Photoinduced transformations of stiff-stilbene-based discrete metallacycles to metallosupramolecular polymers

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PHYSICAL SCIENCES: Chemistry

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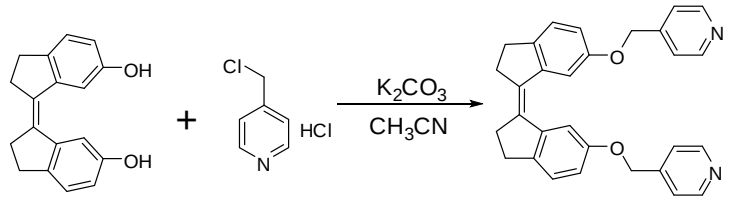
Section A. Materials/General Methods/Instrumentation

All reagents were commercially available and used as supplied without further purification. Deuterated solvents were purchased from Cambridge Isotope Laboratory (Andover, MA). Compounds **2**,[S1] **3**,[S1] and **8**[S2] were prepared according to the published procedures. NMR spectra were recorded with a Bruker Avance DMX 500 spectrophotometer or a Bruker Avance DMX 400 spectrophotometer with use of the deuterated solvent as the lock and the residual solvent or TMS as the internal reference. ^{1}H and ^{13}C NMR chemical shifts are reported relative to residual solvent signals, and $^{31}P\{^{1}H\}$ NMR chemical shifts are referenced to an external unlocked sample of 85% H_3PO_4 (δ 0.0). The two-dimensional diffusion-ordered (2D DOSY) NMR spectra were recorded on a Bruker DRX500 spectrometer. Dynamic light scattering (DLS) was carried out on a Malvern Nanosizer S instrument at room temperature. Mass spectra were recorded on a Micromass Quattro II triple-quadrupole mass spectrometer using electrospray ionization with a MassLynx operating system. UV-vis spectra were collected on a Shimadzu UV-2550 UV-vis spectrophotometer. The fluorescence experiments were conducted on a RF-5301 spectrofluorophotometer (Shimadzu Corporation, Japan). Transmission electron microscopy (TEM) investigations were carried out on a JEM-1200EX instrument. The samples for TEM experiments (Fig. 5, images *A* and *B*) were prepared by placing one drop of a dichloromethane solution of DMC **4** (or **5**) onto a carbon-coated grid. The samples for TEM experiments (Fig. 5, images *C* and *D*) were prepared by placing one drop of a dichloromethane solution of MSP **6** (or **7**) onto a carbon-coated grid.The melting points were collected on a SHPSIC WRS-2 automatic melting point apparatus.

Section B. Synthetic Protocols

*1. Synthesis of stiff stilbene ligand **Z-1***



8 **Z-1**

Scheme S1

Into a 150 mL round-bottomed flask were added compound **8** (200 mg, 0.757 mmol), 4-(chloromethyl)pyridine hydrochloride (273 mg, 1.66 mmol), and K_2CO_3 (1.05 g, 7.57 mmol) in 80 mL of CH_3CN. After heating at reflux under N_2 for 16 h, the solvent was removed and CH_2Cl_2 was added. The mixture was washed with water and brine, and then purified by flash column chromatography (dichloromethane/methanol, 100:1 *v*/*v*) to stilbene ligand ***Z*-1** as a yellow solid (253 mg, 75%). Mp 126.4–127.6 °C. The ^{1}H NMR spectrum of ***Z*-1** is shown in Figure S1. ^{1}H NMR (CD_2Cl_2, room temperature, 500 MHz) δ (ppm): 8.40 (d, J = 5.5 Hz, 4H), 7.66 (d, J = 2.0 Hz, 2H), 7.18 (d, J = 5.5 Hz, 4H), 7.13 (d, J = 8.0 Hz, 2H), 6.70–6.75 (m, 2H), 4.97 (s, 4H), 2.80–2.88 (m, 4H), 2.70–2.773 (m, 4H). The ^{13}C NMR spectrum of ***Z*-1** is shown in Figure S2. ^{13}C NMR (CD_2Cl_2, room temperature, 125 MHz) δ (ppm): 32.40, 37.88, 71.23, 112.53, 116.76, 124.06, 128.39, 138.21, 144.26, 144.32, 148.86, 152.51, and 159.29. LRESIMS is shown in Figure S3: *m*/*z* 447.0 $[M + H]^+$. HRESIMS: *m*/*z* calcd for $[M]^+$ $C_{30}H_{26}N_2O_6$, 446.1994; found 446.1996, error 0.4 ppm.

