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PAPER

Supramolecular light-emitting polymers for solution-processed optoelectronic devices[†]

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Supramolecular light-emitting polymers (SLEPs) based on host-guest interactions were developed for solution processed organic electronic devices. The dibenzo-24-crown-8 functionalized blue-emitting conjugated oligomer 1 and green-emitting conjugated oligomer 3 were used as the host materials, and the dibenzylammonium salt functionalized blue-emitting conjugated oligomer 2 was used as the guest material. The resulting linear SLEPs were obtained from the self-organization of the host and guest oligomers, which were confirmed by the nuclear magnetic resonance, viscosity and differential scanning calorimetry studies. Highly fluorescent SLEP nanofibers can be easily obtained by drawing or electronspinning from the equimolar solution of the host and guest oligomers. The photophysical and electroluminescence properties of the resulting SLEPs were fully investigated. It was found that the SLEPs' emission colors can be well tuned from blue to green with significantly enhanced photoluminescent efficiencies by using 3 as the dopant, which is due to the efficient energy transfer caused by the exciton trapping on narrow band gap host oligomer 3 in the SLEPs. As a result, the designed SLEPs showed comparable electroluminescence device performances to those analogous traditional conjugated polymers. Considering the precisely defined starting monomers and catalyst-free polymerization process for the designed SLEPs, combining the good device performances, the present study provides a promising alternative route to develop solution processed semiconductors for optoelectronic applications.

Introduction

Conjugated polymers (CPs) have attracted considerable attention from both academic and industrial communities because of their versatile applications in optoelectronic devices, such as polymer light-emitting diodes (PLEDs) and polymer solar cells (PSCs).1 Compared to traditional inorganic and small molecule organic semiconductor based devices, the CP-based devices can be fabricated through a low cost solution process and thereby possess unique advantages in the production of low cost, large area, flexible optoelectronic devices.² Significant progress has been made in CP-based devices, where high efficiency PLEDs and PSCs have been successfully demonstrated by all spincoating or a roll to roll process.³ Despite promising progress, there are still many challenges in developing high performance and long lifetime CP-based optoelectronic devices. For example, most CPs are synthesized by the transition-metal-catalyzed cross-coupling reactions. Since it has been proven that the

remaining traces of metal catalysts have a detrimental effect on the resulting thin film device performance, time consuming purification techniques have to be performed to remove the remaining metal catalyst among the conjugated polymers.⁴ In addition, the molecular weights as well as polydispersity of CPs that also play an important role on the performance of the resulting devices are hard to be defined during the polymerization process, which usually generate the batch to batch variation.⁵

To overcome these challenges, a possible solution is to replace the traditional CPs with supramolecular light-emitting polymers (SLEPs).⁶ The supramolecular polymers are generally formed from the monomeric units by directional and reversible secondary interactions such as hydrogen bonding, π - π stacking, host-guest interactions, hydrophobic interactions, etc., and the employment of SLEPs would present several potential advantages in device applications: (1) the polymerization starts from the precisely defined monomers without using any metal catalyst; (2) the comparable viscosity of the supramolecular polymers to the traditional polymers ensure good solution processability, which maintains the key advantage of polymer-based electronics; and (3) the strong interactions among the monomers ensure supramolecular polymers a good morphology stability compared to those solution-processed small molecules, which is important for optoelectronic device applications. Despite all these potential

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advantages, most of the research on SLEPs only focus on their photophysical properties, while the application of supramolecular polymers in optoelectronic devices has been rarely reported.⁷ Meijer *et al.* reported the pioneering work of using hydrogenbonded supramolecular copolymers for PLEDs, while the resulting devices exhibited poor performances with low luminance efficiencies less than 0.1 cd $A^{-1.7d}$ It is challenging to develop high performance supramolecular copolymers for optoelectronic device applications.

Herein we report the first use of host-guest interaction-based SLEPs for PLEDs. The supramolecular polymers based on hostguest interactions have advantages of highly directional binding interactions at well-defined positions and interlocking bonds to afford rotaxane- and catenane-type mechanically interlocked structures.^{6j,8} The dibenzo-24-crown-8 (DB24C8) and dibenzylammonium salt (DBA) functionalized blue-emitting fluorenebased conjugated oligomers 1 and 2 were used as the host and guest of the resulting SLEPs respectively (Scheme 1). The resulting linear SLEPs can be obtained from the self-organization 1 and 2 in solution.^{6j,8} Moreover, another green-emitting host monomer **3** was developed as a dopant unit in SLEPs. It was found that the resulting SLEPs' emission colors can be well tuned and their photoluminescent (PL) efficiencies are significantly enhanced upon the doping of 3, due to the efficient energy transfer caused by the exciton trapping effect.9 As a result, the resulting SLEPs device performances were greatly improved and are comparable to those analogous traditional conjugated polymers.

