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Synthesis and characterization of quinoline-based copolymers for light emitting diodes

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Two new electroluminescent copolymers containing biquinolines and 2,2-diphenylhexafluoropropane (F-PQ) or pyridine (Py-PQE) moieties were prepared. They possess excellent thermal stability (decomposition temperature greater than 500 °C), good electrochemical reversibility in reduction reactions, and high electron affinity. The energy levels for HOMO and LUMO determined by cyclic voltammetry were -5.80 and -2.89 eV for F-PQ, and -5.88 and -2.66 eV for Py-PQE, respectively. Electrical characterization of a double layer light emitting diode (LED) based on the structure of ITO/copper phthalocyanine (CuPc)/F-PQ/Al showed good performance (a rectification ratio greater than 10^5 and a low turn-on voltage of 6.2 V). A single layer LED fabricated with Py-PQE as an emitting layer and air-stable aluminium as a cathode exhibited a balanced injection/transport of hole and electron. A luminance of 94.0 cd m^{-2} was observed from a double layer LED of ITO/CuPc/Py-PQE/Al at a current density of 141.4 mA cm^{-2}.

Introduction

Following the first report that poly(cyanovinyleneterephthalylidene), a dialkoxy-substituted poly(*p*-phenylenevinylene) (PPV) derivative with cyano-groups on the vinylene units, possesses higher electron affinity and shows high internal efficiency (4%) in polymeric light-emitting diodes (LEDs),[1] there has been great interest in these materials[2–11] and their potential for making large area flat color displays. The operation of organic/polymeric LEDs involves the injection of electrons from the cathode into the lowest unoccupied molecular orbital (LUMO) of the electroluminescence (EL) materials and holes from the anode into the highest occupied molecular orbital (HOMO), transporting charge through the devices; capture of opposite charges forms an exciton which emits light during radiative decay. From this picture, the energy barriers between electrodes and LUMO–HOMO are crucial for charge injection. However, most of the EL polymers have higher LUMO levels (near the vacuum level) due to their π-excessive nature. In those cases, the energy barrier between the cathode and the EL material is larger than the energy barrier between the anode and the EL material. This leads to an imbalance in the injection and transport of electrons and holes and limits the efficiency of LEDs severely. The injection of electrons can be improved either by use of low work function metal contact (*e.g.* calcium) or by incorporating an electron-transporting/hole-blocking layer between the cathode and the EL layer. However, the low work function metal is highly susceptible to atmospheric degradation and the fabrication of multilayer devices is technically difficult in practice. Therefore, the approach of employing a high affinity polymer is useful for injecting and transporting electrons for the development of highly efficient and stable LEDs. On the other hand, as a high performance EL material, it should have a combination of high EL efficiency, good thermal, chemical, electrochemical and optical stability, excellent film-forming ability, high purity and low cost. Polyquinolines (PQ) have outstanding thermal stability, low relative permittivities, low moisture absorption, and good film-forming properties.[12–14] A blue EL device using a fluorinated polyquinoline (PQ-100) as the emitting layer has been reported.[15] However, this device possessed a very high turn-on voltage (50 V). More recently, hole-blocking/electron-transporting properties of quinoline-contained copolymers[16] and voltage-tunable multicolor emission polyquinoline-based heterojunction LEDs[17] have also been reported. On the other hand, 2,2-diphenylhexafluoropropane and pyridine, which are π-deficient, have a rather high electron affinity. In the hope of combining both the blue light-emitting and good film-forming properties of the bisquinoline and the high electron-affinitive behavior of the 2,2-diphenylhexafluoropropane–pyridine into a single polymer to enhance the overall performance of an EL device, we have copolymerized these two functional moieties *via* the Friedländer condensation reaction. In this paper, we report the synthesis, characterization of this polymer, and preliminary results of their EL behavior.

