

## Supporting Information for

# Donor-Acceptor Star-Shaped Conjugated Macroelectrolytes: Synthesis, Light-Harvesting Properties and Self-Assembly-Induced FRET

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## 1. Materials and Synthesis

### 1.1 Materials

All reagents and solvents, unless otherwise specified, were obtained from Aldrich, Acros, and TCI Chemical Co. and were used as received. TrNBr and its precursor compounds were synthesized as the procedures described in our previous work.<sup>1</sup>

### 1.2 Synthesis of 4FNaT, 4FNBrT, and 4FNOHT

#### Synthesis of 1 and 2:

2-bromo-9H-fluorene (2.0 g, 7.87 mmol, 1.0 equiv.) and tetrabutylammoniumbromide (TBAB) (0.51 g, 1.57 mmol, 0.20 equiv.) were dissolved in anhydrous DMSO (20 mL). 50 wt% KOH in H<sub>2</sub>O (1.2 g) was dropwise added *via* syringe, followed by the addition of ethyl 4-bromobutanoate (3.897 g, 23.61 mmol, 3 equiv.) to obtain **1** or ethyl 4-bromobutanoate (3.37 mL, 23.61 mmol, 3 equiv.) to gain **2**. After stirring at room temperature for 5 h, the reaction mixture was cooled to room temperature. Then water (10 mL) and dichloromethane (10 mL) were added. The organic layer was separated and the aqueous layer was extracted with dichloromethane. The organic portions were combined, washed with brine (12 mL), dried over anhydrous magnesium sulfate, and filtered. The filtrate was collected and the solvent was removed. The residue was purified by column chromatography over silica using petroleum as eluent to give compound **1** (2.60 g, 58.0%) and **2** (2.07 g, 55.6%) as a white solid.

**1:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.81 (d, 1H), 7.71 (dd, 3H), 7.36–7.29 (m, 3H), 3.26 (t, 4H), 1.99 (td, 4H), 1.71–1.57 (m, 4H), 1.15 (dd, 4H), 1.04 (dd, 4H), 0.58 (dd, 4H).

**2:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.69 – 7.63 (m, 1H), 7.56 (d, 1H), 7.48 – 7.43 (m, 2H), 7.38 – 7.28 (m, 3H), 4.03 (q, 4H), 2.00 (d, 8H), 1.19 (d, 6H), 0.95 – 0.90 (m, 4H).

### Synthesis of **3** and **4**:

A flask charged with compound **1** (2 g, 3.50 mmol, 1.0 equiv.) to obtain **3** or **2** (1.66 g, 3.50 mmol, 1.0 equiv.) to obtain **4**, bis(pinacolato)diborane (1.78 g, 7.0 mmol, 2.0 equiv.), potassium acetate (1.37 g, 14.0 mmol, 4.0 equiv.), PdCl<sub>2</sub>(dppf)<sub>2</sub> (80 mg, 5% equiv.) and 20 mL of anhydrous dioxane was degassed for 15 min. The mixture was deoxygenated (by placing under vacuum and backfilling with argon) and then heated at 100°C under argon for 24 h. The resultant reaction mixture was poured into 100 mL iced water, extracted with DCM. The combined organic layers

were dried over anhydrous  $\text{MgSO}_4$ . After the solvent was evaporated, the residue was purified by chromatography using silica gel to afford **3** (1.18 g, 54.6%) and **4** (1.17 g, 52.3%) as a white solid.

**3:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.81 (d, 1H), 7.71 (dd, 3H), 7.36–7.29 (m, 3H), 3.26 (t, 4H), 1.99 (td, 4H), 1.71–1.57 (m, 4H), 1.39 (s, 12H), 1.15 (dd, 4H), 1.04 (dd, 4H), 0.58 (dd, 4H).

**4:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.79 (d,  $J = 7.6$  Hz, 1H), 7.73 (s, 1H), 7.66 (d, 2H), 7.34–7.21 (m, 3H), 3.94 (m, 4H), 1.99 (t, 8H), 1.33 (s, 12H), 1.09 (t, 6H), 0.93 – 0.83 (m, 4H).

### Synthesis of **5**:

To a 250 mL dried round bottom flask was added triphenylamine (5.00 g, 20.38 mmol, 1.0 equiv.) and dichloromethane (150 mL). The flask was wrapped with aluminium foil. The solution was cooled to  $0^\circ\text{C}$  in a mixed bath of ice and water.  $\text{Br}_2$  (3.26 g, 2.76 mL, 3.0 equiv.) was added slowly to the mixture. The stirred solution was allowed to warm to room temperature and stirred overnight. The mixture was washed with  $\text{Na}_2\text{S}_2\text{O}_3$  and extracted with dichloromethane, then dried with  $\text{MgSO}_4$  to afford the crude product, which was then recrystallized from ethanol twice to give compound **5** (9.33 g, 95%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.40–7.31 (m, 6H), 6.97–6.88 (m, 6H).

### Synthesis of **6** and **7**:

Monomer **3** (2.48 g, 4.36 mmol, 2.1 equiv.) to obtain **6** or **4** (2.27 g, 4.36 mmol, 2.1 equiv.) to obtain **7**, monomer **5** (1.0 g, 2.07 mmol, 1.0 equiv.), TBAB (50 mg, 0.15 mmol, 20% equiv.) and  $\text{Pd}(\text{PPh}_3)_4$  (62 mg) were placed in a 250 mL vessel. A mixture of 2 M  $\text{K}_2\text{CO}_3$  aqueous solution (7 mL) and tol (21 mL) was added to the vessel. The mixture was then heated at  $95^\circ\text{C}$  under argon for 12 h. After the mixture was cooled to room temperature, water (10 mL) and dichloromethane (10 mL) were added. The organic layer was separated. The aqueous layer was extracted with

dichloromethane ( $3 \times 10$  mL). The organic portions were combined, dried over anhydrous magnesium sulfate, and filtered. The filtrate was collected and the solvent was removed. The residue was purified by column chromatography over silica to give compound **6** (0.67 g, 24.7%) and **7** (0.501 g, 21.7%) as a white solid.

**6:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.79–7.70 (m, 4H), 7.62–7.52 (m, 8H), 7.40–7.30 (m, 8H), 7.22 (d, 4H), 7.08 (d, 2H), 4.07–3.96 (m, 8H), 2.17–1.95 (m, 16H), 1.16 (t, 12H), 1.01 (d, 8H).

**7:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.74 (d, 4H), 7.58 (d, 8H), 7.41–7.29 (m, 8H), 7.23 (d, 4H), 7.09 (d, 2H), 3.27 (t, 8H), 2.09–1.93 (m, 8H), 1.70–1.61 (m, 8H), 1.19 (d, 8H), 1.12–1.04 (m, 8H), 0.67 (d, 8H).

