4}, Na\textsubscript{2}CO\textsubscript{3}, \Delta; ii) 9,9-dihexylfluorene-2,7-diboronic acid 169, THF, Pd(PPh\textsubscript{3})\textsubscript{4}, Na\textsubscript{2}CO\textsubscript{3}, \Delta.](image)

In summary, this work establishes that heteroaromatics bearing a primary amine group are suitable substrates for Suzuki cross-coupling reactions under standard conditions, without the need for protection/deprotection steps that are traditionally considered to be necessary for these reactions to proceed cleanly. The presence of the primary amine group offers attractive prospects for further synthetic transformations as well as supramolecular and coordination chemistry.\textsuperscript{134}
3.2.1.3 Additional Heteroaromatic Oligomers

The versatility of the Suzuki cross-coupling reaction was further demonstrated by the synthesis of a series of heteroaromatic oligomers, the structures of which are shown below (Scheme 78). The same cross-coupling conditions were used starting from the aryl halide (bromo or iodo precursor) and the diboronic acids 169 and 207. Compounds 210-214 were prepared in moderate yields with 212 and 213 having terminal bromines being the most significant as they have the capacity to undergo further cross-coupling reactions. The high melting points of compounds 210 (235 °C), 211 (232 °C), 212 (192 °C) and 213 (153 °C) demonstrate that such compounds are not feasible for use in OLEDs. It is generally considered that low-molar-mass-materials and oligomers that are oils preclude practical device applications, so we have not explored 214 further in this context.\(^{135}\)

![Scheme 78: Structures of additional heteroaromatic oligomers 210-214.](image)

3.2.1.4 Phenylene-2,5-dimethylpyrazine co-Oligomers

We chose 2,5-dibromo-3,6-dimethylpyrazine 219 as our starting material with the expectation that steric effects of the methyl substituents would restrict backbone planarity in the derived 2,5-diaryl-3,6-dimethylpyrazine systems, thereby achieving a wider energy band gap and hence shifting emission into the blue region of the spectrum. New blue emitters are much sought after not only because blue is a primary colour and emission in this region of the
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spectrum is crucial for full-colour displays,\textsuperscript{136} but also as energy transfer donors in conjunction with lower bandgap fluorophores.\textsuperscript{137}

Our initial synthesis of 2,5-dibromo-3,6-dimethylpyrazine 219 began from commercially available 2,5-dimethylpyrazine 215 and its oxidation with hydrogen peroxide in aqueous acetic acid gave the di-N-oxide 216 (50\% yield) (Scheme 79). Compound 216 was subsequently refluxed in POCl\textsubscript{3} to give 2,5-dichloro-3,6-dimethylpyrazine 217 in accordance with the literature.\textsuperscript{138} After initial difficulties in forming the di-N-oxide 216 we experienced extremely low yields for the conversion to the dichloro derivative 217 whilst mostly isolating the monochloro product. We therefore sought an alternative synthesis of 2,5-dichloro-3,6-dimethylpyrazine 217.

\[
\text{Scheme 79: Synthesis of 2,5-dichloro-3,6-dimethylpyrazine 217 according to Newbold and Spring}\textsuperscript{138}: \text{i) } \text{H}_2\text{O}_2, \text{AcOH (aq); ii) } \text{POCl}_3. \\
\]

Alanine anhydride 218 can be dehydrated in refluxing POCl\textsubscript{3} to gave 2,5-dichloro-3,6-dimethylpyrazine 217.\textsuperscript{139} Although this reaction step was low yielding (17\%) we were able to perform this reaction on a 20 g scale which produced sufficient 217 for the synthesis of 2,5-dibromo-3,6-dimethylpyrazine 219 by halogen exchange (69\% yield) (Scheme 80).\textsuperscript{140}

\[
\text{Scheme 80: Synthesis of 2,5-dibromo-3,6-dimethylpyrazine 219 : i) } \text{POCl}_3; \text{ii) } \text{PBr}_3. \\
\]

Following the unsuitability of compounds 208-214 in device applications we progressed to side-group substituted oligomers. Incorporation of tert-butyl side chains enhances oligomer solubility, increases the viscosity of the thin film and promotes a glassy state thus inhibiting thin film crystallisation.\textsuperscript{135} Suzuki cross-coupling methodology is known to be a versatile route to oligo(arylenes)\textsuperscript{99} and reaction of 219 with benzeneboronic acid 164, 2-
New Pyrazine co-Oligomers

methoxybenzeneboronic acid 203 and 4-tert-butybenzeneboronic acid 220 gave products 221 (73% yield), 222 (73% yield) and 224 (39% yield) respectively (Scheme 81). Further reaction of 224 with 2,5-dimethoxy-1,4-benzeneboronic acid 207 gave the linear penta-arylene system 225 (16% yield). A second reaction of 219 with 2-methoxybenzeneboronic acid 203 (0.5 equivalents) gave compound 226 (52% yield). However a subsequent reaction 226 with 2,5-dimethoxy-1,4-benzeneboronic acid 207 failed to give the second linear penta-arylene system 227 in sufficient purity. Analogous reaction of 219 with 2-methoxy-5-pyridylboronic acid 228 gave the 2,5-dipyridylpyrazine derivative 229 (73% yield). This last reaction establishes that Suzuki reactions of 219 should enable a range of heteroaryl moieties to be incorporated into the oligomer chain: also the methoxy substituents in 229 should be amenable to further useful synthetic transformations. Reaction of 222 with tetrafluoroboric acid afforded the crystalline diprotonated bis(tetrafluoroborate) salt 223.

Scheme 81: Reagents and conditions: i) benzeneboronic acid 164, THF, Pd(PPh3)4, Na2CO3, Δ; ii) 2-methoxybenzeneboronic acid 203, THF, Pd(PPh3)4, Na2CO3, Δ; iii) HBF4, MeCN; iv) 4-tert-
New Pyrazine co-Oligomers

butylbenzeneboronic acid 220, THF, Pd(PPh₃)₄, Na₂CO₃, Δ; v) 2,5-dimethoxy-1,4-diboronic acid 207, THF, Pd(PPh₃)₄, Na₂CO₃, Δ; vi) 2-methoxybenzeneboronic acid 203, THF, Pd(PPh₃)₄, Na₂CO₃, Δ; vii) 2,5-dimethoxy-1,4-diboronic acid 207, THF, Pd(PPh₃)₄, Na₂CO₃, Δ; vii) 2-methoxy-5-pyridylboronic acid 228, THF, Pd(PPh₃)₄, Na₂CO₃, Δ.

3.2.2 X-ray Crystal Structures of Compounds 208, 222, 223 and 229.

Crystal structures were solved by Dr A. Batsanov. Compound 208 crystallized from DMF/ethanol as a 208·DMF solvate. The structure contains two crystallographically non-equivalent molecules of 208, both located at inversion centres, but adopting different conformations (Figure 19). The dihedral angle between the central benzene and the pyrazine ring is 25.6° in molecule A and nil in molecule B. In both cases, the methoxy group lies in a syn-position to the CH, rather than N, probably due to attractive electrostatic H...O interactions. The methoxy groups deviate from the ideal in-plane conformations by the rotations of 3.0° and 8.0° around the C(2)–O(1) and C(10)–O(2) bonds, respectively.

Figure 19: Independent molecules of 208 and DMF in the structure of 208 DMF (showing 50% thermal ellipsoids).

Molecules 222 and 229 and the dication in 223 have crystallographic C₁ symmetry and adopt twisted conformations: dihedral angles between the phenyl and pyrazine rings are 74.0° (222), 56.4° (223) and 44.6° (229) (Figure 20).
Dication 223 is the first reported diprotonated pyrazine derivative in which the hydrogen atoms were actually located (cf. the four tetramethylpyrazinium salts reported previously). There are relatively strong N-H...F hydrogen bonds with the tetrafluoroborate anions [N-H 0.88(3), N...F 2.701(2), H...F 1.83(3) Å, N-H-F angle 172(3)°] but no intramolecular hydrogen bonds. Protonation widens the C-N-C angle from 118.1(1)° (222) to 126.2(2)° (223),
while the C–N bond lengths are unaffected, viz. N–C(8) 1.339(2) and N–C(9') of 1.344(2) Å in 222 against 1.341(3) and 1.339(3) Å, respectively, in 223.

### 3.2.3 Optical Absorption and Photoluminescence

The absorption spectra in ethanol solution show the lowest energy bands at wavelengths characteristic of twisted oligoaryl structures: viz. compound 221 $\lambda_{max}$ 300 nm; 222 $\lambda_{max}$ 330 nm; 225 $\lambda_{max}$ 315 nm; 229 $\lambda_{max}$ 322 nm (Table 2). Upon addition of H$_2$SO$_4$ to these solutions, there is a red shift of this band to $\lambda_{max}$ 340, 360 and 342 nm for compounds 221, 222 and 225, respectively, but essentially no change was seen for compound 229. This shift is consistent with protonation of the pyrazine unit of 221, 222 and 225, leading to a reduction in the HOMO–LUMO gap. Evidence in favour of diprotonation (not monoprotonation) in these studies is provided by the identical spectra of the isolated salt 223 and that obtained in situ from 222 and H$_2$SO$_4$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Neutral UV-Vis Absorption, $\lambda_{max}$/nm</th>
<th>Protonated UV-Vis Absorption, $\lambda_{max}$/nm</th>
<th>PL, $\lambda_{max}$/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>221</td>
<td>300</td>
<td>340</td>
<td>Not Recorded</td>
</tr>
<tr>
<td>222</td>
<td>330</td>
<td>360</td>
<td>372</td>
</tr>
<tr>
<td>225</td>
<td>315</td>
<td>342</td>
<td>418</td>
</tr>
<tr>
<td>229</td>
<td>322</td>
<td>322</td>
<td>387</td>
</tr>
</tbody>
</table>

Table 2: UV-Vis absorption and emission $\lambda_{max}$ values for compounds 221, 222, 225 and 229 in ethanol, 20°C.
Figure 21: UV-Vis absorption of spectra of 225 in EtOH before and after the addition of H₂SO₄; PL spectra of 225 in EtOH, λₘₐₓ 312 nm.

For compound 229 we suggest that protonation occurs at both of the terminal pyridyl nitrogens, rather than at the central pyrazinyl sites. This would be consistent with literature pKₐ values in aqueous solution: viz. 2-methoxypyridine 3.28; pyrazine 0.51 and -6.6, for mono- and di-protonation, respectively.¹⁴³ The experimental evidence for this is that upon addition of tetrafluoroboric acid to 229 the ¹H NMR spectrum showed protonation of the pyridyl nitrogen atom at δH 7.18 ppm accompanied by a small downfield shift of all protons (and the OMe protons) on the pyridyl ring (Figure 22).
Photoluminescence (PL) spectra in ethanol, with excitation at 312 and 346 nm, show violet-blue emission: 222 $\lambda_{\text{max}}$ 372 nm; 225 $\lambda_{\text{max}}$ 418 nm (Figure 21); 229 $\lambda_{\text{max}}$ 387 nm. The wavelength of PL emission was unaffected by the addition of H$_2$SO$_4$ to the solutions, although the intensity was reduced. This is probably due to the presence of a mixture of emissive neutral species and non-emissive protonated species. When isolated salt 223 was dissolved in ethanol the PL spectrum of the solution was identical to that of neutral precursor 222, although of significantly lower intensity, suggesting that partial deprotonation had occurred to give some neutral 222 in the solution. This is in contrast to the stability of related protonated diarylpyridine systems under these conditions.\textsuperscript{63} Protonation of some nitrogen heterocycles is known to reduce drastically their fluorescence quantum yield.\textsuperscript{136h}
3.2.4 Electroluminescence

Initial studies by Dr T. Sato show that OLEDs can be fabricated using 225 as the emissive layer. A single-layer device was obtained by spin-coating 225 (50-60 nm thick layer) from CHCl₃ solution onto an ITO substrate followed by evaporation of a Ca cathode. The EL emission peak (blue colour; λₘₐₓ 444 nm) was slightly red shifted from the solid state PL (λₘₐₓ 430 nm; Φₑₘ 0.36).¹⁴⁴ No long-wavelength π-aggregates/exciton emission was observed, probably due to the non-planar structure of 225. A common problem with blue emitting materials is the difficulty of charge injection leading to low device efficiency. One strategy is to modify the anode with a thin layer of poly(3,4-ethylenedioxythiophene) (PEDOT).¹⁴⁵ For the device structure ITO/PEDOT/225/Ca blue light emission was observed with an onset of 6.5 V, brightness 110 cd m⁻² at a current density of 40 mA cm⁻²; a maximum EL quantum efficiency of 0.09% was attained.

![Figure 23: Thin film PL λₘₐₓ 350 nm (thin line) and EL spectra (dashed line) of compound 225 in the device configuration ITO/PEDOT/225/Ca.](image)

3.3 CONCLUSIONS

We have successfully demonstrated that pyrazine heteroaromatics bearing a primary amine group are suitable substrates for Suzuki cross-coupling reactions under standard conditions, without the need for protection/deprotection steps as verified by X-ray crystallography for compound 208. The first well-defined pyrazine-containing tertaryl and penta-aryl oligomers have been synthesised by Suzuki methodology, and their structures confirmed by X-ray crystallography for compounds 222, 223 and 229. Blue luminescence has been observed in PL and EL experiments, with no long wavelength emission arising from π-aggregates or
excitons. The applicability of compound 225 as an emissive layer in OLEDs has been established.\textsuperscript{146}
4 NEW 2,5-DIPHENYL-1,3,4-OXADIAZOLES AND 2-PHENYL-5-(2-THIENYL)-1,3,4-OXADIAZOLES

4.1 INTRODUCTION

2,5-Diphenyl-1,3,4-oxadiazole derivatives have been widely studied in diverse areas of chemistry. In particular, due to the electron-deficient properties of the oxadiazole ring, their luminescence properties and their good thermal and chemical stabilities, a range of derivatives (e.g. low molecular weight monomers, star-shaped oligomers and polymers) have been used as emissive materials and/or electron-transporting/hole-blocking compounds in organic light emitting devices (OLEDs). Furthermore, many 1,3,4-oxadiazole derivatives are biologically-active and continue to find applications in medicinal chemistry. This combination of properties ensures that new functionalised derivatives are of considerable interest.

Very recently, the first 2,5-diphenyl-1,3,4-oxadiazole derivative possessing an alkyne substituent, was reported independently by Cha et al. and by workers in our group. From a synthetic viewpoint, the ethynyl substituent offers unprecedented scope for functionalisation reactions, which will extend the π-conjugation at the periphery of the framework. Compound is, therefore, a very attractive building block in the light of the current interest in conjugation of aryl/heteroaryl rings through sp hybridised carbon linkages and the study of ethynyl derivatives of arenes and heteroarenes as “molecular wires”. In this chapter we report the synthesis of the novel thienyl analogue and describe organometallic cross-coupling reactions at the terminal alkyne positions of and to obtain heteroaryl-functionalised derivatives possessing extended π-electron conjugation. We also demonstrate that 2-iodo-5-bromo-pyrimidine is a useful synthetic intermediate in selective palladium catalysed cross-coupling reactions. The optical absorption and photoluminescence properties of these products are reported, along with X-ray crystal structures for compounds and and . In addition EL from a OLED fabricated using a 50% blend of MEH-PPV and a new 2,5-diaryl-1,3,4-oxadiazole-fluorene hybrid compound is also reported.
4.2 RESULTS AND DISCUSSION

4.2.1 Synthesis

Our initial reaction of 230 with 2-bromopyrimidine 170 under standard Sonogashira conditions\textsuperscript{153} [Pd(PPh\textsubscript{3})\textsubscript{2}Cl\textsubscript{2}, triethylamine, CuI, THF] yielded only the self-coupling product 231 which indicated that heteroaryl bromides were not sufficiently reactive for this type of organometallic cross-coupling reaction (Scheme 82). Compound 230 was therefore reacted with a series of heteroaryl iodides under the same standard conditions to afford products 232a-g\textsuperscript{1} in 40-79% yields. Electron-deficient heterocycles (pyridyl, pyrazyl and pyrimidyl: a-e) and electron-rich thienyl derivatives (f,g) reacted similarly.

\begin{center}
\includegraphics[width=\textwidth]{scheme82.png}
\end{center}

Scheme 82: Sonogashira cross-coupling reactions of 230: i) Pd(PPh\textsubscript{3})\textsubscript{2}Cl\textsubscript{2}, CuI, NEt\textsubscript{3}/THF.

To explore the effect of replacing the alkynylphenyl moiety of compound 230 with an alkynylthienyl moiety, a series of novel 2-phenyl-5-(2-thienyl)-1,3,4-oxadiazole derivatives was synthesised as shown in Scheme 83.\textsuperscript{154} The readily available thiophene derivative 233\textsuperscript{155} was converted into the hydrazide derivative 234. Reaction of 234 with tert-butylbenzoyl chloride gave the intermediate diacylhydrazine compound 235 which was not purified. The crude product 235 was cyclodehydrated under standard conditions for the formation of 1,3,4-

\textsuperscript{1} Compound 232f was prepared by Dr. D. Kreher in our laboratory.
2,5-Diphenyl-1,3,4-oxadiazoles and 2-phenyl-5-(2-thienyl)-1,3,4-oxadiazoles

oxadiazoles\textsuperscript{156} using phosphorus oxychloride, to give the 2-phenyl-5-(2-thienyl)-1,3,4-oxadiazole system \textbf{236}. Sonogashira reaction of \textbf{236} with 2-methyl-3-butyn-2-ol gave \textbf{237} from which the target alkyne \textbf{238} was obtained (16\% overall yield from compound \textbf{233}). Cross-coupling reactions analogous to those shown in Scheme 82, using the corresponding iodo-heterocycle gave the terminal heteroaryl derivatives \textbf{239a-g} in 33-65\% yields. Two-fold reaction of \textbf{239} with 2,5-diiodothiophene gave the $\pi$-extended bis(ethynylthienyl)thiophene derivative \textbf{240} in 30\% yield. The self-coupling compound of \textbf{238} was not isolated.