Results and discussion

Synthesis and characterization

The synthesis of the copolymers (F-PQ, Py-PQE) is shown in Scheme 1. 2,2-Bis(4-acetylphenyl)hexafluoropropane (**1**) was obtained by a reduction reaction of 2,2-bis(4-carboxyphenyl)-hexafluoropropane with methyllithium in THF followed by hydrolysis with 2 M HCl. 4,4′-Diamino-3,3′-dibenzoylbiphenyl (**2**) and bis(4-amino-3-benzoylphenyl) ether (**3**) were prepared using the procedure that was reported by Stille.[18] The copolymers were prepared by the acid-catalyzed Friedländer condensation reaction between **1** and **2** or 2,6-diacetylpyridine and **3** with a mole ratio of 1 : 1 in diphenyl phosphate and *m*-cresol at 135–140 °C for 48 h under nitrogen (75% yield for F-PQ and 46% for Py-PQE).[19]

F-PQ was readily soluble in common organic solvents, such as chloroform, tetrahydrofuran (THF) and cyclopentanone. Py-PQE was less soluble than F-PQ, however, it could be soluble in chloroform with ultrasonic-assistance for 30 min. The weight average and number average molecular weights of F-PQ, measured by gel permeation chromatography (GPC)

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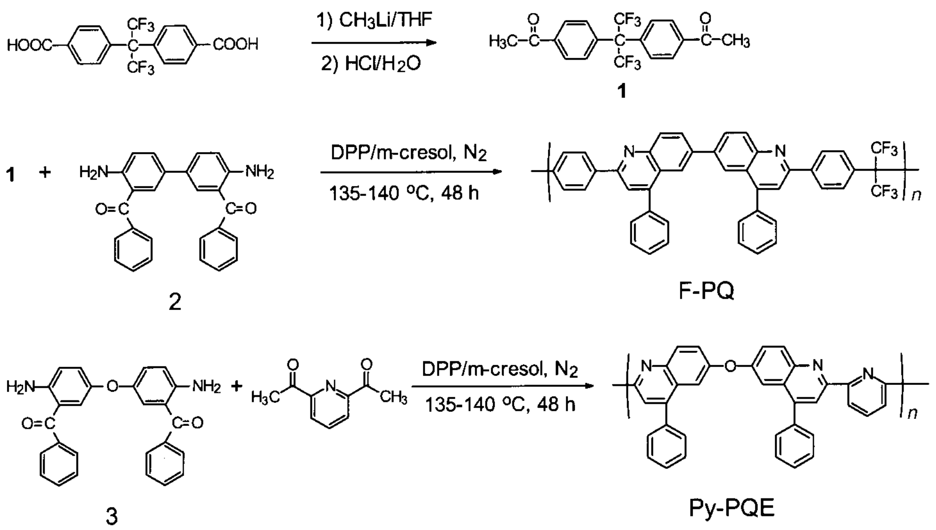

Scheme 1 Synthesis of F-PQ and Py-PQE.

using THF as eluant and polystyrene as standard were $M_w = 59000$, $M_n = 48000$ with a polydispersity index of 1.23. No molecular weight was obtained for Py-PQE since it was not soluble in THF. Homogeneous and pin-hole free thin films were prepared easily by spin-coating technique from their chloroform solutions.

Thermal stability

Thermal properties of the polymers were examined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements. Fig. 1 shows TGA curves of (a) F-PQ and (b) Py-PQE. It shows that the polymers start weight loss at 223 °C for F-PQ and at 528 °C for Py-PQ. 2.1% of weight loss up to 500 °C for F-PQ and 15.0% of weight loss up to 800 °C with a decomposition temperature (T_d) of 561 °C for Py-PQE are observed. It is well known that polyquinoline derivatives are one of the most highly thermally stable polymers,[20,21] and the weight loss for F-PQ in the range of 223–374 °C seems anomalous. To clear this point, a thermal treatment for F-PQ at 350 °C for 10 min was carried out under a nitrogen atmosphere. No obvious weight loss for the second heating process was observed for the treated sample of F-PQ up to 500 °C. The thermally treated F-PQ was still soluble in $CHCl_3$, and no detectable changes were found both for its UV–Vis and ^{1}H-NMR spectra, indicating no chemical change happened during the thermal treatment. Thus, the weight loss in the range of 223–374 °C is probably caused by the release of encapsulated solvents in the polymer. However, the encapsulated solvents were difficult to get rid of by drying at medium temperature (*e.g.* 80 °C) under vacuum. Fig. 2 shows a glass transition temperature (T_g) at 286 °C for Py-PQE. These results demonstrate that F-PQ and Py-PQE possess excellent thermal stability, which are good enough as EL materials.