#### Synthesis of **4FNT** and **4FCT**:

Monomer **6** (1.30 g, 0.10 mmol, 3 equiv.) to obtain **4FNT** or **4** (1.10 g, 0.10 mmol, 3 equiv.) to obtain **4FCT**, monomer **8** (0.21 g, 0.33 mmol, 1 equiv.),  $\text{Pd}(\text{PPh}_3)_4$  (39 mg) were placed in a 250 mL vessel. Toluene (15 mL) was added to the vessel. The mixture was then heated at  $100^\circ\text{C}$  under argon for 36 h. After the mixture was cooled to room temperature, water (10 mL) and dichloromethane (10 mL) were added. The organic layer was separated and the aqueous layer was extracted with dichloromethane ( $3 \times 10$  mL). The organic portions were combined, dried over anhydrous magnesium sulfate, and filtered. The filtrate was collected and the solvent was removed. The residue was purified by column chromatography over silica to give compound **4FNT** (0.24 g, 26.12%) and **4FCT** (0.20 g, 24.12%) as a red solid.

**4FNT:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.15 (d, 2H), 7.91 (s, 2H), 7.78–7.71 (m, 8H), 7.67–7.58 (m, 16H), 7.57 (s, 4H), 7.39–7.28 (m, 22H), 7.24 (d, 4H), 3.28 (t, 16H), 2.02 (d, 16H), 1.70–1.62 (m, 16H), 1.24–1.15 (m, 16H), 1.13–1.05 (m, 16H), 0.68 (d, 16H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$

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152.6, 151.0, 150.5, 147.2, 146.4, 145.3, 140.8, 140.2, 139.4, 138.0, 136.3, 128.7, 128.5, 128.0, 127.0, 126.7, 125.6, 125.2, 124.7, 123.9, 123.4, 122.8, 120.8, 120.1, 119.8, 55.1, 40.3, 34.0, 32.7, 29.1, 27.8, 23.6.

**4FCT:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.15 (d, 2H), 7.90 (s, 2H), 7.75 (d, 8H), 7.68 – 7.61 (m, 16H), 7.59 (s, 4H), 7.40 – 7.29 (m, 24H), 7.24 (s, 2H), 4.03 (t, 16H), 2.08 (d, 32H), 1.17 (t, 24H), 1.02 (d, 16H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  173.4, 152.6, 150.5, 149.6, 147.3, 146.5, 145.4, 140.8, 140.6, 139.7, 138.0, 136.3, 128.8, 128.5, 128.1, 127.3, 126.7, 125.9, 125.7, 125.2, 124.7, 123.8, 123.4, 122.8, 121.0, 120.2, 119.9, 77.3, 77.1, 76.7, 60.1, 54.7, 39.7, 34.4, 29.8, 23.1, 19.4, 14.2, 1.0.

#### Synthesis of 4FNaT:

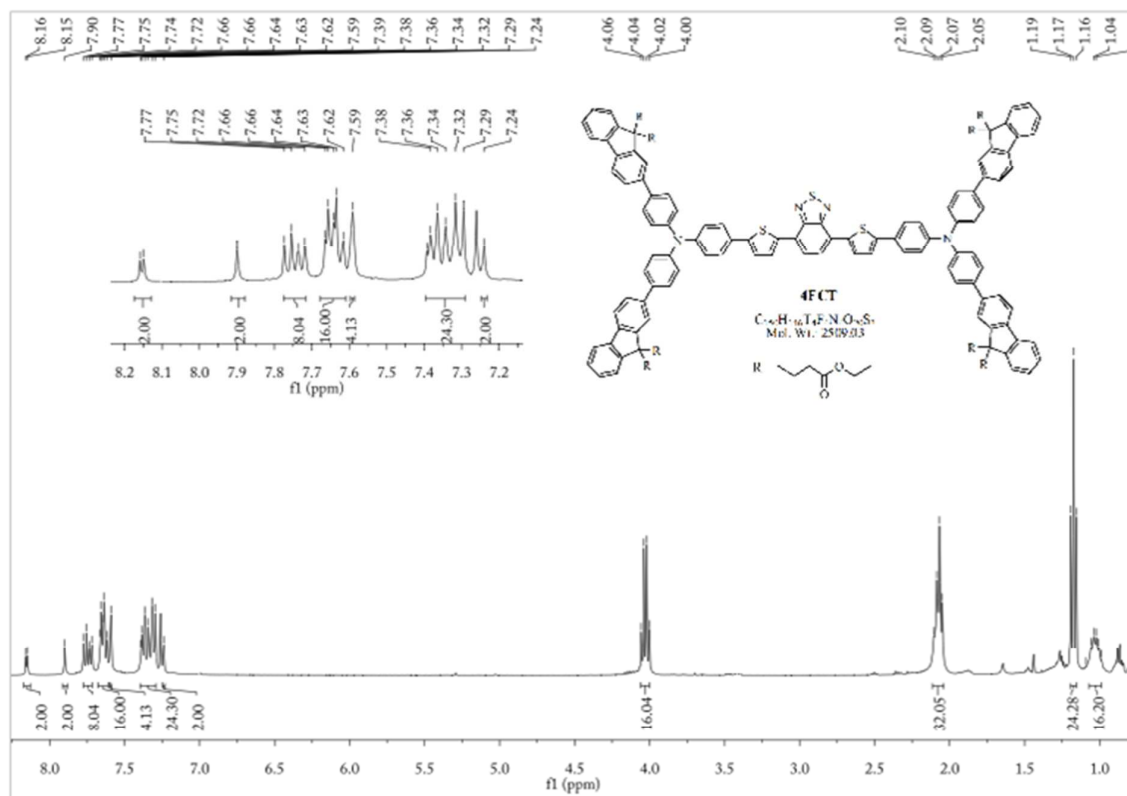
Neutral carboxylate-containing macromolecule **4FCT** was added to a solution of sodium hydroxide in THF; the mixture was refluxed for 2 days. After cooling to room temperature, the THF was removed by rotary evaporation. The red solid was purified by dialyzing against water (Millipore Nanopure<sup>TM</sup>) using a 600-Da MWCO cellulose membrane.  $^1\text{H}$  NMR (400 MHz, MeOD):  $\delta$  8.22 (s, 2H), 8.05 (s, 2H), 7.81 – 7.57 (m, 28H), 7.44 (s, 6H), 7.29 (s, 20H), 2.14 (s, 16H), 1.94 (s, 16H), 0.97 (s, 16H).

#### Synthesis of 4FNOHT:

**4FNT** (100 mg) was dissolved in a mixed solvent of THF (10 mL) and DMF (4 mL), then diethanolamine (2 mL) was added. The mixture was irradiated at 200 W in CEM microwave cavity with cooling mode for 45 min. After the solvent was evaporated, water was added to obtain a red powder (99.54 mg, 93%).  $^1\text{H}$  NMR (400 MHz,  $\text{d}_6\text{-DMSO}$ ):  $\delta$  8.23 – 8.12 (m, 4H), 7.95 (s, 2H), 7.89 – 7.59 (m, 30H), 7.43 (d, 4H), 7.36 – 7.14 (m, 18H), 4.21 (s, 14H), 2.65 (s, 6H), 2.37 (s, 28H), 2.32 (s, 8H), 2.25 (s, 14H), 1.96 (s, 8H), 1.22 (s, 27H), 1.11 (d, 17H), 0.97 (s, 32H), 0.84 (s, 12H).