![Scheme 83: Synthesis of novel 2-phenyl-5-(2-thienyl)-1,3,4-oxadiazole derivatives: i) NH$_2$NH$_2$, H$_2$O, CH$_3$OH; ii) 4-tert-benzoyl chloride, pyridine, 20 °C 1 h, Δ 1 h; iii) POCl$_3$; iv) 2-methyl-3-butyn-2-ol, Pd(PPh$_3$)$_2$Cl$_2$, Cul, NEt$_3$/THF; v) NaOH, Toluene; vi) Pd(PPh$_3$)$_2$Cl$_2$, Cul, NEt$_3$/THF.](image-url)
We recognised the potential for products 232e and 239e to undergo a further Suzuki cross-coupling reactions at the 5-position of the pyrimidine ring. Goodby et al.\textsuperscript{101} had previously reported both Sonogashira and Suzuki cross-coupling reactions of 2-iodo-5-bromopyrimidine 241. An initial reaction of 2-iodo-5-bromopyrimidine 241 with phenylacetylene 242 afforded 243 in 53% yield. Subsequent Suzuki reaction of 243 with benzeneboronic acid gave 244 39%. Compound 232e has poor solubility in organic solvents, we therefore reacted the ethylhexoxy analogue\textsuperscript{157} of compound 230 with 2-iodo-5-bromopyrimidine 241, which afforded 245 in 71% yield. The ethylhexoxy side chain imparts good solubility allowing us to perform a further Suzuki cross-coupling reaction with benzeneboronic acid to yield 246 in a disappointing 10% yield. Due to this last result we did not pursue any further Suzuki cross-coupling reactions with thienyl analogues of 245.

Scheme 84: Sonogashira and Suzuki cross-coupling reactions of 2-iodo-5-bromopyrimidine: i) phenylacetylene Pd(PPh\textsubscript{3})\textsubscript{2}Cl\textsubscript{2}, CuI, NEt\textsubscript{3}/THF; ii) benzeneboronic acid , Pd(PPh\textsubscript{3})\textsubscript{4}, THF, Na\textsubscript{2}CO\textsubscript{3}, Δ; iii) 2-[4-(2-ethylhexyloxy)phenyl]-5-(4-ethynylphenyl)-1,3,4-oxadiazole, Pd(PPh\textsubscript{3})\textsubscript{2}Cl\textsubscript{2}, CuI, NEt\textsubscript{3}/THF; iv) benzeneboronic acid , Pd(PPh\textsubscript{3})\textsubscript{2}, THF, Na\textsubscript{2}CO\textsubscript{3}, Δ.

Suzuki cross-coupling of 2-(4-iodophenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole\textsuperscript{158} 247 with three different diboronic acids afforded new 2,5-diaryl-1,3,4-oxadiazole hybrid compounds 248a-c in moderate yields (Scheme 85).
2,5-Diphenyl-1,3,4-oxadiazoles and 2-phenyl-5-(2-thienyl)-1,3,4-oxadiazoles

Scheme 85: Synthesis of new 2,5-diaryl-1,3,4-oxadiazole hybrids 248a-c: i) 1,4-benzenediboronic acid, Pd(PPh₃)₄, THF, Na₂CO₃, Δ; ii) 2,5-dimethoxy-1,4-benzenediboronic acid, Pd(PPh₃)₄, THF, Na₂CO₃, Δ; iii) 9,9-dihexylfluorene-2,7-diboronic acid, Pd(PPh₃)₄, THF, Na₂CO₃, Δ.

4.2.2 X-ray Crystal Structures of 232d, 232g and 239d.

The molecular structures of 232d, 232g, and 239d, solved by Dr A. S. Batsanov and shown in (Figure 24), can be described as approximately planar. The deviations of all non-hydrogen atoms (except the methyl carbons) from their mean plane average 0.22 Å (232d), 0.21 Å (232g), and 0.15 Å (239d), compared to the total lengths of the molecules, ca. 22.5 Å (232d, 232g), and 23.2 Å (239d). Largely, this planarity is due to the molecule having few degrees of conformational freedom, comprising as it does a number of planar rings on a rigid 'rod'. However, the rings can rotate, and there are substantial differences in the conformations. The asymmetric unit of structure 232d comprises two molecules. In each of them, both benzene rings are nearly coplanar (within 1.5 to 4.8°) to the oxadiazole ring, while the angle between benzene ring B and the pyrazine ring is 42.5 or 39.3°. In molecule 232g the oxadiazole ring is inclined by 24.7 and 18.1° (in opposite sense) to the benzene rings A and B, while the latter is inclined to the thiophene ring by 3.5°. Compound 239d crystallises as a monosolvate, with the asymmetric unit comprising one molecule of 239d and one of CHCl₃, linked by a weak hydrogen bond Cl₃C–H...N(2) (H...N 2.48 Å for the idealised C–H distance of 1.08 Å).
dihedral angles between benzene and oxadiazole rings $13.6^\circ$, oxadiazole and thiophene $6.1^\circ$, thiophene and pyrazine $18.5^\circ$.

Figure 24: X-ray molecular structures of 232d, 232g and 239d.

### 4.2.3 Optical Absorption and Emission Properties

The solution UV-Vis absorption and photoluminescence properties for the two series of compounds 232a-g and 239a-g are collated in Table 3. The Stokes shift in $\lambda_{\text{max}}$ values for all the compounds is in the range 50-80 nm, which agrees with known diphenyl-1,3,4-oxadiazole
derivatives$^{159}$ and diaryl(heteroaryl)ethynes where there is a relatively small conformational change upon photoexcitation.$^{151a}$

<table>
<thead>
<tr>
<th>Compound</th>
<th>UV-Vis Absorption</th>
<th>PL (PLQY)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda_{\text{max}}$ / nm</td>
<td>$\lambda_{\text{max}}$ / nm</td>
</tr>
<tr>
<td>232a</td>
<td>322</td>
<td>354, 374</td>
</tr>
<tr>
<td>232b</td>
<td>319</td>
<td>354, 373</td>
</tr>
<tr>
<td>232c</td>
<td>320</td>
<td>375</td>
</tr>
<tr>
<td>232d</td>
<td>323</td>
<td>380 (24%)</td>
</tr>
<tr>
<td>232e</td>
<td>325</td>
<td>384</td>
</tr>
<tr>
<td>232f</td>
<td>335</td>
<td>389 (10%)</td>
</tr>
<tr>
<td>232g</td>
<td>325</td>
<td>361, 376 (28%)</td>
</tr>
<tr>
<td>239a</td>
<td>352</td>
<td>386, 408</td>
</tr>
<tr>
<td>239b</td>
<td>348</td>
<td>385, 408</td>
</tr>
<tr>
<td>239c</td>
<td>351</td>
<td>388, 409</td>
</tr>
<tr>
<td>239d</td>
<td>353</td>
<td>396, 415 (22%)</td>
</tr>
<tr>
<td>239e</td>
<td>361</td>
<td>420</td>
</tr>
<tr>
<td>239f</td>
<td>355</td>
<td>407, 425</td>
</tr>
<tr>
<td>239g</td>
<td>347</td>
<td>395, 413</td>
</tr>
<tr>
<td>240</td>
<td>400</td>
<td>452, 480</td>
</tr>
</tbody>
</table>

Table 3: UV-Vis absorption and PL ($\lambda_{\text{ex}}$ 350 nm) $\lambda_{\text{max}}$ values for compounds 232a-g, 239a-g and 240 in DCM, 20 °C. PLQY values for 232d, 232f, 232g and 239d shown in brackets. The standards for PLQY measurements were quinine sulfate ($\Phi = 0.577$ in 0.5 M H$_2$SO$_4$) and $\beta$-carbolene ($\Phi = 0.60$ in 0.5 M H$_2$SO$_4$).

An interesting trend is that replacement of a phenyl ring (compounds 232a-g) by the thienyl ring (compounds 232a-g) leads to a red shift in the lowest energy band in both the absorption and emission spectra. This can be explained by a “push–pull effect” of the conjugated electron-donating thiophene ring and the electron-accepting oxadiazole ring lowering the HOMO–LUMO gap.$^{160}$ In the absorption spectra, this shift is largest for the terminal 5-bromo-2-pyrimidyl derivatives 232e/239e (36 nm). For all other derivatives in Table 3 the shift is within the range 21-31 nm. In the PL spectra the red shift which occurs on replacing phenyl with thienyl is remarkably similar for all the analogues [\(\Delta \lambda_{\text{max}}\) (em) 34-37 nm].
An additional feature of the data in Table 3 is a further red shift in the absorption and emission peaks of 240 compared to 239f [$\Delta \lambda_{\text{max}}$ (abs) 45 nm; $\Delta \lambda_{\text{max}}$ (em) 55 nm] which is consistent with extended $\pi$-conjugation through the central bis(ethynylthiophene) unit of 240.\textsuperscript{161} PLQY values were obtained for compounds 232d, 232f, 232g and 239d and fall within the range 10-28% (Table 3). These values are considerably lower than those reported for model compounds which lack the ethynyl bond, viz. 2,5-diphenyl-1,3,4-oxadiazole (89%) and 2-(4-biphenyl)-5-phenyl-1,3,4-oxadiazole (83%) in non-polar solvents,\textsuperscript{162} and are consistent with the data obtained for a series of simpler di(aryl/heteroaryl)ethynl derivatives.\textsuperscript{163}
2,5-Diphenyl-1,3,4-oxadiazoles and 2-phenyl-5-(2-thienyl)-1,3,4-oxadiazoles

Figure 26: UV-Vis absorption and PL spectra for compounds 239f and 240 in DCM, 20 °C.

4.2.4 Electroluminescence from Blended MEH-PPV Devices

Compound 248c is blue-emitting PL $\lambda_{\text{max}}$ 421 nm in solution and has been successfully blended with 50% MEH-PPV into the following device ITO/MEH-PPV:248c (50:50)/Al. Light emission originates from the MEH-PPV, as EL $\lambda_{\text{max}}$ ~580 nm was identical to the pure MEH-PPV device. However, for compound 249 emission is red-shifted to $\lambda_{\text{max}}$ 600 nm.

Scheme 86: 2,5-Diaryl-1,3,4-oxadiazole-fluorene hybrid 249 prepared by Oyston and co-workers.\textsuperscript{164}

We propose that it is the dodecyloxy side chains of 249 that are responsible for the red shift in EL emission which would be in agreement with Baigent et al who also observed a significant Stokes' shift for cyano-derivatives of PPV with increasing side chain length.\textsuperscript{165} A detailed discussion of MEH-PPV blended devices, using 248c and 249 is underway in the laboratories of our collaborators.\textsuperscript{164}
2,5-Diphenyl-1,3,4-oxadiazoles and 2-phenyl-5-(2-thienyl)-1,3,4-oxadiazoles

Figure 27: Emission of pure MEH-PPV and 50% blends of MEH-PPV with 248c and 249.\textsuperscript{164}

4.3 CONCLUSIONS

We have achieved efficient functionalisation of the terminal ethynyl carbon of compound 230 by cross-coupling reactions with a series of heteroaryl iodides using Sonogashira methodology. The first derivatives of 2-phenyl-5-(2-thienyl)-1,3,4-oxadiazole are reported: a five-step sequence from the readily-available 2-iodo-5-methoxycarbonylthiophene gives 2-(4-tert-butylphenyl)-5-(4-ethynlythienyl)-1,3,4-oxadiazole 238 in 13% overall yield. Subsequent functionalisation of 238 proceeds smoothly by analogy with 230. Spectroscopic studies in solution establish that replacement of the phenyl ring (i.e. the 2,5-diphenyl-1,3,4-oxadiazole series 232a-g) by a thienyl ring (i.e. the 2-phenyl-5-thienyl-1,3,4-oxadiazole series 239a-g) leads to a significant red shift in the lowest energy band in both the absorption spectra (21-56 nm shift) and emission spectra (34-37 nm shift). Conjugation is extended further in the bis(ethynlythienyl)thiophene derivative 240. X-Ray crystal structure analyses reveal that the π–systems of compounds 232d, 232g and 239d adopt predominantly planar conformations. This work clearly establishes that the alkynes 230 and 238 are synthetically viable and versatile building-blocks for the construction of extended functional π–electron systems with interesting optoelectronic and structural properties.\textsuperscript{166} We have also successfully fabricated MEH-PPV blend devices with new 2,5-diaryl-1,3,4-oxadiazole-fluorene hybrid compounds 248c and 249 and demonstrated that EL is red shifted with varying side chain length.
5 Experimental Procedures

This chapter details the experimental procedures and analytical data for each of the novel compounds presented in this thesis. This chapter also includes the experimental procedures for some compounds, which were already known in the literature that were used in the course of this work.

5.1 General Methods

All reactions that required inert or dry atmospheres were carried out under a blanket of argon, which was dried by passage through a column of phosphorus pentoxide. All reagents employed were of standard reagent grade and purchased from Aldrich, Lancaster, Avocado, Fluka or Merck and used as supplied unless otherwise stated. The following solvents were dried and distilled immediately prior to use: acetone, over Drierite (CaSO₄), acetonitrile and dichloromethane over calcium hydride, diethyl ether and toluene over sodium metal, tetrahydrofuran over potassium metal. \(N,N\)-Dimethylformamide was dried by standing over 4 Å molecular sieves for at least 48 h and was not distilled prior to use. Ethanol and methanol were dried and distilled over magnesium turnings and stored under dry argon over 3 Å molecular sieves. Pyridine was dried by standing over potassium hydroxide overnight followed by vacuum distillation and stored under dry argon over 3 Å molecular sieves. Chlorobenzene, cyclohexane, ethyl acetate, hexane, and petroleum ether were used without prior purification.

Column chromatography was carried out using Prolabo silica (70-230 mesh). Solvents used for chromatography were distilled prior to use, with the exception of dichloromethane, chloroform and petroleum ether, which were used as supplied. Analytical Thin Layer Chromatography (tlc) was performed on Merck DC-Alufolien Silica gel, 60 F₂₅₄ 0.2 mm thickness or Merck DC-Alufolien oxide neutral (Type E), 60 F₂₅₄ 0.2 mm thickness precoated tlc plates.

Cyclic voltammetry experiments were performed on a BAS CV50W electrochemical analyser with iR compensation. Platinum wire, platinum disk (Ø 1.6 mm) and Ag/Ag⁺ were used as counter, working, and reference electrodes, respectively. CV experiments were performed in
Experimental Procedures

dry dichloromethane with 0.2 M Bu₄N⁺PF₆⁻ as supporting electrolyte; concentrations of compounds were ca. 10⁻³ M⁻¹. The scan rate was varied from 50 to 500 mV s⁻¹. The potentials were referenced to Fe/Fe⁺ couple as the internal reference, which showed a potential of +0.17 V vs. Ag/Ag⁺ in our conditions.

UV-vis spectra were recorded using a Varian Cary 5 spectrophotometer at ambient temperatures. Photoluminescence spectra were recorded using a Jobin-Yvon Horiba Fluolog 3-22 Tau-3 spectrofluorimeter with a 0.5-2 nm bandpass using a Xenon lamp. Spectra were recorded using conventional 90 °C geometry with an excitation at 355 nm. PLQY of thin films were measured using a Jobin-Yvon Fluromax spectrofluorimeter equipped with integrating sphere.¹⁶⁷ The standards for PLQY were quinine sulfate (Φ = 0.577 in 0.5 M H₂SO₄) and β-carbolene (Φ = 0.60 in 0.5 M H₂SO₄).

For fabrication of light-emitting devices using 175 a hole-conducting poly(ethylenedioxythiophene) (PEDOT) layer (30 nm thick) was spun onto an etched ITO glass substrate (20 Ω/□), and then baked overnight in a vacuum oven at 50 °C to remove residual water. A dilute solution of compound 175 in toluene (ca. 0.5 mg/ cm³) was then drop-cast onto the PEDOT to form an active layer (ca. 300 nm thick, as confirmed by AlphaStep measurements). On top of this layer, a cathode of 50 nm thick calcium capped with 50 nm thick aluminium was deposited by evaporation under high vacuum (ca 10⁻⁶ mbar). A single-layer device using 225 was constructed as follows: a layer of 225 (50-60 nm thickness) was assembled by spin-coating a solution of 225 in chloroform onto a ITO substrate, followed by evaporation of the aluminium top electrode (thickness ca 150 nm).