Experimental details

Materials

4-Bromo-dibenzo-24-crown-8 (4),¹⁰ 7,7"-dibromo-2,2':7',2"-ter(9,9-dioctylfluorene) (6),¹¹ and 4,7-bis(7-bromo-9,9-



Scheme 1 Schematic representation of the construction of SLEPs from host 1, guest 2 and host 3.

dioctylfluorene-2-yl)-2,1,3-benzothiadiazole (10)¹² were prepared according to the reported procedures. All chemicals were purchased from commercial sources (Aldrich, Acros, and Alfa Aesar) and used without further purification unless stated otherwise. All the solvents used were further purified prior to use.

Synthesis of 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-dibenzo-24-crown-8 (5)

4-Bromo-dibenzo-24-crown-8 (4) (5.27 g, 10.0 mmol), bis(pinacolato)diboron (3.81 g, 15.0 mmol), and potassium acetate (4.00 g, 40.0 mmol) were added in a 100 mL two-necked roundbottomed flask. Anhydrous 1,4-dioxane (60 mL) and [1,1'-bis-(diphenylphosphino)ferrocene]palladium(II) dichloride [Pd(dppf)Cl₂] (150 mg) were added to the flask. The mixture was refluxed for 36 h under argon. After the mixture was cooled to room temperature, it was poured into brine and extracted twice with dichloromethane. The combined organic layers were dried over MgSO₄ and the solvent was removed. The crude product was purified with column chromatography (silica gel, petroleum ether (60-90 °C)-ethyl acetate-dichloromethane (4/4/1) as eluent) to yield 4.02 g (70%) of 5 as a white semisolid. ¹H NMR $(CDCl_3, 300 \text{ MHz}) \delta$ (ppm): 7.39 (dd, J = 1.3, 7.9 Hz, 1H), 7.28(d, J = 1.4 Hz, 1H), 6.90–6.83 (m, 5H), 4.20–4.12 (m, 8H), 3.92– 3.89 (m, 8H), 3.83 (s, 8H), 1.32 (s, 12H). ¹³C NMR (CDCl₃, 75 MHz) δ (ppm): 151.7, 149.0, 148.2, 129.0, 121.4, 119.6, 114.2, 112.8, 83.6, 71.3, 71.2, 69.9, 69.8, 69.5, 69.4, 69.1, 24.9.

Synthesis of 7,7"-bis(dibenzo-24-crown-8)-2,2':7',2"-ter(9,9dioctylfluorene) (1)

7,7"-Dibromo-2,2':7',2"-ter(9,9-dioctylfluorene) (6) (1.60 g, 1.2 mmol), compound 5 (1.73 g, 3.0 mmol), and tetrakis-(triphenylphosphine)palladium [Pd(PPh₃)₄] (60 mg) were added in a 100 mL two-necked round-bottomed flask. Toluene (40 mL), THF (20 mL) and 20% aqueous tetraethylammonium hydroxide (6 mL) were added to the flask under argon. The mixture was refluxed for 48 h under argon atmosphere. After the mixture was cooled to room temperature, it was poured into brine and extracted twice with dichloromethane. The combined organic extracts were washed three times with water, dried over MgSO₄, evaporated, and purified with column chromatography (silica gel, ethyl acetate-dichloromethane (1/6) as eluent) to yield 1.81 g (73%) of **1** as a light yellow solid. ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 7.84–7.81 (m, 6H), 7.69–7.64 (m, 8H), 7.52 (d, J = 8.1Hz, 4H), 7.22 (d, J = 7.2 Hz, 4H), 6.97 (d, J = 8.6 Hz, 2H), 6.89 (s, 8H), 4.29–4.27 (m, 4H), 4.23–4.21 (m, 4H), 4.18–4.16 (m, 8H), 3.98-3.93 (m, 16H), 3.87 (s, 16H), 2.09-2.05 (m, 12H), 1.26-1.10 (m, 60H), 0.82–0.78 (m, 30H). ¹³C NMR (CDCl₃, 100 MHz) δ (ppm): 151.8, 151.7, 149.2, 149.1, 148.7, 140.5, 140.4, 140.0, 139.7, 135.4, 126.1, 125.7, 121.5, 121.2, 120.3, 119.9, 114.5, 114.3, 113.8, 71.3, 70.0, 69.9, 69.8, 69.7, 69.5, 55.3, 55.2, 40.4, 31.8, 30.0, 29.2, 23.9, 22.6, 14.0. MALDI-TOF (m/z): calcd 2059.34, found $[M]^+$ 2058.90, $[M + Na]^+$ 2081.88.

