ISCI, Volume *19*

Supplemental Information

Dynamic Adaptive Two-Dimensional Supramolecular Assemblies for On-Demand Filtration

Qi Zhang, Ruo-Jie Xing, Wen-Zhi Wang, Yuan-Xin Deng, Da-Hui Qu, and He Tian

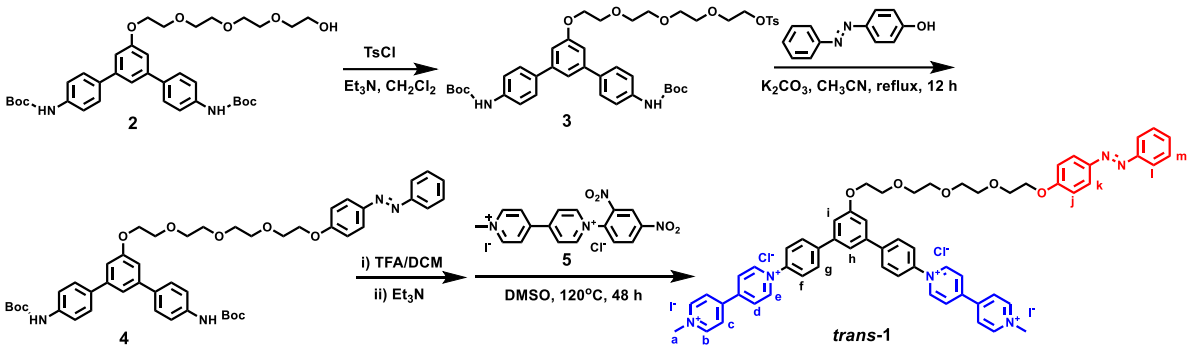
Supplementary Information

CONTENT:

1. Transparent Method

All the reagents were used as received from Adamas®beta, Aladdin and Aldrich. All organic solvents were reagent grade and were dried and distilled prior to use according to standard procedures. Ultrapure water (18.2 MΩ cm) was obtained from a Millipore system (Labconco Corporation, Kansas City, MO, U.S.A). The synthetic products were characterized by ^{1}H NMR, ^{13}C NMR spectroscopies and high resolution electronic spray ionization (ESI) mass spectrometry to confirm the molecular structures. ^{1}H NMR and ^{13}C NMR were obtained from Brüker AV-400 spectrometer employing tetramethylsilane as the internal standard. The ESI mass spectra were acquired on an LCT Premier XE mass spectrometer. UV-Vis absorption spectra were recorded on an Agilent Cary 100 spectrometer (1 cm quartz cells if no specialized note). Dynamic light scattering (DLS) was measured on Beckman Coulter DelsaNano C, 298 K. The morphology of the nano-assemblies was detected on high resolution transmission electron microscopy (HR-TEM) from JEM-1400, JEOL. The sample solutions were dropped onto a copper grid with carbon membrane and evaporated in vacuum oven at corresponding temperature. Surface morphology images of samples were detected by atomic force microscopy (AFM) from Veeco/DI. The sample solution were dropped on a freshly peeled mica sheet and evaporated in vacuum oven at corresponding temperature. The photo-irradiation experiments were performed in a quartz cell under the UV/visible irradiation of a high-power LED lamp with single wavelength output (365 nm or 420 nm), PL-LED100, PerfectLight®. The output power was set as 30 W and the distance between quartze cell and light source was 2 cm. The nanoparticle filter experiments were performed based on the commercial polyethersulfone (PES) filter (Adamas®beta) with average pore diameter of 0.22 μm. The filtration efficiency was calculated based on the relative concentration ratio of the samples before and after filtered, which was required by the relative absorbance at the UV-Vis absorption peaks.

2. Synthetic procedures



Preparation of compound 3: The compound **2** (1.711 g, 2.61 mmol) and p-toluenesulfonyl chloride (0.900 g, 4.72 mmol) were dissolved in CH_2Cl_2 (10 mL). Then, TEA (1 mL) was added into the solution. After stirring for 6 hours at room temperature, the precipitate was removed through filtration, and the filtrate was evaporated. The crude product was purified by chromatography on a silica gel column (PE/EA = 1/1) to yield the compound **3** (1.724 g, 81.6%) as a yellow oily liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.786 (d, J = 8.4 Hz, 2H), 7.558 (d, J = 8.4 Hz, 4H), 7.445 (d, J = 8.4z, 4H), 7.320 (t, 3H), 7.055 (s, 2H), 6.559 (s, 2H), 4.247 (t, J = 4.8 Hz, 2H), 4.144 (t, J = 4.8, 2H), 3.901 (t, J = 4.8 Hz, 2H), 3.743 (m, 2H), 3.674 (m, 4H), 3.586 (m, 4H), 2.416 (s, 3H), 1.534 (s, 18H). ^{13}C NMR (100 M Hz, $CDCl_3$) δ 159.5, 152.7, 144.8, 142.4, 138.0, 135.6, 132.9, 129.8, 128.0, 127.7, 118.7, 118.2, 111.7, 80.6, 70.8, 70.7, 70.7, 70.6, 69.8, 69.3, 68.7, 67.6, 28.4, 21.6. HRMS (ESI) (m/z): $[M + Na]^+$ calcd for $C_{43}H_{54}N_2O_{11}SNa$: 829.3346, found: 829.3369.

Preparation of compound 4: The compound **3** (1.724 g, 2.14 mmol) and p-hydroxyazobenzene (0.508 g, 2.56 mmol) were dissolved in CH_3CN (10 mL) with K_2CO_3 (0.885 g, 6.42 mmol) added in it afterwards. The mixture was refluxed for 12 hours. After the precipitate was filtered and the solvent was evaporated, the crude product was further purified by chromatography on a silica gel column (PE/EA = 1/1) to yield the compound **3** (1.236 g, 69.3%) as a red oily liquid. ^{1}H NMR (400 M Hz, $CDCl_3$) δ (ppm): 7.889 (m, 4H), 7.550-7.431 (m, 11H), 7.314 (s, 1H), 7.055 (s, 2H), 7.007 (d, J = 8.8 Hz, 2H), 6.568 (s, 2H), 4.245 (m, 2H), 4.189-3.908 (m, 6H), 3.766-3.694 (m, 8H), 1.528 (s, 18H). ^{13}C NMR (100 M Hz, $CDCl_3$) δ

171.2, 161.3, 159.5, 152.8, 142.5, 138.0, 135.7, 130.4, 129.8, 129.0, 128.0, 127.7, 124.7, 122.6, 118.8, 114.8, 111.7, 80.6, 70.9, 70.7, 69.8, 69.6, 69.3, 68.7, 67.6,60.4, 28.4. HRMS (ESI) (m/z): $[M + Na]^+$ calcd for $C_{48}H_{56}N_4O_9Na$: 855.3945, found: 855.3942.

