

Solution processable phosphorescent rhenium(I) dendrimers

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A family of (1,10-phenanthroline)rhenium(I)(CO)₃Cl complex cored first generation dendrimers with one, two or three dendrons have been prepared. The first generation dendrons attached to the core complex are comprised of biphenyl units with 2-ethylhexyloxy surface groups at their distal ends. The number and position of attachment of the dendron to the core was found to have an effect on the properties of the dendrimers. When dendrons were attached to both the 2- and 9-positions of the 1,10-phenanthroline ligand, thus straddling the rhenium(I), the dendrimers became more electrochemically stable and less susceptible to solvatochromism. The dendrimers were generally found to have their emission blue-shifted and a higher photoluminescence quantum yield in the solid state than in the solution. The origin of this rigidochromism effect is discussed. A single layer device with a neat dendrimer film was found to have an external quantum efficiency of 0.4% (0.8 cd A⁻¹) and power efficiency of 0.2 lm W⁻¹ at 100 cd m⁻² and 12.8 V.

Introduction

Phosphorescent emitters for organic light-emitting diodes (OLEDs) are being increasingly investigated due to their high device efficiencies that arise from the fact that both singlets and triplets can be captured for emission. Most phosphorescent emitters are based on heavy metal complexes with the most common being iridium(III) complexes.^{1–6} Less investigated are devices that utilize rhenium(I) complexes as the phosphorescent emitter.^{7–15} While much of the work on phosphorescent emitters has been focusing on small molecules^{1–6} there has been an increasing focus on developing phosphorescent light-emitting dendrimers to control the processing and intermolecular interactions that govern device performance.^{16–21} We have shown that by controlling the generation and/or number of dendrons,^{17,18} and dendron type,²² it is possible to control charge transport^{22,23} and light-emission²⁴ in iridium(III) complex cored dendrimers and form simple highly efficient dendrimer light-emitting diodes (DLEDs).¹⁶ OLEDs with solution processed layers comprised of polymers with rhenium(I) units in the backbones or with rhenium(I) complexes blended with a polymer host have generally given very poor performance.^{8,10} The best rhenium(I) containing devices have utilized evaporated layers with the devices including a hole transport layer, blended emissive layer, and an electron transport layer. We were therefore interested in applying the dendrimer technology to rhenium(I) complexes.

Most rhenium(I) complexes studied for light-emission have had a bidentate heteroaromatic ligand such as 2,2'-bipyridine or 1,10-phenanthroline with three carbonyl and one chlorine

ligand. In this paper we describe the synthesis of a series of (1,10-phenanthroline)rhenium(I)tricarbonyl complexes with one, two, or three dendrons attached to the 1,10-phenanthroline ligand (Fig. 1). The first generation dendron used was comprised of biphenyl units and contained 2-ethylhexyloxy surface groups. We discuss the effect of the number and position of the dendrons on the photophysical and electrochemical properties of the materials. We also report the preliminary performance of a DLED incorporating one of the materials.

Results and discussion

Syntheses and physical properties

The synthetic routes to the dendronised rhenium(I) complexes of Fig. 1 are shown in Scheme 1. Two different strategies were used to attach the dendrons to the 1,10-phenanthroline. 1,10-Phenanthroline is susceptible to nucleophilic attack at the 2(9)- and 4(7)-positions and the dendrons were added to the 2- and 9-positions *via* an aryl anion. The dendrons could not be attached to the 3(8)- and 5(6)-positions by the same method and hence a Suzuki reaction was utilized. It should be noted that apart from the 1,10-phenanthroline ligand with the dendron attached to the 5-position (**L2**) it was not possible to isolate the dendronised ligand in an analytically pure form and hence they were reacted to form the complex which could be purified. The key dendron intermediate for this work was 3,5-di[4-(2-ethylhexyloxy)phenyl]phenylbromide (**G1-Br**).²⁵ **G1-Br** was used directly for the formation of **Re3**, **Re5**, and **Re6** but converted to the corresponding boronic acid [**G1-B(OH)₂**] for the formation of **Re2** and **Re4**. **G1-B(OH)₂** was formed by an analogous method as that reported for the formation of an equivalent pinacolate boronate ester.²⁵ **G1-Br** was metallated with *n*-butyllithium at low temperature and then reacted with trimethylborate followed by work-up with dilute aqueous hydrochloric acid. The advantage of this route

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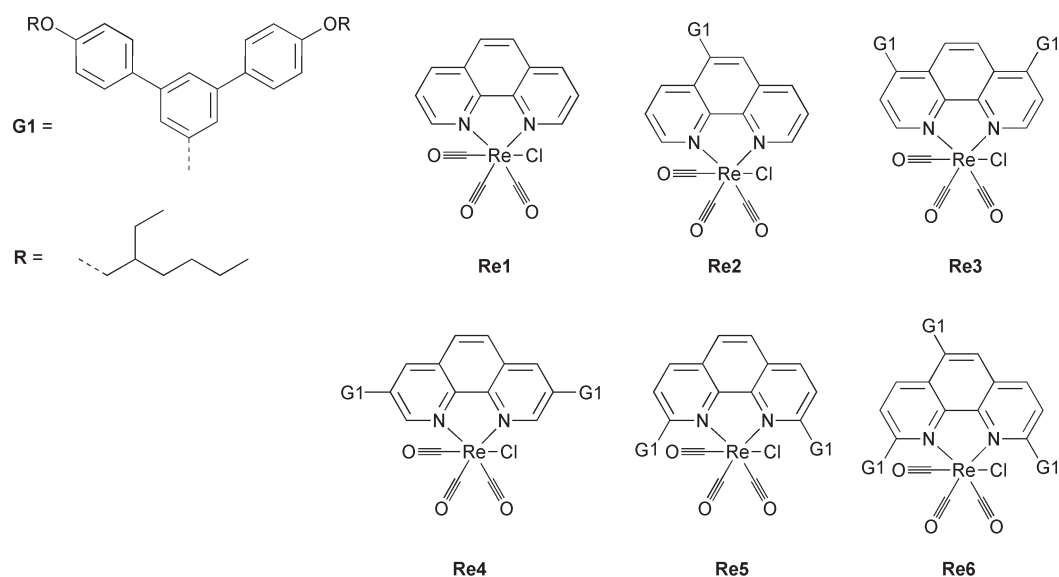
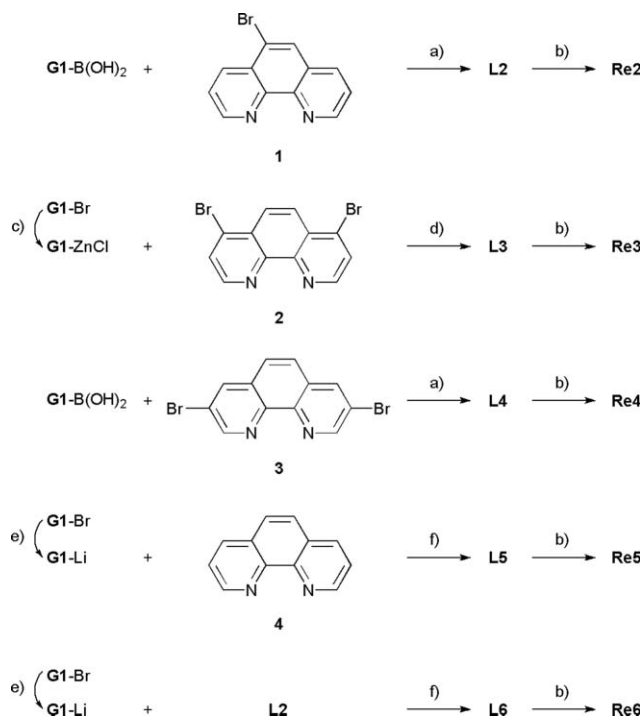


Fig. 1 Chemical structures of the complexes **Re1–6**.



Scheme 1 Synthetic route of the complexes **Re2–6**. *Reagents and conditions:* (a) $\text{Pd}(\text{PPh}_3)_4$, $\text{Na}_2\text{CO}_3\text{aq.}$, EtOH, toluene, $100\text{ }^\circ\text{C}$, 24 h; (b) $\text{Re}(\text{CO})_5\text{Cl}$, toluene, reflux; (c) (i) *n*-BuLi, THF, $-78\text{ }^\circ\text{C}$, 1 h, (ii) ZnCl_2 , THF, $-78\text{ }^\circ\text{C}$; (d) $\text{Pd}(\text{PPh}_3)_4$, THF, $80\text{ }^\circ\text{C}$, 17 h; (e) *n*-BuLi, diethyl ether, 1 h; (f) (i) r.t., (ii) MnO_2 , dichloromethane, 1 h.

over forming the pinacolate boronate ester is that is cheaper to form on a large scale. However, the difficulty is that the product is not a single compound with dimers and cyclic trimers also formed although these can also be used in the Suzuki reaction.