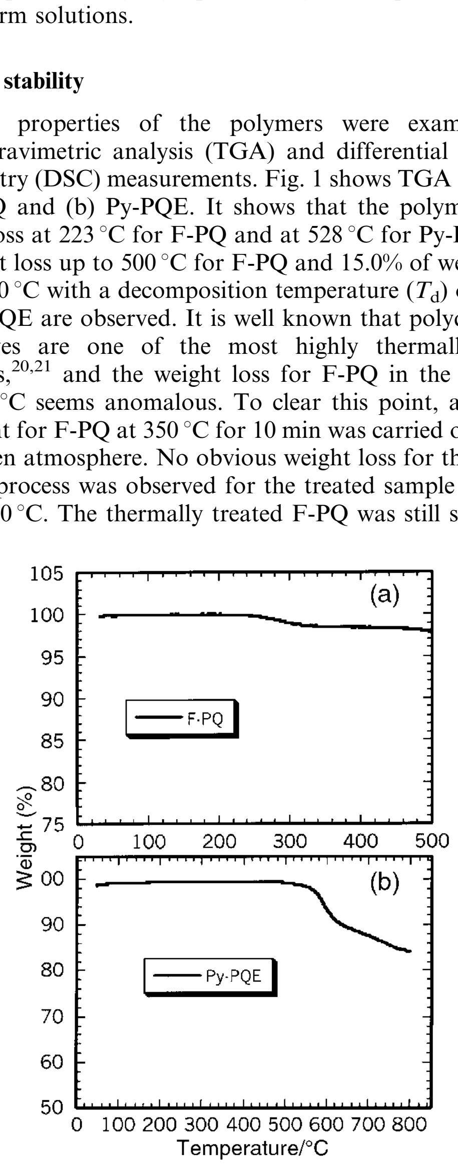

Fig. 1 Thermogravimetric analysis curve of (a) F-PQ and (b) Py-PQE.

Electrochemical properties

The oxidation process corresponds to the removal of electrons from the HOMO band (*p*-doping), whereas the reduction cycle corresponds to the filling of the energy state by electrons to the LUMO band (*n*-doping). Therefore, the onset oxidation and reduction potentials are closely related to the energies of the HOMO and LUMO levels of an organic molecule and thus can provide important information regarding the magnitude of the energy gap. Typical cyclic voltammetry (CV) curves of (a) F-PQ and (b) Py-PQE are shown in Fig. 3. Under a negative scan, two quasi-reversible waves both for F-PQ and Py-PQE (formal potentials $E^{I}_{1/2} = -1.88$ V, $E^{II}_{1/2} = -2.12$ V for F-PQ; $E^{I}_{1/2} = -2.06$ V for Py-PQE *vs.* Ag/Ag$^+$) were observed. However, under a positive scan, only an irreversible anodic wave was observed both for F-PQ and Py-PQE. In general, for conjugated polymers only reduction or oxidation processes are observed or only one process is found to be reversible. In our case, the biquinoline moiety provides a site of reduction at the unbonded electrons on the nitrogen atom because it is relatively electron deficient.

