

## Supporting Information

### Tuning the Luminescence of Polyacrylonitriles by Controlled Polymerization

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## 1. Polymerization of PANs

**2-(((dodecylthio)carbonothioyl)thio)-2-methylpropanoic acid (C<sub>12</sub>H<sub>25</sub>-CTA).** The synthesis was performed according to the previous literature. In a 250 ml three-necked flask, add 3.5 g (16.5 mmol) potassium phosphate and disperse it in 50 mL acetone. Then 5.0 mL (21.0 mmol) of 1-dodecanethiol was dissolved in 10 mL of acetone and added dropwise for approximately 30 min. 2.7 mL (44.9 mmol) of carbon disulfide was dissolved in 10 mL of acetone and added dropwise for approximately 10 min. Dissolve 2.5 g (15.0 mmol) of 2-bromo-2-methylpropionic acid in 10 mL of acetone, add dropwise, and react overnight. The resulting product was concentrated, dissolved in dichloromethane and washed three times with saturated sodium chloride solution, followed by one more extraction with 1 M dilute hydrochloric acid solution. The product was again concentrated and recrystallized from n-hexane to give CTA as crystals. (yield = 90.0 %). <sup>1</sup>H NMR (500 MHz, Chloroform-d) δ 3.27 (t, J = 7.4 Hz 2H), 1.71 (s, 6H), 1.66 (q, J = 7.6 Hz 2H), 1.37 (q, J = 7.25 Hz, 2H), 1.30 - 1.18 (m, 16H), 0.87 (t, J = 6.85 Hz, 3H).

**F1.** In a 100 ml Schlenk bottle, add 3.0 g acrylonitrile (AN), 5 mg AIBN and 20 ml extra dry N, N-dimethylformamide. The mixture in the bottle was frozen and deoxygenated three times, and the reaction bottle was placed in an oil bath at 70 °C to react for 24 hours. After the reaction is over, cool to room temperature, and add 20 ml of DMF to dilute the reaction solution. Drop the diluted reaction solution into 400 ml of methanol to obtain a white precipitate. The precipitates were washed with methanol and dried under vacuum overnight at 70 °C to a constant weight. The polymer yield, relative molecular weight, and PDI are all shown in Table 1. <sup>1</sup>H NMR (500 MHz, DMSO), δ (TMS, ppm): 3.13, 3.08, 2.10, 2.00.

**F2.** In a 100 ml Schlenk bottle, add 3.0 g acrylonitrile (AN), 5 mg AIBN ,0.115 g 1-dodecanethiol and 15 ml extra dry N, N-dimethylformamide. The mixture in the bottle was frozen and deoxygenated three times, and the reaction bottle was placed in an oil bath at 70 °C to react for 24 hours. After the reaction is over, cool to room temperature, and add 20 ml of DMF to dilute the reaction solution. Drop the diluted reaction solution

into 400 ml of methanol to obtain a yellowish white precipitate. The precipitates were washed with hexane and dried under methanol overnight at 70 °C to a constant weight. The polymer yield, relative molecular weight, and PDI are all shown in Table 1. <sup>1</sup>H NMR (500 MHz, DMSO), δ (TMS, ppm): 3.13, 3.08, 2.11, 2.00.

**F3.** In a 100 ml Schlenk bottle, add 3.0 g acrylonitrile (AN), 0.13 g ammonium persulfate ((NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>), 34.0 mg isopropyl alcohol and 20 ml extra dry N, N-dimethylformamide. The mixture in the bottle was frozen and deoxygenated three times, and the reaction bottle was placed in an oil bath at 70 °C to react for 2 hours. After the reaction is over, cool to room temperature, and add 20 ml of DMF to dilute the reaction solution. Drop the diluted reaction solution into 400 ml of methanol to obtain a white precipitate. The precipitates were washed with methanol and dried under vacuum overnight at 70 °C to a constant weight. The polymer yield, relative molecular weight, and PDI are all shown in Table 1. <sup>1</sup>H NMR (500 MHz, DMSO), δ (TMS, ppm): 3.13, 3.08, 2.10, 2.00.

