

Supplementary Information

Synthesis and Properties of Hyperbranched Polymers for Sun Light-Style White Polymer Light Emitting Devices

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Table S1. Electrochemical properties of the hyperbranched polymers.

Section S1. General Experimental Information

Materials and Characterization

In this work, 9,9-Dioctylfluorene-2,7-bis(trimethyleneboronate) (**M2**, 99.5%) was purchased from Synwitech. 2-(4-Bromophenyl)-1H-imidazole (BrPI) was purchased from Energy Chemical. Tetrahydrofuran (THF) and toluene were distilled using standard procedures. Other solvents were used without further purification unless otherwise specified. All reactions were carried out using Schlenk techniques under dry nitrogen atmosphere. ^1H NMR and ^{13}C NMR spectra were measured using a Bruker DRX 600 spectrometer, and chemical shifts were reported in ppm using tetramethylsilane as an internal standard. Elemental analysis (EA) was performed with a Vario EL elemental analyzer. Molecular weights and polydispersities of the copolymers were determined using gel permeation chromatography (GPC) on an HP1100 high performance liquid chromatograph (HPLC) system equipped with a 410 differential refractometer, and a refractive index (RI) detector, with polystyrenes as the standard and THF as the eluent at a flow rate of 1.0 mL/min at 30 °C. The UV-visible absorption spectra were determined on a Hitachi U-3900 spectrophotometer and the PL emission spectra were obtained using a Horiba FluoroMax-4 spectrophotometer at room temperature. The PL lifetime of the hyperbranched porous polymers was measured by Edinburgh Instrument FLS980 spectrometer equipped with an EPL-375 picosecond pulsed diode laser in the 10^{-5} mol/L CH_2Cl_2 solution at

room temperature. Thermogravimetric analysis (TGA) of the copolymers was conducted by a Setaram thermogravimetric analyzer at a heating rate of 10 °C/min under nitrogen atmosphere. Differential scanning calorimetry (DSC) measurements were performed at both heating and cooling rates of 5 °C/min under nitrogen atmosphere, using DSC Q100 V9.4 Build 287 apparatus. Powder X-ray diffraction measurements were performed by a Bruker X-ray diffractometer. Atomic force microscopy (AFM) measurements were performed using an SPA-300HV from Digital Instruments Inc. (Santa Barbara, CA) at a tapping mode. Cyclic voltammetry (CV) measurements were performed on an Autolab/PG STAT302 electrochemical workstation with the thin film of the hyperbranched porous polymers on the working electrode in a solution of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6 , 0.1 M) in acetonitrile (CH_3CN) at a scanning rate of 50 mV/s at room temperature under nitrogen atmosphere. A Pt plate was used as the counter electrode, and a saturated calomel electrode was used as the reference electrode.

Section S2. Device Fabrication and Characterization

Patterned glass substrates coated with indium tin oxide (ITO) ($20 \Omega \text{ square}^{-1}$) were cleaned by a surfactant scrub, washed successively with deionized water, acetone and isopropanol in an ultrasonic bath, and then dried at 120 °C in a heating chamber for 2 h. A 40-nm-thick poly(3,4-ethylenedioxythiophene) : poly(styrenesulfonic acid) (PEDOT:PSS) hole injection layer was spin-coated on top of ITO and baked at 120 °C for 20 min. Thin films (50 nm thick) of the hyperbranched porous polymers as light-emitting layer were deposited on top of the PEDOT:PSS layer by spin-coating the chlorobenzene solution of the hyperbranched porous polymers, followed by thermal annealing at 110 °C for 20 min. Then an electron-transporting layer of 1,3,5-tris(N-phenylbenzimidazol-2-yl)benzene (TPBi, 35 nm), an electron injection layer of LiF (1 nm), and a cathode layer of Al (150 nm) were deposited by vacuum evaporation under a base pressure of $5 \times 10^{-4} \text{ Pa}$. The EL spectra and CIE coordinates were measured with a PR-655 spectra colorimeter. The current-voltage-forward luminance curves were measured using a Keithley 2400 source meter and a BM-7A luminance meter.

Section S3. Preparation of the Monomers

9-(6-bromine hexyl)carbazole (BrhCz)²⁻⁴ (1)

The mixture of carbazole (30 mmol), 1,6-dibromo hexane (90 mmol) and adequacy tetrabutyl ammonium bromide (TBAB) in 50 mL toluene was stirred uniform and then added potassium hydroxide solution (16 mol/L) and heat to reflux for 12 h under nitrogen atmosphere. After cooled to room temperature, the mixture was extracted with water and methylene chloride (CH₂Cl₂), dried by anhydrous magnesium sulfate and then concentrated by rotary evaporation. Finally, it was purified by column chromatography on silica gel with petroleum ether: CH₂Cl₂ = 20:1 as eluent to obtain the white acicular crystal. Yield: 87%. ¹H NMR (CDCl₃) δ: 8.11 (d, *J* = 7.8 Hz, 2H), 7.47 (ddd, *J*₁ = 1.2 Hz, *J*₂ = 7.2 Hz, *J*₃ = 8.4 Hz, 2H), 7.41 (d, *J* = 7.8 Hz, 2H), 7.24 (ddd, *J*₁ = 1.2 Hz, *J*₂ = 7.2 Hz, *J*₃ = 7.8 Hz, 2H), 4.32 (t, *J* = 7.2 Hz, 2H), 3.37 (t, *J* = 6.6 Hz, 2H), 1.93-1.88 (m, 2H), 1.84-1.79 (m, 2H), 1.50-1.45 (m, 2H), 1.43-1.38 (m, 2H). HR-MS: Calcd.329.0799; Found 329.0803.

