## **Supporting Information**

# Controllable Supramolecular Chain Aggregation through Nano-steric Hindrance Functionalization for Multi-color Larger-area Electroluminescence

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### **Experimental Section.**

**Chemicals:** 2,7-dibromo-9-fluorenone, 2,2'-bipyridine, n-octyl bromide, 1,5-cyclooctadiene (COD), bis(1,5-cyclooctadiene)nickel(0) (Ni(COD)<sub>2</sub>), hydrazine hydrate, alumina (Al<sub>2</sub>O<sub>3</sub>), and all solvents were purchased from Aldrich or Adamas Chemicals without further purification. Tetrahydrofuran (THF) was dried over sodium benzophenoneketyl anion radical and distilled under a dry nitrogen atmosphere immediately prior to use. Dimethylformamide (DMF) was dried over calcium hydride (CaH) and distilled under a dry nitrogen atmosphere immediately prior to use. Toluene was dried over Na and distilled under a dry nitrogen atmosphere immediately prior to use. The other solvents were distilled under a dry nitrogen atmosphere immediately prior to use. Anhydrous chloroform was pre-dried over molecular sieves.

#### **Characterization:**

<sup>1</sup>H-NMR were recorded on a Bruker 400 MHz spectrometer in CDCl<sub>3</sub>with tetramethylsilane (TMS) as the interval standard. Mass spectra were recorded on a Shimadzu GCMS 2010 PLUS. Gel permeation chromatography (GPC) analysis was performed on a HP1100 HPLC system equipped with 7911GP-502 and GP NXC columns using polystyrenes as the standard andtetrahydrofuran (THF) as the eluent at a flow rate of 1.0 mL/min at 25 °C. Absorption spectra were measured with a Shimadzu UV-3600 spectrometer at 25 °C, and Photoluminescence emission spectra were recorded on a Shimadzu RF-5301(PC) luminescence spectrometer. DSC measurement was acquired using aShimadzu Instruments DSC-60A. DSCdata were collected from 50 to 250 °C at a rate of 10 °C/min for both of the baseline and sample. Cyclic voltammetric (CV) studies were conducted using an CHI660C Electrochemical Workstation in a typical three-electrode cell with a platinum sheet working electrode, a platinum wire counter electrode, and a silver/silver nitrate (Ag/Ag<sup>+</sup>) reference electrode. All electrochemical experiments were carried out under a nitrogen atmosphere at room temperature in an electrolyte solution of 0.1 M tetrabutylammonium hexafluorophosphate (*n*-Bu<sub>4</sub>NPF<sub>6</sub>) in Acetonitrile (CH<sub>3</sub>CN) at a sweeping rate of 0.05 V/s. According to the redox onset potentials of the CV measurements, the HOMO/LUMO energy levels of the materials are estimated based on the reference energy level of ferrocene (4.8 eV below the vacuum): HOMO/LUMO =  $-[E_{onset} - E_{(Fc/Fc+)} + 4.8]$  eV. The corresponding film thicknesses were measured using a Bruker Dektak XT stylus profiler. The samples were then examined with a field emission SEM (Hitachi, S-4800) at an accelerating voltage of 5 kV.

**Preparation of polymer spin-coated films for analyzing in this work:** Pristine polymer films were spin-coated on quartz substrates from its CHCl<sub>3</sub> solution (6 mg/ml) using KW-4A (from the institute of micro-electronics of Chinese Academy of Science) at 1500 rpm/min for 30 s.

**Preparation of polymer nanospheres and nanowires for analyzing in this work:** 12  $\mu$ L of a fresh DMF solution (typically 0.001 and 5 mg/mL) was dropped onto the Si and quartzes. And the substrates with the DMF solution are allowed overnight for solvent evaporation under an ambient environment (T: 293 K; Humidity: 20%-40% RH).

**PLEDs Device Fabrication and Characterization:** The PLEDs devices were fabricated on ITO-coated glass whose sheet resistance is 10 S/square. The ITO-glass were ultrasonic cleaned sequentially with detergent, 2-propanol, acetone, and demonized water, then dried in an oven, then treated in an ultraviolet-ozone chamber for 5 min. PEDOT: PSS was spin-coated onto the ITO-glass at a speed of 3000 rpm for 60 s annealed then at 120 °C for 20 min. Next, the polymers dissolved in CHCl<sub>3</sub> (6 mg/ml) were spin-coated on the film of PEDOT: PSS in a speed of 2000 rpm for 30 s and then transferred into the glovebox full of N<sub>2</sub> for annealing at 80 °C for 20 min. Finally, TPBi (20 nm), LiF (0.8 nm) and Al (100 nm) were deposited onto the active polymer layer successively using thermal evaporation in vacuum through a shadow mask under a base pressure of ~4 × 10 <sup>-4</sup> torr. The current-voltage luminescence characteristics of the devices were recorded using a combination of a Keithley source meter (model 2602) and a luminance meter. The EL spectra and CIE coordinates of the devices were analyzed with a spectra-scan PR655 spectrophotometer. All the devices were characterized without encapsulation, and all the measurements were carried out in the ambient condition at room temperature

