Synthesis of Host Polymers and Guests for Electrophosphorescence

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Introduction

The discovery of electroluminescence from conjugated polymers has stimulated a wide search for alternative polymeric materials for this application [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. 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 concerning the preparation of solution processible tethered iridium polymer derivatives will be presented. Furthermore our approaches to the design of new high triplet energy conjugated polymer hosts will 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.
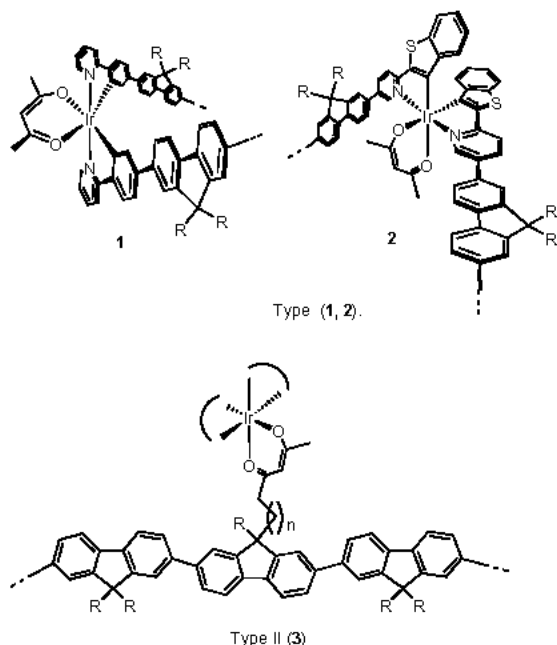
These complexes, which exhibit strong spin-orbit coupling, are able to harvest both the single and triplet excitons within the polymer and emit phosphorescence. It has been proposed that the triplet state emission in phosphorescent dye-doped polymer systems is enhanced due to charge trapping–induced 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 must be higher than that of the metal complex so as to minimise energy back-transfer to the polymer. 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 poly(vinylcarbazole) (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. The limitation faced by a blended system however is that of 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) [6, 7] or by tethering to the polymer backbone through an alkyl pendant (Type II) [8, 9] 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.
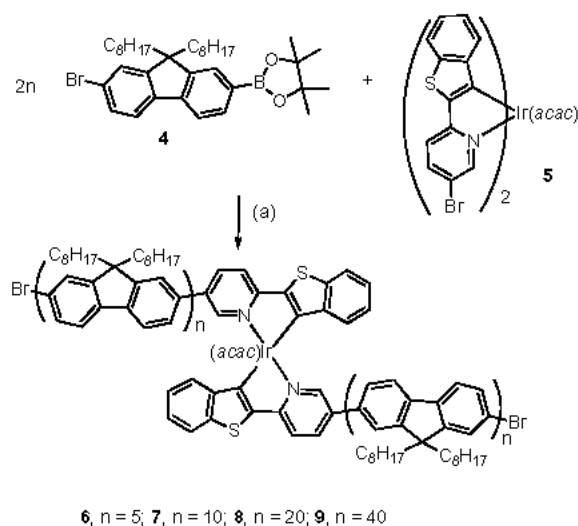

Type (1, 2).

Type II (3)

Figure 1. Illustration of the covalently linked iridium polymers

6, n = 5; **7**, n = 10; **8**, n = 20; **9**, n = 40

Figure 2. Synthesis of fluorene-extended ligands **6**-**9**
Reagents and Conditions: (a) (Pd(OAc)$_2$, PCy$_3$, Et$_4$NOH, toluene, reflux, 24h, 50-60%.

Non-Conjugatively Linked Polymers (Type II)

The strategy for the synthesis of the tethered iridium complexes rests on the synthesis of well-defined macromonomers **11** and **12** carrying the iridium complex tethered by a short (one CH_2 group) or long (eight CH_2 group) chain to the 9-position of the fluorene host. This macromonomer 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.
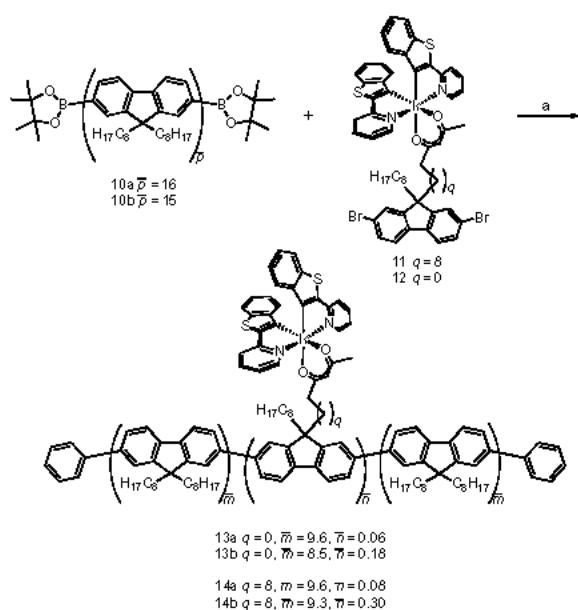

10a $\bar{p}$ = 16
10b $\bar{p}$ = 15

11 q = 8
12 q = 0

13a q = 0, $\overline{m}$ = 9.6, $\overline{n}$ = 0.06
13b q = 0, $\overline{m}$ = 8.5, $\overline{n}$ = 0.18

14a q = 8, m = 9.6, n = 0.08
14b q = 8, $\overline{m}$ = 9.3, $\overline{n}$ = 0.30

Figure 3. Synthesis of tethered iridium copolymers
Reagents and conditions: *a*, Pd(OAc)$_2$, PCy$_3$, chlorobenzene, aq. Et$_4$NOH, 90 °C, 2 h, **13a** *ca.* 77%, **13b** *ca.* 86%, **14a** *ca.* 76%, **14b** *ca.* 78%.

High Triplet Energy Hosts

The high energy triplet host materials were selected on a design principle first enunciated by the Philips group using 3,7-linkages with carbazole derivatives [10]. We selected the 3,6-disubstituted dibenzosilole building blocks **15** and **16** and coupled these materials by Suzuki reaction to afford the host polymer **17**.
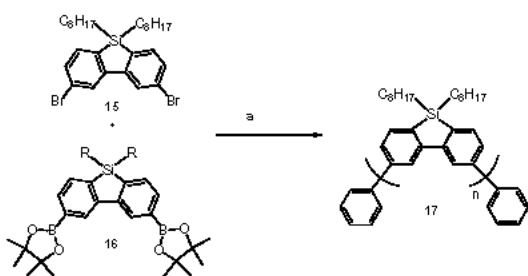

Figure 4. The high triplet energy dibenzosilole host **17**
Reagents and conditions: a) Pd(OAc)$_2$, tricyclohexylphosphine, Et$_4$NOH, toluene, 90 °C, then PhB(OH)$_2$, 2 h, then PhBr, 2 h, 93%

Triplet Energy of Polymer 17

The photoluminescence (PL) spectrum of a thin film of **17** 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 **17** 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) [10]. To investigate the capability of **17** as a high-energy polymer host, *fac*-tris[2-(2-pyridyl-κN)-5-methylphenyl]iridium(III), (Ir(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 **17**.

Conclusion

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

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