## Synthesis of 4FNBrT:

4FNT (100 mg) was dissolved into 10 mL THF. 5 mL trimethylamine (TMA) solution in ethanol (33%) was then added. After stirred at room temperature for 48 h, some solid precipitated. Then 50 % TMA aqueous solution was added to the mixture till the solid was dissolved. After stirring for another 24 h, the solvent were evaporated at vacuum. The resulting solid mixture was washed with THF for three times, collected by centrifugation and dried overnight in vacuum at 50°C to afford **4FNBrT** (118 mg, 90.1%) as a red solid.  $^1\text{H}$  NMR (400 MHz, MeOD):  $\delta$  8.18 (s, 2H), 8.02 (s, 2H), 7.79 (s, 8H), 7.71 (s, 16H), 7.66 (s, 4H), 7.47 – 7.28 (m, 23H), 7.22 (s, 4H), 3.20 – 3.15 (m, 17H), 3.02 (s, 82H), 2.13 (s, 19H), 1.54 (s, 21H), 1.15 (s, 41H), 0.88 (s, 8H).



**Figure S1a.**  $^1\text{H}$  NMR spectra of 4FCT.

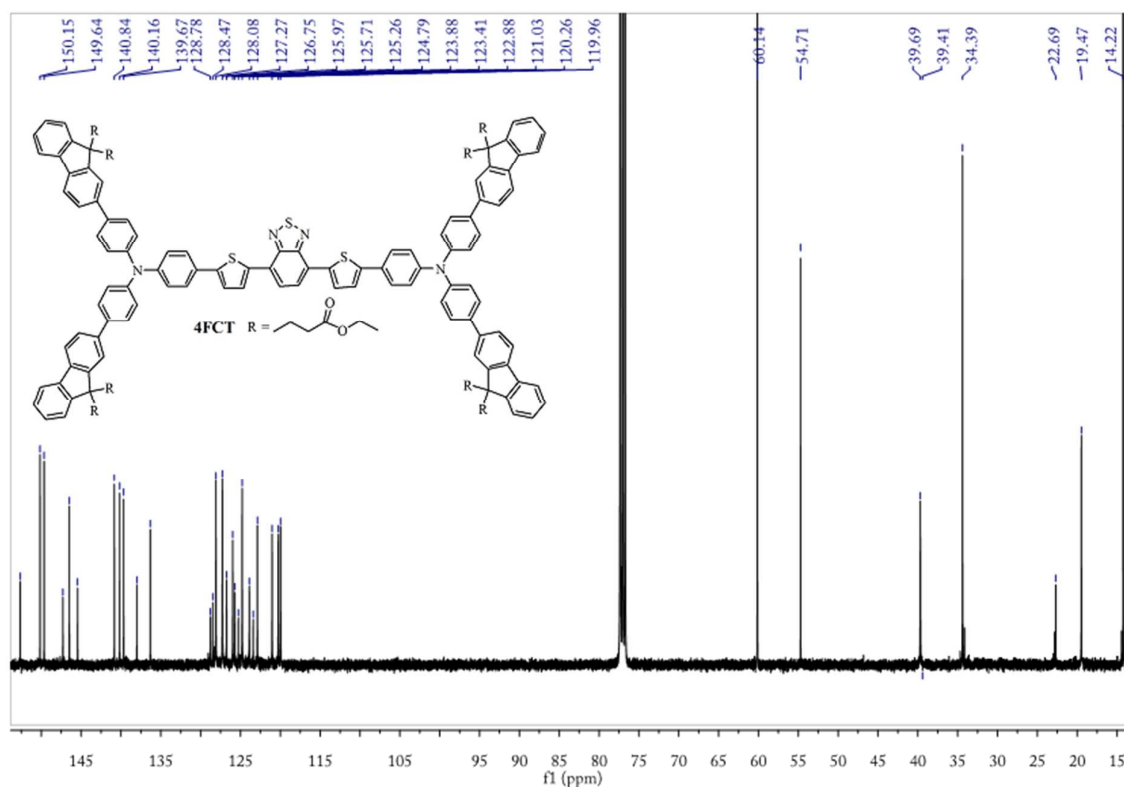


Figure S1b. <sup>13</sup>C NMR spectra of 4FCT.

