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Carbazole-based conjugated polymer with tethered acetylene groups: Synthesis and characterization

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ABSTRACT

A novel carbazole-based conjugated polymer with tethered acetylenes, poly [(9,9-dioctyl)-2,7-fluorene-(*N*-octyl-3,6-carbazole)]-*co*-[(9,9-dioctyl)-2,7-fluorene-(*N*-4-phenylacetylene)-3,6-carbazole)] (**P-2**), was successfully synthesized through the desilylation of triisopropylsilyl (TIPS) protected precursor polymer, poly [(9,9-dioctyl)-2,7-fluorene-(*N*-octyl-3,6-carbazole)]-*co*-[(9,9-dioctyl)-2,7-fluorene-(*N*-4-triisopropylsilyl-phenylacetylene)-3,6-carbazole)] (**P-1**). Thermally induced crosslinking between periphery acetylenes attached on **P-2** began to occur when heating temperature above 220 °C, and the solubility of **P-2** decreased significantly after curing. Nanodispersion of **P-2** in water was readily prepared by reprecipitation protocol. Optical properties of **P-2** in different states were characterized by UV–*vis* and photoluminescence analyses. Acceptable quantum efficiency (QE, 0.13) and binding ability with Hg²⁺ allow **P-2's** nanodispersion to act as optical probe for the detection of Hg²⁺ in aqueous phase. Primary investigation for the application of **P-2** as hole-transport layer (HTL) in multilayer polymeric light-emitting devices (PLEDs) shown that the device with the insertion of **P-2** between PEDOT:PSS and emissive layer affords better performance as compared to that of PEDOT:PSS-based one HTL device.

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1. Introduction

Conjugated polymers (CPs) have drawn extensive attention in recent years due to their potential applications in a variety of fields, such as polymeric light-emitting diodes (PLEDs) [1–4], polymeric solar cells [5–7], bio-sensors [8–11] and chemosensors [12–15]. In these CPs, carbazole-based CPs attracted particular attention owing to their unique properties, such as excellent hole-transporting capability and high luminescence efficiency [16–19]. The efficient conjugation length of carbazole-based CPs can be tuned conveniently by the alteration of substitution position, i.e., the 3,6- and 2,7-site [19–22]; corresponding optoelectronic properties can be thus controlled to meet requirements for different usages.

A series of carbazole-based hole-transport polymers [16,23–25] have been successfully synthesized, and the corresponding device performance improved significantly with the introduction of these hole-transporting layers (HTLs). Despite of

the excellent hole-transporting capability these carbazolederivatives possess, how to realize the retaining of such organic solvent-soluble HTL in multilayer PLEDs is still a challenging question and needs to be resolved. In the fabrication of multilayer devices, the solvent-resistivity is an extra requirement for highperformance HTL, that is, the HTL shouldn't be erased during the coating of subsequent emitting layer (EML). One of the efficient ways to overcome the inter-mixing between HTL and EML is to prepare cross-linkable HTLs. After post-treatment, these HTLs will become insoluble without compromising their hole-transport capability. Two main groups of crosslinkable HTLs have been reported, which containing thermally (such as organosiloxanes [26], styrenes [27,28], trifluorovinylethers [29,30], benzocyclobutenes [31]) and photo-crosslinkable (such as cinnamates, chalcones [32,33] and oxetanes [34,35]) groups, respectively. With the introduction of above-mentioned crosslinkable groups into HTLs, improved performance in solution processed PLEDs can be obtained by application of them.

Acetylene (\equiv H) is an important group of unsaturated component and can be crosslinked both with thermal and photo-treatment. Crosslinking reaction between acetylenes will produce conjugated double bonds [36] or aromatic ring derivatives [37], thus the efficient conjugation chain length of acetylene-substituted





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material will be increased after crosslinking. A series of acetylenecontaining, silole-based CPs have been successfully synthesized recently and their thermal-crosslinking, photopatterning and sensoring properties have been systematically investigated [38]. Lee et al. [36] have synthesized two kinds of acetylene-containing triphenylamine-based small molecules; these materials can be cured both by heating and UV irradiation. Improved electroluminescent efficiency has been obtained after cure treatment of these smallmolecular HTLs as compared to the corresponding device with un-crosslinked HTL (devices' structure: ITO/HTL/Alq3/Al). But the film-forming process of these small-molecular HTLs needs vacuum deposition, which is tedious and cost-waste relative to spin-coating process. However, spin-coatable, acetylene-substituted crosslinkable polymer as hole-transporting material has not been reported by far and will be interesting to be explored.