Electron Impact (EI) mass spectra were recorded on a Micromass Autospec spectrometer operating at 70 eV with the ionisation mode as indicated. Electrospray (ES) mass spectra were recorded on a Micromass LCT spectrometer. Gas Chromatography Mass Spectra (GCMS) were recorded on a Finnigan Trace MS spectrometer using a HP5MS column (30 L, ID 0.25 mm, Film 0.25 μm).
Experimental Procedures

$^1$H NMR spectra were recorded on a Varian Unity 300 at 300 MHz, a Varian VXR 400s at 400 MHz or a Varian Inova 500 at 500 MHz using deuterated solvent as lock. Chemical shifts are quoted in ppm, relative to tetramethylsilane (TMS), using TMS or the residual solvent as internal reference. $^{13}$C NMR were recorded using broad band decoupling, using Varian VXR 400s or Varian Inova 500 spectrometer at 100 MHz and 125 MHz, respectively. The following abbreviations are used in listing NMR spectra: s = singlet, d = doublet, dd = doublet of doublets, dt = doublet of triplets, t = triplet, m = multiplet, br = broad.

Elemental analyses were obtained on an Exeter Analytical Inc. CE-440 elemental analyser. Melting points were recorded on a Stuart Scientific SMP3 melting points apparatus.
5.2 EXPERIMENTAL PROCEDURES OF CHAPTER 2

5.2.1 Suzuki Cross-Coupling: General Method

The boronic acid, the halide, and the catalyst (5 mol% relative to the boronic acid) were added sequentially to distilled organic solvent (30 cm³) in the absence of light. The reaction mixture was stirred at 20 °C for 30 min. Degassed aqueous base was added and the reaction mixture was heated at reflux under a blanket of argon until tlc monitoring showed that the reaction was complete, typically 36 h. Solvent was evaporated and water (50 cm³) was added to the residue, which was extracted into DCM (3 x 50 cm³). The organic layer was dried (MgSO₄) then concentrated under reduced pressure and purified by chromatography on a silica column.

2-Chloro-5-bromopyrimidine 162

\[
\text{Br-} \begin{array}{c} \text{N} \\ \text{Cl} \end{array} \text{N} \begin{array}{c} \text{Cl} \\ \text{N} \end{array} \text{Br}
\]

2-Hydroxypyrimidine hydrochloride 160 (12.5 g, 93.4 mmol) was dissolved in a Na₂CO₃ solution (5.0 g, 47.2 mmol) in water (275 cm³). Bromine (5.0 cm³, 97.6 mmol) was added slowly and the reaction stirred at 20 °C for 30 min. The water was removed in vacuo to leave a yellow solid. Toluene (225 cm³) was added and the solution refluxed via an azeotropic distillation (24 h). Toluene was removed by distillation and the resultant solid, dried under vacuum (24 h). Phosphorus oxychloride (45.0 cm³) and N,N-dimethylaniline (4.5 cm³) were added and the reaction heated under reflux (8 h). Excess phosphorus oxychloride was removed under reduced pressure with any residual hydrolysed with external cooling. The product was extracted into diethyl ether (150 cm³) and washed with saturated Na₂CO₃ solution and dried over MgSO₄. The solution was concentrated and purified by silica column chromatography (eluent DCM-hexane, 1:1 v/v) and then recrystallised from hexane to yield 162 as colourless crystals (8.26 g, 45%) m.p 78-78.6 °C (lit. 79 °C).¹⁰⁰ m/z (El) 196 (M⁺, 18%, ⁸¹Br, ³⁷Cl), 194 (M⁺, 100%, ⁸¹Br, ³⁵Cl, or ⁷⁹Br, ³⁷Cl), 192 (M⁺, 57%, ⁷⁹Br, ³⁷Cl). δH (CDCl₃) 8.68 (s, 2H). δc (CDCl₃) 118.82, 159.90, 160.04.

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2,5-Dibromopyrimidine 163

2-Chloro-5-bromopyrimidine 162 (8.00 g, 41.4 mmol) dissolved in dichloromethane (25 cm³) was added to stirred 48% hydrobromic acid (25 cm³), along with a few drops of Aliquat 336. The two-phase system was stirred at 20 °C for 72 h. A white solid was visible after 24 h. The solvent was removed in vacuo and extracted into diethyl ether (150 cm³), neutralised with saturated Na₂CO₃ (aq), and dried over MgSO₄. Diethyl ether was removed in vacuo to leave a white solid, which was recrystallised from hexane to yield 163 as white crystalline needles (6.33 g, 64%). m.p 84 °C (lit. 81-83 °C). m/z (EI) 240 (M⁺, 40%, 81Br, 81Br), 238 (M⁺, 84%, 81Br, 79Br), 236 (M⁺, 44%, 79Br, 79Br). δH (CDCl₃) 8.63 (s, 2H). δC (CDCl₃) 119.70, 150.84, 159.90.

5-Bromo-2-phenylpyrimidine 165 and 2,5-Diphenylpyrimidine 166

In accordance with the general method for Suzuki cross-coupling reactions; 2,5-dibromopyrimidine 163 (190 mg, 0.80 mmol), benzeneboronic acid 164 (293 mg, 2.4 mmol), THF (15 cm³), Pd(PPh₃)₄ (40 mg) and Na₂CO₃ (1M, degassed, 2.0 cm³). After cooling to 20 °C, THF was evaporated and the resulting aqueous suspension of compounds 165 and 166 was suction filtered to obtain a white solid which was washed with water then hexane. Chromatography (eluent DCM-hexane 1:1 v/v) gave a colourless solid which was recrystallised from toluene to yield 2,5-diphenylpyrimidine 166 as colourless crystals (60 mg, 32%), m.p 185.0-185.5 °C (lit. 180-181 °C). m/z (EI) 232 (M⁺, 100%). δH (500 MHz, CDCl₃) 7.45 (t, 2H, J = 8.0 Hz), 7.52 (m, 4H), 7.64 (d, 2H, J = 8.0 Hz), 8.50 (dd, 2H, J = 2.0, 7.58 Hz), 9.03 (s, 2H). δC (500 MHz, CDCl₃) 127.07, 128.11, 128.76, 129.55, 130.70, 155.41, 155.91.

The combined mother toluene liquor and DCM-hexane eluent (apart from the DCM-hexane solution of product 166) was evaporated and the residue was chromatographed (eluent DCM-hexane 1:1 v/v) gave to yield 165 as a white solid which was recrystallised from ethanol to yield 165 as a white crystalline solid (80 mg, 43%), m.p 104.0-104.6 °C, (lit. 103b, 104-105 °C). m/z (EI) 234 (M⁺ [79Br], 100%), 236 (M⁺ [79Br], 93%). δH (500 MHz, CDCl₃) 7.50 (m, 3H),
Experimental Procedures

8.40 (m, 2H), 8.84 (s, 2H). δ_C (500 MHz, CDCl_3) 118.29, 128.13, 128.69, 131.12, 136.45, 157.82, 162.84.

2,7-Dibromo-9,9-dihexylfluorene 168

2,7-Dibromofluorene 167 (3.24 g, 10 mmol) and bromohexane (7.0 cm³, 50 mmol) were added to freshly distilled THF (80 cm³), which was subsequently cooled to 0 °C. Potassium tert-butoxide (1M 10 cm³) was added slowly with stirring (30 min) resulting in a pink suspension. After stirring at 0 °C for 1 h an additional portion of potassium tert-butoxide (1M, 10.5 cm³) was added and the solution was stirred at 20 °C overnight. THF was removed _in vacuo_, dry DCM (100 cm³) was added and the inorganic salts were removed by filtration. The organic solution was concentrated and purified by chromatography (eluent hexane) to give a light yellow oil, which was recrystallised from ethanol to yield white plates of compound 168 (4.1 g, 83%), mp 72-73 °C (lit 67.5-68.5 °C).  97b Anal. calcd. for C_{25}H_{32}Br_2 C, 60.99, H, 6.60. Found: C, 60.89, H, 6.60%. m/z (EI) 490 (M⁺, 79 Br, 79 Br, 13%), 492 (M⁺, 79 Br, 81 Br, 100%), 494 (M⁺, 81 Br, 81 Br, 13%). δ_H (500 MHz, CDCl₃) 0.59 (m, 4H), 0.79 (m, 6H), 1.10 (m, 12H), 1.93 (m, 4H, CH₂-C(Ar)₂-CH₂), 7.46 (m, 4H), 7.53 (m, 2H). δ_C (500 MHz, CDCl₃) 13.98, 22.56, 23.61, 29.56, 31.44, 40.17, 55.65, 121.09, 121.43, 126.12, 130.10, 139.01, 152.50.

9,9-Dihexylfluorene-2,7-diboronic acid 169

To a solution of 168 (2.46 g, 5.00 mmol) in dry THF (10 cm³) was added _n_-butyllithium solution in hexane (1.6M, 6.8 cm³, 11.04 mmol) dropwise at −78 °C. The mixture was stirred at −78 °C under argon for an additional 6 h to give a white suspension. Triisopropyl borate (5.0 cm³) was syringed in quickly at −78 °C and the mixture was stirred overnight with a cooling bath allowing the temperature to rise gradually to 20 °C. Water (30 cm³) was added to the white suspension and the mixture was stirred at 20 °C for a further 4 h. THF was removed _in vacuo_. Water (100 cm³) was added and the product extracted into diethyl ether (3x 50 cm³) and dried (MgSO₄). Diethyl ether was removed _in vacuo_ giving a white solid, which was recrystallised from acetonitrile to yield a white crystalline solid 169 (1.68 g, 80%), mp 297-298 °C (lit 294-295 °C). 106c Anal. calcd. for C_{25}H_{32}B₂O₄ C, 71.12, H,
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8.60. Found C, 71.62, 8.70%. δ _H_ (400 MHz, DMSO-d6) 0.45 (s, 4H), 0.68 (m, 6H, J = 6.6 Hz), 0.98 (m, 12H), 1.93 (m, 4H, CH2-C(Ar)2-CH2), 7.73 (m, 4H, J = 1.8 Hz) 7.81 (s, 2H) 8.00 (s, 4H). δ _C_ (400 MHz, DMSO-d6) 13.78, 21.95, 23.43, 29.00, 30.93, 54.17, 119.01, 128.37, 132.88, 142.31, 149.36.

2,7-Bis(2-pyrimidyl)-9,9-dihexylfluorene 172

In accordance with the general method for Suzuki cross-coupling reactions: 2-bromopyrimidine 170 (0.28 g, 1.78 mmol), 9,9-dihexylfluorene-2,7-diboronic acid 169 (0.25 g, 0.60 mmol), THF (30 cm³), Pd(PPh3)4 (69.35 mg) and Na2CO3 (1 M, degassed, 2.5 cm³). Followed by column chromatography (eluent DCM: ethyl acetate 9:1 v/v) to yield compound 172 as a yellow solid (100 mg, 34%), mp 155.1-156.9 °C. m/z (EI) 490 (M⁺, 100%). HRMS (EI) (M⁺) 490.3094 (calcd. for C33H38N4: 490.3096).

UV-Vis Amax 317.0, 337.5, 352.5 nm, PL Amax 366, 384 nm.

2,7-Bis(5-pyrimidyl)-9,9-dihexylfluorene 173

By analogy with the synthesis of 172. 5-bromopyrimidine 171 (0.28 g, 1.78 mmol), 9,9-dihexylfluorene-2,7-diboronic acid 169 (0.25 g, 0.60 mmol), THF (30 cm³), Pd(PPh3)4 (69.35 mg) and Na2CO3 (1 M, degassed, 2.5 cm³). Followed by column chromatography (eluent DCM: ethyl acetate 9:1 v/v) to yield compound 173 as a yellow solid (93 mg, 32%), mp 157-157.8 °C. m/z (EI) 490 (M⁺, 100%). HRMS (EI) (M⁺) 490.3101 (calcd. for C33H38N4: 490.3096). δ _H_ (400 MHz, CDCl3) 0.65 (m, 10H), 1.00 (m, 12H), 2.01 (m, 4H, CH2-C(Ar)2-CH2), 7.50 (s, 2H), 7.53 (d, 2H, J = 8.0 Hz), 7.81 (d, 2H, J = 4.9 Hz). δ _C_ (400 MHz, CDCl3) 13.95, 22.56, 23.71, 29.69, 31.48, 40.36, 55.55, 118.84, 120.35, 122.44, 127.40, 136.75, 143.28, 152.07, 157.23, 164.97. UV-Vis λmax 317.0, 337.5, 352.5 nm, PL λmax 366, 384 nm.
2,7-Bis(5-bromo-2-pyrimidyl)-9,9-dihexylfluorene 174

By analogy with the synthesis of 172. 2,5-dibromopyrimidine 163 (0.28 g, 1.78 mmol), 9,9-dihexylfluorene-2,7-diboronic acid 169 (0.25 g, 0.60 mmol), THF (30 cm³) Pd(PPh₃)₄ (69.0 mg) and Na₂CO₃ (1 M, degassed, 2.5 cm³). Followed by column chromatography (eluent DCM: petroleum ether, 9:1 v/v) giving a white solid, which was recrystallised from hexane to yield compound 174 as white needles (87 mg, 23%). m.p 179.3-179.8°C. m/z (EI) 646 (M⁺, 79 Br, 79 Br, 46%), 648 (M⁺, 79 Br, 81 Br, 100%), 648 (M⁺, 81 Br, 81 Br, 13%). HRMS (EI) (M⁺) 646.1304 (calcd. for C₃₃H₃₆Br₂N₄: 646.1306).

δ_H (500 MHz, CDCl₃) 0.71 (m, 10H), 1.07 (m, 12H), 2.12 (m, 4H, CH₂-C(Ar)₂-CH₂), 7.85 (d, 2H, J = 8.5 Hz), 8.41 (s, 2H), 8.47 (d, 2H, J = 8.2 Hz), 8.86 (s, 4H). δ_C (500 MHz, CDCl₃) 13.96, 22.55, 23.81, 29.66, 31.48, 40.28, 55.55, 117.95, 120.48, 122.51, 127.48, 135.86, 143.45, 152.18, 157.78, 163.08. UV-Vis λ_max 348.0, 365.0 nm, PL λ_max 377, 396 nm.

2,7-Bis(5-phenyl-2-pyrimidyl)-9,9-dihexylfluorene 175

A solution of 2,7-bis(5-bromo-2-pyrimidyl)-9,9-dihexylfluorene 174 (100 mg, 0.154 mmol), benzeneboronic acid 164 (60 mg, 0.46 mmol), THF (30 cm³), Pd(PPh₃)₄ (53.5 mg) and Na₂CO₃ (1 M, degassed, 2.0 cm³). Followed by column chromatography (eluent DCM: petroleum ether 4:1 v/v) yielded compound 175 as a white/yellow solid (35 mg, 35%), m.p 185.5-186.5°C. m/z (EI) 642 (M⁺, 100%). HRMS (EI) (M⁺) 642.3719 (calcd. for C₄₅H₴₆N₄: 642.3722). δ_H (400 MHz, CDCl₃) 0.71 (m, 10H), 1.07 (m, 12H), 2.19 (m, 4H, CH₆-C(Ar)₂-CH₂), 7.47 (m, 2H), 7.54 (t, 4H, J = 7.0 Hz), 7.65 (d, 4H, J = 11.50 Hz), 7.91 (d, 2H, J = 8.0 Hz), 8.53 (s, 2H), 8.58 (d, 2H, J = 8.0 Hz), 9.07 (s, 4H). δ_C (400 MHz, CDCl₃) 13.96, 22.57, 23.85, 29.72, 31.53, 40.41, 55.58, 120.41, 122.38, 126.70, 127.40, 129.40, 131.38, 134.59, 136.54, 143.28, 152.12, 155.17, 163.69. UV-Vis λ_max 365.5, 371.5 nm, PL λ_max 391, 412 nm.
5.3 Experimental Procedures of Chapter 3

Pyrazine-2,3-dicarboxylic acid anhydride 182

Pyrazine-2,3-dicarboxylic acid 181 (49.8 g, 0.30 mole) was added to acetic anhydride (128 cm$^3$) and heated under reflux for 2 h. Once the solution was a dark brown colour refluxing was continued for an additional 10 min. The mixture was then cooled in an ice bath. The product was separated by filtration and washed with diethyl ether (3 x 50 cm$^3$) to yield 182 as white needles (40.8 g, 92%), mp 218-219 °C (lit 125 221-222 °C). m/z (EI) 150 (M$^+$, 100%). $\delta_H$ (250 MHz DMSO-d$_6$) 9.19 (s, 2H). $\delta_C$ (250 MHz DMSO-d$_6$) 146.09, 151.56, 166.84.

Pyrazine-2-carboxylic acid-3-methyl ester 183

Pyrazine-2,3-dicarboxylic acid anhydride 182 (38.8 g, 0.26 moles) was added to methanol (125 cm$^3$). The resultant yellow solution was stirred at 20 °C overnight. Methanol was evaporated revealing a white solid, which was dissolved in ethyl acetate and purified by chromatography (eluent ethyl acetate). The organic solvent was removed in vacuo and the resulting white solid recrystallised from toluene to yield 183 as a white crystalline solid (41.7 g, 89%), mp 115.9-117.8 °C (lit 125 115-116 °C). m/z (EI) 182 (M$^+$, 100%). $\delta_H$ (250 MHz DMSO-d$_6$) 3.95 (s, 3H), 9.01 (d, 2H, $J = 12.3$ Hz). $\delta_C$ (250 MHz DMSO-d$_6$) 53.02, 144.51, 144.72, 145.93, 146.10, 164.99, 165.57.

