

Synthesis of Host Polymers and Guests for Electrophosphorescence

Scott E. Watkins^{1*}, Khai Leok Chan^{1,2}, Sung Yong Cho^{1,2}, Nicholas R. Evans², Andrew C. Grimsdale¹, Andrew B. Holmes^{1,3*}, Chris S. K. Mak², Albertus J. Sandee², and Charlotte K. Williams³

¹School of Chemistry, Bio21 Institute, University of Melbourne, Parkville, Vic. 3010, Australia

²Melville Laboratory, Department of Chemistry, Lensfield Road, Cambridge CB2 1EW, UK.

³Department of Chemistry, Imperial College, South Kensington, London SW7 2AZ, UK.

Received October 9, 2006; Revised November 9, 2006

Abstract: Significant progress has been realized in the design and synthesis of light emitting polymers that emit over the entire visible spectrum. However, up to seventy-five percent of charge recombination events can lead to triplet states that decay non-radiatively. Following the pioneering work in the field of small molecule organic light emitting devices, it has been found that solution processible iridium polymer complexes can be used to harness the wasted triplet energy. In this paper, new results with respect to the electrophosphorescence of solution processible tethered iridium polymer derivatives are presented. Furthermore, our approaches to the design of new high triplet energy conjugated polymer hosts are also reported.

Keywords: conjugated polymers, electrophosphorescence, synthesis, characterization, device physics.

Introduction

The discovery of electroluminescence from conjugated polymers has stimulated an intense area of research.^{1,2} Significant progress has been realised in the design and synthesis of light emitting polymers with emission over the whole range of the visible spectrum. However, up to seventy-five percent of charge recombination events can lead to triplet states that decay non-radiatively. In order to compete with continuing advances in other display technologies there is growing interest in harnessing this lost energy to improve device efficiencies. Following the pioneering work in the field of small molecule organic light emitting devices it has been found that solution processible iridium polymer complexes can be used to harness the wasted triplet energy. In this paper, two approaches to the preparation of solution processible iridium-containing polymer derivatives will be presented. Our approaches to the design of new high triplet energy conjugated polymer hosts will also be reported.

Electrophosphorescent Polymer Complexes

The design criteria for electrophosphorescent polymer complexes have been inspired by the work of Forrest and Thompson and colleagues in the field of small molecule

devices where they have demonstrated that incorporation of tris-cyclometallated iridium complexes in the emissive layer can capture the triplet energy from electron-hole recombination that is then re-emitted as phosphorescence.³ Heavy metal complexes have been introduced into conducting polymer matrices in order to use all the triplet and singlet excitons.

These complexes, which exhibit strong spin-orbit coupling, are able to harvest both the single and triplet excitons within the polymer and emit phosphorescence. It has been proposed that the triplet state emission in phosphorescent dye-doped polymer systems is enhanced due to charge trapping-induced direct recombination on the phosphorescent dopants rather than long-range Förster energy transfer alone.⁴

An added requirement for the observation of electrophosphorescence is that the triplet energy level of the polymer should be higher, or close to, that of the metal complex so as to minimise energy back-transfer to the polymer. To this end, several groups have reported phosphorescent PLEDs using poly(vinylcarbazole) (PVK) as the host polymer. Gong *et al.*⁵ have studied Ir complexes with different triplet energies (from green to red) blended into PVK and polyfluorene hosts. Devices with PVK as the polymer host demonstrated stable guest EL and a higher device efficiency than those of polyfluorene, which has poor host to guest energy transfer and triplet confinement as a result of the low triplet energy level. Very recently Cao *et al.* have reported efficient electrophosphorescence from a blend of a blue phosphorescent iridium complex and a high triplet energy polymer host.⁶ The limitation faced by a blended system however is that of

*Corresponding Authors. E-mail: s.watkins@unimelb.edu.au or aholmes@unimelb.edu.au