2-(4-Bromophenyl)-1-[6-(9-carbazolyl)hexyl]-imidazole (CzhBrPI) (2)

Under nitrogen atmosphere, the mixture of BrCz (4 mmol), BrPI (5mmol) and Toluene (30 mL) was stirred uniform and then of potassium hydroxide solution (2 mol/L) was added and appropriate TBAB to react for 30 min at room temperature. The reaction solution was cooled to room temperature and extracted with water and methylene chloride (CH₂Cl₂), dried by anhydrous magnesium sulfate and then concentrated by rotary evaporation after it was heated to reflux for 24 h. Finally, it was purified by column chromatography on silica gel with ethyl ether: CH₂Cl₂ = 4:1 as eluent to obtain the light yellow powder. Yield: 76%. ¹H NMR (CDCl₃) δ: 8.10 (d, *J* = 7.8 Hz, 2H), 7.63 (ddd, *J*₁ = 2.4 Hz, *J*₂ = 4.2 Hz, *J*₃ = 9.0 Hz, 2H), 7.54 (ddd, *J*₁ = 2.4 Hz, *J*₂ = 4.2 Hz, *J*₃ = 9.0 Hz, 2H), 7.45 (ddd, *J*₁ = 1.2 Hz, *J*₂ = 7.2 Hz, *J*₃ = 8.4 Hz, 2H), 7.34 (d, *J* = 7.8 Hz, 2H), 7.30 (dd, *J*₁ = 2.4 Hz, *J*₂ = 7.2 Hz, 2H), 7.23 (dd, *J*₁ = 0.6 Hz, *J*₂ = 7.8 Hz, 2H), 4.25 (t, *J* = 7.2 Hz, 2H), 4.14 (t, *J* = 7.2 Hz, 2H), 1.84~1.79 (m, 2H), 1.75~1.70 (m, 2H), 1.32~1.25 (m, 2H), 1.24~1.19 (m, 2H).

2-(5-(4-fluorinated phenyl)-1,3,4-triazole)pyridine (fpptz) (3)

Under nitrogen atmosphere, the mixture of 2-cyanopyridine (50 mmol), hydrazine

hydrate (50 mmol) and ethanol (25 mL) was reacted for 8 h at low temperature to produce viscous light yellow paste and cooled to room temperature. The redundant ethanol was removed in vacuum. The obtained solid was washed by a small quantity of diethyl ether, suction filtered and dried for 3 h to obtain white crystal (2-pyridine)amidrazone.

Under nitrogen atmosphere, the mixture of (2-pyridine)amidrazone (30 mmol), Na_2CO_3 (30 mmol), 2-Fluorobenzoyl chloride (30 mmol) and THF (30 mL) were reacted for 6 h and filter. The filter mass was heated to elevated temperature for 30 min in 30 ml ethylene glycol to dehydrate, dried for 8 h under vacuum. Then it was recrystallized by ethanol to obtain the white acicular crystal. Yield 92%. ^1H NMR (DMSO-d_6) δ : 14.87 (s, 1H), 8.74 (d, $J = 4.8$ Hz, 1H), 8.18 (d, $J = 7.8$ Hz, 1H), 8.15-8.11 (d, $J = 7.8$ Hz, 2H), 8.04 (dt, $J_1 = 1.2$ Hz, $J_2 = 7.2$ Hz, 1H), 7.57 (ddd, $J_1 = 0.6$ Hz, $J_2 = 4.8$ Hz, $J_3 = 5.4$ Hz, 1H), 7.34 (t, $J = 9.0$ Hz, 2H).

