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Supramolecular Phosphorescent Polymer Iridium Complexes for High-Efficiency Organic Light-Emitting Diodes

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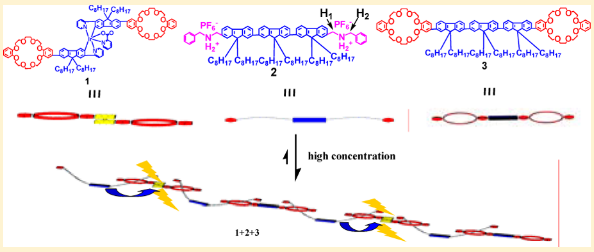

ABSTRACT: The synthesis of supramolecualr phosphorescent polymers (SPPs) as a novel class of solution-processable electroluminescent (EL) emitters was presented. The SPPs were formed by utilizing the efficient nonbonding self-assembly of luminescent iridium monomer **1** and "terfluorenyl"-based monomers **2** and **3**, tethered with either a crown ether or dibenzylammonium unit. The supramolecular assembly process was monitored and illustrated by ^{1}H nuclear magnetic resonance (NMR) and viscosity measurement. Moreover, the SPPs exhibit an intrinsic glass transition with a glass-transition temperature (T_g) of 72.5−81.5 °C, which is absent in the monomers. The characterization of organic light-emitting diodes that consisted of these SPPs as an emitter gave an efficiency of 14.6 cd A^{-1} at a luminance of 450 cd m^{-2}. Considering the good solution processability and catalyst-free polymerization process for the designed SPPs, combining the good device performances, the present study provide a promising alternative route to develop solution processed phosphorescent light-emitting materials for optoelectronic applications.

KEYWORDS: *iridium complex, organic light-emitting diodes, phosphorescence, solution process, supramolecular polymer*

■ INTRODUCTION

Phosphorescent organic light-emitting diodes (OLEDs) have been recognized as one of the most promising candidates for flat-panel displays and solid-state lighting.[1] In order to obtain high-efficiency OLEDs, phosphorescent complexes have been extensively developed as the emissive materials, since they can harvest both singlet and triplet excitons, which can potentially ensure nearly 100% internal quantum efficiency.[2] In particular, cyclometalated iridium complexes show short lifetimes in excited states (on the order of microseconds) and high luminescence efficiencies.[3] Recently, solution-processable electroluminescent (EL) emitters have been the subject of increasing interest for low-cost and large-area OLED displays and lighting.[4] In this context, electrophosphorescent polymers, where the iridium complexes are incorporated into the polymeric main chain[5] or side chain[6] via covalent bonds, have attracted considerable interest. Compared with the physical blends of polymer hosts and phosphors of iridium complexes, this strategy can effectively prohibit phase segregation. However, some challenges still exist in developing high-performance solution-processed phosphorescent organic light-emitting diodes (PHOLEDs). For example, a trace of metal catalyst remaining in the polymers would inevitably impede the improvement of device performances.[7] In addition, it is difficult to control the distribution and exact content of the iridium complex in the polymer, which plays an important role in the properties of the resulting PHOLEDs.[4b,8]

The programmed supramolecular assembly of functional components might open up a new avenue toward well-controlled supramolecular polymers, which exhibit many advantages, such as easy control of the ratio of monomers in the alternating copolymer and no residual metal catalyst contamination, with respect to conventional polymers, prepared through metal-catalyzed polymerization.[9] Thus far, there have been only occasional reports on supramolecular polymers as EL emitters.[10] Meijer et al. first utilized self-assembled light-emitting polymers based on UPy-functionalized fluorescent monomers (UPy = 2-ureido-4[1H]-pyrimidinone), while the resulting luminous efficiency (LE) was <0.1 cd A^{-1}.[10a] Recently, we reported on supramolecular fluorescent polymers by harnessing the efficient nonbonding interaction between functionalized dibenzo-24-crown-8 and dibenzylammonium salt, which produced a LE value of ~4 cd A^{-1}.[10b]

In this contribution, we describe a phosphorescent small-molecule crown ether-functionalized iridium monomer and its successful incorporation into a luminescent supramolecular polymer (see Scheme 1). The optical, morphological, and EL properties of the resulting polymers, as well as the supramolecular assembly process, were discussed. The supramolecualr phosphorescent polymers (SPPs) exhibit an intrinsic glass transition with a glass-transition temperature (T_g) of 72.5−81.5 °C. A high LE of 14.6 cd A^{-1} at a current density of 3.1 mA cm^{-2}, and a maximal brightness of 2863 cd m^{-2} were obtained based on the single-emissive-layer polymer light-emitting diodes with SPP50 as the emitter. This work opens a new avenue in the development of solution-processable

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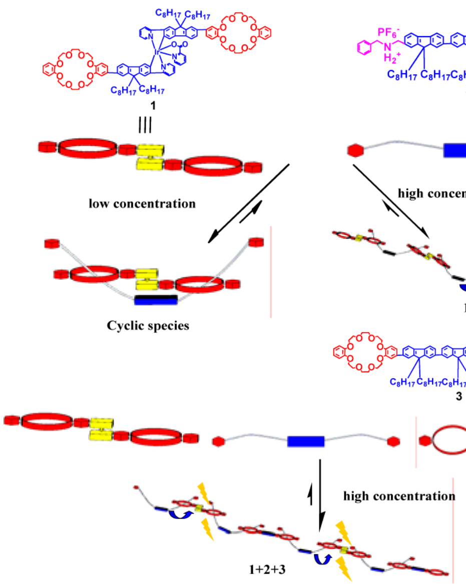
Scheme 1. Schematic Representation of the Construction of SPPs from Monomers 1, 2, and 3



electrophosphorescent polymers for organic light-emitting diodes.