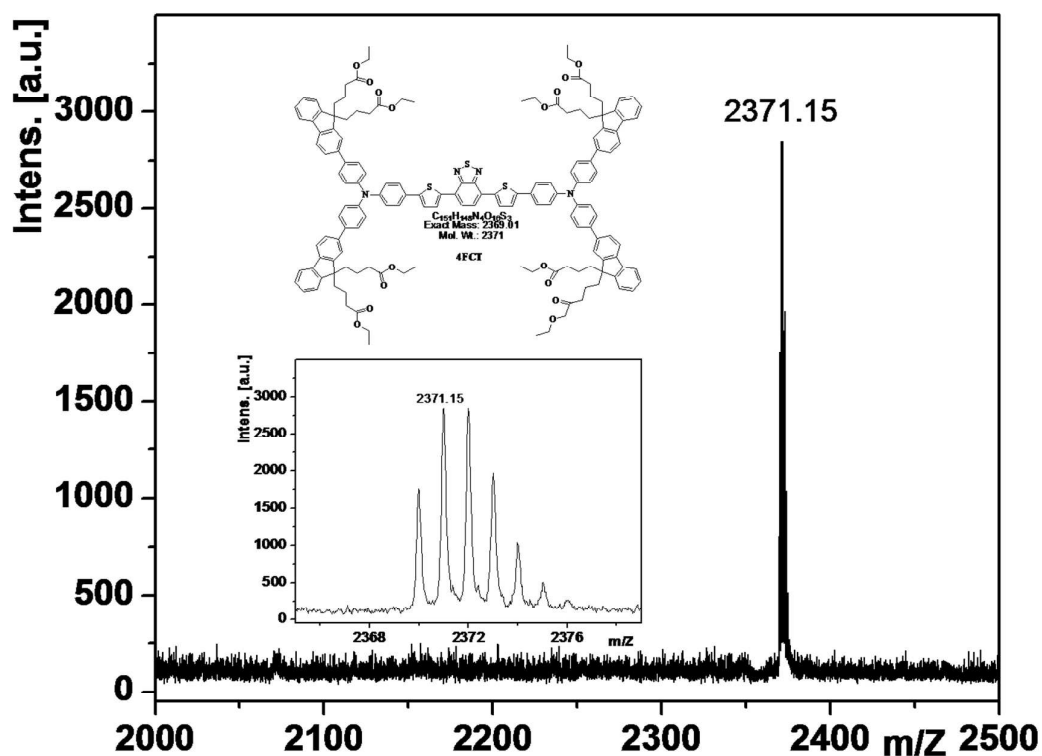
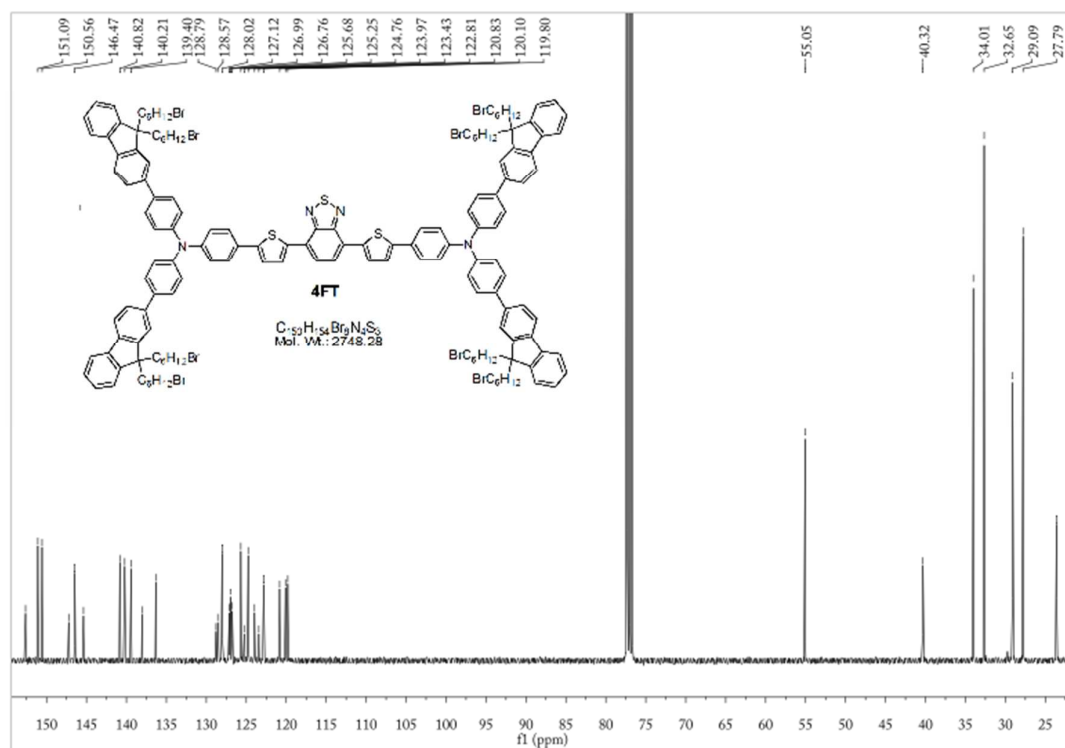
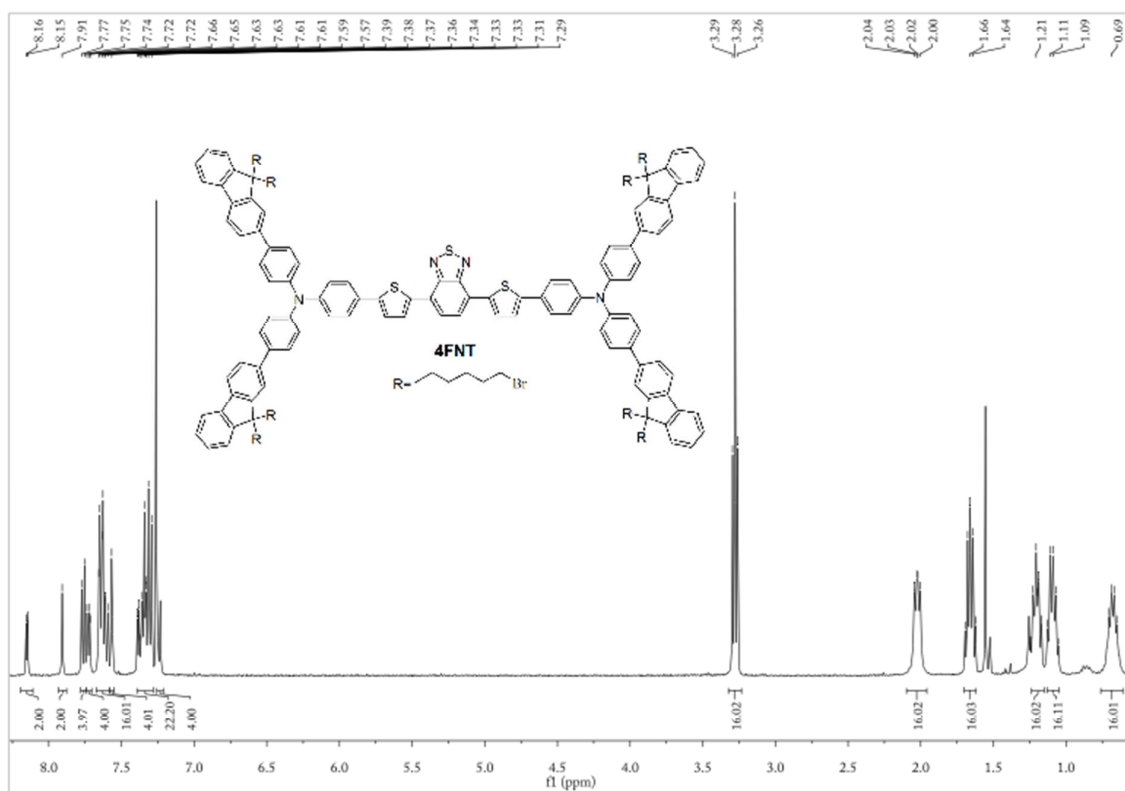