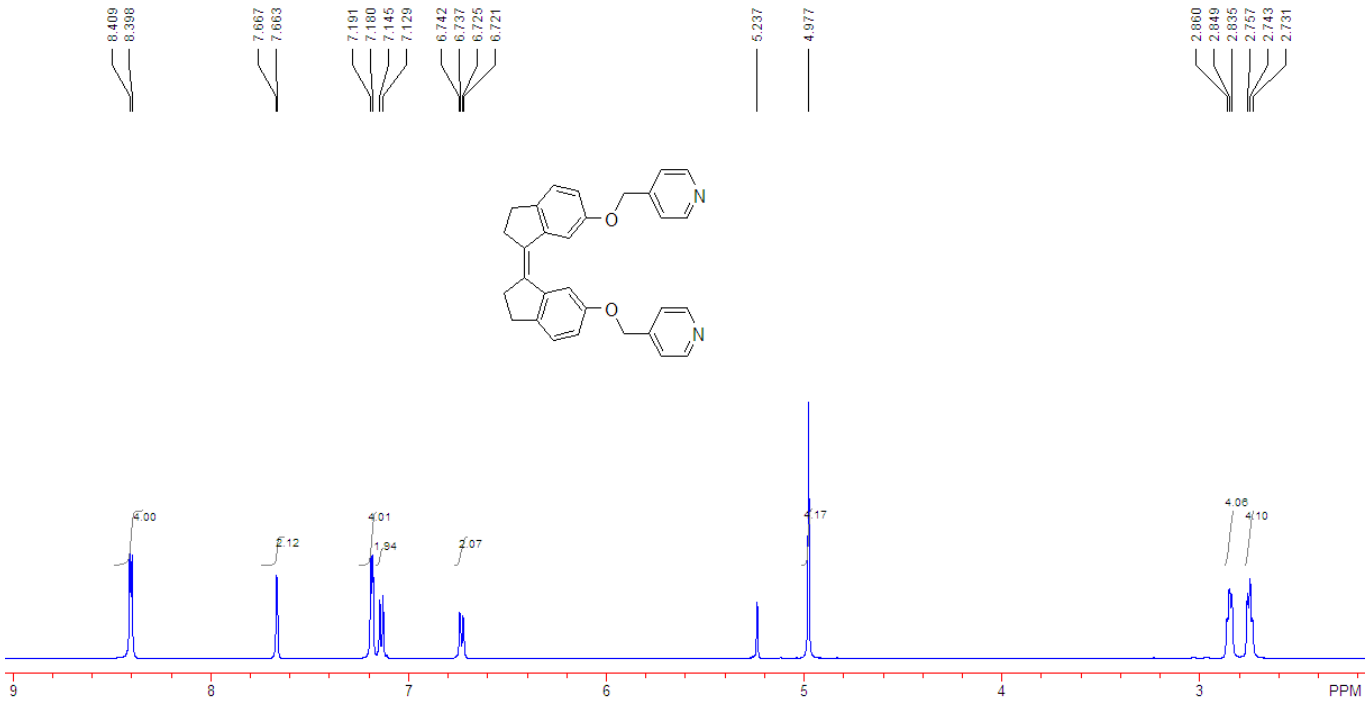


Figure S1. ^{1}H NMR spectrum (CD_2Cl_2, room temperature, 500 MHz) of ***Z*-1**.