Synthesis of 7,7^{''}-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2[']:7['],2^{''}-ter(9,9-dioctylflourene) (7)

To a solution of compound **6** (6.0 g, 4.5 mmol) in 150 mL THF in a 250 mL three-necked round-bottomed flask at -78 °C was

added dropwise 4.5 mL of n-butyllithium (2.5 M in hexane). The mixture was stirred at -78 °C for 1 h and 2-isoproxoy-4,4,5,5,tetramethyl-1,3,2-dioxaborolane (5 mL, 24.5 mmol) was added rapidly to the solution. The resulting mixture was warmed to room temperature and stirred overnight. The mixture was poured into brine, extracted with dichloromethane three times and dried over MgSO₄, evaporated, and purified with column chromatography (silica gel, petroleum ether-ethyl acetate (1/20) as eluent) to yield 4.8 g (75%) of 7 as a white solid. ¹H NMR $(CDCl_3, 300 \text{ MHz}) \delta$ (ppm): 7.83 (d, J = 7.7 Hz, 4H), 7.78 (d, J =4.1 Hz, 4H), 7.73 (d, J = 7.6 Hz, 2H), 7.67–7.63 (m, 8H), 2.08– 2.03 (m, 12H), 1.40 (s, 24H), 1.22-1.07 (m, 60H), 0.83-0.70 (m, 30H). ¹³C NMR (CDCl₃, 100 MHz) δ (ppm): 152.1, 151.8, 150.2, 143.8, 141.0, 140.5, 140.1, 140.0, 133.8, 128.9, 126.2, 126.0, 121.5, 120.3, 119.9, 119.0, 83.7, 55.3, 55.2, 40.3, 40.2, 31.8, 30.0, 29.2, 24.9, 23.9, 23.8, 22.6, 14.0. MADLI-TOF (m/z): calcd 1419.12 found [M]+ 1418.92.

Synthesis of 4,4'-(2,2':7',2''-ter(9,9-dioctylflourene))-7,7'diyldibenzaldehyde (8)

Compound 7 (4.3 g, 3.0 mmol), 4-bromo-benzaldehyde (1.3 g, 7.0 mmol), sodium carbonate (2.6 g, 24.0 mmol), and Pd(PPh₃)₄ (105 mg) were added in a 150 mL two-necked round-bottomed flask. Toluene (60 mL) and deionized water (10 mL) were added to the flask under argon. The mixture was refluxed for 24 h under argon atmosphere. After the mixture had been cooled to room temperature, it was poured into brine and extracted twice with dichloromethane. The combined organic layers were dried over MgSO₄ and the solvent was removed. The crude product was purified with column chromatography (silica gel, petroleum ether-ethyl acetate (20/1) as eluent) to yield 4.2 g (82.5%) of 8 as a light yellow solid. ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 10.09 (s, 2H), 8.00 (d, J = 8.4 Hz, 4H), 7.87–7.82 (m, 10H), 7.71–7.64 (m, 12H), 2.12–2.07 (m, 12H), 1.25–1.10 (m, 60H), 0.81–0.77 (m, 30H). ¹³C NMR (CDCl₃, 100 MHz) δ (ppm): 191.8, 152.0, 151.9, 151.8, 147.7, 141.4, 141.0, 140.4, 140.1, 139.6, 138.4, 135.1, 130.3, 127.7, 126.5, 126.3, 126.2, 121.7, 121.5, 120.3, 120.0, 55.4, 55.3, 40.3, 31.8, 30.0, 29.2, 23.9, 22.6, 14.0. MADLI-TOF (m/z): calcd 1376.01, found [M]+ 1375.91.

