Two novel supramolecular metallogels constructed by platinum(II) coordination and pillar[5]arene-based host–guest interactions

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Electronic Supplementary Information

1. Materials and methods

All reagents were commercially available and used as supplied without further purification. Compounds **2**,[S1] **3**,[S2] **4**,[S3] and **6**[S4] were synthesized by published literature procedures. NMR spectra were recorded with a Bruker Avance DMX 500 spectrophotometer with use of the deuterated solvent as the lock and the residual solvent or TMS as the internal reference. Low-resolution electrospray ionization (LRESI) mass spectra were obtained on a Bruker Esquire 3000 plus mass spectrometer (Bruker-Franzen Analytik GmbH Bremen, Germany) equipped with an ESI interface and an ion trap analyzer. High-resolution electrospray ionization mass spectra (HRESI-MS) were obtained on a Bruker 7-Tesla FT-ICR mass spectrometer equipped with an electrospray source (Billerica, MA, USA). MALDI-TOF MS was performed with a Bruker UltrafleXtreme instrument. Dynamic light scattering (DLS) was carried out on a Malvern Nanosizer S instrument at room temperature. Scanning electron microscopy (SEM) investigations were carried out on a JEOL 6390LV instrument. Rheological behaviors of gels were analyzed by using an ARG-2 rheometer (TA Instruments, USA). The disc-shaped gels with thickness of 1 mm and diameter of 20 mm were adhere to the plates and surrounded by silicone oil. Frequency sweeps were performed to the samples with strain amplitude of 0.05%.

*2. Synthetic route to compound **1***

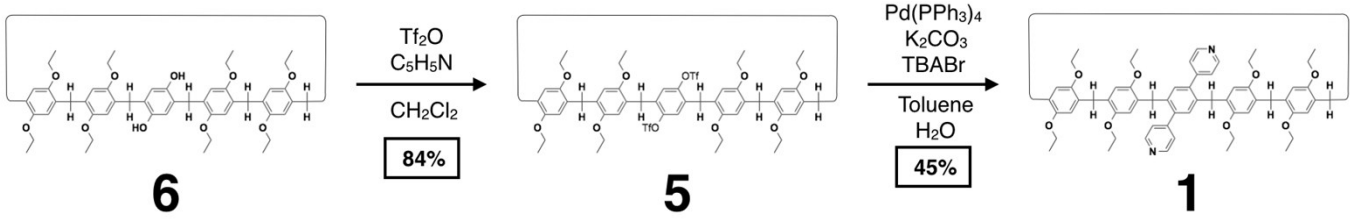


Figure S1. Synthetic route to compound **1**.

Trifluoromethanesulfonic anhydride (2 mL) was added dropwise to a mixture of **6** (500 mg, 0.69 mmol) and C_5H_5N (dry, 1 mL) in CH_2Cl_2 (dry, 20 mL), cooled to 0 ˚C and then allowed to stir at room temperature for 12 h. The reaction mixture was concentrated under vacuum and subjected to silca gel chromatography (1:1 hexane/CH_2Cl_2) to give **5** as a white powder (520 mg, 84%). The ^{1}H NMR spectrum of **5** is shown in Figure S2. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ = 7.38 (1H, s), 6.79 (1H, s), 6.76 (1H, s), 6.75 (1H, s), 6.67 (1H, s), 3.95−3.79 (14H, m), 1.42−1.22 (12 H, m). The ^{13}C NMR spectru of **5** is shown in Figure S3. ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ = 148.88, 148.77, 148.75, 148.54, 145.05, 133.11, 128.96, 127.77, 127.02, 123.77, 123.19, 119.13, 115.95, 113.96, 113.66, 113.16, 62.81, 62.77, 62.36, 52.22, 29.64, 28.59, 28.12, 14.12, 14.04, 13.53. LRESIMS is shown in Figure S4: *m*/*z* 1116.4 [M + NH_4^+]$^+$. HRESIMS: *m*/*z* calcd for [M + H]$^+$ $C_{53}H_{61}O_{14}F_6S_2^+$, 1099.34069; found 1099.34181; error 1 ppm.

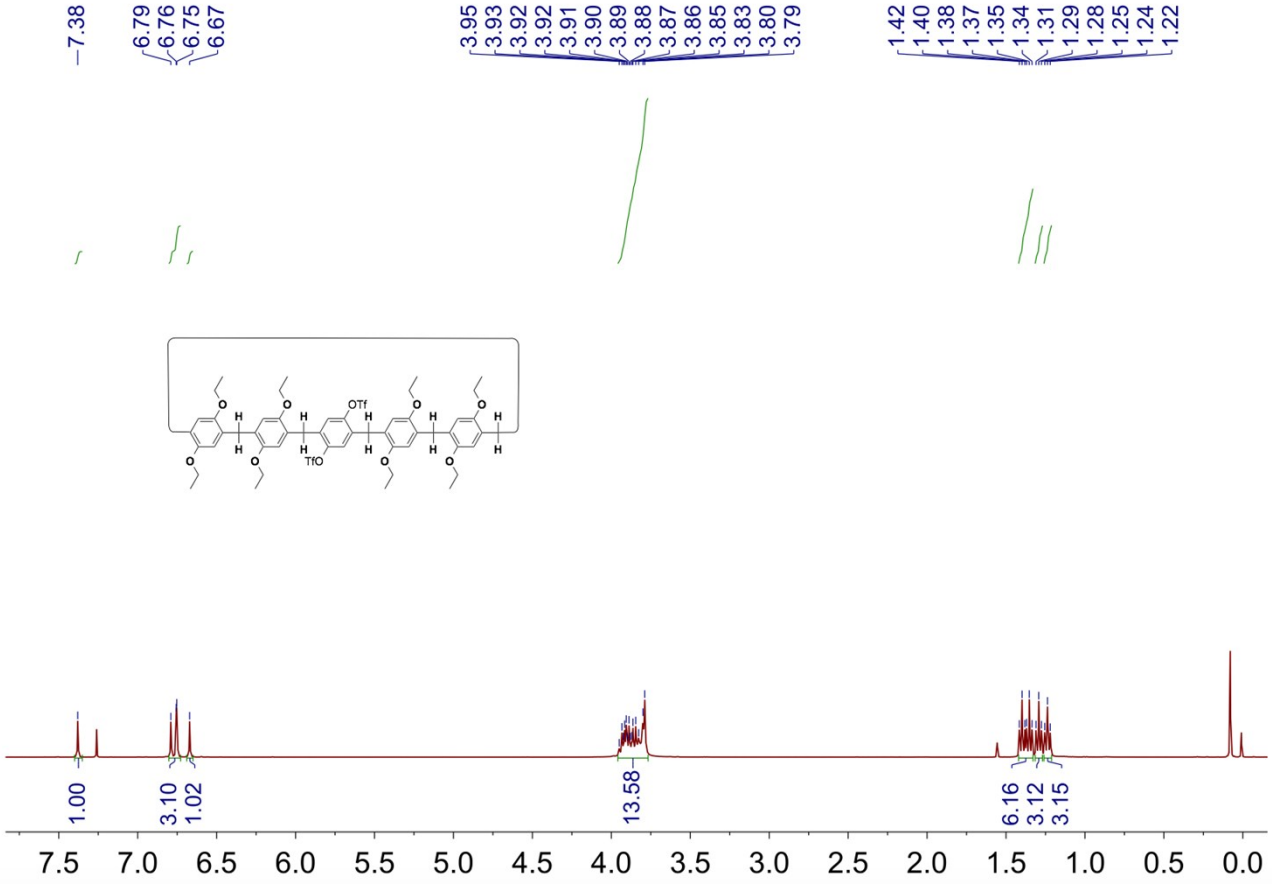


Figure S2. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **5**.