Preparation of compound *trans*-1: The compound **4** (300 mg, 0.36 mmol) was dissolved in CH_2Cl_2 (5.0 mL) and then trifluoroacetic acid (0.412 g, 3.6 mmol) was added and the mixture was stirred for 4 hours. After the removal of the solution, triethylamine (2 mL) was added to deprotonate the amino groups. Dissolved in CH_2Cl_2, the mixture was washed with water (3 × 20 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure to yield some red oily liquid. Then, it was dissolved with **5** (364 mg, 0.727 mmol) in DMSO (3 mL) and stirred at 120℃ for 2 days. The mixture was added into acetone (150 mL), and the result powder was filtered, washed by hot acetone (3 × 60 mL), and recrystallized in EtOH/H_2O twice to yield the compound **4** (89 mg, 19.5%) as a dark red solid. ^{1}H NMR (400 M Hz, D_2O) δ (ppm): 9.311 (d, J = 7.2 Hz, 4H), 9.086 (d, J = 6.8 Hz, 4H), 8.667 (d, J = 6.8 Hz, 4H), 8.564 (d, J = 6.8 Hz, 4H), 8.045 (d, J = 8.8 Hz, 4H), 7.859 (d, J = 8.8 Hz, 4H), 7.680 (s, 1H), 7.535 (m, 4H), 7.393 (m, 5H), 6.865 (d, J = 9.2 Hz, 2H), 4.524 (s, 6H), 4.390 (t, J = 4.4 Hz, 2H), 4.039 (t, J = 4.0 Hz, 2H), 3.935 (t, J = 4.0 Hz, 2H), 3.863 (t, J = 3.2 Hz, 2H), 3.783 (m, 2H), 3.734 (m, 4H), 3.688 (m, 2H). ^{13}C NMR (600 M Hz, DMSO-d_6) δ 161.7, 160.3, 152.4, 151.5, 149.7, 148.2, 147.2, 146.3, 145.8, 143.2, 142.1, 140.9, 131.3, 129.9, 129.2, 126.9, 126.8, 125.8, 125.0, 122.7, 122.6, 115.5, 70.5, 70.4, 70.4, 70.3, 69.5, 69.3, 68.1, 68.1, 48.6. HRMS (ESI) (m/z): $[M – 2I]^{2+}$ calcd for $C_{60}H_{58}N_6O_5Cl_2$: 506.1917, found: 506.1910.

2. Supporting Figures

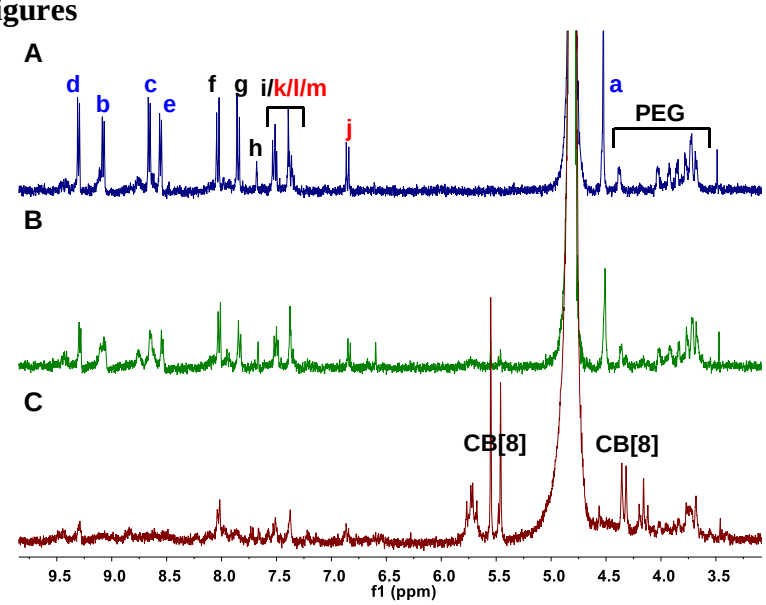


Figure S1. ^{1}H NMR titration experiments (D_2O, 400 MHz, 298K), related to Figure 2. (a) *trans*-**1**, (b) *trans*-**1** + CB[8] (1 : 0.75), (c) *trans*-**1** + CB[8] (1 : 1.5). Concentration of *tran*-**1** was 1 mM.

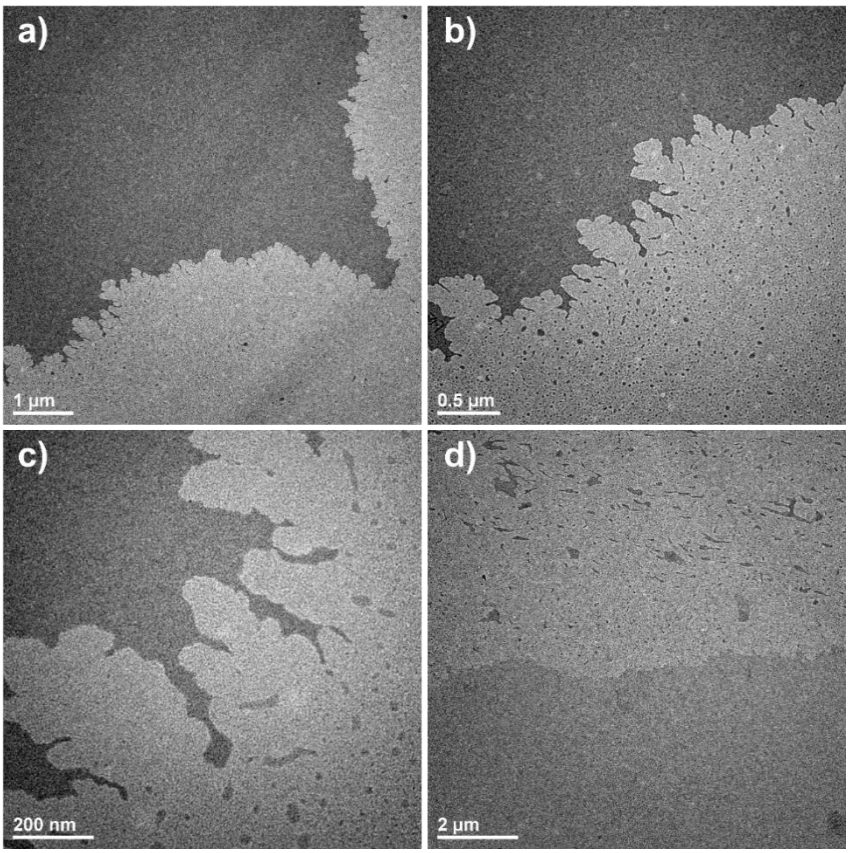


Figure S2. TEM images with different magnifications of the resulting supramolecular films, related to Figure 2.

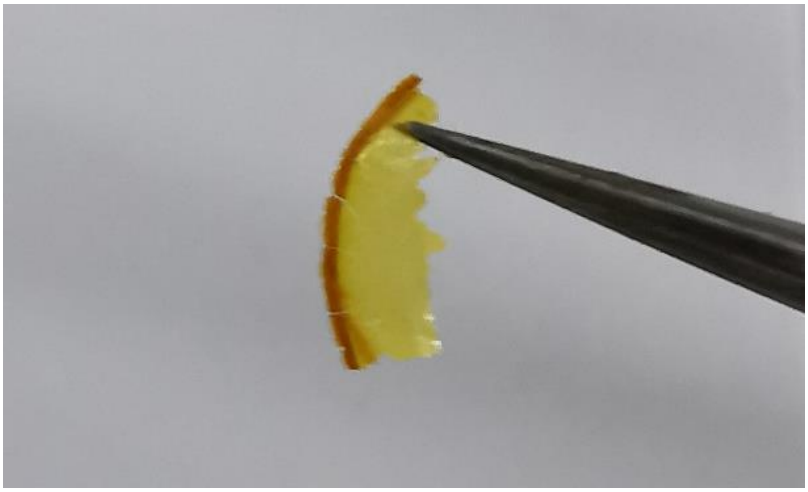


Figure S3. Photograph shows the free-standing film prepared by drop-casting method of the supramolecular assemblies solution, related to Figure 2.