Synthesis of di-tert-butyl(((2,2':7',2''-ter(9,9-dioctylflourene)-7,7''-diyl)bis(4,1-phenylene))bis(methylene)) bis(benzylcarbamate) (9)

Compound **8** (3.0 g, 2.2 mmol) and benzylamine (0.54 g, 5.0 mmol) were heated together in refluxing toluene (50 mL) for 20 h under argon. The reaction mixture was cooled to room temperature, and the solvent was evaporated under vacuum. The residue was redissolved in THF (20 mL) and added in a 100 mL two-necked round-bottomed flask. MeOH (60 mL) and NaBH₄ (0.74 g, 15.0 mmol) were added, and the mixture was heated under reflux for 8 h. The reaction mixture was quenched with aqueous NaHCO₃ and extracted with dichloromethane. The two phases were separated, and the water phase was extracted twice with dichloromethane. The combined organic extracts were washed three times with water, dried over MgSO₄ and filtered. The filtrate was evaporated to dryness. The obtained oil was stirred together with (Boc)₂O (1.8 g, 8.0 mmol) and a catalytic

amount of DMAP in dry 50 mL dichloromethane for 12 h at room temperature. The solution was evaporated and the residue was purified by column chromatography (silica gel, petroleum ether–ethyl acetate (50/1) as eluent) to yield **9** as a white semisolid (3.0 g, 78%). ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 7.84–7.81 (m, 4H), 7.80 (d, J = 2.5 Hz, 2H), 7.70–7.67 (m, 6H), 7.66–7.64 (m, 6H), 7.62–7.59 (m, 4H), 7.38–7.27 (m, 14H), 4.48 (s, 4H), 4.40 (s, 4H), 2.11–2.06 (m, 12H), 1.54 (s, 18H), 1.20–1.10 (m, 60H), 0.85–0.78 (m, 30H). ¹³C NMR (CDCl₃, 100 MHz) δ (ppm): 156.1, 151.8, 140.7, 140.6, 140.5, 140.2, 140.0, 139.9, 139.7, 138.0, 137.0, 128.6, 128.0, 127.5, 127.3, 127.2, 126.2, 126.0, 121.5, 120.0, 80.1, 55.3, 49.0, 40.4, 31.8, 30.0, 29.2, 28.5, 23.9, 22.6, 14.0. MADLI-TOF (*m*/*z*): calcd 1758.27, found [M]⁺ 1758.07.

Synthesis of *N*,*N'*-(((2,2':7',2''-ter(9,9-dioctylflourene)-7,7''-diyl) bis(4,1-phenylene))bis(methylene))bis(1-phenylmethanaminium) hexafluorophosphate(v) (2)

TFA (3.0 mL, 39.0 mmol) was added to a solution of 9 (2.8 g, 1.6 mmol) in dichloromethane (30 mL) and the mixture was stirred for 12 h at room temperature. A saturated aqueous solution of NH₄PF₆ was added to the reaction mixture. On removal of the volatile solvents, a precipitate was formed which was filtered off and dissolved in acetonitrile. Afterwards, the acetonitrile solution was also treated with the aqueous NH_4PF_6 solution to yield 2 (2.67 g, 90%) as a light yellow solid. ¹H NMR (DMSO, 300 MHz) δ (ppm): 7.93 (d, J = 7.5 Hz, 6H), 7.85 (d, J = 7.9 Hz, 4H), 7.78-7.70 (m, 12H), 7.61 (d, J = 8.0 Hz, 4H), 7.51-7.47 (m, 10H), 4.27 (s, 4H), 4.22 (s, 4H), 2.08 (m, 12H), 0.99 (m, 60H), 0.67 (m, 30H). ¹³C NMR (CD₃COCD₃, 100 MHz) δ (ppm): 162.1, 151.9, 151.7, 142.5, 140.9, 140.6, 140.4, 140.2, 140.0, 138.8, 131.1, 130.8, 131.1, 130.8, 130.2, 129.9, 129.6, 129.1, 127.4, 126.2, 126.0, 121.3, 120.3, 120.2, 55.4, 55.3, 51.5, 51.3, 39.9, 35.4, 31.5, 30.2, 29.6, 23.7, 22.3, 13.4. MADLI-TOF (m/z): calcd $[M - 2PF_6]^+$ 1560.18, found $[M - 2PF_6^-]^+$ 1556.96.