■ EXPERIMENTAL SECTION

Materials. 2-(7-Bromo-9,9-dioctylfluoren-2-yl)pyridine (BrFPy),[11] 4-(boronic acid pinacol ester)-dibenzo-24-crown-8,[10b] 7-bromo-9,9-dioctylfluorene-2-carbaldehyde,[12] 9,9-dioctylfluorene-2,7-bis(boronic acid pinacol ester),[13] and monomer **3**[10b] were prepared according to the reported procedures. All reactions were performed under nitrogen. All solvents were carefully dried and distilled from appropriate drying agents prior to use. Commercially available reagents were used without further purification, unless otherwise stated.

Synthesis of (BrFPy)$_2$Ir(Pic). A mixture of iridium trichloride hydrate (0.35 g, 1.0 mmol) and 2-(7-bromo-9,9-dioctylfluoren-2-yl)pyridine (BrFPy) (1.36 g, 2.50 mmol) in 2-ethoxyethanol (24 mL) and water (8 mL) was heated and refluxed for 24 h under nitrogen atmosphere. After being cooled to room temperature, the resulting precipitate was collected, and then washed respectively with water, ethanol, and petroleum ether to afford 1.18 g of chlorine-bridged iridium dimer [(BrFPy)$_2$IrCl]$_2$ as an orange powder. The dimer was directly used in the following procedure.

A mixture of [(BrFPy)$_2$IrCl]$_2$ (1.18 g, 0.447 mmol), picolinic acid (138 mg, 1.12 mmol), Na_2CO_3 (572 mg, 5.4 mmol) in 2-ethoxyethanol (20 mL) was refluxed for 24 h under nitrogen atmosphere, then was allowed to cool to room temperature and mixed with water (40 mL). The mixture was extracted with dichloromethane (3 × 30 mL). The resulting organic layers were dried over $MgSO_4$ and evaporated to remove the solvents under vacuum. The residue was purified by column chromatography (ethyl acetate/dichloromethane = 1/1 (v/v)) to obtain (BrFPy)$_2$IrPic as an orange solid in 67% yield (842 mg). ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ (ppm): 8.87–8.86 (d, J = 4.8 Hz, 1H), 8.34–8.31 (d, J = 7.47 Hz, 1H), 8.01–7.98 (d, J = 8.16 Hz, 1H), 7.94–7.92 (d, J = 8.04 Hz, 1H), 7.89–7.85 (t, J = 6.71 Hz, 1H), 7.80–7.74 (m, 2H), 7.67–7.65 (d, J = 4.77 Hz, 1H), 7.58–7.52 (m, 3H), 7.39 (s, 1H), 7.35 (s, 1H), 7.31–7.14 (m, 5H), 7.10–7.07 (d, J = 8.07 Hz, 1H), 6.95–6.91 (t, J = 6.57 Hz, 1H), 6.73 (s, 1H), 6.55 s, 1H), 2.10–1.91 (m, 8H), 1.25–1.02 (m, 40H), 0.85–0.63 (m, 20H). Anal. Calcd. for $C_{74}H_{90}Br_2IrN_3O_2$: C, 63.23; H, 6.45; N, 2.99; Found: C, 63.29; H, 6.35; N, 2.93.