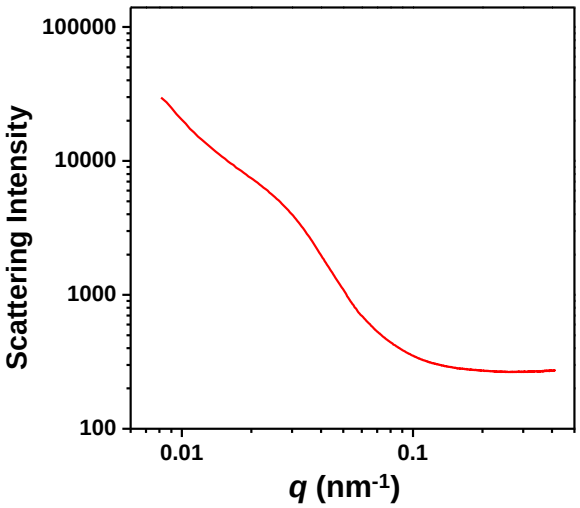


Figure S4. Synchrotron radiation SAXS pattern of the resulting supramolecular films, related to Figure 2.

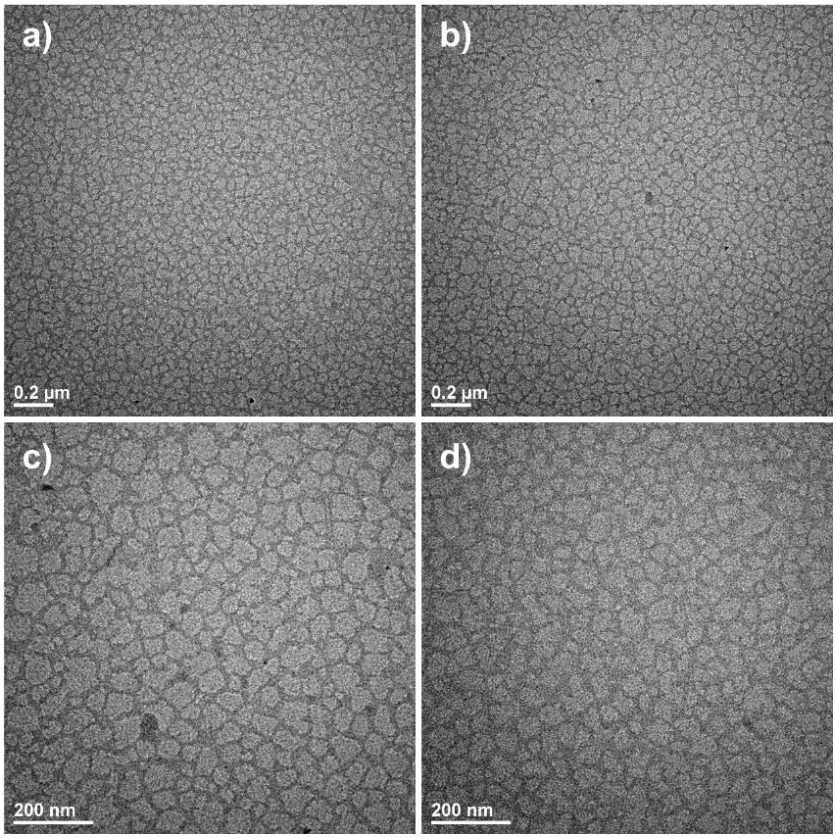


Figure S5. TEM images with different magnifications of the resulting supramolecular films at high temperature (40ºC), related to Figure 3.

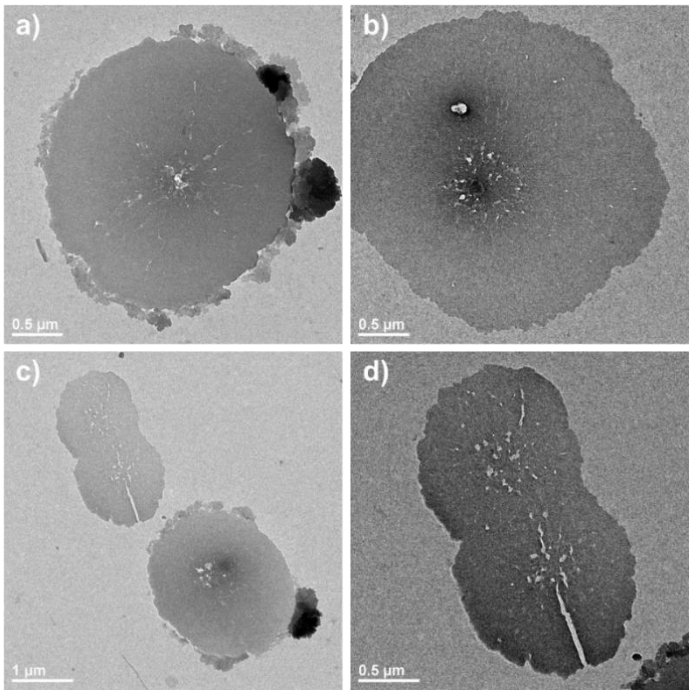


Figure S6. TEM images with different magnifications of the resulting supramolecular films at low temperature (0ºC), related to Figure 3.

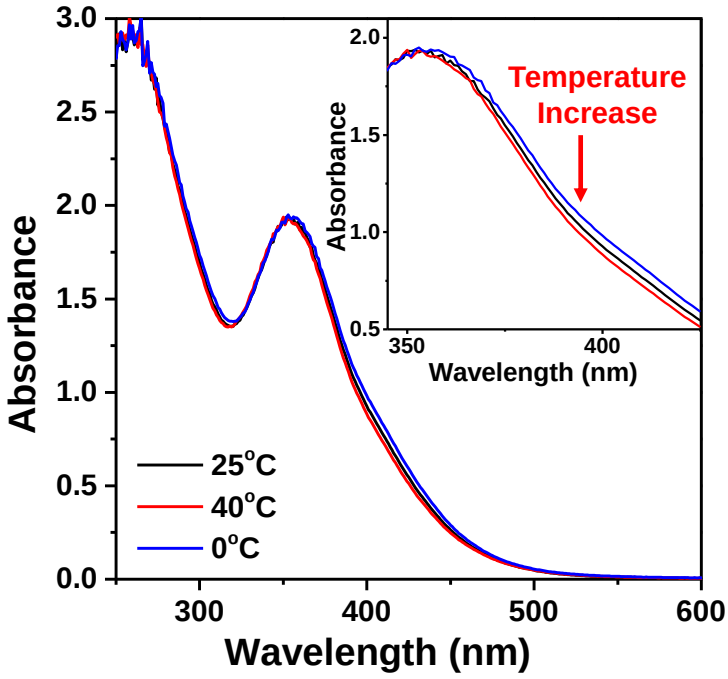


Figure S7. UV-Vis absorption spectra of the supramolecular polymers *trans*-1@CB[8] solution (1 mM, H_2O) under different temperature, related to Figure 3. Cuvette with short path length (1 mm) was used in this experiment due to the high concentration of solutes. The inset spectra show the amplified curve shifts at varied temperature.