The 5-substituted complex (**Re2**) was formed from 5-bromo-1,10-phenanthroline in two steps. In the first step it was coupled with **G1-B(OH)₂** under Suzuki conditions to give the

ligand with the dendron on the 5-position (**L2**) in a 54% yield. **L2** was then reacted with pentacarbonylchlororhenium(I) in toluene heated at reflux to give **Re2** in a 52% yield. **Re4** with dendrons in the 3- and 8-positions on the ligand was formed in a similar manner with **G1-B(OH)₂** being reacted with 3,8-dibromo-1,10-phenanthroline under Suzuki conditions to give **L4**. **L4** was then reacted with pentacarbonylchlororhenium(I) in refluxing toluene to give **Re4** in a 24% yield for the two steps. While in principle the dendronised ligand **L3** could be formed from the Suzuki reaction of **G1-B(OH)₂** with 4,7-dibromo-1,10-phenanthroline, we found that the **L3** formed was very difficult to purify. However, by converting the **G1-Br** into the corresponding zinc reagent (**G1-ZnCl**) by metallation and reaction with zinc chloride it was possible to carry out a Negishi coupling to give **L3**. **L3** was then reacted with pentacarbonylchlororhenium(I) giving **Re3** in a 14% yield for the two steps. **Re5** with the dendrons in the 2- and 9-positions was prepared by reaction of the lithium salt of **G1-Br**, **G1-Li**, with 1,10-phenanthroline followed by oxidation with manganese dioxide and subsequent complex formation in an overall 43% yield. **Re6** with dendrons in the 2-, 5-, and 9-positions was made in a 17% yield by an analogous method to **Re5** except that **L2** was used as the starting phenanthroline. All the dendritic complexes, **Re2–Re6**, showed good solubility in common organic solvents such as tetrahydrofuran, dichloromethane, and toluene.

Infrared analysis of the complexes in the carbonyl region ($1880\text{--}2025\text{ cm}^{-1}$, Table 1) revealed that there were three stretches, which was consistent with the complexes only having the *facial* configuration.²⁶ In the *facial* configuration there are only two carbonyl environments and two of the stretches correspond to the symmetric and asymmetric stretches of the two carbonyls in the same plane, with the third stretch due to the third carbonyl which is opposite the chlorine atom. If the complexes were the *mer* isomers only two stretches would be infrared active. The ¹³C-NMR confirmed that there was only one isomer present. Interestingly **Re3**, **Re4**, and **Re5** all had two peaks due to the carbonyl carbons in the region of

Table 1 ^{13}C -NMR chemical shift and IR stretching frequencies of the carbonyl groups, and decomposition (T_d) temperatures of the complexes

	δ/ppm^a	$\nu/\text{cm}^{-1}{}^b$	$T_d/^\circ\text{C}^c$
Re1		2017, 1930, 1897	348, 358
Re2	189.4, 196.98, 197.03	2020, 1916, 1893	306, 339
Re3	189.7, 197.2	2020, 1920, 1888	344, 393
Re4	189.8, 197.1	2023, 1923, 1883	276, 307
Re5	192.1, 192.6	2019, 1921, 1884	320, 357
Re6	192.2, 192.7	2022, 1926, 1885	365, 392

^a 125 MHz, CDCl_3 . ^b Film on NaCl. ^c 5 and 10% weight loss.

189–199 ppm. In contrast the ^{13}C -NMR spectrum of **Re2** exhibited three carbonyl signals because of the asymmetric nature of its structure, caused by the 1,10-phenanthroline ligand being substituted by the dendron in the 5-position. The ^1H -NMR spectra were also consistent with the structures of the complexes. There was an important difference between the ^1H -NMR spectra of **Re5** and **Re6** and the other complexes. The ^1H -NMR spectra showed that the symmetry of the protons in the dendrons had been broken (Fig. 2 illustrates the aromatic region of **Re5**). This means that when the dendrons are attached to the 2- and 9-positions their rotation is hindered by the other ligands on the metal. That is, the dendrons are encapsulating the rhenium(I) at the centre. As will be discussed later this imparts important properties to the rhenium(I) complex cores.

The thermal properties of the dendrimers were studied by Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). TGA of all the complexes showed that they had high thermal stability with 5% weight loss occurring at temperatures greater than 275 $^\circ\text{C}$ (Table 1). Both **Re2** and **Re3** had clearly observable glass transition temperatures at 114 $^\circ\text{C}$ (heating rate = 30 $^\circ\text{C min}^{-1}$) and 121 $^\circ\text{C}$

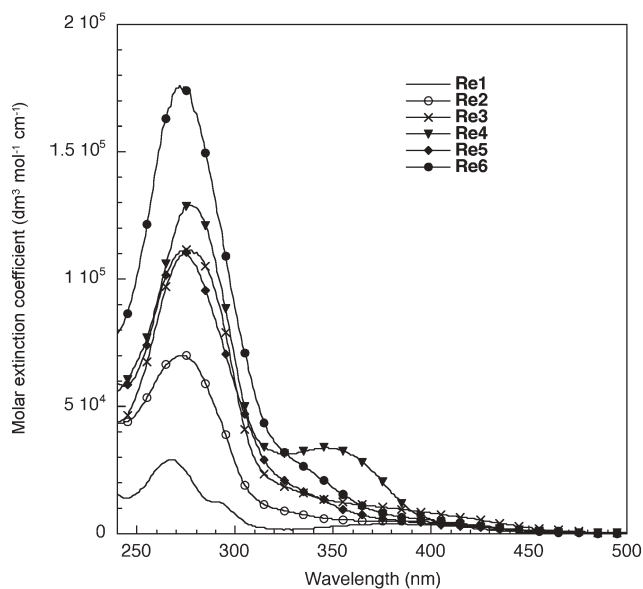


Fig. 3 UV-visible spectra in dichloromethane of **Re1–Re6**.

(heating rate = 100 $^\circ\text{C min}^{-1}$) respectively. **Re4** had a more crystalline appearance and had a melting point at 260–263 $^\circ\text{C}$ while the thermal properties of **Re5** and **Re6** were much more complex with overlapping transitions observed.

Photophysical properties

The first step in the photophysical study of the dendrimers was to understand their UV-visible absorption spectra, which are shown in Fig. 3. The parent complex (**Re1**) has an absorption peak at 267 nm and a broad absorption between 320 nm and 440 nm. The absorption at short wavelengths is primarily due to the π - π^* transition of the 1,10-phenanthroline in the

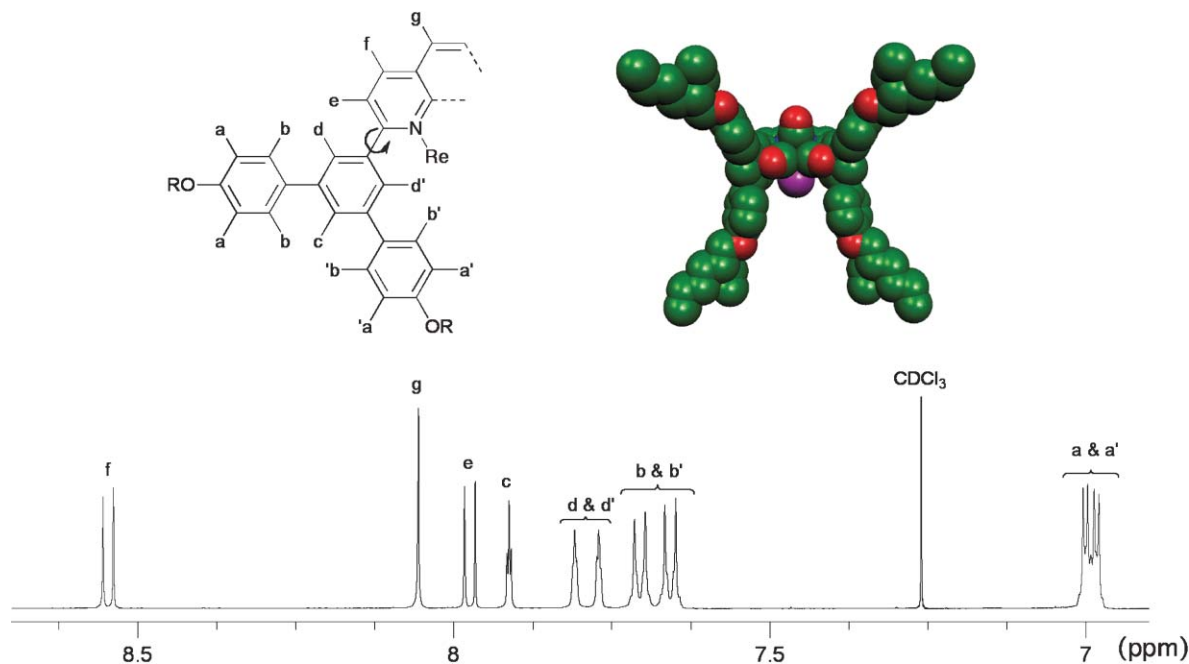


Fig. 2 ^1H -NMR and molecular model of **Re5**.

