

# Supporting Information

*for*

**Dual-stimuli responsive fluorescent supramolecular polymer based on a diselenium-bridged pillar[5]arene dimer and an AIE-active tetraphenylethylene guest**

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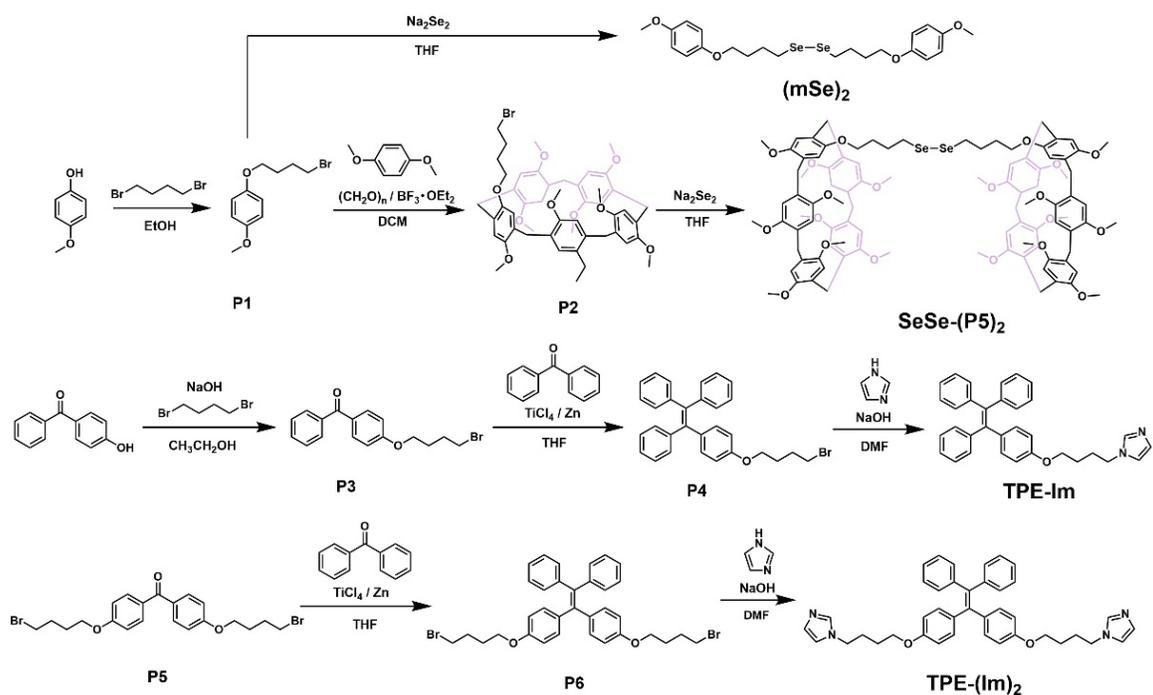
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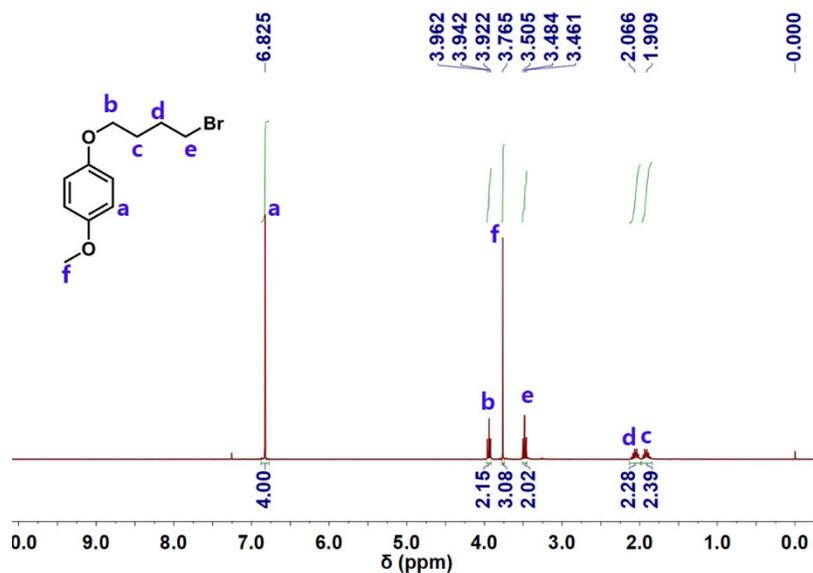
## Syntheses of $\text{SeSe-(P5)}_2$ , $\text{TPE-(Im)}_2$ , $\text{TPE-Im}$ and $(\text{mSe})_2$



**Scheme 1.** Synthetic procedures of  $\text{SeSe-(P5)}_2$ ,  $\text{TPE-(Im)}_2$ ,  $\text{TPE-Im}$  and  $(\text{mSe})_2$

**P1:** 4-Methoxyphenol (12.4 g, 0.1 mol) and  $\text{K}_2\text{CO}_3$  (22 g, 0.16 mol) were dispersed in acetonitrile (200 mL) and the mixture was stirred at room temperature for 30 min. Then, KI (0.2 g, 10 mmol) and excess 1, 4-dibromobutane (14.2 mL, 0.12 mol) were added to the solution. The mixture was added to reflux condenser and reacted for 16 hours. The solution was concentrated under vacuum, and subjected to silica gel chromatography (10:1 petroleum ether (PE) / ethyl acetate (EA)) to give the product 1-(4-bromobutyl-4-methoxybenzene) **P1** (17.87 g, yield: 90%).

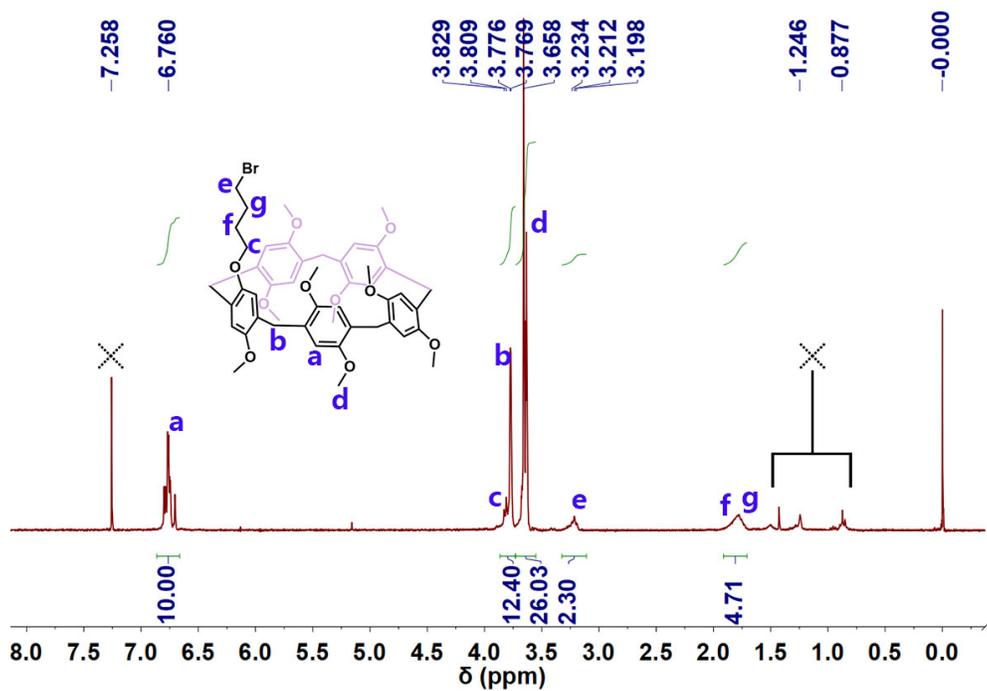
$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.825 (s, 4H), 3.942 (t, 2H), 3.765 (s, 3H), 3.484 (t, 2H), 2.124 – 2.011 (m, 2H), 1.958 – 1.873 (m, 2H).



**Figure S1.**  $^1\text{H}$  NMR (300 MHz, 298 K,  $\text{CDCl}_3$ ) spectrum of **P1**.

**P2:** **P1** (1.04 g, 4 mmol), 1,4-dimethoxybenzene (2.75 g, 20 mmol),  $(\text{CH}_2\text{O})_n$  (2.52 g, 84 mmol) and dichloromethane (DCM, 180 mL) were added into a flask under ice-water bath and stirred for 30 min. Then  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  (3.6 mL) was added into the flask. After the color of solution changed from white to light yellow to olivine to dark-green (ca. 40 min), water (300 mL) was poured into solution to quench the reaction. The pure monobromo-substituted pillar[5]arene product was obtained as white power (556 mg, yield: 15%) over silicon gel column chromatography (PE:DCM:EA=90:30:1).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.814 – 6.691 (m, 10H), 3.865 – 3.738 (m, 12H), 3.714 – 3.552 (m, 27H), 3.212 (t, 2H), 1.913 – 1.716 (m, 4H).



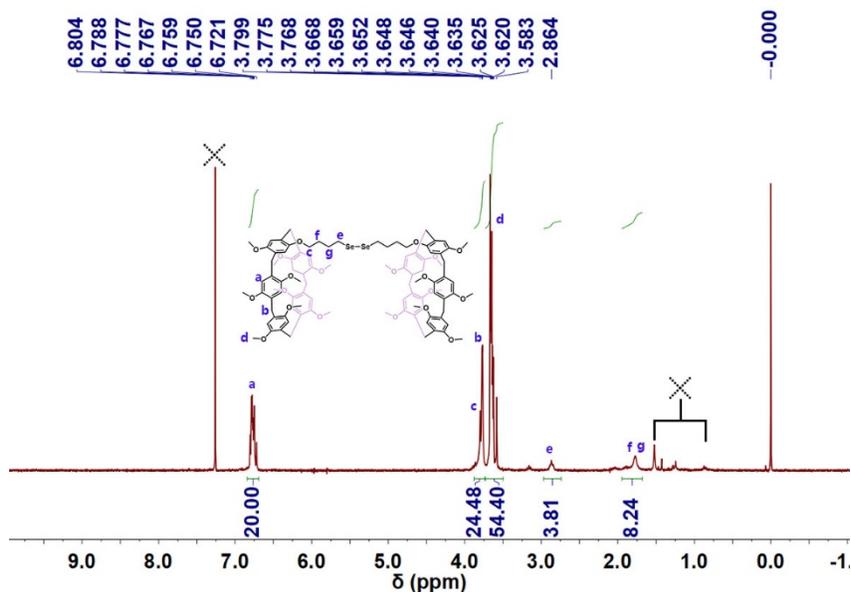
**Figure S2.**  $^1\text{H}$  NMR (300 MHz, 298 K,  $\text{CDCl}_3$ ) spectrum of **P2**.