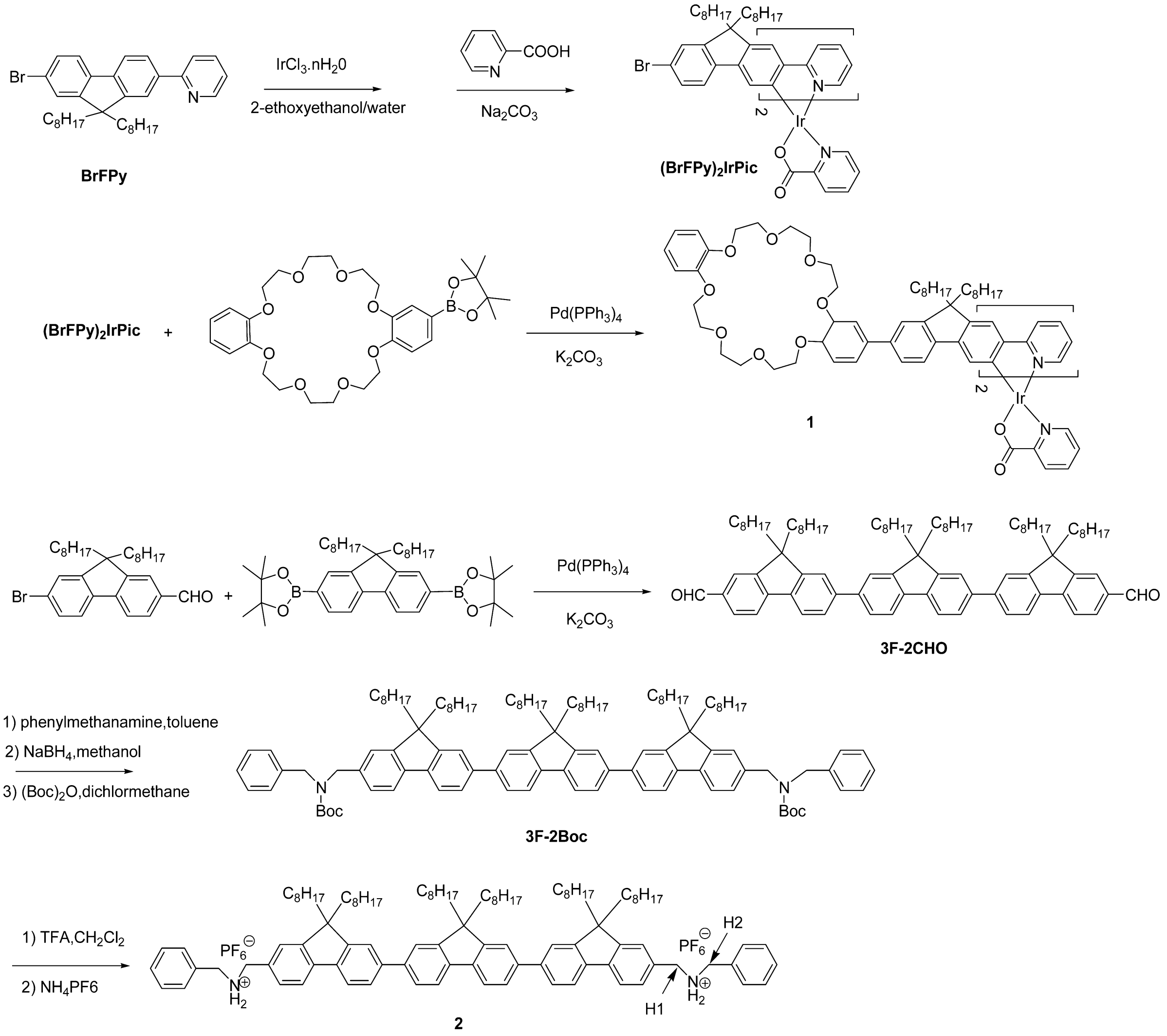
Synthesis of Monomer 1. Pd(PPh$_3$)$_4$ (105 mg, 0.09 mmol) was added to a mixture of (BrFPy)$_2$IrPic (842 mg, 0.6 mmol), 4-(boronic acid pinacol ester)-dibenzo-24-crown-8 (1.03 g, 1.8 mmol), and 2.0 M K_2CO_3 solution (20.0 mL) in toluene (30.0 mL) and ethanol (10.0 mL). The mixture was degassed and heated to 80 °C with vigorously stirring for 48 h under N_2. After being cooled to room temperature, the mixture was poured into water. The organic phase was separated and the aqueous phase was extracted with dichloromethane (3 × 30 mL). The combined organic layers were dried over $MgSO_4$ and evaporated to remove the solvents under vacuum. The residue was purified by column chromatography (ethyl acetate/dichloromethane = 2/1 (v/v)) to provide monomer **1** (617 mg) as an orange solid in 48% yield. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ (ppm): 8.90–8.88 (d, J = 5.82 Hz, 1H), 8.34–8.31 (d, J = 7.92 Hz, 1H), 8.02–8.00 (d, J = 8.43 Hz, 1H), 7.95–7.93 (d, J = 8.52 Hz, 1H), 7.88–7.82 (t, J = 7.96 Hz, 1H), 7.80–7.74 (m, 2H), 7.70–7.68 (d, J = 5.25 Hz, 1H), 7.58 (s, 2H), 7.55–7.53 (d, J = 5.82 Hz, 2H), 7.42 (s, 1H), 7.35 (s, 1H), 7.31–7.07 (m, 9H), 6.95–6.91 (d, J = 7.23 Hz, 1H), 6.87 (s, 10H), 6.73 (s, 1H), 6.55 (s, 1H), 4.23 (m, 16H), 3.93 (s, 16H), 3.84 (s, 16H), 2.00–1.84 (m, 8H), 1.25–0.98 (m, 40H), 0.82–0.68 (m, 20H). Anal. Calcd. for $C_{122}H_{156}IrN_3O_{18}$: C, 68.32; H, 7.33; N, 1.96; Found: C, 68.39; H, 7.35; N, 1.92. MALDI-TOF (m/z): calcd for $[M]^+$ 2142.10, found $[M + Na]^+$ 2164.20.

Synthesis of 3F-2CHO. A mixture of 9,9-dioctylfluorene-2,7-bis(boronic acid pinacol ester) (1.6 g, 2.5 mmol), 7-bromo-9,9-dioctylfluorene-2-carbaldehyde (2.8 g, 5.6 mmol), potassium carbonate (7.7 g, 56.0 mmol), and Pd(PPh$_3$)$_4$ (130 mg) in toluene (50 mL) and deionized water (28 mL) was refluxed for 24 h under argon atmosphere. After being cooled to the room temperature, the mixture was poured into brine and extracted twice with dichloromethane. The combined organic layers were dried over $MgSO_4$ and the solvent was removed. The crude product was purified with column chromatography (petroleum ether/dichloromethane = 4/1 (v/v)) to afford a light yellow solid in 72% yield (2.2 g). ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 10.08 (s, 2H), 8.11 (d, J = 8.4 Hz, 2H), 7.88 (s, 4H), 7.86–7.85 (d, J = 2.22 Hz, 2H), 7.82 (s. 2H), 7.73–7.72 (d, J = 1.44 Hz, 2H), 7.69 (s, 2H), 7.66–7.64 (d, J = 4.62 Hz, 4H), 2.12–2.07 (m, 12H), 1.25–1.07 (m, 60H), 0.81–0.77 (m, 30H).