Another unique property of acetylene is its binding capability with some heavy metals [39], this endows acetylene-substituted materials with potential probing properties toward these metals. Along with this line, some researchers have synthesized a series of small molecular optical probes based on acetylene-substituted materials to realize Hg²⁺ detection in organic or aqueous environment [40–42]. It has been acknowledged that the sensitivity of CPs is superior to that of small molecules due to their signalamplification effect [15]. But to our knowledge, there is no literature about the application of acetylene-substituted CP to detect Hg^{2+} . One of the questions still laid before us is that a majority of reported mercuric sensors have poor water solubility, and hardly to be used in pure aqueous environment (which is undoubtedly of very importance due to the existence of Hg²⁺ is in water in most cases). Preparation of water-soluble conjugated polyelectrolytes [43–45] is a protocol to solve this problem. But the synthesis and purification of such polyelectrolytes are time-waste and difficult to realize, and the remaining counter-ions correlated with polymer backbone may endow unfavorable effect to their photoluminescent (PL) and detective properties. An alternative way to overcome the hydrophobic intrinsic of CPs is to transform them into nanoparticles in aqueous phase, in other words, is to take advantage of their size effect. Various CPs-based nano-sized aqueous dispersions [46–48] have been readily prepared *via* simple post-treatment, such as reprecipitation, with acceptable PL quantum efficiency. Based on these finding, a kind of water-dispersed fluorescent small molecular organic nanoparticle [49] has been prepared and was proven to act as efficient sensor for Hg^{2+} .

In this effort, a kind of novel carbazole-based polymer with periphery acetylene substituents was successfully synthesized. The corresponding aqueous nano-suspension of this polymer was prepared by reprecipitation method and the response to various metal ions was investigated here. Results show that this polymer can be act as potential probe for Hg²⁺ ion, and the lowest detection of limit is $\sim 3.3 \times 10^{-6}$ M. With thermal crosslinking treatment, this polymer can also be used as solvent-resistant HTL in multilayer PLEDs. Preliminary analyses indicate that the device with this material as buffer layer on PEDOT:PSS shows better performance as compared to that of the PEDOT:PSS-based one HTL device.

2. Experimental section

2.1. Materials

All reagents, unless otherwise specified, were purchased from Aldrich, Acros and TCI Chemical Co. and used without further purification. Diisopropylamine, toluene and tetrahydrofuran (THF) were distilled from sodium at the presence of benzophenone and degassed before use. 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene was synthesized as the reported literature [20]. Solutions of Al³⁺, Ba²⁺, Co²⁺, Cu²⁺, K⁺, Mg²⁺, Na⁺, Ni²⁺, Sn⁴⁺, and Zn²⁺ were prepared from their chloride salts; Hg²⁺, Ca²⁺, Pb²⁺ were prepared from their acetate salts; Fe³⁺ and Cd²⁺ were prepared from their sulfate salts, and Ag⁺ was prepared from its nitrate salts. Concentrations of metal solutions were controlled at 10^{-1} M in deionized water and were diluted subsequently to different concentration stocks for next use.

2.2. Measurements and characterization

IR spectra were recorded on an EQUINOX 55 FT-IR spectrometer with KBr pellets. ¹H NMR and ¹³C NMR spectra were collected on a VARIAN INOVA-400 spectrometer operating respectively at 400 MHz (for ¹H) and 100 MHz (for ¹³C) in deuterated chloroform solution with tetramethylsilane as reference. Number-average (M_n) and weight-average (M_w) molecular weights were determined by Waters GPC 2410 in tetrahydrofuran (THF) using a calibration curve of polystyrene standards. UV-vis absorption spectra were recorded on a SHIMADZU UV-2450 UV-vis spectrophotometer. PL spectra were recorded on HITACHIF-4500 spectrophotometer. Cyclic voltammetry was carried out on a CHI660C electrochemical workstation with platinum electrodes at scan rate of 50 mV/s against a saturated calomel reference electrode with nitrogen-saturated solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) in acetonitrile (CH₃CN). Thermogravimetric analysis (TGA) and differential scanning calorimetric (DSC) analyses were conducted on a NETZSCH STA 449C and 204F1 at a heating rate of 10 °C/min, respectively. Transmission electron microscope (TEM) and dynamic light scattering (DLS) were conducted on JEM-2100 (JEOL) and Zetasizer Nano S90, respectively.