Methyl-3-aminopyrazine carboxylate 186

Pyrazine-2-carboxylic acid-3-methyl ester 183 (38.52 g, 0.21 moles) was added to SOCl$_2$ (43 cm$^3$), and the mixture heated under reflux for 2 h followed by a second addition of SOCl$_2$ (2.6 cm$^3$) and reflux for an additional 1 h. The excess SOCl$_2$ was removed by distillation with toluene (3 x 25 cm$^3$) leaving a brown oil. Acetone (analytical grade, 100 cm$^3$) was added followed by NaN$_3$ (33.5 g, 0.48 moles) dissolved in H$_2$O (110 cm$^3$), which was added in portions over 1 h. Water (90 cm$^3$) was
added and the mixture was stirred at 0 °C for 18 h. The organic portion was extracted into benzene (4 x 50 cm³) and the combined extracts heated under reflux for 24 h. Benzene was removed in vacuo and the resulting, yellow solid was dissolved in methanol and filtered via a celite bed whilst hot. Upon filtration, the product crystallized. The product was therefore directly recrystallised from the mother liquor and separated by filtration to yield 186 as golden yellow needles (10.83 g 33%), mp 170.3-171.1 °C (lit125 172-173 °C). m/z (EI) 95 (M+, 100%) 153 (M⁺, 64%). δ H (250 MHz DMSO-d₆) 3.96 (s, 3H), 7.43 (s, 2H), 7.93 (d, 1H, J= 2.2 Hz), 8.26 (d, 1H, J= 2.0 Hz). δ C (250 MHz DMSO-d₆) 52.06, 123.13, 132.43, 147.77, 155.84, 166.43.

2-Amino-5-bromopyrazine-3-carboxylic acid methyl ester 187

Method 1

3-Aminopyrazine carboxylic acid methyl ester 186 (3.00 g, 1.95 mmol) was added to warm glacial acetic acid (16.5 cm³). Bromine (1.05 cm³, 2.00 mmol) was added dropwise during 15 min and the reaction mixture was allowed to stand at 20 °C for 30 min. The reaction mixture was washed with K₂CO₃ (aq), then extracted into ethyl acetate and dried (MgSO₄). Purification by chromatography (eluent DCM-ethyl acetate 3:1 v/v) gave a yellow solid, which was recrystallised from ethanol. An insoluble impurity was removed by hot filtration. The product, which precipitated from the filtrate, was recrystallised from the ethanol mother liquor to yield long yellow needles of 187 (1.63 g, 36%), mp 172-173.5 °C (lit126 175.3-175.9 °C). Spectroscopic data were identical to those obtained by method 2.

Method 2

3-Aminopyrazine carboxylic acid methyl ester 186 (10.0 g, 65.3 mmol) was dissolved in DMF (79 cm³), to which a solution of NBS (11.6 g, 65.3 mmol) in DMF (77 cm³) was added and the mixture was stirred overnight at 20 °C. Sodium metabisulfite (2.9 g) dissolved in H₂O (73 cm³) was added, a precipitate formed immediately. Water (60 cm³) was added and the crude product was extracted into DCM (250 cm³) and dried over MgSO₄. Purification by column chromatography (eluent
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DCM-diethyl ether 1:1 v/v). Solvent was removed in vacuo leaving pale a yellow solid, which was recrystallised from ethanol to yield 187 as long yellow needles (12.4 g, 82%), mp 175.4-176.7 °C (lit\textsuperscript{126} 175.3-175.9 °C). m/z (EI) 231 (M\textsuperscript{+}, 79 Br, 78%), 233 (M\textsuperscript{+}, 81 Br, 76%). δ\textsubscript{H} (250 MHz DMSO-d\textsubscript{6}) 3.96 (s, 3H), 7.54 (s, 2H), 8.46 (s, 1H). δ\textsubscript{C} (250 MHz DMSO-d\textsubscript{6}) 52.27, 122.34, 122.59, 150.05, 154.88, 165.30.

2-Amino-5-bromopyrazinoic acid 188

2-Amino-5-bromopyrazine carboxylic acid methyl ester 187 (10.0 g, 43 mmol) was added to NaOH (5% aq) (200 cm\textsuperscript{3}) and heated under reflux for 2 h. The mixture was acidified with HBr (48% aq, 28 cm\textsuperscript{3}). The product 188 that precipitated was recrystallised from the aqueous mother liquor and isolated as green needles (7.30 g, 78%), mp 182.1-182.3 °C (lit\textsuperscript{126} 184-186 °C). m/z (EI) 217 (M\textsuperscript{+}, 79 Br, 65%), 219 (M\textsuperscript{+}, 81 Br, 65%). δ\textsubscript{H} (250 MHz DMSO-d\textsubscript{6}) 7.60 (s, 2H), 8.41 (s, 1H). δ\textsubscript{C} (250 MHz DMSO-d\textsubscript{6}) 122.45, 123.30, 149.61, 155.16, 166.90.

2-Amino-5-bromopyrazine 189

Method 1

2-Amino-5-bromopyrazinoic acid 188 (4.55 g, 20 mmol) was added to tetralin (35 cm\textsuperscript{3}) and heated under reflux for 2.5 h. Petroleum ether (bp 100-120 °C) (20 cm\textsuperscript{3}) was added causing product precipitation, which was separated by filtration, then dissolved in diethyl ether and purified by chromatography (eluent diethyl ether) to give a yellow solid, which was recrystallised from toluene / petroleum ether to yield 189 as yellow crystals (2.45 g, 67%), mp 113.7-115.0 °C (lit\textsuperscript{126} 113 °C). Data were identical to that obtained by method 2.

Method 2

Aminopyrazine 190 (5.00 g, 52.5 mmol) was added to DCM (150 cm\textsuperscript{3}), which had previously been cooled to 0 °C. NBS (9.40 g, 52.5 mmol) was added and the reaction mixture was stirred at 0 °C for 20 h. Saturated Na\textsubscript{2}CO\textsubscript{3} (aq) was added followed by water (50 cm\textsuperscript{3}). The organic component was then
washed with water, dried (MgSO₄), then concentrated under reduced pressure and purified by
column chromatography (eluent DCM-ethyl acetate, 1:1 v/v) to give a yellow solid which was
recrystallised from toluene / petroleum ether (bp 100-120 °C) to yield 189 as golden needles
(3.25 g, 36%), mp 114.3-115.9 °C (Lit¹²⁶ 113 °C). m/z (GCMS)172.9 (¹⁷⁹Br), 174.9 (¹⁸¹Br). δ_H
(400 MHz CDCl₃) 4.68 (s, 2H), 7.76 (d, 1H, J = 1.6 Hz), 8.07 (d, 1H, J = 1.6 Hz). δ_C (400
MHz CDCl₃) 127.06, 131.76, 144.12, 153.37.

2,5-Dibromopyrazine 191

HBr solution (48% aq 5 cm³) was cooled to 0 °C. 2-Amino-5-bromopyrazine
189 (0.5 g, 2.87 mmol) was added in small portions with stirring until a clear
solution was obtained. Bromine (0.2 cm³, 3.90 mmol) was added dropwise over a 20 min
period. The reaction was stirred at 0 °C for 30 min. NaN₃O (0.91 g, 13.2 mmol) dissolved in
water (1.5 cm³) was added dropwise ensuring that the internal reaction flask temperature did
not rise above 0 °C. After stirring for 30 min, Na₂SO₃ (0.63 g, 5.00 mmol) dissolved in water
(6.5 cm³) was added again whilst maintaining a reaction temperature below 0 °C. The
solution was made alkaline (pH 9) with the addition of 10% Na₂CO₃ (aq) and extracted into
diethyl ether (3 x 25 cm³). The combined organic extracts were dried (MgSO₄) and the
solvent removed in vacuo to yield 191 as a yellow solid (100 mg, 15%), mp 40-42 °C (lit¹²⁶
38-44 °C). δ_H (200 MHz CDCl₃) 8.47 (s, 2H). δ_C (200 MHz CDCl₃) 139.25, 147.46. This
reaction proved to be capricious, and on some occasions no pure product could be isolated.

2-Amino-5-chloropyrazine carboxylic acid methyl ester 193

3-Aminopyrazine carboxylic acid methyl ester 186 (10.0 g, 53.3 mmol)
was added to a mixture of glacial acetic acid (69 cm³) and H₂O (292 cm³).
The reaction mixture was heated to give a clear yellow solution. With
external cooling Cl₂ (g) was bubbled into the solution for 10 min forming a white solid. The
resulting chloroamine 192 was isolated by filtration and added to a solution of sodium
bisulfite (10.73 g) in H₂O (65 cm³). The white suspension was stirred at 20 °C for 1.5 h. A
light yellow solid was isolated by filtration and washed with water and isopropyl alcohol and
identified as 193 (5.40 g, 56%), mp 158-159 °C (lit¹²⁹ 159-161 °C). m/z (GCMS) 186.9 (¹⁵Cl),
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188.8 (13Cl). δH (500 MHz DMSO-d6) 3.83 (s, 3H), 7.54 (s, 2H), 8.37 (s, 1H). δC (500 MHz DMSO-d6) 52.35, 120.97, 132.74, 147.65, 154.79, 165.40.

2-Amino-5-chloropyrazinoic acid 194

Cl
N
CO2H

2-Amino-5-chloropyrazine carboxylic acid methyl ester 193 (5.21 g, 30 mmol) was added to NaOH (10% aq) solution (50 cm3) and heated under reflux for 1.5 h. The sodium salt was removed by filtration and dissolved in water (30 cm3), boiled then acidified with conc HCl precipitating 194 as yellow needles (4.03 g, 84%), mp 179-180 °C (lit13o 177-180 °C). m/z (GCMS) 172.9 (13Cl), 174.8 (37Cl). δH (300 MHz DMSO-d6) 7.54 (s, 2H), 8.34 (s, 1H). δC (500 MHz DMSO-d6) 121.94, 132.58, 147.24, 155.07, 167.01.

2-Amino-5-chloropyrazine 195

Cl
N
NH2

2-Amino-5-chloropyrazine acid 194 (3.18 g, 18.32 mmol) was added to tetralin (48 cm3) and heated under reflux for 2.5 h. The solution was cooled in an ice bath for 1 h. 195 was isolated as a yellow solid (1.75 g, 74%), mp 130-131 °C (lit13o 129-130 °C). m/z (GCMS) 128.9 (13Cl), 130.8 (37Cl). δH (500 MHz CDCl3) 4.61 (s, 2H), 7.76 (d, 1H, J = 0.5 Hz), 8.01 (d, 1H, J = 0.5 Hz). δC (500 MHz CDCl3) 130.72, 137.52, 141.36, 153.09.

3-Chloropyrazine-1-Oxide 199

O
N
Cl

Chloropyrazine 198 (5.50 cm3, 61.2 mmol) was added to a solution of glacial acetic acid (18.5 cm3) and hydrogen peroxide (aq 35%) (10.5 cm3) and refluxed for 17 h. The reaction volume was reduced by 50% and diluted with an equal volume of water. The product was extracted into chloroform (3 x 25 cm3) and dried (MgSO4). Solvent was evaporated in vacuo to give a white solid, which was recrystallised from ethanol to yield 199 as white needles (3.97 g, 50%), mp 97-99 °C (lit131 95-96 °C). m/z (EI) 130 (M+ 35Cl, 100%), 132 (M+ 35Cl, 47%). δH (400 MHz CDCl3) 8.02 (dd, 1H, J = 4.0, 1.0 Hz), 8.15 (d, 1H, J = 0.5 Hz), 8.25 (d, 1H, J = 4.0 Hz). δC (400 MHz CDCl3) 133.18, 133.51, 145.97, 151.77.
2,5-Dichloropyrazine 197

3-Chloropyrazine-1-oxide 197 (2.00 g, 15.32 mmol) was added to POCl₃ (5.0 cm³) and refluxed for 1 h. The solution was cooled to 20 °C and poured cautiously onto crushed ice with good stirring. The product was extracted with DCM (3 x 25 cm³) washed with water (50 cm³) and 5% NaHCO₃ (50 cm³), dried (MgSO₄). Solvent was removed under reduced pressure and the product was purified by chromatography (eluent DCM) to give a colourless oil (0.23 g). m/z (GCMS) 147.9 (35Cl, 35Cl), 149.8 (35Cl, 37Cl), 151.7 (37Cl, 37Cl). δ_H (400 MHz CDCl₃) 8.32 (s, 2H), 8.39 (s, 2H), 8.52 (s, 2H). δ_C (400 MHz CDCl₃) 141.76, 142.43, 143.79, 147.83, 148.03. These NMR data showed that the product was a mixture of isomers 197, 200 and 201 see page 74.

2-Amino-5-phenylpyrazine 202

In accordance with the general method for Suzuki cross-coupling reactions. 2-amino-5-bromopyrazine 189 (1.00 g, 5.75 mmol), benzeneboronic acid 164 (0.84 g, 6.29 mmol), THF (30 cm³), Pd(PPh₃)₄ (398 mg) and Na₂CO₃ (1 M, degassed, 5 cm³). Followed by column chromatography (eluent DCM-diethyl ether, 1:2 v/v) gave a pale yellow solid which was recrystallised from toluene to yield compound 202 as off-white needles (0.58 g, 59%), mpt 147-149 °C. Anal. calcd. for C₁₀H₉N₃: C, 70.16; H, 5.30; N, 24.54. Found: C, 70.35; H, 5.32; N, 24.41%. m/z (EI) 171 (M⁺, 100%). δ_H (400 MHz CDCl₃) 7.36 (m, 1H), 7.45 (t, 2H, J = 7.2 Hz), 7.87 (d, 2H, J = 7.2 Hz), 8.07 (d, 2H, J = 1.6 Hz), 8.45 (d, 2H, J = 1.6 Hz). δ_C (400 MHz CDCl₃) 125.63, 128.17, 128.82, 131.60, 136.93, 139.01, 142.96, 153.02.

2-Amino-5-(2-methoxyphenyl)pyrazine 204

By analogy with the synthesis of 202, 2-amino-5-bromopyrazine 189 (0.27 g, 1.44 mmol), 2-methoxybenzeneboronic acid 203 (0.26 g, 1.72 mmol), THF (30 cm³), Pd(PPh₃)₄ (99.4 mg) and Na₂CO₃ (1 M, degassed, 4.5 cm³). Followed by column chromatography (eluent DCM-diethyl ether, 1:2 v/v) gave a yellow oil which crystallised under vacuum. This product was recrystallised from toluene / hexane mixture to yield 204 as yellow crystals (0.12 g, 35%), mp 100-102 °C. Anal.
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calcd. for C_{11}H_{11}N_3O: C, 65.66; H, 5.51, N, 20.88. Found: C, 65.55; H, 5.52; N, 20.88%. m/z (GCMS) 201.1. δ_H (400 MHz CDCl₃) 3.85 (s, 3H), 4.69 (s, 2H), 6.98 (d, 1H, J = 7.9 Hz), 7.06 (td, 1H, J = 7.6, 1.2 Hz), 7.33 (ddd, 1H, J = 8.8, 8.0, 7.2 Hz), 7.73 (dd, 1H, J = 7.6, 1.6 Hz), 8.07 (d, 1H, J = 1.6 Hz), 8.58 (d, 1H, J = 1.6 Hz). δ_C (400 MHz CDCl₃) 55.48, 111.20, 121.02, 126.24, 129.36, 130.15, 131.39, 141.13, 143.15, 152.51, 156.60.

2-Amino-5-(4-methoxyphenyl)pyrazine 206

By analogy with the synthesis of 202, 2-amino-5-bromopyrazine 189 (1.00 g, 5.74 mmol), 4-methoxybenzenearboronic acid 205 (1.05 g, 6.89 mmol), THF (30 cm³), Pd(PPh₃)₄ (398 mg) and Na₂CO₃ (1M, degassed, 21.0 cm³). Followed by column chromatography (eluent DCM-diethyl ether, 1:1 v/v) gave a yellow solid which was recrystallised from toluene / petroleum ether (bp 100-120 °C) mixture to yield compound 206 as pale yellow crystals (0.27 g, 23%), mp 98-100 °C. Anal. calcd. for C_{11}H_{11}N_3O: C, 65.66; H, 5.51, N, 20.88. Found: C, 65.64; H, 5.50; N, 21.02%. m/z (GCMS) 201.0. δ_H (400 MHz CDCl₃) 3.85 (s, 3H), 6.98 (d, 2H, J = 8.8 Hz), 7.80 (d, 2H, J = 8.8 Hz), 8.03 (d, 1H, J = 1.6 Hz), 8.39 (d, 1H, J = 1.6 Hz). δ_C (400 MHz CDCl₃) 55.32, 114.21, 126.88, 129.66, 131.39, 138.41, 142.94, 152.60, 159.78.