ligand with the longer wavelength absorption being assigned to metal-to-ligand charge transfer transitions.²⁷ Each of the dendrimers have a similar absorption pattern although there are some important differences. At short wavelengths (≈ 270 nm) the absorption of the dendrimers is stronger than that of **Re1** and that is due to the biphenyl units in the dendrons that also absorb at that wavelength. The strength of the absorption is generally in line with the number of dendrons (biphenyl units) attached to the core. **Re2** has a single dendron and hence has a lower molar absorption coefficient at ≈ 270 nm than **Re3**, **Re4**, and **Re5** that have two dendrons. **Re6** with three dendrons attached to the core has the largest absorption in this part of the UV-visible spectrum. It might be thought that the attachment of the conjugated dendrons would have a large effect on the MLCT transitions. However, it is important to remember that the branching in the dendrons means that while they are fully conjugated the π -electrons are not fully delocalised. In fact the MLCT transitions of **Re2**, **Re3**, **Re5**, and **Re6** occur at similar wavelengths and have similar molar extinction coefficients to **Re1**. This can be easily understood for **Re3**, **Re5**, and **Re6** where in principle the first phenyl ring of the dendron could be conjugation with the 1,10-phenanthroline ring. For these dendrimers though, the plane of the dendrons is orthogonal to that of the 1,10-phenanthroline due to steric interactions and hence there is less overlap of the dendron and ligand π -orbitals. The UV-visible spectrum of **Re4** was different from the other dendrimers at longer wavelengths. For **Re4** there is a second absorption peak at 346 nm and this is most probably due to the fact that when the dendrons are attached to the 3- and 8-positions there are less steric interactions meaning that the first phenyl rings of the two dendrons increases the conjugation length of the ligand. The fact that the molar absorption coefficient is of order of $33\,000\text{ M}^{-1}\text{ cm}^{-1}$ strongly suggests that it has significant π - π^* transition character although it is undoubtedly overlapping MLCT transitions.

One of the features of rhenium(I) complexes is that they can show solvatochromism, with non-polar solvents causing a red shift in the MLCT transitions in the UV-visible absorption spectrum.²⁷ It has been reported that this may be due to interactions of the solvent with the bidentate ligand orbitals or a 'charge separated excited state'.²⁶ We therefore investigated whether the dendritic structure could create an environment that gives control over the interactions that lead to solvatochromism. The UV-absorption spectra of the dendrimers in dichloromethane and a toluene–heptane mixture (4 : 96 v/v) were compared. For the dendrimers with dendrons further away from the rhenium (**Re2**, **Re3**, and **Re4**) there was a red shift in the absorption spectra in the less polar toluene–heptane mixture (the spectra of **Re2** are shown in Fig. 4). In contrast there was little change in the wavelengths of the absorption spectra for **Re5** (Fig. 4) and **Re6** indicating that having the shielding dendrons decrease the solvatochromism observed in the absorption spectra.

The solution photoluminescence (PL) spectra of the dendrimers are shown in Fig. 5. The spectra of the dendrimers are all broad and similar to that of the parent complex **Re1**, except that of **Re6**, which shows a second emission peak at the shorter wavelength of 421 nm. We believe that the small

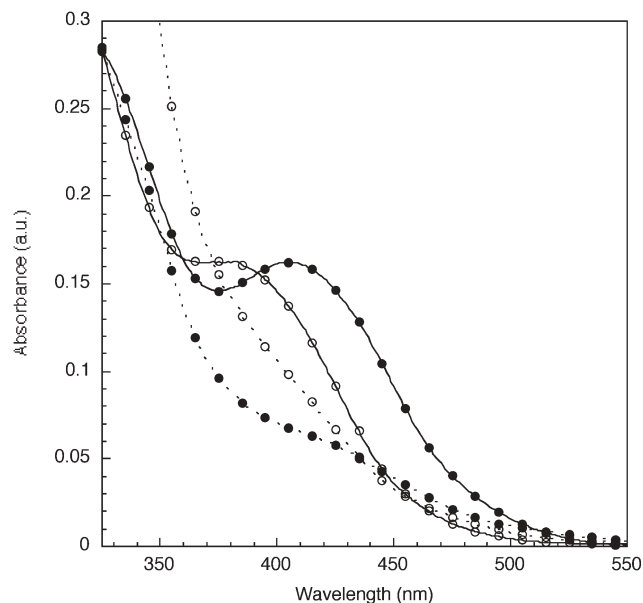


Fig. 4 Comparison of the UV-visible spectra of **Re2** (solid line) and **Re5** (dotted line) in dichloromethane (open circle) and toluene–heptane (4 : 96 v/v) (filled circle).

emission at 421 nm is probably due to a small amount of free ligand that remained after purification and illustrates the power of luminescence spectroscopy to identify different emissive species when a weakly emitting chromophore, in this case the rhenium(I) complex, is present. Indeed this analytical technique allowed us to compare the purity of different batches. Fascinatingly, the solvatochromism observed in absorption spectra does not occur in the PL spectra, which is almost independent of solvent. The extent of solvatochromism effects on the luminescence appear to be dependent on the bidentate nitrogen containing ligand used.^{26,27}

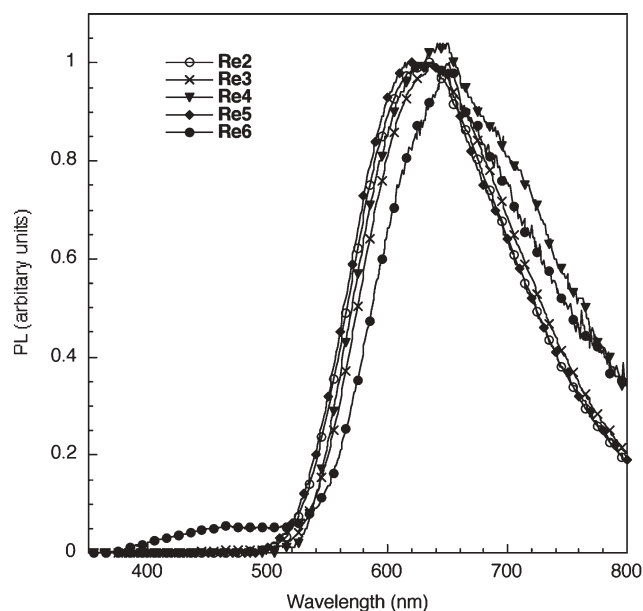


Fig. 5 Solution PL spectra of **Re2–6** (the spectra have been normalized).

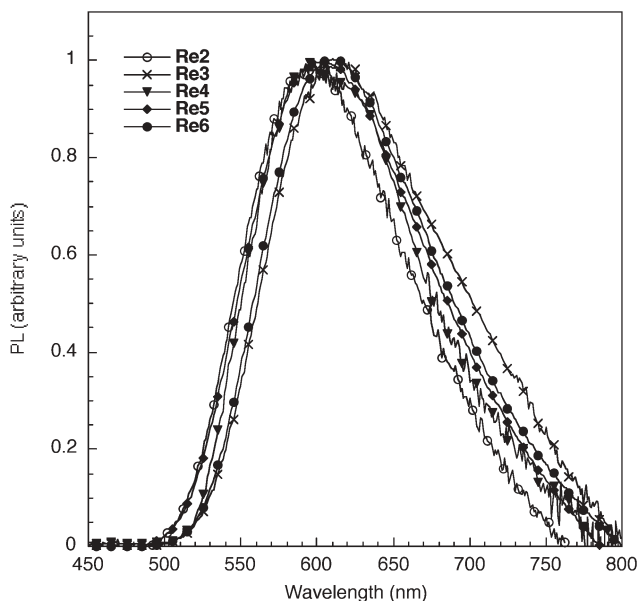


Fig. 6 Film PL spectra of **Re2–6** (the spectra have been normalized).