Synthesis of 3F-2Boc. Compound 3F-2CHO (2.2 g, 1.8 mmol) and benzylamine (0.48 g, 4.5 mmol) were heated together in refluxing toluene (40 mL) for 20 h under argon. The reaction mixture was cooled to room temperature, and the solvent was evaporated off under vacuum. The residue was redissolved in tetrahydrofuran (THF) (20 mL) and added in a 100-mL two-necked round-bottomed flask. Methanol (MeOH) (60 mL) and $NaBH_4$ (0.28 g, 7.2 mmol) were added, and the mixture was heated to reflux for 8 h. The reaction mixture was quenched with aqueous $NaHCO_3$ 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 $MgSO_4$, and filtered. The filtrate was evaporated to dryness. The obtained oil was stirred together with (Boc)$_2$O (1.04 g, 4.7 mmol) and catalytic amount of DMAP in dry dichloromethane (50 mL) for 12 h at room temperature. The solution was evaporated and the residue was purified by column chromatography (petroleum ether/ethyl acetate = 20/1 (v/v)) to afford a colorless liquid in 86.7% yield (3.0 g). ^{1}H NMR ($CDCl_3$, 300 MHz, tetramethylsilane (TMS)) δ (ppm): 7.82–7.80 (d, J = 7.86 Hz, 2H), 7.78–7.75 (d, J = 7.86 Hz, 2H), 7.69–7.61 (m, 8H), 7.35–7.24 (m, 16H), 4.52–4.34 (m, 8H), 2.12–2.07 (m, 12H), 1.54 (s, 18H), 1.25–1.07 (m, 60H), 0.81–0.77 (m, 30H).

Synthesis of Monomer 2. TFA (3.0 mL, 39.0 mmol) was added to a solution of 3F-2Boc (1.57 g, 1.0 mmol) in dichloromethane (30 mL), and the mixture was stirred for 12 h at room temperature. A saturated aqueous solution of NH_4PF_6 was added to the reaction mixture. Upon removal of the volatile solvents, a precipitate was formed which was filtered off and dissolved in acetonitrile. After the acetonitrile solution was also treated with the aqueous NH_4PF_6 solution to afford a white solid in 85% yield (1.44 g). ^{1}H NMR (DMSO, 300 MHz, TMS) δ (ppm): 9.17 (s, 4H), 7.94–7.92 (d, J = 7.26 Hz, 6H), 7.79 (s, 8H), 7.57 (s, 2H), 7.48 (s, 2 H), 7.46 (s, 10 H), 4.27 (s, 4H), 4.15 (s, 4H), 1.98–1.90 (m, 12H), 1.10–1.02 (m, 60H), 0.72–0.64 (m, 30H). MALDI-TOF (m/z): calcd for $[M - 2PF_6]^+$ 1406.12, found $[M - 2PF_6]^+$ 1405.90.

Scheme 2. Synthetic Route to Monomers 1 and 2



Synthesis of Supramolecular Phosphorescent Polymers. Monomers **1**, **2**, and **3** are dissolved at a certain ratio in a solution of $CHCl_3$−CH_3CN (1/1 (v/v)). The resulting solution was left for evaporation at room temperature. The obtained supramolecular phosphorescent polymers are denoted as SPP5, SPP10, SPP25 and SPP50, corresponding to the monomer molar ratios of **1**:**2**:**3** as 0.5:5:4.5, 1:5:4, 2.5:5:2.5, and 5:5:0, respectively, without any further purification.

Measurements and Characterization. ^1H spectra were recorded on a Bruker 300 or 400 MHz spectrometer operating at 300 or 400 MHz at room temperature. Chemical shifts were reported as δ values (ppm), relative to an internal 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 system. Differential scanning calorimetry (DSC) measurements were carried out with a Netzsch Model DSC 204 system under N_2 flow at heating and cooling rates of 10 °C min^{-1}. The T_g value was determined from the second heating scan. The viscosity was measured with a digital viscometer from Brookfield Engineering Laboratories, Inc. (Model LVDV-I+). Ultraviolet-visible light (UV−vis) absorption spectra were measured on a Hewlett−Packard Model HP 8453 spectrophotometer. Photoluminescence (PL) spectra were recorded on a Hitachi Model F-4500 fluorescence spectrophotometer. The phosphorescence quantum yield of monomer **1** was determined in CH_2Cl_2 solution at 293 K against *fac*-[Ir(ppy)$_3$] (Hppy = 2-phenylpyridine) as a reference (Φ_p = 0.90).[14] Cyclic voltammetry was carried out on a CHI Instruments Model 660A electrochemical workstation in a solution of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) (0.1 M) in acetonitrile at a scan rate of 50 mV/s at room temperature, under the protection of argon. A platinum electrode was used as the working electrode. A platinum wire was used as the counter electrode, and a saturated calomel electrode (SCE) was used as the reference electrode. The PL quantum yields of SPPs and monomer **1** in neat film were measured by an absolute method.[15] The measurements were carried out on a SENS-9000 Fluorosens System with an integrating sphere at ambient temperature, using a 380-nm excitation wavelength. The photoluminescent lifetime was investigated on a Model FLS920 spectrometer demonstration system.