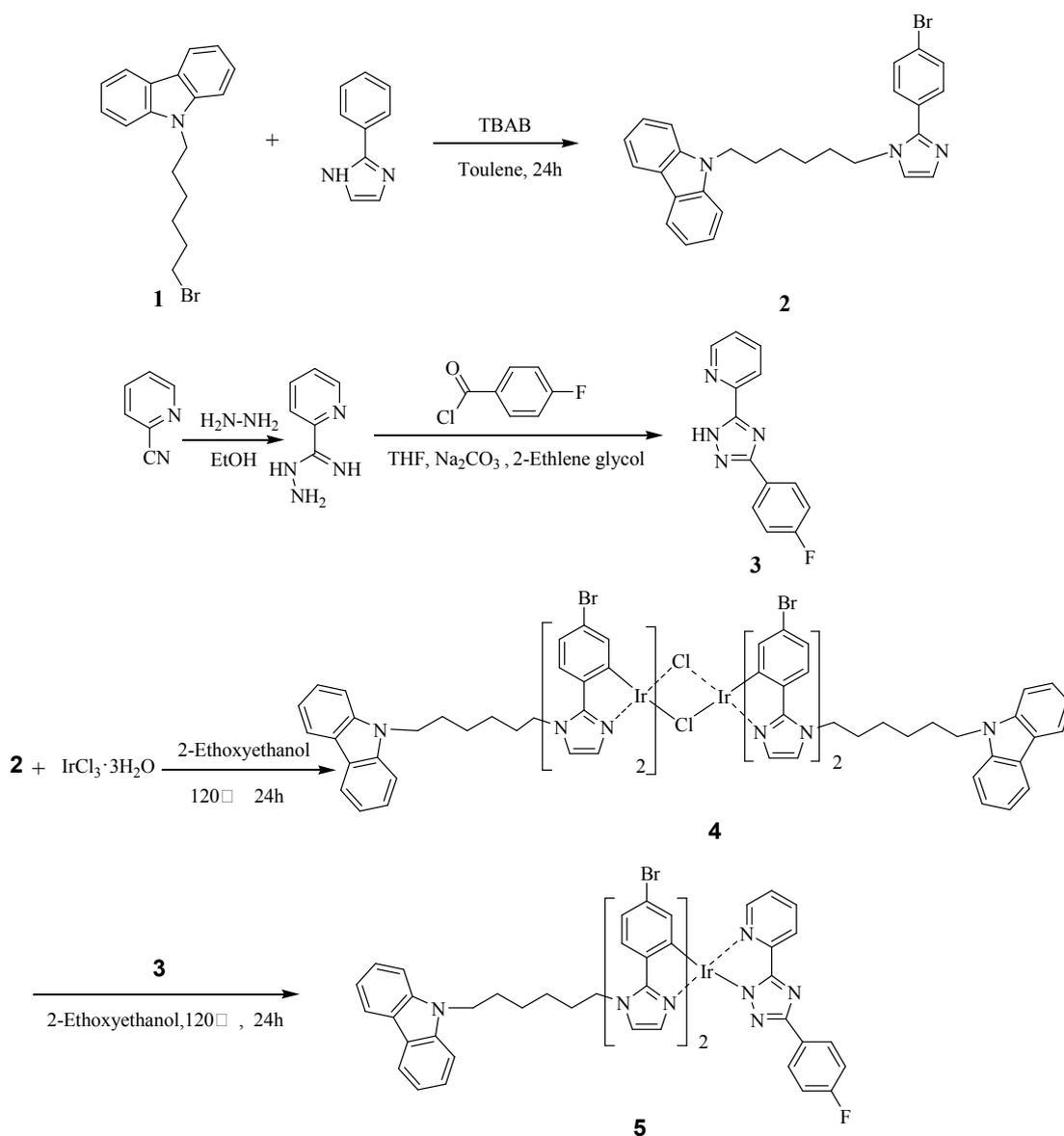
2-(4-Bromophenyl)-1-[6-(9-carbazolyl)hexyl]-imidazole chloro-bridge iridium dimers $[(\text{CzhBrPI})_2\text{Ir}(\mu\text{-Cl})_2\text{Ir}(\text{CzhBrPI})_2]$ (4)

The mixture trihydrate trichloride iridium ($\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$) (0.1 mmol) in 2-ethoxyethanol (24 mL) and deionized water (8 mL) and 2-(4-Bromophenyl)-1-[6-(9-carbazolyl)hexyl]-imidazole (0.25 mmol) was heated to reflux for 24 h under nitrogen atmosphere. After cooling to room temperature, the deionized water (200 mL) was poured into the reaction solution to separate out atrovirens flocculent solid, filtered and washed with deionized water and ethanol. The crude product was dried for 12 h at 45 °C under vacuum to obtain the green solid.

2.3.6 $(\text{CzhBrPI})_2\text{Ir}(\text{fpptz})$ (5)

The solution of the chloro-bridged iridium (0.1 mmol) in 2-ethoxyethanol (25 mL), the 2-(5-(4-fluorinated phenyl)-1,3,4-triazole)pyridine (0.25 mmol) and anhydrous potassium carbonate (2.0 mmol) were stirred at 100 °C for 24 h under nitrogen atmosphere. After cooling to room temperature, Deionized water was added to separate out green flocculent solid, and then purified by column chromatography on silica gel with petroleum ether : $\text{CH}_2\text{Cl}_2 = 10:1$ as eluent to obtain the green solid

power. Yield: 70%. $^1\text{H NMR}$ (CDCl_3) δ : 8.15 (dd, $J_1 = 3.0$ Hz, $J_2 = 6.6$ Hz, 1H), 8.10 (ddd, $J_1 = 4.2$ Hz, $J_2 = 7.8$ Hz, $J_3 = 11.4$ Hz, 4H), 7.82 (ddd, $J_1 = 5.4$ Hz, $J_2 = 9.6$ Hz, $J_3 = 36$ Hz, 1H), 7.71-7.61 (m, 2H), 7.49-7.40 (m, 4H), 7.36-7.29 (m, 4H), 7.23 (dt, $J_1 = J_2 = 6.6$ Hz, $J_3 = 13.2$ Hz, 4H), 7.17 (dd, $J_1 = 7.8$ Hz, $J_2 = 13.8$ Hz, 2H), 7.12 (t, $J = 7.8$ Hz, 1H), 7.06 (ddd, $J_1 = 2.4$ Hz, $J_2 = 11.4$ Hz, $J_3 = 13.2$ Hz, 1H), 7.01-6.88 (m, 4H), 6.80 (t, $J = 7.2$ Hz, 1H), 6.68 (dd, $J_1 = 7.2$ Hz, $J_2 = 14.4$ Hz, 1H), 6.44 (dd, $J_1 = 7.8$ Hz, $J_2 = 16.2$ Hz, 1H), 6.37 (dd, $J_1 = 9.6$ Hz, $J_2 = 18.0$ Hz, 1H), 6.33 (dd, $J_1 = 4.2$ Hz, $J_2 = 12.0$ Hz, 1H), 5.77 (ddd, $J_1 = 7.8$ Hz, $J_2 = 12.0$ Hz, $J_3 = 19.8$ Hz, 1H), 4.66~4.44 (m, 4H), 4.31~4.18 (m, 4H), 2.04-1.79 (m, 8H), 1.43~1.35 (m, 8H).



Scheme S1. Synthesis of the green light emitting group $(\text{CzhBrPI})_2\text{Ir}(\text{fpptz})$.