(R.T.). The emission area of the devices is  $1600 \text{ mm}^2$  or  $40 \times 40 \text{ mm}^2$  as defined by the overlapping area of the ITO films and top electrodes.

**Memory Device Fabrication**: ITO-glass substrates were precleared by ultrasonication for 10 min each in deionized water, acetone, and ethanol. PPFOH-*co*-ThC60 and PPFOH was added to CHCl<sub>3</sub> to get a solution of 6 mg mL<sup>-1</sup>, which was spin coated onto the ITO-glass substrate to form the planar switching layer in N<sub>2</sub> filled glove box. Then the PPFOH-*co*-ThC60 or PPFOH coated substrate was transferred to a hot plate at 80 °C for 1 h to remove the residual solvent also in the glove box. Finally, a 70 nm thick Al TE (or anode) with a diameter of 250  $\mu$ m was thermally evaporated on the PPFOH-*co*-ThC60 or PPFOH layer using a shadow mask at 10<sup>-4</sup> Pa. The electrical characteristics of the devices were measured using a Keithley 4200A-SCS in an ambient atmosphere. A Motic PSM-1000 Microscope connecting with a charged-coupled device (CCD) camera was used to ensure the light touch between probe tip/Al electrode and monitor the dynamic changes. During the measurement, the positive bias was defined by the current flowing from the bottom (ITO) to the top (Al) electrode, and the negative bias was defined by the opposite direction.

#### Synthetic experimental procedures of our four polymer.

**Preparation of PPFOH-***co***-DF8.** Various ratios of DBrPFOH (0.38 mmol, 0.20 g, PPFOH monomer) and DBrDF8 (0.38 mmol, 0.21 g) were added to mixture of DMF (10 mL) and toluene (10 mL) solution containing Ni(COD)<sub>2</sub> (0.50 g, 1.82 mmol), 1,5-cyclooctadiene (COD) (0.24 mL, 1.82 mmol) and 2,2'-bipyridine (0.28 g, 1.82 mmol) in a 50 mL Schlenktube under argon, respectively. The reaction mixture was stirred for 96 hrs at 85 °C to obtain a dark blue solution. Then, bromobenzene was added to the solution for a final reaction. After the final product cooled to room temperature, 10 ml of THF and 1.0 mL of hytrazine hydrate were added for quenching reaction. The precipitate was separated by filtration. The solution had further purification subjected to Al<sub>2</sub>O<sub>3</sub> column chromatography eluting with THF to afford PPFOH-*co*-DF8 with the weights and total yields of (0.22 g, 78.31%). GPC:  $M_n$  of 3.11 × 10<sup>4</sup> with the PDI of 1.61. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$  (ppm): 7.89-7.31 (m, ArH), 6.92-6.75

(m, ArH), 3.91 (s, -OCH<sub>2</sub>-), 2.12 (s, -CH<sub>2</sub>-), 1.76 (s, -CH<sub>2</sub>-), 1.63 (s, -CH<sub>2</sub>-), 1.52-1.10 (m, -CH<sub>2</sub>-), 1.01-0.68 (m, -CH<sub>2</sub>- and CH<sub>3</sub>).

**Preparation of PPFOH**-*co*-**DBF**. Polymer was prepared analogously above with green powder (0.17 g, total yield of 61.07%). GPC:  $M_n$  of 3.49 × 10<sup>4</sup> with the PDI of 1.84. <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>, 298 K)  $\delta$  (ppm): 7.95-7.86 (m, ArH), 7.75-7.51 (m, ArH), 7.55-7.27 (m, ArH), 7.21-7.01 (m, ArH), 6.95-6.80 (m, ArH), 3.82 (s, -OCH<sub>2</sub>-), 1.71-1.63 (m, -CH<sub>2</sub>-), 1.45-1.25 (m, -CH<sub>2</sub>-), 0.89-0.80 (m, CH<sub>3</sub>).