**F4.** In a 100 ml Schlenk bottle, add 3.0 g acrylonitrile (AN), 0.13 g ammonium persulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>), 34.0 mg isopropyl alcohol and 15 ml extra dry N, N-dimethylformamide. The mixture in the bottle was frozen and deoxygenated three times, and the reaction bottle was placed in an oil bath at 70 °C to react for 1 hours. After the reaction is over, cool to room temperature, and add 20 ml of DMF to dilute the reaction solution. Drop the diluted reaction solution into 400 ml of methanol to obtain a white precipitate. The precipitates were washed with methanol and dried under vacuum overnight at 70 °C to a constant weight. The polymer yield, relative molecular weight, and PDI are all shown in Table 1. <sup>1</sup>H NMR (500 MHz, DMSO), δ (TMS, ppm): 3.13, 3.08, 2.10, 2.00.

**F5.** In a 100 ml Schlenk bottle, add 3.0 g acrylonitrile (AN), 20 mg AIBN, 1.0 mg NaOH and 20 ml extra dry N, N-dimethylformamide. The mixture in the bottle was frozen and deoxygenated three times, and the reaction bottle was placed in an oil bath at 70 °C to react for 6.0 hours. After the reaction is over, cool to room temperature. Drop the reaction solution into 200 ml of methanol to obtain a bright yellow precipitate.

The precipitates were washed with methanol and dried under vacuum overnight at 70 °C to a constant weight. The polymer yield, relative molecular weight, and PDI are all shown in Table 1. <sup>1</sup>H NMR (500 MHz, DMSO), δ (TMS, ppm): 3.13, 3.08, 2.66, 2.10, 2.00.

**R1.** In a 100 ml Schlenk bottle, add 3.0 g acrylonitrile (AN), 46.5 mg AIBN, 0.23 g C<sub>12</sub>H<sub>25</sub>-CTA and 20 ml extra dry N, N-dimethylformamide. The mixture in the bottle was frozen and deoxygenated three times, and the reaction bottle was placed in an oil bath at 70 °C to react for 24 hours. After the reaction is over, cool to room temperature, and add 10 ml of DMF to dilute the reaction solution. Drop the diluted reaction solution into 400 ml of methanol to obtain a yellowish white precipitate. The precipitates were washed with methanol and dried under vacuum overnight at 70 °C to a constant weight. The polymer yield, relative molecular weight, and PDI are all shown in Table 1. <sup>1</sup>H NMR (500 MHz, DMSO), δ (TMS, ppm): 3.13, 3.08, 2.11, 2.03, 1.99. The synthesis method of **R2 - R4** is the same as that of **R1**.

F1-(NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, F1-Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, F1-H<sub>2</sub>SO<sub>4</sub> and F1-NaOH are the products of F1 reacted with (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, H<sub>2</sub>SO<sub>4</sub>, and a trace NaOH under the above polymerization conditions, respectively.

## 2. Theoretical calculations

Density functional theory (DFT) calculations were performed using Gaussian 16 program Package. The geometry optimization and frequency calculations of hydrolyzed PANs were performed with Gaussian 16 at B3LYP/6-31G level.<sup>1</sup> The energy of different states and corresponding transition states was calculated at PBE0/def2-SV(P) with def2/J and def2-SVP/C. Spin-orbit coupling (SOC) constants were obtained through ORCA 5.0 based on the TD-DFT results.<sup>2-3</sup> Frontier molecular orbitals analysis were carried out by Multiwfn<sup>4</sup> and results were plotted via VMD software for visualization<sup>5</sup>.

