

Electronic Supplementary Information

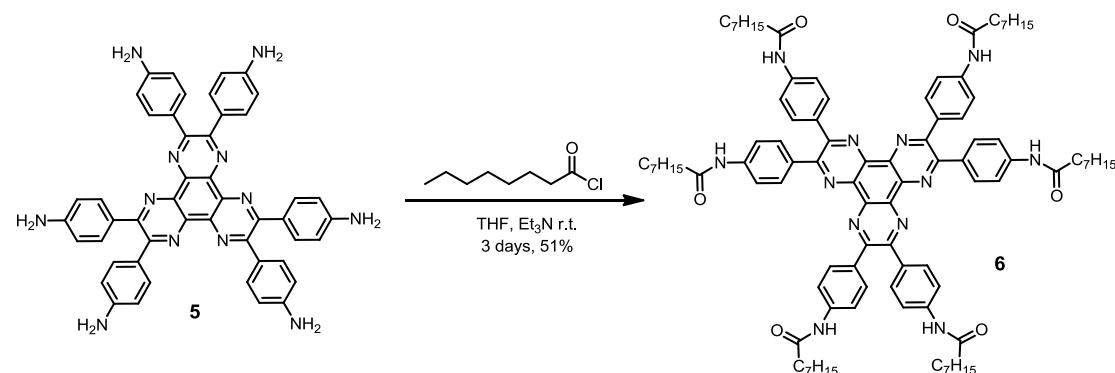
The construction of supramolecular polymers through anion bridging: from frustrated hydrogen-bonding network to well-ordered linear arrays

Tian-Guang Zhan, Tian-You Zhou, Qiao-Yan Qi, Jian Wu, Guang-Yu Li
and Xin Zhao*

Key Laboratory of Synthetic and Self-assembly Chemistry for Organic Functional Molecules, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences
345 Lingling Road, Shanghai 200032, China

E-mail: xzhao@mail.sioc.ac.cn.

Experimental Section



Compound 6. A mixture of compound 5 (0.155 g, 0.2 mmol) and octanoyl chloride (3.72 g, 18.96 mmol) were dissolved in 150 mL anhydrous THF, and 10 mL anhydrous Et_3N was added, which was then stirred at room temperature under argon atmosphere for 3days. When the reaction was completed monitored by TLC, the solvent was removed under reduced pressure, the resulting solid was washed by water and ethyl ether, respectively, and dried. Compound 6 was obtained as a yellow

solid (0.155 g, 51%). ^1H NMR (400 MHz, DMSO- d_6): δ (ppm) 10.06 (s, 6 H), 7.69-7.61 (dd, J_1 = 8 Hz, J_2 = 8 Hz 24 H), 2.34 (t, J = 16 Hz, 12 H), 1.61 (s, 12 H), 1.35-1.19 (m, 48 H), 0.87 (t, J = 16 Hz, 18 H). ^{13}C NMR (100 MHz, DMSO- d_6): δ 171.60, 152.73, 140.28, 139.12, 132.91, 130.47, 118.55, 36.51, 28.67, 28.50, 25.06, 23.18, 22.09, 13.94. MS (MALDA-TOF): m/z 1561.0[M + H + Na] $^+$, 1540.0[M + 3H] $^+$, 1412.9[M - C₈H₁₅O + 3H] $^+$, 1286.8[M - 2C₈H₁₅O + 3H] $^+$, 1159.6[M - 3C₈H₁₅O + 3H] $^+$, 1033.5[M - 4C₈H₁₅O + 3H] $^+$. HRMS (MALDA-TOF): Calcd. for C₉₆H₁₂₀N₁₂O₆Na [M + Na] 1559.9334, Found: 1559.9346.

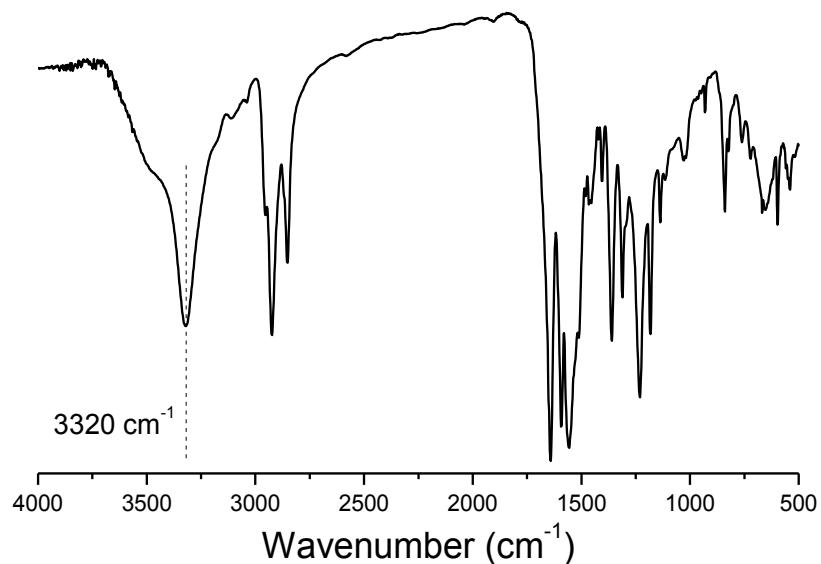


Figure S1. FT-IR spectrum of compound **1**.

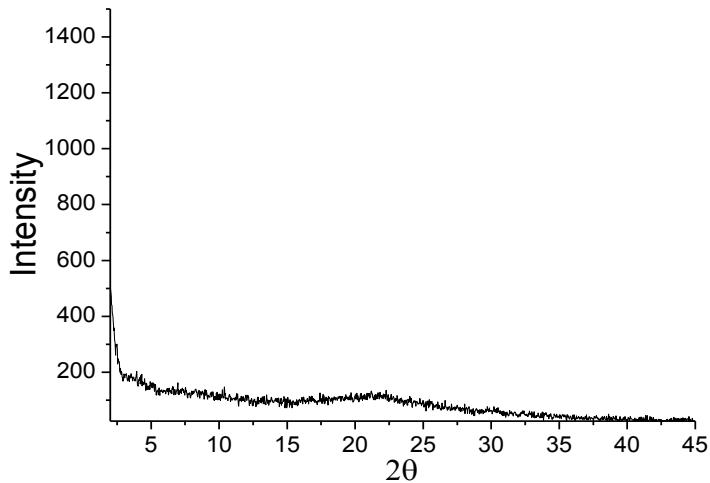


Figure S2. Powder XRD pattern of compound **1** in solid state.

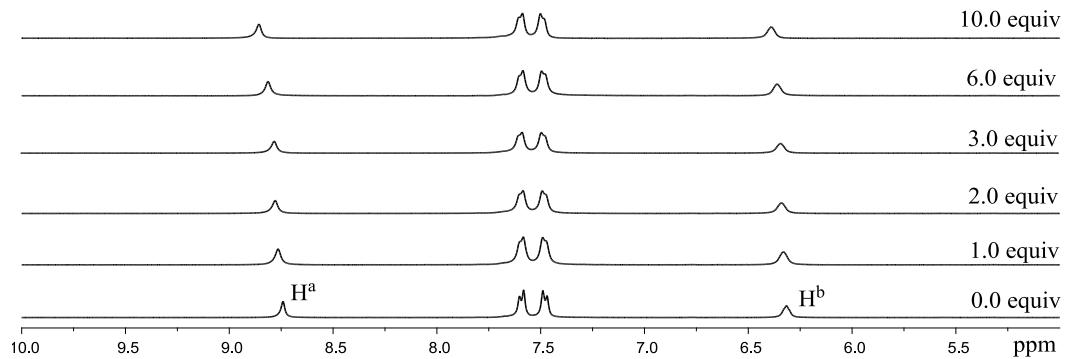


Figure S3. Partial ^1H NMR (400 MHz) spectra of compound **1** (6.0 mM) upon addition of TBABr in $\text{DMSO}-d_6$ at 25 °C.