The energy levels of the polymers were calculated using the ferrocence (FOC) value of −4.8 eV as the standard.[22,23] The onset potentials of the oxidation and the reduction (Fig. 3)

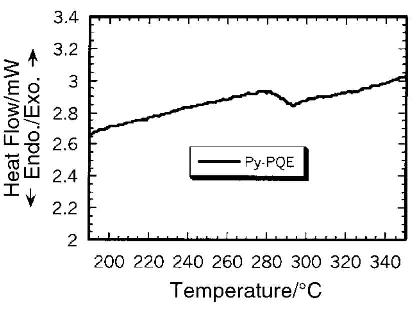

Fig. 2 Differential scanning calometry curve of Py-PQE.

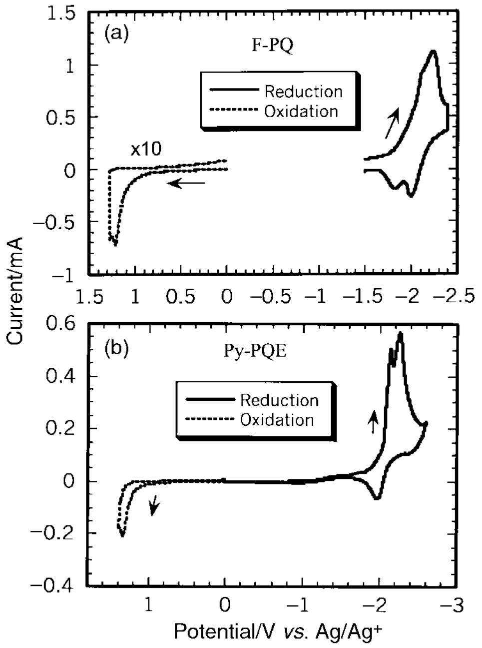

Fig. 3 Cyclic voltammetry of TPDPQ-FPQ spun-coated on ITO glass in an acetonitrile solution of TBAP (0.1 M) at a scan rate of 40 mV s^{-1}.

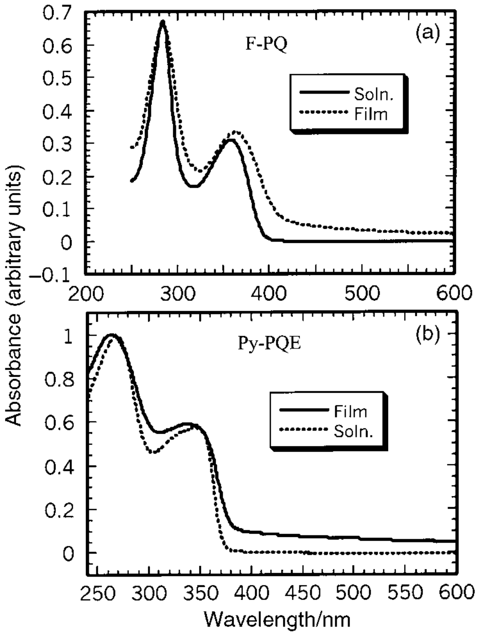

Fig. 4 UV–Vis absorption spectra. (a) F-PQ in chloroform (solid line) and as film (dotted line), (b) Py-PQE in chloroform (dotted line) and as film (solid line).

were determined to be +1.12 and −1.79 V *vs.* Ag/Ag$^+$ for F-PQ, and +1.20 and −2.02 V for Py-PQE. The formal potential of FOC was measured to be 0.12 V against Ag/Ag$^+$. Therefore, the HOMO, LUMO energy levels and the band gap (E_g^{EC}) were −5.80, −2.89 and 2.91 eV for F-PQ, and −5.88, −2.66 and 3.22 eV for Py-PQE, respectively. It is worth noting that as a result of the introduction of the 2,2-diphenylhexafluoropropane and pyridine moieties into the polymer main chain both F-PQ and Py-PQE have a high electron affinity (F-PQ, LUMO = −2.89 eV; Py-PQE, LUMO = −2.66 eV). This is useful in designing new highly electron affinitive copolymers.