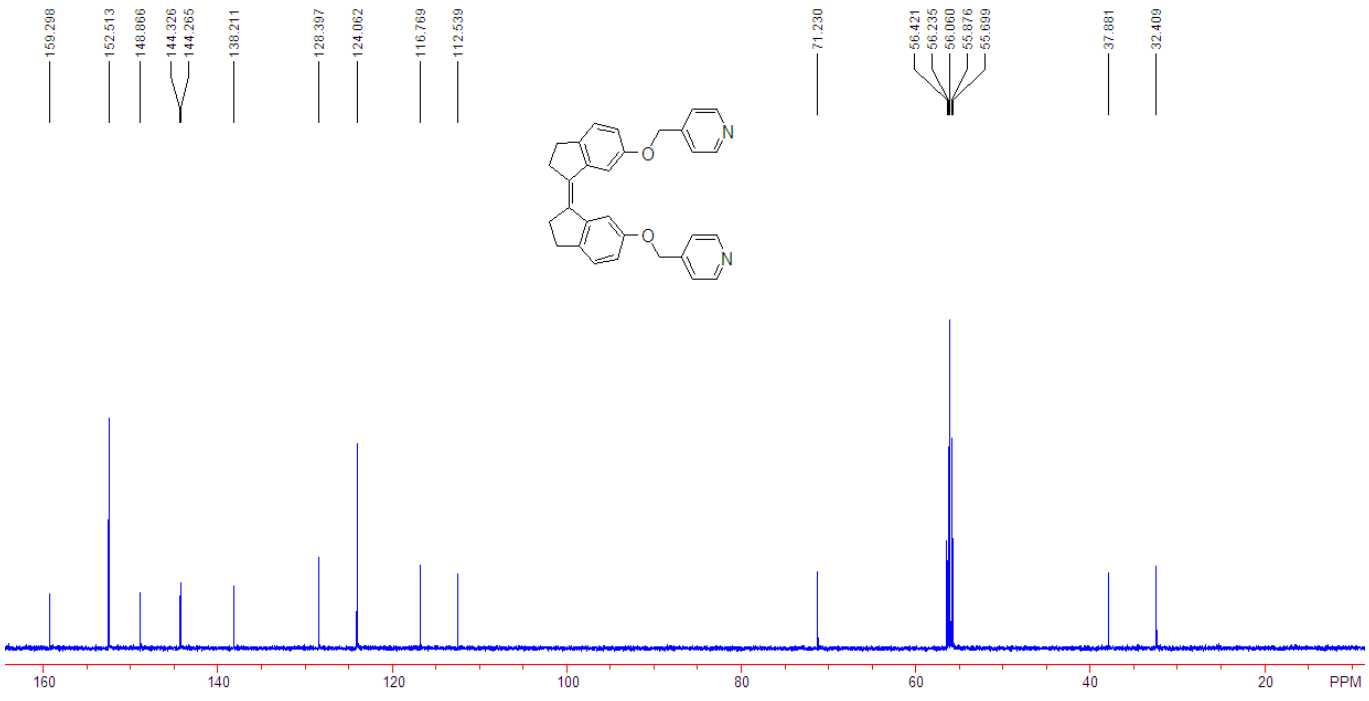


Figure S2. ^{13}C NMR spectrum (CD_2Cl_2, room temperature, 125 MHz) of ***Z*-1**.