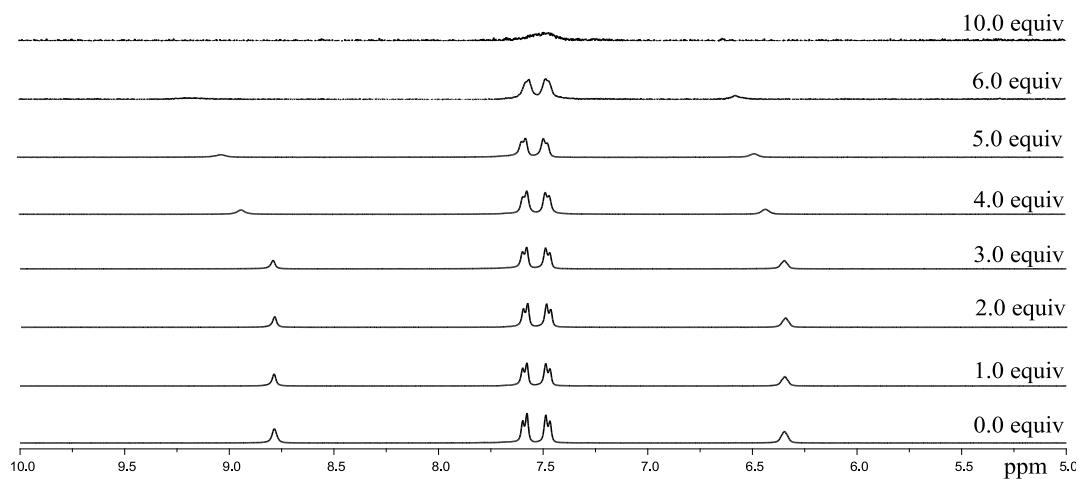


Figure S4. Partial ^1H NMR (400 MHz) spectra of **1** (6.0 mM) upon addition of TBAF in $\text{DMSO}-d_6$ at 25 °C.

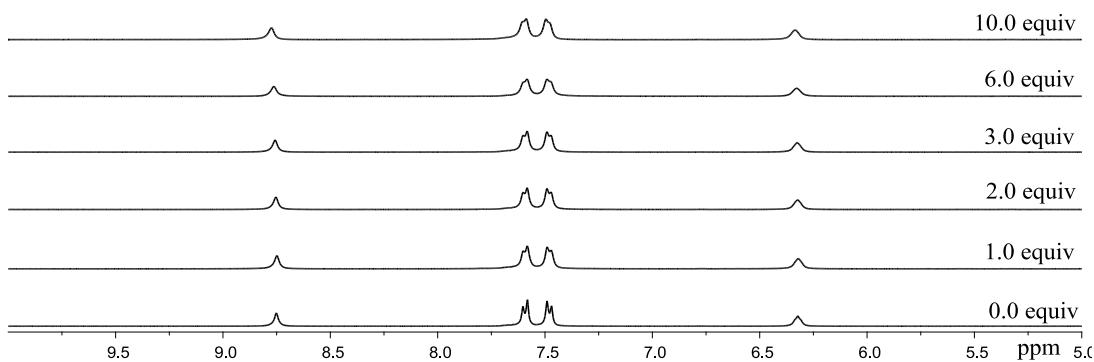


Figure S5. Partial ^1H NMR (400 MHz) spectra of **1** (6.0 mM) upon addition of TBAl in $\text{DMSO}-d_6$ at 25 °C.

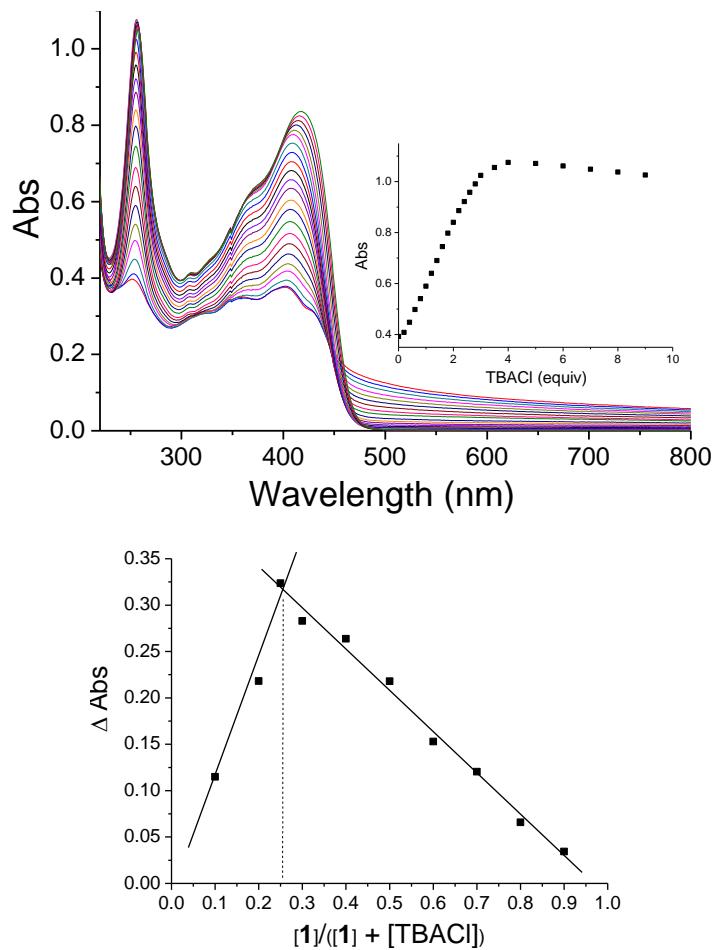


Figure S6. UV-vis absorption spectra of **1** (0.015 mM) upon addition of TBACl (from 0 to 9 equiv) in THF at 25 °C (Inset: the plot of the absorbance at 255 nm vs [TBACl]) (top), and Job's plot indicating a 1:3 stoichiometry for **1** and Cl^- (bottom). The total concentration for conducting Job's plot was 0.03 mM.

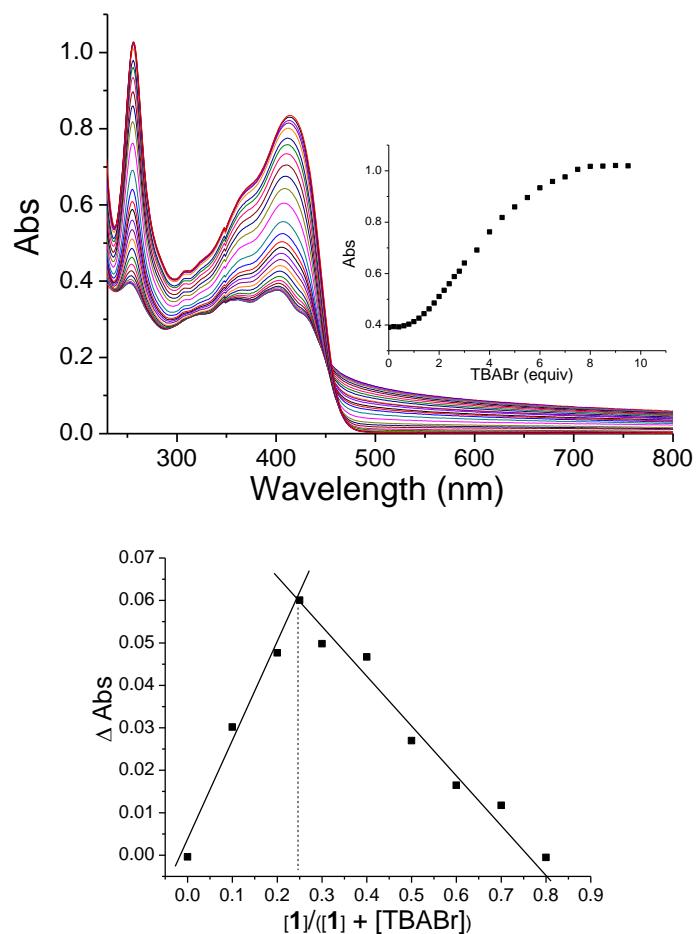


Figure S7. UV-vis absorption spectra of **1** (0.015 mM) upon addition of TBABr (from 0 to 9 equiv) in THF at 25 °C (inset: the plot of the absorbance at 255 nm vs [TBABr]) (top), and Job's plot indicating a 1:3 stoichiometry for **1** and Br⁻ (bottom). The total concentration for conducting Job's plot was 0.03 mM.