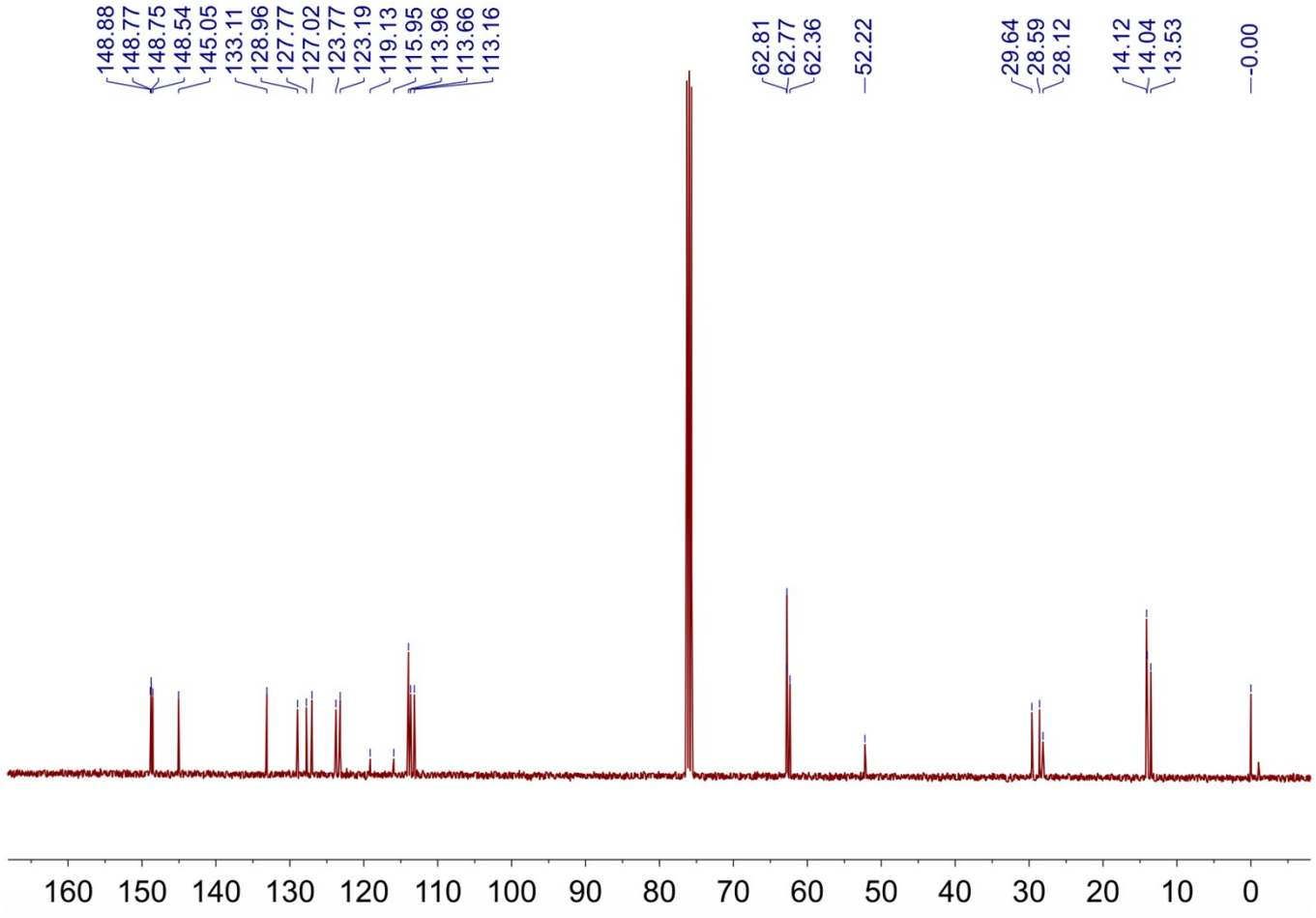


Figure S3. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **5**.

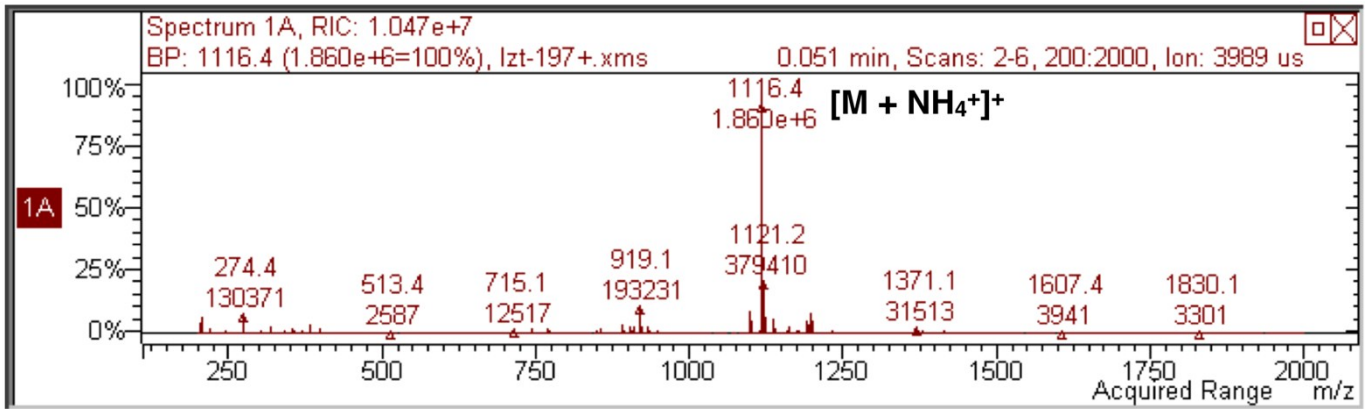


Figure S4. LRESIMS spectrum of **5**.

$Pd(PPh_3)_4$ (266 mg, 0.230 mmol) was added to a mixture of **5** (1.04 g, 1.01 mmol), 4-pyridinyl boronic acid (738 mg, 6.00 mmol), and K_2CO_3 (2.49 g, 1.80 mmol) in 80.0 mL of a mix solvent (Toluene/H_2O, 3:1 *v*/*v*). The mixture was stirred at 100 ˚C for 24 h. After cooling to room temperature, the excess solvent was removed on a rotary evaporator at reduced pressure. After adding 200 mL of CH_2Cl_2, the solution was washed with H_2O (2 × 100 mL), brine (100 mL), and dried (Na_2SO_4) then concentrated under vacuum, and finally subjected to silica gel chromatography (CH_2Cl_2/MeOH, 100:1 *v*/*v*) to give **1** (0.37 g,

45%). The ^{1}H NMR spectrum of **5** is shown in Figure S5. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ = 8.45 (4H, s), 6.89 (6H, s), 6.86 (2H, s), 6.74 (2H, s), 6.53 (2H, s), 5.95 (2H, s), 3.95−3.56 (26H, m), 1.46−1.43 (6H, t, *J* = 7.5 Hz), 1.26−1.24 (6H, t, *J* = 5.0 Hz), 1.17−1.15 (6H, t, *J* = 5.0 Hz), 0.97−0.94 (6H, t, *J* = 7.5 Hz). The ^{13}C NMR spectru of **1** is shown in Figure S6. ^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ = 150.02, 149.99, 149.69, 149.52, 149.28, 138.59, 136.91, 131.45, 129.83, 128.98, 128.64, 126.81, 124.24, 115.22, 115.16, 114.97, 114.58, 64.12, 64.05, 63.23, 33.10, 30.96, 29.95, 29.61, 15.34, 15.19, 14.86, 14.56. MOLDI-TOF is shown in Figure S7: *m*/*z* 957.120 $[M + H^+]^+$.