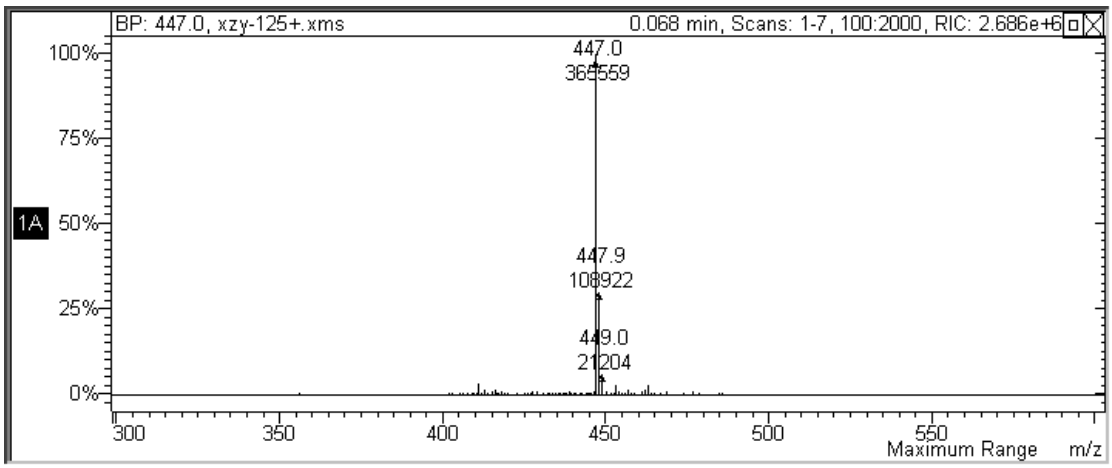
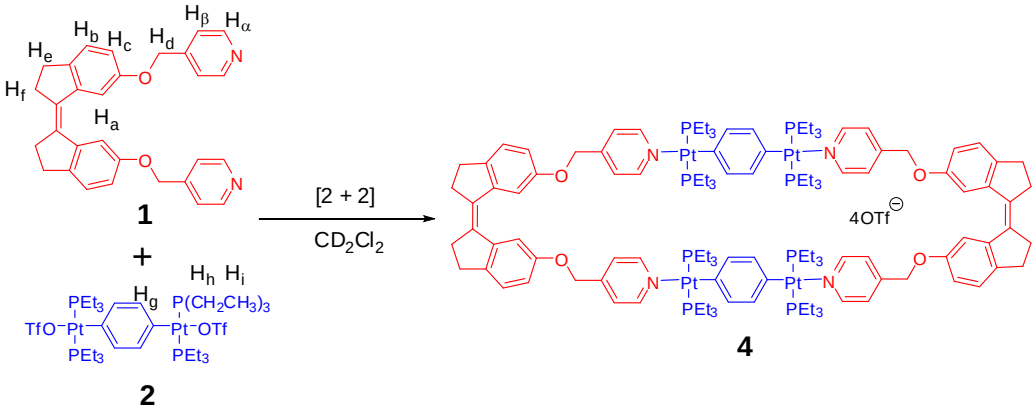


Figure S3. Electrospray ionization mass spectrum of ***Z*-1**.

*2. Synthesis of stilbene-based metallacycle **4***



Scheme S2

In a 1:1 molar ratio, stiff stilbene ligand **1** (2.23 mg, 5.00 μmol) and 180° diplatinum acceptor **2** (6.18 mg, 5.00 μmol) were dissolved in 1.00 mL of CH_2Cl_2 in a 2 mL dram vial. The reaction mixture was allowed to stir for 8 h at room temperature. To the resulting homogeneous solution, diethyl ether was added to precipitate the product, which was then isolated and dried under reduced pressure and re-dissolved in CD_2Cl_2 for characterization. The ^{1}H NMR spectrum of metallacycle **4** is shown in Figure S4. ^{1}H NMR (CD_2Cl_2, room temperature, 500 MHz) δ (ppm): 8.50 (d, J = 5.5 Hz, 8H), 7.68 (d, J = 5.5 Hz, 8H), 7.57 (s, 4H), 7.16 (d, J = 8.5 Hz, 4H), 6.92 (s, 8H), 6.76–6.83 (m, 4H), 5.29 (s, 8H), 2.83 (t, J = 6.3 Hz, 8H), 2.72 (t, J = 6.3 Hz, 8H), 1.12–1.30 (m, 48H), 0.89–1.06 (m, 72H). The ^{31}P{^{1}H} NMR spectrum of metallacycle **4** is shown in Figure S5. ^{31}P{^{1}H} NMR (CD_2Cl_2, room temperature, 202.3 MHz) δ (ppm): 12.79 ppm (s, ^{195}Pt satellites, $^1J_{Pt-P}$ = 2725.0 Hz). ESI-MS is shown in Figure S6: m/z 692.26 [M – 4OTf]$^{4+}$, 702.77 [M – 3OTf – HOTf + K]$^{4+}$, 986.67 [M – 2OTf – HOTf + K]$^{3+}$, 1534.47 [M – 2OTf]$^{2+}$, 1554.48 [M – OTf – HOTf + K]$^{2+}$.