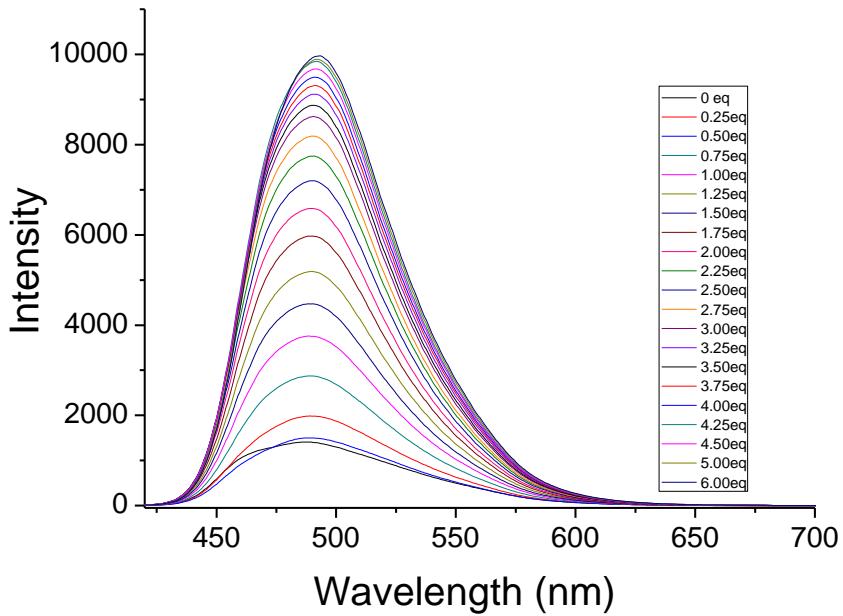


Figure S8. Fluorescence emission spectra of **1** (6.0 μM) upon addition of TBACl (from 0 to 6 equiv) in THF at 25 $^{\circ}\text{C}$. $\lambda_{\text{ex}} = 400 \text{ nm}$.

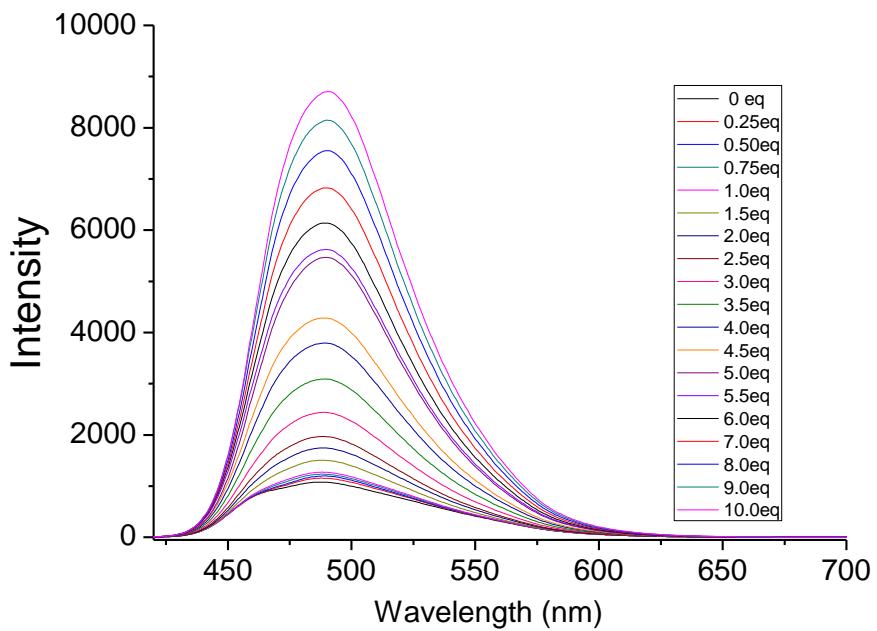


Figure S9. Fluorescence emission spectra of **1** (6.0 μM) upon addition of TBABr (from 0 to 10 equiv) in THF at 25 $^{\circ}\text{C}$. $\lambda_{\text{ex}} = 400 \text{ nm}$.

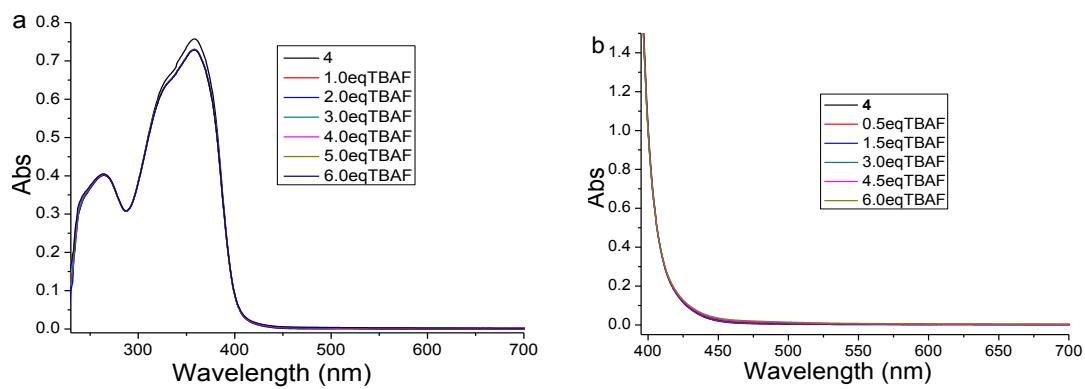


Figure S10. UV-vis absorption spectra of compound **4** (a) 0.01 mM and (b) 0.1 mM upon addition of TBAF in THF at 25 °C

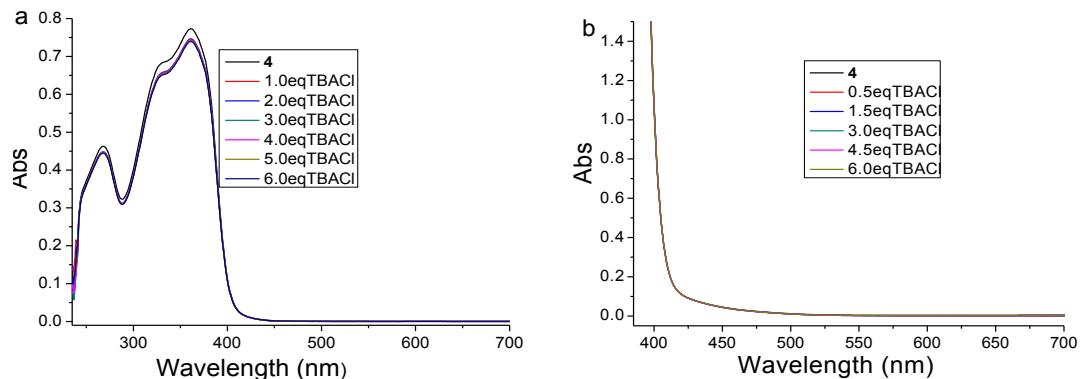


Figure S11. UV-vis absorption spectra of compound **4** (a) 0.01 mM and (b) 0.1 mM upon addition of TBACl in THF at 25 °C.