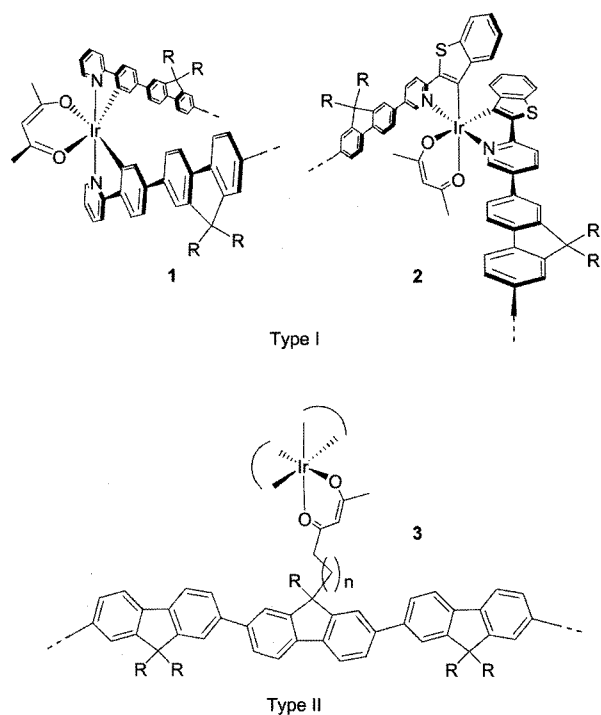


Figure 1. Illustration of the covalently linked iridium polymers.

phase separation, i.e. aggregation of the phosphorescent dopant in the conjugated-polymer film, resulting in reduced emission efficiency through concentration quenching. Our intention was to prepare solution processible polymer hosts in which the phosphorescent emitters were incorporated into the polymer chain through covalent linking via the ligands on the metal complex by conjugation (Type I)^{7,8} or by tethering to the polymer backbone through an alkyl pendant (Type II)^{9,10} to give devices that were expected to exhibit superior efficiencies compared with the blends (see Figure 1).

Conjugatively Linked Polymers (Type I). Since energy transfer from the conjugated host to the mixed metal to ligand charge transfer orbitals must be downhill, the benzo[*b*]thienylpyridyl complexes (2) were considered the most suitable for evaluation. The synthesis strategy for these polymers depended on constructing functionalized benzo[*b*]thienylpyridyl ligands from which oligo- and polyfluorene arms could be grown by chain extension using Suzuki cross-coupling reactions. Well-defined oligomeric structures were selected to obtain information on the influence of triplet energies as a function of the extent of chain extension. The general strategy for polymer synthesis is illustrated in Figure 2.

Non-Conjugatively Linked Polymers (Type II). The strategy for the synthesis of the tethered iridium complexes rests on the synthesis of well-defined macromonomers **10** and the iridium-functionalized monomers **11** and **12** carrying the iridium complex tethered by a short (one CH₂ group) or

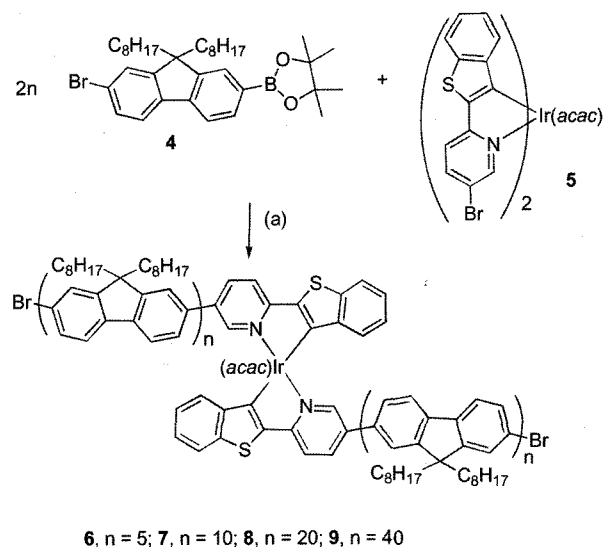


Figure 2. Synthesis of fluorene-extended complexes 6-9. Reagents and Conditions: (a) Pd(OAc)₂, PCy₃, Et₄NOH, toluene, reflux, 24 h, 50-60%.