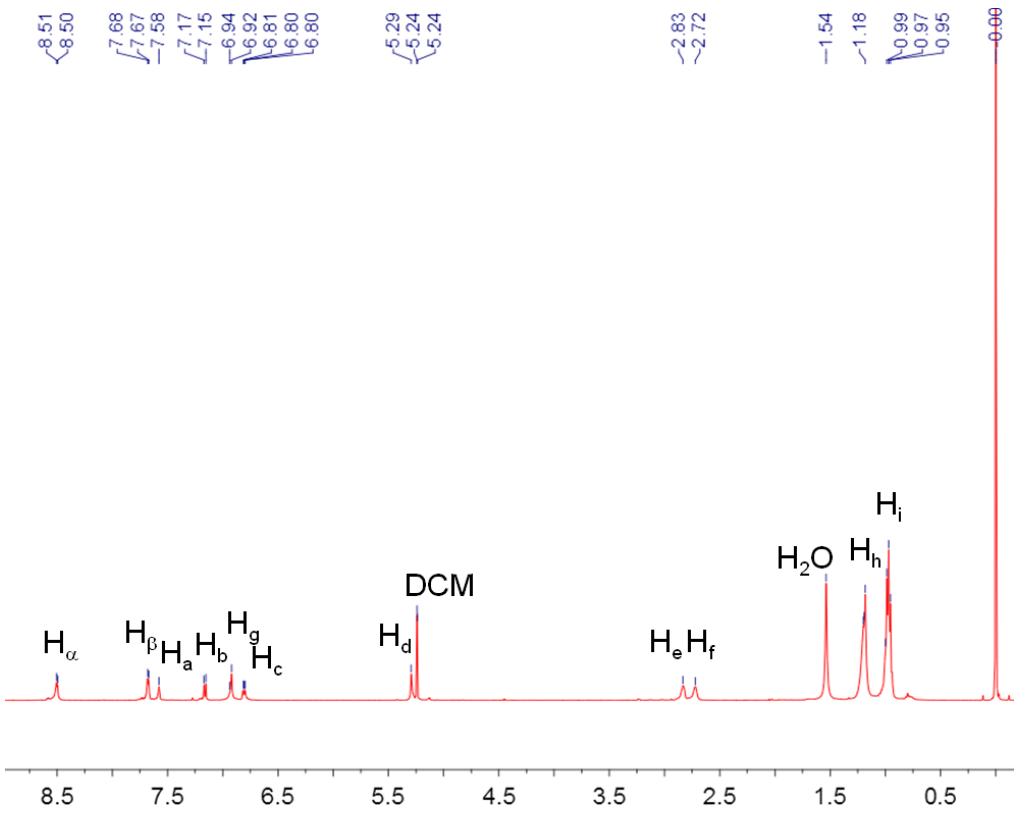


Figure S4. ^{1}H NMR spectrum (CD_2Cl_2, room temperature, 500 MHz) of metallacycle **4**.