PLEDs Fabrication and Measurements. The ITO-coated glass substrates were ultrasonically cleaned with deionized water, acetone, detergent, deionized water, and isopropyl alcohol. A layer of 40-nm-thick poly(3,4-ethylenedioxythiophene):poly(styrene sulfonic acid) (PEDOT:PSS) (H.C. Starck, 4083) then was spin-coated onto the precleaned and O_2-plasma-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 glovebox under the argon-protected environment. SPPs + PBD (30 mg mL^{-1} in *o*-DCB) were spin-coated onto PEDOT:PSS at a speed of 2000 rpm to yield emitting layers 90 nm thick. The samples were transferred into a chamber and kept under vacuum (3.0×10^{-4} Pa) for 2 h. Cesium fluoride (CsF) with a thickness of 1.5 nm and aluminum with a thickness of 100 nm, then were subsequently deposited on top of the EML to form the cathode. The current density (*J*) and brightness (*L*) versus voltage (*V*) data were collected using a Keithley Model 236 source meter and silicon photodiode. After typical encapsulation with UV epoxy and cover glass, the devices were taken out from the drybox 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 synthesis of monomers **1** and **2** is presented in Scheme 2. Monomer **3** was reported by us recently.[10b] The new phosphorescent monomer **1** was obtained by a bis-Suzuki coupling of bis(2-(7-bromo-9,9-dioctylfluoren-2-yl)pyridine)Ir(picolinate) with 4-(boron acid pinacol ester)-dibenzo-24-crown-8. The bis-ammonium monomer **2** that contains a linear-conjugated terfluorenyl unit was prepared by a modified procedure, starting from 3F-2CHO.[10b,16]

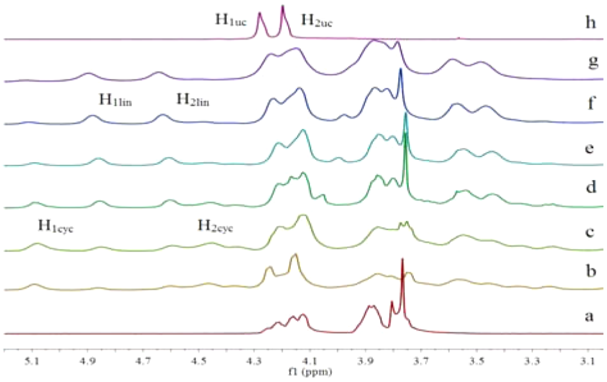


Figure 1. Stacked ^1H NMR spectra (400 MHz, $CDCl_3$−CD_3CN, 1/1 (v/v), 22 °C) of solutions of **1** and **2** at different concentrations: (a) **1**, (h) **2**, and equimolar solutions of **1** and **2** at concentrations of (b) 2, (c) 5, (d) 10, (e) 20, (f) 30, and (g) 50 mM L^{-1}. Peaks of linear polymer, cyclic dimer, and uncomplexed monomer are designated as lin, cyc, and uc, respectively.

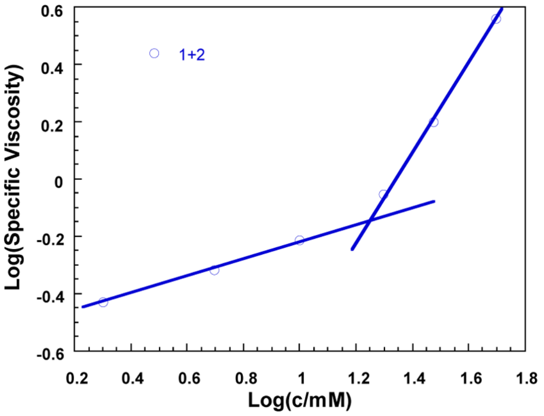


Figure 2. Specific viscosity of equimolar mixtures of **1** and **2** in $CHCl_3$−CH_3CN (1/1 (v/v)) solution.

^1H NMR studies show that the formation of linear supramolecular polymers is favored at high monomer concentrations, in contrast to cyclic structures. For an equimolar solution of monomers **1** and **2**, the H_1 and H_2 of monomer **2** undergo a downfield shift at low concentrations, splitting into two sets of signals, namely, H_{cyc} and H_{lin} (Figure 1), which is attributed to the coexistence of both cyclic and linear assemblies.[17] With increasing concentration, the signal of H_{lin} increased while that of H_{cyc} decreased. Meanwhile, the broadening of the H_{lin} signal may imply the formation of high-molecular-weight polymeric structures.

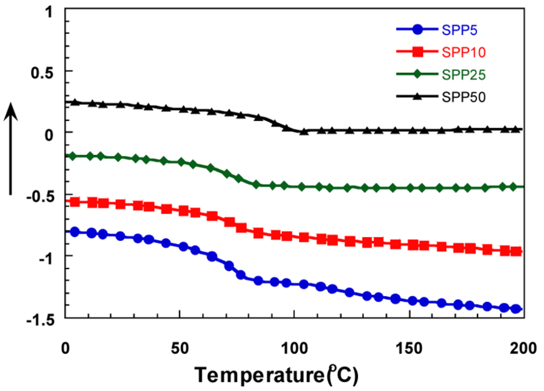


Figure 3. Differential scanning calorimetry (DSC) plots of SPP5, SPP10, SPP25, and SPP50.