2,5-Dimethoxy-1,4-benzenediboronic acid 207

To a solution of 1,4-dibromo-2,5-dimethoxybenzene (4.34 g, 14.8 mmol) in dry THF (150 cm³) was added nBuLi solution in hexane (1.6 M, 20.2 cm³, 32.32 mmol) dropwise at −78 °C under argon. The mixture was stirred and allowed to warm to 20 °C over 9 h to give a clear light yellow solution. Triisopropylborate (14.8 cm³) was syringed in quickly at −78 °C and the mixture was stirred for 12 h with a cooling bath allowing the temperature to rise gradually to 20 °C. HCl solution (5%) (30 cm³) was syringed in and the reaction stirred at 20 °C for 0.5 h. THF was evaporated and the white solid was isolated and washed with a large volume of water. The solid was recrystallised from acetonitrile / water mixture to yield 207 as white needles (84 mg, 25%), mp 268 °C (Lit.61 > 250 °C). δ_H (300 MHz DMSO-d₆) 3.72 (s, 6H), 7.10 (s, 2H), 7.75 (s, 4H). δ_C (300 MHz DMSO-d₆) 55.84, 116.86, 124.56, 157.47.
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1,4-Dimethoxy-2,5-bis[2-(5-aminopyrazyl)]benzene 208

By analogy with the synthesis of 202, 2-amino-5-bromopyrazine 189 (0.42 g, 2.44 mmol), 2,5-dimethoxy-1,4-benzenediboronic acid 207 (0.25 g, 1.11 mmol), THF (30 cm³), Pd(PPh₃)₄ (128 mg) and Na₂CO₃ (1 M, degassed, 7.0 cm³). The crude reaction residue was recrystallised from DMF / ethanol to yield 208 as brown crystals (0.20 g, 56%), mp >300 °C. m/z (EI) 324 (M⁺, 100%). HRMS (EI) (M⁺) 324.1338 (calcd., for C₁₆H₁₈N₆O₂ 324.1334). δH (400 MHz DMSO-d₆) 3.81 (s, 6H), 6.51 (s, 4H), 7.49 (s, 2H), 7.98 (d, 2H, J = 1.6 Hz), 8.54 (d, 2H, J = 1.6 Hz). δC (400 MHz DMSO-d₆) 56.71, 113.20, 126.42, 132.11, 137.81, 143.47, 151.13, 154.99.

2,7-Bis[2-(5-aminopyrazyl)]-9,9-dihexylfluorene 209

By analogy with the synthesis of 202, 2-amino-5-bromopyrazine 189 (0.50 g, 2.88 mmol), THF (30 cm³), Pd(PPh₃)₄ (55.5 mg), 9,9-dihexylfluorene-2,7-diboronic acid 169 (0.50 g, 0.50 mmol) and Na₂CO₃ (1 M, aqueous, degassed, 5.0 cm³). Followed by column chromatography [eluent ethyl acetate-petroleum ether (bp 40-60 °C) 1:1 v/v] gave a golden solid which was recrystallised from toluene / hexane mixture to yield compound 209 as pale golden crystals (0.32 g, 51%), mp 161.5-163.5 °C. m/z (ES⁺) 521.3, 543.3 (M⁺, Na). HRMS (ES⁺) (M⁺) 521.3387 (calcd. for C₃₃H₄₁N₆ 521.3393). δH (400 MHz CDCl₃) 0.71 (m, 1OH), 1.04 (m, 12H), 2.06 (m, 4H, CH₂-C(Ar)₂-CH₂), 4.68 (s, 4H), 7.80 (d, 2H, J = 8.8 Hz), 7.87 (m, 4H), 8.10 (d, 2H, J = 1.6 Hz), 8.53 (d, 2H, J = 1.2 Hz). δC (400 MHz CDCl₃) 13.95, 22.55, 23.77, 29.67, 31.46, 40.40, 55.41, 119.90, 120.15, 124.46, 131.43, 135.87, 139.22, 140.84, 143.37, 151.86, 152.91.

1,4-Dimethoxy-2,5-bis(2-pyrazyl)benzene 210

By analogy with the synthesis of 202, iodopyrazine (0.62 g, 3.00 mmol), 2,5-dimethoxy-1,4-benzenediboronic acid 207 (0.23 g, 1.00 mmol), THF (30 cm³), Pd(PPh₃)₄ (116 mg) and Na₂CO₃ (1 M, degassed, 6.0 cm³). The product was isolated as white needles by filtration of the reaction
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mother liquor and washed with a large amount of water to yield 210 (0.35 g, 84%), mp 235-237 °C. m/z (El) 294 (M⁺, 74%), 277 (M⁺, 100%). HRMS (El) (M⁺) 294.1110 (calcd. for C₁₆H₁₄N₄O₂ 294.1116). δH (400 MHz DMSO-d₆) 3.88 (s, 6H), 7.61 (s, 2H), 8.59 (d, 2H, J = 2.4 Hz), 8.77 (dd, 2H, J = 2.4, 1.6 Hz), 9.18 (d, 2H, J = 2.4 Hz). δC (400 MHz DMSO-d₆) 56.27, 114.43, 127.06, 142.59, 143.95, 145.26, 149.94, 151.08.

1,4-Dimethoxy-2,5-bis(2-pyrimidyl)benzene 211

By analogy with the synthesis of 202, 2-bromopyrimidine 170 (0.48 g, 3.00 mmol), 2,5-dimethoxy-1,4-benzenediboronic acid 207 (0.23 g, 1.00 mmol), THF (30 cm³), Pd(PPh₃)₄ (116 mg) and Na₂CO₃ (1 M, degassed, 6.0 cm³) and preparative tlc (eluent ethyl acetate-acetonitrile 1:1 v/v) gave 211 as a pale green solid (56 mg, 19 %), mp 232-234 °C. m/z (El) 294 (M⁺, 100%). HRMS (El) (M⁺) 294.1117 (calcd. for C₁₆H₁₄N₄O₂ 294.1116). δH (400 MHz DMSO-d₆) 3.73 (s, 6H), 7.33 (s, 2H), 7.46 (t, 2H, J = 4.8 Hz), 8.90 (d, 4H, J = 4.8 Hz). δC (400 MHz DMSO-d₆) 57.10, 116.21, 120.30, 130.73, 151.66, 157.97, 165.18.

1,4-Dimethoxy-2,5-bis[2-(5-bromopyridyl)]benzene 212

By analogy with the synthesis of 202, 2,5-dibromopyridine (0.94 g, 3.98 mmol), 2,5-dimethoxy-1,4-benzenediboronic acid 207 (0.30 g, 1.33 mmol), THF (30 cm³), Pd(PPh₃)₄ (154 mg), Na₂CO₃ (1 M, degassed, 8.0 cm³). Followed by column chromatography (eluent DCM-hexane 1:1 v/v) gave a yellow solid which was recrystallised from a toluene / hexane mixture to yield 212 as a yellow solid (0.13 g, 22%), mp 192-194 °C. m/z (El) 448 (M⁺, 50%, ₇⁹Br, ₇⁹Br), 450 (M⁺, 100%, ₇⁹Br, ₈¹Br), 452 (M⁺, 49%, ₈¹Br, ₈¹Br). HRMS (El) (M⁺) 447.9421 (calcd. for C₁₆H₁₄Br₂N₂O₂ 447.9422). δH (400 MHz CDCl₃) 3.91 (s, 6H), 7.57 (s, 2H), 7.83 (dd, 2H, J = 8.4, 2.4 Hz), 7.92 (dd, 2H, J = 8.4, 0.8 Hz), 8.75 (dd, 2H, J = 2.4, 0.8 Hz). δC (500 MHz CDCl₃) 56.24, 114.21, 119.11, 126.47, 128.78, 138.37, 150.35, 151.36, 153.54.
1,4-Dimethoxy-2,5-bis[2-(5-bromopyrimidyl)]benzene 213

By analogy with the synthesis of 202, 2,5-dibromopyrimidine 163 (0.47 g, 2.00 mmol), 2,5-dimethoxy-1,4-benzenediboronic acid 207 (0.15 g, 0.70 mmol), THF (30 cm³), Pd(PPh₃)₄ (70 mg) and Na₂CO₃ (1 M, degassed, 4.0 cm³) and chromatography [eluent DCM-Petroleum ether (bp 40-60) 9:1 v/v] gave 213 as a white solid (75 mg, 25%), mp 153-154 ºC. m/z (EI) 450 (M⁺, 44%, 79 Br, 79 Br), 452 (M⁺, 84%, 79 Br, 81 Br), 454 (M⁺, 40%, 81 Br, 81 Br). HRMS (EI) (M⁺) 449.9333 (calcd. for C₁₆H₁₂Br₂N₄O₂ 449.9326). δH (500 MHz CDCl₃) 3.92 (s, 6H), 7.53 (s, 2H), 8.92 (s, 4H). δC (500 MHz CDCl₃) 57.26, 116.62, 118.63, 129.65, 152.26, 157.90, 163.34.

2,7-Bis(2-pyrazyl)-9,9-dihexylfluorene 214

By analogy with the synthesis of 202, iodopyrazine (0.37 g, 0.60 mmol), 9,9-dihexylfluorene-2,7-diboronic acid 169 (0.25g, 0.60 mmol), THF (30 cm³), Pd(PPh₃)₄ (68 mg) and Na₂CO₃ (1 M, degassed, 3.0 cm³). Followed by column chromatography (eluent DCM-ethyl acetate, 9:1 v/v) gave 214 as a yellow oil (0.35 g, 40%). m/z (EI) 490 (M⁺, 79%), 405 (M⁺, 100%). HRMS (EI) (M⁺) 490.3076 (calcd. for C₃₃H₃₈N₄ 490.3096). δH (500 MHz CDCl₃) 0.71 (m, 10H), 1.05 (m, 12H), 2.04 (m, 4H, CH₂-C(Ar)₂-CH₂), 7.88 (d, 2H, J = 7.5 Hz), 8.05 (m, 4H), 8.52 (d, 2H, J = 2.5 Hz), 8.68 (dd, 2H, J = 2.5, 1.5 Hz), 9.12 (d, 2H, J = 1.5 Hz). δC (500 MHz CDCl₃) 14.21, 22.80, 24.08, 29.90, 31.73, 40.60, 55.94, 121.00, 121.59, 126.28, 135.86, 142.46, 142.53, 142.86, 144.44, 152.56, 153.34.

2,5-Dimethylpyrazine-N,N-Dioxide 216

2,5-Dimethylpyrazine 215 (2.65 g, 24.5 mmol) was dissolved in acetic acid (15 cm³). Hydrogen peroxide (35%) (25 cm³) was added and the solution heated at 80 ºC for 24 h. Solvent was removed in vacuo to give a white solid. Methanol (25 cm³) was added and the residue was heated vigorously for 2 h, then cooled to 20 ºC and the white solids were isolated by suction filtration and washed with a large volume of methanol. The white solids were then recrystallised from an acetic acid /
methanol mixture to yield 216 as white crystals (1.72 g, 50%). mp 283-284 °C (lit.138 280 °C). m/z (EI) 140 (M+, 100%). δ_H (500 MHz, D_2O) 2.40 (s, 6H), 8.46 (s, 2H). δ_C (500 MHz, D_2O) 14.06, 136.42, 146.29.

**2,5-Dichloro-3,6-dimethylpyrazine 217**

2,5-Dichloro-3,6-dimethylpyrazine 217 (4.60 g, 25.80 mmol) was added to PBr_3 (23 cm³) and the mixture was heated under reflux for 4 days. The excess PBr_3 was removed by vacuum distillation. With external cooling, water (75 cm³) was added slowly to the white/pink residue, which was extracted into DCM (3 x 50 cm³). The organic layer was dried (MgSO₄) then concentrated under reduced pressure and purified by chromatography (eluent diethyl ether) to give 219 as a yellow solid (3.22 g, 47%), mp 79-81 °C (lit. 140 80-81 °C). m/z (GCMS) (EI) 263.8 (M+ 79 Br), 265.8 (M+ 79 Br, 81 Br), 267.7 (M+ 79 Br, 81 Br), 268.9 (M+ 81 Br). δ_H (400 MHz, CDCl₃) 2.62 (s, 6H). δ_C (400 MHz, CDCl₃) 22.96, 138.77, 152.41.

**2,5-Dibromo-3,6-dimethylpyrazine 219**

2,5-Dibromo-3,6-dimethylpyrazine 219 (0.10 g, 0.38 mmol), benzeneboronic acid 164 (0.18 g, 1.50 mmol), THF (30 cm³), Pd(PPh₃)₄ (173 mg) and Na₂CO₃ (1 M, degassed, 7.5 cm³). Followed by column chromatography (eluent DCM) gave
221 as a white solid (69 mg, 70%), mp 178-180 °C. \( m/z \) (EI) 260 (M⁺ 100%). \( \delta_H \) (400 MHz, CDCl₃) 2.65 (s, 6H), 7.48 (m, 6H), 7.63 (m, 4H). \( \delta_C \) (400 MHz, CDCl₃) 22.62, 128.44, 128.56, 129.02, 138.66, 147.82, 151.04.

2,5-Bis(2-methoxyphenyl)-3,6-dimethylpyrazine 222

By analogy with the synthesis of 202, 2,5-dibromo-3,6-dimethylpyrazine 219 (0.10 g, 0.38 mmol), 2-methoxybenzeneboronic acid 203 (0.14 g, 0.94 mmol), THF (30 cm³), Pd(PPh₃)₄ (109 mg) and Na₂CO₃ (1 M, degassed, 6.0 cm³) and chromatography (eluence DCM) gave 222 as a yellow solid (92 mg, 76%), mp 232-236 °C. \( m/z \) (EI) 320 (M⁺, 100%). HRMS (EI) (M⁺) 320.1524 (calcd. C₂₀H₂₀N₂O₂ 320.1524). \( \delta_H \) (500 MHz, CDCl₃) 2.42 (s, 6H), 3.83 (s, 6H), 7.00 (d, 2H, \( J = 8.5 \) Hz), 7.10 (t, 2H, \( J = 7.0 \) Hz), 7.38 (d, 2H, \( J = 7.0 \) Hz), 7.42 (t, 2H, \( J = 7.0 \) Hz). \( \delta_C \) (500 MHz, CDCl₃) 21.51, 55.32, 110.76, 120.95, 128.22, 130.00, 130.89, 149.43, 149.48, 156.67.

2,5-Bis(2-methoxyphenyl)-3,6-dimethylpyrazinium bis(tetrafluoroborate) salt 223

To a solution of 2,5-bis(2-methoxyphenyl)-3,6-dimethylpyrazine 222 (10 mg) in chloroform (10 cm³) was added a few drops of tetrafluoroboric acid. After 1 h at 20 °C the solvent was evaporated and the residue was recrystallised from acetonitrile. After a few days crystals of salt 223 were collected. Anal. cald. for C₂₀H₂₂B₂F₂N₂O₂: C, 48.43; H, 4.47; N, 5.65. Found C, 48.30; H, 4.22; N, 5.85%.

2-Bromo-5-(tert-butylphenyl)-3,6-dimethylpyrazine 224

By analogy with the synthesis of 202, 2,5-dibromo-3,6-dimethylpyrazine 219 (0.90 g, 3.37 mmol), 4-tert-butylbenzeneboronic acid 220 (0.50 g, 2.81 mmol), THF (30 cm³), Pd(PPh₃)₄ (325 mg) and Na₂CO₃ (1 M, degassed, 8.5 cm³) and chromatography (eluence DCM hexane, 1:1 v/v) gave compound 224 as a white solid (0.35 g, 39%), mp 69 °C. \( m/z \) (EI) 319 (M⁺, \(^{81}\)Br 44%), 317 (M⁺, \(^{79}\)Br 44%). HRMS (EI) (M⁺) 318.0726 (calcd.
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C_{16}H_{19}BrN_{2} 318.0731. δ_{H} (500 MHz, CDCl_{3}) 1.35 (s, 9H), 2.59 (s, 3H), 2.68 (s, 3H), 7.49 (s, 4H). δ_{C} (500 MHz, CDCl_{3}) 22.70, 23.38, 31.24, 34.72, 125.50, 128.58, 134.59, 138.40, 149.22, 150.94, 151.54, 152.03.

1,4-Dimethoxy-2,5-bis{2(5-tert-butylphenyl-3,6-dimethylpyrazinyl)benzene} 225

By analogy with the synthesis of 202, 2-bromo-5-(tert-butylphenyl)-3,6-dimethylpyrazine 224 (0.57 g, 1.78 mmol), 2,5-dimethoxy-1,4-benzenediboronic acid 207 (0.17 g, 0.75 mmol), THF (30 cm^3), Pd(PPh_{3})_{4} (77 mg) and Na_{2}CO_{3} (1 M, degassed, 4.5 cm^3) and chromatography (eluent DCM-ethyl acetate, 9.5 : 0.5 v/v) gave compound 225 as a white solid (0.18 g, 16%), mp 348-350 °C. Anal. calcd. for C_{40}H_{46}N_{4}O_{2}: C, 78.14; H, 7.54; N, 9.11. Found: C, 77.98; H, 7.48; N, 9.01%. m/z (EI) 614 (M^{+}, 100%). δ_{H} (500 MHz, CDCl_{3}) 1.37 (s, 18H), 2.49 (s, 6H), 2.69 (s, 6H), 3.83 (s, 6H), 7.04 (s, 2H), 7.58 (d, 4H, J = 8.5 Hz), 7.59 (d, 4H, J = 8.0 Hz). δ_{C} (500 MHz, CDCl_{3}) 21.70, 22.68, 31.31, 34.71, 55.94, 113.82, 125.41, 128.74, 129.07, 135.92, 147.50, 148.61, 150.07, 150.86, 151.48, 151.55.