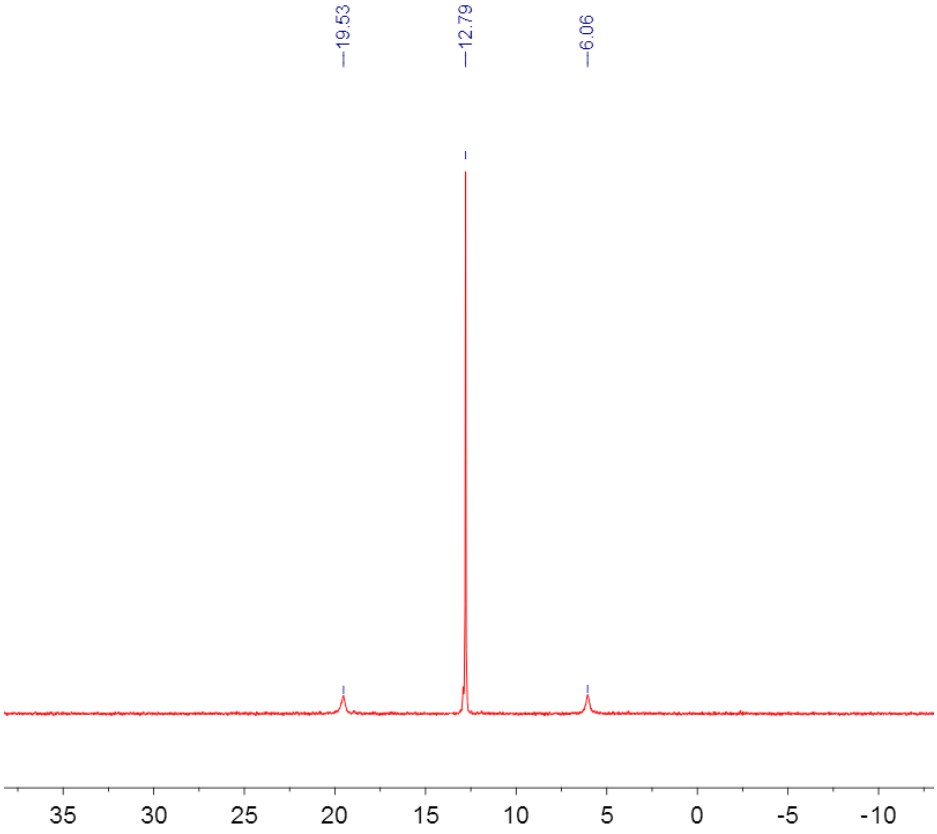
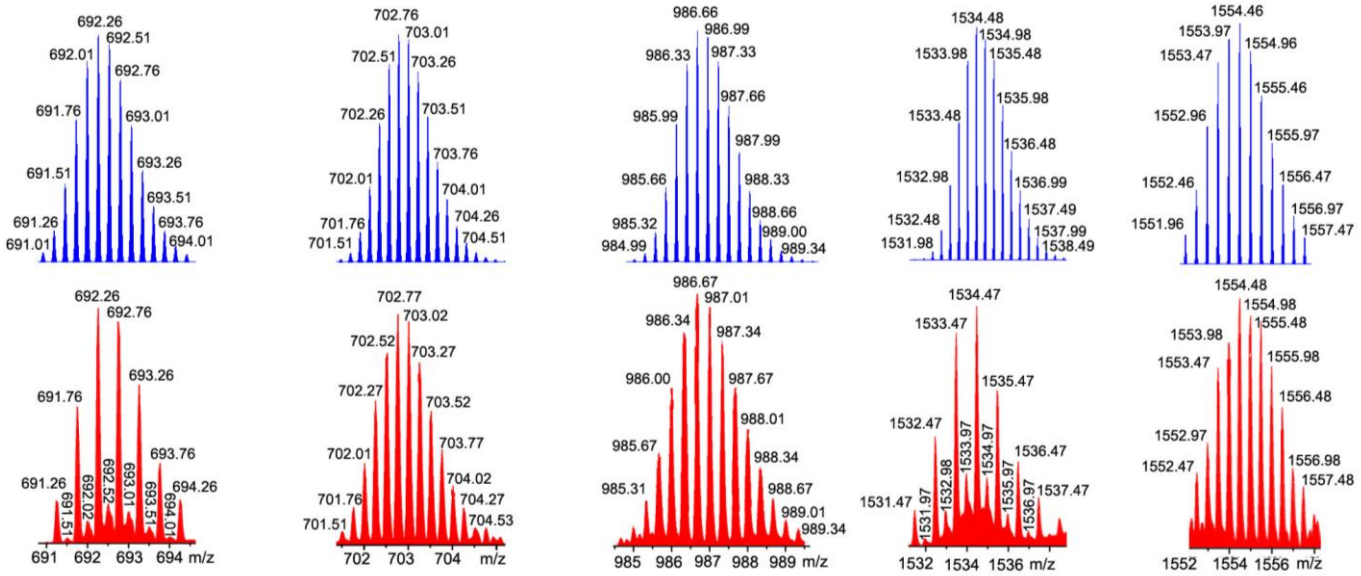