Synthesis of 4,7-bis(7-(dibenzo-24-crown-8)-9,9-dioctylfluorene-2-yl)-2,1,3-benzothiadiazole (3)

4,7-Bis(7-bromo-9,9-dioctylfluorene-2-yl)-2,1,3-benzothiadiazole (10) (1.3 g, 1.2 mmol), compound 5 (1.73 g, 3.0 mmol), and Pd(PPh₃)₄ (40 mg) were added in a 100 mL two-necked roundbottomed flask. Toluene (20 mL), THF (40 mL) and 40% aqueous tetraethylammonium hydroxide (3 mL) were added to the flask under argon. The mixture was refluxed for 36 h under argon atmosphere. After the mixture had been cooled to room temperature, the mixture was poured into brine, extracted with dichloromethane three times and dried over MgSO4, evaporated, and purified with column chromatography (silica gel, ethyl acetate-dichloromethane (1/6) as eluent) to yield 0.58 g (27%) of **3** as a orange solid. ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 8.06 (dd, J = 1.4, 7.9 Hz, 2H), 7.97 (s, 2H), 7.88 (d, J = 8.6 Hz, 4H),7.80 (d, J = 8.0 Hz, 2H), 7.54 (d, J = 7.8 Hz, 4H), 7.24–7.21 (m, 4H), 6.97 (d, J = 8.5 Hz, 2H), 6.89 (s, 8H), 4.30–4.27 (m, 4H), 4.24-4.21 (m, 4H), 4.18-4.13 (m, 8H), 3.99-3.93 (m, 16H), 3.87 (s, 16H), 2.09–2.05 (m, 8H), 1.19–1.10 (m, 40H), 0.88–0.76 (m, 20H). ¹³C NMR (CDCl₃, 100 MHz) δ (ppm): 154.4, 152.0, 151.3, 149.2, 149.1, 148.7, 141.0, 140.0, 139.6, 136.1, 133.6, 128.2, 127.9, 125.8, 124.0, 121.5, 121.3, 120.3, 120.2, 119.7, 114.4, 114.3, 113.9,

71.3, 70.0, 69.9, 69.6, 69.5, 55.3, 40.3, 31.8, 30.1, 29.2, 24.0, 22.6, 14.0. MADLI-TOF (*m*/*z*): calcd 1805.02, found [M]⁺ 1805.01, [M + Na]⁺ 1828.00, [M + K]⁺ 1843.98.

Measurement and characterization

¹H and ¹³C NMR were recorded by using a Bruker-300 and 400 spectrometer operating at 300 or 400 and 75 or 100 MHz at 295 K. Chemical shifts were reported as δ values (ppm) relative to an internal tetramethylsilane (TMS) standard. Time-of-flight mass spectrometry (TOF-MS) was performed in the positive ion mode with a matrix of dithranol using a Bruker-autoflex III smartbeam. The differential scanning calorimetry (DSC) measurements were carried out with a Netzsch DSC 204 under N2 flow at heating and cooling rates of 10 °C min⁻¹. The viscosity was measured with a digital viscometer from Brookfield Engineering Laboratories, Inc. (model LVDV-I+). UV-vis absorption spectra were measured on a HP 8453 spectrophotometer. PL spectra were recorded on an Instaspec IV CCD spectrophotometer (Oriel Co.) under 325 nm excitation of a HeCd laser. The confocal laser scanning microscope micrograph was performed on a Lecia TCS SP5 scanning microscope (Mannheim, Germany) under 405 nm excitation of a 405 diode laser. The electrospinning fibers were fabricated by an electrospinning forming machine ESF-Y1.

Electrospinning of SLEP 1 + 2 nanofiber

The concentration of SLEP 1 + 2 was 150 mM in CHCl₃– CH₃CN (1/1, v/v). During electrospinning, the solution was placed in a 1 mL syringe and was fed by a syringe pump at a rate of 400 rpm. The metallic needle was connected to a grounded counter electrode. A power supply was connected to the aluminium collector. The distance between the tip of the capillary and the collector was 13 cm. The collecting target was a quartz substrate placed on the top of the aluminium electrode. The spinning voltage was set at 13 kV, and all experiments were carried out at room temperature.

