Solution Processable Phosphorescent Red Luminescent Polymer for OLED Devices

Raju Adhikari†, Almar Postma†, Juo-Hao Li†, Kazuya Arima†, Tadahiko Hirai‡, Hideyuki Shimizu‡, Mark Bown‡ and Kazunori Ueno†

Abstract This study reports on the synthesis of red phosphorescent, solution processable chain-end functional, mid-chain- and three-arm star polymers from a functionalized styryl monomer host and a RAFT agent containing a tris-cyclometalated Ir(III) complex phosphorescent group (dopant). The polymerization was carried out in toluene at 120 °C, and the resulting polymers showed a narrow molecular weight distribution (D<1.3) and contained approximately 6-11 mol% of the Ir(piq)₃ complex. All polymers showed good solubility in non-polar organic solvents and exhibited red emission. Of these polymers, the three-arm star polymer showed better energy transfer (in film) compared to the midchain functional and end chain functional polymers. No significant difference in optical properties and energy levels was found for the end functional vs the mid-chain and three-arm star polymers. Preliminary device evaluation of the end functional Ir(piq)₃ poly(host) showed a current efficiency of 0.4 cd/A at 10 mA/cm² and a voltage of 10.5 V with color CIE 1931 coordinate (0.68, 0.31).

Keywords: Electrophosphorescent, Solution processable, Red PhoLEDs, RAFT, Device, Polymer OLEDp-5

1. Preface

Organic light-emitting diodes (OLEDs) are being considered as the next generation technology of flat-panel display. The development of red phosphorescent Ir(III) complexes with high quantum yields compared to green emitters has been found to be relatively challenging because they are intrinsically less emissive. Although Ir(piq)₃ and Ir(btp)₃ (acetoacetonate) are well known as red phosphorescent emitters (piq and btp; 1-phenylisoquinolinato-N,C₂0 and 2-(20-benzo[b]thienyl)pyridinato-N,C₃0 ligands, respectively), their photoluminescence quantum yields in solution are not more than 0.26. In order to achieve high device performance of red emitting OLEDs, highly emissive red phosphorescent materials and suitable small molecules host are required.

The recent focus has been towards making polymer based red phosphorescent light-emitting diodes (P-PhoLEDs) in comparison to small molecules because they have the advantage of being easily fabricated using wet processes such as spin-coating and ink-jet printing. In polymer based devices, polymer phosphorescent (P-PhoLEDs) have been reported with higher efficiencies as compared to polymeric light emitting diodes (PLEDs) because of the better usage of excitons for the phosphorescent dyes. However, in the polymer based devices, unbalanced charged carriers (electrons and holes) and their unmatched mobility are often considered to be the main problem which needs to be addressed to achieve high efficiency.

Initially the focus on material for PLEDs has mostly been on conjugated polymers. Suzuki cross coupling and Yamamoto coupling have been widely used as the method of choice for making these polymers. The external quantum efficiency of PLEDs based on conjugated polymer doped with phosphorescent dyes has generally been reported to be much lower when compared to small molecules. This low efficiency is attributed to the phosphorescent quenching phenomenon in conjugated polymers, generally due to low triplet energy. To date, the highest efficiency, 16.9 cd/A and 17.6 lm W⁻¹ at 220 cd m⁻², was reported using Ir(C8piq)₃, Ir(4F5MPiq)₃ dopants and polyfluorene host derivatives. Polyvinylcarbazole (PVK) type host polymer has also been studied widely and the efficiencies are reported to be poor compared to green PLED. For most of the red P-PhoLED devices,
quantum efficiency has been reported to drop rapidly with increasing current density and brightness, attributed to the long phosphorescent lifetime, causing potential saturation of the emission sites triplet-triplet annihilation (TTA)\textsuperscript{20}).

Recently, the focus has shifted towards making pendant type polymers due to their reported higher triplet energy compared to conjugated polymers. With the advent of living radical polymerisation techniques\textsuperscript{22)}, polymers can now be prepared with control over molecular weight, molecular weight dispersities, end-group(s) and topology. Of the living polymerisation techniques, reversible-addition fragmentation chain transfer (RAFT)\textsuperscript{23)} was chosen for its suitability with a range of polymerisation conditions, monomer functionalities, lack of metal impurities and prior success in synthesizing electroactive polymers\textsuperscript{24)–27}).

