Supporting Information

One-Step Preparation of Conjugated Homopolymer Sub-Microsphere via Controllable Supramolecular Approach Toward Optoelectronic Applications

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 ^cDepartment of Physics and Centre for Plastic Electronics, The Blackett Laboratory, Imperial College London, Prince Consort Road, London SW7 2AZ, UK **Experimental Section**

Chemicals: All solvents were purchased from Aldrich or J&K Chemicals without further purification. Anhydrous THF (HPLC grade) was collected from Solvent Purification Systems (Innovative Technology, Inc.). Anhydrous chloroform was pre-dried over molecular sieves. DMF was dried over calcium hydride (CaH) 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.

Characterization: Absorption spectra were measured with a Shimadzu UV-3600 spectrometer at 25°C, and emission spectra were recorded on a Shimadzu RF-5301(PC)S luminescence spectrometer. The quartz cells of 10 mm thickness were used to measure the spectra. The samples were then examined with a field emission SEM (Hitachi, S-4800) at an accelerating voltage of 5 kV. TEM studies were performed in a JEM 2010F JEOL, operating at an accelerating voltage of 120 kV.A drop of 5 μ L DMF solution(1 mg/mL) was deposited on a carbon-coated copper grid. GIXD measurements were performed with An X-ray beam impinged onto the sample at a grazing angle above and below the critical angle of the thinfilm ($\alpha_c = 0.16$) but below the critical angle of the silicon substrate ($\alpha c = 0.22$). The wavelength of X-rays used was 1.240 Å, and the scattered intensity was detected by PILATUS 1M detector.The input laser pulses were focused by a lens (f = 20 cm) on the samples solution in a 1-mm-thick quartz cell (beam spot ~1 mm inside the cell). The emission from the samples was collected at a back scattering angle of 150° by a pair of lenses and directed to an OptronisOptoscopeTM streak camera system which has an ultimate temporal resolution of 6 ps.

Preparation of PPFOH CPSMs: 12 μ L of a fresh DMF or other solvents solution (typically 1 mg/mL, 10 mg/mL, 30 mg/mL and 50 mg/mL) was dropped onto the Si, quartzes, glass and Cu net. And the substrates with the DMF or other solvents solution are allowed overnight for solvent evaporation under an ambient environment (dark condition, T: 293 K; Humidity:

20%-40% RH). PPFOH CPSMs films for optical analysis were prepared via drop-coating method from PPFOH/DMF solutions on the quartz plates.

Device fabrication and evaluation: The device configuration was Au/*p*-SiC/PPFOH CPSMs films /ITO. Briefly, on a clean *p*-SiC substrate, a Au contact (size of about $5 \times 5 \text{ mm}^2$, ~120 nm thick for Au) was deposited by using electron beam evaporation at room temperature. The emission layers of PPFOH CPSMs were prepared via drop-coating (DMF solution, 1 mg/mL) on the other side of the *p*-SiC substrates. The spectra were measured by connecting the cathode and anode of a rectangle pulse voltage source (with repetition rate and pulse width of 7.5 Hz and 80 ms respectively) to the ITO and Au (120 nm) metal contacts, respectively. Light was collected from the surface of the ITO glass by an objective lens.



Figure S1. Comparison of partial ¹H NMR spectra of TFOHC8 and mixed solution of DMF/ TFOHC8 in CDCl₃.



Figure S2. SEM images of other conjugated polymers with the hydroxyl group self-assembled CPSMs. Scale bars are 200 nm.



Figure S3. SEM images of the PPFOH self-assembled CPSMs on other substrates. (a) quartz plate, (b) glass. Concentration: 1 mg/mL. Scale bars are 500 nm.



Figure S4. TEM images of the PPFOH self-assembled CPSMs prepared via solvent evaporation-induced interface self-assembly on Cu net. Concentration: 1 mg/mL. Scale bars are 100 nm.



Figure S5. GIXD diffraction pattern of PPFOH CPSMs.



Figure S6. SEM images of PPFOH CPSMs obtained in (a-b) DMSO and (c-d) DMAc solutions. Concentration: 1 mg/mL. Scale bars are 200 nm.



Figure S7. PPFOH films obtained in other different solvents, such as (a) CHCl₃, (b) THF and (c) toluene solutions. Concentration: 1 mg/mL. Scale bars are 1 μ m.



Figure S8. SEM images of PPFOH CPSMs prepared in different humidity conditions, (a) high humidity near the water, (b) dryer, (c) dry box and (d) glove box. Concentration: 1 mg/mL. Scale bars are 500 nm.



Figure S9. SEM analysis of PPFOH film spin-coated from DMF solution. Scale bar is 1 μ m.



Figure S10. Absorption and PL spectra of PPFOH CPSMs films with different diameters via solvent evaporation-induced interface self-assembly. Excited at 380 nm.



Figure S11. PL decays of the PPFOH CPSMs film in different wavelengths, as 450 nm (black), 560 nm (red).

Samples	State	λ_{abs} [nm]	$\lambda_{\rm PL}$ [nm]	τ[ns]	${{{{\pmb \Phi }}_{{ m{PLQY}}}}^{\left[{{\mathfrak c}} ight]}}$
				(λ[nm])	
PPFOH	Solution ^[b]	390	423, 448, 480	0.48 (460)	72
PPFOH CPSMs ^[a]	film	409	458, 540	2-4, 6-9(560)	18

Table S1. Photophysical data of PPFOH CPSMs.

[a] the size of 150-2000 nm, [b] in DMF, [c] The Φ_{PLQY} of PFO amorphous phase film was about 43% in our lab under the same experimental conditions.