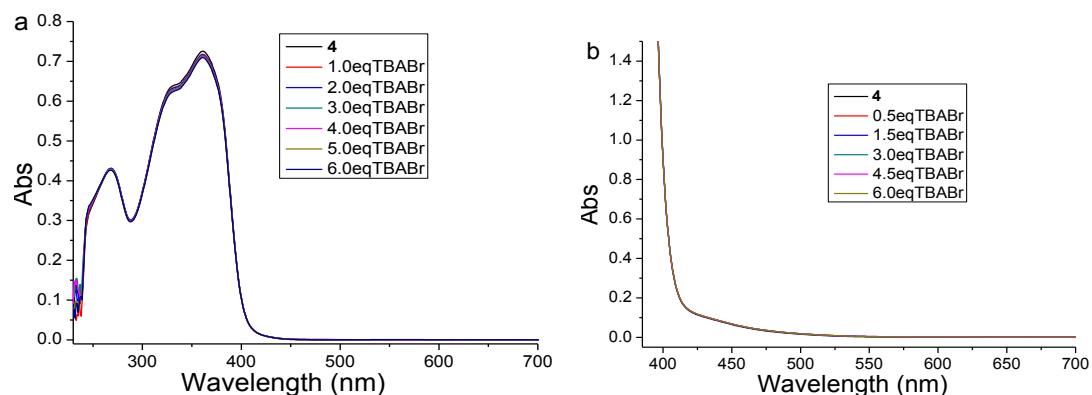


Figure S12. UV-vis absorption spectra of compound **4** (a) 0.01 mM and (b) 0.1 mM upon addition of TBABr in THF at 25 °C.

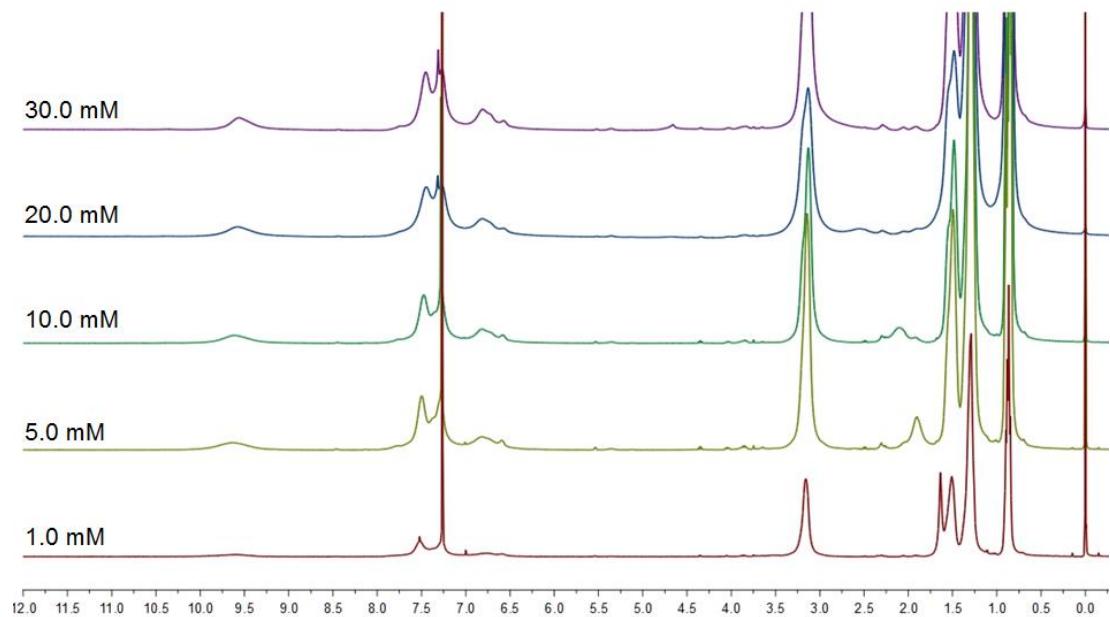


Figure S13. The ^1H NMR (400 MHz) dilution spectra of a mixture of **1** and TBACl (1:3) in CDCl_3 at 25°C.

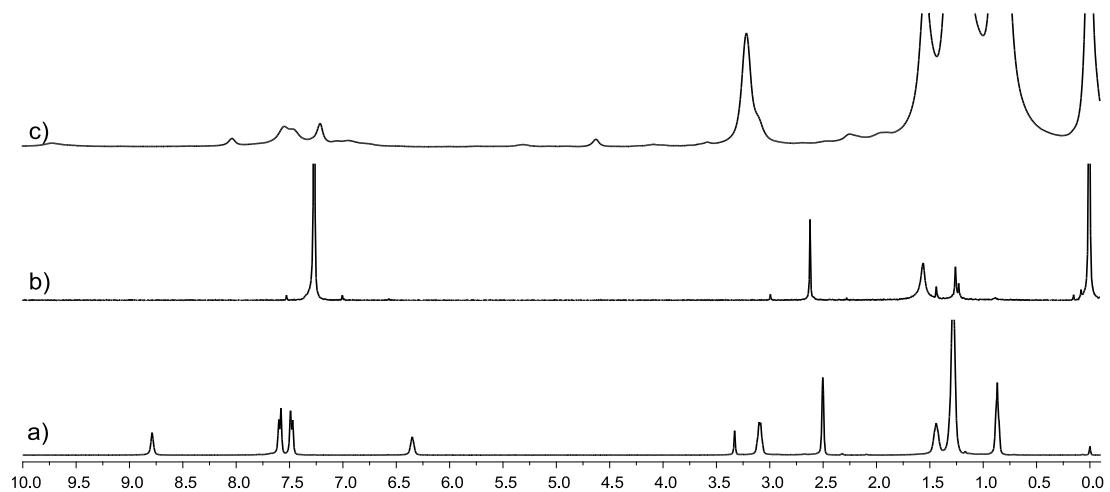
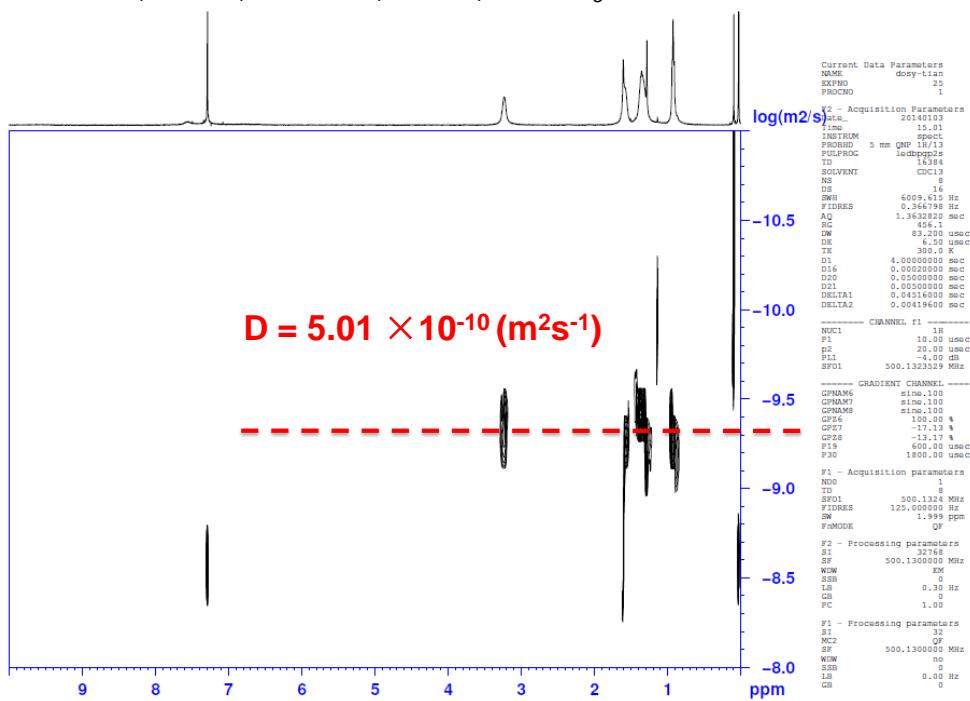


Figure S14. Partial ^1H NMR (400 MHz) spectra of (a) **1** in $\text{DMSO}-d_6$, (b) suspension of **1** in CDCl_3 , and (c) **1** + TBABr (1:3) in CDCl_3 at 25 °C.