Table 1. Ultraviolet (UV), Photoluminenscence (PL), and Thermal Performances of SPP5, SPP10, SPP25, and SPP50

SPP	monomer ratio (**1**/**2**/**3**)	λ_{abs} (nm)[a]	λ_{PL} (nm)[a]	Φ_{PL} (%)[a]	T_g (°C)
SPP5	0.5:5:4.5	358, 456	416, 438, 562, 604	17	72.5
SPP10	1:5:4	358, 456	416, 438, 562, 604	17	73.4
SPP25	2.5:5:2.5	358, 456	416, 562, 604	20	75.0
SPP50	5:5:0	358, 456	562, 604	21	81.5

[a] Measured in the neat film at room temperature.

The linear self-assembly process was further evidenced by viscosity measurements. The double logarithmic plot of specific viscosity versus the initial concentrations of equimolar solutions of monomers **1** and **2** is shown in Figure 2. At low concentrations, the curve has a slope of 0.31, which is characteristic for noninteracting assemblies of constant size.[18] As the concentration increases, the curve exhibits a sharp rise with a slope of 1.55, indicating the emergence of linear supramolecular polymers. The critical polymerization concentration at ~18 mM L^{-1} indicates a transition from cyclic species to linear supramolecular polymers. Furthermore, the viscosity measurements reveal that the resulting SPPs possess excellent solution processability for optoelectronics.

The differential scanning calorimetry (DSC) measurements show that the as-prepared phosphorescent polymers SPP5−SPP50 are inherently amorphous with a glass-transition temperature of T_g = 72.5−81.5 °C (see Figure 3 and Table 1), which is absent in the monomers.[10b] This amorphous morphology is desirable for EL purposes.[19]

Photophysical Properties. The absorption and photoluminescence (PL) spectra of monomers **1**−**3** in solution (**1** and **3** in CH_2Cl_2 and **2** in CH_3CN) and those of the SPPs as films are shown in Figure 4, and relevant data are presented in Tables 1 and 2. The iridium monomer gives a weak absorption band above 400 nm, which corresponds to an admixture of ^{1}MLCT, ^{3}MLCT, and $^3\pi$−π^* excited states, caused by the heavy-metal effect of Ir center, leading to strong spin−orbital coupling.[20] The PL spectrum shows a maximal phosphorescent peak at 566 nm at ambient temperature, excited at a wavelength of 380 nm. The triplet emission displays a large Stokes shift from the lowest energy absorption peak. The phosphorescence quantum yield (Φ_P), recorded in degassed CH_2Cl_2 solution

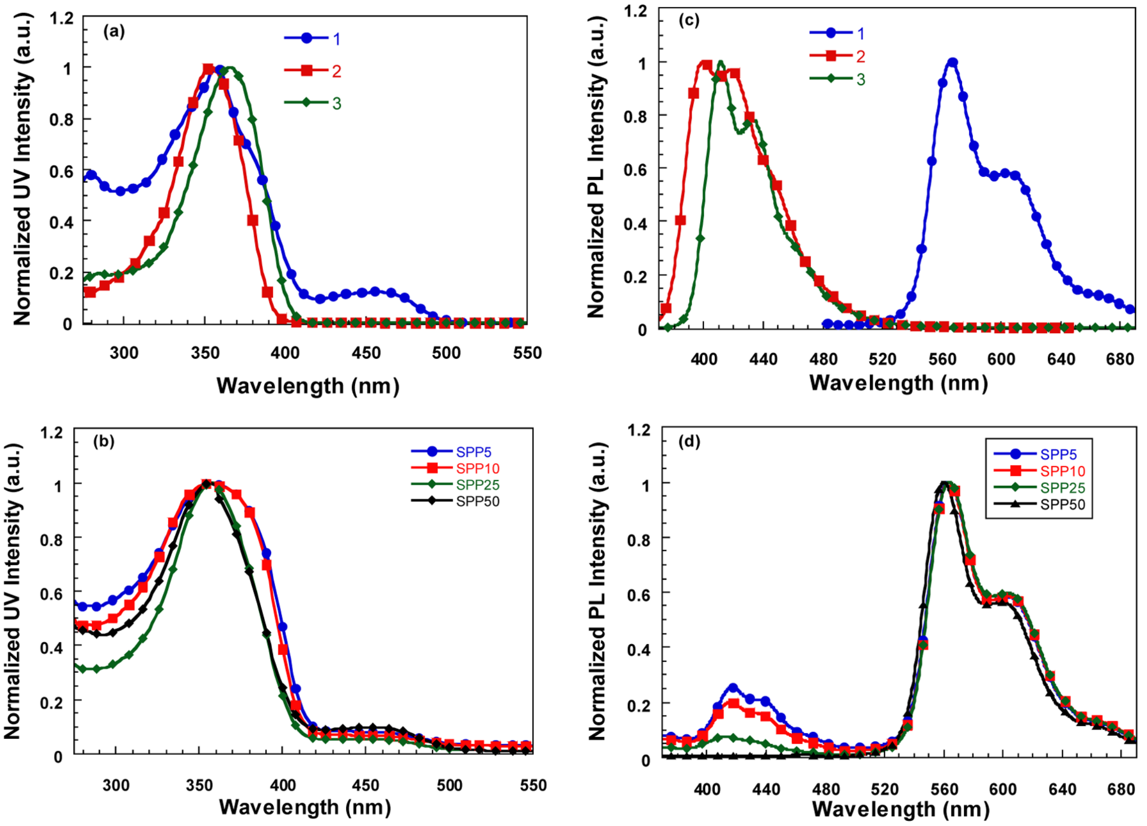


Figure 4. Normalized UV−vis absorption spectra of monomer **1**−**3** (a) in solution and (b) SPPs in neat film; normalized PL spectra of monomer **1**−**3** (c) in solution and (d) SPPs in neat film at room temperature.