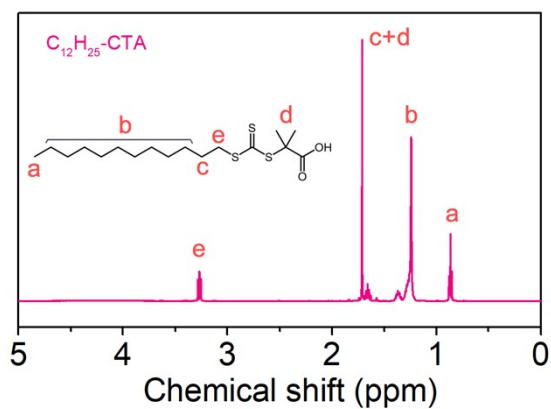


Figure S1.  $^1\text{H}$  NMR spectrum of RAFT CTA initiator.

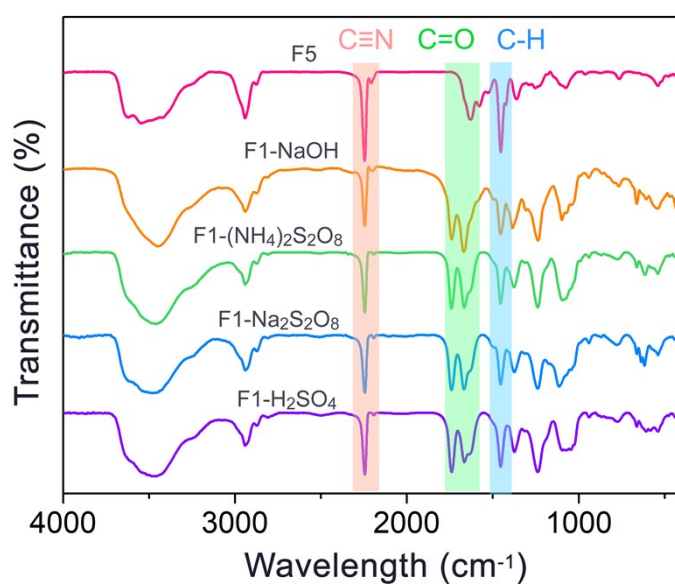


Figure S2. FT-IR spectra of PAN samples.

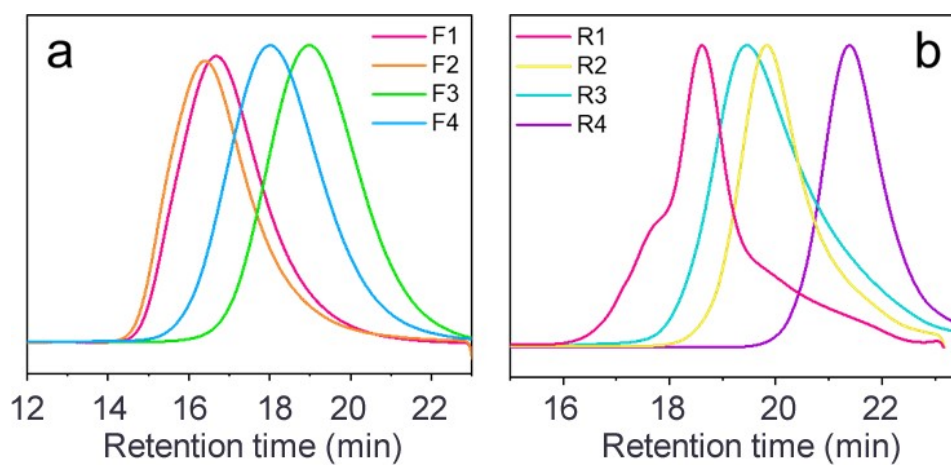


Figure S3. GPC curves of F1-F4 (a) and R1-R4 (b).

Table S1. Optimal emission wavelengths and their respective fluorescence lifetimes and quantum yields of F1-F3 and R1 DMF solutions with different concentrations.