Figure S5. ^{31}P {^{1}H} NMR spectrum (CD_2Cl_2, room temperature, 202.3 MHz) of metallacycle **4**.



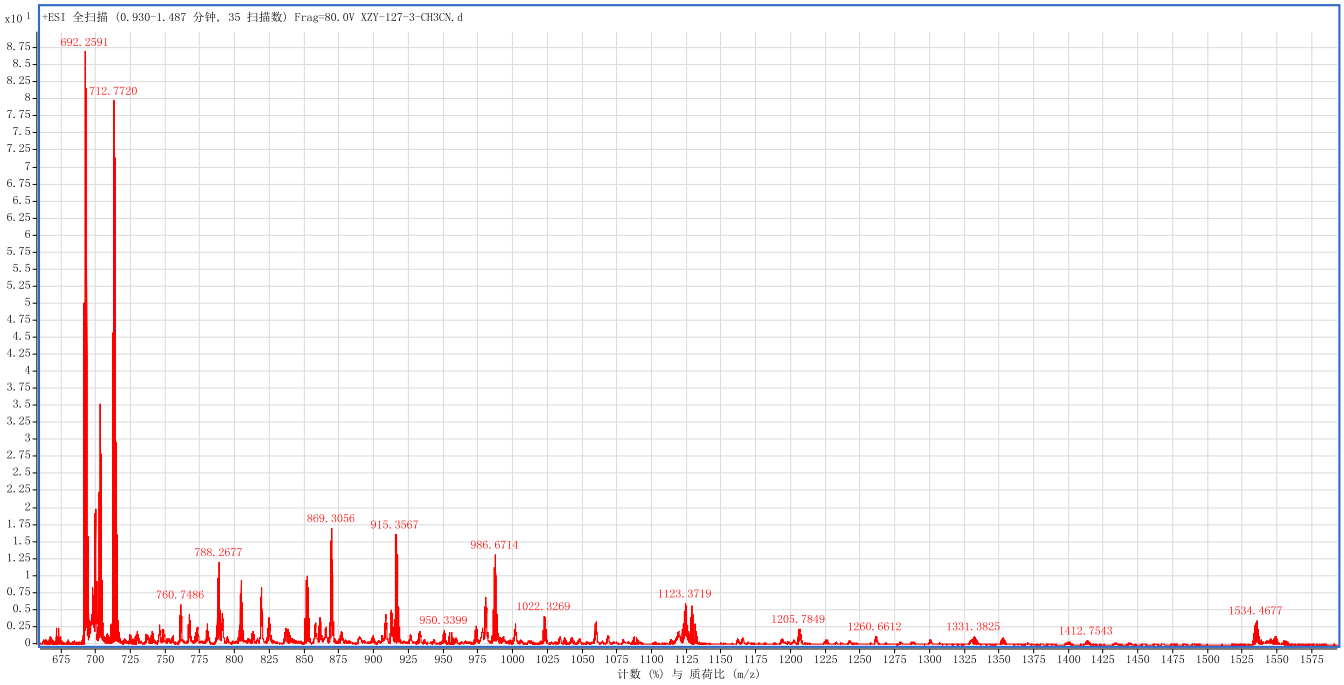
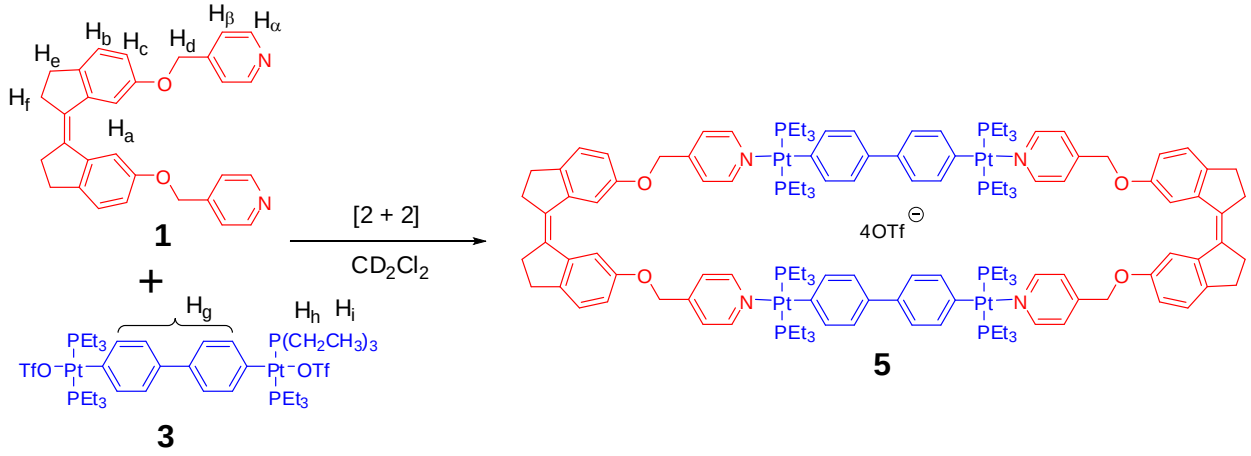