2.3. LED fabrication and characterization

PLEDs with P-2 as HTL were investigated. Devices' structures were ITO/(PEDOT:PSS)/(**P-2**)/emissive polymer/CsCO₃/Al. Patterned indium tin oxide (ITO) coated glass substrates were cleaned with acetone, detergent, distilled water and isopropanol in an ultrasonic bath, and were treated with oxygen plasma before use. About 1 wt.% of P-2 was dissolved in toluene, filtered through a 0.45 µm filter and spin-coated on top of anode inside a dry box. The film thicknesses of P-2 were around 40 nm, as measured with a profilometry (XP-2). Emissive material was dissolved in toluene, filtered through a 0.45 μ m filter and spin-coated on top of HTL to form a film of 70 nm. CsCO₃(2 nm) and Al(100 nm) layers were vacuum-evaporated on the top of EML layer in a vacuum of 3×10^{-4} Pa. **P-2** containing devices were subjected to thermal treatment at different temperatures before the spin-coating of EML. For comparative purpose, device with a structure of ITO/PEDOT:PSS (40 nm)/emissive polymer (70 nm)/ CsCO₃/Al was made as reference. In control device, a 40-nm layer of PEDOT-PSS was spin-coated on the cleaned ITO from aqueous emulsion of PEDOT:PSS (Baytron P, Bayer A.G.) [Poly(3,4ethylenedioxythiophene) (PEDOT) doped with poly(styrenesulfonic acid) (PSS)] followed by drying in a vacuum oven at 90 °C for 8 h. The current density-voltage-luminance (J-V-L) characteristics were measured by a Keithley 2400 source measurement unit and a calibrated silicon photodiode which was calibrated for luminance by a PR-705 SpectraScan Spectrophotometer (Photo Research). The external EL quantum efficiency (QE) was collected by measuring the total light output in all directions in an integrating sphere (IS-080, Labsphere).

2.4. Synthesis

Synthetic route of target polymer is outlined in Scheme 1. 3,6dibromo-9-octyl-carbazole (**3**) and 9-(4-iodophenyl) carbazole (**4**) were prepared and purified *via* similar procedures in reported literature [50–52].

2.4.1. Synthesis of 3,6-dibromo-9-(4-iodophenyl) carbazole (5)

9-(4-iodophenyl) carbazole (**4**) (0.738 g, 2 mmol) and DMF (10 mL) were placed in a 50 mL round bottom flask equipped with a Teflon covered magnetic stir bar. The above mixture was degassed for several minutes. *N*-bromo-succinimide (NBS) (0.783 g, 4.4 mmol) was dissolved into DMF (10 mL) and added dropwise with syringe, and the mixture was stirred overnight at room temperature under nitrogen atmosphere. The product was purified by column chromatography using petroleum ether as eluent to give final product as white solid (0.536 g). Yield: 51%. ¹H NMR: ¹H NMR (400 MHz, CDCl₃). δ (ppm): 8.18–8.17 (d, *J* = 2.0 Hz, 2H), 7.95–7.92 (d, *J* = 11.2 Hz, 2H), 7.51–7.49 (dd, *J* = 8.0 Hz, 2H), 7.26–7.21(t, *J* = 20.0 Hz, 4H).

2.4.2. Synthesis of 3,6-dibromo-9-(4-triisopropylsilyl-phenylacetylene) carbazole (**6**)

3,6-dibromo-9-(4-iodophenyl) carbazole (**5**) (0.527 g, 1 mmol), Pd(PPh₃)₂Cl₂ (0.035 g, 0.08 mmol) and CuI (0.019 g, 0.1 mmol) were added in a 50 mL round bottom flask. After purged with nitrogen for 5 min, dry toluene (10 mL) and diisopropylamine (5 mL) were placed *via* syringe. The mixture was degassed and stirred for 20 min under nitrogen and triisopropylsilyl acetylene (TIPSA) (0.225 g, 1.2 mmol) was injected. The above mixture was stirred at room temperature overnight. The crude product was purified by column chromatography using petroleum ether as eluent to give final product as white solid (1.664 g). Yield: 83%. FT-IR (KBr, cm⁻¹): 3435, 3064, 2941, 2863, 2721, 2154, 1505, 1466, 1314, 1278, 1228, 1175,

1104, 1072, 1007, 830, 727. ¹H NMR (400 MHz, CDCl₃). δ (ppm): 8.18 (d, J = 2.0 Hz, 2H), 7.72–7.70 (d, J = 8.0 Hz, 2H), 7.52–7.49 (dd, J = 12.0 Hz, 2H), 7.45–7.43 (dd, J = 8.0 Hz, 2H), 7.26–7.23 (t, J = 12.0 Hz, 2H), 1.18–1.17(s, J = 4.0 Hz, 21H). ¹³C NMR (100 MHz, CDCl₃). δ (ppm): 139.57, 136.54, 133.77, 129.52, 126.52, 124.08, 123.33, 113.32, 111.40, 105.87, 92.52, 124.08, 123.33.