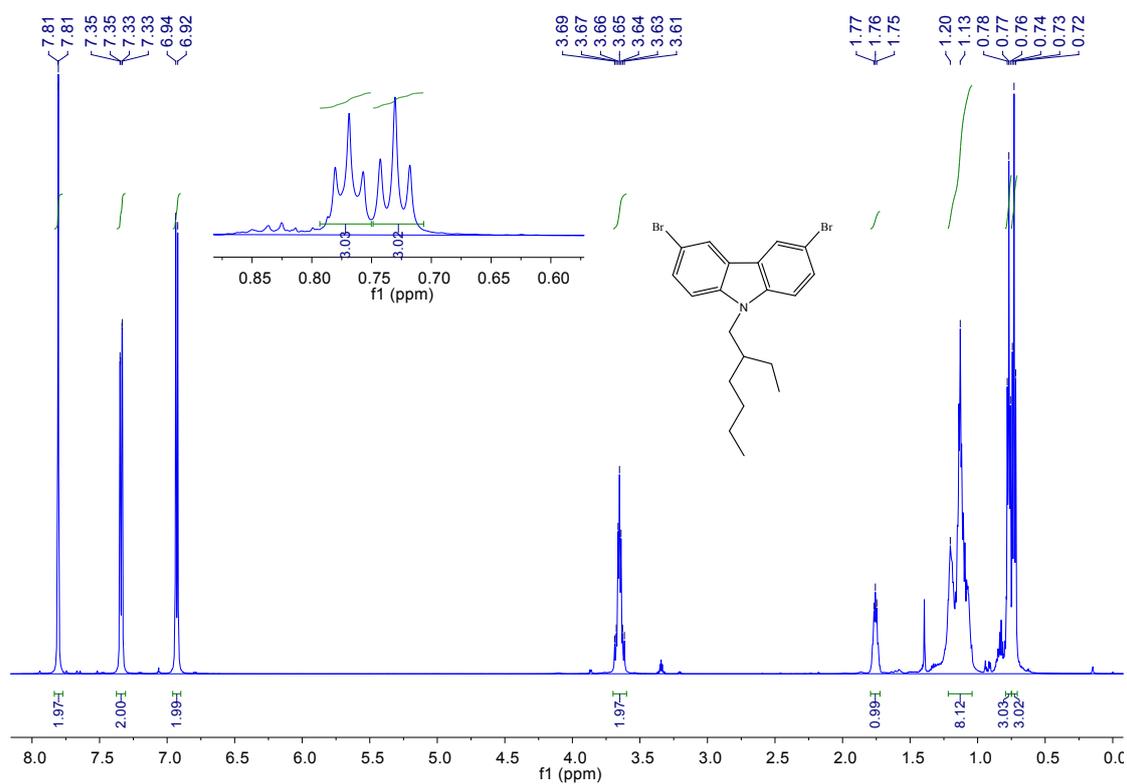


Figure S1. ^1H NMR spectrum of DBrCz.

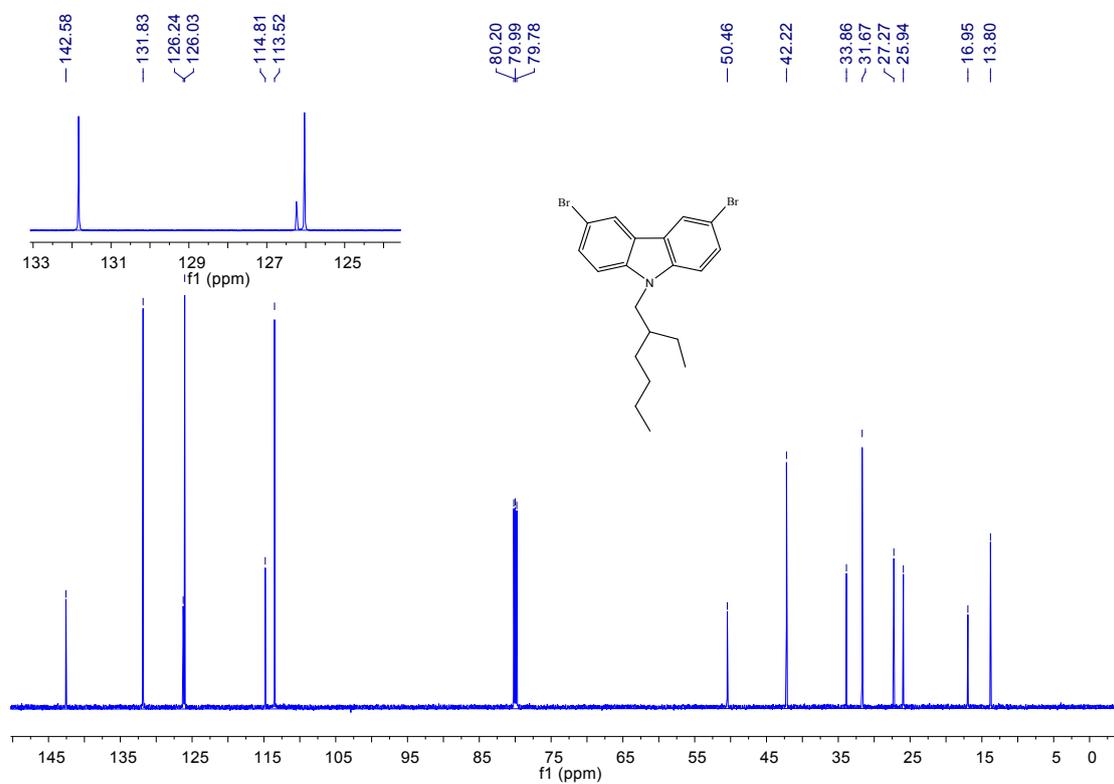


Figure S2. ^{13}C NMR spectrum of DBrCz.