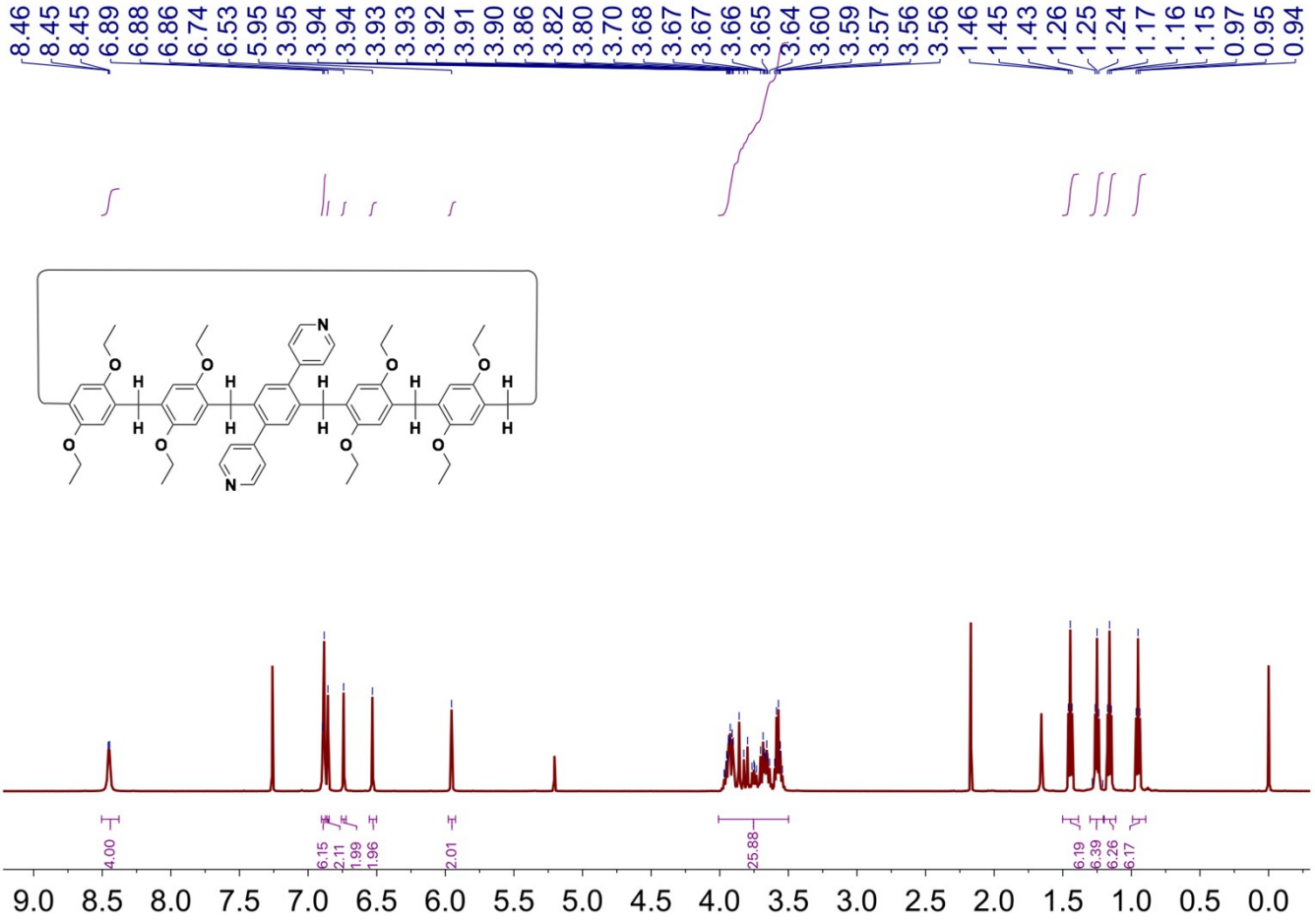


Figure S5. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **1**.

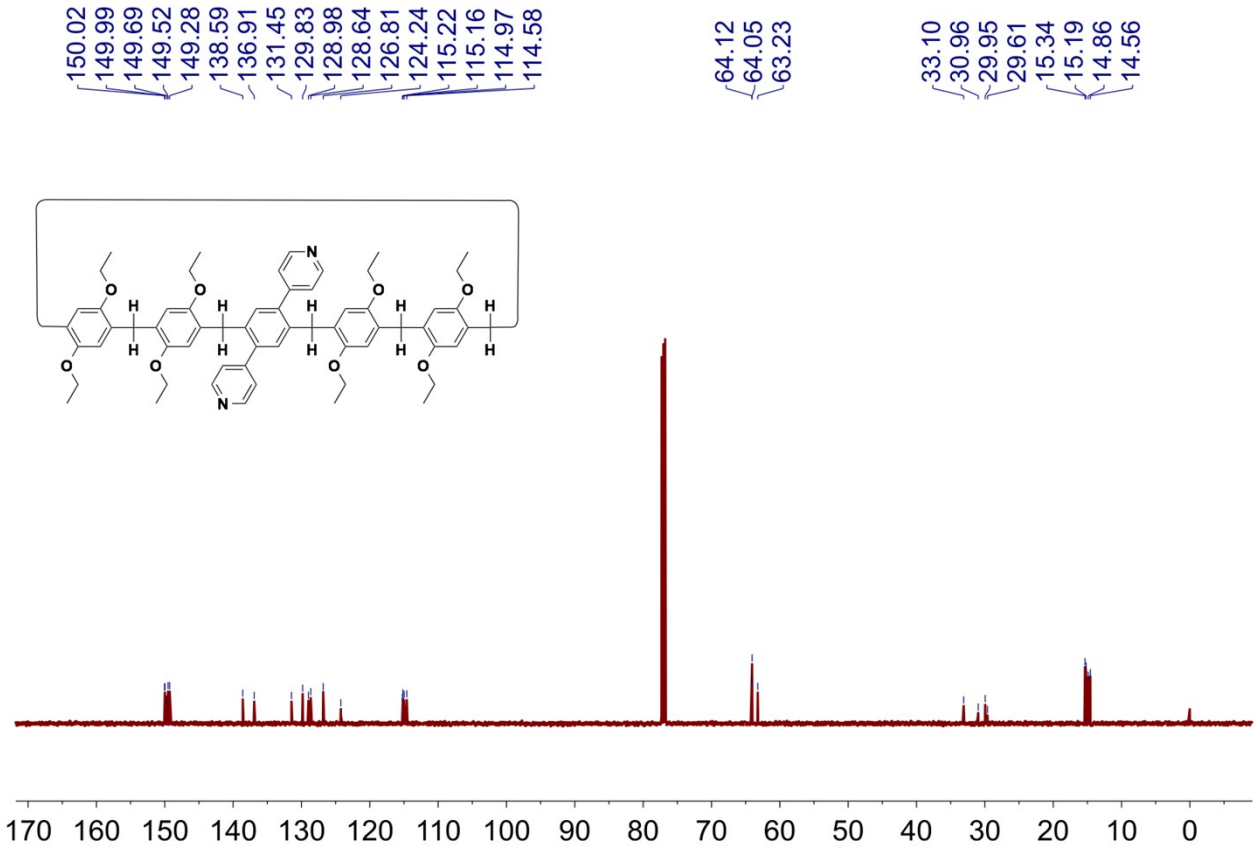


Figure S6. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **1**.