2.4.3. Synthesis of poly [(9,9-dioctyl)-2,7-fluorene-(N-octyl-3,6-carbazole)]-co-[(9,9-dioctyl)-2,7-fluorene-(N-4-triisopropylsilyl-phenylacetylene)-3,6-carbazole] (**P-1**)

Under nitrogen, 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (0.193 g, 0.3 mmol), 3 (0.105 g, 0.24 mmol) and 6 (0.035 g, 0.06 mmol) were added in degassed toluene (8 mL) and 0.2 M potassium carbonate aqueous solution (1.5 mL). Pd(OAc)₂ (0.003 g, 0.013 mmol) and 3 drops of Aliguat 336 were placed later. The above mixture was degassed for several times, tricyclohexyl phosphine (0.006 g, 0.021 mmol) was added afterward. The reaction was refluxed at 90 °C for 72 h before it was cooled to room temperature. The crude product was purified by flash column chromatography, using toluene as eluent, then concentrated to a volume of 3 mL, and reprecipitated into methanol (50 mL). The formed precipitate was recovered by filtration. The obtained polymer was further purified by washing with acetone in a Soxhlet apparatus for 24 h to remove oligomers and catalyst residues and was dried after vacuum drying at 50 °C overnight (0.090 g). Yield: 44%. FT-IR (KBr, cm⁻¹): 2921, 2850, 2155, 1886, 1602, 1462, 1351, 1268, 1153, 803. ¹H NMR (400 MHz, CDCl₃), δ (ppm): 8.54–8.52 (m. 1.8H), 8.35–8.32 (m. 0.6H), 7.85-7.33 (m. 10H), 4.40-4.32 (m. -N-CH₂-, 1.8H), 2.14-0.76 (m. alkyl H, 48H).



Scheme 1. Synthetic route of monomers and polymers.

2.4.4. Synthesis of poly [(9,9-dioctyl)-2,7-fluorene-(N-octyl-3,6-carbazole)]-co-[(9,9-dioctyl)-2,7-fluorene-(N-4-phenylacetylene)-3,6-carbazole] (**P-2**)

A solution of **P-1** (0.090 g) in anhydrous THF (8 mL) was vigorously stirred under nitrogen atmosphere in a round-bottom flask and tetrabutylammoniumfluoride (0.5 mL, 0.5 mmol) was added to this solution. The mixture was stirred at room temperature overnight. The crude product was purified by flash column chromatography, using toluene as an eluent, then concentrated and reprecipitated in methanol. The final product was obtained after vacuum drying at 50 °C overnight (0.082 g). Yield: 95%. FT-IR (KBr, cm⁻¹): 3300 (C=C–H), 3050, 2919, 2849, 2109, 1870, 1581, 1603, 1462, 1351, 1267, 1134, 1005, 802. ¹H NMR (400 MHz, CDCl₃). δ (ppm): 8.54–8.51 (m, 1.8H), 8.35–8.32 (m, 0.6H), 7.85–7.33 (m, 10H), 4.40–4.32 (m, –N–CH₂–, 1.80H), 3.20 (m, =C–H, 0.11H), 2.14–0.76 (m, alkyl H, 47H).

2.4.5. Preparation of P-2 nanoparticles in aqueous phase

Polymer nanoparticles in aqueous phase were prepared follow procedures in previous literature [46–48]. Briefly, 4 mg of **P-2** was added to a flask containing 100 mL of THF, and keep stirring at room temperature overnight. 2 mL of above-mentioned solution was filtered *via* 0.45 μ m filter and added to 8 mL of deionized water with ultrasonic processing (40 kHz) for 20 min. THF was removed by heating at 60 °C from this mixture to give the final aqueous dispersion.

2.4.6. Fluorescence titration of P-2 nanoparticle with metal ions

Nanoparticles in aqueous phase of **P-2** (with concentration of $\sim 1 \times 10^{-5}$ M) were prepared as stated before. Solutions of metal ions were prepared in deionized water with different concentrations. A stock solution of **P-2** (3.0 mL) was placed in a quartz cell (10.0 mm width). Metal ions solutions were introduced with micropipette with aimed volumes, and fluorescence intensity changes (excitation wavelength of 350 nm) and UV–*vis* absorption were recorded after 3 min with the addition of ions each time.

3. Results and discussion

3.1. Synthesis and characterization

The synthetic route of intermediates and target polymer is shown in Scheme 1.