**SeSe-(P5)<sub>2</sub>**: First, Na<sub>2</sub>Se<sub>2</sub> solution was obtained by dissolving NaBH<sub>4</sub> (37.87 mg, 1 mmol) into H<sub>2</sub>O (3 mL) and then adding Se (78.96 mg, 1 mmol) into the solution. The solution was crimson after reacting for about 15 minutes.

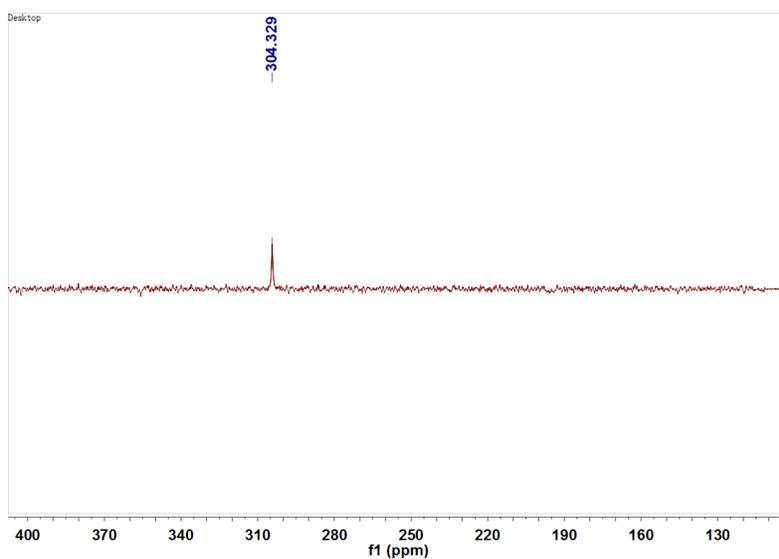
Then, **P2** (0.51g) and THF (30 mL) were added into the crimson solution, after that, the temperature was increased to 50 °C and maintained for 10 hours. During this period, the solution changes from crimson to yellow. After silicon gel column chromatography (PE:DCM:EA=15:10:1), the final Se-Se-bridged bis(pillar[5]arene)s product was obtained as yellow power (962 mg, yield: 90%).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 6.824 – 6.690 (m, 20H), 3.854 - 3.735 (m, 24H), 3.722 – 3.545 (m, 54H), 2.868 (t, 4H), 1.899 – 1.690 (m, 8H).

<sup>77</sup>Se NMR (95 MHz, CDCl<sub>3</sub>): δ 304.329.



**Figure S3.** <sup>1</sup>H NMR (300 MHz, 298 K, CDCl<sub>3</sub>) spectrum of SeSe-(P5)<sub>2</sub>.



**Figure S4.** <sup>77</sup>Se NMR (500 MHz, 298 K, CDCl<sub>3</sub>) spectrum of SeSe-(P5)<sub>2</sub>.

**P3:** 4-Hydroxybenzophenone (4.95 g, 25 mmol) and NaOH (1 g, 25 mmol) were dissolved in EtOH (240 mL) and added into a flask. After stirred for 30 mins at the room temperature, 1,4-dibrombutane (8.9 mL, 75 mmol) was added into the flask. The mixture was stirred at 85 °C for 14 h. After the reaction mixture was cooled to room temperature, EtOH was evaporated and the raw product was purified by column chromatography with PE: EA = 20:1. The final product was obtained as a white solid (6.2 g, yield: 85%).

$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.929 – 7.684 (dd, 4H), 7.634 – 7.385 (m, 3H), 6.951 (d, 2H), 4.088 (t, 2H), 3.507 (t, 2H), 2.244 – 1.912 (m, 4H).

$^{13}\text{C NMR}$  (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  195.51, 162.51, 138.28, 132.57, 131.89, 130.19, 129.71, 128.19, 113.99, 77.26, 77.04, 76.83, 67.13, 33.28, 29.36, 27.77.

HRESIMS is shown in Figure S7:  $m/z$  calcd for  $[\text{P3}+\text{H}]^+ \text{C}_{17}\text{H}_{17}\text{BrO}_2$ , 335.0465; found 335.0454.

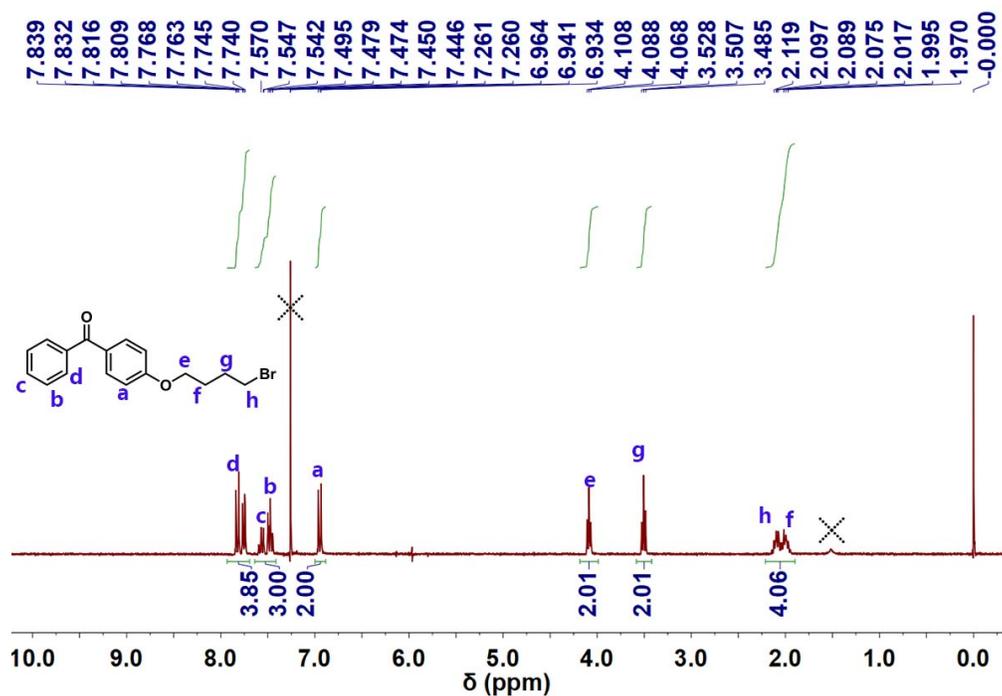
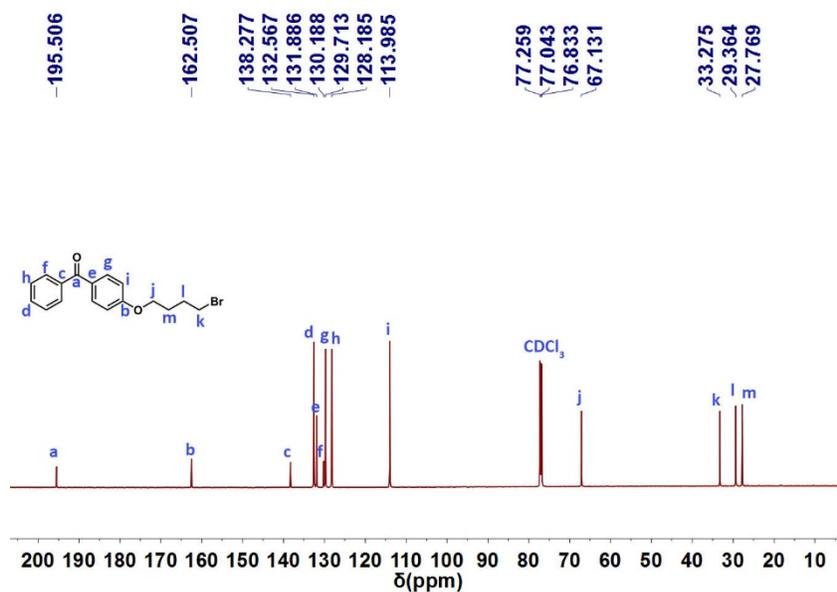


Figure S5.  $^1\text{H NMR}$  (300 MHz, 298 K,  $\text{CDCl}_3$ ) spectrum of P3.



**Figure S6.**  $^{13}\text{C}$  NMR (151 MHz, 298 K,  $\text{CDCl}_3$ ) spectrum of **P3**.



**Figure S7.** HRESIMS of **P3**.

**P4:** Dry THF (200 mL) and Zn (6.8g, 100 mmol) were added into a flask. Then  $\text{TiCl}_4$  (6.6 ml, 60 mmol) was added dropwise in ice bath. After 30 minutes, **P3** (3.33 g, 10 mmol) and benzophenone (1.82 g, 10 mmol) were dissolved in dry THF (40 mL) and added into the reaction flask, then the mixture was reacted at 85 °C for 8h. After that,  $\text{K}_2\text{CO}_3$  (8.3 g, 60 mmol) dissolved in water and added to quench the reaction. Then the reaction mixture was filtered off and the filtrate was collected. THF was evaporated from the filtrate and the crude product was extracted by DCM. After removing DCM, the crude product was purified by column chromatography (PE:DCM = 4:1) to give a white powder (1.1g, yield: 21%).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.193 – 6.839 (m, 16H), 6.614 (d, 2H), 3.914 (t, 2H), 3.472 (t, 2H), 2.164 – 1.812 (m, 4H).