Ultraviolet–visible absorption and photoluminescence (PL) spectra

UV–Vis spectra both from the spin coated film on a quartz plate and a solution of the polymer are given in Fig. 4. The absorption spectra exhibit similar absorption spectra with two peaks either in solution (λ_{max}: 283, 360 nm for F-PQ; λ_{max}: 267, 347 nm for Py-PQE) or in the film state (λ_{max}: 283, 363 nm for F-PQ; λ_{max}: 263, 340 nm for Py-PQE). Note that the UV–Vis spectra of the films have a long absorption tail. This will affect the PL spectra reducing the shortest wavelength emissions. The optical band gaps (E_g^{OPT}) determined by the absorption edge of the film are 3.02 eV (λ_{onset} = 410 nm) for F–PQ and 3.26 eV (λ_{onset} = 380 nm) for Py–PQE. Obviously, in the case of Py–PQE, the band gap values obtained from optical methods and from electrochemical data are in excellent agreement (E_g^{EC} = 3.22 eV), however, in case of F-PQ, there is slight difference between them (E_g^{EC} = 2.91 eV, E_g^{OPT} = 3.02 eV). Such a difference has been reported in the literature.[24,25] Huang *et al.*[25] thought the optical value corresponds to the pure band gap between the valence band and the conduction band, while the electrochemical data may be the result of the optical band gap coupled with the interface barrier between the polymer film and the electrode surface, which leads to a larger value. In contrast to their results, we found the electrochemical value was smaller than the optical value. Although the cause is still unclear, the real situation could be even more complex. We assume that the difference might be not only due to the two different approaches used but also should depend on the polymer itself. Another possibility may be related to the oxidation process since the oxidation is irreversible. This raises the question of whether it is really oxidation of the polymer or some other electrochemical process; in the latter case the discrepancy would not be surprising.

PL spectra are shown in Fig. 5. The PL spectrum of F-PQ in chloroform has a maximum at 408 nm with a well defined vibronic feature at 424 nm and a weak shoulder at around 495 nm when it was excited at 366 nm, while the thin film has a maximum at 528 nm with a well defined vibronic feature at 450 nm. The fluorescence quantum yield of F-PQ in chloroform solution was measured to be φ_{PL} = 0.385, using dilute quinine sulfate in 0.5 M H_2SO_4 as a reference by assuming its PL efficiency of 0.546 at 365 nm excitation. For Py-PQE, in chloroform the emission spectrum peaked at 398 nm and is

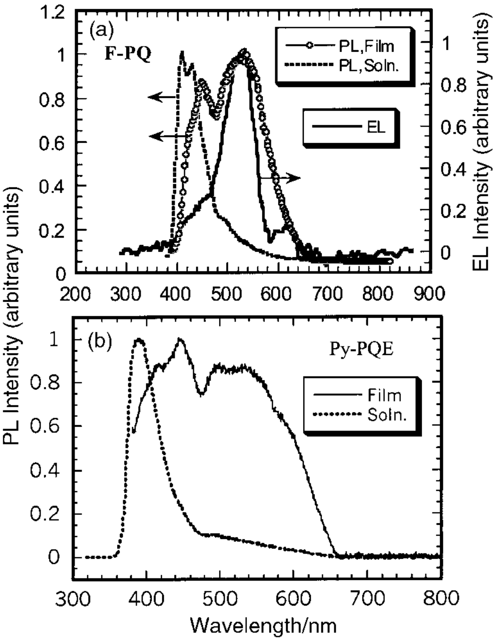

Fig. 5 Photoluminescence and electroluminescence spectra. (a) PL spectra of F-PQ in chloroform (dotted line) and as film (solid with circle line), EL spectrum of an ITO/CuPc/F-PQ/Al device; (b) PL spectra of Py-PQE in chloroform (dotted line) and as film (solid line).

narrow with a full width at half maximum (FWHM) of 50 nm, however, the spin coated film shows a very broad emission spectrum with peaks at 440, 500 and 536 nm and an FWHM of 230 nm. The weaker broad emission peaks at 500 and 536 nm might be assigned as the excimer emission.[26] Indeed, a large difference in PL between solution and film was observed, suggesting that aggregates or excimer formation existed in the film, which are usually deleterious to PL.