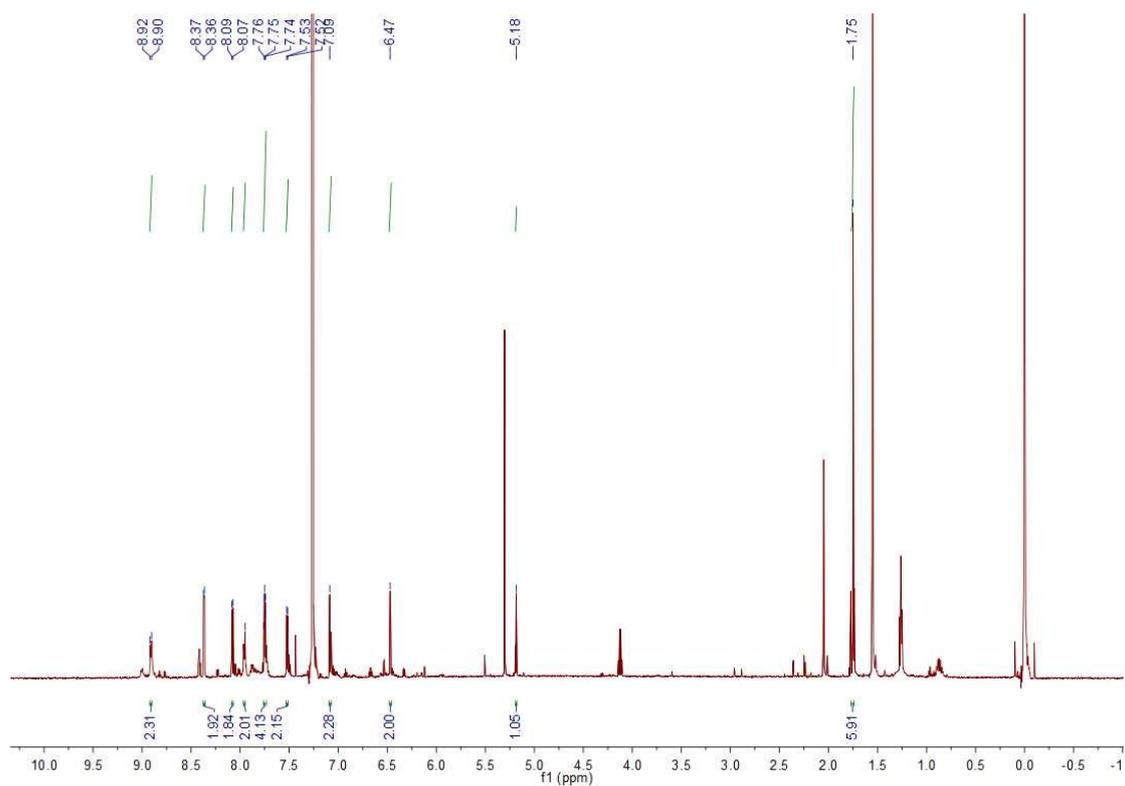


Figure S3. ^1H NMR spectrum of $\text{Ir}(\text{Brpiq})_2\text{acac}$.