$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  157.39, 144.04, 143.98, 140.51, 140.12, 136.20, 132.56, 131.40, 131.36, 131.34, 127.73, 127.61, 126.37, 126.25, 113.56, 66.63, 33.51, 29.52, 27.94.

HRESIMS is shown in Figure S10:  $m/z$  calcd for  $[\text{P4}+\text{H}]^+ \text{C}_{30}\text{H}_{27}\text{BrO}$ , 485.1302; found 485.1265.

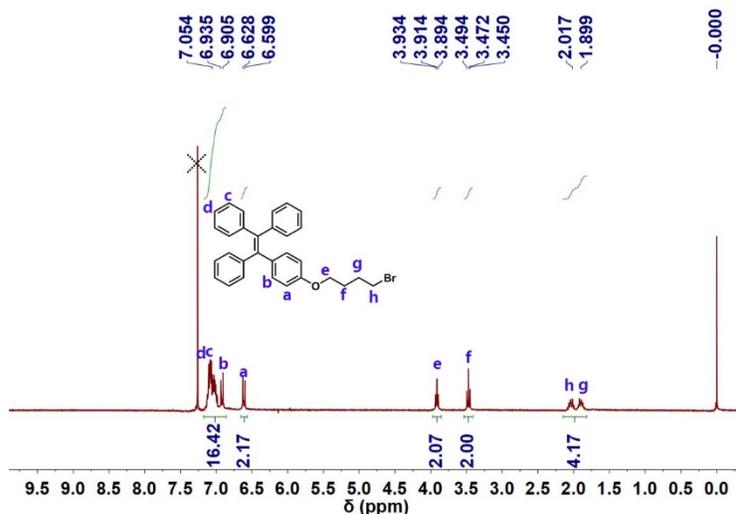


Figure S8.  $^1\text{H}$  NMR (300 MHz, 298 K,  $\text{DMSO}-d_6$ ) spectrum of P4.

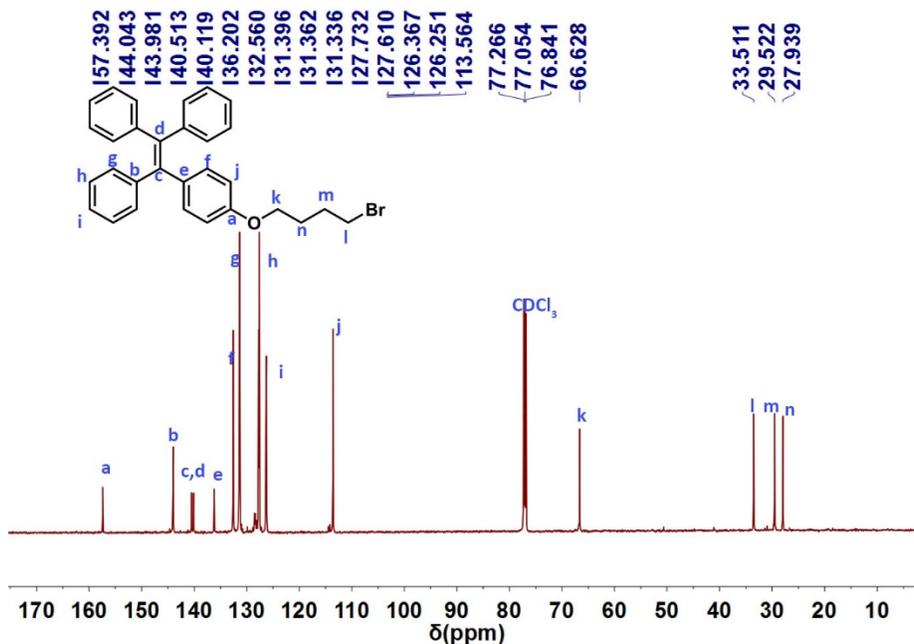


Figure S9.  $^{13}\text{C}$  NMR (151 MHz, 298 K,  $\text{DMSO}-d_6$ ) spectrum of P4.

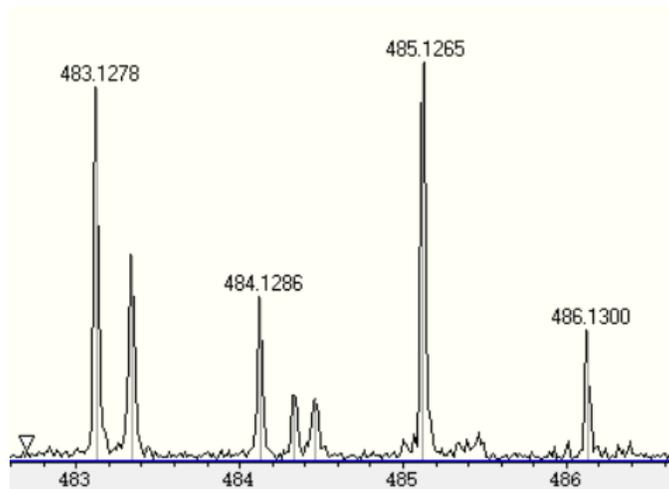


Figure S10. HRESIMS of P4.

**P5:** 4,4-Dihydroxybenzophenone (4.28 g, 20 mmol) and NaOH (1.6 g, 40 mmol) were dissolved in 240 mL EtOH and kept stirring for 30 mins at the room temperature. Then, 1,4-dibrombutane (14.2 mL, 120 mmol) was added and stirred at 85 °C for 14h. The raw product was filter off and filter cake was collected. After washing with EtOH and water for 3 times, white solid was obtained (8.3 g, yield: 87%).

$^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ ):  $\delta$  7.704 (d, 4H), 7.083 (d, 4H), 4.121 (t, 4H), 3.627 (t, 4H), 2.094 – 1.811 (m, 8H).

$^{13}\text{C}$  NMR (151 MHz, DMSO- $d_6$ ):  $\delta$  193.58, 162.30, 132.27, 130.45, 114.66, 67.47, 35.24, 29.49, 27.75, 19.02.

HRESIMS is shown in Figure S13:  $m/z$  calcd for  $[\text{P5}+\text{H}]^+ \text{C}_{21}\text{H}_{24}\text{Br}_2\text{O}_3$ , 485.0146; found 485.0213.

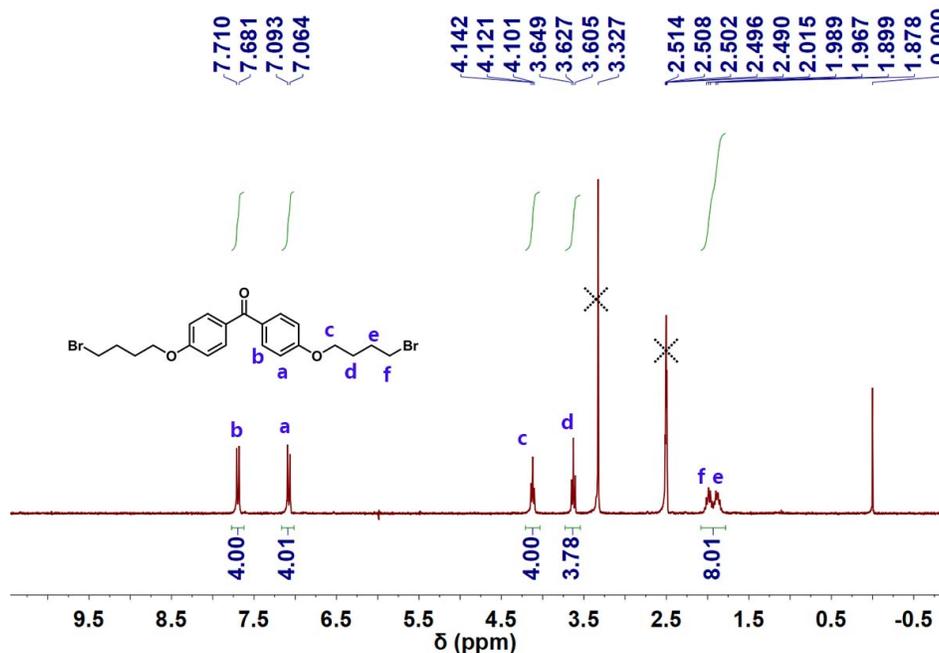


Figure S11.  $^1\text{H}$  NMR (300 MHz, 298 K,  $\text{CDCl}_3$ ) spectrum of P5.

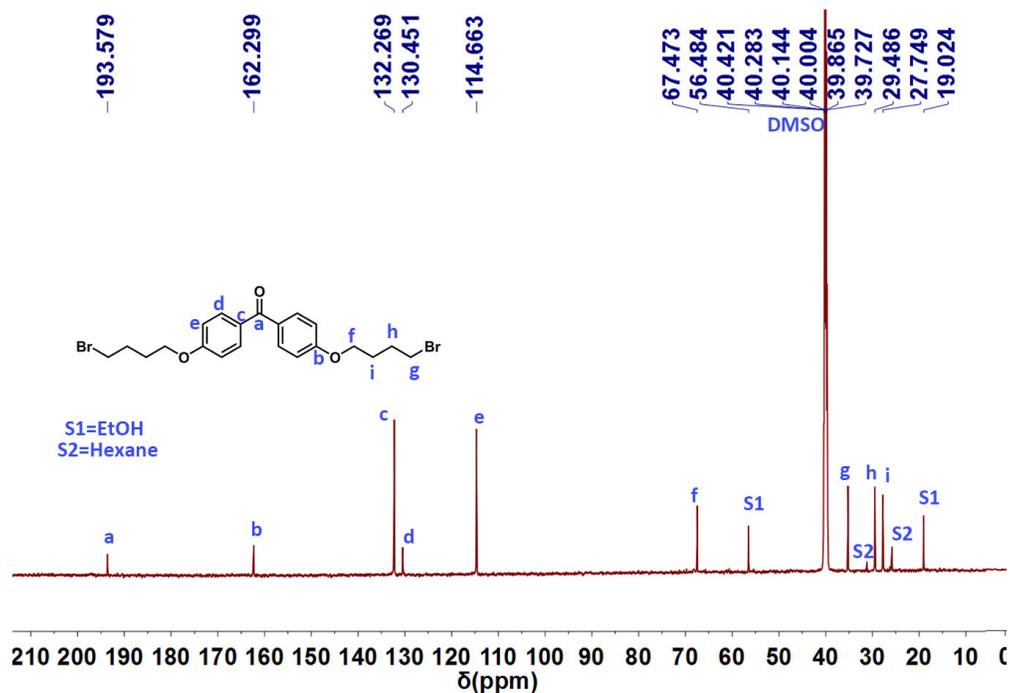


Figure S12.  $^{13}\text{C}$  NMR (151 MHz, 298 K,  $\text{CDCl}_3$ ) spectrum of P5.