Table 2. Electrochemical and Photophysical Data of Monomers 1, 2, and 3

monomer	E_{ox} (V)[a]	E_{red} (V)	HOMO (eV)	LUMO (eV)	E_g (eV)	λ_{abs} (nm)[b]	λ_{PL} (nm)[b]
1	0.85	−1.69	−5.25	−2.71	2.54	358, 454	566, 605
2	1.4	−1.75	−5.8	−2.65	3.15	355	400, 417
3	1.16	−1.88	−5.56	−2.52	3.04	365	411, 432

[a] Measured in a solution of Bu_4NPF_6 (0.1 M) in acetonitrile at a scan rate of 50 mV/s at room temperature. [b] Measured in CH_2Cl_2 solution at room temperature.

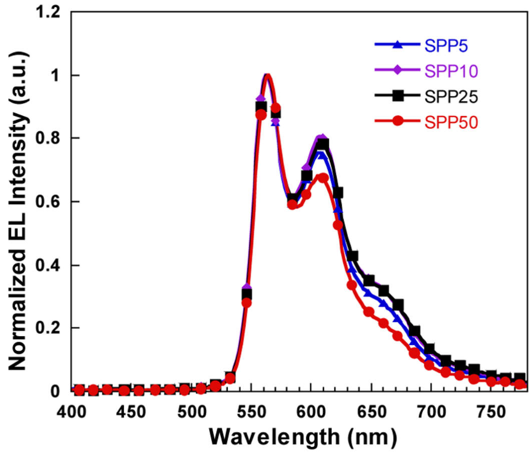


Figure 5. Electroluminescent (EL) spectra of SPP5, SPP10, SPP25, and SPP50 in the OLEDs (ITO/PEDOT/EMLs/CsF/Al).

excited at 380 nm, is 0.41, relative to a *fac*-[Ir(ppy)$_3$] standard (Φ_P = 0.9, Hppy = 2-phenylpyridine).[14] The emission lifetime (τ_p) in CH_2Cl_2 was well fitted to a single-exponential decay at room temperature and measured as 1.7 μs, which is shorter than that of [Ir(Flpy)$_3$] (2.8 μs).[20c] Accordingly, the radiative lifetime (τ_r) of the triplet excited state was 4.1 μs, deduced from $\tau_r = \tau_p/\Phi_p$. The triplet radiative and nonradiative rate constant (k_r and k_{nr}, calculated from Φ_p and τ_p, using the expressions $\Phi_p = \Phi_{ISC}[k_r/(k_r + k_{nr})]$ and $\tau_p = (k_r + k_{nr})^{-1}$, are 2.4×10^5 and 3.5×10^5 s^{-1}, respectively, assuming that the Φ_{ISC} is unity.

The PL spectra of the SPPs show a similar intense emission at 562 nm with a shoulder at 604 nm, characteristic of the iridium monomer. Nevertheless, the presence of an additional emission peak at ca. 430 nm indicates an incomplete energy transfer from the terfluorenyl to iridium units at a low iridium content (for instance, in SPP5, SPP10, and SPP25). On the other hand, the PL quantum efficiencies (Φ_{PL}) of the SPPs in neat film enhanced from 17% to 21% with increasing iridium content from 5 mol % to 50 mol % (Table 1). By contrast, the Φ_{PL} of the iridium monomer in neat film is 7.7%.

Electrochemical Properties. The electrochemical behaviors of monomers **1**, **2**, and **3** were studied by cyclic voltammetry in order to estimate the potential charge injection/transport properties of the SPPs (see Table 2). The iridium monomer **1** shows a reversible anodic wave at 0.85 V vs SCE, attributed to the oxidation of the iridium(III). The onset

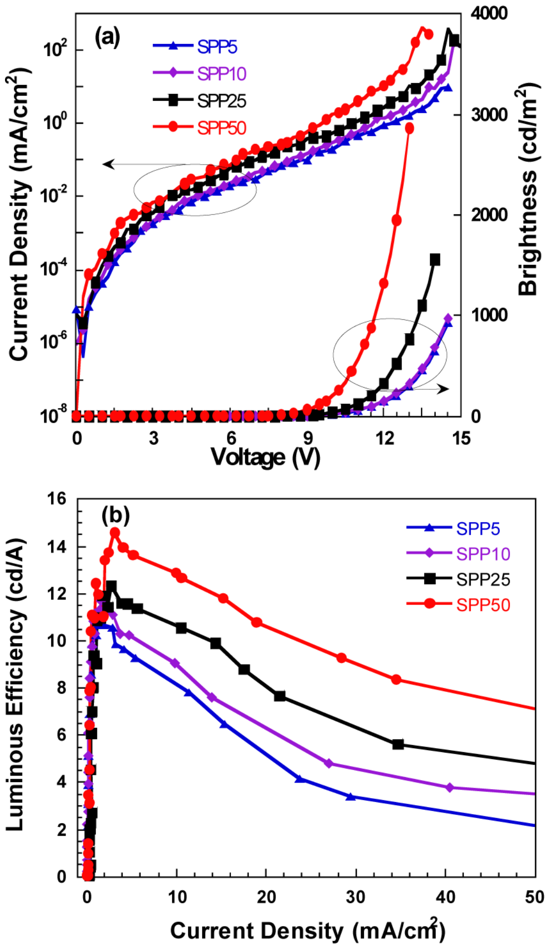


Figure 6. (a) Current density (J) and brightness (L) versus voltage (V) characteristics (J−L−V) and (b) luminous efficiency−current density−luminance (LE−J−L) characteristics of SPP5, SPP10, SPP25, and SPP50 in the devices with configuration of ITO/PEDOT:PSS/EMLs/CsF/Al).