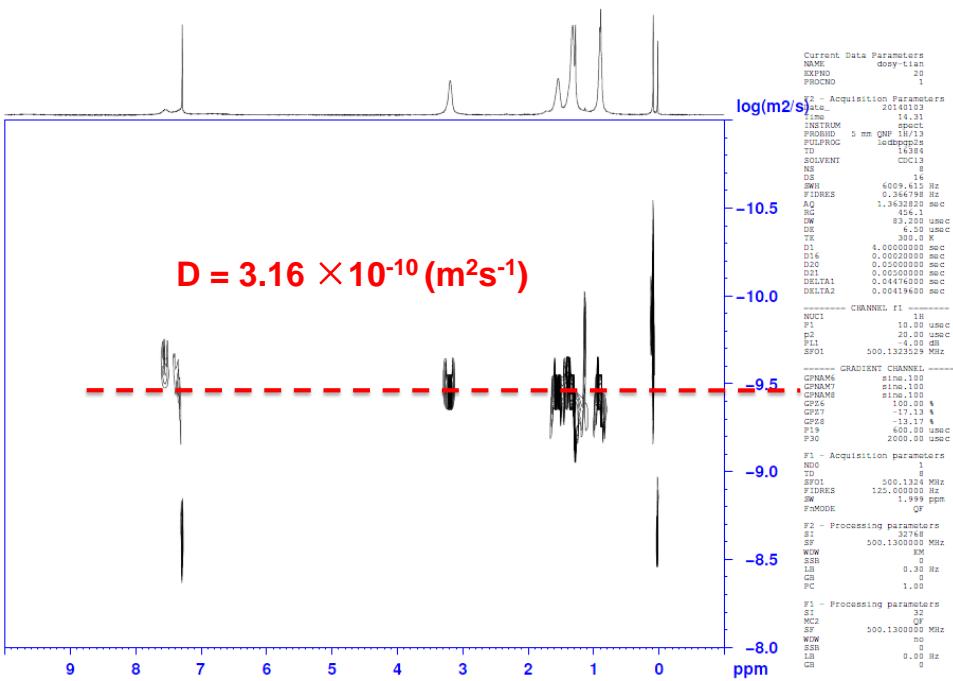


Figure S15. Picture for the organogel fabricated from **1** and TBACl (1:3) in CHCl₃.

Mixture of **1** (1.0 mM) + TBACl (3.0 mM) in CDCl₃



Mixture of **1** (5.0 mM) + TBACl (15.0 mM) in CDCl_3



Mixture of **1** (10.0 mM) + TBACl (30.0 mM) in CDCl_3

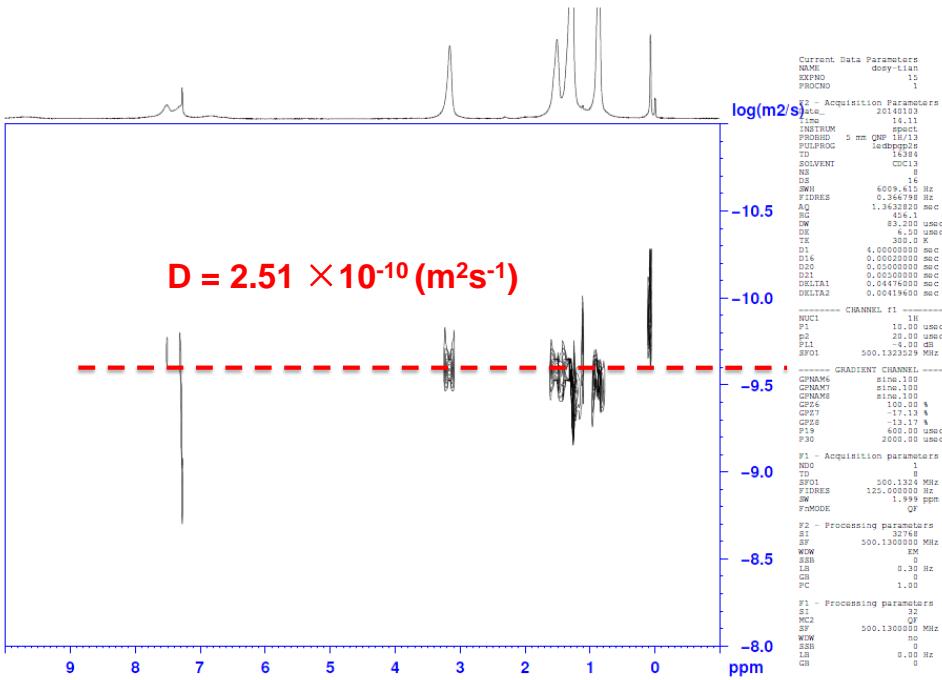


Figure S16. DOSY-NMR spectra of the solution of **1** and TBACl (1:3) in CDCl_3 at different concentrations at 25 °C.