2-Bromo-5-(2-methoxyphenyl)-3,6-dimethylpyrazine 226

By analogy with the synthesis of 202, 2,5-dibromo-3,6-dimethylpyrazine 219 (1.05 g, 4.00 mmol), 2-methoxybenzeneboronic acid 203 (0.5 g, 3.30 mmol), THF (30 cm^3), Pd(PPh_{3})_{4} (190 mg) and Na_{2}CO_{3} (1 M, degassed, 10.0 cm^3) and chromatography (eluent DCM-petroleum ether (bp 60-80 °C) 9.0 : 1.0 v/v) gave compound 226 as a yellow solid (0.6 g, 52 %), mp 134-135 °C. Anal. calcd. for C_{13}H_{13}BrN_{2}O: C, 53.26; H, 4.47; N, 9.56. Found: C, 53.80; H, 4.48; N, 9.32%. m/z (EI) 292 (M^{+}, ^{79}Br 67%), 294 (M^{+}, ^{81}Br 63%). δ_{H} (400 MHz, CDCl_{3}) 2.28 (s, 3H), 2.60 (s, 3H), 3.72 (s, 3H), 6.90 (d, 1H, J = 8.0 Hz), 7.00 (t, 1H, J = 8.0 Hz), 7.21 (d, 1H, J = 8.0 Hz), 7.35 (t, 1H, J = 8.0 Hz). δ_{C} (400 MHz, CDCl_{3}) 21.12, 23.39, 55.34, 110.89, 121.02, 126.83, 130.47, 130.54, 139.02, 149.93, 150.64, 151.35, 156.47.
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2,5-Bis(6-methoxypyridin-3-yl)-3,6-dimethylpyrazine 229

By analogy with the synthesis of 202, 2,5-dibromo-3,6-dimethylpyrazine 219 (0.10 g, 0.38 mmol), 2-methoxy-5-pyridylboronic acid\textsuperscript{141} 228 (0.14 g, 0.90 mmol), THF (30 cm\textsuperscript{3}), Pd(PPh\textsubscript{3})\textsubscript{4} (103 mg) and Na\textsubscript{2}CO\textsubscript{3} (1M, degassed, 5.50 cm\textsuperscript{3}) and chromatography (eluent initially DCM followed by DCM-ethyl acetate 9.0:1.0 v/v) gave compound 229 off-white needles (88 mg, 73%), mp 179-181 °C. \textit{m/z} (EI) 321 (M⁺, 100%).

HRMS (EI) (M⁺) 322.1429 (calcd. for C\textsubscript{18}H\textsubscript{18}N\textsubscript{4}O\textsubscript{2} 322.1429).

\(\delta\text{H} (500 \text{ MHz CDCl}_3)\) 2.66 (s, 6H), 4.01 (s, 6H), 6.88 (d, 2H, \(J = 9.0 \text{ Hz}\)), 7.91 (dd, 2H, \(J = 2.5, 8.5 \text{ Hz}\)), 8.47 (d, 2H, \(J = 2.0 \text{ Hz}\)).

\(\delta\text{C} (500 \text{ MHz CDCl}_3)\) 22.72, 53.74, 110.70, 127.60, 139.40, 147.26, 148.05, 148.17, 164.15.

Protonation of compound 229. To a solution of compound 229 in methanol was added tetrafluoroboric acid (50% aqueous) dissolved in ether dropwise at 20 °C. The white precipitate which formed was collected and dissolved in DMSO-d\textsubscript{6}. \(\delta\text{H} (400 \text{ MHz DMSO-d}_6)\) 2.59 (s, 6H), 3.93 (s, 6H), 6.99 (d, 2H, \(J = 8.4 \text{ Hz}\)), 7.18 (s, br, 2H), 8.07 (dd, 2H, \(J = 2.8, 2.4 \text{ Hz}\)), 8.50 (d, 2H, \(J = 2.6 \text{ Hz}\)).

\(\delta\text{C} (400 \text{ MHz DMSO-d}_6)\) 22.40, 53.75, 110.31, 127.45, 140.26, 146.99, 147.49, 147.86, 163.51.
5.4 Experimental Procedures of Chapter 4

5.4.1 Sonogashira Cross-Coupling: General Method

The alkyne, the halide, the catalyst and CuI (10 mol% relative to the alkyne) were added sequentially to a degassed solution of THF/Et₃N [50 cm³ (3:2 v/v)] and the mixture was stirred at 20 °C overnight under a blanket of argon until tlc monitoring showed that the reaction was complete. Solvent was evaporated and the residue was dissolved in chloroform. The organic layer was purified by chromatography on a silica column.

**Attempted Synthesis of 2-(4-tert-Butylphenyl)-5-{4-[2-(2-pyrimidyl)ethynyl]phenyl}-1,3,4-oxadiazole**

![Structure](image)

Synthesis in accordance with the general Sonogashira cross-coupling method. 2-Bromopyrimidine 170 (0.32 g, 1.98 mmol), 230 (0.20 g, 0.66 mmol), Pd(PPh₃)₂Cl₂ (46 mg), CuI (12 mg) and chromatography (eluent DCM-diethyl ether, 9.5:0.5 v/v) gave a white solid (0.15 g) which was identified as the self coupling product 231.

**Bis-[4-[2-(4-tert-butylphenyl)-1,3,4-oxadiazol-5-yl]-phenyl]-butadiyne 231**

![Structure](image)

(mp 307-309 °C, \(\text{lit}^{168} 308-309 ^\circ\text{C} \)). \(m/z\) (El) 602 (M⁺ 100%). \(\delta_H\) (300 MHz CDCl₃) 1.37 (s, 9H), 7.54 (d, 4H, \(J = 8.7 \text{ Hz}\)), 7.67 (d, 4H, \(J = 8.7 \text{ Hz}\)), 8.04 (d, 4H, \(J = 8.7 \text{ Hz}\)), 8.11 (d, 4H, \(J = 8.4 \text{ Hz}\)). \(\delta_C\) (300 MHz CDCl₃) 31.10, 35.12, 74.69, 81.91, 120.80, 124.42, 124.74, 126.09, 126.79, 126.81, 133.11, 155.58, 163.61, 164.94.
2-(4-tert-Butylphenyl)-5-[4-[(2-pyridyl)ethynyl]phenyl]-1,3,4-oxadiazole 232a

2-Iodopyridine (0.22 g, 1.05 mmol), 230 (0.32 g, 1.05 mmol), Pd(PPh₃)₂Cl₂ (74 mg), CuI (20 mg) and chromatography (elucent DCM-diethyl ether, 9.5:0.5 v/v) gave a yellow solid which was recrystallized from petroleum ether (bp 100-120 °C) yielding 232a as a yellow solid (0.30 g, 73%), mp 180-181 °C. m/z (ES+) 380.3. HRMS (ES+) (M⁺) 380.1790 (calcd. for C₂₅H₂₁N₃O 380.1763). δH (400 MHz acetone-d₆) 1.38 (s, 9H), 7.42 (ddd, 1H, J = 7.6, 4.8, 1.2 Hz), 7.69 (m, 3H), 7.86 (m, 3H), 8.12 (d, 2H, J = 8.8 Hz), 8.23 (d, 2H, J = 8.4 Hz), 8.65 (ddd, 1H, J = 4.8, 2.4, 1.6 Hz). δC (400 MHz acetone-d₆) 31.29, 35.64, 87.92, 92.23, 122.09, 124.37, 125.25, 126.34, 127.08, 127.53, 127.72, 128.34, 133.42, 137.29, 143.65, 151.15, 156.24, 164.51, 165.55.

2-(4-tert-Butylphenyl)-5-[4-[(3-pyridyl)ethynyl]phenyl]-1,3,4-oxadiazole 232b

3-Iodopyridine (0.22 g, 1.05 mmol), 230 (0.32 g, 1.05 mmol), Pd(PPh₃)₂Cl₂ (74 mg), CuI (20 mg) and chromatography (elucent DCM-Diethyl ether, 9.5:0.5 v/v) gave a yellow solid which was recrystallized from petroleum ether (bp 100-120 °C) yielding 232b as a yellow solid (0.23 g, 56%), mp 182-183 °C. Anal. calcd. for C₂₅H₂₁N₃O: C, 79.13; H, 5.58; N, 11.07. Found: C, 78.60; H; 5.56; N, 10.83%. m/z (EI) 379 (M⁺ 100%). δH (500 MHz acetone-d₆) 1.38 (s, 9H) 7.46 (dd, 1H, J = 7.5, 4.5 Hz), 7.68 (d, 2H, J = 8.5 Hz), 7.82 (d, 2H, J = 8.5 Hz), 7.99 (dt, 1H, J = 8.0, 2.0 Hz), 8.11 (d, 2H, J = 8.5 Hz), 8.22 (d, 2H, J = 8.5 Hz), 8.61 (d, 1H, J = 3.5 Hz), 8.79 (s, 1H). δC (500 MHz acetone-d₆) 31.30, 35.64, 89.39, 92.07, 120.46, 122.10, 124.27, 125.10, 126.54, 127.08, 127.52, 127.71, 133.21, 139.26, 150.19, 152.89, 156.24, 164.51, 165.54.
2-(4-tert-Butylphenyl)-5-{4-[2-(4-pyridyl)ethynyl]phenyl}-1,3,4-oxadiazole 232c

4-Iodopyridine (0.22 g, 1.05 mmol), 230 (0.32 g, 1.05 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (74 mg), CuI (20 mg) and chromatography (eluent DCM-diethyl ether, 9.5:0.5 v/v) gave a yellow solid which was recrystallized from petroleum ether (bp 100-120 °C) yielding 232c as a yellow solid (0.16 g, 40%), mp 196-198 °C. Anal. calcd. for C$_{25}$H$_{21}$N$_3$O: C, 79.13; H, 5.58; N, 11.07. Found: C, 78.60; H, 5.56; N, 10.83%. m/z (EI) 379 (M$^+$ 100%). $\delta_H$ (500 MHz acetone-d$_6$) 1.38 (s, 9H), 7.53 (d, 2H, $J$ = 5.0 Hz), 7.68 (d, 2H, $J$ = 8.5 Hz), 7.84 (d, 2H, $J$ = 8.5 Hz), 8.12 (d, 2H, $J$ = 8.0 Hz), 8.24 (d, 2H, $J$ = 8.5 Hz), 8.66 (s, br, 2H). $\delta_C$ (500 MHz acetone-d$_6$) 31.30, 35.64, 89.76, 93.03, 122.08, 125.49, 126.02, 126.22, 127.09, 127.75, 131.11, 133.44, 150.98, 156.28, 164.47, 165.59.

2-(4-tert-Butylphenyl)-5-{4-[2-(2-pyrazyl)ethynyl]phenyl}-1,3,4-oxadiazole 232d

Iodopyrazine (0.22 g, 1.05 mmol), 230 (0.32 g, 1.05 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (74 mg), CuI (20 mg) and chromatography (eluent DCM-diethyl ether, 9.5:0.5 v/v) gave a yellow solid which was recrystallized from Petroleum Ether (100—120 °C) yielding 232d as thin yellow needles (0.28 g, 69%), mp 190-192 °C. Anal. calcd. for C$_{24}$H$_{20}$N$_4$O: C, 75.77; H, 5.30; N, 14.73. Found: C, 75.65; H, 5.34; N, 14.60%. m/z (ES$^+$) 381.3. $\delta_H$ (500 MHz CDCl$_3$) 1.37 (s, 9H), 7.55 (d, 2H, $J$ = 8.5 Hz), 7.77 (d, 2H, $J$ = 8.5 Hz), 8.06 (d, 2H, $J$ = 8.5 Hz), 8.17 (d, 2H, $J$ = 8.5 Hz), 8.53 (d, 1H, $J$ = 3.0 Hz), 8.16 (dd, 1H, $J$ = 2.5, 1.5 Hz), 8.80 (d, 1H, $J$ = 1.5 Hz). $\delta_C$ (500 MHz CDCl$_3$) 31.09, 35.11, 88.15, 92.05, 120.82, 124.65, 124.69, 126.11, 126.83, 126.87, 132.74, 139.88, 143.24, 144.59, 147.85, 155.59, 163.66, 164.98.
Experimental Procedures

2-(4-tert-Butylphenyl)-5-{4-[2-(5-bromo-2-pyrimidine)ethynyl]phenyl}-1,3,4-oxadiazole 232e

2-Iodo-5-bromopyrimidine (0.32 g, 1.05 mmol), 230 (0.32 g, 1.05 mmol), Pd(PPh₃)₂Cl₂ (74 mg), CuI (20 mg) and chromatography (elucent DCM-diethyl ether, 9.5:0.5 v/v) gave a pale yellow solid which was recrystallized from chlorobenzene to yield 232e as a white solid (0.35 g, 72%), mp 268-270 °C. m/z (EI) 458 (M⁺ ⁷⁹Br, 43%), 459 (M⁺ 100%), 460 (M⁺ ⁸¹Br, 42%). HRMS (EI) (M⁺) 458.0730 (calcd. for C₂₄H₁₉BrN₄O 458.0742).

1H (400 MHz CDCl₃) 1.37 (s, 9H), 7.55 (d, 2H, J = 8.4 Hz), 7.81 (d, 2H, J = 8.4 Hz), 8.06 (d, 2H, J = 8.8 Hz), 8.16 (d, 2H, J = 8.8 Hz), 8.83 (s, 2H).

2-(4-tert-Butylphenyl)-5-{4-[3-thienyl]ethynyl}phenyl)-1,3,4-oxadiazole 232g

3-Iodothiophene (0.22 g, 1.05 mmol), 230 (0.32 g, 1.05 mmol), Pd(PPh₃)₂Cl₂ (74 mg), CuI (20 mg) and chromatography (elucent DCM-diethyl ether, 9.8:0.2 v/v) gave a yellow solid which was recrystallized from ethanol yielding 232g as off white plates (0.16 g, 40%), mp 169-170 °C. m/z (EI) 384 (M⁺ 100%). HRMS (EI) (M⁺) 384.1299 (calcd. for C₂₄H₂₀N₂O₃S 384.1296). δH (500 MHz acetone-d₆) 1.39 (s, 9H), 7.30 (dd, 1H, J = 5.0, 1.0 Hz), 7.60 (dd, 1H, J = 5.0, 3.0 Hz), 7.68 (d, 2H, J = 8.5 Hz), 7.76 (d, 2H, J = 8.5 Hz), 7.84 (dd, 1H, J = 3.0, 1.0 Hz), 8.12 (d, 2H, J = 8.5 Hz), 8.20 (d, 2H, J = 8.5 Hz).

δC (500 MHz acetone-d₆) 31.29, 35.62, 88.15, 88.60, 122.11, 122.42, 124.52, 127.06, 127.24, 127.28, 127.49, 127.64, 130.51, 130.78, 132.90, 156.18, 164.57, 165.44.
Experimental Procedures

5-Iodothiophene-2-carboxylic acid methyl ester 233

To a solution of methyl thiophene-2-carboxylate (10.0 g, 70.3 mmol) and CCl₄ (89.0 cm³) was added I₂ (8.93 g, 35.2 mmol) and bis-(trifluoroacetoxy)iodobenzene (16.4 g, 38.2 mmol) and the mixture was stirred at 20°C overnight to give a deep purple solution. The reaction was then refluxed at 70 °C for 3 h and allowed to cool to 20 °C. Solvent was evaporated and the residue dissolved in DCM (150 cm³), washed with saturated KI (100 cm³) and sodium thiosulfate (100 cm³) and dried (MgSO₄). The organic layer was concentrated under reduced pressure and purified by chromatography on a silica column (elucent DCM-hexane, 1:1 v/v) to give a white solid which was recrystallised from cyclohexane to yield 233 as white crystalline solid (11.0 g, 58%), mp 84-85 °C, (lit 155 mp 89 °C). m/z (EI) 268 (M⁺ 92%), 237 (M⁺ 100%). δH (500 MHz acetone-d₆) 3.84 (s, 3H), 7.43 (d, 1H, J = 4.0 Hz), 7.46 (d, 1H, J = 4.0 Hz). δC (500 MHz acetone-d₆) 52.46, 83.81, 135.38, 139.05, 139.91, 161.39.

5-Iodothiophene-2-carboxylic acid hydrazide 234

233 (10.0 g, 37.3 mmol) was dissolved in methanol (70 cm³). NH₂NH₂·H₂O (7.23 cm³, 149.2 mmol) was added. The reaction was heated under reflux overnight. Solvent was evaporated to ca 50% of the original volume and the yellow solid was isolated by suction filtration and air-dried. The dried solid was recrystallised from methanol to yield 234 as yellow crystals (4.60 g, 46%), mp 146-147 °C. Anal. calcd. for C₅H₅IN₂O: C, 22.40; H, 1.88; N, 10.45. Found: C, 22.35; H, 1.87; N, 10.49%. m/z (EI) 268 (M⁺ 100%). δH (500 MHz DMSO-d₆) 4.44 (s, 2H), 7.34 (d, 1H, J = 4.0 Hz), 7.37 (d, 1H, J = 4.0 Hz), 9.77 (s, 1H). δC (500 MHz DMSO-d₆) 82.43, 129.09, 137.72, 144.08, 160.02.

2-(4-tert-Butylphenyl)-5-(5-iodothienyl)-1,3,4-oxadiazole 236

234 (7.50 g, 27.9 mmol) was dissolved in pyridine (20 cm³) and 4-tert-butylbenzoyl chloride (5.50 g, 27.9 mmol) was added. The mixture was stirred at 20 °C under Ar for 1 h then refluxed for 1 h. Pyridine was removed in vacuo, to leave a white residue. Methanol
Experimental Procedures

(100 cm$^3$) was added to the suspension and boiled for 2 min. The white solid 235 was separated by suction filtration and dried under vacuum overnight. This intermediate product was mixed with phosphorus oxychloride (75 cm$^3$) and the mixture gently refluxed for 3 h. The excess POCl$_3$ was removed by vacuum distillation. The viscous residue was crystallised from a chloroform-ethanol mixture, yielding 236 as light yellow plates (6.04 g, 53%), mp 170-172 $^\circ$C. Anal. calcd. for C$_{16}$H$_{15}$N$_2$O$_5$: C, 46.84; H, 3.69; N, 6.83. Found: C, 46.58; H, 3.62; N, 6.73%. m/z (EI) 410 (M$^+$ 100%). $\delta$H (400 MHz CDCl$_3$) 1.37 (s, 9H), 7.33 (d, 1H, $J$ = 4.0 Hz), 7.46 (d, 1H, $J$ = 4.0 Hz), 7.52 (d, 2H, $J$ = 8.4 Hz), 8.00 (d, 2H, $J$ = 8.4 Hz). $\delta$C (400 MHz CDCl$_3$) 31.08, 35.09, 79.61, 120.60, 126.08, 126.79, 130.67, 1311.10, 137.99, 155.55, 159.44, 164.16.