of irreversible reduction potential located at −1.69 V, while the reduction occurs primarily on the ligands. On the basis of the redox data and the formulas of $E_{\mathrm{HOMO}} = -(E_{\mathrm{ox}} + 4.4)$ eV, $E_{\mathrm{LUMO}} = -(E_{\mathrm{red}} + 4.4)$ eV, and $E_{\mathrm{LUMO}} = E_{\mathrm{HOMO}} + E_g$,[21] the E_{HOMO} and E_{LUMO} values of monomer **1** are calculated as −5.25 and −2.71 eV, respectively. The reversible oxidation waves of **2** and **3** were observed at 1.4 and 1.16 V, respectively, corresponding to E_{HOMO} values of −5.8 and −5.56 eV. Based on their absorption onset, $E_{\mathrm{LUMO}} = -2.65$ eV for **2** and −2.52 eV for **3**. Thus, the iridium monomer shows a substantially higher HOMO level by 0.3−0.55 eV than monomers **2** and **3**, implying that the iridium unit in the SPPs could be a strong hole trap in OLEDs.

Electroluminescent Devices. As a first attempt, we introduce the SPPs into OLEDs as a phosphorescent emitter (ITO/PEDOT:PSS/SPPs(70 wt %) + PBD(30 wt %)/CsF/Al). Poly(3,4-ethylenedioxythiophene) poly(styrene sulfonate) (PEDOT:PSS) was used as a hole-injection layer. The electron-transporting/hole-blocking material 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) was blended with the SPPs in order to balance electron/hole injection in the emitting layer. A vacuum-deposited cesium fluoride (CsF) layer was used as an electron-injection layer.

The EL spectra of the SPPs are identical with a maximal emission peak at 562 nm and a shoulder at 605 nm, arising from the iridium monomer (Figure 5). Relative to PL spectra, the EL emission from monomers **2** and **3** is completely quenched with the iridium content as low as 5 mol % in the supramolecular polymer. The substantial difference of energy transfer efficiencies between PL and EL spectra of the SPPs implies that different mechanisms are involved.[22] Under photoexcitation, the singlet excited states are created on monomers **2** and **3** and then transferred to the iridium monomer by Förster energy transfer.[23] In contrast, under electrical excitation, charge trapping is considered as dominant, since the iridium monomer is a more efficient hole trap, as indicated by the electrochemical experiments.[24] Consequently, holes and electrons are likely to recombine directly on the iridium unit, leading to pure electrophosphorescent emission.

Moreover, the highly efficient PHOLEDs were almost all obtained when the guest is doped into the host materials with a low concentration (usually lower than 10 wt %), because of the concentration quenching and triplet−triplet (T-T) annihilation of the guest, which leads to lower efficiency when the concentration of the guest is too high.[25] In contrast, it was found that the EL performances of the SPPs seem to improve as the iridium complex content in the active layer blend increases from ca. 4 wt % to 39 wt % (see Figure 6 and Table 3). For instance, the device that contained SPP50 showed a lowest turn-on voltage of 6.6 V (defined at a luminance of 1 cd m^{-2}) and a highest luminous efficiency (LE) of 14.6 cd A^{-1} at a luminance of 450 cd m^{-2}, corresponding to an external efficiency of 6.9%. At a current density of 20 mA cm^{-2}, LE remained at 10.8 cd A^{-1}. This observation further suggests that the incorporated "iridium monomer" in the SPPs efficiently traps hole charges and thereby serves as hole carriers. It is also worthy of note that the present supramolecular polymer structure considerably shields the iridium luminescent centers from concentration quenching.

■ CONCLUSIONS

In summary, we have developed the first supramolecular phosphorescent polymers (SPPs) for organic light-emitting diodes. These SPPs are formed through efficient nonbonding interactions between designed small-molecule monomers. It

Table 3. EL Performances of SPP5, SPP10, SPP25, and SPP50

SPP	dopant (wt %)^a	λ_{EL} (nm)	turn-on voltage, $V_{\text{turn-on}}$ (V)^b	maximum external quantum efficiency, EQE (%)	maximum luminous efficiency, LE$_{\max}$ (cd A^{-1})	maximum brightness, $L_{\max}$ (cd m^{-2})^c
SPP5	4	563, 608	7.8	5.4	10.7	936 (270)
SPP10	8	563, 608	7.7	6.1	11.7	967 (187)
SPP25	20	563, 608	7.7	6.5	12.3	1556 (330)
SPP50	39	563, 608	6.6	6.9	14.6	2863 (450)

^{a}Weight ratio of monomer **1** in the active layer blend. ^{b}Turn-on voltage at a brightness of 1 cd m^{-2}. ^{c}Data in parentheses were recorded at LE$_{\max}$.

was shown that incorporation of an iridium monomer can afford promising electroluminescent (EL) properties. Furthermore, the high photoluminescence (PL) and EL efficiencies of the SPP with 50 mol % contents indicate that this type of self-assembly process may afford a new class of high-performance solution-processable EL emitters.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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