Electroluminescence properties

Fig. 6 shows the current–voltage (*I–V*) characteristics for a device of ITO/copper phthalocyanine (CuPc)/F-PQ/Al. The device revealed an excellent diode behavior, *i.e.*, under the forward bias (a positive voltage that was applied to the ITO electrode), the current increased superlinearly with the increase of applied voltage after exceeding the turn-on voltage. Moreover, under reverse bias, no obvious increase of current was observed when the applied voltage was increased. The turn-on voltage and rectification ratio were determined to be 6.2 V, and 1.8×10^5 (at ±6.5 V). The EL spectra for the device of ITO/CuPc/F-PQ/Al exhibited an emission peak (λ_{max} = 523 nm) and a weak shoulder at around 440 nm. Yellow–green light emission was observed in daylight under forward bias.

Fig. 7 shows the current–voltage–brightness (*I–V–B*) characteristics for two LEDs of (a) ITO/Py-PQE/Al and (b) ITO/CuPc/Py-PQE/Al. The rectification ratios were 2.0×10^3 at ±7.8 V for ITO/Py-PQE/Al and 17.1 at ±11.5 V for ITO/CuPc/Py-PQE/Al. In addition, under reverse bias the current increased superlinearly when the applied voltage (absolute value) was larger than 11.5 V. The most significant feature derived from the *I–V–B* curves was that for a single layer device of ITO/Py-PQE/Al the turn-on voltages both for current and light were almost the same at 5.9 V, indicating a balanced injection/transport of hole and electron, while for the double layer device of ITO/CuPc/Py-PQE/Al the turn-on voltages for current and light were at 9.7 and 8.1 V, respectively, when CuPc was used as the hole injection/transport layer. As a result of rather high electron affinity of the Py-PQE polymer, the overall charge injection/transport of the single layer device may be balanced without an additional hole or electron transport layer (Fig. 7a). The external quantum efficiency of ITO/Py-PQE/Al was 0.002%, the same as that using poly{[2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylene]vinylene} (MEH-PPV) as the emitting layer in the same device configuration,[27] which has been widely investigated in organic LEDs. The luminance was 32 cd m^{-2} at 6 mA, corresponding to a current density of 84.9 mA cm^{-2}. In the case of the double layer device ITO/CuPc/Py-PQE/Al, the external quantum efficiency was slightly increased to 0.003% (Fig. 7b), and the luminance was 94.0 cd m^{-2} at a current density of 141.4 mA cm^{-2}.

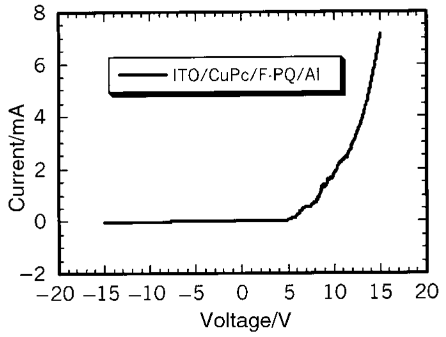

Fig. 6 Current–voltage characteristic for the light emitting device of ITO/CuPc/F-PQ/Al.

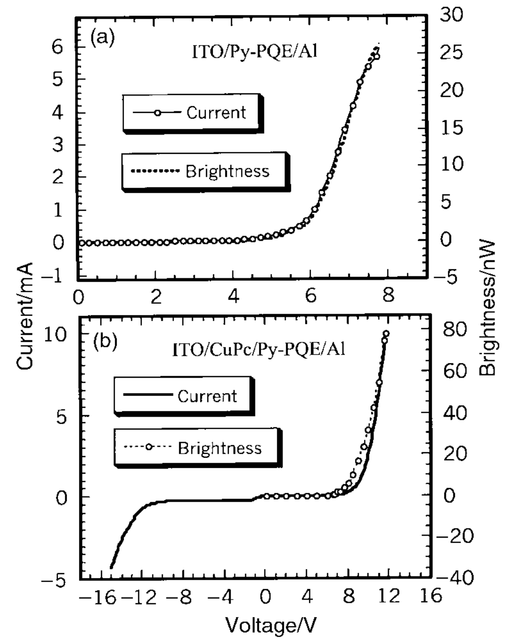

Fig. 7 Current–voltage–brightness characteristics for light emitting devices. (a) ITO/Py-PQE/Al, (b) ITO/CuPc/Py-PQE/Al.