Sample	5.3 mg/mL			53 mg/mL			106 mg/mL		
	lifetime (ns)	quantum yield (%)	$\lambda_{Em}$ (nm)	lifetime (ns)	quantum yield (%)	$\lambda_{Em}$ (nm)	lifetime (ns)	quantum yield (%)	$\lambda_{Em}$ (nm)
F1	3.56	7.09	403	3.39	3.44	407	4.08	2.93	424
F2	3.90	5.03	404	4.02	10.21	413	3.68	8.70	417
R1	3.13	0.71	432	7.80	3.09	482	7.43	1.00	520
F3	4.79	6.94	503	5.01	2.07	591	6.11	1.70	631

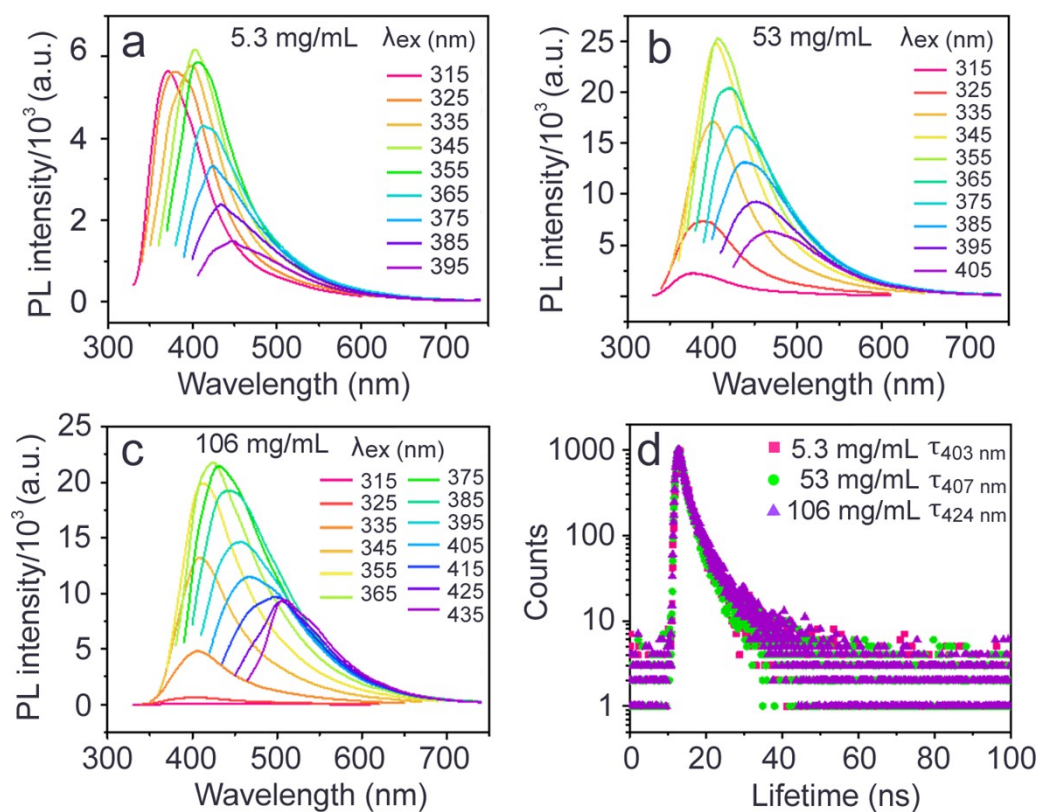


Figure S4. Excitation-dependent spectra of F1 in DMF solution and the fluorescence lifetimes of optimal emission wavelengths at different concentrations.