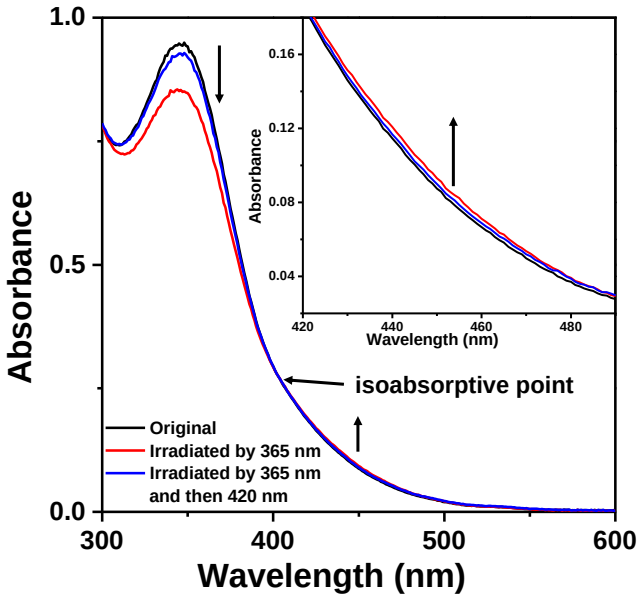


Figure S8. UV-Vis absorption spectra (50 μM in H_2O) detecting the photo-isomerization process of the azobenzene units, related to Figure 4. The inset image shows the amplified region of the increasing absorbance attributed to the *cis*-azobenzene.

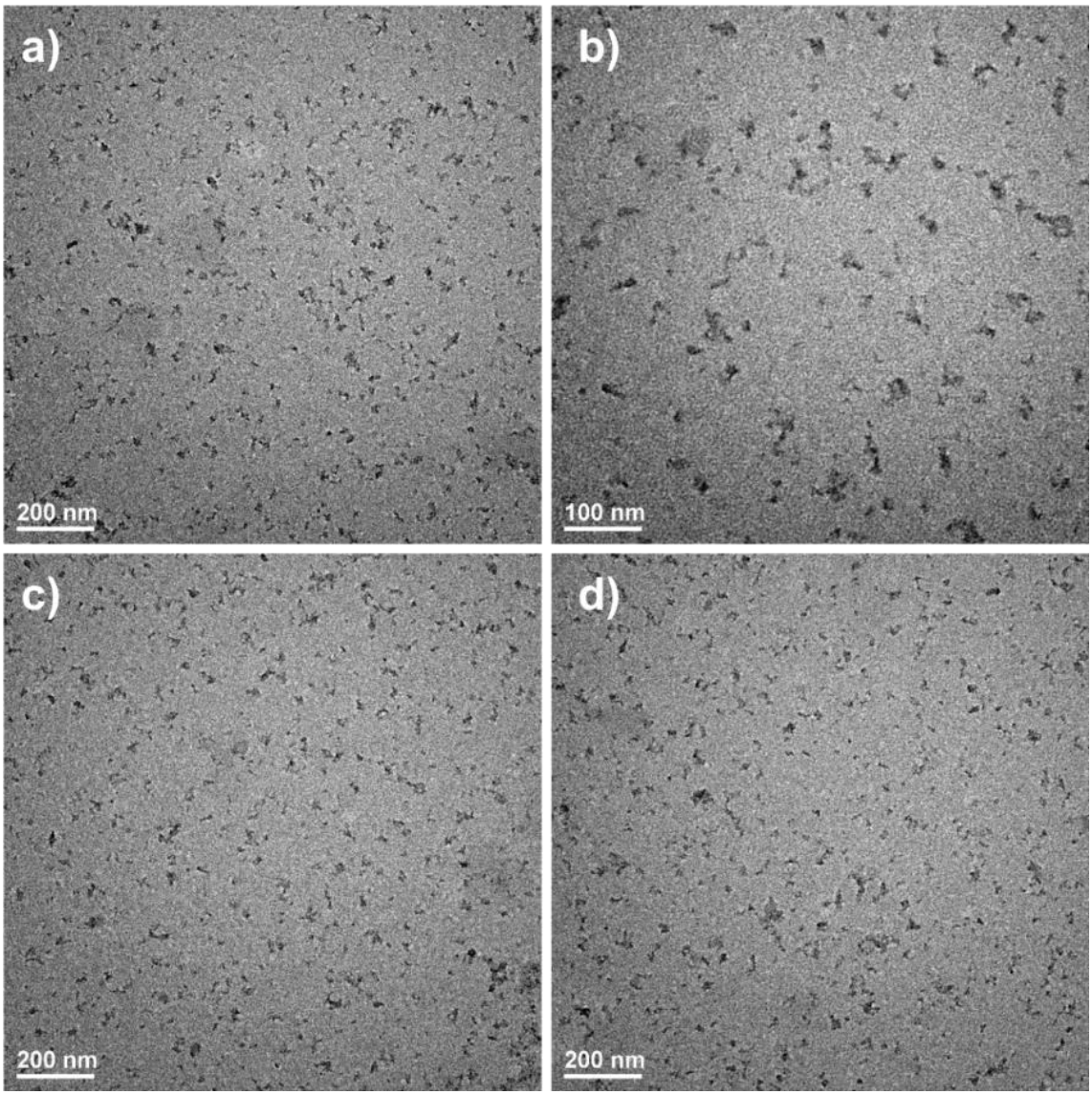


Figure S9. TEM images of the UV-induced disassemblies, related to Figure 4.