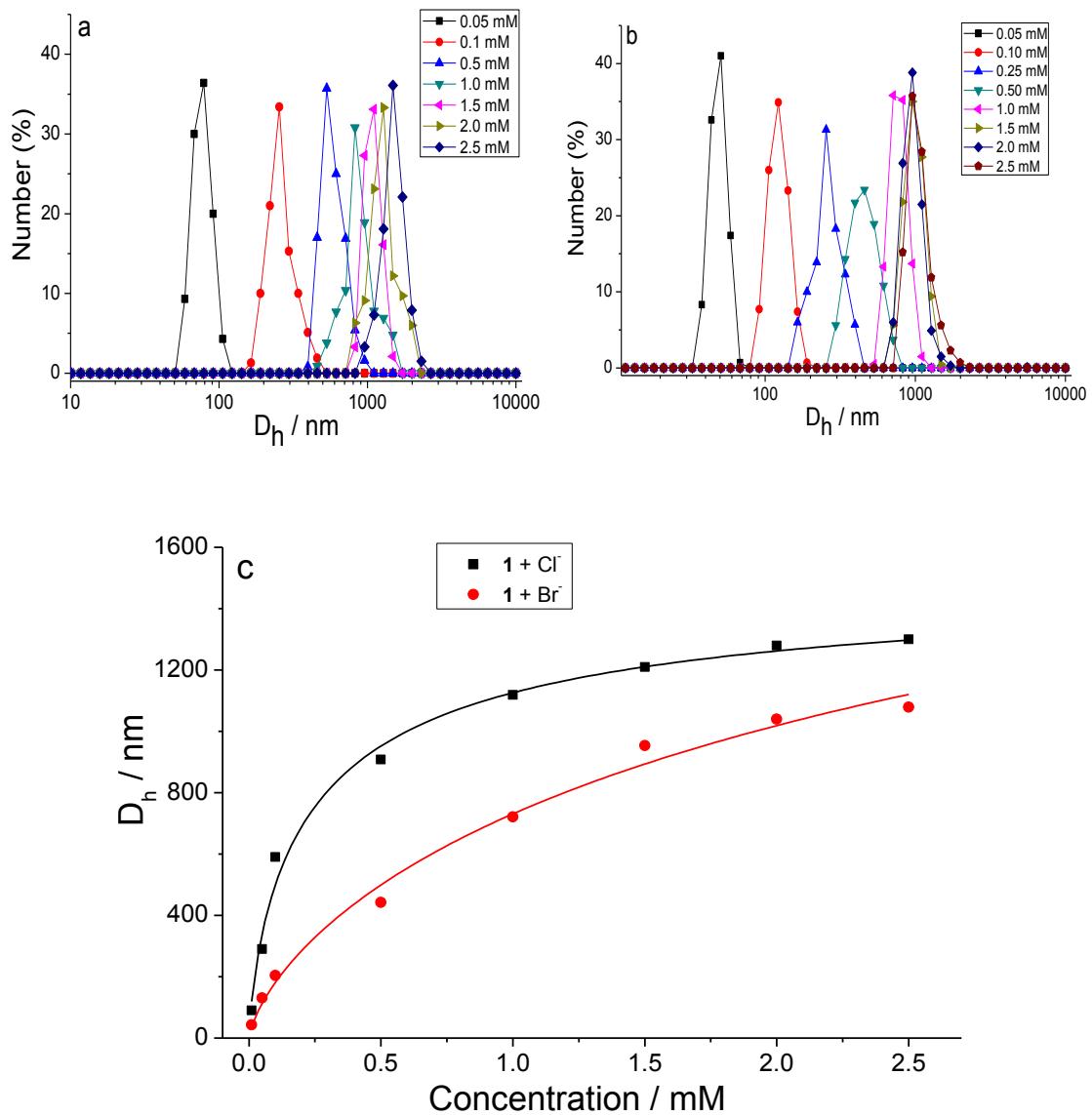


Figure S17. DLS profiles of the mixtures of **1** with 3.0 equiv of (a) TBACl, (b) TBABr in CHCl₃ at different concentrations at 25 °C, and (c) plots of hydrodynamic diameter (D_h) versus concentration.



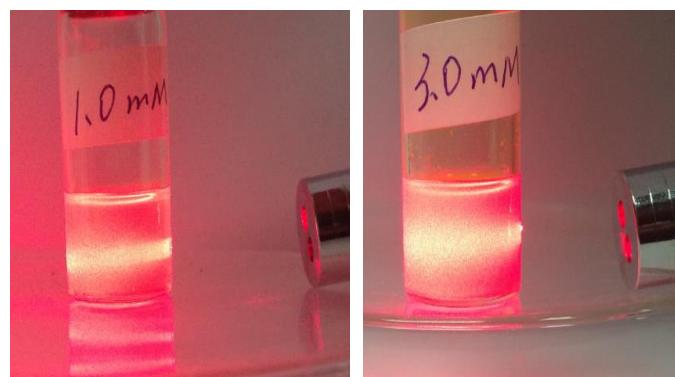


Figure S18. Pictures for the Tyndall effect of the solutions prepared from the mixtures of **1** with 3.0 equiv of TBACl (top) and TBABr (bottom).

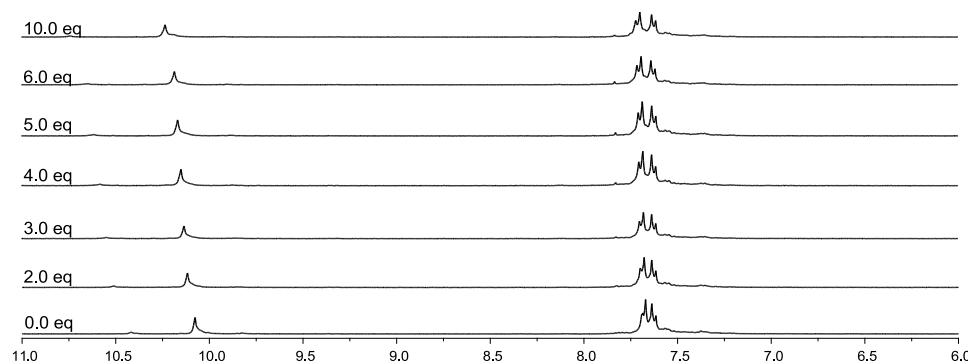


Figure S19. Partial ^1H NMR (400 MHz) spectra of **6** (6.0 mM) upon addition of TBACl in $\text{DMSO}-d_6$ at 25 °C.

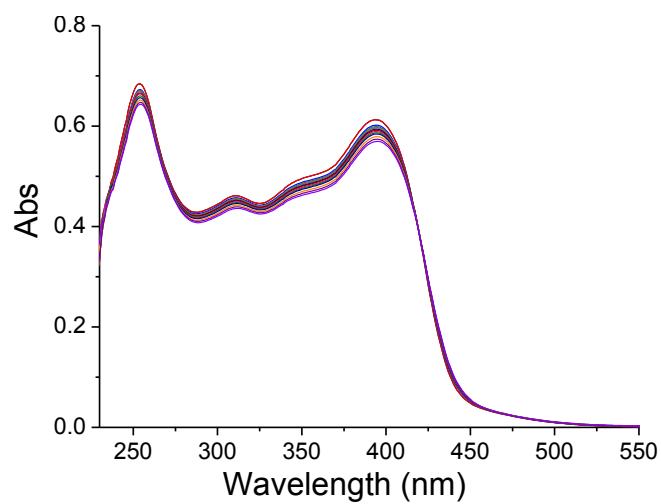


Figure S20. UV-vis absorption spectra of **6** (0.02 mM) upon addition of TBACl (from 0 to 8 equiv) in THF at 25 °C.

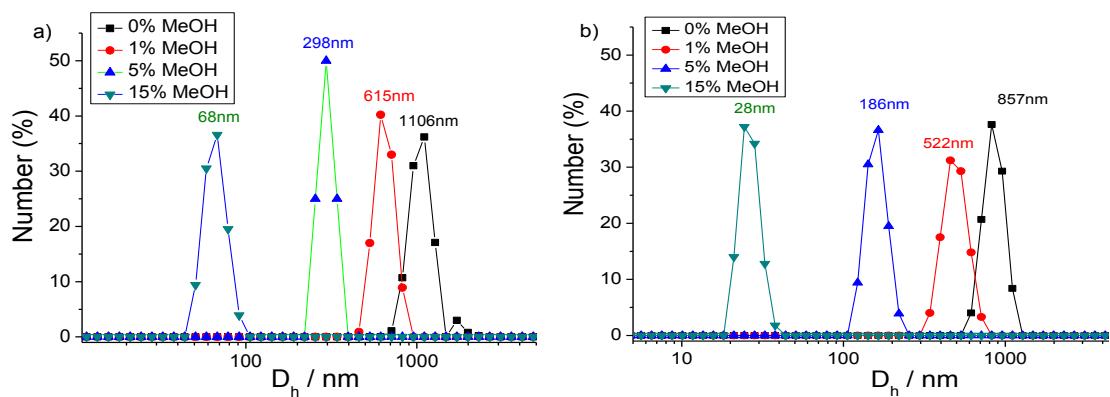


Figure S21. DLS profiles of **1** with 3.0 equiv of (a) TBACl and (b) TBABr upon adding different amount of methanol in their CHCl_3 solution at 25 °C.

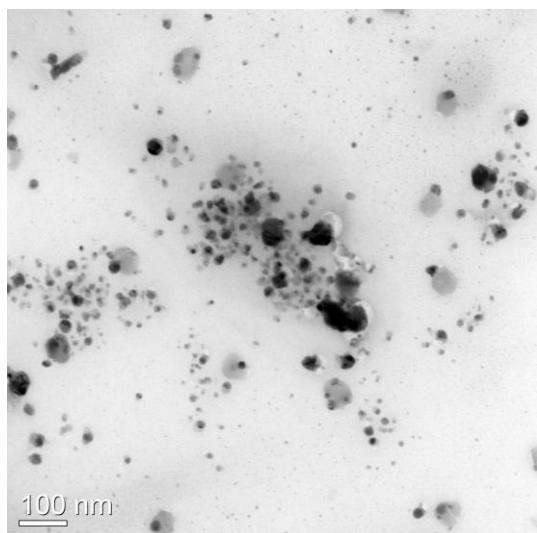


Figure S22. TEM image of the sample after the introduction of Ag^+ into the solution of supramolecular polymer prepared from **1** and TBACl.