We herein report for the first time the synthesis of end-functional, mid-functional and three-arm star polymers from styrenic functionalised host monomer. Polymerised under the control of mono, bis or tri thio-carbonylthio-functional Ir(piq)\textsubscript{3} RAFT agents (Figs. 1, 2, 3), allowing for the specific placement of the dopant within the polymer chain. We chose homoleptic cyclometalated iridium phenylisoquinoline[Ir(piq)\textsubscript{3}] complex as the dopant due to its reported high efficiency. Conjugating it onto polymer chains would mitigate its poor solubility and solution processability issues. The polymer was solution processed as an emissive layer in the construction of a red P-PhoLED device.

2. Main Section

2.1 Synthesis: Dopant and RAFT agents

Mono (1), bis (2) and tri thio-carbonylthio-functional (3) Ir(piq)\textsubscript{3} RAFT agents (Fig.1) were synthesised from vinyl functionalised isopicolinic acid monomer in overall 16% yield, via the single monomer addition synthetic method previously published\textsuperscript{25)}. The RAFT agents were purified by column chromatography using silica gel and their structures were confirmed by \textsuperscript{1}H NMR and mass spectra.

In a typical synthetic procedure, Ir(piq)\textsubscript{2}(piq-vinyl) (4) (150 mg, 0.14 mmol), 2-cyanopropan-2-yl methyl carbonitrile (0.069 g, 0.90 mmol), 2,2’-azodiisobutyronitrile (0.009 g, 0.14 mmol) was weighed into a glass ampoule. Toluene (2.0 mL) was added to the ampoule and warmed to dissolve the reaction mixture. The reaction mixture was then degassed by three freeze-pump-thaw cycles prior to the ampoule being sealed. After heating the reaction mixture for 24 hr at 80 °C, the ampoule was cooled to room temperature and the solvent was removed under rotary evaporation. The crude product was purified by column chromatography (chloro-
form:ethyl acetate = 7:3) to give the product 1 (0.30 g, Yield = 17%). The bis and tri thiocarbonylthio-functional RAFT agents (2, 3) were also prepared by this method. As shown in Scheme 1, the synthesis of the above RAFT agent precursor Ir(piq)2 (piq-vinyl) monomers 4, 5 and 6 were prepared by reacting 1-(4-vinylphenyl)isoquinoline (B') with cyclometalated Ir(III) chloro-bridge dimers (B) prepared from 1-phenylisoquinoline (A) following literature procedures. The reaction yielded a mixture of mono, bis and tri vinyl-functional compounds (4, 5 and 6) which were purified by column chromatography using silica gel with chloroform and petroleum ether (CHCl3:PE) as eluent. The starting material 1-(4-vinylphenyl)isoquinoline monomer (B') was in turn prepared by Suzuki coupling reaction of 1-chlorophenylisoquinoline (A') in quantitative yield (94%).

2.2 Host monomer

Styrene functionalised host monomer was synthesised by reacting p-bromo host compound with the styrylboronic acid in about 46% yield. (The structure of the host compound is not disclosed here due to confidentiality agreements). UV and PL spectra of host monomer film and solution are shown in Fig.2. The synthesized host monomer showed high quantum yield (QY) 0.96 and showed blue emission with the PL peak around 411 nm.

2.3 RAFT polymerisation

Solution blending of the dopant in different ratios with the host monomer in toluene at room temperature was carried out to investigate the energy transfer from host to dopant. On the basis of the doping experiments, the energy transfer from host to dopant was found to reach an optimum at 6 mol% and saturated at 10 mol% dopant concentration to host. Accordingly, 6 mol% dopant concentrations were targeted in the polymerisation formulations. The host monomer was polymerised using Ir(piq)3 RAFT agents (1, 2, 3). The overall monomer conversion in the series was found to be between 48 to 77% and polymers showed Mn in the range of 12700 to 37500 and polydispersities (D) between 1.17 to 1.37. The end-functional, mid chain-functional and three-arm star polymers showed good solubility (solubility parameters. i.e. mg/mL) in non-polar organic solvents such as toluene, chloroform, and chlorobenzene. The compositions and properties of synthesised polymers are summarised in Table 1.

In a typical procedure for the synthesis of the end-functional poly(host)-Ir(piq)3, styrene functionalised host monomer (50 mg, 0.353 M), Ir(piq)2(piq-RAFT) (1.2 mg, 3.53 mM) and VR110 initiator (0.027 mg, 0.35 mM) were transferred to an ampoule with toluene (0.3 mL). The ampoule was degassed, sealed and heated at 120 ˚C for 20.5 h. The ampoule was cooled to room temperature and the sample taken for NMR conversion analysis showed 77% conversion. The reaction mixture was diluted with additional chloroform and precipitated into hexane:chloroform (1:1), 2 times for removal of the unreacted monomer by precipitation, to give the final polymer (24 mg), $M_n^{Th} = 37400, M_n^{GPC} = 16600, D = 1.28$. 