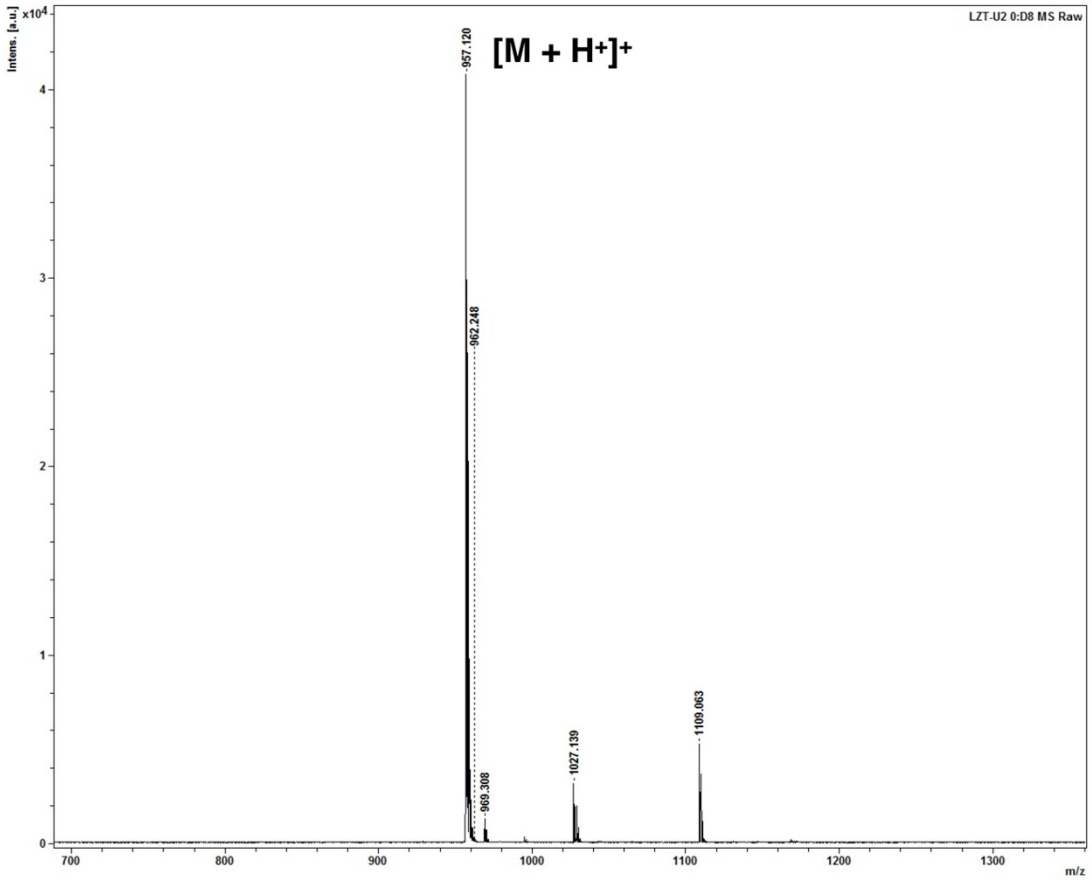


Figure S7. MOLDI-TOF spectrum of **1**.

*3. $^{31}P\{^{1}H\}$ NMR spectra of **3** and assemblies*

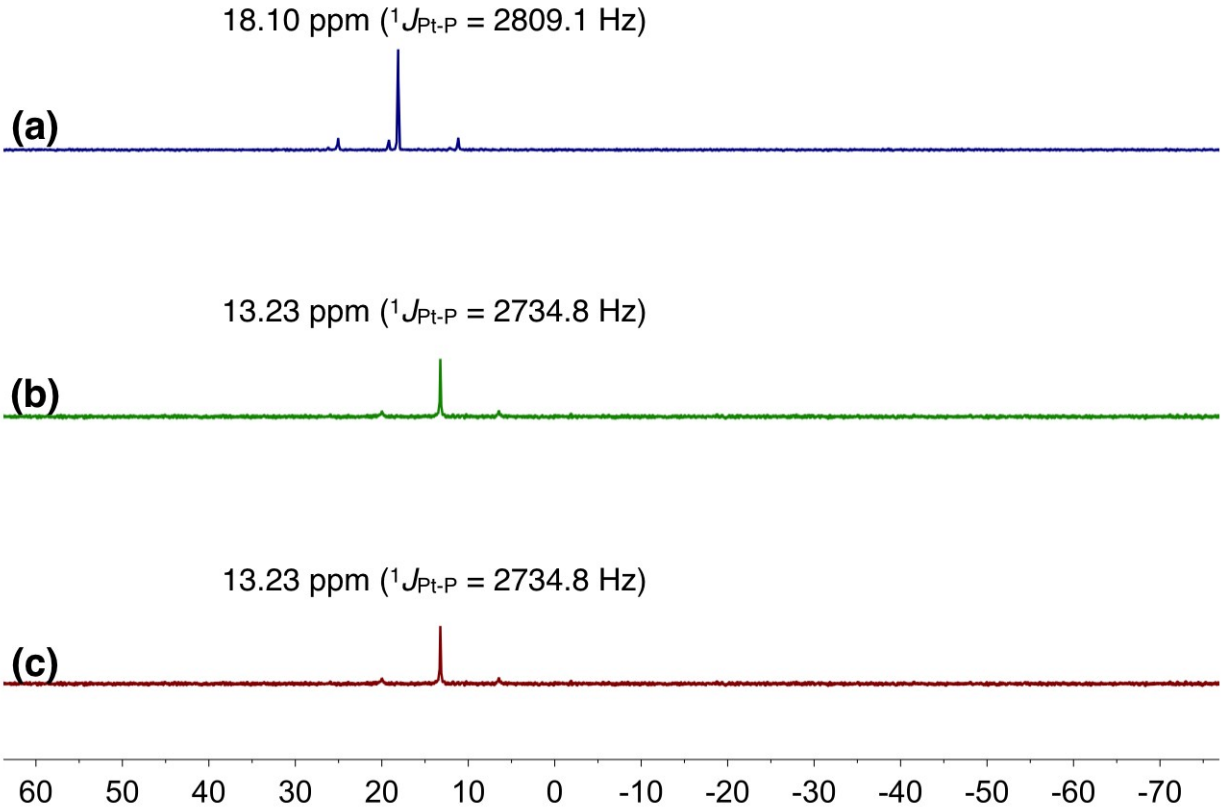
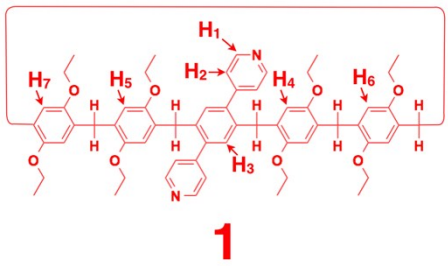
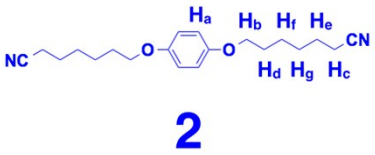


Figure S8. Partial $^{31}P\{^{1}H\}$ NMR spectra (202.3 MHz, acetone-d_6, 298 K): (a) **3**; (b) **1** + **3**; (c) **1** + **3** + **2**. *c* = 5.00 mM.

*4. ^{1}H NMR spectra of **1**, **2**, and **1** + **2***





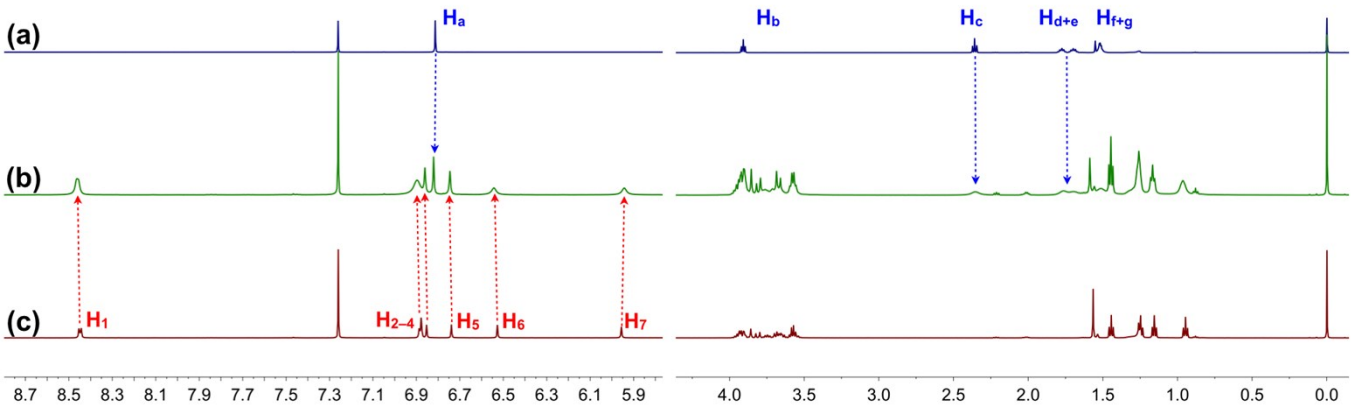


Figure S9. Partial ^{1}H NMR spectra (500 MHz, $CDCl_3$, 298 K): (a) **2**; (b) **1** + **2**; (c) **1**. *c* = 5.00 mM.