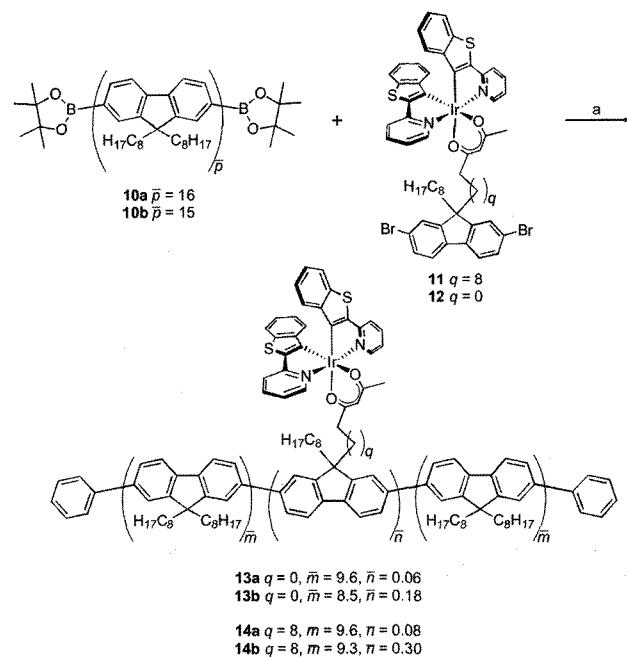


Figure 3. Synthesis of tethered iridium copolymers. Reagents and conditions: a, Pd(OAc)₂, PCy₃, chlorobenzene, aq. Et₄NOH, 90 °C, 2 h, **13a** ca. 77%, **13b** ca. 86%, **14a** ca. 76%, **14b** ca. 78%.

long (eight CH₂ group) chain to the 9-position of the fluorene host. As shown in Figure 3 the resulting macro-monomer was then copolymerised by Suzuki reaction with boronate- and bromo-substituted fluorene comonomers to give statistical copolymers carrying a distribution of iridium-tethered fluorene units in the host fluorene polymer. The polymers were end capped with phenyl substituents.

Relative Electroluminescent Efficiencies. Under relatively similar conditions the total electroluminescence quantum efficiency of the octamethylene-tethered iridium complex **14a**⁹ is about 30% higher than for the conjugatively linked complex **9**.⁷

High Triplet Energy Hosts. The host polymers illustrated in Figure 1 are all based on the 9,9-dialkylfluorene unit, the homopolymer of which has previously been reported to have a triplet energy of 2.1 eV.¹¹ Polyfluorene is therefore a suitable host for phosphorescent guests that emit at energy lower than 2.09 eV (i.e. red emitters). To investigate host materials for high energy green and blue phosphorescent emitters the low temperature phosphorescence spectra of a series of silicon-based polyfluorene analogues were recorded. To validate this approach we were able to obtain the triplet energy level of poly(9,9-dioctyl-2,7-fluorene) by measuring its phosphorescence spectrum at 77 K using a cryostat fitted to a Varian Cary Eclipse fluorescence spectrometer with the capability of producing pulsed excitations and recording time-delayed emission. The emission spectrum consists of a sharp band centering at 2.09 eV (Figure 5) that is taken as a measure of the homopolymer triplet energy level. This value is consistent with that reported by Bässler *et al.* (2.1 eV).¹¹ The fully conjugated poly(2,7-disubstituted dibenzosilole) **17** was prepared via a Suzuki cross-coupling reaction, Figure 4.¹² Whilst poly(9,9-dihexyl-2,7-dibenzosilole) **17** has emerged as a more colour-stable polymer than polyfluorene the photophysical characteristics of **17** were comparable with that of polyfluorene. The triplet energy level of polymer **17** was found by a similar technique to the one described above to be 2.14 eV (Figure 5), making **17** also an ideal host for red emitters. Although the triplet energy is favorably higher than that of polyfluorene by 0.05 eV, this is still insufficient to allow **17** to be a host for higher-energy green and blue electrophosphorescent emitters.