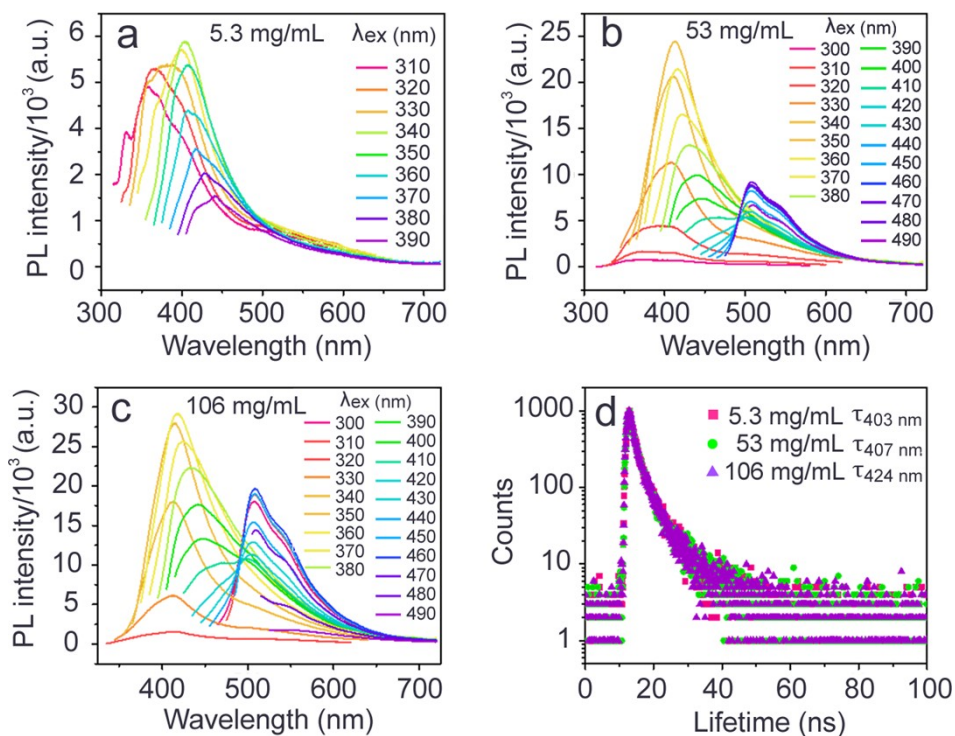


Figure S5. Excitation-dependent spectra of F2 and fluorescence lifetimes of optimal emission wavelengths at different concentrations.