The film PL spectra are shown in Fig. 6 and the key difference is that the film PL spectra are blue shifted relative to the solution spectra by approximately 20 nm. A blue shift in the solid state relative to the solution PL spectra of rhenium(I) complexes has been reported previously for a complex in a frozen solvent or in a polymer blend and has been termed ‘rigidochromism’.^{27,28} Here, we are observing a similar effect, but in a neat film of the material. The second difference between the solution and solid state PL spectra occurs for **Re6**, which only shows emission from the core complex. This can be explained by the fact that intermolecular energy transfer between any free ligand and the dendrimer core can occur easily in the solid state.

We further probed the photophysical properties of the dendrimers by measuring their PL quantum yields (PLQYs) in tetrahydrofuran with the results summarized in Table 2. The solution PLQYs of the dendrimers ranged between 0.5 and 3% which is similar to that for the parent complex **Re1** (2%) and typical of such complexes. It should be noted that the solution PLQY of **Re6** also contains a component from the ligand fluorescence. In neat film, the PLQYs of all the dendrimers were found to increase relative to their solution values and were in the range from 7% for **Re6** to 19% for **Re2** (Table 2). This is very unusual behaviour; in most complexes, intermolecular interactions in neat films results in extra quenching with respect to the solution.

Table 2 Photoluminescence data

	PL (THF)/nm	PL (film)/nm	EL/nm	PLQY (THF) (%)	PLQY (film) (%)
Re1	629 ^a	—	—	2	—
Re2	632 ^{a,b}	598	612	2	19
Re3	637 ^b	616	613	3	13
Re4	639 ^b	602	596	0.5	10
Re5	632	603	601	1	11
Re6	451, 645 ^a	608	612	0.5	7

^a Excitation wavelength = 360 nm. ^b Excitation wavelength = 300 nm.

We propose that the differences in spectrum and PLQYs between the solution and the solid state are due to differences in molecular geometry and vibronic coupling. In solution the geometry of the molecules is less constrained than in the solid state, and so they can reach a more fully relaxed geometry, resulting in the red shift of solution PL spectra with respect to the film PL spectra. Non-radiative decay can arise from overlap of ground and excited state vibronic wavefunctions with the same energy. Since relaxation energy is proportional to vibronic coupling,²⁹ this non-radiative decay process is stronger in the solution than in the solid state. This explains the lower PLQYs in solution and accounts for the effect of rigidochromism which has not been fully understood. Normally the dendrons would be expected to control the intermolecular interactions in the solid state that lead to quenching of the luminescence with the best case being where the solution and solid state PLQYs are the same.¹⁶ However, with these rhenium(I) complex cored dendrimers it is more difficult to elucidate the role of the dendrons as the PLQY is larger in the solid state when compared to solution. For example, when **Re2** was blended with *m*-bis(carbazolyl)benzene the film PLQY increased to 32%. However, this was associated with a larger blue shift than the neat film and hence the increased PLQY could be due to smaller relaxation and vibronic coupling as well as decreasing the intermolecular interactions that quench the luminescence.

Electrochemical properties

The redox properties of the dendrimers were studied by cyclic voltammetry (CV) (Fig. 7 and Table 3). The redox potentials are quoted against the ferrocenium/ferrocene couple.³⁰ All the complexes showed a chemically reversible reduction at a scan rate of 100 mV s⁻¹ in *N,N*-dimethylformamide. For rhenium(I) complexes the LUMO is predominantly on the heterocyclic ligand, in this case the 1,10-phenanthroline ligand. In spite of the different substitution patterns of the dendrons of the dendrimer there was not a large difference in the reduction potentials of the materials with the reduction $E_{1/2S}$ falling in the range of -1.63 V to -1.76 V. Many neutral rhenium(I) complexes have less chemically reversible oxidations at the usual scan rates used in cyclic voltammetry,³¹ which is in contrast to iridium(III) complexes whose oxidations are generally stable. The first oxidation rhenium(I) complexes undergo is normally associated with the rhenium(I)/rhenium(II) redox couple. For example, **Re1** has been reported to have an essentially chemically irreversible oxidation at scan rates of 1 V s⁻¹ but at a scan rate of 50 V s⁻¹ the redox process becomes more chemically reversible.³¹ We found that dichloromethane was the best solvent for the oxidation studies. We also observed that **Re1** had a chemically irreversible oxidation with E_{pa} (potential of the peak on the anodic scan) of 0.93 V when a scan rate of 100 mV s⁻¹ was used. Attachment of a dendron to the 5-, 3- and 8-, and 4- and 7-positions was found to have no effect on the chemical reversibility of the oxidation processes and no cathodic process was observed for the oxidized species for dendrimers, **Re2**, **Re3**, and **Re4**. In contrast, for **Re5** and **Re6** a cathodic wave was observed for the oxidation with a scan rate of 100 mV s⁻¹ (Fig. 7). However, even under the best

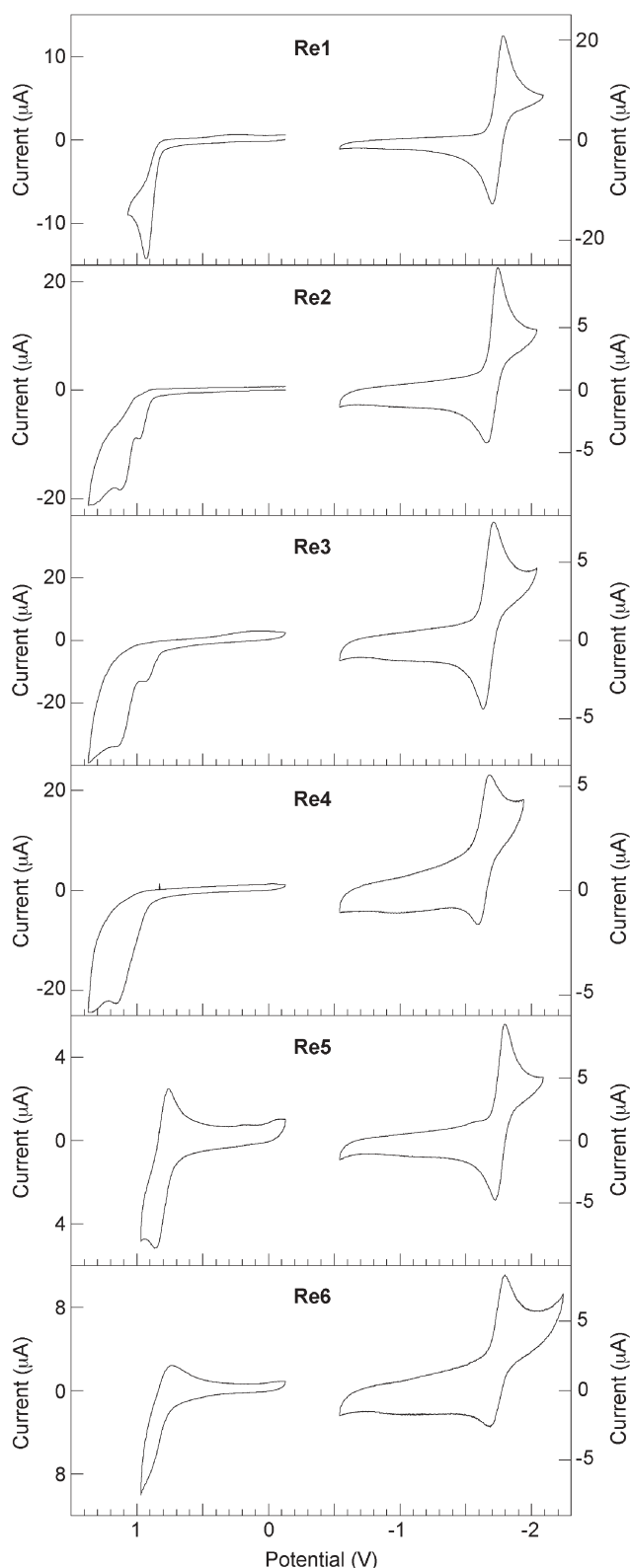


Fig. 7 Cyclic voltammograms of **Re1–6** (the currents for the oxidations and reductions for each material are shown on the left and right axes respectively).

conditions the current decreased on consecutive scans indicating that the redox process was still not fully chemically reversible under the experimental conditions. Nevertheless,

Table 3 Electrochemical data

	$E_{1/2}$ (oxidation)				$E_{1/2}$ (reduction)			
	E_{onset}	E_{pa}	E_{pc}	$E_{1/2}$	E_{onset}	E_{pa}	E_{pc}	$E_{1/2}$
Re1	0.82	0.93			-1.68	-1.70	-1.79	-1.74
Re2	0.81	0.94			-1.66	-1.66	-1.74	-1.70
Re3	0.82	0.92			-1.60	-1.63	-1.71	-1.67
Re4	0.93	1.15			-1.56	-1.60	-1.67	-1.63
Re5	0.73	0.86	0.76	0.81	-1.70	-1.72	-1.80	-1.76
Re6	0.76	0.88	0.75	0.82	-1.68	-1.69	-1.78	-1.74

this is an important step forward as it shows that the bulky **G1** dendrons on the 2- and 9-positions of the 1,10-phenanthroline enhance the stability of the core complex. The $E_{1/2}$ s of **Re5** and **Re6** were just over 0.8 V (Table 3).