2-((4-tert-Butylphenyl)-5-[5-(3-hydroxy-3-methylbutynyl)thienyl]-1,3,4-oxadiazole 237

$\text{N-N} \quad \text{S} \quad \text{S} \quad \text{O} \quad \text{OH}$

236 (5.0 g, 12.2 mmol), 2-methyl-3-butyn-2-ol (2.6 cm$^3$, 26.7 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (0.86 g), Cul (0.23 mg) were added to a THF/Et$_3$N (100 cm$^3$, 1:1 v/v) mixture, stirred at 20 $^\circ$C overnight then refluxed for 3 h, followed by chromatography (eluent DCM-diethyl ether, 9.5:0.5 v/v) to give a yellow solid which was recrystallized from ethanol-H$_2$O mixture yielding 237 as golden needles (3.2 g, 72%), mp 161-163 $^\circ$C. Anal. calcd. for C$_{21}$H$_{22}$N$_2$O$_2$: C, 68.82; H, 6.05; N, 7.64. Found: C, 68.61; H, 6.00, N, 7.54%. m/z (EI) 366 (M$^+$ 100%). $\delta$H (500 MHz CDCl$_3$) 1.41 (s, 9H), 1.69 (s, 6H), 2.30 (s, 1H), 7.20 (d, 1H, $J$ = 3.5 Hz), 7.53 (d, 2H, $J$ = 8.0 Hz), 7.66 (d, 1H, $J$ = 4.0 Hz), 8.01 (d, 2H, $J$ = 8.0 Hz). $\delta$C (500 MHz CDCl$_3$) 31.08, 31.16, 65.74, 74.59, 100.59, 120.62, 125.70, 126.08, 126.80, 127.32, 129.20, 132.64, 155.55, 159.87, 164.26.

2-(4-tert-Butylphenyl)-5-(5-ethylthiophene)-1,3,4-oxadiazole 238

$\text{N-N} \quad \text{S} \quad \text{S} \quad \text{O} \quad \text{H}$

237 (2.62 g, 7.15 mmol) was dissolved in dry toluene (40 cm$^3$). Sodium hydroxide powder (freshly ground from pellets) (0.34 g) was added and the mixture was stirred in an oil bath at 130 $^\circ$C, under Ar, for 40 min, until the reaction was complete (tlc monitoring). Toluene was removed in vacuo and the residue dissolved in DCM (15 cm$^3$), followed by chromatography (eluent DCM-diethyl ether, 9.8:0.2 v/v) to give a pale yellow
solid, which was recrystallized from ethanol-H2O mixture yielding 238 as golden needles (1.54 g, 72%), mp 165-166 °C. Anal. calcd. for C18H16N2O5S: C, 70.10; H, 5.23; N, 9.08. Found: C, 69.93; H, 5.22; N, 8.93%. m/z (EI) 308 (M+ 100%). δH (500 MHz CDCl3) 1.36 (s, 9H), 3.51 (s, 1H), 7.31 (d, 1H, J = 3.5 Hz), 7.53 (d, 2H, J = 8.0 Hz), 7.67 (d, 1H, J = 3.5 Hz), 8.01 (d, 2H, J = 9.0 Hz). δC (500 MHz CDCl3) 31.08, 35.10, 75.85, 84.30, 120.59, 126.28, 126.41, 126.83, 129.05, 133.71, 155.60, 159.76, 164.35.

2-(4-tert-Butylphenyl)-5-{5-[2-(2-pyridyl)ethynyl]thienyl}-1,3,4-oxadiazole 239a

2-Iodopyridine (0.10 g, 0.50 mmol), 238 (0.15 g, 0.50 mmol), Pd(PPh3)2Cl2 (34 mg), CuI (10 mg) and chromatography (eluent DCM-diethyl ether, 9:8 v/v) gave a orange solid which was recrystallised from a ethanol-H2O mixture yielding 239a as copper coloured needles (86.3 mg, 46%), mp 158-160 °C. m/z (EI) 385 (M+ 100%). HRMS (EI) (M+) 385.1247 (calcd. for C23H19N3O5S 385.1248). δH (500 MHz CDCl3) 1.37 (s, 9H), 7.28 (dd, 1H, J = 7.0, 5.5 Hz), 7.41 (d, 1H, J = 4.0 Hz), 7.54-7.57 (m, 3H), 7.71-7.74 (m, 2H), 8.03 (d, 2H, J = 8.5 Hz), 8.56 (s, br 1H). δC (500 MHz CDCl3) 31.09, 35.12, 81.37, 95.20, 120.60, 123.36, 126.11, 126.65, 126.86, 127.27, 129.36, 133.91, 136.32, 142.53, 150.28, 155.61, 159.84, 164.39. δC (500 MHz CD2Cl2) 31.15, 35.36, 81.12, 95.37, 121.02, 123.76, 126.53, 126.82, 127.02, 127.29, 127.67, 129.74, 134.32, 136.60, 142.77, 150.65, 156.06, 160.18, 164.76.

2-(4-tert-Butylphenyl)-5-{5-[2-(3-pyridyl)ethynyl]thienyl}-1,3,4-oxadiazole 239b

3-Iodopyridine (0.10 g, 0.50 mmol), 238 (0.15 g, 0.50 mmol), Pd(PPh3)2Cl2 (34 mg), CuI (10 mg) and chromatography (eluent DCM-diethyl ether, 9:8 v/v) gave a orange solid 239b (61.6 mg, 33%), mp 164-166 °C. Anal. calcd. for C23H19N3OS: C, 71.66; H, 4.97; N, 10.90. Found: C, 71.29, H, 5.24, N, 10.31%. m/z (EI) 385 (M+ 100%). δH (500 MHz acetone-d6) 1.38 (s, 9H), 7.46 (dd, 1H, J = 8.0, 5.0 Hz), 7.56 (d, 1H, J = 4.0 Hz), 7.68 (d, 2H, J = 8.0 Hz), 7.90 (d, 1H, J = 4.0 Hz), 8.00 (dt, 1H, J = 8.0, 2.5 Hz), 8.07 (d, 2H, J = 8.5 Hz), 8.62 (d, 1H, J = 3.5 Hz), 8.79 (s, br 1H). δC (500 MHz
acetone-$d_6$) 31.28, 35.65, 84.93, 93.29, 119.93, 121.80, 124.31, 127.08, 127.12, 127.53, 127.55, 130.81, 134.75, 139.18, 150.46, 152.69, 156.38, 160.50, 165.10.

2-(4-tert-Butylphenyl)-5-{5-[2-(4-pyridyl)ethynyl]thienyl}-1,3,4-oxadiazole 239c

\[
\begin{align*}
\text{4-Iodopyridine (0.10 g, 0.50 mmol), 238 (0.15 g, 0.50 mmol), Pd(PPh}_3\text{)Cl}_2 (34 mg), CuI (10 mg) and chromatography (eluent DCM-diethyl ether, 9.8:0.2 v/v) gave 239c as an orange solid (61.8 mg, 33%), mp 198-199 °C. Anal. calcd. for C\text{\textsubscript{23}}H\text{\textsubscript{19}}N\text{\textsubscript{3}}O\text{\textsubscript{5}}: C, 71.66; H, 4.97; N, 10.90. Found: C; 71.74, H; 4.89, N, 10.34%. m/z (EI) 385 (M$^+$ 100%).} \\
\delta_\text{H} (500 MHz acetone-$d_6$) 1.38 (s, 9H), 7.52 (d, 2H, J = 6.0 Hz), 7.60 (d, 1H, J = 4.0 Hz), 7.67 (d, 2H, J = 8.8 Hz), 7.91 (d, 1H, J = 4.0 Hz), 8.06 (d, 2H, J = 8.8 Hz), 8.66 (d, 2H, J = 6.0 Hz). \delta_\text{C} (500 MHz acetone-$d_6$) 31.27, 35.65, 85.93, 93.64, 121.74, 125.87, 126.42, 127.11, 127.53, 128.19, 130.49, 130.83, 135.44, 152.00, 156.39, 160.43, 165.14.
\end{align*}
\]

2-(4-tert-Butylphenyl)-5-{5-[2-(2-pyrazyl)ethynyl]thienyl}-1,3,4-oxadiazole 239d

\[
\begin{align*}
\text{Iodopyrazine (0.10 g, 0.50 mmol), 238 (0.15 g, 0.50 mmol), Pd(PPh}_3\text{)Cl}_2 (34 mg), CuI (10 mg) and chromatography (eluent DCM-diethyl ether, 9.8:0.2 v/v) gave a yellow solid which was recrystallised from ethanol to yield 239d as fine yellow needles (0.10 g, 54%), mp 197-198 °C. Anal. calcd. for C\text{\textsubscript{22}}H\text{\textsubscript{18}}N\text{\textsubscript{4}}O\text{\textsubscript{5}}: C, 68.37; H, 4.69; N, 14.50. Found: C; 67.90; H; 4.68; N, 14.34%. m/z (EI) 386 (M$^+$ 100%).} \\
\delta_\text{H} (500 MHz CDC\text{\textsubscript{3}}) 1.37 (s, 9H), 7.47 (d, 1H, J = 4.0 Hz), 7.54 (d, 2H, J = 8.5 Hz), 7.75 (d, 1H, J = 4.0 Hz), 8.03 (d, 2H, J = 9.0 Hz), 8.54 (d, 1H, J = 2.5 Hz), 8.61 (dd, 1H, J = 2.5, 1.5 Hz), 8.79 (d, 1H, J = 1.0 Hz). \delta_\text{C} (500 MHz CDC\text{\textsubscript{3}}) 31.09, 35.13, 85.31, 92.06, 120.58, 125.63, 126.14, 126.90, 127.78, 129.35, 134.58, 139.57, 143.35, 144.64, 147.69, 155.74, 159.70, 164.53.
\end{align*}
\]

2-(4-tert-Butylphenyl)-5-{5-[2-(5-bromo-2-pyrimidine)ethynyl]thienyl}-1,3,4-oxadiazole 239e

\[
\begin{align*}
\text{2-Iodo-5-bromopyrimidine (0.14 g, 0.50 mmol), 238 (0.15 g, 0.50 mmol), Pd(PPh}_3\text{)Cl}_2 (34 mg), CuI (10 mg) and chromatography (eluent DCM-diethyl ether, 9.8:0.2 v/v) gave 239e as an orange solid (65.7 mg, 33%), mp 194-195 °C. Anal. calcd. for C\text{\textsubscript{22}}H\text{\textsubscript{18}}N\text{\textsubscript{4}}O\text{\textsubscript{5}}Br: C, 65.59; H, 4.69; N, 14.50. Found: C; 65.71, H; 4.67, N, 14.53% m/z (EI) 427 (M$^+$ 100%).} \\
\delta_\text{H} (500 MHz acetone-$d_6$) 1.38 (s, 9H), 7.52 (d, 2H, J = 6.8 Hz), 7.60 (d, 1H, J = 4.0 Hz), 7.67 (d, 2H, J = 8.8 Hz), 7.91 (d, 1H, J = 4.0 Hz), 8.06 (d, 2H, J = 8.8 Hz), 8.66 (d, 2H, J = 6.0 Hz). \delta_\text{C} (500 MHz acetone-$d_6$) 31.28, 35.65, 84.93, 93.29, 119.93, 121.80, 124.31, 127.08, 127.12, 127.53, 127.55, 130.81, 134.75, 139.18, 150.46, 152.69, 156.38, 160.50, 165.10.
\end{align*}
\]
chromatography (eluent DCM-diethyl ether, 9.8:0.2 v/v) gave a yellow solid which was recrystallised from ethanol to yield 239e as a yellow crystalline solid (0.14 g, 65%), mp 200 °C (dec). m/z (EI) 464 (M+ 79Br, 49%), 465 (M+ 100%), 466 (M+ 81Br, 49%). HRMS (EI) (M+) 464.0317 (calcd. for C22H17BrN4O4S: 464.0306). 

2-((4-tert-Butylphenyl)-5-[5-[(2-thienyl)ethynyl]thienyl]-1,3,4-oxadiazole 239f

2-Iodothiophene (0.10 g, 0.50 mmol), 238 (0.15 g, 0.50 mmol), Pd(PPh3)2Cl2 (34 mg), CuI (10 mg) and chromatography (eluents DCM-diethyl ether, 9.9:0.1 v/v) gave a pale yellow solid which was recrystallised from ethanol to yield 239f as yellow plates (72 mg, 38%), mp 168-169 °C. Anal. calcd. for C22H18N2O4S: C, 67.66; H, 4.65; N, 7.17. Found: C, 67.62; H, 4.61; N, 7.19%. m/z (EI) 390 (M+ 100%). δH (500 MHz acetone-d6) 1.38 (s, 9H), 7.16, (dd, 1H, J = 5.0, 1.5 Hz), 7.46 (dd, 1H, J = 3.5, 0.5 Hz), 7.50 (d, 1H, J = 4.0 Hz), 7.67 (m, 3H), 7.87 (d, 1H, J = 4.0 Hz), 8.06 (d, 2H, J = 8.5 Hz). δC (500 MHz acetone-d6) 31.28, 35.64, 81.43, 92.09, 130.

2-((4-tert-Butylphenyl)-5-[5-[(3-thienyl)ethynyl]thienyl]-1,3,4-oxadiazole 239g

3-Iodothiophene (0.10 g, 0.50 mmol), 238 (0.15 g, 0.50 mmol), Pd(PPh3)2Cl2 (34 mg), CuI (10 mg) and chromatography (eluents DCM-diethyl ether, 9.9:0.1 v/v) gave a yellow solid which was recrystallised from ethanol to yield 239g as yellow plates (70 mg, 36%), mp 161-162 °C. Anal. calcd. for C22H18N2O4S: C, 67.66; H, 4.65; N, 7.17. Found: C, 67.54; H, 4.61; N, 7.22%. m/z (EI) 390 (M+ 100%). δH (500 MHz acetone-d6) 1.38 (s, 9H), 7.29 (dd, 1H, J = 5.0, 1.5 Hz), 7.46 (d, 1H, J = 4.0 Hz), 7.61 (dd, 1H, J = 5.0, 3.0 Hz), 7.67 (d, 2H, J = 8.5 Hz), 7.86 (d, 1H, J = 4.0 Hz), 7.88 (dd, 1H, J = 3.0, 1.0 Hz), 8.06 (d, 2H, J = 8.5 Hz). δC (500 MHz acetone-d6) 31.28, 35.64, 81.43, 92.09,
Experimental Procedures

121.75, 121.83, 126.74, 127.11, 127.49, 127.98, 130.33, 130.79, 131.36, 133.91, 156.32, 160.55, 165.00.

2,5-Bis-{5-[4-tert-butylphenyl]-1,3,4-oxadiazol-5-yl}thien-2yl]-thiophene 240

![Chemical structure image]

2,5-iodothiophene (0.30 g, 0.50 mmol), 238 (0.16 g, 1.00 mmol), Pd(PPh₃)₂Cl₂ (68 mg), CuI (18.52 mg) and chromatography (eluent DCM-diethyl ether, 9.8:0.2 v/v) gave a yellow solid which was recrystallised from toluene to yield 240 as a yellow crystalline solid (70 mg, 30%), mp decomposed at 288 °C. m/z (EI) 696 (M⁺ 100%). HRMS (EI) (M⁺) 696.1697 (calcd for C₄₀H₃₂N₄O₂S₃ 696.1687). δ_H (400 MHz CDCl₃) 1.37 (s, 1H), 7.25 (s, 2H), 7.34 (d, 2H, J = 4.0 Hz), 7.54 (d, 4H, J = 8.8 Hz), 7.73 (d, 2H, J = 4.0 Hz), 8.02 (d, 4H, J = 8.4 Hz). δ_C (400 MHz CDCl₃) 31.09, 35.13, 86.95, 88.74, 120.60, 124.47, 126.12, 126.58, 126.84, 126.88, 129.43, 132.84, 133.12, 155.63, 159.82, 164.39.

2-Iodo-5-bromopyrimidine 241

To a solution of 2-chloro-5-bromopyrimidine 162 (1.40 g, 0.72 mmol) in DCM (10 cm³) cold hydroiodic acid (57% aq 0.6 cm³, 4.60 mmol) was added. The solution was stirred at 0 °C for 24 h then neutralised with solid sodium carbonate. The organic layer was separated and the aqueous layer washed with DCM (3 x 50 cm³). The combined organic washings were dried (MgSO₄) and the solvent evaporated. The residue was recrystallised from hexane yielding 241 as off-white flakes (0.12 g, 58%), mp 99-100 °C (lit¹⁰¹ 101-102 °C). m/z (EI) 284 (M⁺, 79Br, 44%), 286 (M⁺, 81Br, 46%). δ_H (400 MHz CDCl₃) 8.52 (s, 2H). δ_C (400 MHz CDCl₃) 120.99, 125.87, 159.20.