*5. ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra of **4** and assemblies*

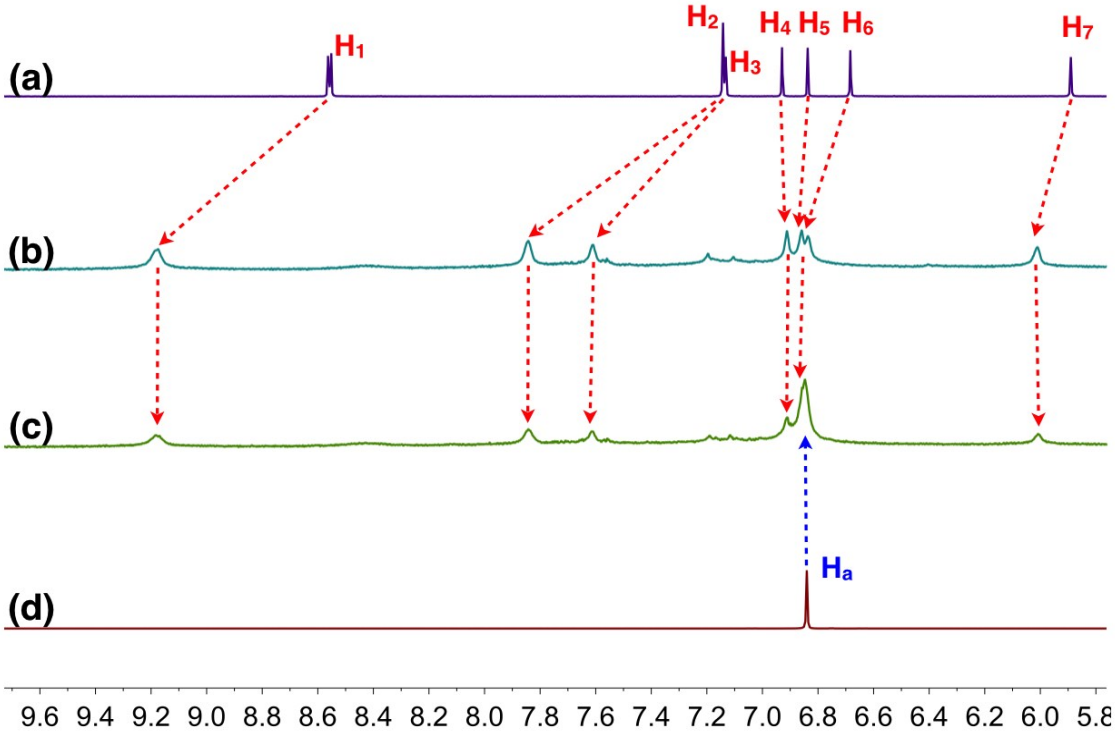


Figure S10. Partial ^{1}H NMR spectra (500 MHz, acetone-d_6, 298 K): (a) **1**; (b) **1** + **4**; (c) **1** + **4** + **2**; (d) **2**. c = 5.00 mM.

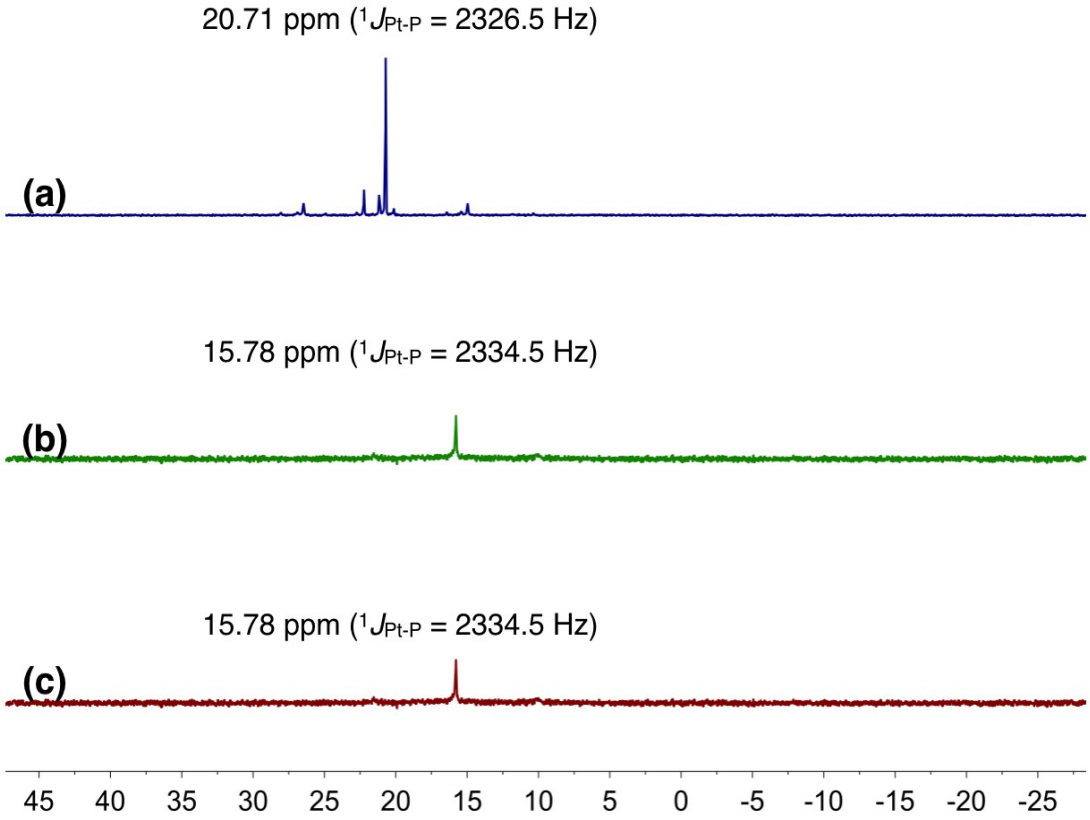


Figure S11. Partial $^{31}P\{^{1}H\}$ NMR spectra (202.3 MHz, acetone-d_6, 298 K): (a) **4**; (b) **1** + **4**; (c) **1** + **4** + **2**. c = 5.00 mM.

6. Partial DOSY NMR spectra of supramolecular assemblies

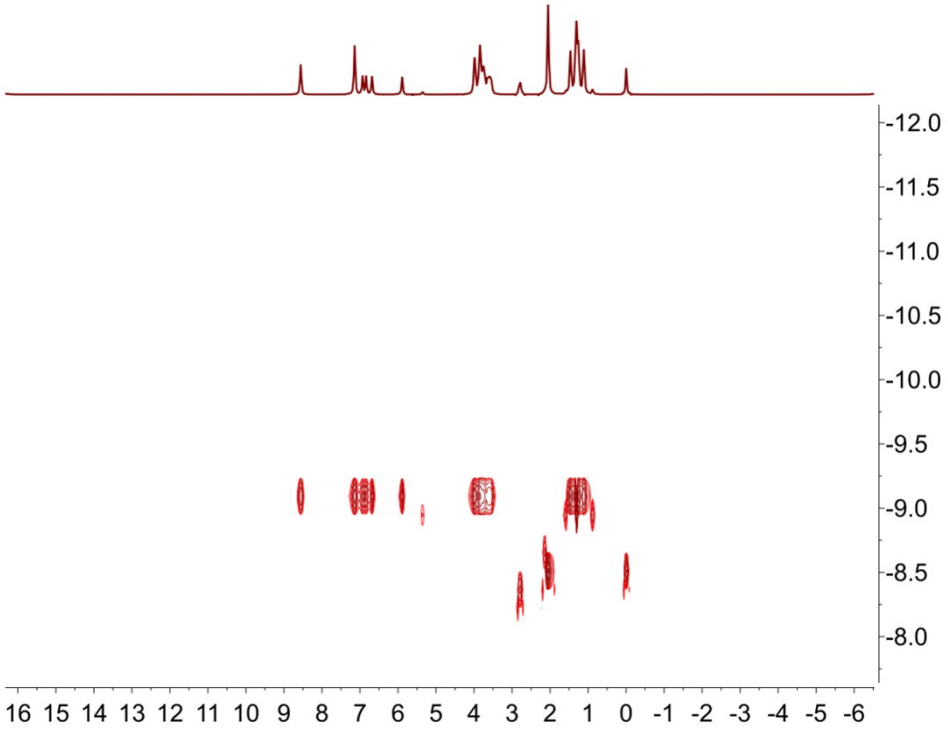


Figure S12. Partial DOSY NMR spectrum (500 MHz, acetone-d_6, 298 K) of **1** at 5.00 mM.