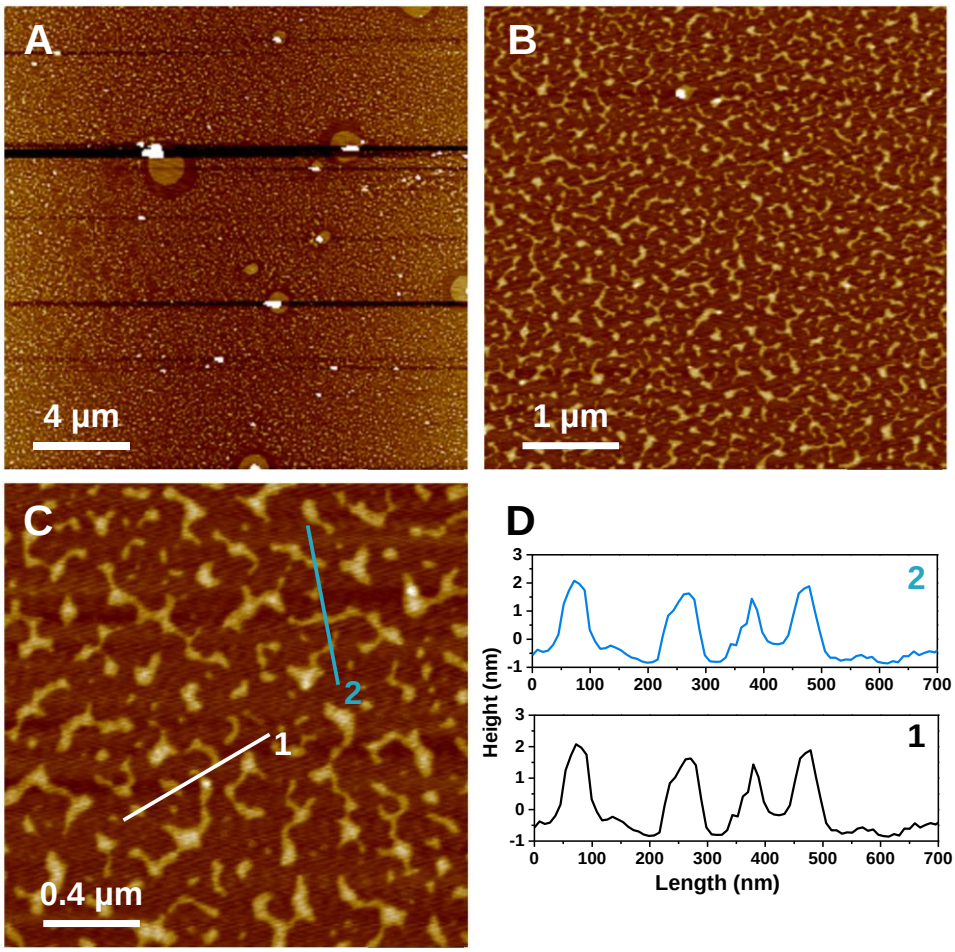


Figure S10. AFM images of the UV-induced disassemblies, related to Figure 4.

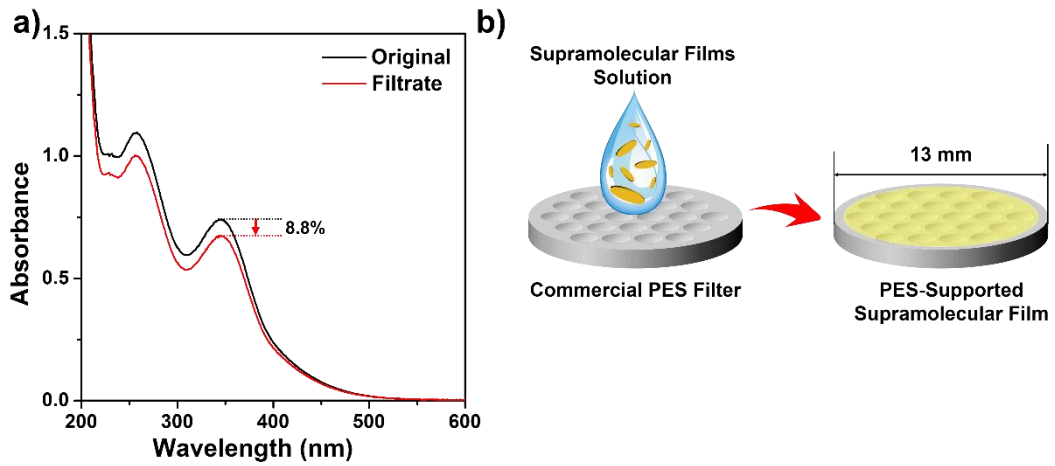


Figure S11. UV-Vis absorption spectra of the supramolecular film solution before and after filtrated by PES filter, related to Figure 5. The original concentration was 0.33 mM. The volume was 1 mL. Scheme of the filtration process (b). The diameter of the PES substrate was 13 mm.

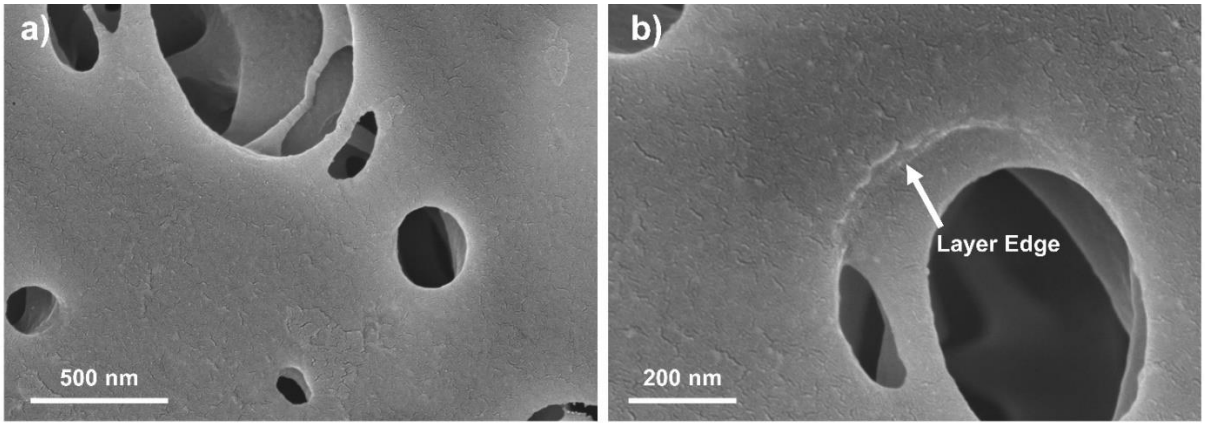


Figure S12. SEM images of the 2D network attached on the PES filter, related to Figure 5. The visible pores with hundreds of nanometers belong to the PES filter. A visible layer edge is showed in a higher magnification (b), showing the nano-sized thickness of the layered 2D network. Images with the larger amplification times are not available because of the instability of the 2D network under high-energy electron beam.

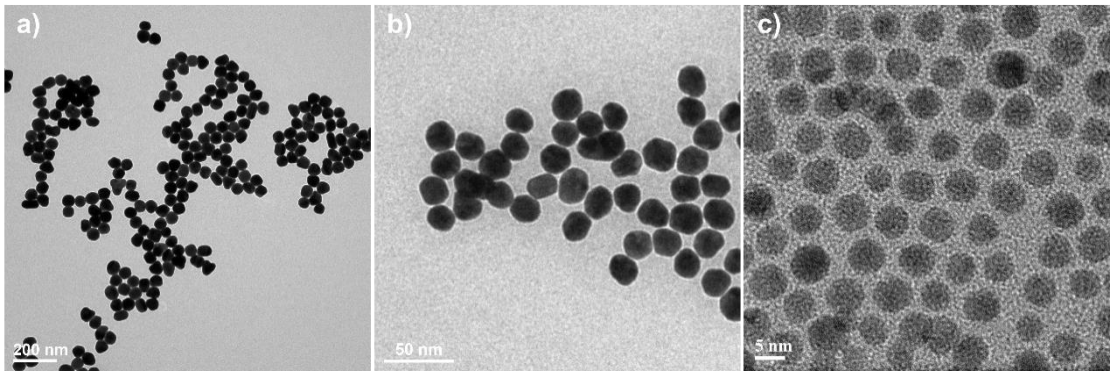


Figure S13. TEM images of the tested gold NPs with different sizes, related to Figure 5. (a) 60 nm; (b) 20 nm; (c) 5.5 nm.