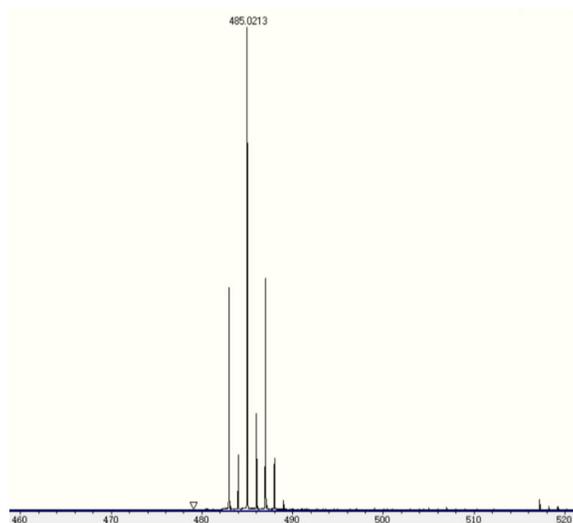


Figure S13. HRMSIMS of P5.

**P6:** Dry THF (200 mL) and Zn (3.4g, 50 mmol) were added into a flask. Then  $\text{TiCl}_4$  (3.3 mL, 30 mmol) was added dropwise under ice bath. After 30 mins, **P5** (2.42 g, 5 mmol) and benzophenone (0.91 g, 5 mmol) were dissolved in dry THF (40 mL) and added into the flask. Then the temperature was increased to 85 °C and kept for 6h.  $\text{K}_2\text{CO}_3$  (8g) and water were added to quench the reaction, and then the reaction mixture was filtered off and the filtrate was collected. THF was evaporated from the filtrate and the crude product was extracted by DCM. After removing DCM, the crude product was purified by column chromatography (PE:DCM = 5:1) to give a white power (0.8 g, yield: 25%).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  7.166 – 6.887 (m, 14H), 6.613 (d, 4H), 3.914 (t, 4H), 3.470 (t, 4H), 2.301 – 1.693 (m, 8H).

$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  157.35, 144.28, 140.04, 139.26, 136.42, 132.60, 131.36, 127.67, 126.07, 113.51, 66.62, 33.51, 29.51, 27.93.

HRESIMS is shown in Figure S16:  $m/z$  calcd for  $[\text{P6}] \text{C}_{34}\text{H}_{34}\text{Br}_2\text{O}_2$ , 634.0902; found 634.0912.

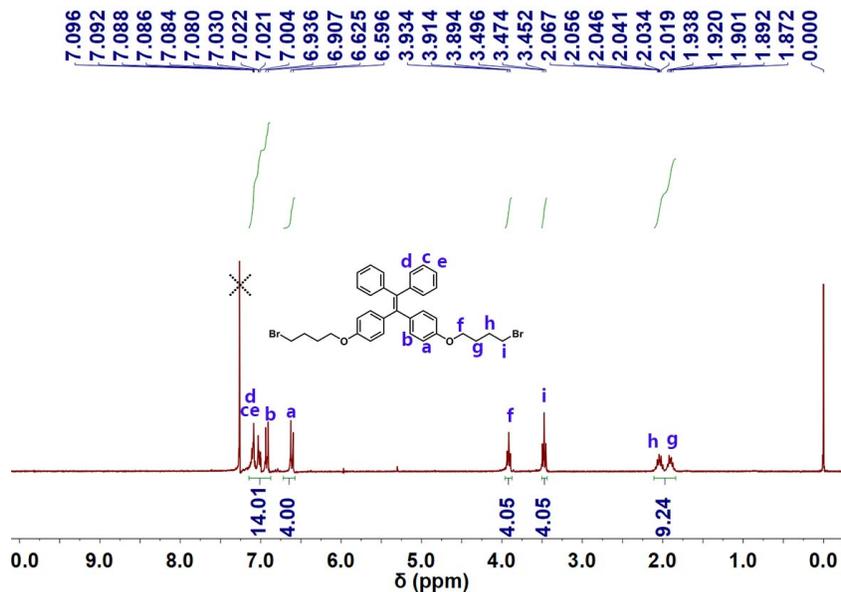


Figure S14.  $^1\text{H}$  NMR (300 MHz, 298 K,  $\text{CDCl}_3$ ) spectrum of P6.

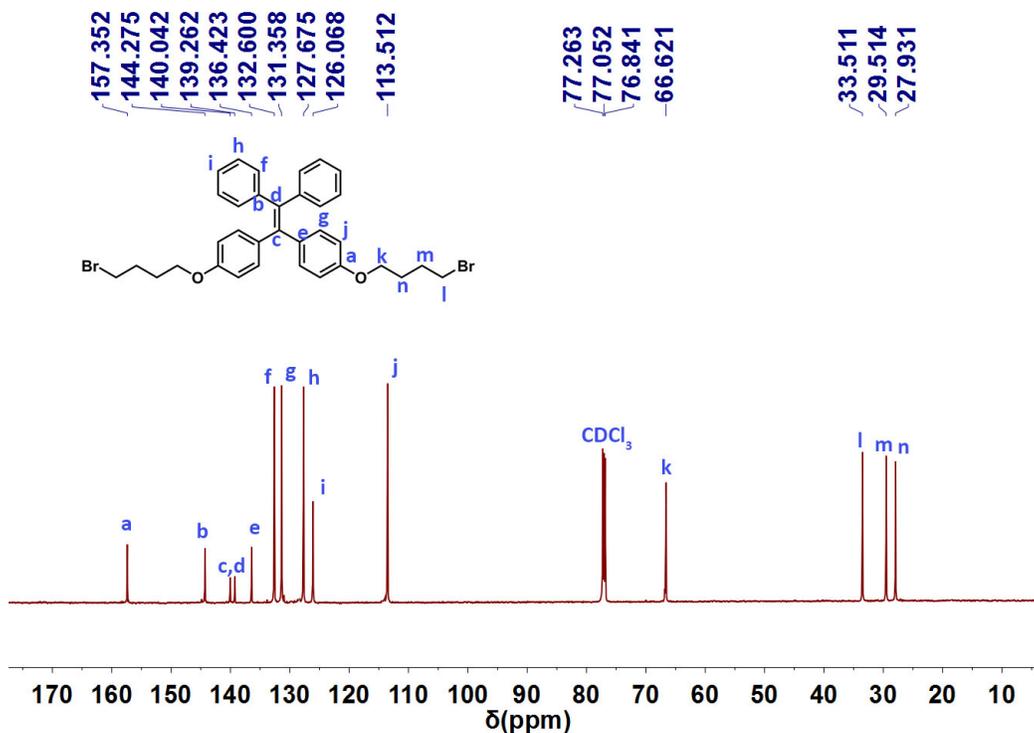
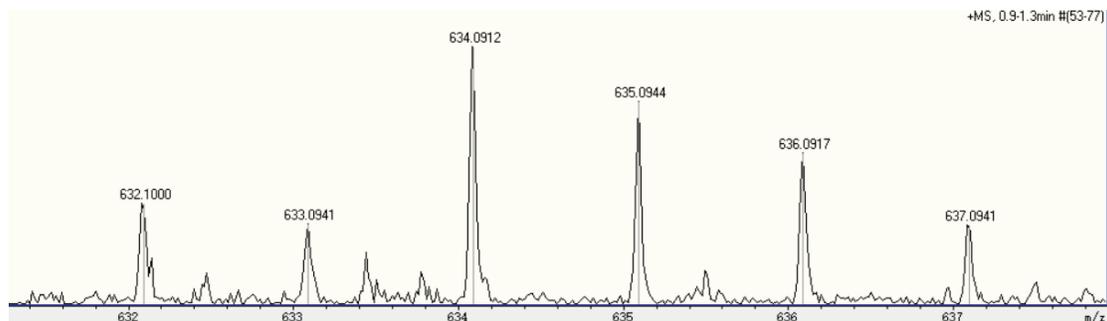


Figure S15.  $^{13}\text{C}$  NMR (151 MHz, 298 K,  $\text{CDCl}_3$ ) spectrum of P6.



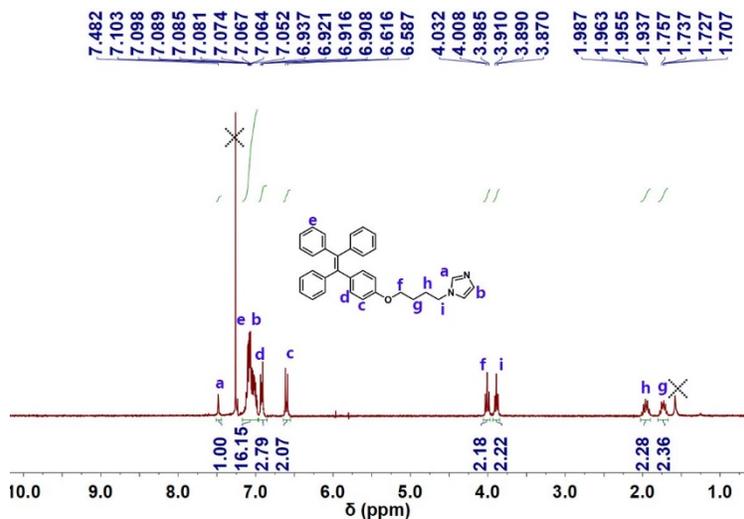
**Figure S16.** HRESIMS of **P6**.