Electroluminescent properties

We prepared simple single layer devices comprised of indium tin oxide/neat dendrimer film/calcium/aluminium. Of the six dendrimers **Re5** gave the best device performance with an external quantum efficiency of 0.4% (0.8 cd A^{-1}) and power efficiency of 0.2 lm W^{-1} at 100 cd m^{-2} and 12.8 V. With a solid state PLQY of 11% the maximum external quantum efficiency of the device could be 2.5% taking into account an outcoupling of light of 20% from the device. We can understand the lack of optimum performance from the device by considering the HOMO and LUMO energies of **Re5** relative to Irppy₃. The oxidation of **Re5** is around 0.5 V more positive than that of Irppy₃ meaning that its HOMO energy is around 6.13 eV. In contrast the reduction potential of **Re5** is approximately 1.1 V less negative than Irppy₃ meaning that the LUMO has an energy of 3.6 eV. The electrochemical results therefore suggest that a calcium cathode should have at least an ohmic contact with the dendrimer while there will be a large barrier to hole injection. That is, there will be an imbalance of charge injection with electrons being injected more readily than holes. The performance of the devices could be improved by the use of an insoluble hole transport layer and by blending the dendrimers with a host material.

Conclusion

We have demonstrated that the light-emitting dendrimer technology can be used in conjunction with rhenium(I) complex emitters. By attaching dendrons strategically to the ligands of rhenium(I) it is possible to prepare solution processable materials that have enhanced electrochemical stability and control the intermolecular interactions that cause solvatochromism in solution and PL quenching in the solid state. Finally, we have shown that in spite of modest solid state PLQYs and unbalanced charge injection reasonably efficient devices can be prepared.

Experimental

Unless otherwise noted, all chemicals were obtained from commercial suppliers and used as received. Melting points

were measured on a Leica Galen III hotstage and are uncorrected. The $^1\text{H-NMR}$ spectra were measured in deuterated solvents with either Bruker DPX 400 MHz, AVB 400 MHz, or AVC 500 MHz spectrometers. All J values are quoted in Hertz to the nearest 0.5 Hz. The phenyl rings in the dendron are denoted sp-H (surface phenyl H) and bp-H (branch phenyl H), and the ligand protons are described as L-H. Microanalyses were carried out in the Inorganic Chemistry Laboratory, Oxford University, UK or by the Elemental Analysis Service, London Metropolitan University, UK. The UV-visible absorption spectra were recorded as solutions in HPLC grade dichloromethane with a Perkin-Elmer UV-vis Lambda 25 spectrometer. IR spectra were recorded on a Perkin Elmer Paragon 1000 Infrared spectrometer as film on a sodium chloride plate. Mass spectra were recorded on an Applied Biosystems Voyager matrix-assisted laser desorption/ionisation-time-of-flight (MALDI-TOF) from *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenyldiene] malononitrile (DCTB) in positive reflectron mode or a Finnigan MAT 95XP at the EPSRC National Mass Spectrometry Centre, Swansea, UK, or a Bruker FT-MS Apex III (EI). Thermal gravimetric analysis was performed on a Perkin-Elmer thermogravimetric analyzer TGA7. Differential Scanning Calorimetry (DSC) was performed on a Perkin Elmer Pyris 1. The samples for DSC analysis were prepared by transferring a toluene solution of the dendrimer into the aluminium DSC pan and then the toluene was removed by heating at 100 °C. The sample was then dried under vacuum at room temperature for 1 h before the measurement. Light petroleum refers to the fraction of boiling point 40–60 °C. When solvent mixtures are used for chromatography over silica, the proportions are given by volume. The alumina used for chromatography was basic Brockmann grade I. Electrochemistry was performed using an EG&G Princeton Applied Research potentiostat/galvanostat model 263A. All measurements were made at room temperature on samples dissolved in dichloromethane or *N,N*-dimethylformamide with 0.1 M tetra-*n*-butylammonium tetrafluoroborate as the electrolyte. The sample concentration was 1 mM, and a platinum working electrode, platinum counter electrode in 0.1 M tetra-*n*-butylammonium tetrafluoroborate in the same solvent as used for the sample, and a Ag/0.1 M AgNO₃ in acetonitrile reference electrode were used. The scan rate was 100 mV s⁻¹. The electrolyte was purified by recrystallization from a mixture of ethylacetate and diethylether. The solutions were deoxygenated with argon. The ferricinium/ferrocene couple was used as the standard³⁰ and the ferrocene was purified by sublimation. All potentials are quoted relative to the ferricinium/ferrocene couple. In all cases several scans were carried out to confirm the chemical reversibility of the redox processes. For room temperature photoluminescence measurements, samples were dissolved in spectroscopic grade tetrahydrofuran in quartz degassing cuvettes, degassed by three freeze–pump–thaw cycles, sealed under vacuum, and warmed to nominal room temperature in a bath of tepid water. The optical density (OD) of the samples and standard were similar and small (≤ 0.1 at ≥ 360 nm). Photoluminescence spectra in solution were recorded using a Jobin Yvon Fluoromax 2 fluorimeter, at the highest spectral resolution, using an excitation wavelength

of 300 or 360 nm. Spectra were corrected after measurement using the emission calibration obtained from measuring a calibrated lamp spectrum. PLQYs were measured by a relative method using quinine sulfate in 0.5 M sulfuric acid as a standard.³² The error in this method is estimated to be approximately 10% of the measured value. Films for the solid state PLQYs were spin-coated from a chloroform or dichloromethane solution with a dendrimer concentration of 10 mg ml⁻¹ at 1000 rpm for 1 min to give a thickness of about 150 nm. Their PLQYs were measured using an integrating sphere in accordance with Greenham *et al.* with a Helium Cadmium laser (Kimmon) as the excitation source.³³ The excitation intensity was 0.2 mW at 325 nm and the sphere was purged with nitrogen during the measurements.

Devices were made from solutions spin-coated at 20 mg ml⁻¹ concentration using chloroform or dichloromethane onto cleaned and plasma etched ITO substrates. The samples were then transferred to a vacuum evaporator capable of base pressures of $< 2 \times 10^{-6}$. A metal cathode of 20 nm of calcium followed by a capping layer of 100 nm of aluminium was deposited.

L2. A mixture of **G1** boronic acid (3.72 g, 7.01 mmol), 5-bromo-1,10-phenanthroline³⁴ (1.24 g, 4.79 mmol), tetrakis-(triphenylphosphine)palladium(0) (162 mg, 0.140 mmol), aqueous sodium carbonate (2.1 M, 2.5 cm³), ethanol (2.5 cm³), and toluene (13 cm³) was degassed and placed under nitrogen, and then heated at 100 °C for 24 h. The mixture was allowed to cool to room temperature and then dichloromethane (100 cm³) was added. The organic layer was washed with water (3 \times 100 cm³), dried over magnesium sulfate, and filtered. The solvent was removed and the residue was purified by column chromatography over silica using a methanol–ethyl acetate mixture (1 : 10) as eluent to give **L2** (1.70 g, 54%). Found: C, 83.15; H, 8.0; N, 4.7. C₄₆H₅₂N₂O₂ requires C, 83.1; H, 7.9; N, 4.2%; $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 271 [$\log \epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ (5.1)]; $\delta_{\text{H}}(500 \text{ MHz}, \text{CDCl}_3)$ 0.87–1.03 (12 H, m, CH₃), 1.32–1.59 (16 H, m, CH₂), 1.77 (2 H, m, CH), 3.92 (4 H, m, OCH₂), 7.02 (4 H, 1/2AABB', sp-H), 7.61 (1 H, dd, $J = 8$, $J = 4$, L-H), 7.62–7.65 (6 H, m, sp-H and bp-H), 7.68 (1 H, dd, $J = 8$, $J = 4$, L-H), 7.86 (1 H, s, L-H), 7.87 (1 H, dd, $J = 1.5$, $J = 1.5$, bp-H), 8.28 (1 H, dd, $J = 8.5$, $J = 1.5$ Hz), 8.43 (1 H, dd, $J = 8.5$, $J = 1.5$, L-H), and 9.23 (2H, m, L-H); $\delta_{\text{C}}(125 \text{ MHz}, \text{CDCl}_3)$ 11.1, 14.1, 23.0, 23.9, 29.1, 30.5, 39.4, 70.6, 114.9, 122.9, 123.4, 124.8, 126.49, 126.52, 128.0, 128.1, 128.2, 132.8, 134.7, 136.0, 139.0, 139.7, 141.8, 145.6, 146.3, 150.1, 150.2, 159.3. m/z (EI: M⁺) Found: 664.4 (24%). C₄₆H₅₂N₂O₂ requires 664.9.