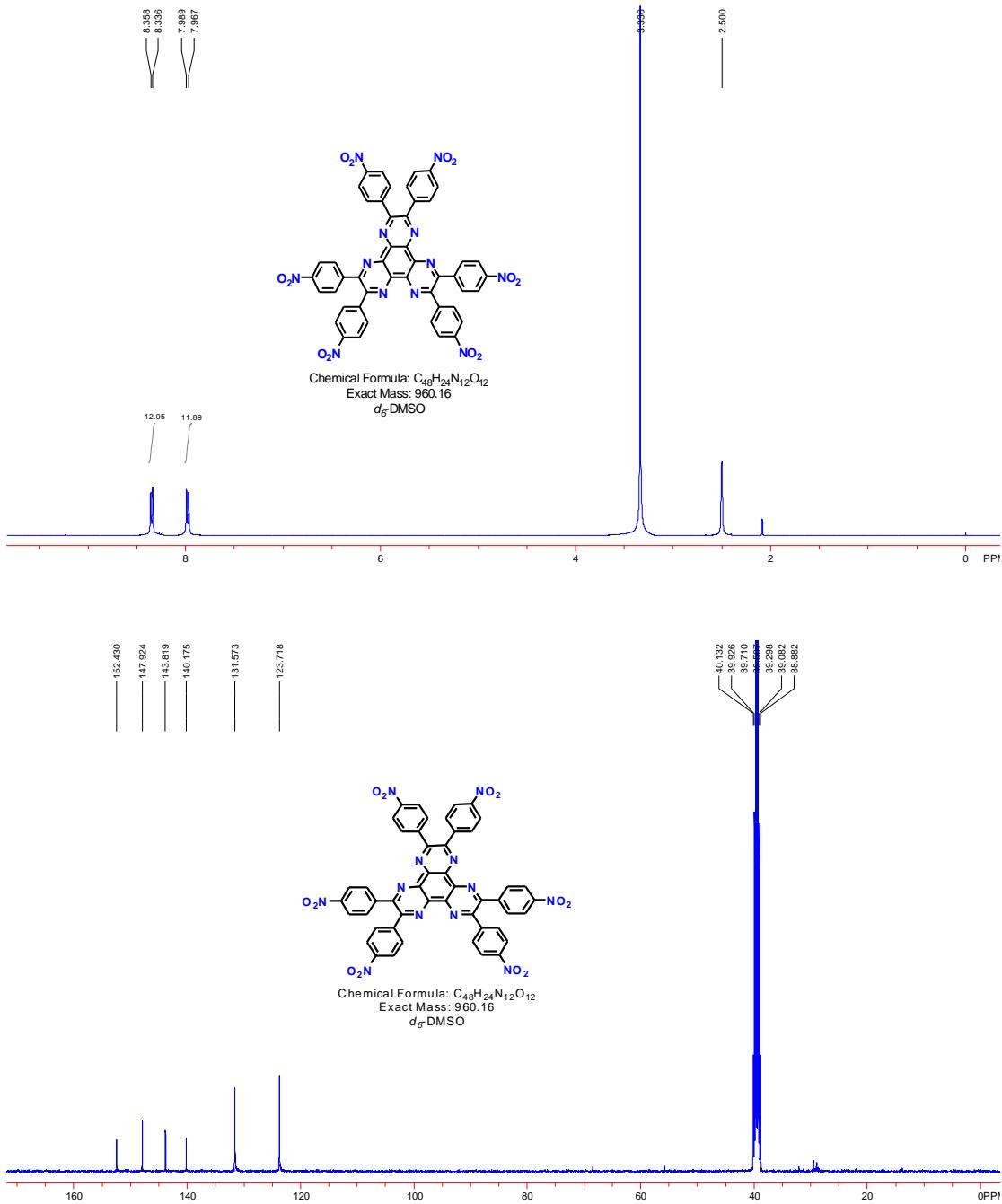


Figure S23. ^1H NMR and ^{13}C NMR spectra of compound **4** in $\text{DMSO}-d_6$.

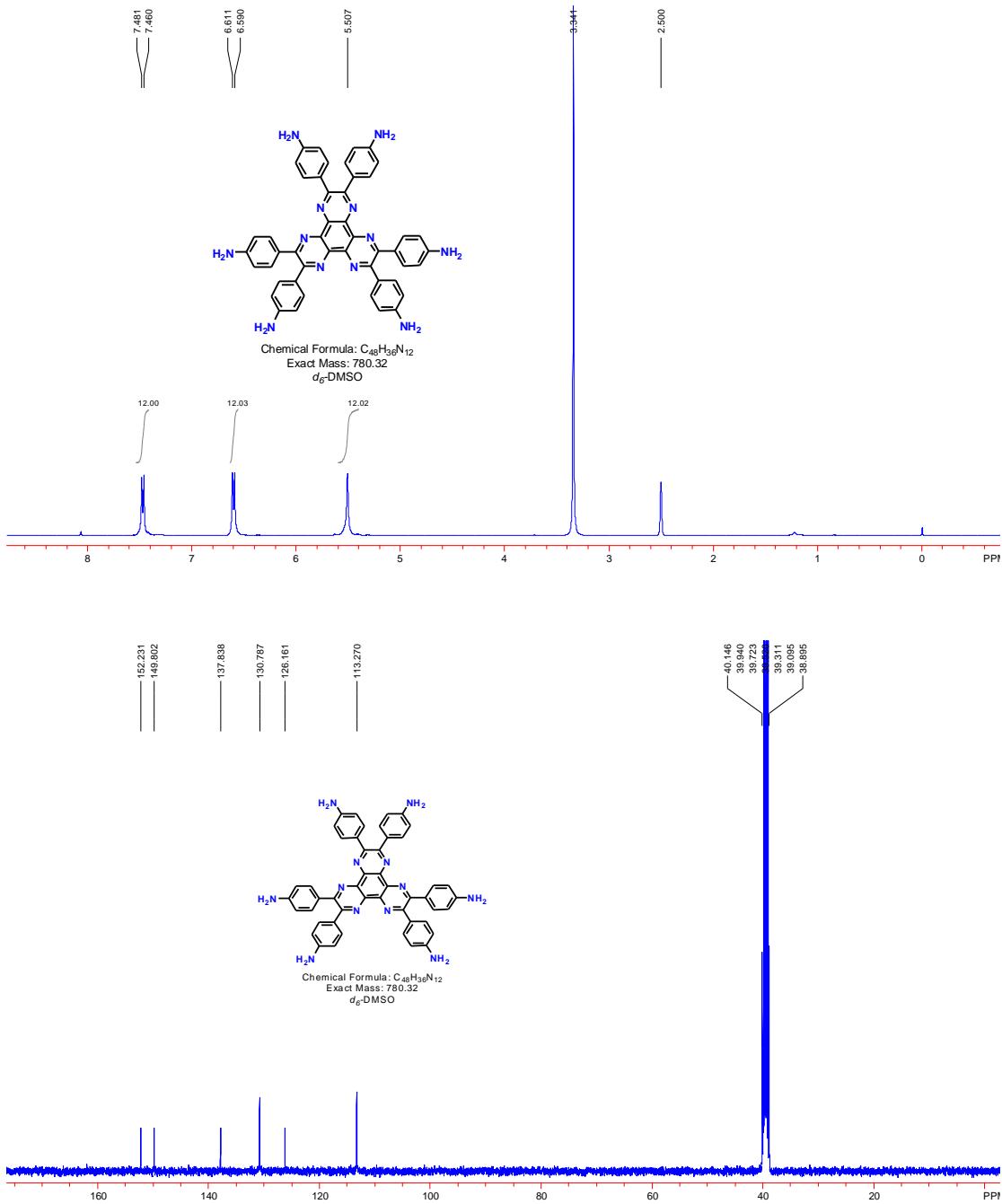


Figure S24. ^1H NMR and ^{13}C NMR spectra of compound **5** in $\text{DMSO}-d_6$.