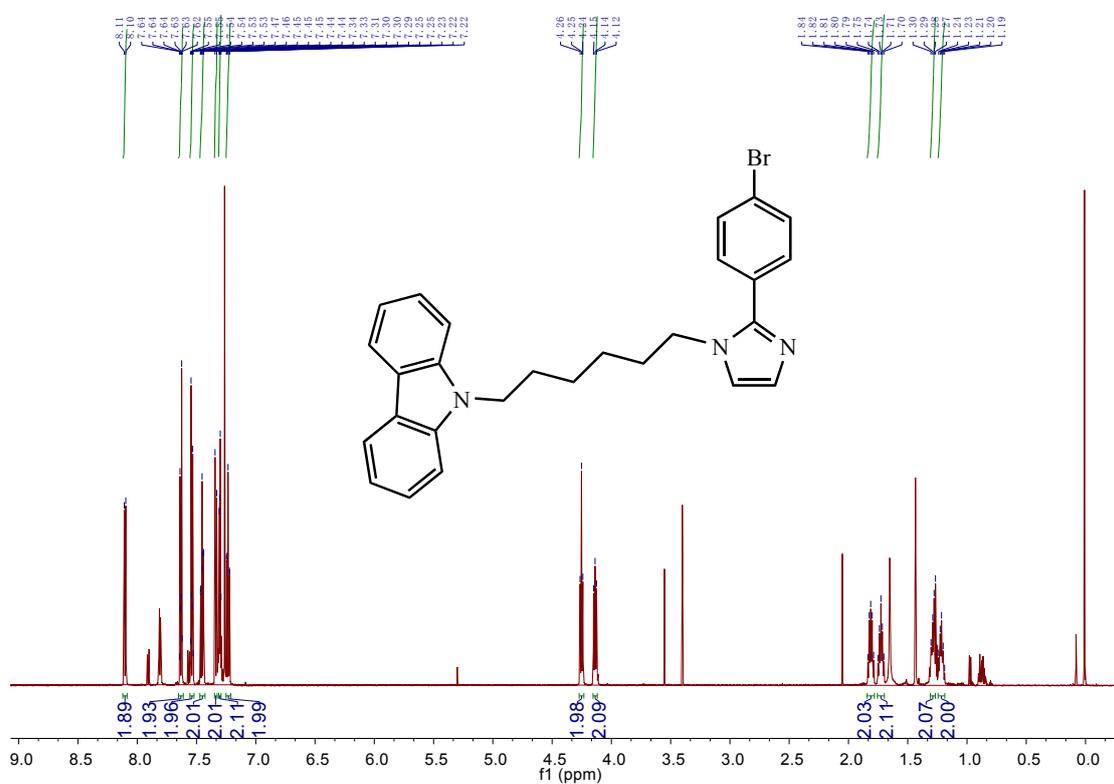
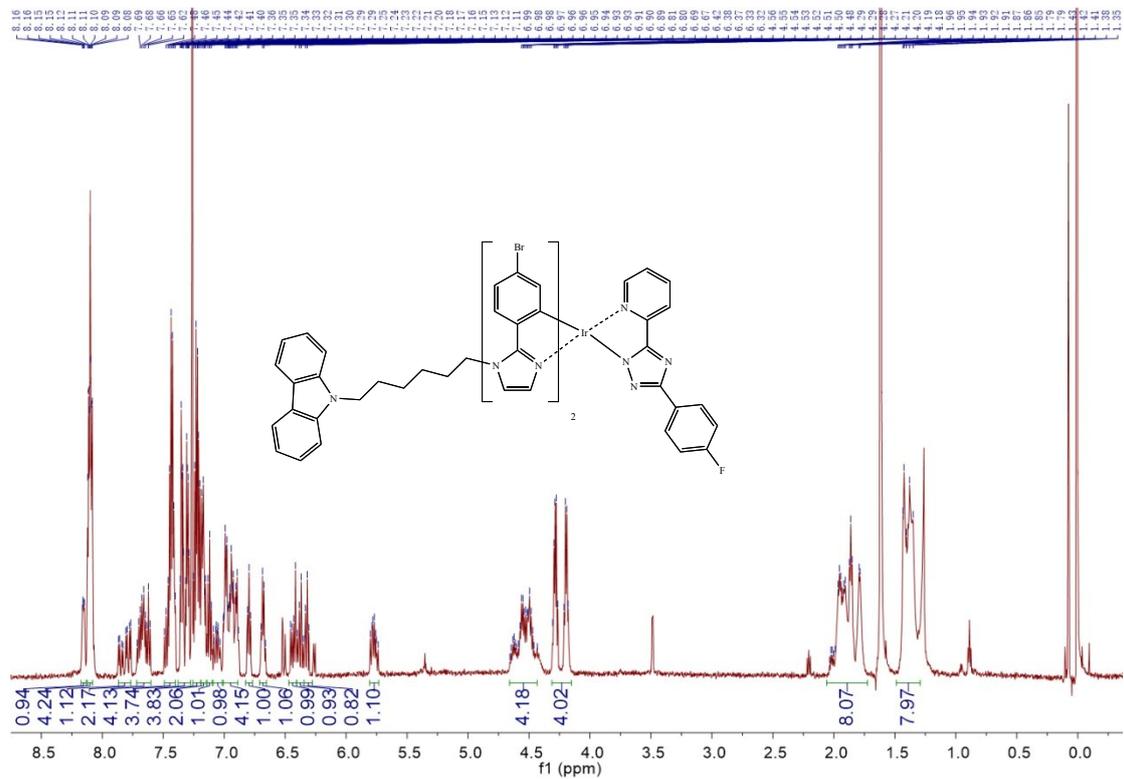


Figure S4. ^1H NMR spectrum of CzhBrPI .