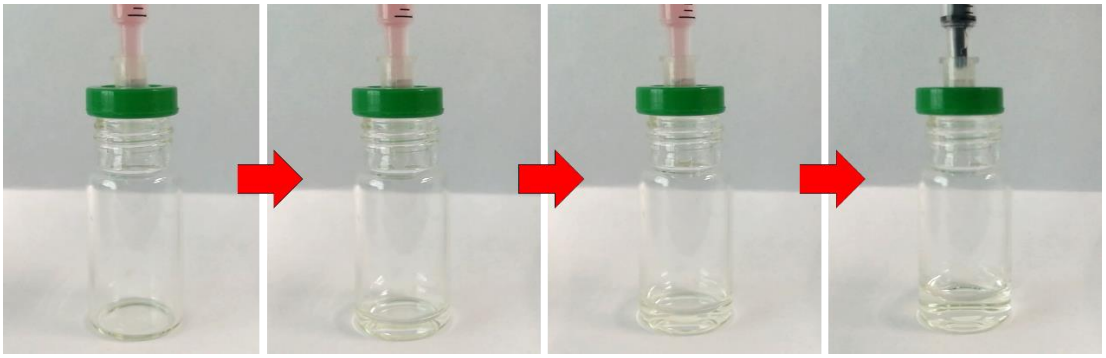


Figure S14. Photographs of the filtration process for 1 mL gold NPs solution (20 nm), related to Figure 5.

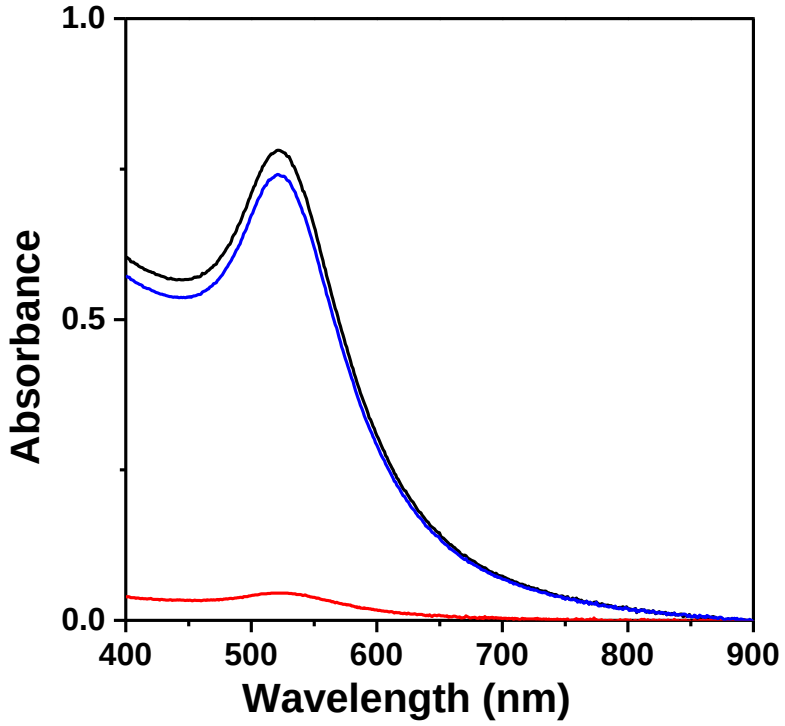


Figure S15. UV-Vis absorption spectra of the 5.5 nm gold NPs solution before (black curve) and the filtrate after filtration by commercial PES film (blue curve) and by PES-supported supramolecular film filter (red curve), related to Figure 5.

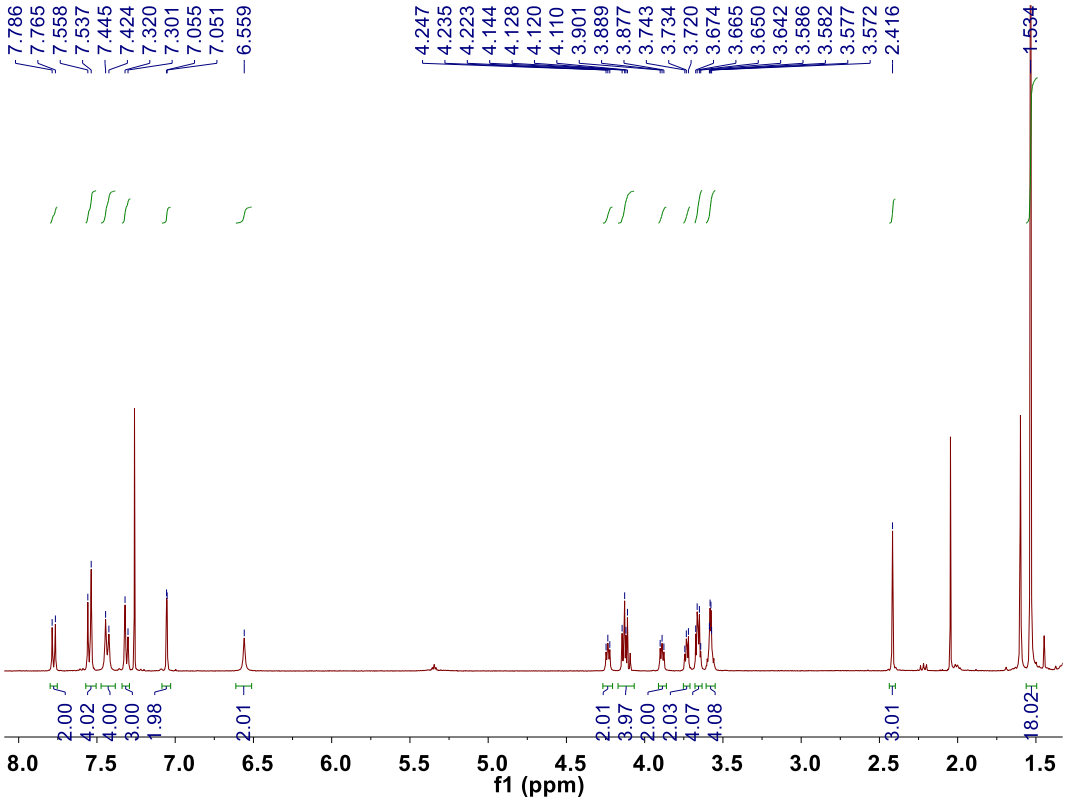


Figure S16. ^{1}H NMR spectrum of **3** ($CDCl_3$, 400 MHz, 298 K), related to Figure 1.