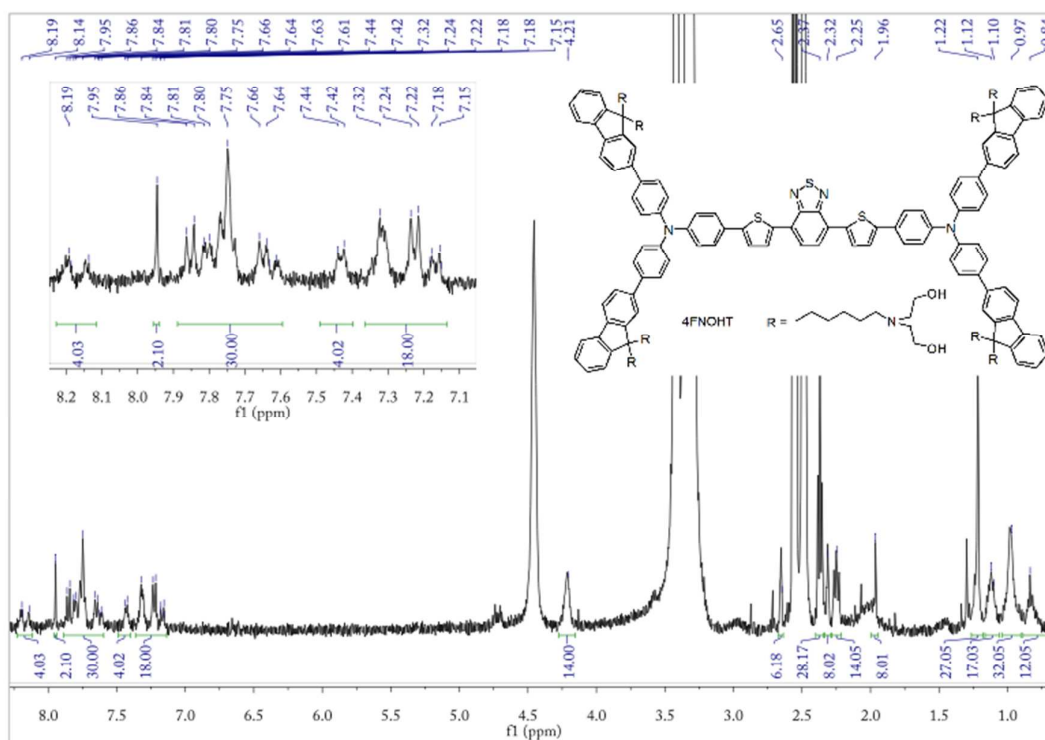
Figure S1c. MALDI-TOF spectra of 4FCT



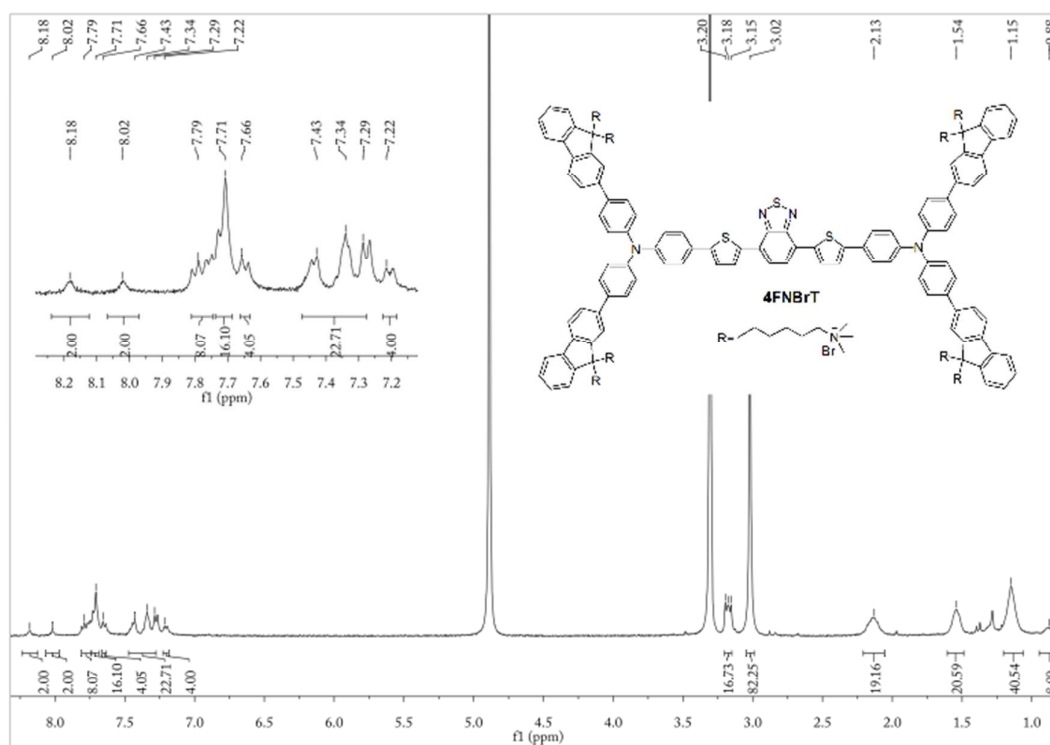
**Figure S2b.**  $^{13}\text{C}$  NMR spectra of 4FNT  
S8