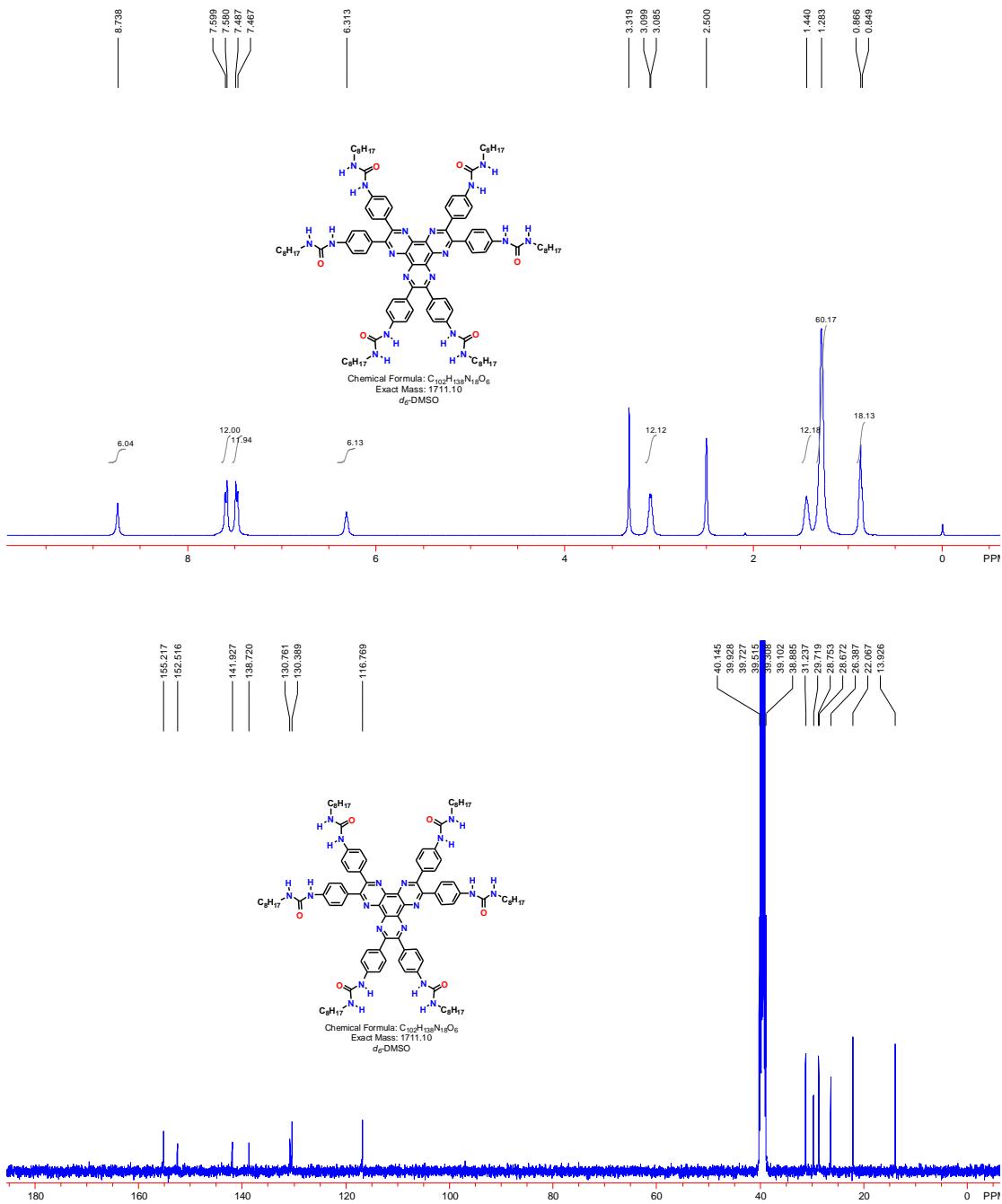


Figure S25. ^1H NMR and ^{13}C NMR spectra of compound **1** in $\text{DMSO}-d_6$.

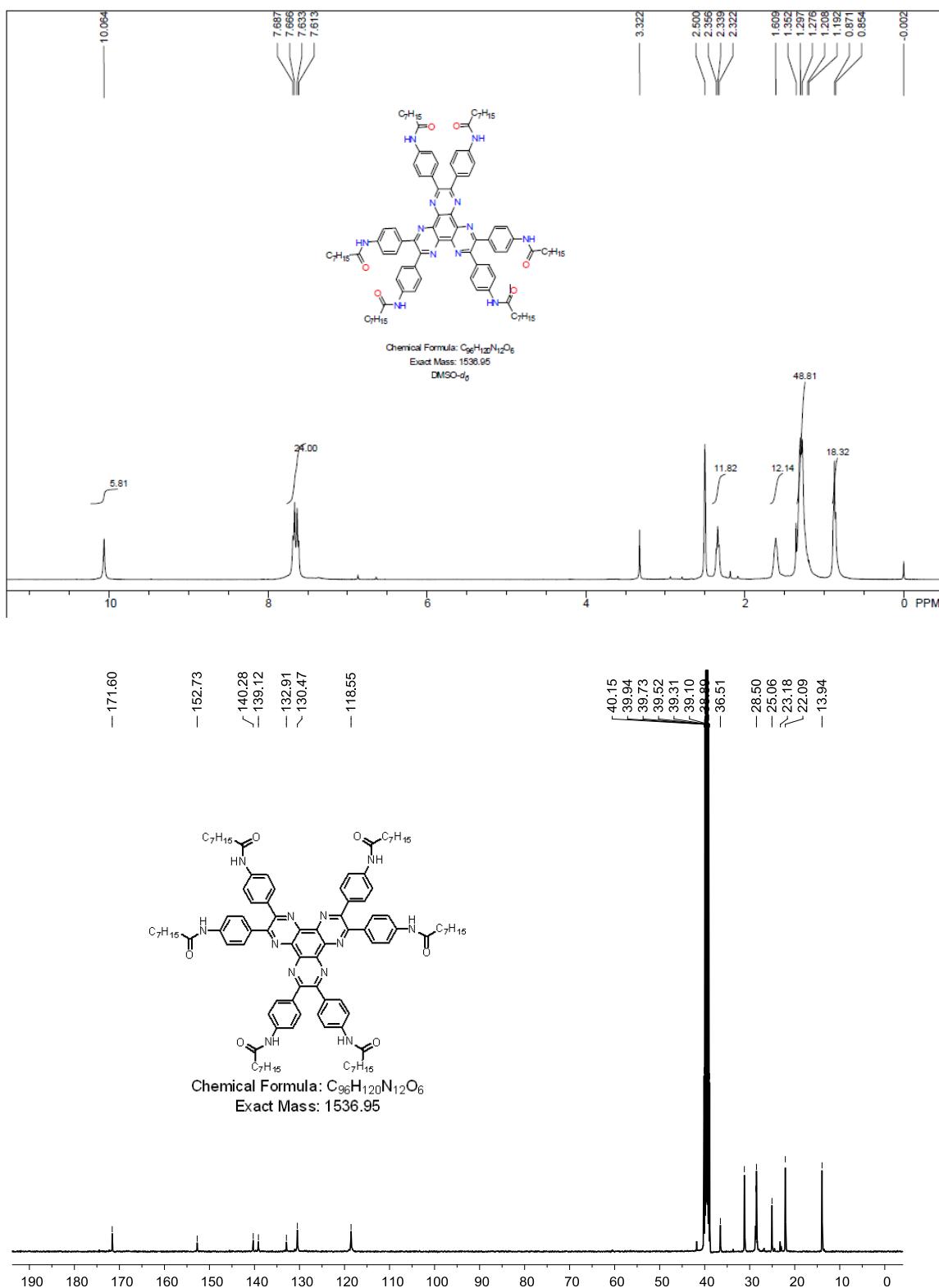


Figure S26. 1H NMR and ^{13}C NMR spectra of compound 6 in $DMSO-d_6$.