Polymer light-emitting diodes fabrication and characterization

The ITO-coated glass substrates were ultrasonically cleaned with deionized water, acetone, detergent, deionized water, and isopropyl alcohol. Then a layer of 40 nm thick poly(3,4-ethylenedioxythiophene):poly(styrene sulfonic acid) (PEDOT:PSS) (H.C.Stack, 4083) was spin-coated onto the pre-cleaned and O₂plasma-treated ITO substrates. After that, the PEDOT:PSS layer was baked at 150 °C for 20 min to remove residual water, and then the devices were moved into a glove box under the argon-protected environment. SLEPs 1 + 2, 1 + 2 + 3 (10%), and 1 + 2 + 3 (30%) (30 mg mL⁻¹ in *o*-DCB) were spin-coated onto PEDOT:PSS at the speed of 2000 r per min to yield 90 nm thickness light emitting layers. In SLEP 1 + 2 + 3 (10%), the molar ratios of 1, 2, and 3 are 40%, 50% and 10%, respectively. In SLEP 1 + 2 + 3 (30%), the molar ratios of 1, 2, and 3 are 20%, 50% and 30%, respectively. The samples were transferred into a chamber and kept under vacuum (3.0×10^{-4} Pa) for 2 h. 30 nm TPBI thickness was sublimed as the hole blocking layer, and then caesium fluoride (CsF) with a thickness of 1.5 nm and aluminium with a thickness of 100 nm were subsequently

deposited on top of the TPBI to form the cathode. The current density (J) and brightness (L) versus voltage (V) data were collected using a Keithley 236 source meter and silicon photodiode. After typical encapsulation with UV epoxy and cover glass, the devices were taken out from the dry box and the luminance was calibrated by a PR-705 SpectraScan Spectrophotometer (Photo Research) with simultaneous acquisitions of the EL spectra.

Results and discussion

Synthesis and characterization

The synthetic routes of the monomers are shown in Scheme 2. The host monomers 1 and 3 were synthesized from compounds 5 with 6 or 10 by Suzuki condensation reactions, respectively. The guest monomer 2 was synthesized from compound 6 by a four-step procedure with a high yield. Because of the presence of a ring strain, the rigid aromatic linker units are favorable to form the linear SLEPs compared with the flexible aliphatic linker units.8g,h,13 Therefore, the critical polymerization concentration (CPC) which exhibited a ring-chain transition from the formation of the cyclic to linear polymers is low. To get some insight into the complexation of the designed host and guest monomers, the NMR studies were performed. The concentration-dependent ¹H NMR spectra of an equimolar solution of host 1 and guest 2 in CDCl₃-CD₃CN (1/1, v/v) at 22 °C are shown in Fig. 1. At low concentrations (below 10 mM), the benzyl protons H_4 on the fast-exchanging units (Scheme 1) have two sets of well-defined signals standing for the cyclic and liner species. As the concentrations increased, the signals for the cyclic dimer decreased, and further disappeared at 20 mM. At high concentrations, all the signals are broad, confirming the formation of high molecular weight aggregates driven by host-guest interactions between host 1 and guest 2.8 Moreover, the large chemical shift change of benzyl protons H₄ exhibited that a percentage of complexed species was concentration-dependent.14

The viscosity study can provide the direct physical evidence for the formation of large supramolecular polymers by the monomers. Therefore, viscosity measurements were performed in CHCl₃-CH₃CN (1/1, v/v) solution. As shown in Fig. 2a, a double logarithmic representation of specific viscosity versus the concentration of equimolar solution of 1 and 2 was observed. In the low concentration range, the curve had a slope of 0.176, revealing a linear relationship between specific viscosity and concentration, which is characteristic for noninteracting assemblies of constant size.15 As the concentrations increase, the curve exhibited a sharp rise with a slope of 2.059, indicating the formation of linear supramolecular polymers. The CPC for SLEP 1 + 2 was about 10 mM as evidenced by the clear change of slope, indicating a ring-chain transition from the formation of cyclic dimer to ordered linear SLEP. It was found that the CPC of the SLEPs based on a rigid aromatic linker was significantly lower than those of the supramolecular polymers based on a flexible aliphatic linker, owing to the presence of ring strain.^{8g,h,13c,16} Clearly, the viscosity study results show that the designed SLEPs will have good film formation abilities for solution processed organic electronic devices.



Scheme 2 Synthesis of host 1, guest 2 and host 3.