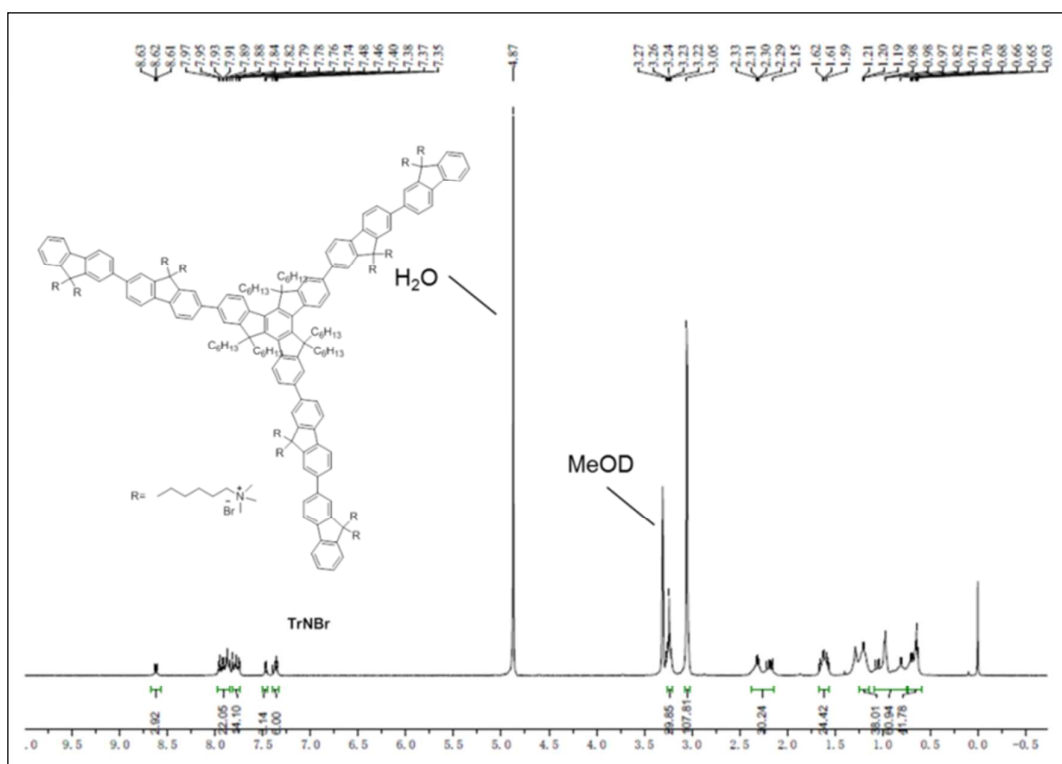




**Figure S4.  $^1\text{H}$  NMR spectra of 4FNOHT.**

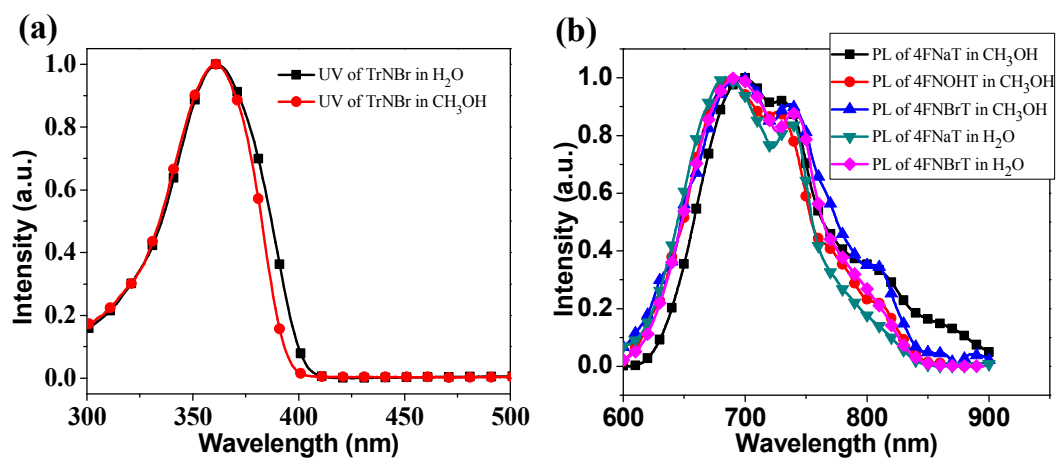


**Figure S5.  $^1\text{H}$  NMR spectra of 4FNBrT.**

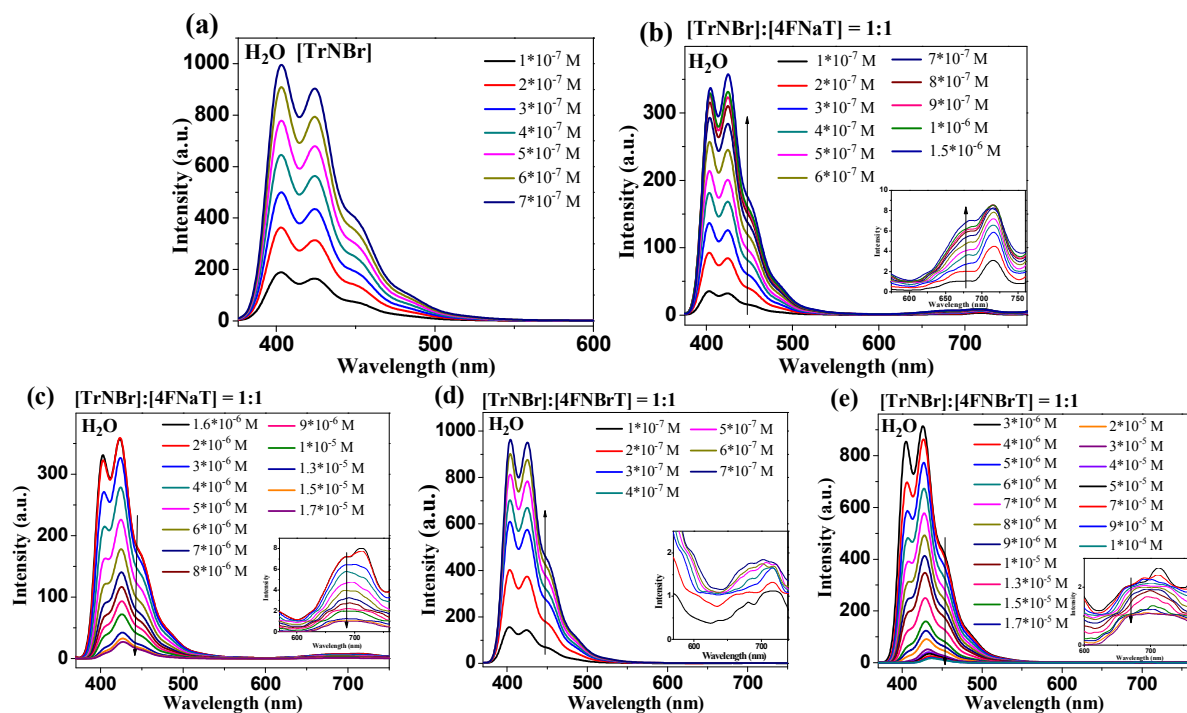


**Figure S6.**  $^1\text{H}$  NMR spectra of TrNBr.

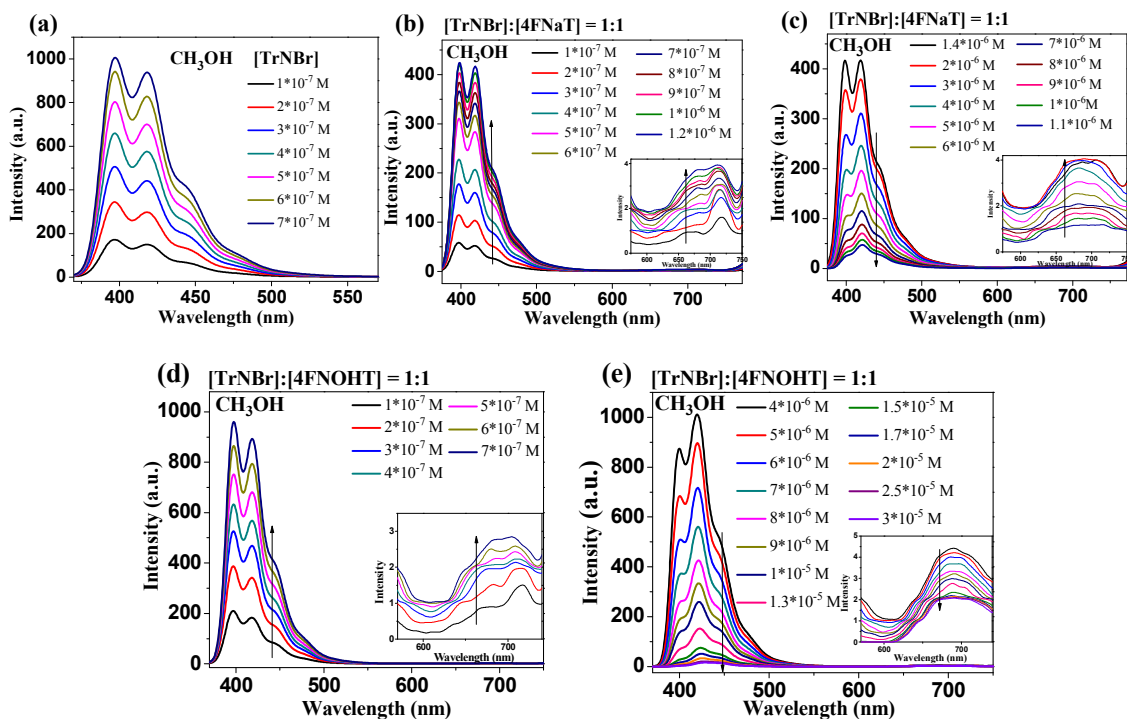
## 2. Absorption and Emission Spectra

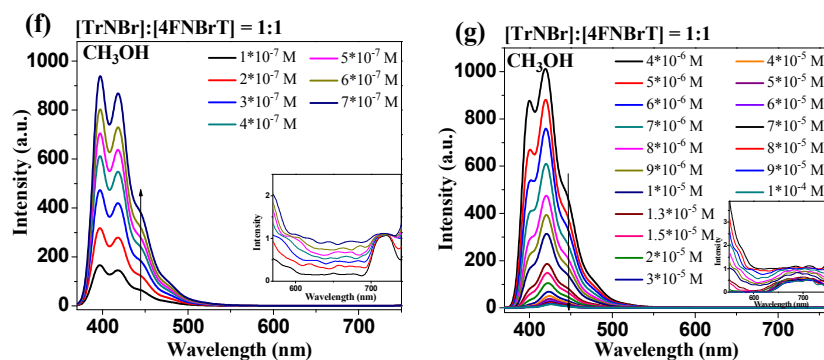


**Figure S7.