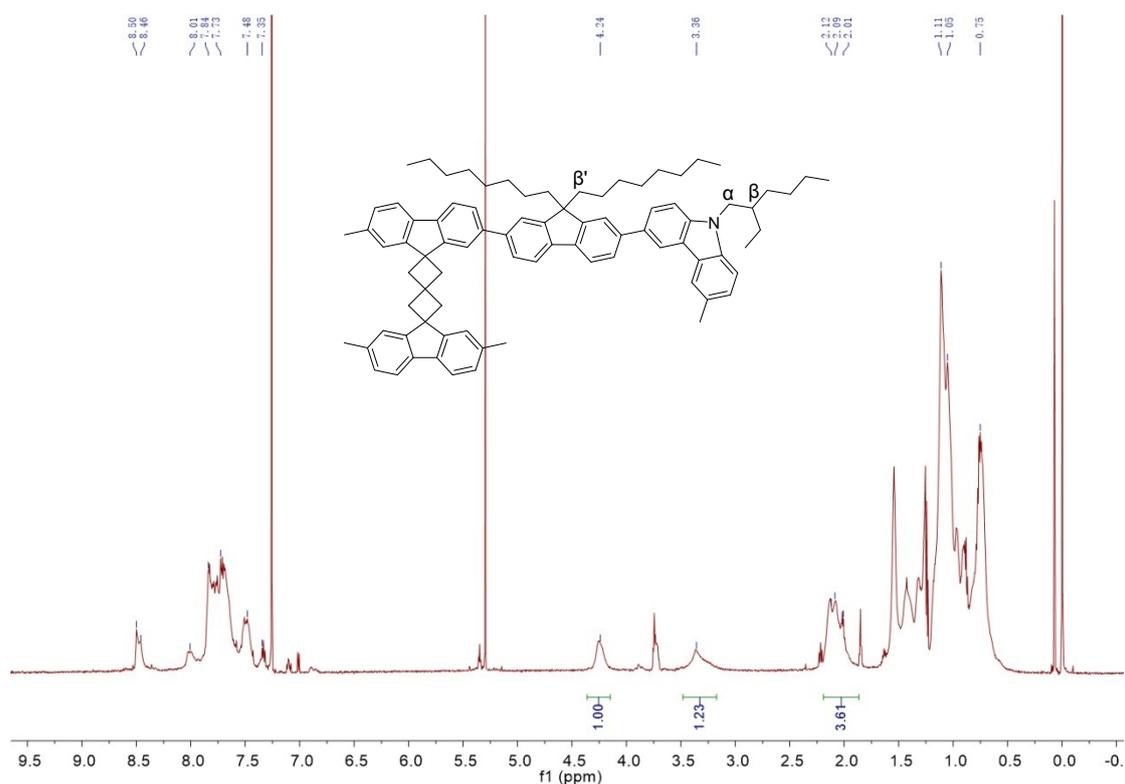


Figure S7. ^1H NMR spectra of **PFCzSDF10R8G24**.

Section S4. Electroluminescent properties

In the preliminary work, we synthesized a series of hyperbranched polymers with fluorene-carbazole as the main chain and red light emitting group **Ir(Brpiq)₂acac** as adjust light emitting unit. It is named **PFCzSDF10Ir6**, **PFCzSDF10Ir7**, **PFCzSDF10Ir8** and **PFCzSDF10Ir9** based on the amount of red light group **Ir(Brpiq)₂acac** of 0.06 mol%, 0.07 mol%, 0.08 mol% and 0.09 mol%, respectively. It can be seen from the EL spectra in Figure S8 that the feed ratios of 0.08 mol% is the optimum proportion of red light added to achieve white-light emission.

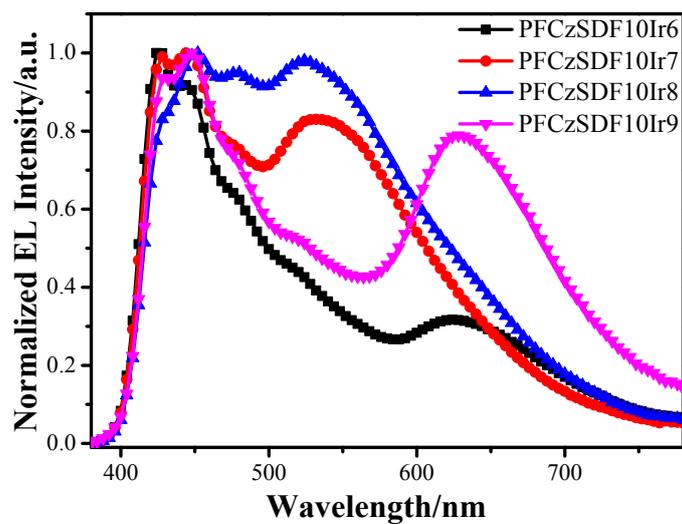


Figure S8. EL spectra of the copolymer PLEDs at 14 V.

Section S5. Fluorescence Lifetime

Figure S9 shows the PL lifetime decay curve of the hyperbranched polymers at room temperature. The four hyperbranched polymers demonstrated the same fluorescence lifetime at 6.5 ns because of their similar main structure, only put up slightly shortened gradually with the increasing of green phosphor. This is owing to energy transfer from blue light fluorescent group **PFCz** to green light phosphorescent group **(CzhBrPI)₂Ir(fpptz)**. But phosphorescent complexes play an important role in enhancing fluorescence intensity and fluorescence life.

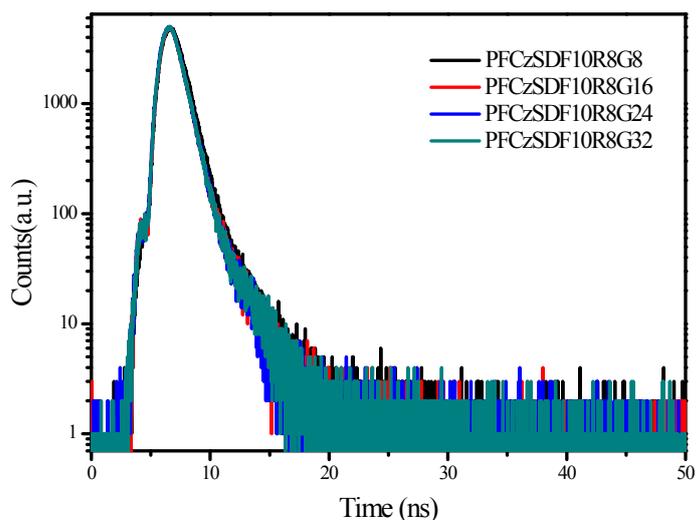


Figure S9. Time-resolved fluorescence spectra of the polymers $\lambda_{ex} = 375$ nm.

Section S6. Electrochemical characteristics

The electrochemical behaviors of the resulting hyperbranched polymers were investigated by cyclic voltammetry (CV), as shown in Figure S10 and Table 1. The oxidation potentials (E_{ox}) vary slightly from 0.80 to 0.87 V. The HOMO levels of polymers are calculated according to the empirical formulas $E_{HOMO} = -(E_{ox} + 4.5)$ (eV)⁵. The LUMO levels are deduced from the HOMO levels and the optical band gaps (E_g) determined from the onset value of the absorption spectrum in film in the long-wavelength direction ($E_g = 1240/\lambda_{edge}$). The HOMO levels of the hyperbranched polymers are at about -5.30 eV, which are relatively close to the work function of PEDOT (-5.2 eV) and thus facile hole injection into the emission layer (EML) can be expected⁶. On the other hand, the LUMO levels of the hyperbranched polymers (from -2.30 eV to -2.40 eV) are awfully approach to the work function of LiF/Al (-2.9 eV), indicating that the barrier for electron injection is reduced. The results demonstrate that the incorporation of the green group **(CzhBrPI)₂Ir(fpptz)** into the backbone could effectively lower the LUMO level and increases the electro-transporting ability of the materials, and at the same time, the hole-transporting ability is unaffected.