9-(4-iodophenyl) carbazole (4) was synthesized from carbazole as the starting material by Ullmann reaction in the presence of copper and potassium carbonate [52]. Compound 5 was readily obtained by the bromination of **4** in DMF. Due to the much higher reactivity of iodide-site as compared to that of bromine-sites toward Sonogashira reaction, the introduction of TIPS group is happened exclusively at iodide-site. The attempt to obtain target polymer, P-2, by using acetylene-substituted dibromo-carbazole directly as monomer failed after several trials. This might due to the formation of complexes between acetylene and Pd-catalyst during polymerization under Suzuki reaction condition. Acetylene groups can be under good protection with the introduction of TIPS in this effort. High chemical stability of TIPS endows it with sufficient tolerance for Suzuki polymerization condition. Along with this line, P-2 was obtained through two-step reaction (protection and deprotection). Acetylene proportion in polymer can be tuned by the alternation of feed ratio of carbazole comonomers, and in this effort it was controlled at 10%. The obtained TIPS-protected polymer precursor P-1 was successfully synthesized and purified by conventional procedure. TIPS in P-1 can be deprotected by the desilvlation of Bu₄NF in THF at room temperature to give **P-2** with high yield. Both P-1 and P-2 are readily soluble in common organic



Fig. 1. FT-IR spectra of **P-1** and **P-2** (inset is the amplified region from wavenumber of 2200 to 2050 cm⁻¹).

solvents such as THF, chloroform, and toluene at room temperature. The number-average molecular weight (M_n) of **P-2** was measured by gel permeation chromatography (GPC) analysis using THF as eluant against polystyrene standards, to be 8200 and with the polydispersity of 2.1.

Chemical structures of intermediates and polymers were verified by FT-IR and NMR analyses. Fig. 1 shows FT-IR spectra of polymers. There is a clear difference in FT-IR spectra between **P-1** and **P-2**. For **P-1**, a weak absorption signal appeared at ~2155 cm⁻¹, which corresponds to the C \equiv C stretching vibration, weakened significantly in the spectrum of **P-2** and moved to ~2109 cm⁻¹ after the desilylation reaction. New band at ~3300 cm⁻¹ is observed exclusively in the spectrum of **P-2**, which can be assigned to the typical stretching absorption signal of \equiv C–H in **P-2**.

¹H NMR spectra of polymers are shown in Fig. 2. Signals at 4.40–4.32 ppm in both curves can be ascribed to the $-CH_2$ – groups attached directly to the *N* atoms of carbazole moieties (depicted as $-N-CH_2-$). By comparison of these two spectra one can find that a small peak at ~3.20 ppm appeared only in the spectrum of **P-2**, which can be ascribed to the signal of substituted acetylene. This result is consistent with the finding in FT-IR analysis, by which one can conclude that the desilylation reaction successfully realized.



Fig. 2. ¹H NMR spectra of **P-1** and **P-2** in deuterated chloroform (inset is the integration ratio of protons of $-N-CH_2-$ to $\equiv C-H$ of **P-2**).

Integration ratio of protons of $-N-CH_2-$ against $\equiv C-H$ (as can be seen from the inset of NMR spectrum of **P-2**) in **P-2** was evaluated as ~ 16.4 (1.80/0.11), which is nearly double of the theoretical result (8.0, as calculated by the feed ratio of monomer **3** and **6**), suggesting that the actual composition ratio of $\equiv C-H$ groups in whole polymer was ~ 10%. This presumably was brought by the different reactivity between monomers **3** and **6** in the copolymerization process. The other alkyl and aromatic protons signals are also reasonable and match well with their chemical structures.

Nano-dispersion of **P-2** in water can be conveniently obtained by reprecipitation procedure as reported by previous literature [46–48]. As can be seen from Fig. 3, the corresponding nanodispersion is uniform and with good transparency under natural light (Fig. 3a). It emits bright blue light when excited by UV light (365 nm, visual photograph was shown in Fig. 3b). Its detailed optical property will be discussed in following section. Morphology of the resulted dispersion was characterized by TEM analysis. As revealed by Fig. 3c, **P-2** nanoparticles with shapes approximate to spherical (with average diameter of \sim 60 nm, as obtained by the average counting of more than one hundred particles), and with moderate aggregation. DLS analysis was also conducted and the result was shown in Fig. 3d, which revealed larger average sizes (~130 nm) of particles than that of TEM result. Similar phenomenon was also found in previous literature [53]. After drying, shrinkage of nanoparticle happened in TEM test while in DLS the wet environment (may with little residue of THF) may induce the swollen of particles and gives larger sizes.

3.2. Thermal properties

Thermal properties of **P-2** were examined by thermogravimetric analysis (TGA) (Fig. 4a) and differential scanning calorimetry (DSC) (Fig. 4b). As shown in Fig. 4b, the degradation temperature of **P-2** is appeared at ~402 °C, which may due to the crack of alkyl attachments. In Fig. 4b, during the first heating scan, **P-2** exhibits a glasstransition temperature (T_g) of ~85 °C, and an apparent exothermic process was revealed at the onset of ~220 °C and with the peak at ~270 °C. According to TGA analysis one can conclude that this process is not due to the degradation of polymer, and this can be assigned to the crosslinking reaction between acetylene groups on the periphery of **P-2** according to previous report [37,38]. On the second heating, there is no obvious thermal feature appeared from



Fig. 3. Photograph under natural light (a), ultraviolet light (b), TEM image (c) and DLS analysis (d) of P-2 aqueous dispersion.