** (a) Normalized UV-Vis absorption spectra of TrNBr in  $\text{H}_2\text{O}$  and  $\text{CH}_3\text{OH}$ . (b) Normalized fluorescence spectra of 4FNaT, 4FNBBrT in  $\text{H}_2\text{O}$  and 4FNaT, 4FNOHT and 4FNBBrT in  $\text{CH}_3\text{OH}$ .

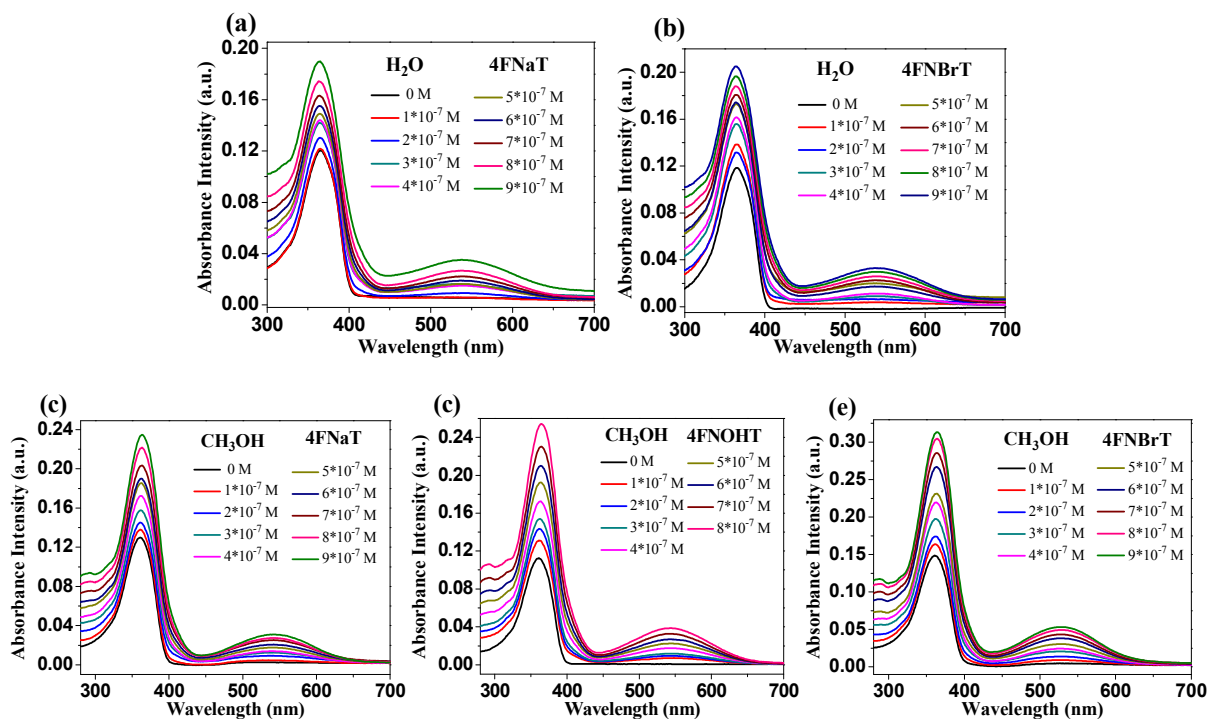


**Figure S8.** The changes of emission spectra of the systems ([TrNBr] (a), [TrNBr]:[4FNaT] = 1:1 (b, c) and [TrNBr]:[4FNBrT] = 1:1 (d, e)) with their simultaneous increasing concentrations in H<sub>2</sub>O. The emission spectra were collected at  $\lambda_{ex} = 361$  nm.