5-Bromo-2-(phenylethynyl)-pyrimidine 243

2-Iodo-5-bromopyrimidine 241 (0.2 g, 0.70 mmol), phenylacetylene 242 (0.16 g, 1.54 mmol), Pd(PPh₃)₂Cl₂ (49 mg), CuI (14 mg) and chromatography (eluent DCM-hexane, 8:2 v/v) gave 243 as a golden solid
Experimental Procedures

(96 mg, 53%), mp 143-145 °C. Anal. calcd. for C_{12}H_{7}BrN_{2}: C, 55.63; H, 2.72; N, 10.81.

Found: C, 55.20; H, 2.73; N, 10.30%. m/z (GCMS) 257.8 (M⁺ {^{79}Br}), 261.0 (M⁺ {^{81}Br}). δ_{\text{H}} (400 MHz acetone-d₆) 7.49-7.52 (m, 3H), 7.66-7.69 (m, 2H), 8.95 (s, 2H). δ_{\text{C}} (400 MHz acetone-d₆) 88.46, 120.07, 121.95, 129.70, 130.91, 133.08, 151.75, 159.06. δ_{\text{C}} (400 MHz C₆D₆) 88.84, 88.96, 119.10, 121.79, 128.58, 129.67, 132.75, 151.72, 157.77.

5-Phenyl-2-phenylethynyl-pyrimidine 244

5-Phenyl-2-phenylethynyl-pyrimidine 244

[Diagram: 5-Phenyl-2-phenylethynyl-pyrimidine 244]

2-[4-(2-Ethylhexyloxy)phenyl]-5-{4-[2-(5-bromo-2-pyrimidine)ethynyl]phenyl}-1,3,4-oxadiazole 245

[Diagram: 2-[4-(2-Ethylhexyloxy)phenyl]-5-{4-[2-(5-bromo-2-pyrimidine)ethynyl]phenyl}-1,3,4-oxadiazole 245]

2-Iodo-5-bromopyrimidine 241

(0.30 g, 1.05 mmol), 2-[4-(2-ethylhexyloxy)phenyl]-5-(4-ethynylphenyl)-1,3,4-oxadiazole (0.39 g, 1.05 mmol), Pd(PPh₃)₂Cl₂ (74 mg), Cul (20 mg) and chromatography (eluent DCM-diethyl ether, 9.5:0.5 v/v) gave a white solid which was recrystallized from cyclohexane yielding 245 as a white crystalline solid (0.40 g, 71%), mp 180-182 °C. m/z (GCMS) 530 (M⁺ {^{79}Br}, 13%), 531 (M⁺ 41%), 532 (M⁺ {^{81}Br}, 13%). HRMS (EI) (M⁺) 530.1313 (calcd. for C_{29}H_{27}BrN_{4}O_{2} 530.1317). δ_{\text{H}} (400 MHz CDCl₃) 0.95 (m, 6H), 1.31-1.58 (m, 8H), 1.76 (m, 1H), 3.91 (d, 2H, J = 5.9 Hz), 7.01 (d, 2H, J = 8.8 Hz), 7.79 (d, 2H, J = 8.8 Hz), 8.05 (d, 2H, J = 8.8 Hz), 8.14 (d, 2H, J = 8.8 Hz), 8.83 (s, 2H). δ_{\text{C}} (400 MHz CDCl₃) 11.09, 14.08, 23.01, 23.78, 26.88, 29.04, 30.43, 39.27, 70.72, 88.02, 89.31, 115.03, 115.75, 124.09, 126.75, 128.73, 133.11, 133.15, 150.73, 158.16, 162.36, 163.34, 164.95.
Experimental Procedures

2-[4-(2-Ethylhexyloxy)phenyl]-5-[4-[2-(5-phenyl-2-pyrimidine)ethynyl]phenyl]-1,3,4-oxadiazole 246

245 (0.20 g, 0.38 mmol), benzene boronic acid 164 (0.14 g, 1.12 mmol), THF (30 cm³), Pd(PPh₃)₄ (50.3 mg) and Na₂CO₃ (1 M degassed 4 cm³) and chromatography (eluent DCM-diethyl ether, 9.5:0.5 v/v) gave an off white solid which was recrystallized from toluene yielding 246 as a white solid (20 mg, 10%), mp 233-235 °C. m/z 528 (M⁺ 28%). HRMS (EI) (M⁺) 528.2549 (calcd. for C₃₄H₃₂N₄O₂ 528.2525).

δ_H (500 MHz CDCl₃) 0.95 (m, 6H), 1.35-1.58 (m, 8H), 1.76 (m, 1H), 3.95 (d, 2H, J = 5.9 Hz), 7.01 (d, 2H, J = 8.9 Hz), 7.50 (d, 1H, J = 6.9 Hz), 7.55 (t, 2H, J = 7.9 Hz), 7.62 (d, 2H, J = 6.9 Hz), 7.83 (d, 2H, J = 7.9 Hz), 8.06 (d, 2H, J = 8.5 Hz), 8.16 (d, 2H, J = 7.9 Hz), 9.00 (s, 2H).

δ_C (500 MHz CDCl₃) 11.10, 14.08, 23.02, 223.80, 29.05, 30.46, 39.29, 70.74, 87.10, 90.17, 115.05, 115.82, 124.52, 124.80, 126.75, 126.94, 128.74, 129.36, 129.55, 132.70, 133.16, 133.66, 151.39, 155.27, 162.36, 163.43, 164.93.

1,4-Bis-[2-phenyl-5-(4-tert-butylphenyl)-1,3,4-oxadiazole]-benzene 248a

1,4-Benzenediboronic acid (80 mg, 0.48 mmol), 2-(4-iodophenyl)-5-(4-tert-butyrylphenyl)-1,3,4-oxadiazole 247 (0.3 g, 0.74 mmol), THF (30 cm³), Pd(PPh₃)₄ (50.3 mg) and Na₂CO₃ (1 M degassed 4 cm³). A white highly insoluble precipitate of 248a was isolated from the reaction flask (68 mg, 15%), mp >300 °C. m/z (EI) 630 (M⁺ 8%), 41 (M⁺ 100%). HRMS (EI) (M⁺) 630.2997 (calcd. for C₄₂H₃₈N₄O₂ 630.2994).

δ_H (500 MHz TCE-d₂) 1.30 (s, 18H), 7.49 (d, 4H, J = 8.0 Hz), 7.73 (s, 4H), 7.77 (d, 4H, J = 8.0 Hz), 7.99 (d, 4H, J = 8.0 Hz), 8.14 (d, 4H, J = 7.5 Hz). δ_C (500 MHz TCE-d₂) 31.32, 35.22, 121.65, 123.70, 126.24, 127.15, 127.69, 127.82, 127.91, 139.96, 143.87, 155.88, 164.45, 165.03.
Experimental Procedures

1,4-Bis-[2-phenyl-5-(4-tert-butylphenyl)-1,3,4-oxadiazole]-2,5-dimethoxybenzene 248b

2,5-Dimethoxy-1,4-benzenediboronic acid 207 (100 mg, 0.48 mmol), 2-(4-iodophenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole 247 (0.3 g, 0.74 mmol), THF (30 cm³) Pd(PPh₃)₄ (50.5 mg) and Na₂CO₃ (1 M degassed 4 cm³) and chromatography (eluuent initially DCM-ethyl-acetate, 9.9:0.1 v/v, then DCM-ethyl-acetate, 1:1 v/v) gave 248b as a yellow solid (80 mg, 24%), mp 224-226 °C. m/z (EI) 690 (M⁺ 100%).

HRMS (EI) (M⁺) 690.3227 (calcd. for C₄₄H₃₂N₄O₄ 690.3206).

δ_H (500 MHz CDCl₃) 1.37 (s, 18H), 3.86, (s, 6H), 7.05 (s, 2H), 7.56 (d, 4H, J = 8.5 Hz), 7.77 (d, 4H, J = 8.5 Hz), 8.08 (d, 4H, J = 8.5 Hz), 8.21 (d, 4H, J = 8.5 Hz). δ_C (500 MHz CDCl₃) 31.11, 35.09, 56.47, 114.46, 121.10, 122.67, 126.06, 126.67, 126.77, 129.84, 130.11, 141.50, 150.77, 155.34, 164.32, 164.67.

1,4-Bis-[2-phenyl-5-(4-tert-butylphenyl)-1,3,4-oxadiazole]-9,9-dihexylfluorene 248c

9,9-Dihexylfluorene-2,7-diboronic acid 169 (0.20 g, 0.48 mmol), 2-(4-iodophenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole 247 (0.3 g, 0.74 mmol), THF (30 cm³) Pd(PPh₃)₄ (55.48 mg) and Na₂CO₃ (1 M degassed 4 cm³) and (eluuent initially DCM-ethylacetate, 9.9:0.1 v/v, then DCM-ethylacetate, 1:1 v/v) gave a yellow oil; crystallisation from cyclohexane/hexane mixture precipitated a yellow solid impurity which was removed by suction filtration. The filtrate was removed in vacuo to yield 248c as a white solid (70 mg, 11%), mp 187-189 °C. m/z (ES+) 887.7. HRMS (ES+) (M⁺) 886.5184 (calcd. for C₆₁H₆₆N₄O₂ 886.5186).

δ_H (500 MHz CDCl₃) 0.75 (m, 10H), 1.06 (m, 12H), 1.39 (s, 18H), 2.08 (m, 4H, J = 8.0 Hz), 7.57 (d, 4H, J = 8.0 Hz), 7.65-7.68 (m, 4H), 7.83-7.86 (m, 6H), 8.09 (d, 4H, J = 8.5 Hz), 8.24 (d, 4H, J = 8.5 Hz). δ_C (500 MHz CDCl₃) 13.98, 22.54, 23.79, 29.64, 31.11, 31.43, 35.09, 40.36, 55.45,
Experimental Procedures

120.40, 121.11, 121.46, 122.63, 126.06, 126.25, 126.78, 127.35, 127.70, 138.92, 140.68, 144.70, 151.98, 155.34, 164.31, 164.68.
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Comparative values for solid state PL efficiencies of other blue emitters: poly[2,8-(indenofluorene-co-anthracene)] \( \Phi_{em}^{0.35} \); 3,3'-5,5'-tetraethoxycarbonyl-4,4'-diphenyl-2,2'-bipyrrrole \( \Phi_{em}^{1.0} \); poly(4,4'-biphenylylene-\( \alpha \)-phenyvinylene) \( \Phi_{em}^{0.42} \); polymers containing 9,10-di(2-naphthyl)anthracene chromophores \( \Phi_{em}^{0.22-0.37} \).

The parent 2-phenyl-5-(2-thienyl)-1,3,4-oxadiazole system is known: Hayes, F. N.; Rogers, B. S.; Ott, D. G. *J. Amer. Chem. Soc.* **1955**, 77, 1850-1852. During the course of our work, 2-furyl-5-phenyl-1,3,4-oxadiazole derivatives were synthesised using different methodology from that shown in Scheme 82.


Synthesis of 2-[4-(2-ethylhexyloxy)phenyl]-5-(4-ethynylphenyl)-1,3,4-oxadiazole: Wang, C.; Batsanov, A. S.; Bryce, M. R. manuscript in preparation. For other reactions of this compound see Ref 150b.

Synthesis of 2-(4-iodophenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole: See Ref 157.


Beeby, A.; Findlay, K. S.; Rutter, S. personal communication.


Compound 231 was identical with a sample obtained previously in our laboratory: Wang, C. unpublished results.
1 Appendix One: New Pyrimidine- and Fluorene-Containing Oligo(arylene)S: Ab Initio Calculations

1.1 Quantum Chemical Calculations

These calculations were performed by Dr. I. Perepichka. For modelling compounds 172, 173 and 175, geometries and electronic structures were calculated for compounds 172E, 173E, and 175E which have ethyl substituents at C(9) instead of hexyl. In addition, the same calculations were performed for derivatives 176E–180E, to study the influence of the position and the number of nitrogen atoms in the heterocycle attached to the fluorene moiety (Scheme A).

Ab initio calculations of the geometries and electronic structures were performed at the HF and DFT levels of theory at HF/6-31G(d,p), B3LYP/6-31G(d,p) and B3PW91/6-31G(d,p). Both DFT methods (B3LYP and PW91) gave similar results for the optimised geometries and electronic structures of the compounds (Table A). Electronic structures were also calculated at the HF/6-31G(d,p)//B3LYP/6-31G(d,p) level (Figure A).
Both HF and DFT calculations indicate that the 2-pyrimidyl ring in the optimised geometries of 172E and 175E is in the plane of the fluorene moiety ($\omega_1 \approx 0^\circ$). These results correspond well with experimental X-ray structural data for 175, which showed only small deviations of the pyrimidine rings from the plane of the fluorene moiety [5.1° and 5.6° (Figure 14)]. These small experimental distortions could probably be a result of crystal packing (in any case, the expected energy loss for such distortions is quite low). Their isomers 173E and 178E, however, have a twisted structure with the dihedral angle between the 1,3-pyrimidin-5-yl ring and fluorene moiety $\omega_1$ ca. 45° (HF) or 37° (DFT) (Table A). Again, these values are in the normal range of distortions in biphenyls (see Crystal Structures section in Chapter 2). On the other hand, the $\omega_2$ dihedral angle in 175E between the phenyl ring and the planar pyrimidine-fluorene moiety is also pronounced ($\approx 45^\circ$ and $\approx 37^\circ$ by HF and DFT, respectively) whereas in 178E the phenyl-pyrimidine moiety is completely planar ($\omega_2 = 0^\circ$). Thus, as seen in the crystal structures (Figures 12, 13 and 14), the nitrogen atoms in the pyrimidine fragment decrease the steric repulsion which exists between adjacent benzene rings in biphenyl derivatives resulting in planarisation and hence facilitating conjugation between the aromatic rings in oligo(arylenes). This effect is clearly illustrated by the fluorene-tetrazine derivative 180E which represents a fully planar system ($\omega_1 = \omega_2 = 0^\circ$). Pyrazine derivatives 176E and 179E, which have only one nitrogen atom adjacent to the fluorene or phenyl ring, have dihedral angles $\omega_1$ and $\omega_2$ of 28 – 29° and 19 – 21° by HF and DFT, respectively (Table A) which are intermediate between those observed for phenyl and 2-phenylpyrimidine moieties.
Table A: Calculated energy parameters and dihedral angles for compounds 172E, 173E, and 175E–180E.

A HOMO–LUMO energy diagram (Figure B) shows that at both HF and DFT levels of theory HOMO energies are monotonously decreased in the sequence 172E > 176E > 173E > 177E (and for phenyl-substituted derivatives 175E > 178E > 179E > 180E). In contrast, changes in LUMO energies are less pronounced for pyrimidine and pyrazine derivatives (172E, 173E, 175E, 176E, 178E, 179E) but decreased for tetrazine derivatives 177E and 180E. At HF level, the addition of terminal phenyl substituents in all these series increased the HOMO and decreased the LUMO orbital energies, thus resulting in a contraction of the HOMO-LUMO
A similar tendency was observed in the DFT calculations, however, for tetrazine derivatives addition of terminal phenyl substituents (177E → 180E) resulted in increasing LUMO energy (nevertheless HOMO-LUMO gap decreased). Although the exact physical meaning of DFT orbital energies is a controversial subject and B3LYP/6-31G(d,p) gave too high energies for the HOMO orbitals, it gives quite reliable HOMO-LUMO energy gaps, consistent with the spectroscopic data.

Analysis of the frontier orbitals reveals that for all these compounds the HOMOs, which are located at the fluorene moiety, populate on the same carbon atoms of the benzene rings whereas the LUMOs are localised at C–C bonds between the 6-membered aromatic rings. Therefore, HOMO–LUMO excitation should increase the quinoidal character of the system, especially the central fluorene moiety. As a result of planarity between the pyrimidine and fluorene rings in 172E and 175E the population of the LUMO on the C–C bonds between these rings is more pronounced than that for 173E and 178E, where the dihedral angle ω1 is quite large (Table A).

1.2 Computational Procedure

The \textit{ab initio} computations were carried out with the Gaussian 98 package of programs at both Hartree-Fock and density-functional theory levels using Pople's 6–31G split valence basis set supplemented by \textit{d}-polarisation functions on heavy atoms and \textit{p}-polarisation functions on hydrogens. DFT calculations were carried out using Becke's three-parameter hybrid exchange functional with either Lee–Yang–Parr correlation functional (B3LYP) or Perdew–Wang 1991 gradient-corrected correlation functional (B3PW91). Geometries were
optimised with HF/6-31G(d,p), B3LYP/6-31G(d,p) and B3PW91/6-31G(d,p) and electronic structures were calculated at the same levels. Contours of HOMO and LUMO orbitals were also calculated at HF/6-31G(d,p)//B3LYP/6-31G(d,p) level and visualisation of frontier orbital populations was performed using Mølekel v.4.2 program. No constraints of bonds/angles/dihedral angles were applied in the calculations and all the atoms were free to optimise.
HF/6-31G(d) calculated dihedral angles between the phenyl substituents and the fluorene moiety in 2,7-diphenyl-9,9-dioctylfluorene were found to be 45.5°: Belletete, M.; J.-F. Morin, J.-F.; Beaupre, S.; Leclerc. M.; Durocher, G. *Synth. Met.* 2002, 126, 43-51.