Fig. 4. TGA (a) and DSC (b) studies of P-2.

50 to 300 °C, suggesting that all of the acetylene groups have participated in curing in the first heating.

3.3. Optical properties

UV–*vis* absorption properties of **P-2** in THF, aqueous dispersion, and as film were shown in Fig. 5a. From it one can find that there is apparent red-shift and broaden of absorption curve in aqueous phase and film as compared to the corresponding one in THF. This indicates that aggregation of polymer chains happened in nanoparticle and film state. Absorption maxima of **P-2** in THF, aqueous phase and film were found at ~347, 351 and 360 nm, respectively. UV spectra of **P-2** film with thermal crosslinking treatment at 240 °C under N₂ for 1 h, with and without rinsed by a large amount of THF, were compared in Fig. 5b. It reveals that the solubility of **P-2** decreased dramatically after crosslinking, and ~75% of absorption intensity was preserved after washing.

Fig. 6 shows photoluminescent (PL) properties of **P-2** in different states. Emission maxima of **P-2** in THF and in aqueous phase were found at \sim 420 nm in both cases. The emission peak red-shifts to 451 nm in solid film, suggests stronger intermolecular aggregation in solid state relative to that in water phase. After thermally crosslinking, the emission peak red-shifts further to 468 nm and the emission curve is broader as compared to that of pristine film. This may be caused by the formation of conjugated linkage between polymer chains in crosslinked film after the thermally induced reaction between periphery acetylenes. Fluorescence



Fig. 5. Normalized UV–*vis* spectra of **P-2** in THF (4×10^{-4} M), aqueous phase (1×10^{-5} M) and as film on glass substrate (a), crosslinked film with and without washing by a large mount of THF (b).

quantum efficiency (QE, $\Phi_{\rm f}$) of **P-2** in THF and in aqueous phase was determined using 9,10-diphenylanthracene ($\Phi_{\rm f} = 0.90$ in cyclohexane) as standard, are 0.58 and 0.13, respectively. Although the QE of **P-2** nanoparticle (0.13) is much lower than that in THF solution (this might due to the quenching effect brought by interchains aggregation), this QE is acceptable in terms of CPs-based aqueous nanoparticles according to previous reports [54].

3.4. Electrochemical properties

Electrochemical property of **P-2** was shown in Fig. 7. **P-2** shows one reversible oxidation process, indicative of stable cation radical. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels were calculated



Fig. 6. PL spectra of P-2 in different states.



Fig. 7. Cyclic voltammogram of P-2's film cast on platinum electrode against standard calomel electrode (SCE).

according to an empirical formula of $E_{\text{HOMO}} = -e(E_{\text{oxonset}} + 4.4)$ (eV), and $E_{\text{LUMO}} = E_{\text{HOMO}} - E_g$ in which E_g is the optical band gap (3.08 eV, as calculated by the absorption onset, 403 nm, of **P-2**'s film) [55], to be -5.59 and -2.51 eV, respectively. Such energy level fits reasonably with the required electronic levels for hole-transporting materials.

3.5. Optical response to metal ions by P-2 aqueous nanodispersion

Optical response of **P-2** to different metal ions (Ag⁺, Al³⁺, Ba²⁺, Ca²⁺, Cd²⁺, Co²⁺, Cu²⁺, Fe³⁺, Hg²⁺, K⁺, Mg²⁺, Na⁺, Ni²⁺, Pb²⁺, Sn⁴⁺, Zn²⁺) was detected in aqueous phase. Fig. 8 shows changes of **P-2**'s PL intensity with the addition of different metal ions (the concentration of **P-2** and each ion were controlled at 1×10^{-5} and 3.3×10^{-4} M, PL intensity was recorded 3 min later after the addition of each ion). One can note that compared to other metal ions, Fe³⁺ and Hg²⁺ caused much more pronounced fluorescent quenching.

In view of the situation, the question laid before us is that whether the differentiate detection of Hg^{2+} and Fe^{3+} can be realized by **P-2**. UV–*vis* changes of **P-2** upon titration of Hg^{2+} and Fe^{3+} were investigated to find some clues for afore-mentioned question,



Fig. 8. Fluorescence intensity changes of **P-2** nanoparticle in aqueous phase (with the concentration of 1×10^{-5} M) in the presence of various metal ions (with concentration of 3.3×10^{-4} M). (Excitation wavelength was 350 nm and the slit width was identical in all cases).

and corresponding spectra were shown in Fig. 9. One can note from Fig. 9a that upon the presence of incremental amount of Hg²⁺, just tiny alteration of absorption was detected, that is, shapes of absorption curves of **P-2** were scarcely changed and absorbance intensity was lightly decreased. While for Fe³⁺, substantial changes can be detected when the concentration of Fe³⁺ exceeding ~9.9 × 10⁻⁶ M, and curves upturned during succeeding titration. The combination of PL and UV–*vis* analyses indicated that **P-2** possesses discriminating capability for these two ions to some extent.