![Fig.3 UV-Vis and PL spectra of polymers (Table 1; entries 5, 6, 7; (a), (b) and (c), respectively) in solution and film (excitation wavelength 300 nm).](image-url)
(polystyrene equivalent). The mid chain-functional and three-arm star polymers were also synthesised and purified by above methods, results summarised in Table 1. Differences in $M_n$ and $M_n^{GPC}$ are expected as the hydrodynamic volume of the host polymer differs significantly from that of the polystyrene standards. The three arm star polymer would also have a reduced hydrodynamic volume to its linear counterpart.

### 3. Photophysical properties of the polymers

The UV-vis and PL spectra’s of synthesised polymers were taken in both film and solution. As shown in Fig.3, the absorption peaks around 400 nm may correspond to the typical spin allowed metal to ligand charge transfer transitions. The PL spectrum showed the blue emission of the host at around 400 nm and the emission of the red dopant at 621 nm. The energy transfer is found better in film than in solution in all three polymers, it is most likely because of the shorter distance between the molecules in the solid form resulting in better Förster energy transfer. Further, three-arm star polymer showed better energy transfer (in film) compared to the mid chain and end-functional polymers.

The photo-physical properties of synthesized polymers are shown in Table 2. The highest occupied molecular
orbital (HOMO) was calculated by "AC2 machine (Riken Keiki)" and lowest unoccupied molecular orbital (LUMO) was calculated from the UV-vis absorption spectrum edge and the HOMO. There was found no significant change in the energy levels amongst three polymers. The HOMO/LUMO found to increase slightly in polymer. However, the relative HOMO/LUMO levels of dopants and host polymers are an indicative of efficient energy transfer from host polymers to dopant. All the synthesized polymers exhibited strong red emission (Ex-300 nm) at room temperature.

Of the above polymers, the end-functional poly(host)-Ir(piq)₃ polymers was selected for evaluation in the device without removing the thiocarbonylthio RAFT end-group. The structure of the OLEDs is ITO (130 nm)/PEDOT:PSS (40 nm)/Emitting layer (35 nm)/2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (40 nm)/LiF (1 nm)/Al is shown in Fig.4(a) and the device performances J-V-L characteristic and current efficiency are shown in Fig.5.

The above red OLED device showed a current efficiency of 0.4 cd/A at 10 mA/cm² and a voltage of 10.5 V. The color is deep red and the CIE 1931 coordinate is (0.68, 0.31). Early studies without optimization from the first fabricated simple device structure showed high turn-on voltage with poor efficiency and device structure needs further optimisation. It is reported that the thiocarboxylthio end-group within the polymer may cause the quenching of the light emission²⁵). Also from the current-voltage luminance (Fig.5(a)), one can realise that there is an issue of the charge imbalance which needs the optimisation of the device structure to improve the performance. Further work on device structure and evaluation of polymers is in progress.

4. Conclusions

Polymers were synthesised with controlled molecular weights, architecture and narrow molecular weight dispersions. P-PhoLED device prepared from synthesised linear end functional polymer, containing 6 wt% dopant, showed deep red emission with CIE 1931 coordinate is (0.68, 0.31). The poor device performance from the first fabricated device is largely attributed to the device structure and to the potential quenching from the thio-

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**Table 2** Summary of photophysical properties of host monomer, Ir(piq), and polymers.

<table>
<thead>
<tr>
<th>Compound</th>
<th>HOMO eV</th>
<th>LUMO eV</th>
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<tr>
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</tr>
<tr>
<td>Ir(piq)₂</td>
<td>5.1</td>
<td>3.42</td>
</tr>
</tbody>
</table>

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**Fig.4** Device structure ITO (130 nm)/PEDOT:PSS (40 nm)/polymer (Table 1; entry 5) (35 nm)/BCP (40 nm)/LiF (1 nm)/Al(a). 365 nm Photoemission and CIE coordinate for the polymer (Table 1; entry 5) (enclosed is photo of polymer sample showing red emission (b).
The current-voltage-luminance characteristics of the red Bravybrook, Dr. Jo Cosgriff (Mass spectrometry) & Mr. Roger Mulder, Dr. Jo Cosgriff (NMR), Mr. Carl mize device performance.

without thiocarbonylthio end-groups is planned to opti-

improving device structure and evaluation of polymers carbonylthio end-group in the polymer. Further work on improving device structure and evaluation of polymers without thiocarbonylthio end-groups is planned to optimum device performance.

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[References]


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