Re2. A solution of **L2** (127 mg, 0.191 mmol) and pentacarbonylchlororhenium(i) (77.5 mg, 0.214 mmol) in toluene (10 cm³) was heated at reflux under nitrogen for 2.0 h. The solution was allowed to cool to room temperature and the solvent was removed. The residue was purified by column chromatography over silica using a light petroleum–dichloromethane mixture (1 : 4) to give a yellow solid of **Re2** (96 mg, 52%). Found: C, 60.5; H, 5.5; N, 2.8. C₄₉H₅₂ClN₂O₅Re requires C, 60.6; H, 5.4; N, 2.9%; $\nu_{\text{max}}(\text{thin film})/\text{cm}^{-1}$ 1893 (CO), 1916 (CO), and 2020 (CO); $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 273 [$\log \epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$ (4.85)], 329sh (3.93), and 383sh (3.72); $\delta_{\text{H}}(400 \text{ MHz}, \text{CDCl}_3)$ 0.90–0.99 (12 H, m, CH₃),

1.31–1.60 (16 H, m, CH₂), 1.78 (2 H, m, CH), 3.92 (4 H, m, OCH₂), 7.03 (4 H, 1/2AA'BB', sp-H), 7.59–7.63 (6 H, m, sp-H and bp-H), 7.81 (1 H, dd, *J* = 8.5, *J* = 5, L-H), 7.89–7.92 (2 H, m, bp-H and L-H), 8.06 (1 H, s), 8.56 (1 H, dd, *J* = 8.5, *J* = 1.5, L-H), 8.69 (1 H, dd, *J* = 8.5, *J* = 1.5, L-H), and 9.43 (2 H, m, L-H); δ_{C} (125 MHz, CDCl₃) 11.1, 14.1, 23.0, 23.9, 29.1, 30.5, 39.4, 70.7, 115.1, 125.6, 125.7, 126.1, 126.3, 127.1, 128.2, 130.2, 130.6, 132.3, 137.2, 137.4, 137.9, 141.0, 142.4, 146.5, 147.4, 152.8, 152.9, 159.6, 189.4 (CO), 196.98 (CO), and 197.03 (CO); *m/z* (FAB: M–Cl⁺) Found: 933.5 (64%), 934.5 (36%), 935.5 (100%), 936.5 (52%), 937.5 (17%), and 938.5 (3%). C₄₉H₅₂N₂O₅Re requires 933.3 (54%), 934.3 (31%), 935.3 (100%), 936.3 (53%), 937.3 (15%), and 938.4 (3%); TGA_{5%} 306 °C (2 °C min⁻¹).

Re3. *n*-Butyllithium (1.6 M in hexane, 2.4 cm³, 3.84 mmol) was added to a solution of **G1-Br**²⁵ (2.01 g, 3.55 mmol) in tetrahydrofuran (74 cm³) cooled in an acetone–dry ice bath under nitrogen. The solution was stirred with acetone–dry ice bath cooling for 1 h. Zinc chloride (0.50 g, 3.67 mmol) in tetrahydrofuran (19 cm³) was added to the solution cooled in an acetone–dry ice bath, and then the solution was allowed to warm to room temperature and stirred for 30 min. 4,7-Dibromo-1,10-phenanthroline **2**³⁵ (0.403 g, 1.19 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.026 g, 0.0225 mmol) were added to the solution and then the solution was heated at 80 °C for 17 h. The solvent was removed and the residue was dissolved in dichloromethane (300 cm³). The organic layer was washed with saturated aqueous ethylenediamine tetraacetic acid (3 × 200 cm³) and water (2 × 200 cm³), dried over anhydrous magnesium sulfate, and filtered. The solvent was removed and the residue was partially purified by column chromatography over silica using ethylacetate and then a methanol–dichloromethane mixture (8 : 92) as the eluent to give **L3** as pale brownish solid (≈0.181 g, ≈13%). δ_{H} (400 MHz, CDCl₃) 0.88–0.97 (24 H, m, CH₃), 1.30–1.60 (32 H, m, CH₂), 1.75 (4 H, m, CH), 3.88 (8 H, m, OCH₂), 6.99 (8 H, 1/2AA'BB', sp-H), 7.59–7.63 (12 H, m, sp-H and bp-H), 7.73 (2 H, d, *J* = 4, L-H), 7.85 (2 H, dd, *J* = 1, *J* = 1, bp-H), 8.02 (2H, s, L-H), and 9.32 (2 H, d, *J* = 4, L-H). **L3** was used in the complexation reaction without further purification. A solution of **L3** (0.181 g, 0.157 mmol) and pentacarbonylchlororhenium(I) (0.061 g, 0.169 mmol) in toluene (1.0 cm³) was heated at reflux for 1.5 h. The solution was allowed to cool to room temperature and the solvent removed. The residue was purified by column chromatography over silica using a light petroleum–dichloromethane mixture (1 : 2) as the eluent gave a yellow solid of **Re3** (33 mg, 14%). Found: C, 68.5; H, 6.7; N, 2.0. C₈₃H₉₆ClN₂O₇Re requires C, 68.5; H, 6.65; N, 1.9%; ν_{max} (thin film)/cm⁻¹ 1888 (CO), 1920 (CO), and 2020 (CO); λ_{max} (CH₂Cl₂)/nm 277 [log ϵ /dm³mol⁻¹cm⁻¹ (5.05)], 331sh (4.23), and 385sh (3.98); δ_{H} (400 MHz, CDCl₃) 0.90–0.99 (24 H, m, CH₃), 1.30–1.60 (32 H, m, CH₂), 1.76 (4 H, m, CH), 3.90 (8 H, m, OCH₂), 7.01 (8 H, 1/2AA'BB', sp-H), 7.58–7.62 (12 H, m, sp-H and bp-H), 7.90–7.93 (4 H, m, bp-H and L-H), 8.19 (2 H, s, L-H), and 9.48 (2 H, d, *J* = 5, L-H); δ_{C} (125 MHz, CDCl₃) 11.1, 14.1, 23.0, 23.8, 29.1, 30.5, 39.4, 70.6, 115.1, 125.8, 125.9, 126.1, 126.4, 128.2, 129.2, 132.1, 136.5, 142.5, 147.7, 151.4, 152.5, 159.6, 189.7 (CO), and 197.2 (CO); *m/z* (FAB: M–Cl⁺) Found: 1417.5 (62%), 1418.5 (55%),

1419.4 (100%), 1420.5 (76%), 1421.5 (36%), and 1422.5 (13%). C₈₃H₉₆N₂O₇Re requires 1417.7 (47%), 1418.7 (44%), 1419.7 (100%), 1420.7 (82%), 1421.7 (38%), and 1422.7 (12%); TGA_{5%} 344 °C (5 °C min⁻¹).