Conclusion

In conclusion, two new copolymers composed of alternating biquinoline and 2,2-diphenylhexafluoropropane/pyridine were synthesized *via* a simple Friedländer condensation reaction. These polymers possess excellent thermal stability, good electrochemical reversibility in reduction reaction, high electron affinity and good thin film-forming properties. In addition, a single layer LED device with the relatively air-stable aluminium electrode using Py-PQE as an emitter layer showed a balanced injection/transport of hole and electron and compatible external quantum efficiency (0.002%) with MEH-PPV.[27]

Experimental section

Materials

All solvents used in this study were purified according to standard methods prior to use, all other chemicals were of reagent grade and used as purchased without further purification.

Synthesis

2,2-Bis(4-acetylphenyl)hexafluoropropane (1). To a stirred solution of 2,2-bis(4-carboxyphenyl)hexafluoropropane (19.60 g, 50 mmol) in 30 mL of THF was added methyllithium (1.0 M solution in THF–cumene) (250 mL, 250 mmol, 5 equiv.) by syringe at 0 °C under nitrogen. After the stirring for 2 h, the reaction mixture was poured into a solution of 2 M HCl (600 mL) at 0 °C. The resulting solution was extracted with methylene chloride. The organic layer was separated, washed with water and dried over Na_2SO_4. The solvent was then removed by rotatory evaporation under reduced pressure and the viscous liquid was purified through a packed silica gel column with hexane–methylene chloride (2 : 3) as eluant. The product was a white solid (10.29 g, 53%, mp 78–80 °C). ^1H NMR ($CDCl_3$, ppm): δ 7.49 (d, J = 8.31 Hz, 4H), 7.97 (d, J = 8.31 Hz, 4H), 2.63 (s, 6H). $C_{19}H_{14}F_6O_2$ (388.30): calcd C, 58.77, H, 3.63; found C, 58.54, H, 3.33.

4,4′-Diamino-3,3′-dibenzoylbiphenyl (2) and bis(4-amino-3-benzoylphenyl) ether (3). They were prepared using the procedure that was reported by Stille.[16] **2**, 75% yield. ^{1}H NMR ($CDCl_3$, ppm): δ 7.63 (d, $J = 7.3$ Hz, 4H), 7.54 (q, 4H), 7.41 (d, $J = 2.0$ Hz, 2H), 7.39 (dd, $J = 3.0$, 2.0 Hz, 2H), 7.37 (d, $J = 3.0$ Hz, 2H), 6.76 (d, $J = 8.6$ Hz, 2H), 6.0 (br, 4H). **3**, 38% yield. ^{1}H NMR ($CDCl_3$, ppm): δ 7.90 (d, $J = 8.4$ Hz, 4H), 7.70 (d, $J = 8.8$ Hz, 2H), 7.42–7.55 (m, 6H), 7.21–7.28 (m, 4H).