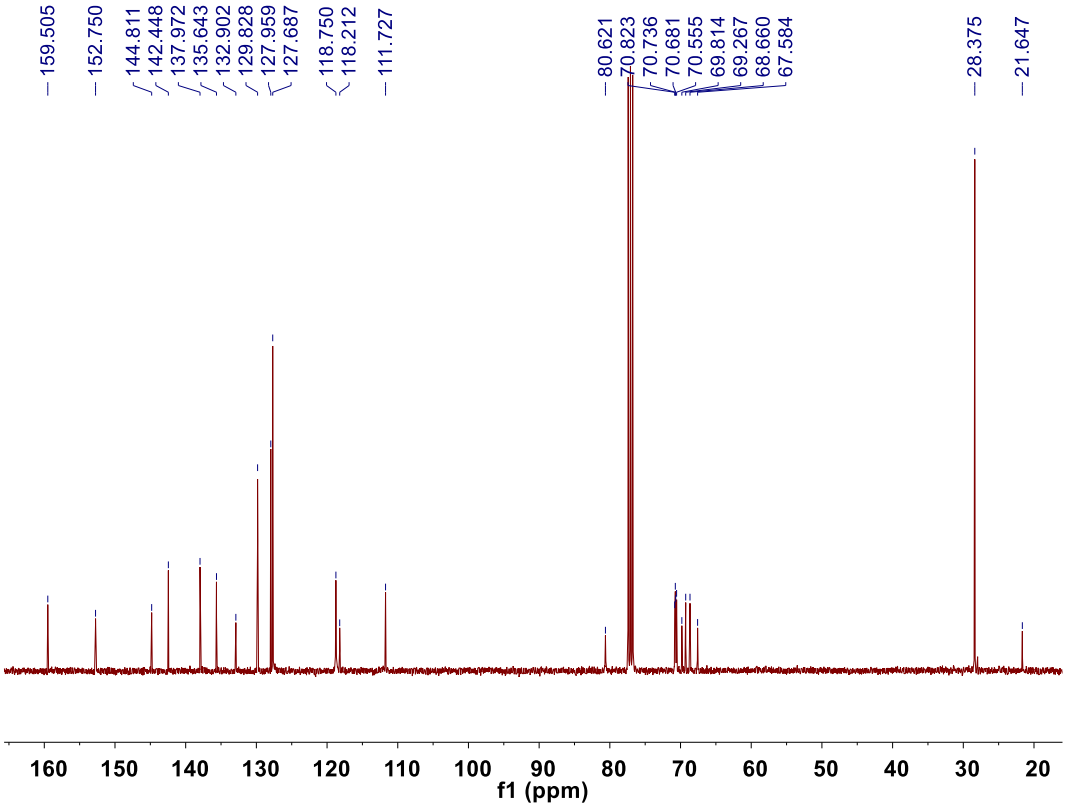


Figure S17. ^{13}C NMR spectrum of **3** ($CDCl_3$, 100 MHz, 298 K), related to Figure 1.

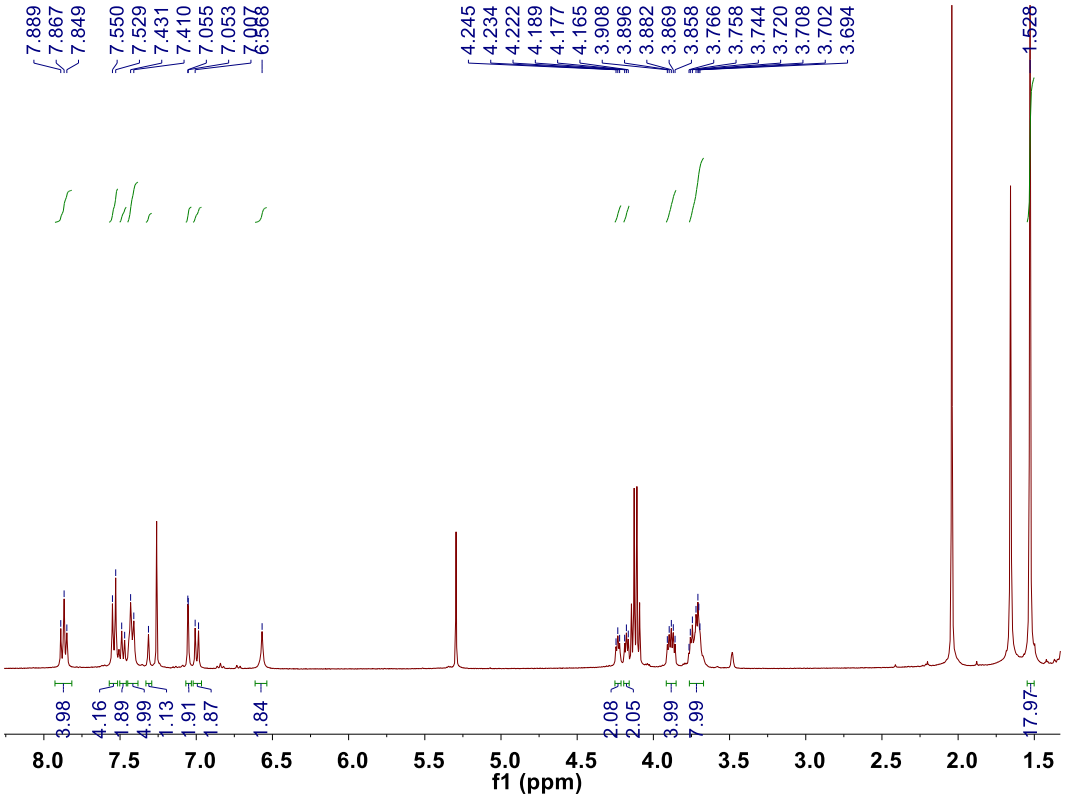


Figure S18. ^{1}H NMR spectrum of **4** ($CDCl_3$, 400 MHz, 298 K), related to Figure 1.