In order to produce host polymers capable of working with high energy green and blue phosphorescent emitters the design principle first enunciated by the Philips group using 3,7-linkages with carbazole derivatives was employed.¹² We

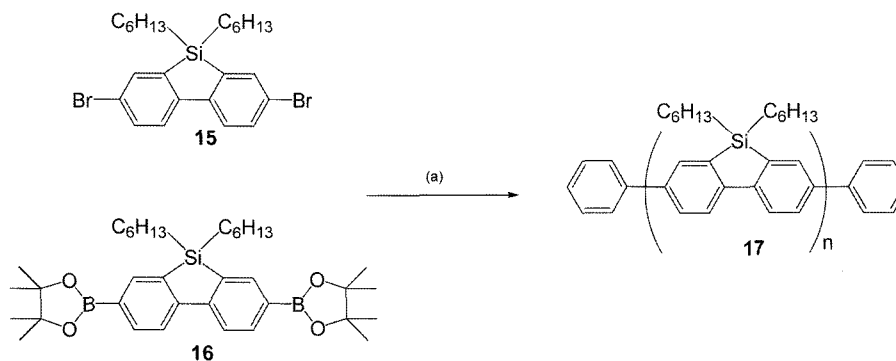


Figure 4. The synthesis of the dibenzosilole polymer **17**. Reagents and conditions: (a) Pd(OAc)₂, tricyclohexylphosphine, Et₄NOH, toluene, 90 °C, then PhB(OH)₂, 2 h, then PhBr, 2 h, 93%.

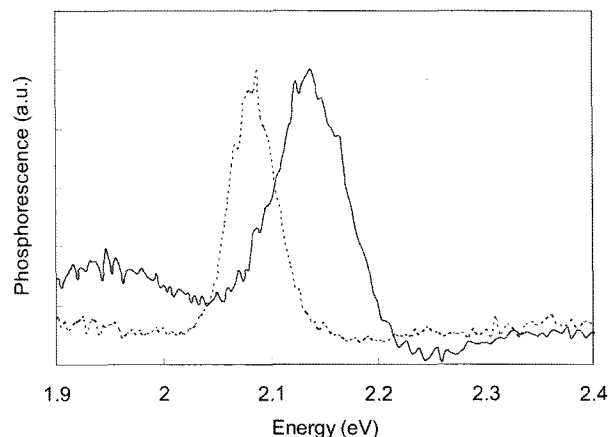


Figure 5. Phosphorescence spectrum of poly(9,9-dioctyl-2,7-fluorene) (---) and poly(9,9-dihexyl-2,7-dibenzosilole) (—).

selected the 3,6-disubstituted dibenzosilole building blocks **18** and **19** and coupled these materials by Suzuki reaction to afford the host polymer **20**, Figure 6.^{13,14}

Triplet Energy of Polymer 20. The photoluminescence (PL) spectrum of a thin film of **20** at 77 K exhibited a 0-0 transition at 3.5 eV and a second maximum at 3.3 eV (excitation at 4.4 eV). The phosphorescence emission spectrum of **20** was obtained at 77 K using a cryostat fitted to a commercially available fluorescence spectrometer. The emission consists of a broad band exhibiting vibronic structure (excitation at 3.9 eV). The onset of the triplet emission of the homopolymer is measured at 2.55 eV and this is taken as a measure of the homopolymer triplet energy level. We have found this method to be a reliable procedure for estimating triplet energies of conjugated polymers. The triplet energy of 2.55 eV implies that the polymer is a potential host for phosphorescent emitters that have a triplet energy level lower than 2.55 eV, without the risk of energy back transfer onto the polymer. This triplet energy is significantly higher than that of commonly used polyfluorenes (2.1 eV), and comparable with that of PCaz (2.6 eV).¹⁵ To investigate the capability