Poly[1,4-phenylene(4,4′-diphenyl-[6,6′-biquinoline]-2,2′-diyl)-1,4-phenylene-1,1-bis(trifluoromethyl)methylene)] (F-PQ). A mixture of **1** (0.1553 g, 0.40 mmol), **2** (0.1570 g, 0.40 mmol), diphenyl phosphate (DPP) (2.50 g, 10.00 mmol), and freshly distilled *m*-cresol (0.48 mL, 4.60 mmol) was placed in a three-necked flask. With the stirring, the reaction mixture was flushed with nitrogen for about 20 min and then heated in an oil bath from room temperature to 135–140 °C in about 30 min. It was maintained at this temperature for 48 h under a nitrogen atmosphere. After cooling, the resulting viscous solution was added dropwise into an agitated solution of 200 mL of methanol containing 10% v/v of triethylamine. The precipitated polymer was re-dissolved in 10 mL of chloroform and reprecipitated by slow addition to a stirred solution of 200 mL of methanol containing 10% v/v of triethylamine. The polymer was collected by suction filtration, continuously extracted in a Soxhlet extractor for 24 h with a methanol solution containing 10% v/v of triethylamine and for 24 h with acetone, and then dried at 100 °C under vacuum for 24 h to afford an off-white polymer (0.21 g, 75%). ^{1}H NMR ($CDCl_3$, ppm): δ 8.38 (br, 2H), 8.17–8.28 (m, 6H), 8.06 (d, 2H), 7.87 (s, 2H), 7.48–7.70 (m, 14H).

Poly[(4-phenylquinoline-2,6-diyl)oxy(4-phenylquinoline-6,2-diyl)pyridine-2,6-diyl] (Py-PQE). It was synthesized using a similar procedure to that described for polymer **F-PQ** using **2** (0.2859 g, 0.70 mmol), 2,6-diacetylpyridine (0.1142 g, 0.70 mmol) as the two monomers. DPP (4.38 g, 17.5 mmol) with *m*-cresol (0.84 mL, 8.1 mmol) was used as the reaction medium. An off-white polymer (0.16 g, 46%) was obtained. ^{1}H NMR ($CDCl_3$, ppm): δ 8.58–8.88 (m, 4H), 7.80–8.55 (m, 5H), 7.28–7.68 (m, 12H).

Characterization and measurement

NMR spectra were obtained on a Varian XL 300 MHz FT NMR spectrometer. UV–Vis spectra were recorded on a Perkin–Elmer Lambda 9 UV/Vis/NIR spectrophotometer. The thermal properties of the copolymers were determined by TGA and DSC at a heating rate of 10 °C min^{-1} under nitrogen on a Shimadzu Thermal Analyzer (TGA-50 and DSC-50). The molecular weights and polydispersities (relative to polystyrene standards) were determined using a Waters 410 gel permeation chromatograph (GPC) with a refractive index detector and HR-4E columns at room temperature (THF as the eluant). Electrochemical measurements were performed on a Voltammetric Analyzer (BAS, CV-50W) using cyclic voltammetry (CV) at room temperature in a conventional three-electrode cell with a polymer thin film spin-coated onto indium tin oxide (ITO) glass as the working electrode ($\sim$3 cm^2). Pt gauze was used as the counter-electrode and Ag/Ag$^+$ was used as the reference electrode, with 0.1 M tetrabutylammonium perchlorate (TBAP) in acetonitrile as the electrolyte. *I–V* characteristics, photo and electroluminescence spectra measurements were carried out on a Semiconductor Parameter Analyzer (Hewlett Packard 4155B) and an InstaSpec IV spectrometer (Oriel Instruments), respectively.

Device fabrication

Three types of LED with the structure of ITO/CuPc/F-PQ/Al, ITO/Py-PQ/Al, and ITO/CuPc/Py-PQE/Al were fabricated. Glass substrates coated with ITO (100 Ω sq^{-1}) were cleaned in an ultrasonic bath of detergent solution, deionized water, methanol and chloroform for 30 min each, and then rinsed with acetone for two hours in a Soxhlet extractor. The CuPc and Al layers were evaporated under vacuum (10^{-6} Torr). Thin films of F-PQ and Py-PQE were spin-coated from a chloroform solution at 2000 rpm for 20 s. The thickness of CuPc, F-PQ and Py-PQE were $\sim$20, $\sim$55 and $\sim$50 nm, and the active areas of the resulted devices were 7.07 mm^2.

Acknowledgements

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