Re4. A mixture of **G1** boronic acid (3.31 g, 6.24 mmol), 3,8-dibromo-1,10-phenanthroline **3**³⁶ (0.846 g, 2.50 mmol), tetrakis(triphenylphosphine)palladium(0) (0.223 g, 0.193 mmol), aqueous sodium carbonate (2.0 M, 3.0 cm³), ethanol (3.0 cm³) and toluene (9 cm³) was degassed and placed under nitrogen. The reaction mixture was heated at 100 °C under nitrogen for 23 h. After the mixture was cooled to room temperature dichloromethane (100 cm³) was added. The organic layer was washed with water (3 × 100 cm³), dried over anhydrous magnesium sulfate, and filtered. The solvent was removed and the residue was purified by column chromatography over alumina with dichloromethane as eluent to give a white solid of **L4** (0.380 g, 13%). δ_{H} (400 MHz, CDCl₃) 0.91–0.98 (24 H, m, CH₃), 1.30–1.60 (32 H, m, CH₂), 1.78 (4 H, m, CH), 3.94 (8 H, m, OCH₂), 7.05 and 7.67 (16 H, AA'BB', sp-H), 7.83 (2 H, dd, *J* = 1.5, *J* = 1.5, bp-H), 7.87 (4 H, d, *J* = 1.5, bp-H), 7.98 (2H, s, L-H), 8.58 (2 H, s, L-H), and 9.60 (2 H, s, L-H). **L4** was used for the complexation reaction without further purification. **L4** (0.419 g, 0.364 mmol) and pentacarbonylchlororhenium(I) (0.133 g, 0.368 mmol) in toluene (18 cm³) was heated at reflux for 2.0 h. After the solution was allowed to cool to room temperature the solvent was removed, and the residue was purified by column chromatography over silica using a light petroleum–dichloromethane mixture (1 : 3) as eluent to give a yellow solid of **Re4** (0.126 g, 24%). Mp 260–263 °C (found: C, 68.6; H, 7.1; N, 2.1. C₈₃H₉₆ClN₂O₇Re requires C, 68.5; H, 6.65; N, 1.9%); ν_{max} (thin film)/cm⁻¹ 1883 (CO), 1923 (CO), and 2023 (CO); λ_{max} (CH₂Cl₂)/nm 277 [log ϵ /dm³mol⁻¹cm⁻¹ (5.11)], 346 (4.53), and 420sh (3.45); δ_{H} (400 MHz, CDCl₃) 0.90–1.00 (24 H, m, CH₃), 1.33–1.61 (32 H, m, CH₂), 1.78 (4 H, m, CH), 3.91 (8 H, m, OCH₂), 7.05 and 7.63 (16 H, AA'BB', sp-H), 7.74 (4 H, d, *J* = 1.5, bp-H), 7.84 (2 H, bm, bp-H), 7.97 (2H, s, L-H), 8.59 (2 H, d, *J* = 1.5, L-H), 9.62 (2 H, d, *J* = 1.5, L-H); δ_{C} (125 MHz, CDCl₃) 11.2, 14.2, 23.2, 23.9, 29.2, 30.6, 39.5, 70.7, 115.1, 124.0, 126.5, 127.9, 128.4, 130.3, 132.2, 135.0, 135.6, 138.9, 143.0, 145.3, 151.8, 159.7, 189.8 (CO), and 197.1 (CO). *m/z* (FAB: M–Cl⁺) Found: 1417.5 (72%), 1418.5 (61%), 1419.4 (100%), 1420.5 (74%), 1421.4 (41%), and 1422.4 (19%). C₈₃H₉₆N₂O₇Re requires 1417.7 (47%), 1418.7 (44%), 1419.7 (100%), 1420.7 (82%), 1421.7 (38%), and 1422.7 (12%); TGA_{5%} 276 °C (2 °C min⁻¹).

Re5. *n*-Butyllithium (1.6 M in hexane, 1.9 cm³, 3.04 mmol) was added to a solution of **G1-Br**²⁵ (1.51 g, 2.67 mmol) in diethyl ether (2.7 cm³) cooled in an acetone–dry ice bath under nitrogen, and then the solution was allowed to warm to room temperature and stirred for 1.0 h. The mixture was then cooled in an acetone–dry ice bath and a solution of 1,10-phenanthroline **4** (0.12 g, 0.67 mmol) in toluene (9 cm³) was added slowly. The reaction mixture was allowed to warm to room temperature and then stirred for 18 h. A small amount of water and dichloromethane (100 cm³) were added, and then the mixture was washed with water (150 cm³), dried over anhydrous magnesium sulfate, and filtered. The solvent was removed and the residue was dissolved in dichloromethane

(12 cm³) and activated manganese dioxide (3.06 g) was added. The mixture was stirred at room temperature for 1.0 h and then the reaction mixture was filtered through celite. The filtrate was collected and the solvent removed. The residue was purified by column chromatography over alumina using a light petroleum–dichloromethane mixture (3 : 1) as the eluent to give a brownish solid of **L5** (0.432 g, 56%). δ_{H} (400 MHz, CDCl₃) 0.90–1.00 (24 H, m, CH₃), 1.33–1.61 (32 H, m, CH₂), 1.78 (4 H, m, CH), 3.85 (8 H, m, OCH₂), 6.89 and 7.71 (8 H, AA'BB', sp-H), 7.81 (2 H, s, L-H), 7.88 (2H, bs, bp-H), 8.25 (2 H, d, $J = 8.5$, L-H), 8.34 (2 H, d, $J = 8.5$, L-H), and 8.58 (4 H, bs, bp-H). **L5** was used for the complexation reaction without further purification. **L5** (0.432 g, 0.376 mmol) and pentacarbonylchlororhenium(i) (0.136 g, 0.376 mmol) in toluene (19 cm³) was heated at reflux for 2.0 h. The solution was allowed to cool and the solvent was removed. The residue was purified by column chromatography over silica using a light petroleum–dichloromethane mixture (1 : 5) as the eluent to give a yellow solid of **Re5** (0.235 g, 43%). Found: C, 68.5; H, 6.65; N, 1.9. C₈₃H₉₆ClN₂O₇Re requires C, 68.5; H, 6.65; N, 1.9%; ν_{max} (thin film)/cm⁻¹ 1884 (CO), 1921 (CO), and 2019 (CO); λ_{max} (CH₂Cl₂)/nm 273 [log ϵ /dm³mol⁻¹cm⁻¹ (5.05)], 340sh (4.18), and 395sh (3.64); δ_{H} (500 MHz, CDCl₃) 0.90–1.00 (24 H, m, CH₃), 1.34–1.60 (32 H, m, CH₂), 1.78 (4 H, m, CH), 3.94 (8 H, m, OCH₂), 6.97–7.02 [8 H, m (2 × 1/2AA'BB'), sp-H], 7.66 (4 H, 1/2AA'BB', sp-H), 7.71 (4 H, 1/2AA'BB', sp-H), 7.77 (2H, bm, bp-H), 7.81 (2 H, bm, bp-H), 7.91 (2 H, dd, $J = 1.5$, $J = 1.5$ bp-H), 7.97 (2 H, d, $J = 8.5$, L-H), 8.06 (2 H, s, L-H), and 8.55 (2 H, d, $J = 8.5$ L-H); δ_{C} (125 MHz, CDCl₃) 11.1, 14.1, 23.0, 23.8, 29.1, 30.5, 39.3, 70.5, 114.9, 125.7, 126.0, 126.88, 126.92, 127.2, 128.4, 128.6, 130.0, 132.61, 132.65, 137.9, 141.5, 142.3, 142.8, 148.2, 159.2, 159.3, 164.8, 192.1, and 192.6; m/z (FAB: M⁺) Found: 1452.4 (58%), 1453.4 (50%), 1454.4 (100%), 1455.4 (79%), 1456.4 (58%), 1457.4 (42%), and 1458.4 (26%). C₈₃H₉₆ClN₂O₇Re requires 1452.6 (41%), 1453.7 (39%), 1454.6 (100%), 1455.7 (83%), 1456.6 (60%), 1457.7 (33%), and 1458.6 (13%); TGA_{5%} 320 °C (2 °C min⁻¹).

Re6. *n*-Butyllithium (2.8 cm³, 1.6 M in hexane, 4.48 mmol) was added to a solution of **G1-Br**²⁵ (2.15 g, 3.80 mmol) in diethyl ether (3.8 cm³) cooled in an acetone–dry ice bath under nitrogen, and then the solution was allowed to warm to room temperature and stirred for 1.0 h. The reaction mixture was then cooled in an acetone–dry ice bath and a solution of **L2** (0.63 g, 0.95 mmol) in toluene (12 cm³) was added slowly. After addition the reaction mixture was allowed to warm to room temperature and was stirred for 21 h. A small amount of water and dichloromethane (100 cm³) were added and the mixture was washed with water (150 cm³). The organic layer was collected, dried over anhydrous magnesium sulfate, and filtered. The solvent was removed and the residue was dissolved in dichloromethane (17 cm³) and activated manganese dioxide (8.0 g) was added. The mixture was stirred at room temperature for 1.0 h before being filtered through celite. The filtrate was collected and the solvent removed. The residue was purified by column chromatography over basic alumina using a light petroleum–dichloromethane mixture (5 : 1) as the eluent to give a yellowish solid of **L6** (0.710 g, 46%). m/z (MALDI: M⁺) Found: 1634.1 (100%). C₁₁₄H₁₄₀N₂O requires