**TPE-Im:** A mixture of NaOH (328 mg, 8.2 mmol) and imidazole (558 mg, 8.2 mmol) in dimethylformamide (DMF, 5 mL) was heated at 60 °C for 2 h, followed that, **P4** (397 mg, 0.82 mmol) was added. The resulting mixture was maintained at 60 °C for another 2h. And then brine (100 mL) was added into the mixture. After extraction with diethyl ether for three times, the combined organic phase was washed with brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed by rotary evaporation to afford product as pale yellow solid (355 mg, yield: 92%).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298 K): δ 7.482 (s, 1H), 7.185 – 6.504 (m, 18H), 6.602 (d, 2H), 4.008 (t, 2H), 3.890 (t, 2H), 2.037 – 1.891 (m, 2H), 1.816 – 1.655 (m, 2H).

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>, 298 K): δ 157.24, 144.00, 143.92, 140.43, 140.18, 136.98, 136.33, 132.58, 131.36, 131.32, 128.97, 127.72, 127.60, 126.37, 126.25, 118.85, 113.51, 66.88, 46.91, 28.09, 26.27.

HRESIMS is shown in Figure S19: m/z calcd for [TPE-Im+H]<sup>+</sup> C<sub>33</sub>H<sub>30</sub>N<sub>2</sub>O, 471.2430; found 471.2413.



**Figure S17.** <sup>1</sup>H NMR (300 MHz, 298 K, CDCl<sub>3</sub>) spectrum of **TPE-Im**.

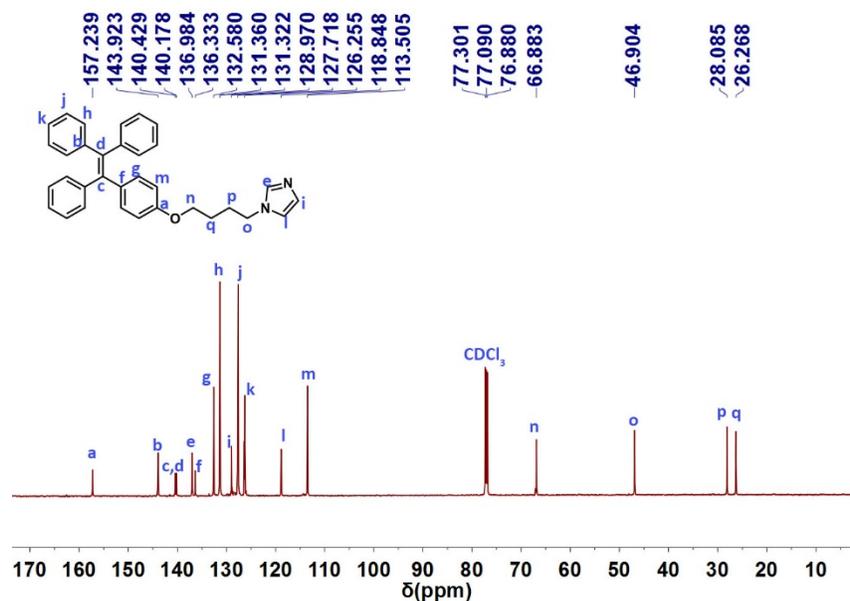


Figure S18.  $^{13}\text{C}$  NMR (151 MHz, 298 K,  $\text{CDCl}_3$ ) spectrum of TPE-Im.

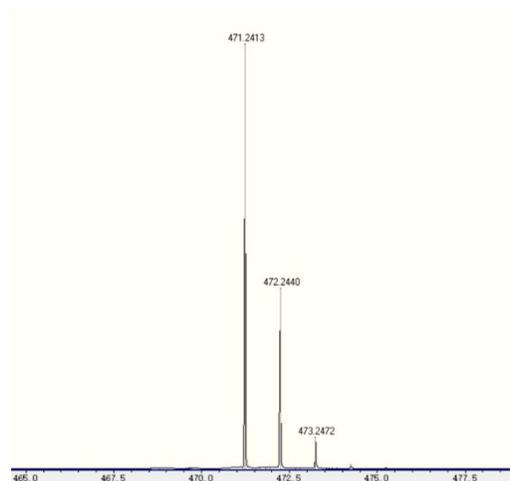


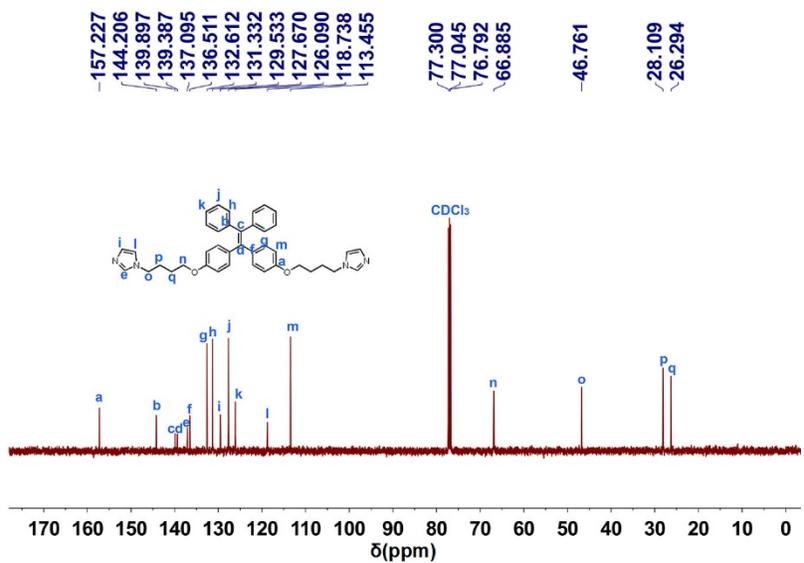
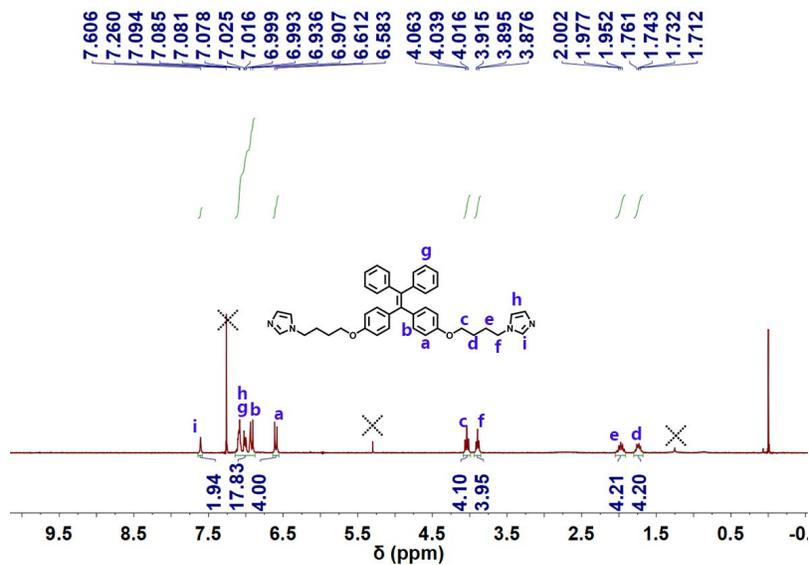
Figure S19. HRESIMS of TPE-Im.

**TPE-(Im)<sub>2</sub>**: A mixture of NaOH (200 mg, 5 mmol) and imidazole (340 mg, 5 mmol) in DMF (5mL) was heated at 60 °C for 2 h, then **P6** (150 mg, 0.25 mmol) was added into the mixture. The mixture was continue heated at 60 °C for another 2h. And then 100 mL brine was added into the mixture. After extraction with diethyl ether for three times, the combined organic phase was washed with brine and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was removed by rotary evaporation to afford product TPE-(Im)<sub>2</sub> as pale yellow solid (140 mg, yield: 92%).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  7.606 (s, 2H), 7.159 – 6.877 (m, 18H), 6.612 (d, 4H), 4.039 (t, 4H), 3.895 (t, 4H), 2.075 – 1.895 (m, 4H), 1.816 – 1.636 (m, 4H).

$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  157.23, 144.21, 139.90, 139.39, 137.09, 136.51, 132.61, 131.33, 129.53, 127.67, 126.09, 118.74, 113.46, 77.30, 77.05, 76.79, 66.89, 46.76, 28.11, 26.29.

HRESIMS is shown in Figure S22: m/z calcd for  $[\text{TPE}-(\text{Im})_2+\text{H}]^+$   $\text{C}_{40}\text{H}_{40}\text{N}_4\text{O}_2$ , 609.3224; found 609.3221.



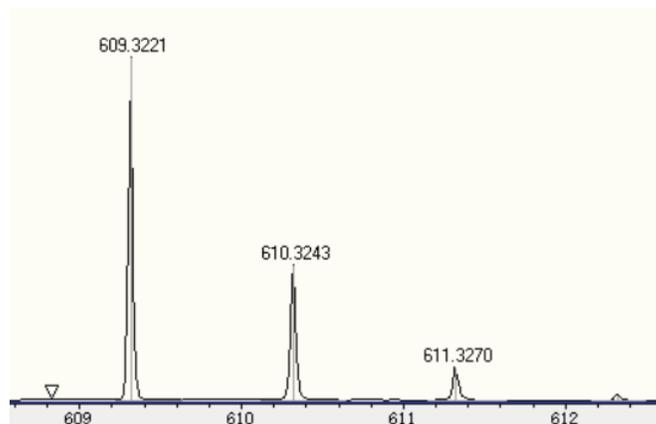


Figure S22. HRESIMS of TPE-(Im)<sub>2</sub>.