Besides the film formation abilities, the film morphology stabilities of the light-emitting polymers are also critical for device application, which will greatly affect the resulting devices' stabilities. Thus, the DSC measurement was carried out. Host **1** is a crystalline solid with a melting point at around 90 °C, while no obvious endotherm–exotherm transition was found across the entire scanning range for guest **2**. In contrast, the solid obtained from the evaporation of solutions **1** and **2** had a repeatable glasstransition temperature (T_g) of 114.5 °C, which was much higher than those of the host–guest supramolecular polymers based on the flexible aliphatic linker¹⁶ and comparable to polyfluorene conjugated polymers.¹⁷ It is interesting that the designed SLEPs based on 1 and 2 exhibited a relatively high T_g compared to traditional conjugated polymers, which will ensure it has a good film morphology stability for device application. Moreover, although no fibers could be drawn from the individual highly concentrated solutions of 1 and 2, rod like fibers with a regular diameter of around 50 µm could easily be drawn from concentrated equimolar solutions of SLEP 1 + 2 (Fig. 3a and b). Furthermore, long thin fibers can be processed by an electrospinning technique, which generally can only be applied for high molecule weight polymers,¹⁸ providing another direct evidence of the formation of supramolecular polymers with high molecular weight (Fig. 3c). Most importantly, the luminescence properties



Fig. 1 The stacked ¹H NMR spectra (400 MHz, CDCl₃–CD₃CN, 1/1, v/v, 22 °C) of solutions of **1** and **2** at different concentrations: (a) **1**, (i) **2**, and equimolar solutions of **1** and **2** at concentrations of (b) 1, (c) 2, (d) 5, (e) 10, (f) 20, (g) 30 and (h) 100 mM. Peaks of linear polymer, cyclic dimer, and uncomplexed monomer are designated by lin, cyc, and uc, respectively.

of the typical fluorene oligomers were well maintained in the supramolecular systems and all these fibers exhibited strong blue fluorescence under the excitation of the UV light, which can be clearly observed by the confocal laser scanning microscope micrograph (Fig. 3a–c).



Fig. 3 (a) A photo of a rod-like fiber drawn from a high concentration of SLEP 1 + 2 in CHCl₃–CH₃CN (1/1, v/v) solution. (b) The confocal laser scanning microscope micrograph of a rod-like fiber drawn from a high concentration of SLEP 1 + 2 in CHCl₃–CH₃CN (1/1, v/v) solution. (c) The confocal laser scanning microscope micrograph of the electrospun SLEP 1 + 2 nanofibers.

Optical properties

The absorption and PL spectra of the monomers and the SLEPs in solid films are shown in Fig. 4. Both host 1 and guest 2 exhibited similar UV-visible absorption and PL spectra to those of typical fluorene trimers.¹⁹ It was noted that guest 2 showed more pronounced emission tails at around 500–600 nm compared to host 1, probably due to the stronger intermolecular interactions caused by the ionic groups among guest 2.²⁰ Different from 1 and 2, 3 exhibited two absorption peaks and a green emission with a peak at around 550 nm. The photophysical properties of the resulting SLEPs were also investigated. The absorption spectrum of SLEP 1 + 2 is similar to those of the monomers, while the SLEPs based on 1, 2 and 3 exhibited a broader main absorption peak at around 360 nm and a small





Fig. 2 (a) Specific viscosity of equimolar mixtures of host 1 and guest 2 in $CHCl_3-CH_3CN$ (1/1, v/v) solution; (b) DSC plots of host 1, guest 2, and SLEP 1 + 2.

Fig. 4 (a) Absorption spectra and (b) PL spectra of host 1, guest 2, host 3, SLEP 1 + 2, SLEP 1 + 2 + 3 (10%) and SLEP 1 + 2 + 3 (30%).



Fig. 5 (a) Current density (J) and brightness (L) versus voltage (V) characteristics (J-L-V) and (b) EL spectra of SLEPs 1 + 2, 1 + 2 + 3 (10%) and 1 + 2 + 3 (30%) in the devices with configuration of ITO/ PEDOT/EMLs/TPBI/CsF/Al.