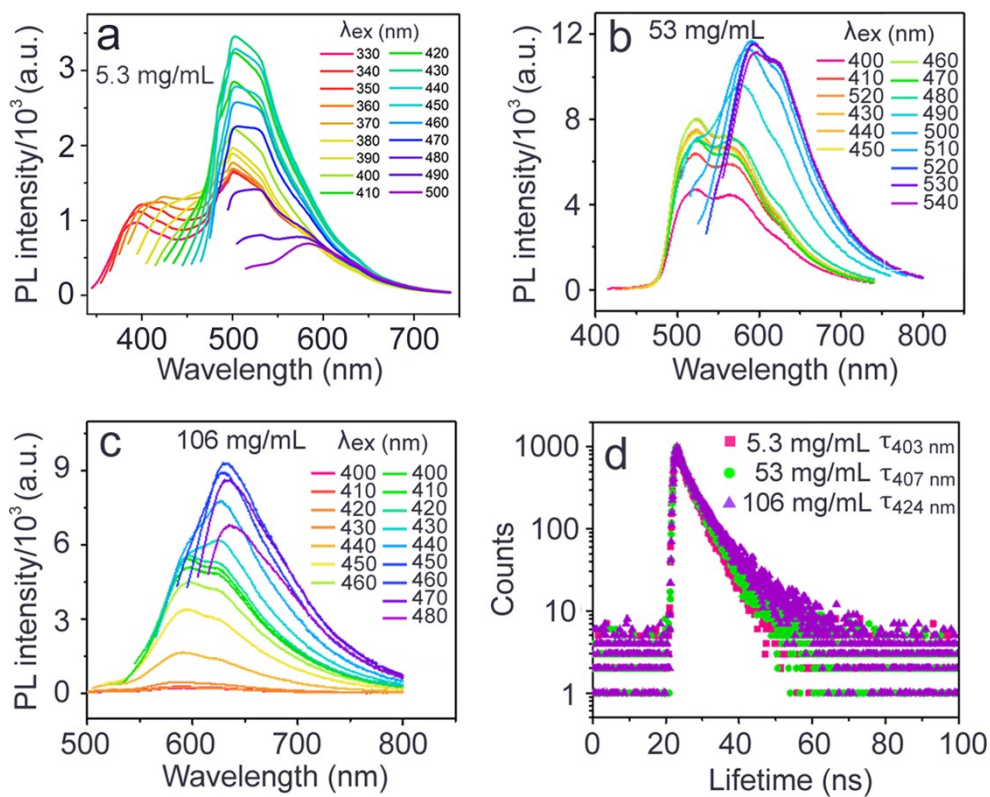


Figure S6. Excitation-dependent spectra of F3 and fluorescence lifetimes of optimal emission wavelengths at different concentrations.

### Possible oxidation in F3 and F4

To investigate the possible oxidation of PAN in the presence of persulfates, the mixtures of F1 and persulfates,  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  and  $\text{Na}_2\text{S}_2\text{O}_8$  were heated under the polymerization conditions (70 °C for 1 hour), termed F1- $(\text{NH}_4)_2\text{S}_2\text{O}_8$  and F1- $\text{Na}_2\text{S}_2\text{O}_8$ , respectively. As shown in Figure S13, the absorption and PL spectra of F1- $(\text{NH}_4)_2\text{S}_2\text{O}_8$  and F1- $\text{Na}_2\text{S}_2\text{O}_8$  are the same as that of original F1 in both solution and solid states. In addition, we also prepared F1 treated with  $\text{H}_2\text{SO}_4$ , termed F1- $\text{H}_2\text{SO}_4$ , and the emission peak was 425 nm (Figure S13d). These results indicate that the red-shifted emission of F3 and F4 is not ascribed to the oxidation of PAN by persulfates.

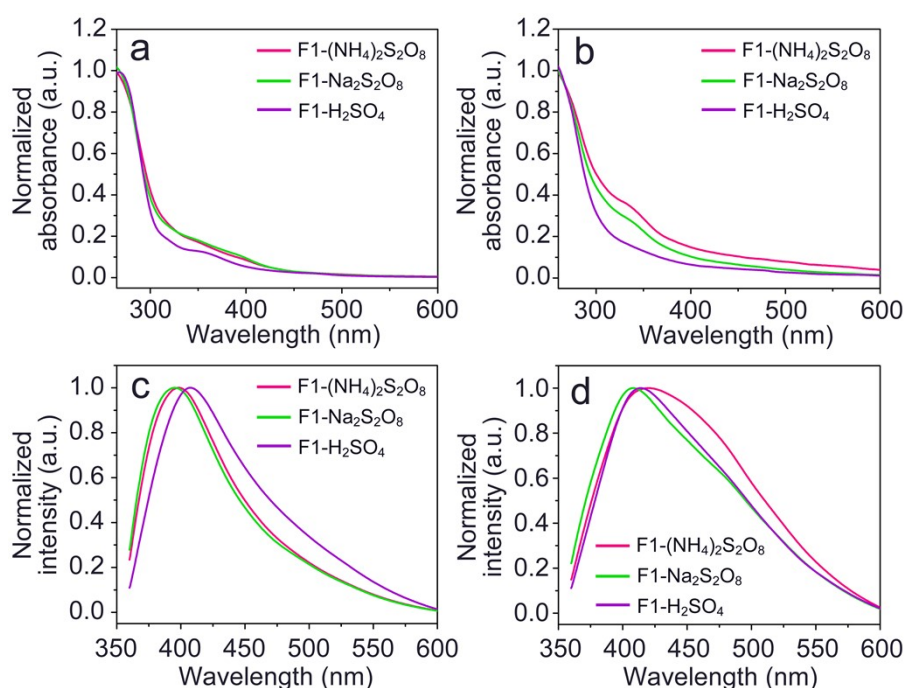


Figure S7. Normalized UV-vis (a, b) and PL spectra (c, d) of F1 treated with  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ,  $\text{Na}_2\text{S}_2\text{O}_8$ , and  $\text{H}_2\text{SO}_4$  at 70 °C for 1 hour in DMF solution (a, c) and in solid film (b, d), excitation at 345 nm.