**(mSe)<sub>2</sub>**: First, Na<sub>2</sub>Se<sub>2</sub> solution was obtained by dissolving NaBH<sub>4</sub> (37.87 mg, 1 mmol) into H<sub>2</sub>O (3 mL) and then adding Se (78.96 mg, 1 mmol) into the solution. The solution was crimson after reacting for about 15 minutes.

Then, **P1** (0.26 g, 1 mmol) and DMF (30 mL) were added into the crimson solution, after that, the temperature was increased to 50 °C and maintained for 10 hours. During this period, the solution changes from crimson to yellow. After silicon gel column chromatography (PE:EA=20:1), (mSe)<sub>2</sub> was obtained as yellow powder (464 mg, yield: 90%).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298 K): δ 6.821 (s, 8H), 3.929 (t, 4H), 3.763 (s, 6H), 2.983 (t, 4H), 1.933-1.842 (m, 8H).

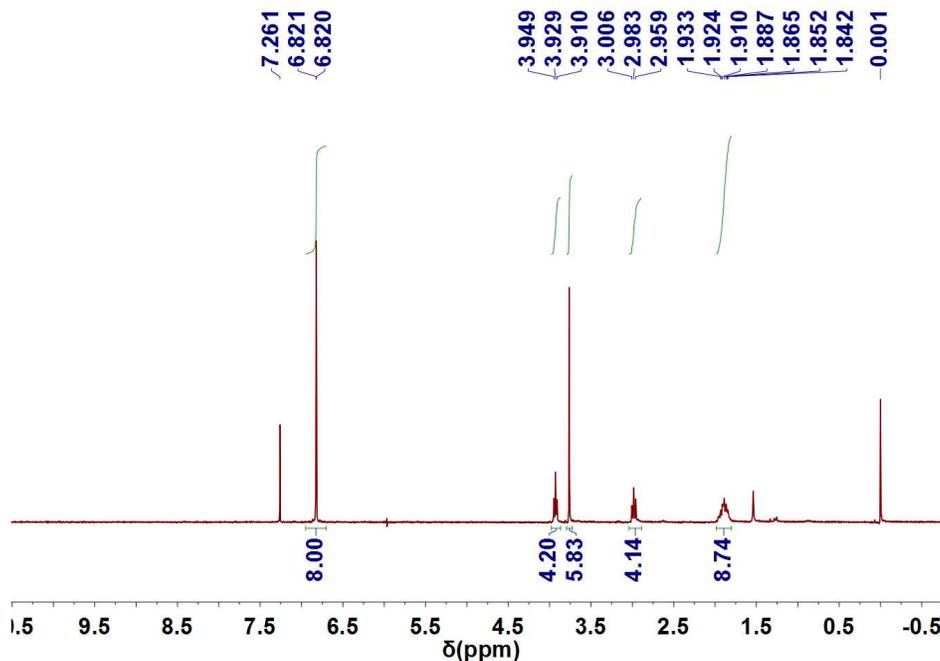
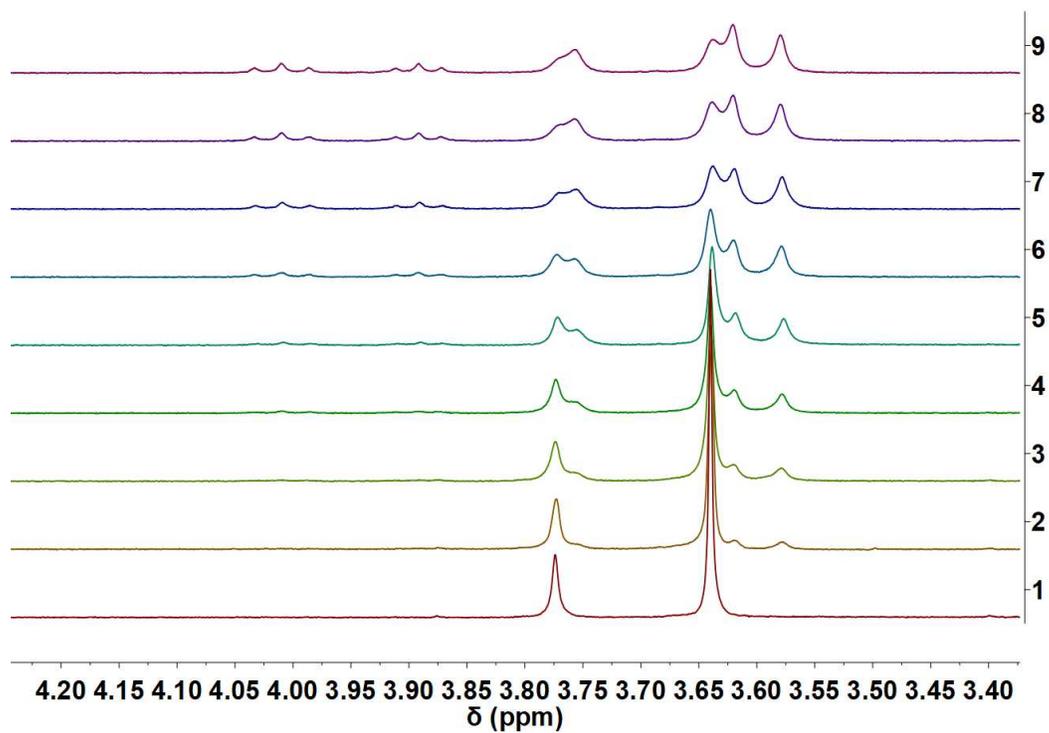


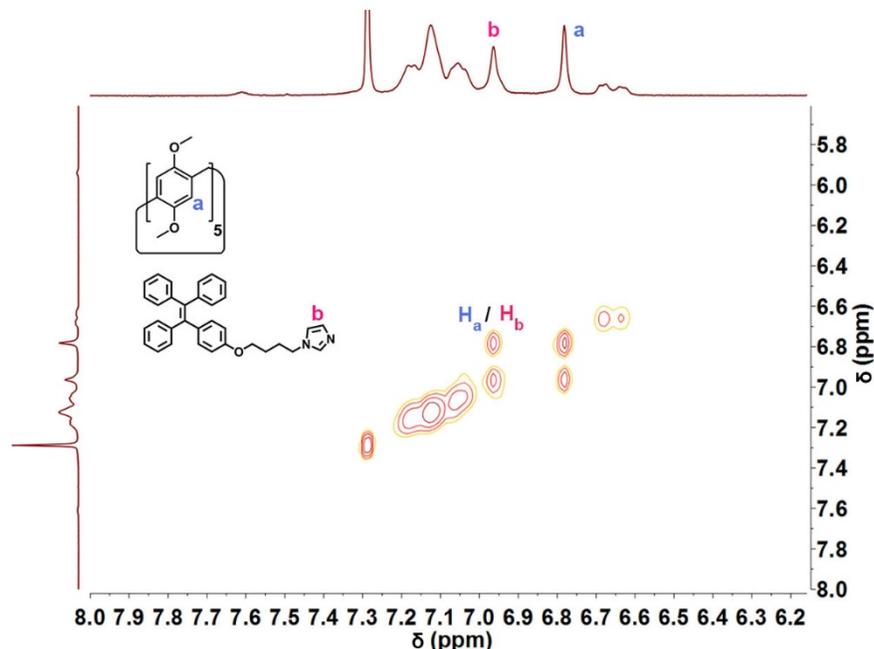
Figure S23. <sup>1</sup>H NMR (300 MHz, 298 K, CDCl<sub>3</sub>) spectrum of (mSe)<sub>2</sub>.

## NMR titration test of DMP[5] with TPE-Im



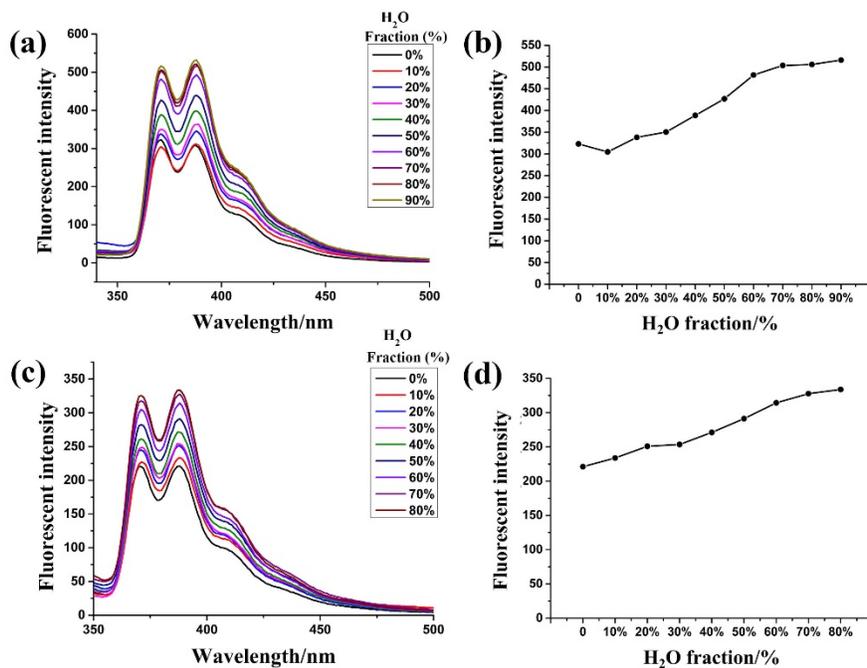
**Figure S24.** <sup>1</sup>H NMR (300 MHz, 298 K, CDCl<sub>3</sub>) titration test of **DMP[5]** (fixed concentration, 2 mM) upon addition of **TPE-Im** (from 0 to 2 mM gradually raised).