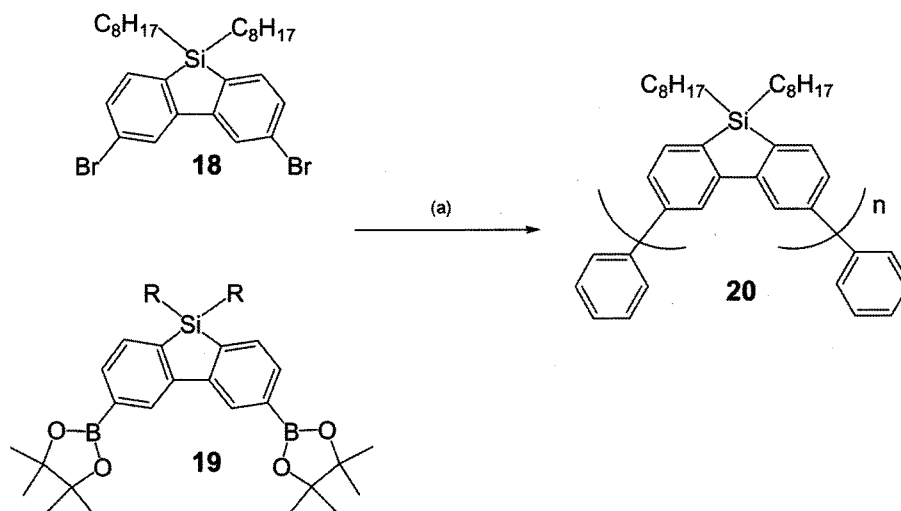


Figure 6. The synthesis of the dibenzosilole polymer **20**. Reagents and conditions: (a) $\text{Pd}(\text{OAc})_2$, tricyclohexylphosphine, Et_4NOH , toluene, 90°C , then $\text{PhB}(\text{OH})_2$, 2 h, then PhBr , 2 h, 93%.

of **20** as a high-energy polymer host, *fac*-tris[2-(2-pyridyl- κN)-5-methylphenyl]iridium(III), ($\text{Ir}(\text{m-ppy})_3$), which has a triplet energy of 2.4 eV, was blended into a toluene solution of the polymer (8 wt%) to provide a green phosphorescent dopant. The electroluminescence emission from an unoptimised neat emissive layer device of the configuration ITO/PEDOT:PSS/polymer blend/LiF/Al showed complete energy transfer from the polymer host to the green dopant at a drive voltage of 4 V, and the absence of any emission from **20**.¹³

Experimental

The conjugated triplet emitting polymers **6-9** were prepared by Suzuki chain extension reactions using an AB monomer with the bromo-substituted iridium complexes.⁷ The tethered triplet emitting polymers **13** and **14** were prepared by statistical co-polymerization of fluorene macromonomers as the bis(boronates) with a dibromofluorene carrying the iridium complex tethered at the 9-position.⁹ The poly(dibenzosiloles) **17** and **20** were prepared by conventional Suzuki cross coupling polymerizations as used for polyfluorene itself.^{12,13}

The triplet energy of polymers **17** and **20** were measured by spin-coating a 10 mg/cm^3 toluene solution of each of the polymers at 2,500 rpm onto a glass microscope slide. The slide was mounted on a glass holder and inserted into an Oxford Instruments Optistat DN cryostat. The cryostat was evacuated, the sample chamber was filled with helium gas and then cooled to 77 K. The cryostat was mounted on a baseplate inside the sample chamber of a Varian Cary Eclipse fluorescence spectrometer. The phosphorescence spectrum was recorded in "phosphorescence mode" with the number of flashes set to 50, a delay of 5 ms and a gate of 100 ms. This allowed the weak phosphorescence peak to be separated from the high intensity, but rapidly decaying, flu-

orescence signal.

Conclusions

In conclusion this work has illustrated the potential for the synthesis of covalently linked solution processible electrophosphorescent polymers based on fluorene hosts and the design of polydibenzosilole host polymers with high triplet energy.

Acknowledgements. We thank the Gates Cambridge Trust and the Universities UK (scholarships to K.L.C.), the Croucher Foundation (Fellowship to CSKM), the Engineering and Physical Sciences Research Council (UK), the European Commission, the Australian Research Council, CSIRO and VESKI for generous financial support. We thank Prof. A. Köhler (University of Potsdam), Ms Lekshmi Sudha Devi, Dr C. E. Boothby, Prof. Sir Richard Friend (University of Cambridge), Dr C. Towns, Dr M. J. McKiernan (CDT) and Prof. K. P. Ghiggino (University of Melbourne) for their contributions to this work.

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