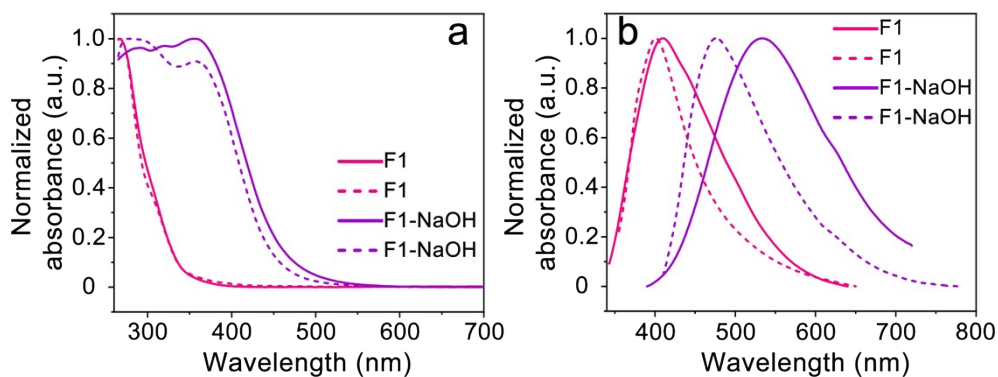


Figure S8. Normalized UV-vis (a) and PL (b) spectra of F1 and F1-NaOH, solid line: film sample; dash line: solution sample.

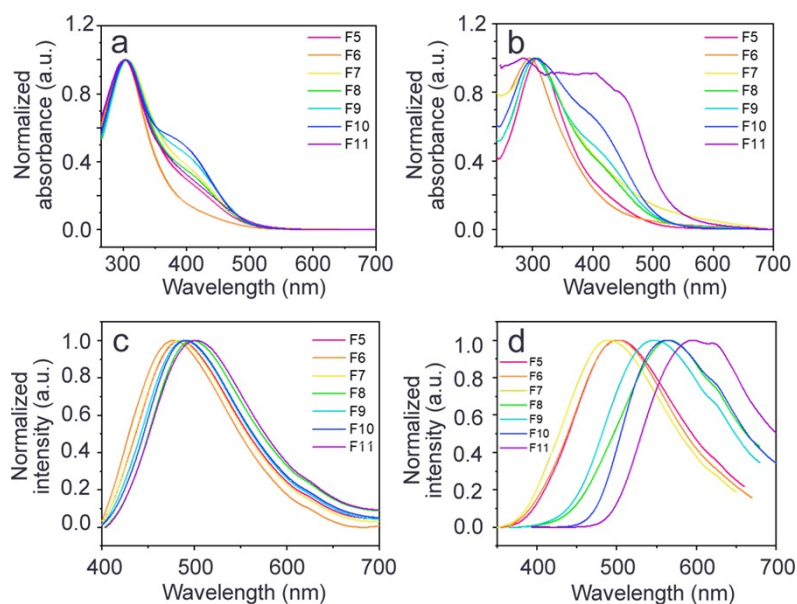


Figure S9. Normalized UV-vis (a, b) and PL spectra (c, d) of F5-F11 in DMF solution (a, c) and in solid film (b, d).