## 2D nuclear Overhauser effect NMR spectroscopy of DMP[5] with TPE-Im



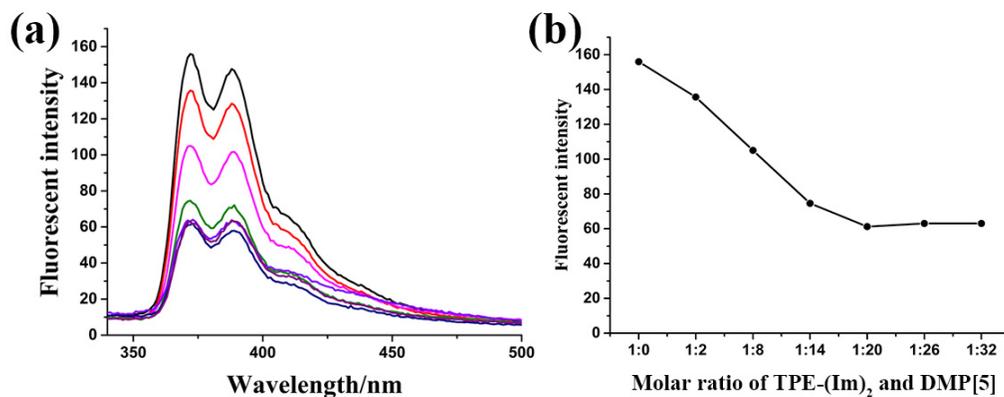
**Figure S25.** Partial NOESY spectrum (600 MHz,  $\text{CDCl}_3$ , 298 K, concentration = 2 mM) of **DMP[5]** and **TPE-Im**.

### Contrast/control fluorescent experiments

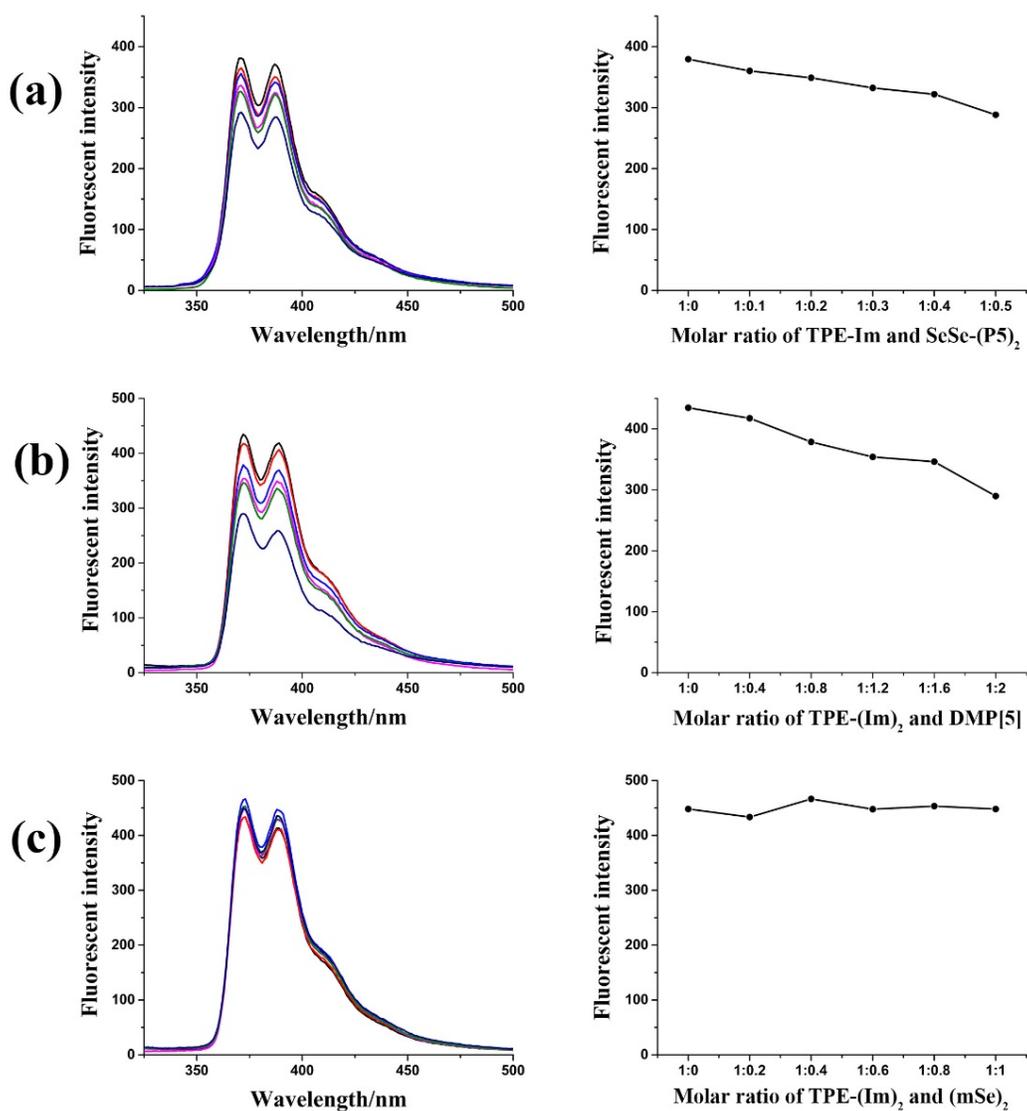


**Figure S26.** Fluorescent emission spectra of (a) **TPE-(Im)<sub>2</sub>** (8  $\mu\text{M}$ ;  $\lambda_{\text{ex}} = 265 \text{ nm}$ ;  $\lambda_{\text{em}} = 372 \text{ nm}$ ; slit widths: ex. 5 nm, em. 5 nm; 25  $^\circ\text{C}$ ) and (c) **P6** (8  $\mu\text{M}$ ;  $\lambda_{\text{ex}} = 268 \text{ nm}$ ;  $\lambda_{\text{em}} = 370 \text{ nm}$ ; slit widths: ex. 5 nm, em. 5 nm; 25  $^\circ\text{C}$ ) in the mixed solvent of THF- $\text{H}_2\text{O}$  with different fractions of  $\text{H}_2\text{O}$  ranging from 0 to 90% or 0 to 80%.

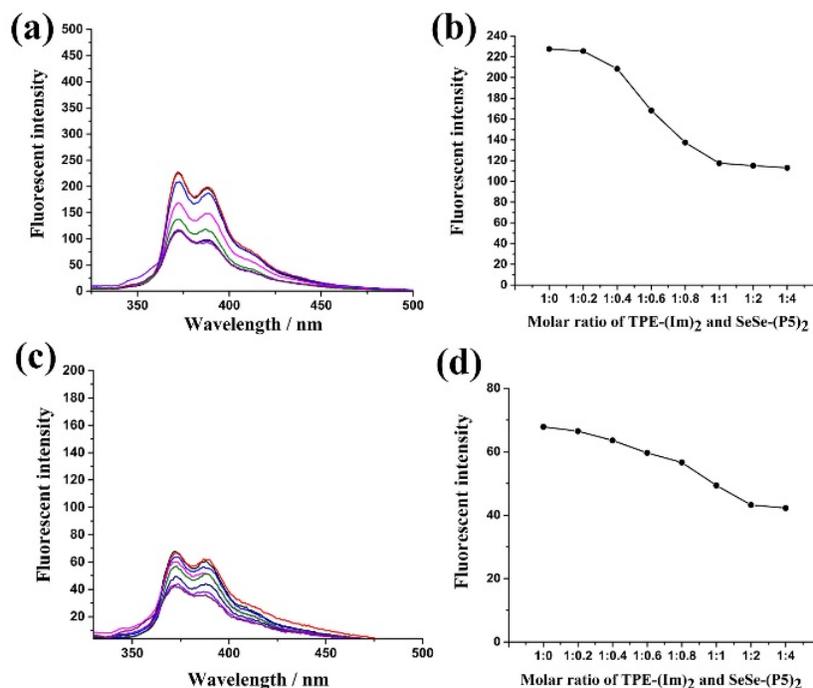
A plot of fluorescence intensity of (b) **TPE-(Im)<sub>2</sub>** and (d) **P6** at 372 nm or 370 nm vs. the fraction of H<sub>2</sub>O in the mixed solvent of THF-H<sub>2</sub>O.



**Figure S27.** (a) Fluorescent emission spectra of mixed **TPE-(Im)<sub>2</sub>** and excessive **DMP[5]** ( $\lambda_{\text{ex}} = 265$  nm;  $\lambda_{\text{em}} = 372$  nm; slit widths: ex. 5 nm, em. 5 nm; 25 °C, fixed  $[\text{TPE-(Im)}_2] = 5 \mu\text{M}$ ). (b) A plot of fluorescence intensity at 372 nm versus molar ratio of **TPE-(Im)<sub>2</sub>** and **DMP[5]**.