absorption peak at around 440 nm, caused by the doped host 3. The PL studies on the SLEPs interestingly show that SLEP 1 + 2showed similar emission main peaks to those of monomers 1 and 2, while its emission tail at around 500-600 nm was largely suppressed. That indicates that the intermolecular interactions among monomers 1 and 2 were decreased in the SLEPs which were desirable for PLED application. By doping 10% of 3 into the supramolecule system, SLEP 1 + 2 + 3 (10%) exhibited a green emission at around 550 nm with a small peak at around 420 nm, which is from the 1 + 2 hosts. With the increase in content of 3, the emission of SLEP 1 + 2 + 3 (30%) is dominated by a green emission that peaked at around 550 nm, indicating the efficient energy transfer from 1 and 2 to 3, which is very similar to those traditional conjugated copolymers.²¹ The PL quantum yields of SLEPs were determined in an integrating sphere with 325 nm excitation of the HeCd laser. PL efficiencies were increased from 20.2% for SLEP **1** + **2** to 65% for SLEP **1** + **2** + **3** (10%) and 60% for SLEP **1** + **2** + **3** (30%), respectively. The significantly enhanced PL efficiencies of SLEPs upon doping with **3** were attributed to the efficient intra- and inter-molecular energy transfer among the SLEPs.²¹

Electroluminescence properties

The electroluminescence (EL) properties of the SLEPs are investigated. All the SLEPs were used as the emissive layers (EMLs) in light-emitting devices. Fig. 5a compares the current density (J) and brightness (L) versus voltage (V) characteristics between different SLEPs. The SLEPs based on 1, 2 and 3 exhibited much higher device performances than the SLEPs based on 1 and 2, which possess higher brightness and efficiencies at the same voltage and current density. As shown in Table 1, the devices of SLEPs based on 1, 2 and 3 showed maximum luminance efficiencies (LE) more than 3 cd A^{-1} , which is much higher than that of devices of SLEPs based on 1 and 2. Fig. 5b shows the EL spectra of the devices. It can be found that compared to its PL emission, the device of SLEPs based on 1 and 2 showed a largely red-shifted EL emission, which is attributed to the excimer formation as typical polyfluorene homopolymers.²² By using 3 as an additional dopant host, the excimer emissions are completely quenched and the resulting devices emit an exclusively green emission of host 3. Besides, host 3 has a smaller band gap compared to 1 and 2, and will act as a "charge trap" in the resulting SLEPs. That will cause efficient energy transfer among the SLEPs and enhance the hole-electron recombination ratios in the devices, resulting in the greatly improved device performances. It is interesting that all the SLEPs showed comparable device efficiencies to those analogous traditional conjugated polymers such as polyfluorene homopolymers^{17,23} or polyfluorene copolymers with 2,1,3-benzothiadiazole.²⁴ It was noted that the resulting devices' brightness is not as high as those analogous traditional conjugated polymers, which is probably due to mobile ions among these SLEPs.²⁵ Nevertheless, this can be potentially addressed by tuning the counterions of the SLEPs^{6i,25a} and the related work is in progress.

Conclusions

In summary, the conjugated oligomers 1–3 were developed and used as the starting monomers to build the SLEPs for PLED application. The formation of the SLEPs was confirmed by the NMR, viscosity and DSC studies. Photophysical studies indicate that the luminescence properties of the typical conjugated oligomers can be well maintained in the supramolecular systems and highly fluorescent fibers can be obtained by drawing or by

Table 1 EL Performance of the SLEPs in the devices with configuration of ITO/PEDOT:PSS/EML/TPBI/CsF/Al

EMLs	$V_{\rm on}{}^a$ [V]	B^b [cd m ⁻²]	LE^c [cd A^{-1}]	B_{\max}^{d} [cd m ⁻²]	LE_{max}^{e} [cd A ⁻¹]
1 + 2 1 + 2 + 3 (10%) 1 + 2 + 3 (30%)	10	23.6	0.37	79.6	0.49
	9.25	121.8	1.45	384.0	3.40
	9.25	156.8	1.66	439.0	4.07

^{*a*} Turn-on voltage corresponding to 1 cd m⁻². ^{*b*} Brightness at current density around 10 mA cm⁻². ^{*c*} Luminous efficiency at current density around 10 mA cm⁻². ^{*c*} Maximum brightness. ^{*e*} Maximum luminance efficiency.

electro-spinning from the SLEP solutions. The doping strategy was successfully applied in SLEPs, resulting in largely enhanced PL efficiencies. PLED device studies show that the designed SLEPs had comparable device performances to those analogous traditional conjugated polymers. Considering the perfectly defined starting monomers and catalyst-free polymerization process for the designed SLEPs, combining the good device performances, the present study provides a promising alternative route to develop solution processed semiconductors for optoelectronic applications.

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