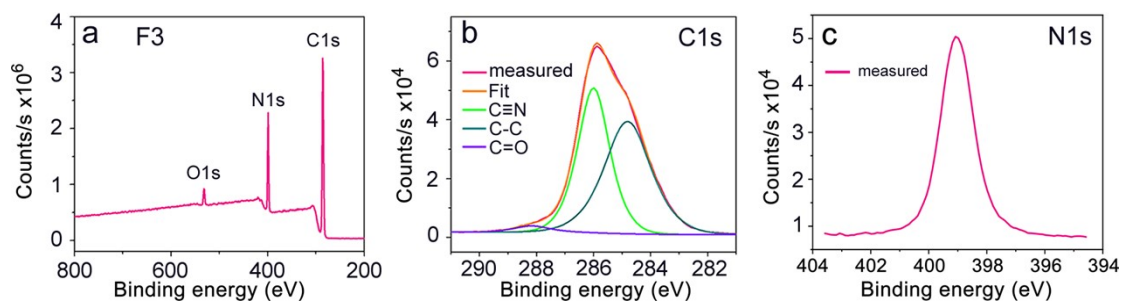


Figure S10. (a) XPS spectrum of F3 and (b-c) F3 high-resolution XPS spectra of C 1s

and N 1s.

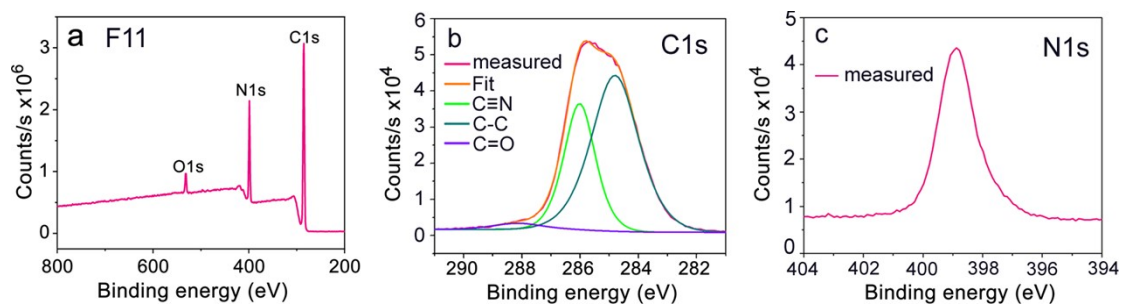


Figure S11. (a) XPS spectrum of F11 and (b-c) F11 high-resolution XPS spectra of C 1s and N 1s.

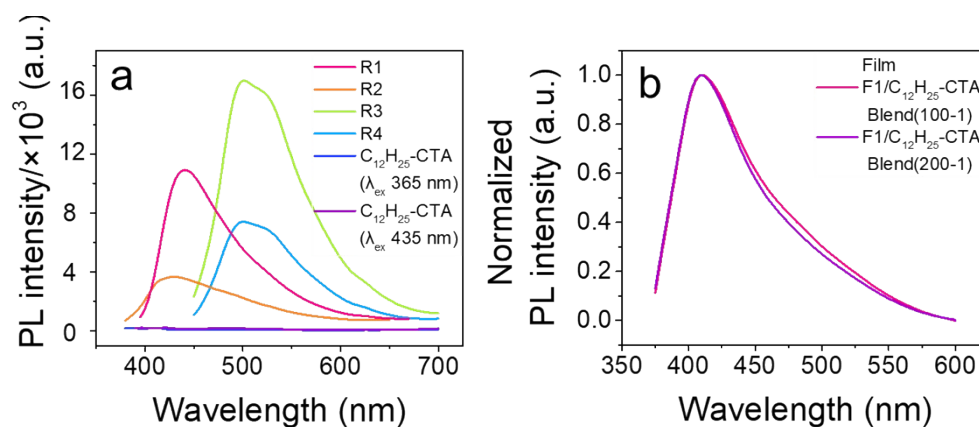


Figure S12. (a) PL spectra of R1-R4 and C<sub>12</sub>H<sub>25</sub>-CTA in DMF solution; excitation wavelengths of R1-R4 are 381 nm, 367 nm, 435 nm and 435 nm, respectively. (b) F1 blend different ratio C<sub>12</sub>H<sub>25</sub>-CTA film PL spectra. Excitation by 360 nm.

## References:

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