1634.3. **L6** was used for the complexation reaction without further purification. **L6** (0.204 g, 0.125 mmol) and pentacarbonylchlororhenium(i) (0.050 g, 0.14 mmol) in toluene (1.0 cm³) was heated at reflux for 1.0 h. The solution was cooled to room temperature and the solvent removed. The residue was purified by column chromatography over silica using a light petroleum–dichloromethane mixture (1 : 2) as the eluent to give a yellow solid of **Re6** (0.042 g, 17%). Found: C, 72.5; H, 7.2; N, 1.5. C₁₁₇H₁₄₀ClN₂O₉Re requires C, 72.4; H, 7.3; N, 1.4%; ν_{max} (thin film)/cm⁻¹ 1885 (CO), 1926 (CO), and 2022 (CO); λ_{max} (CH₂Cl₂)/nm 272 [log ϵ /dm³mol⁻¹cm⁻¹ (5.25)], 338sh (4.40), and 400sh (3.73); δ_{H} (400 MHz, CDCl₃) δ 0.90–1.00 (36 H, m, CH₃), 1.27–1.61 (48 H, m, CH₂), 1.76 (6H, m, CH), 3.90 (12 H, m, OCH₂), 6.97–7.10 [12 H, m (3 × 1/2AA'BB'), sp-H], 7.63–7.75 (14 H, m, sp-H and bp-H), 7.77–7.81 (3 H, m, bp-H), 7.83 (1 H, bs, bp-H), 7.90–7.94 (4 H, m, bp-H and L-H), 8.01 (1 H, d, $J = 8.5$, L-H), 8.12 (1 H, s, L-H), 8.57 (1 H, d, $J = 8.5$, L-H), and 8.73 (1 H, d, $J = 8.5$, L-H); m/z (MALDI: M⁺) Found: 1937.0 (38%), 1938.0 (48%), 1939.0 (97%), 1940.0 (100%), 1941.0 (74%), 1942.0 (45%), 1943.0 (24%), and 1944.0 (10%). C₁₁₇H₁₄₀ClN₂O₉Re requires 1937.0 (33%), 1938.0 (44%), 1939.0 (95%), 1940.0 (100%), 1941.0 (80%), 1942.0 (50%), 1943.0 (25%), and 1944.0 (9%); TGA_{5%} 356 °C (5 °C min⁻¹).

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References

- M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson and S. R. Forrest, *Nature*, 1998, **395**, 151.
- C. Adachi, M. A. Baldo, S. R. Forrest and M. E. Thompson, *Appl. Phys. Lett.*, 2000, **77**, 904.
- W.-Y. Wong, C.-L. Ho, Z.-Q. Gao, B.-X. Mi, C.-H. Chen, K.-W. Cheah and Z. Lin, *Angew. Chem., Int. Ed.*, 2007, **46**, 1558.
- S.-Y. Takizawa, Y. Sasaki, M. Akhtaruzzaman, H. Echizen, J.-I. Nishida, T. Iwata, S. Tokito and Y. Yamashita, *J. Mater. Chem.*, 2007, **17**, 841.
- S.-Y. Kim, J.-H. Kim, Y. Ha, S.-H. Lee, J.-H. Seo and Y.-K. Kim, *Curr. Appl. Phys.*, 2007, **7**, 380.
- S.-C. Lo, C. P. Shipley, R. N. Bera, R. E. Harding, A. R. Cowley, P. L. Burn and I. D. W. Samuel, *Chem. Mater.*, 2006, **18**, 5119.
- Y.-Y. Lu, C.-C. Ju, D. Guo, Z.-B. Deng and K.-Z. Wang, *J. Phys. Chem. C*, 2007, **111**, 5211.
- N. J. Lundin, P. J. Walsh, S. L. Howell, J. J. McGarvey, A. G. Blackman and K. C. Gordon, *Inorg. Chem.*, 2005, **44**, 3551.
- Z. Ming, L. Ping, X. M. Wang, H. Lin, X. Hong, Z. Wu, Y. Bing, L. L. Liu, Y. Li, Y. Min, Y. G. Ma, J. K. Feng, D. J. Wang and N. Tamai, *J. Phys. Chem. B*, 2004, **108**, 13185.
- B. Li, M. T. Li, Z. R. Hong, W. L. Li, T. Z. Yu and H. Z. Wei, *Appl. Phys. Lett.*, 2004, **85**, 4786.
- F. Li, M. Zhang, G. Cheng, J. Feng, Y. Zhao, Y. G. Ma, S. Y. Liu and J. C. Shen, *Appl. Phys. Lett.*, 2004, **84**, 148–150.
- S. Ranjan, S. Y. Lin, K. C. Hwang, Y. Chi, W. L. Ching, C. S. Liu, Y. T. Tao, C. H. Chien, S. M. Peng and G. H. Lee, *Inorg. Chem.*, 2003, **42**, 1248.
- Y. Q. Li, Y. Liu, J. H. Guo, F. Wu, W. J. Tian, B. F. Li and Y. Wang, *Synth. Met.*, 2001, **118**, 175.
- W. K. Chan, P. K. Ng, X. Gong and S. J. Hou, *Appl. Phys. Lett.*, 1999, **75**, 3920.
- X. Gong, P. K. Ng and W. K. Chan, *Adv. Mater.*, 1998, **10**, 1337.

- 16 J. P. J. Markham, S.-C. Lo, S. W. Magennis, P. L. Burn and I. D. W. Samuel, *Appl. Phys. Lett.*, 2002, **80**, 2645.
- 17 T. D. Anthopoulos, J. P. J. Markham, E. B. Namdas, J. R. Lawrence, I. D. W. Samuel, S.-C. Lo and P. L. Burn, *Org. Electron.*, 2003, **4**, 71.
- 18 S.-C. Lo, T. D. Anthopoulos, E. B. Namdas, P. L. Burn and I. D. W. Samuel, *Adv. Mater.*, 2005, **17**, 1945.
- 19 G. J. Zhuo, W.-Y. Wong, B. Yao, Z. Y. Xie and L. X. Wang, *Angew. Chem., Int. Ed.*, 2007, **46**, 1149.
- 20 T. Tsuzuki, N. Shirasawa, T. Suzuki and S. Tokito, *Jpn. J. Appl. Phys.*, 2005, **44**, 4151.
- 21 J. Ding, J. Gao, Y. Cheng, Z. Xie, L. Wang, D. Ma, X. Jing and F. Wang, *Adv. Funct. Mater.*, 2006, **16**, 575.
- 22 S.-C. Lo, E. B. Namdas, C. P. Shipley, J. P. J. Markham, T. D. Anthopoulos, P. L. Burn and I. D. W. Samuel, *Org. Electron.*, 2006, **7**, 85.
- 23 J. P. J. Markham, I. D. W. Samuel, S. C. Lo, P. L. Burn, M. Weiter and H. Bässler, *J. Appl. Phys.*, 2004, **95**, 438.
- 24 E. B. Namdas, A. Ruseckas, I. D. W. Samuel, S.-C. Lo and P. L. Burn, *J. Phys. Chem. B*, 2004, **108**, 1570.
- 25 S.-C. Lo, E. B. Namdas, P. L. Burn and I. D. W. Samuel, *Macromolecules*, 2003, **36**, 9721.
- 26 P. J. Giordano and M. S. Wrighton, *J. Am. Chem. Soc.*, 1979, **101**, 2888.
- 27 M. Wrighton and D. L. Morse, *J. Am. Chem. Soc.*, 1974, **96**, 998.
- 28 T. G. Kotch, A. J. Lees, S. J. Fuerniss, K. I. Papatomas and R. W. Snyder, *Inorg. Chem.*, 1993, **32**, 2570.
- 29 M. Pope and C. E. Swenberg, *Electronic Processes in Organic Crystals and Polymers*, Oxford University Press, New York, 2nd edn, 1999.
- 30 G. Gritzner and J. Kuta, *Pure Appl. Chem.*, 1984, **56**, 461.
- 31 J. C. Luong, L. Nadjo and M. S. Wrighton, *J. Am. Chem. Soc.*, 1978, **100**, 5790.
- 32 J. N. Demas and G. A. Crosby, *J. Phys. Chem.*, 1971, **75**, 991.
- 33 N. C. Greenham, I. D. W. Samuel, G. R. Hayes, R. T. Phillips, Y. Kessener, S. C. Moratti, A. B. Holmes and R. H. Friend, *Chem. Phys. Lett.*, 1995, **241**, 89.
- 34 M. Hissler, W. B. Connick, D. K. Geiger, J. E. McGarrah, D. Lipa, R. J. Lachicotte and R. Eisenberg, *Inorg. Chem.*, 2000, **39**, 447.
- 35 G. I. Graf, D. Hastreiter, L. E. da Silva, R. A. Rebelo, A. G. Montalban and A. McKillop, *Tetrahedron*, 2002, **58**, 9095.
- 36 Y. Saitoh, T. Koizumi, K. Osakada and T. Yamamoto, *Can. J. Chem.*, 1997, **75**, 1336–1339.

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