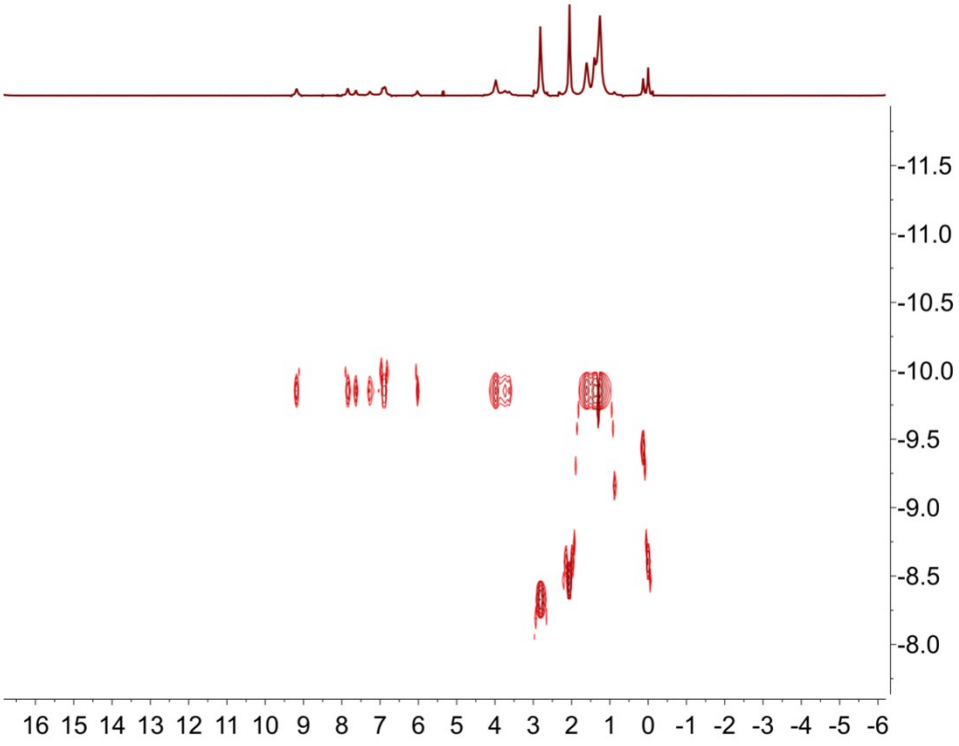


Figure S13. Partial DOSY NMR spectrum (500 MHz, acetone-d_6, 298 K) of **1** + **3** at 5.00 mM.

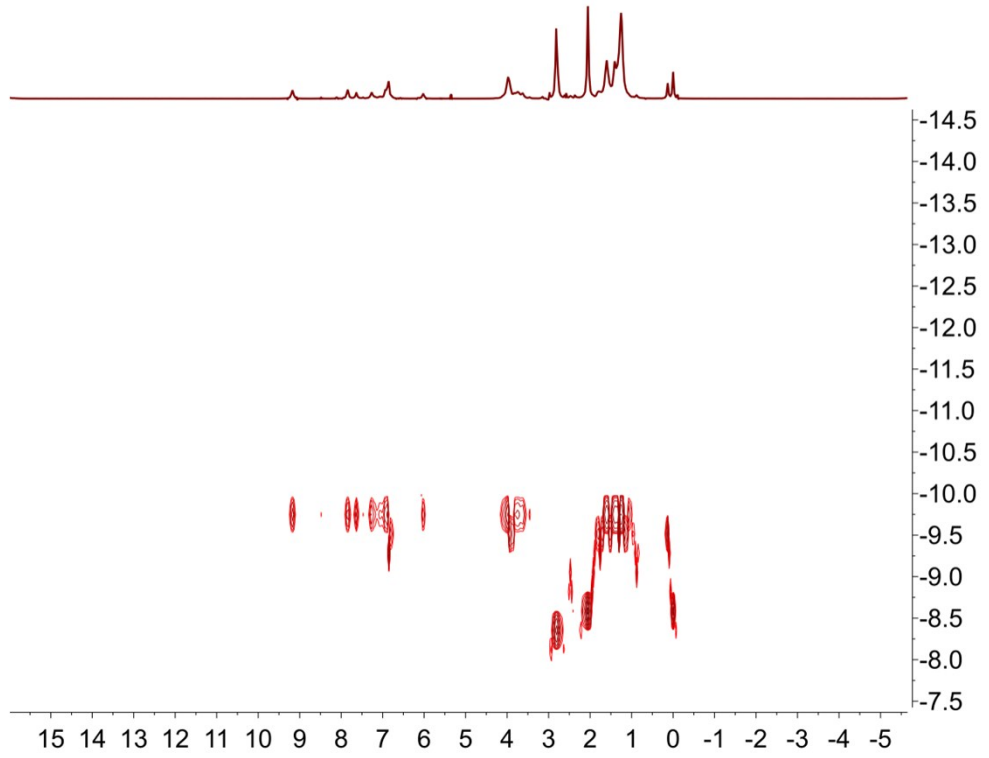


Figure S14. Partial DOSY NMR spectrum (500 MHz, acetone-d_6, 298 K) of **1** + **3** + **2** at 5.00 mM.

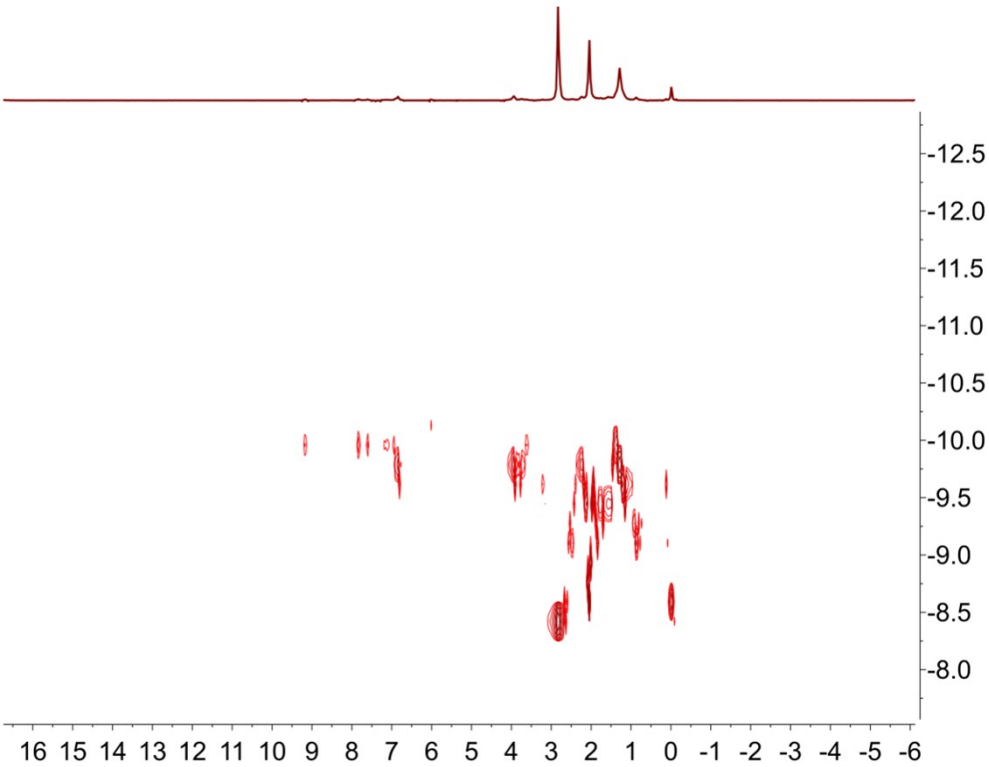


Figure S15. Partial DOSY NMR spectrum (500 MHz, acetone-d_6, 298 K) of **1** +**4** at 5.00 mM.