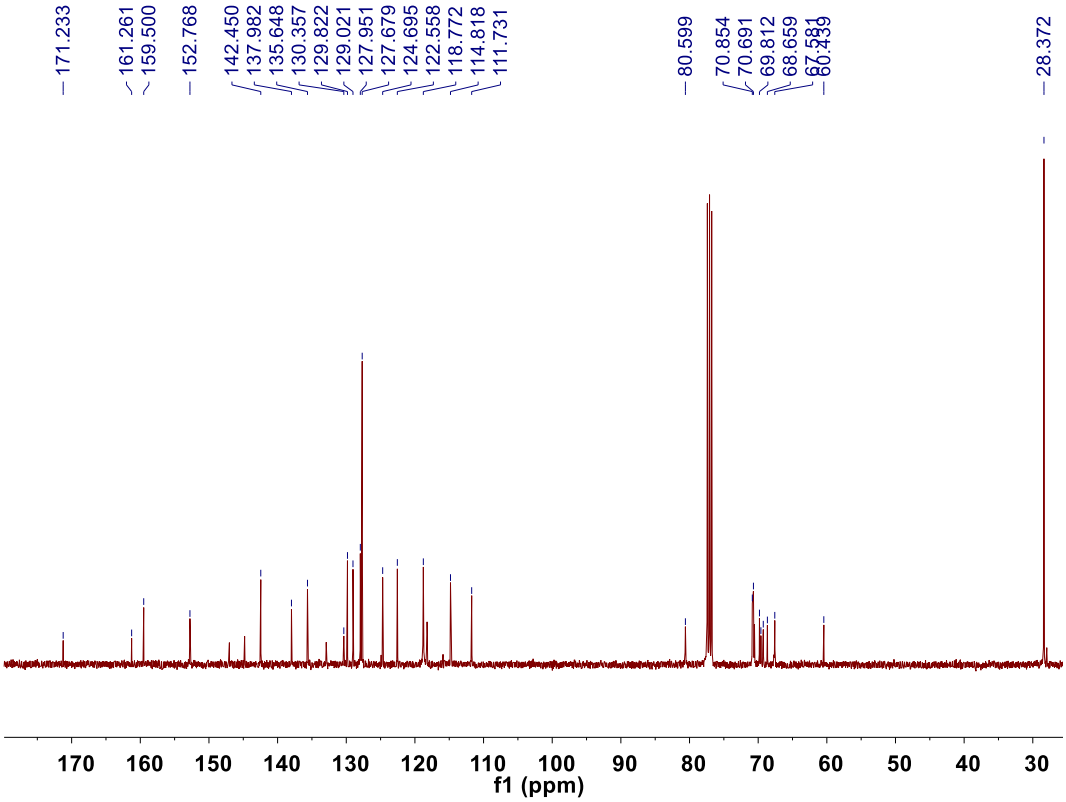


Figure S19. ^{13}C NMR spectrum of **4** ($CDCl_3$, 100 MHz, 298 K), related to Figure 1.

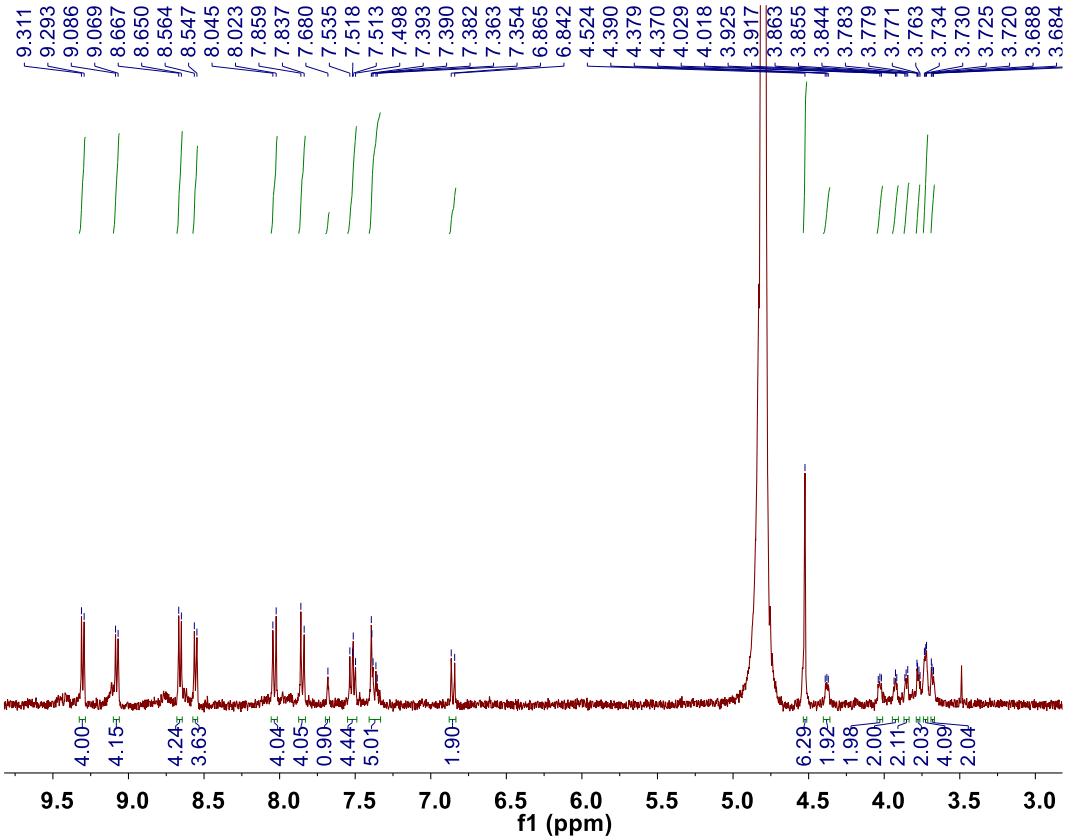


Figure S20. ^{1}H NMR spectrum of *trans*-**1** (D_2O, 400 MHz, 298 K), related to Figure 1.

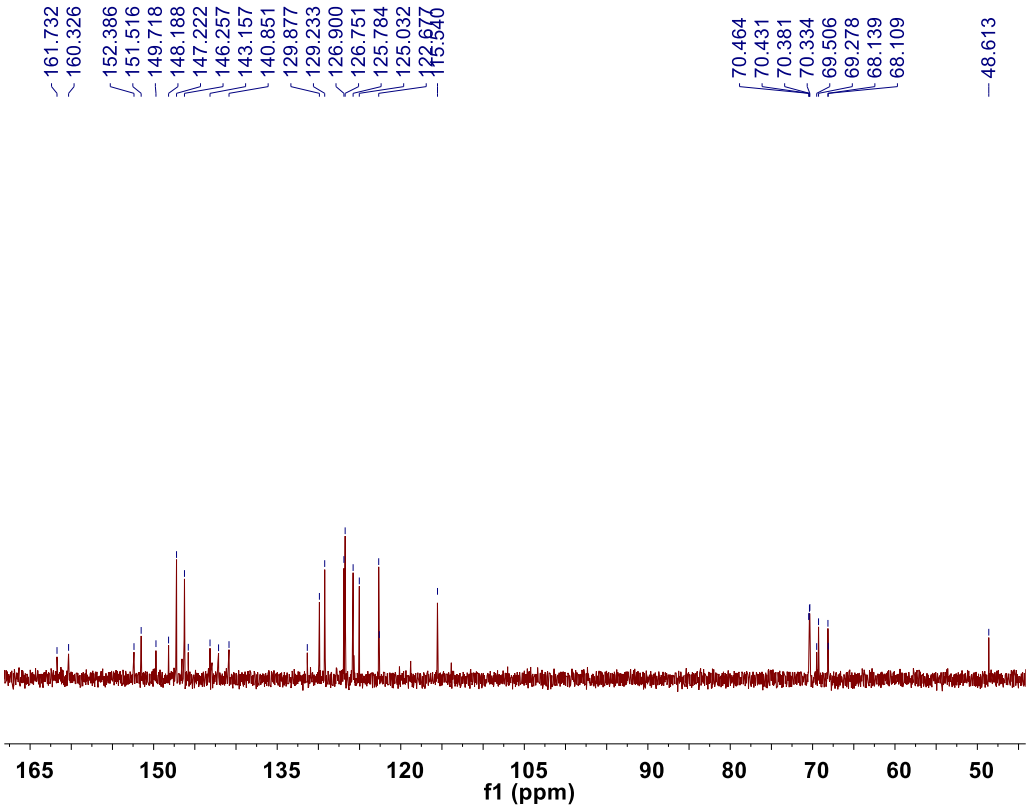


Figure S21. ^{13}C NMR spectrum of *trans*-**1** (D_2O, 600 MHz, 298 K), related to Figure 1.