Fig. 10a illustrates detailed fluorescence changes of **P-2** upon gradual titration of Hg²⁺ ion in increasing concentrations. Around 75% of PL intensity of **P-2** was quenched when the concentration of Hg²⁺ reached 1.3 \times 10⁻³ M. The quenching efficiency can be reflected by K_{sv} constant, which can be obtained by the calculation of the slope of linear region of quenching plot (Fig. 10b) at low concentration region (with Hg²⁺ concentration below 10⁻⁵ M), to be 5.1 \times 10⁴ M⁻¹ and with the lowest detection limit (LDL) in the range of ~3 \times 10⁻⁶ M.

Another issue is that what's the most important moiety in **P-2** is responsible for the quenching toward Hg^{2+} . As discussed in Introduction section, complex can be formed between acetylene derivatives and Hg^{2+} . In the current case, PL quenching of **P-2** toward Hg^{2+} is also presumable due to the interaction of tethered acetylene groups in **P-2** with Hg^{2+} . To find some traces for such



Fig. 9. UV–vis spectra of **P-2** (with the concentration of 1×10^{-5} M) in the presence of incremental Hg²⁺ (a) and Fe³⁺ (b) in deionized water.



Fig. 10. Fluorescence spectra of **P-2** nanoparticle $(1 \times 10^{-5} \text{ M})$ upon incremental addition of Hg²⁺ (0–1.78 × 10⁻³ M) in deionized water (a), and the corresponding I_0/I values versus Hg²⁺ concentration (b) (inset shows the linear region of **P-2**'s PL intensity versus Hg²⁺ (concentration in the range of 1.65–9.9 × 10⁻⁶ M)). Excitation was controlled at 350 nm, and each spectrum was recorded 3 min after adding Hg²⁺.

speculation, P-1 aqueous nanoparticle suspension (DLS and TEM spectra of P-1 suspension can be seen in Fig. S1 in supporting information) was prepared with the same condition as adopted for P-2, and florescence alteration of P-1 with the incremental amount of Hg²⁺ was also investigated to make comparison. The corresponding spectra were shown in Fig. 11. With the introduction of Hg^{2+} , against from the pronounced monotonous quenching for **P-2**, PL intensity of P-1 altered relatively slightly under the same circumstance (fluorescence intensity of P-1 increased firstly and then decreased within a narrow range during the titration process). Considering the same backbone and alkyl attachments of these two polymers, and previous report has proven that PL intensity of carbazole-based compound was not affected by the addition of Hg²⁺ [56]. Different responding manner between **P-1** and **P-2** is presumably brought by the difference in their acetylenesubstituent. Binding with Hg²⁺ will quench **P-2**'s intensity while for P-1 this effect didn't work due to the presence of TIPS protecting groups. Not all of PL intensity of P-2 was quenched and there is ~25% of intensity remained even with ~100 eq of Hg²⁺. This may be explained by the possibility that not all of molecular chains in P-2 contain acetylene groups due to the low ratio of monomer 6 controlled in polymerization process. In other words, some chains in P-2 might be not attached by acetylene and their intensity preserved during titration.

Interference of other metal ions for **P-2** against Hg^{2+} was also investigated. Fig. 12 shows PL responses of **P-2** to various background metal ions before/after the addition of Hg^{2+} . Majority of



Fig. 11. Fluorescence response of **P-1** nanoparticle in aqueous phase $(1.0 \times 10^{-5} \text{ M})$ upon incremental addition of Hg²⁺ $(0-7.8 \times 10^{-4} \text{ M})$. Excitation was 350 nm. Spectra were recorded 3 min after adding Hg²⁺.

ions in this case brought insignificant effect to the quenching for the adding of Hg^{2+} , while Al^{3+} , Ba^{2+} , Cu^{2+} , Mg^{2+} and Zn^{2+} had relatively stronger interference. In all cases the addition of Hg^{2+} caused stronger quenching as compared to those only with background metals. For Fe³⁺, additive quenching was detected with the introduction of Hg^{2+} . Considering that these spectra were recorded 3 min later with the addition of each ion and Hg^{2+} without longtime standing, **P-2** might be act as a potential immediacy optical probe for Hg^{2+} . Its anti-interference and sensitivity might be modified by tuning its backbone structure and acetylene composition, and the relating work is in progress.