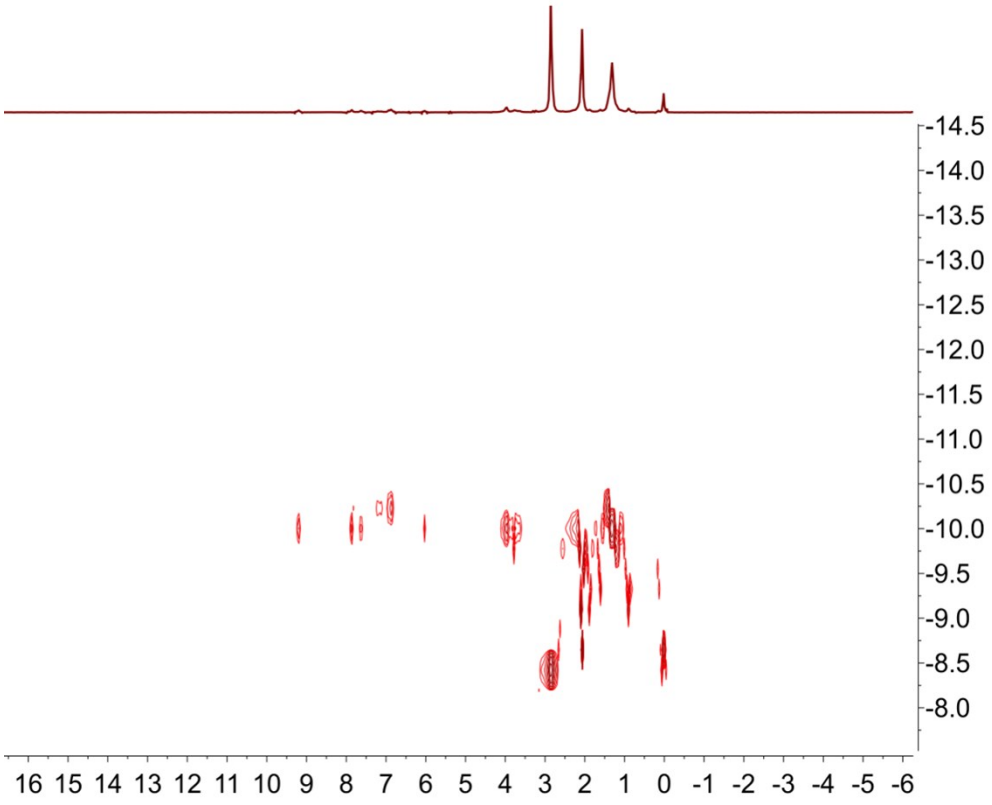


Figure S16. Partial DOSY NMR spectrum (500 MHz, acetone-d_6, 298 K) of **1** +**4** + **2** at 5.00 mM.

*7. DOSY and DLS results of **1**, **1** + **4**, and **1** + **4** + **2***

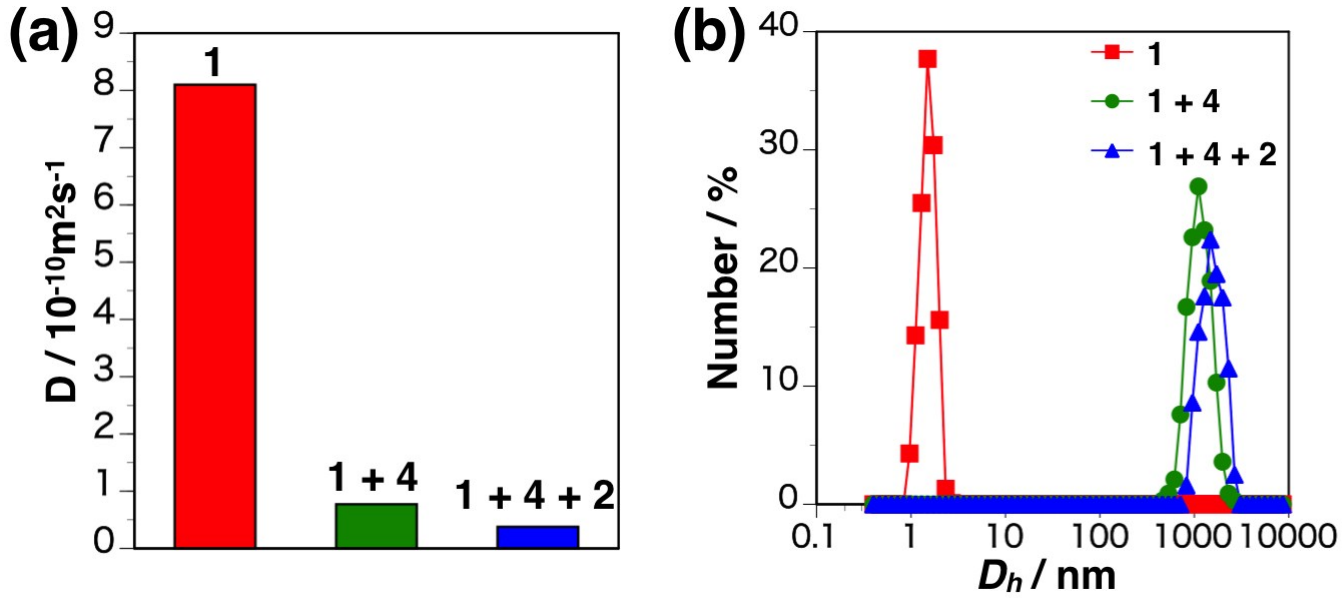


Figure S17. (a) Diffusion coefficient D values (500 MHz, acetone-d_6, 298 K) of **1**, **1** + **4**, and **1** + **4** + **2**. (b) Size distributions of **1**, **1** + **4**, and **1** + **4** + **2**. *c* = 5.00 mM.

*8. SEM images of **1** + **4** and **1** + **4** + **2***

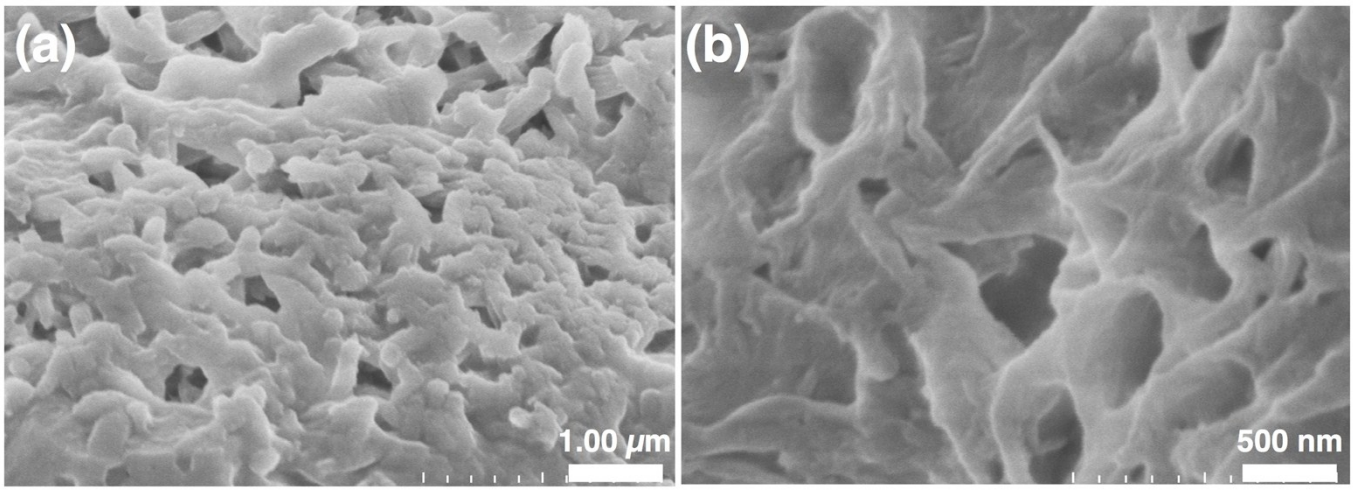


Figure S18. SEM image of (a) **1** + **4** and (b) **1** + **4** + **2** in acetone at 100 mM.