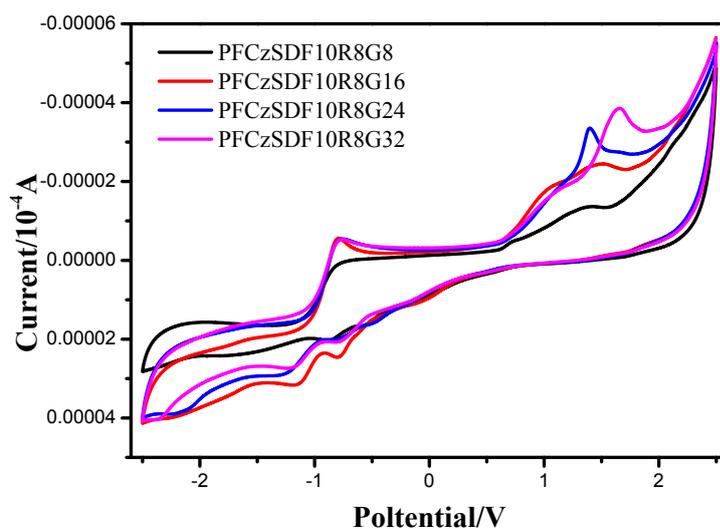


Figure S10. Cyclic voltammograms of the hyperbranched polymers.

Table S1. Electrochemical properties of the hyperbranched polymers

Copolymers	$\lambda_{\text{abs}}(\text{onset})$ (nm)	E_{g} (eV)	$E_{\text{onset/OX}}$ (V)	HOMO (eV)	LUMO (eV)
PFCzSDF10R8G8	418	2.97	0.87	-5.37	-2.40
PFCzSDF10R8G16	415	2.99	0.80	-5.30	-2.31
PFCzSDF10R8G24	416	2.98	0.81	-5.31	-2.33
PFCzSDF10R8G32	414	3.00	0.80	-5.30	-2.30

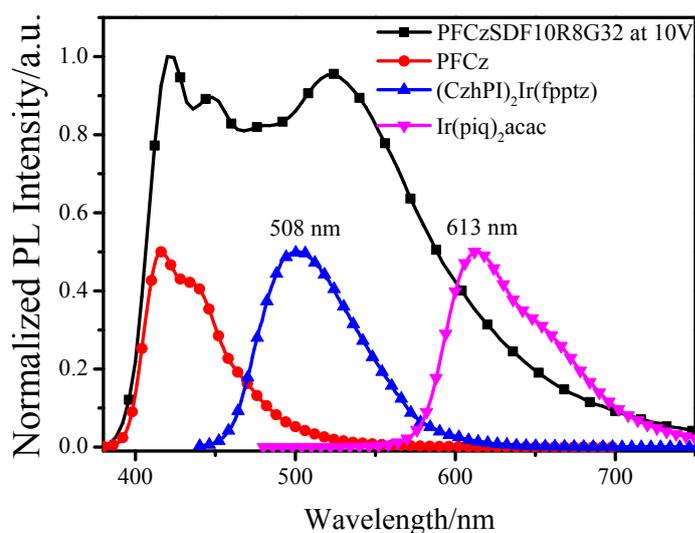


Figure S11. Electroluminescence spectra of the hyperbranched polymers

PFCzSDF10R8G32 PLEDs at 10 V and PL spectra of PFCz, (CzhPI)₂Ir(fpptz) and Ir(piq)₂acac in CHCl₃ solution (10⁻⁵ M).

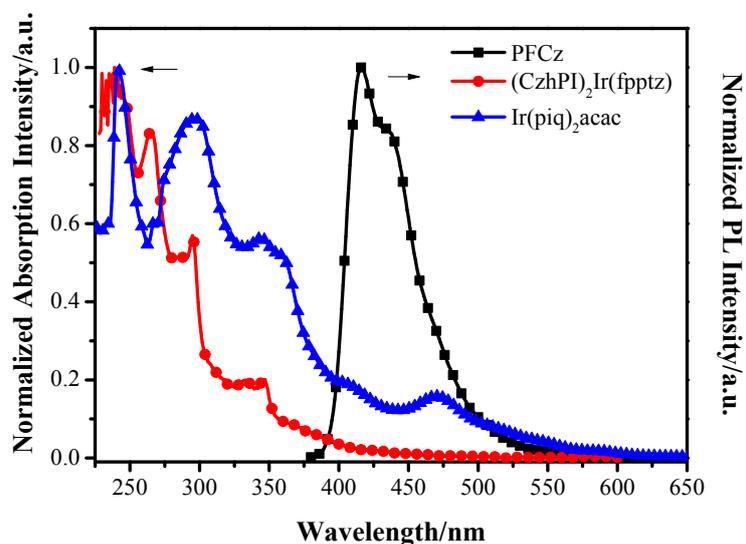


Figure S12. PL spectra of PFCz and UV-vis spectra of (CzhPI)₂Ir(fpptz) and Ir(piq)₂acac in CHCl₃ solution (10⁻⁵ M).

References and Notes

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