3.6. Primary investigation of hole-transporting property of P-2

It's well-known that carbazole derivatives have good holetransporting capability, and the energy level of **P-2** (as evaluated by its CV and absorption property) seems suitable for the application



Fig. 12. Fluorescence quenching of **P-2** nanoparticle in aqueous phase (with concentration of 1.0 \times 10⁻⁵ M) in the presence of various background metal ions (with concentration of 3.3 \times 10⁻⁴ M for each ion, from 1 to 16: Ag⁺, Al³⁺, Ba²⁺, Ca²⁺, Cd²⁺, Co²⁺, Cu²⁺, Fe³⁺, K⁺, Mg²⁺, Na⁺, Ni²⁺, Pb²⁺, Sn⁴⁺, Zn²⁺ and Hg²⁺) and with sequential addition of Hg²⁺ (3.3 \times 10⁻⁴ M). The excitation wavelength is 350 nm.

as HTL in multilayer PLEDs. To evaluate the hole-transporting property of **P-2**, four parallels of electroluminescence (EL) devices, with structures of ITO/PEDOT:PSS/Emitting layer (EML)/Cs2CO3/Al (Device I), ITO/P-2/EML/Cs2CO3/A1 (Device II), ITO/PEDOT:PSS/P-2/ EML/Cs₂CO₃/Al (270) (Device III), ITO/PEDOT:PSS/P-2/EML/Cs₂CO₃/ Al (240) (Device IV) were constructed to make comparison. The EML used here is a kind of fluorene derivative reported previously by our group [57]. The choice of this polymer is based on its relatively weaker intrinsic hole-transporting capability as deduced by its relative higher HOMO level (with ~5.8 eV). In Devices II and III, P-2 was spin-coated onto anode and was thermally annealed at 270 °C under N₂ for 1 h. Device IV was fabricated under the same condition, except the heating temperature was controlled at 240 °C. Similar EL spectra were obtained by these devices, indicating hole-electron combination zone was not affected by the insertion of different HTLs. Devices' performance curves were shown in Fig. 13. From Fig. 13, one can find that Device I shows much higher current density than the other devices with a given voltage, which may caused by the high conductivity of PEDOT:PSS. Turn-on voltages of Devices I–IV were at \sim 4.0, 7.5, 9.2 and 4.7 V, respectively, as recorded by Fig. 13b. The maximum brightness of Devices I–IV reached \sim 460 (at 7.3 V), 155 (at 11.3 V), 17 (at 12.0 V) and 440 (at 10.3 V) cd/m², respectively. As revealed by Fig. 13c, the maximum luminescence efficiency (LE) of Devices I–IV were 0.11 (at 110 mA/cm²), 0.13 (at



Fig. 13. Device characteristics of PLEDs, (a) voltage–current density, (b) voltage– brightness and luminescence efficiency–current density (c) characteristics.

18.5 mA/cm²), 0.13 (at 12.0 mA/cm²) and 0.14 (at 76.6 mA/cm²), respectively. Whole devices' performance in this effort is inferior to our previous report [57], which presumably due to the different cathode structures (Ba/Al in previous work and Cs₂CO₃/Al in current case) and different experimental conditions in two cases. The parallel devices' performance in this case indicates that type IV device shows better performance than those of the others. Type III device shows the poorest performance, which may due to the high heating temperature (270 °C) treatment during device's fabrication process, the underneath PEDOT:PSS film fabricated in previous step will degraded significantly as reported by previous report [58]. This will unfavorable to device's performance and the corresponding device is tending to breakdown under relatively lower current density. According to the solubility analysis of P-2 film in previous section, thermal treatment at 240 °C has endowed it with good solvent-resistivity. Along with this line, lower curing temperature was adopted in Device IV; this temperature will not damage excessively the applied PEDOT: PSS layer. With this modification, the corresponding performance was improved as compared to that of Device I, which may due to the hole-transporting and electronblocking effect brought by P-2 as revealed by its HOMO and LUMO energy levels. These primary analyses indicate that P-2 can be used as potential HTL in multilayer PLEDs. Another merit acetylenederivatives possess is that they can also be cured by ultra-violet radiation. Thermal degradation problem encountered in abovementioned discussion might be readily overcome by photocrosslinking protocol and the related investigation is underway.

4. Conclusion

In summary, a crosslinkable conjugated fluorescent poly (carbazole–fluorene) polymer with tethered acetylenes was successfully prepared *via* protection–deprotection two-step protocols. Corresponding polymer nanoparticle in aqueous phase with reasonable QE was prepared and has the potential to be used as Hg²⁺ optical probe in pure water phase. Besides, good solvent-resistivity together with suitable hole-transport and electron-block capability endows this polymer with the potential to be used as HTL in multilayer PLEDs.

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Appendix A. Supporting information

Supplementary data related to this article can be found online at http://dx.doi.org/10.1016/j.dyepig.2012.07.010.

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