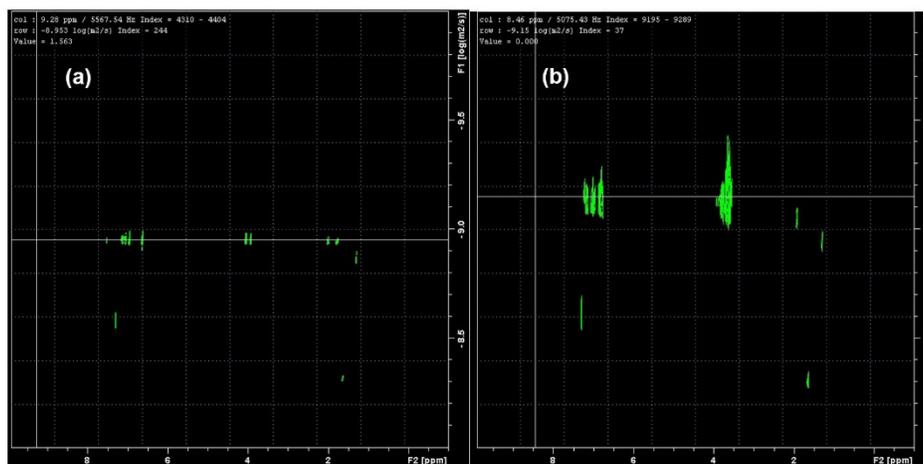


**Figure S28.** Fluorescent intensity spectra of different control host-guest pairs at various molar ratio ( $\lambda_{\text{ex}} = 265 \text{ nm}$ ;  $\lambda_{\text{em}} = 372 \text{ nm}$ ; slit widths: ex. 5 nm, em. 5 nm; 25 °C) and its plot graph at 372 nm. (a) Fixed [TPE-Im] = 10  $\mu\text{M}$ , [SeSe-(P5)<sub>2</sub>] = 0, 1, 2, 3, 4 and 5  $\mu\text{M}$  from top to bottom; (b) Fixed [TPE-(Im)<sub>2</sub>] = 10  $\mu\text{M}$ , [DMP[5]] = 0, 4, 8, 12, 16 and 20  $\mu\text{M}$  from top to bottom; (c) Fixed [TPE-(Im)<sub>2</sub>] = 10  $\mu\text{M}$ , [(mSe)<sub>2</sub>] = 0, 2, 4, 6, 8 and 10  $\mu\text{M}$  from top to bottom.

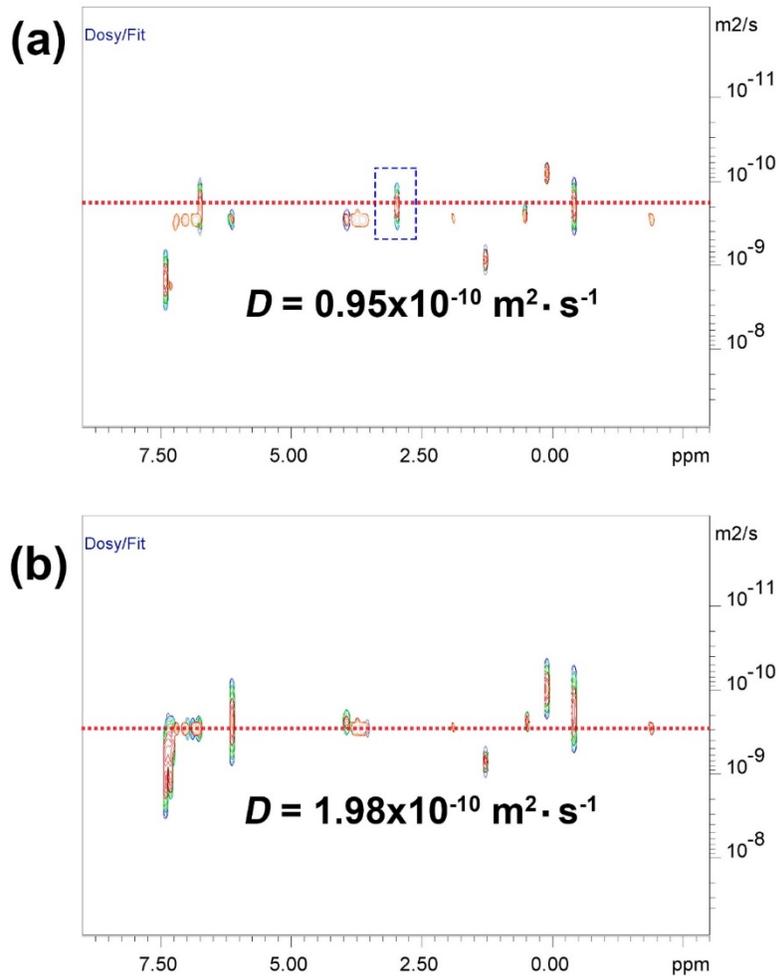


**Figure S29.** Fluorescence emission spectra of the host-guest supramolecular polymer system in  $\text{CHCl}_3$  at various concentrations of TPE-(Im)<sub>2</sub> and SeSe-(P5)<sub>2</sub> pairs ( $\lambda_{\text{ex}} = 265 \text{ nm}$ ;  $\lambda_{\text{em}} = 372 \text{ nm}$ ; slit widths: ex. 5 nm, em. 5 nm; 25 °C). (a) [TPE-(Im)<sub>2</sub>] = 5  $\mu\text{M}$ , fixed for all traces; [SeSe-(P5)<sub>2</sub>] = 0  $\mu\text{M}$ , 1  $\mu\text{M}$ , 2  $\mu\text{M}$ , 3  $\mu\text{M}$ , 4  $\mu\text{M}$ , 5  $\mu\text{M}$ , 10  $\mu\text{M}$ , 20  $\mu\text{M}$  from top to bottom). (c) [TPE-(Im)<sub>2</sub>] = 1  $\mu\text{M}$ , fixed for all traces; [SeSe-(P5)<sub>2</sub>] = 0  $\mu\text{M}$ , 0.2  $\mu\text{M}$ , 0.4  $\mu\text{M}$ , 0.6  $\mu\text{M}$ , 0.8  $\mu\text{M}$ , 1  $\mu\text{M}$ , 2  $\mu\text{M}$ , 4  $\mu\text{M}$  from top to bottom). (b) and (d) Plots of fluorescent intensity at 372 nm *versus* the molar ratio of TPE-(Im)<sub>2</sub> and SeSe-(P5)<sub>2</sub> in the cases of (a) and (c), respectively.

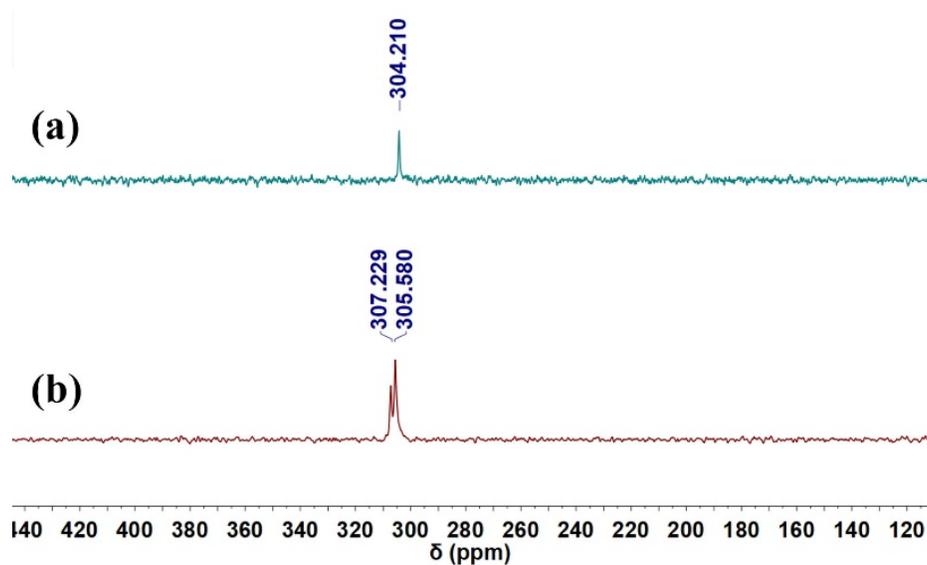
## Stimuli-responsive experiments



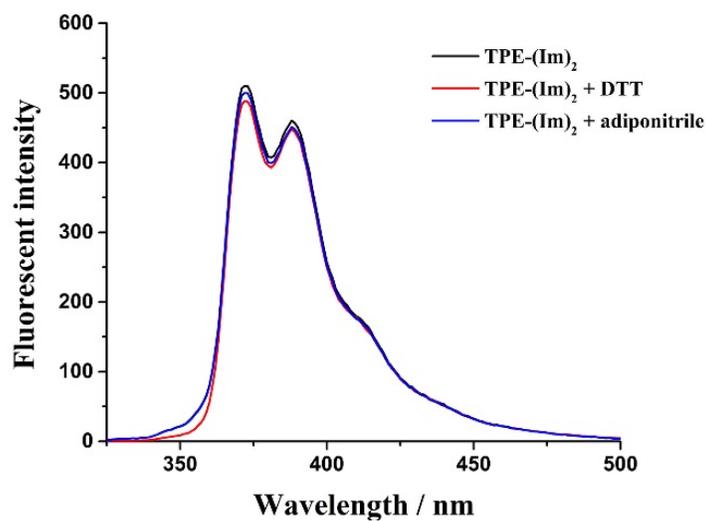
**Figure S30.** DOSY spectra (600 MHz,  $\text{CDCl}_3$ , 298K, concentration = 2 mM) of (a) TPE-(Im)<sub>2</sub>, and (b) equimolar TPE-(Im)<sub>2</sub> and SeSe-(P5)<sub>2</sub>.



**Figure S31.** DOSY spectrum (600 MHz,  $\text{CDCl}_3$ , 298K) of (a) 50 mM **TPE-(Im)<sub>2</sub>** and 50 mM 50 **SeSe-(P5)<sub>2</sub>**; (b) 50 mM **TPE-(Im)<sub>2</sub>**, 50 mM **SeSe-(P5)<sub>2</sub>**, and 20 mM **DTT**.



**Figure S32.**  $^{77}\text{Se}$  NMR (500 MHz, 298 K,  $\text{CDCl}_3$ ) spectra of the supramolecular polymer ( $\text{TPE}-(\text{Im})_2 / \text{SeSe}-(\text{P5})_2$  1:1 molar ratio, 30 mM) (a) in the absence of any stimuli and (b) in the presence of DTT.



**Figure S33.** Fluorescent emission spectra ( $\lambda_{\text{ex}} = 265 \text{ nm}$ ;  $\lambda_{\text{em}} = 372 \text{ nm}$ ; slit widths: ex. 5 nm, em. 5 nm; 25  $^\circ\text{C}$ ,  $[\text{TPE}-(\text{Im})_2] = 10 \mu\text{M}$ ) of  $\text{TPE}-(\text{Im})_2$  upon the addition of 1 eq. DTT or 50 eq. competitive guest (adiponitrile).