9. Multi-responsiveness of gels

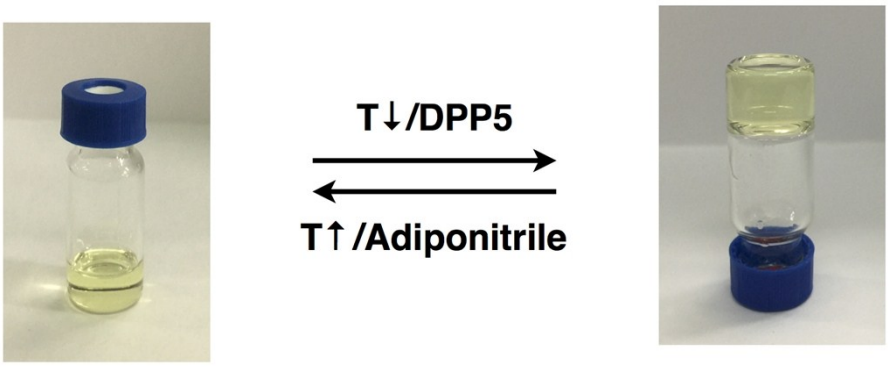


Figure S19. The gel–sol transitions of the supramolecular gel triggered by different stimuli.

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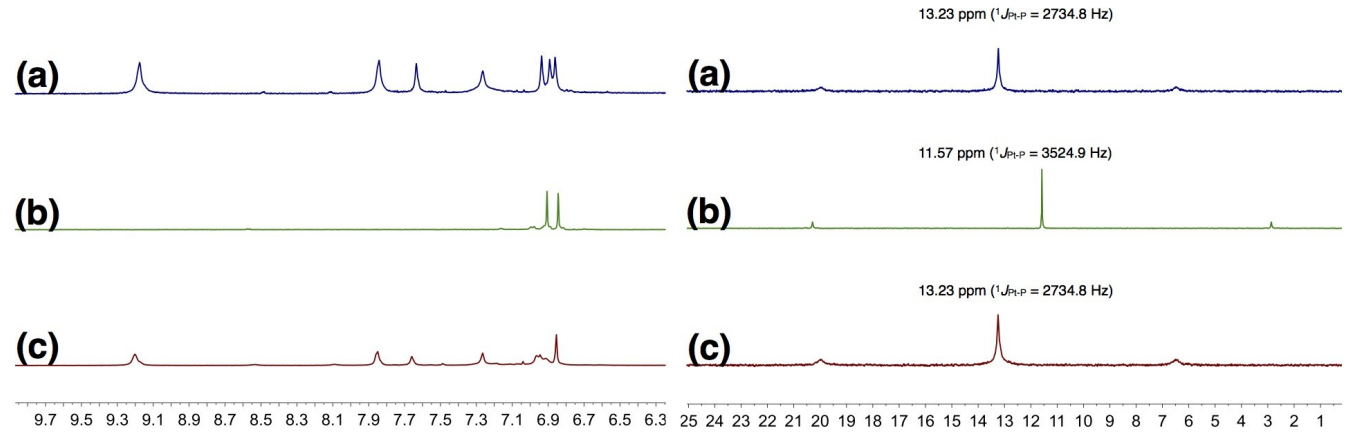

Figure S20. Partial ^{1}H NMR (500 MHz, acetone-d_6, 298 K) (left) and ^{31}P{^{1}H} NMR (202.3 MHz, acetone-d_6, 298 K) (right) spectra of (a) **1** + **3** + **2**; (b) after the addition of 2 equiv of TBABr to a; (c) after subsequent addition of 4 equiv of AgOTf to b. c = 5.00 mM.

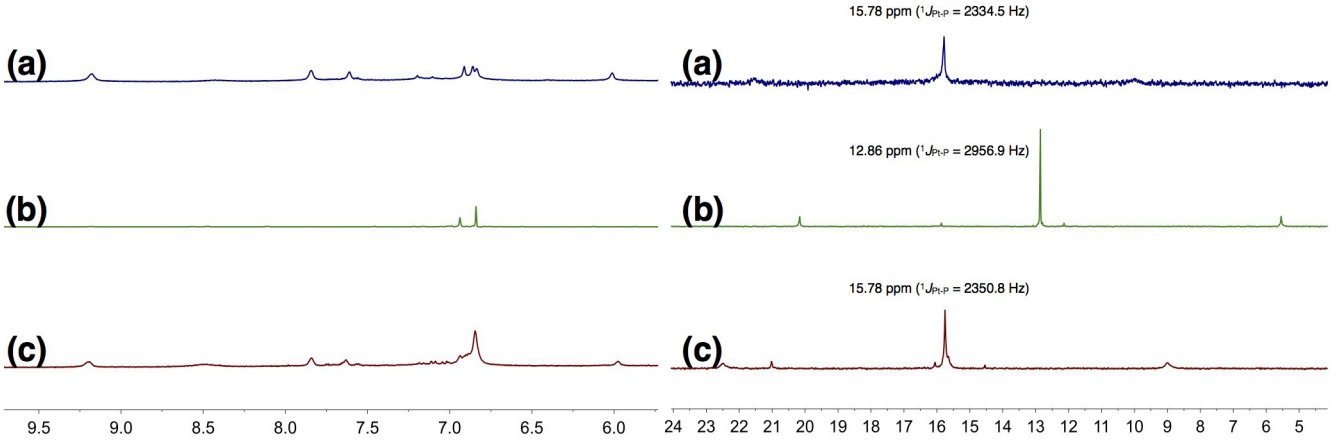

Figure S21. Partial ^{1}H NMR (500 MHz, acetone-d_6, 298 K) (left) and ^{31}P{^{1}H} NMR (202.3 MHz, acetone-d_6, 298 K) (right) spectra of (a) **1** + **4** + **2**; (b) after the addition of 2 equiv of TBABr to a; (c) after subsequent addition of 4 equiv of AgOTf to b. c = 5.00 mM.

*10. X-ray analysis data for **1***

Crystallographic data: prism, colourless, 0.448 × 0.350 × 0.252 mm^3, $C_{61}H_{68}N_2O_8{\cdot}2C_3H_6O$, *FW* 1073.33, orthorhombic, space group *P*–1, a = 25.3293(7), b = 20.1695(5), c = 23.6895(6) Å, α = 90°, β = 90°, γ = 90°, V = 12102.5(5) Å^3, Z = 8, D_c = 1.178 g cm^{-3}, T = 150(1) K, μ = 0.078 mm^{-1}, 28854 measured reflections, 9828 independent reflections, 1359 parameters, 59 restraints, F(000) = 4608, R_1 = 0.1727, wR_1 = 0.3001 (all data), R_2 = 0.0889, wR_2 = 0.2365 [$I > 2\sigma(I)$], max. residual density 0.792 e•Å^{-3}, and goodness-of-fit (F^2) = 1.015. CCDC 1522035.

11. References:

S1. Z. Li, Y. Zhang, C. Zhang, L. Chen, C. Wang, H. Tan, Y. Yu, X. Li and H.-B. Yang, *J. Am. Chem. Soc.,* 2014, **136**, 8577.

S2. P. Wei, J. Li, X. Yan and Q. Zhou, *Org. Lett.,* 2014, **16**, 126.

S3. P. Wei, S. Li, Y. Zhang, Y. Yu and X. Yan, *Polym. Chem.,* 2014, **5**, 3972.

S4. T. Ogoshi, D. Yamafuji, D. Kotera, T. Aoki, S. Fujinami and T. Yamagishi, *J. Org. Chem.*, 2012, **77**, 11146.