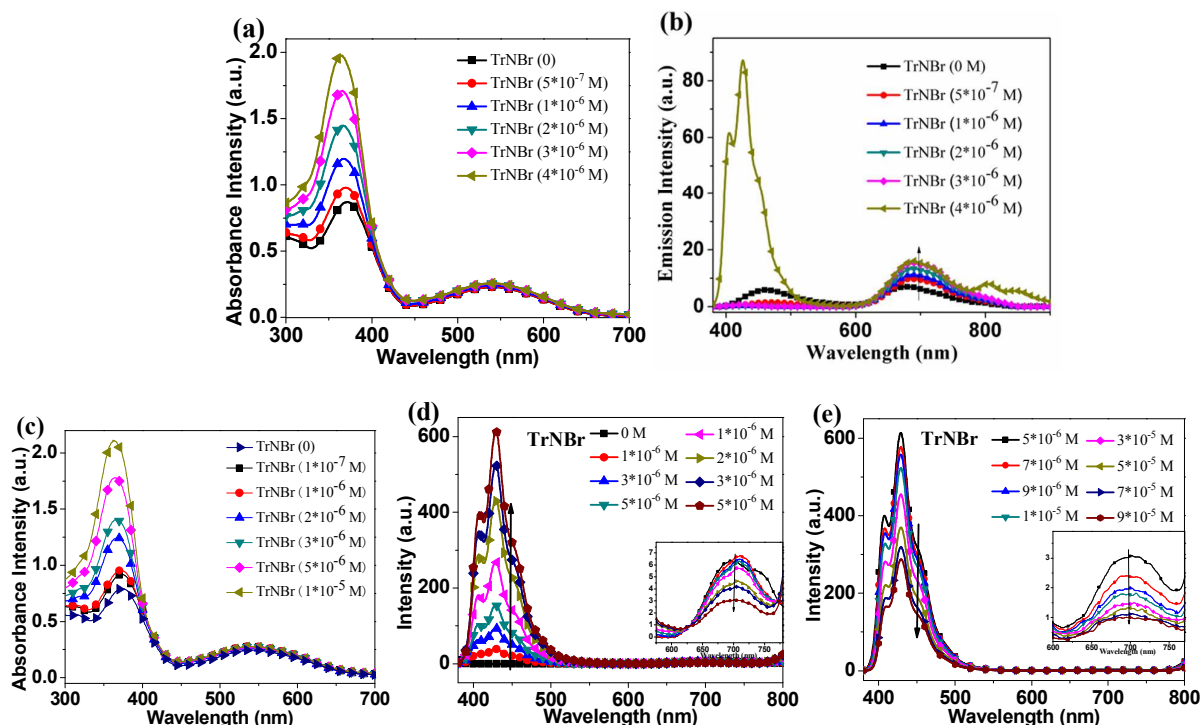




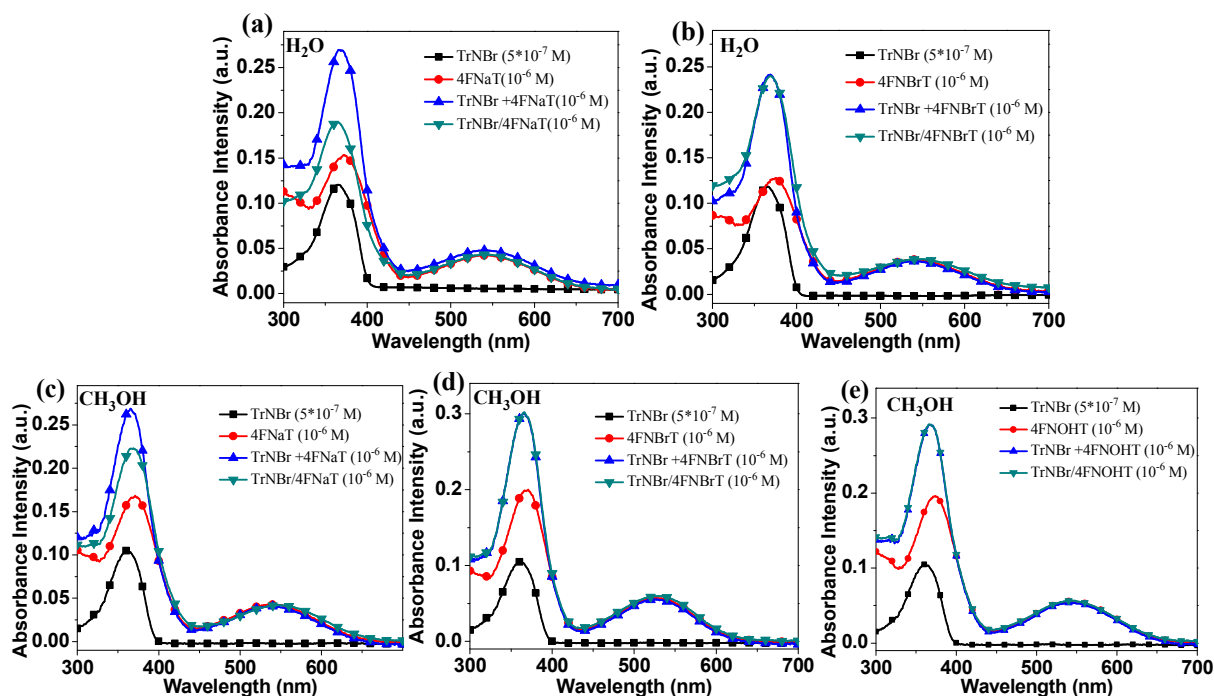
**Figure S9.** The changes of emission spectra of the systems ([TrNBBr] (a), [TrNBBr]:[4FNaT] = 1:1 (b, c), [TrNBBr]:[4FNOHT] = 1:1 (d, e) and [TrNBBr]:[4FNaBrT] = 1:1 (f, g)) with their simultaneous increasing concentrations in CH<sub>3</sub>OH. The emission spectra were collected at  $\lambda_{ex}$  = 360 nm.



**Figure S10.** Absorption spectra of TrNBBr ( $5 \times 10^{-7}$  M) with increasing concentrations of 4FNaT (a), 4FNaBrT (b) in H<sub>2</sub>O and increasing concentrations of 4FNaT (c), 4FNOHT (d), 4FNaBrT (e) in CH<sub>3</sub>OH. The emission spectra were collected at  $\lambda_{ex}$  = 361 nm (H<sub>2</sub>O) and  $\lambda_{ex}$  = 360 nm (CH<sub>3</sub>OH).

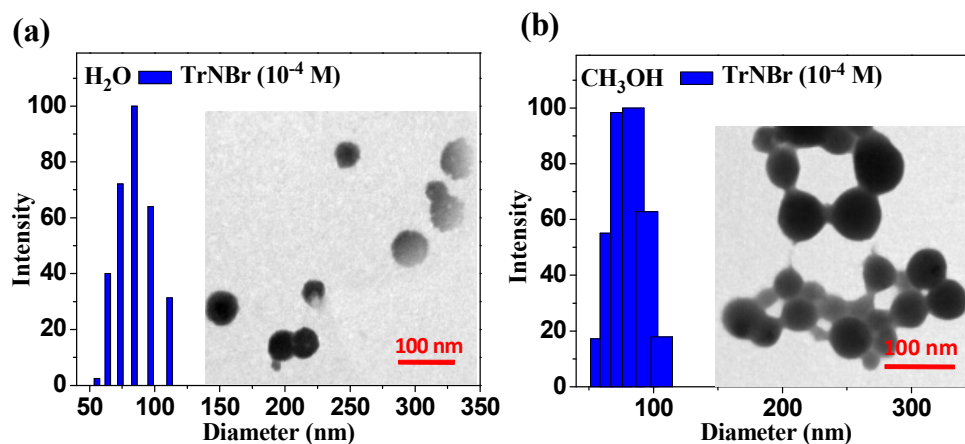


**Figure S11.** Absorption and emission spectra of 4FNaT ( $10^{-5}$  M) (a, b) and 4FNBrT ( $10^{-5}$  M) (c, d, e) in  $H_2O$  with increasing concentrations of TrNBr. The emission spectra were collected at  $\lambda_{ex} = 361$  nm.



**Figure S12.** Absorption spectra of TrNBr ( $5 \times 10^{-7}$  M), 4FTs ( $10^{-6}$  M) and TrNBr/4FTs mixed

system. The sum of TrNBr and 4FTs absorption spectra is also presented. (a) 4FTs = 4FNaT in H<sub>2</sub>O; (b) 4FTs = 4FNBrT in H<sub>2</sub>O; (c) 4FTs = 4FNaT in CH<sub>3</sub>OH; (d) 4FTs = 4FNBrT in CH<sub>3</sub>OH; (e) 4FTs = 4FNOHT in CH<sub>3</sub>OH.



**Figure S13.** DLS analysis of TrNBr in H<sub>2</sub>O (a) and CH<sub>3</sub>OH (b) with the inset showing the corresponding TEM images.

- (1) Xu, W. D.; Kan, Z. P.; Ye, T. L.; Zhao, L.; Lai, W. -Y.; Xia, R. D.; Lanzani, G.; Keivanidis, P. E.; Huang, W. Well-Defined Star-Shaped Conjugated Macroelectrolytes as Efficient Electron-Collecting Interlayer for Inverted Polymer Solar Cells. *ACS Appl. Mater. Interfaces* **2015**, *7*, 452-659.