**Preparation of PPFOH**-*co*-**ThC60.** Polymer was prepared analogously above with pale powder (0.125 g, total yield of 48.21%). The reaction amounts of DBrPFOH and ThC60 are about 0.38 mmol (0.20 g) and 0.10 mmol (0.134 g). For the better solubility of ThC60 in toluene, we have added more amount of toluene as solvent in our Yamamoto reaction (DMF (10 mL) and toluene (50 mL) mixed solution). GPC:  $M_n$  of 3.84 × 10<sup>4</sup> with the PDI of 1.55. The number ratio of S/O is about 0.028. <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>, 298 K)  $\delta$  (ppm): 7.95-6.52 (m, ArH), 3.89 (s, -OCH<sub>2</sub>-), 3.52 (s, -CH<sub>3</sub>), 1.89-1.52 (m, -CH<sub>2</sub>-), 1.49-1.11 (m, -CH<sub>2</sub>-), 1.00-0.75 (m, CH<sub>3</sub>).







**Figure S1.** Chemical structures and <sup>1</sup>H-NMR spectra of polymer PPFOH-*co*-DF8, PPFOH-*co*-DBF and PPFOH-*co*-ThC60.



Figure S2. GPC curves of polymer PPFOH, PPFOH-co-DF8, PPFOH-co-DBF and PPFOH-co-ThC60.



Figure S3. DSC curves of PPFOH, PPFOH-*co*-DF8, PPFOH-*co*-DBF and PPFOH-*co*-ThC60.



**Figure S4**. Thermogravimetric curves of PPFOH, PPFOH-*co*-DF8, PPFOH-*co*-DBF and PPFOH-*co*-ThC60. Heating rate was 10 K/min. under a nitrogen atmosphere.



Figure S5. CV curves of polymer PPFOH-co-DF8, PPFOH-co-DBF and PPFOH-co-ThC60.



Figure S6. Concentration-depdent PL spectra of PPFOH-co-DF8.



**Figure S7.** UV-*vis* absorption and PL spectra of the PPFOH THF solutions (0.1 mg/ml) before and after adding a small amount of MeOH.



**Figure S8**. UV-vis absorption spectra of four polymer films (a) spin-coating from CHCl<sub>3</sub> solution and nanosphere films drop-coating from DMF solution (b).



Figure S9. Current density-voltage curves of four polymer-based polymer light-emitting diodes (PLEDs).



**Figure S10**. Charge-trapped ability in PPFOH-*co*-ThC60 and PPFOH. I–V characteristics of the diode device fabricated with PPFOH (a) and PPFOH-*co*-ThC60 (b). (c) Stimulus effect of read pulse of -2 V on the ON, and OFF states.

Polymers	$M_n$	PDI	$T_g/T_d$ (°C)	$\lambda_{abs}$ (nm)	$\lambda_{em}$ (nm)	HOMO/LUMO (eV)	Φ
PPFOH	3.64×10 <sup>4</sup>	1.70	120/402	396	454, 547	-5.79/-2.58	13
PPFOH-co-DF8	3.11×10 <sup>4</sup>	1.61	118/407	384	434, 455, 530	-5.77/-2.59	30
PPFOH-co-DBF	3.49×10 <sup>4</sup>	1.84	-/447	386	435, 461, 521	-5.72/-2.60	38
PPFOH-co-ThC60	3.84×10 <sup>4</sup>	1.55	-/517	387	34, 465, 489	-5.76/-2.69	16

**Table S1.** Photophysical and Electrochemical Properties of the Polymers

<b>Table S2.</b> Summary of the Devices Performance	ce
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EML	$V_{on}^{a}(V)$	$L_{\max}^{b}$ (cd m <sup>-2</sup> )	$\eta_{c.max}^{c}(cd A^{-1})$	$\operatorname{CIE}(x, y)^d$	Color
PPFOH	5.22	383.62	0.54	(0.53, 0.41)	Orange-Red
PPFOH-co-DF8	4.11	1266	1.06	(0.38, 0.39)	Yellow
PPFOH-co-DBF	3.58	1770	1.17	(0.28, 0.35)	Cyan
PPFOH-co-ThC60	7.32	546.56	0.34	(0.24, 0.26)	Blue

<sup>*a*</sup>Turn-on voltage at a brightness of 1 cd/m<sup>2</sup>. <sup>*b*</sup>Maximum luminance. <sup>*c*</sup>Maximum current efficiency. <sup>*d*</sup> Measured at 8 V.