Figure S6. Experimental (red) and calculated (blue) electrospray ionization mass spectra of metallacycle **4**.

*3. Synthesis of stilbene-based metallacycle **5***



Scheme S3

In a 1:1 molar ratio, stiff stilbene ligand **1** (2.23 mg, 5.00 μmol) and 180° diplatinum acceptor **3** (6.57 mg, 5.00 μmol) were dissolved in 1.00 mL of CH_2Cl_2 in a 2 mL dram vial. The reaction mixture was allowed to stir for 8 h at room temperature. To the resulting homogeneous solution, diethyl ether was added to precipitate the product, which was then isolated and dried under reduced pressure and re-dissolved in CD_2Cl_2 for characterization. The ^{1}H NMR spectrum of metallacycle **5** is shown in Figure S7. ^{1}H NMR (CD_2Cl_2, room temperature, 500 MHz) δ (ppm): 8.52 (d, J = 5.0 Hz, 8H), 7.70 (d, J = 5.0 Hz, 8H), 7.59(s, 4H), 7.29 (s, 16H), 7.17 (d, J = 10.0 Hz, 4H), 6.81–6.83 (m, 4H), 5.32 (s, 8H), 2.84 (t, J = 6.3 Hz, 8H), 2.72 (t, J = 6.3 Hz, 8H), 1.15–1.28 (m, 48H), 0.94–1.06 (m, 72H). The ^{31}P{^{1}H} NMR spectrum of metallacycle **5** is shown in Figure S8. ^{31}P{^{1}H} NMR (CD_2Cl_2, room temperature, 202.3 MHz) δ (ppm): 13.49 ppm (s, ^{195}Pt satellites, $^1J_{Pt-P}$ = 2692.6 Hz). ESI-MS is shown in Figure S9: m/z 730.77 $[M - 4OTf]^{4+}$, 740.78 $[M - 3OTf - HOTf + K]^{4+}$, 1037.69 $[M - 2OTf - HOTf + K]^{3+}$, 1610.50 $[M - 2OTf]^{2+}$, 1630.51 $[M - OTf - HOTf + K]^{2+}$.

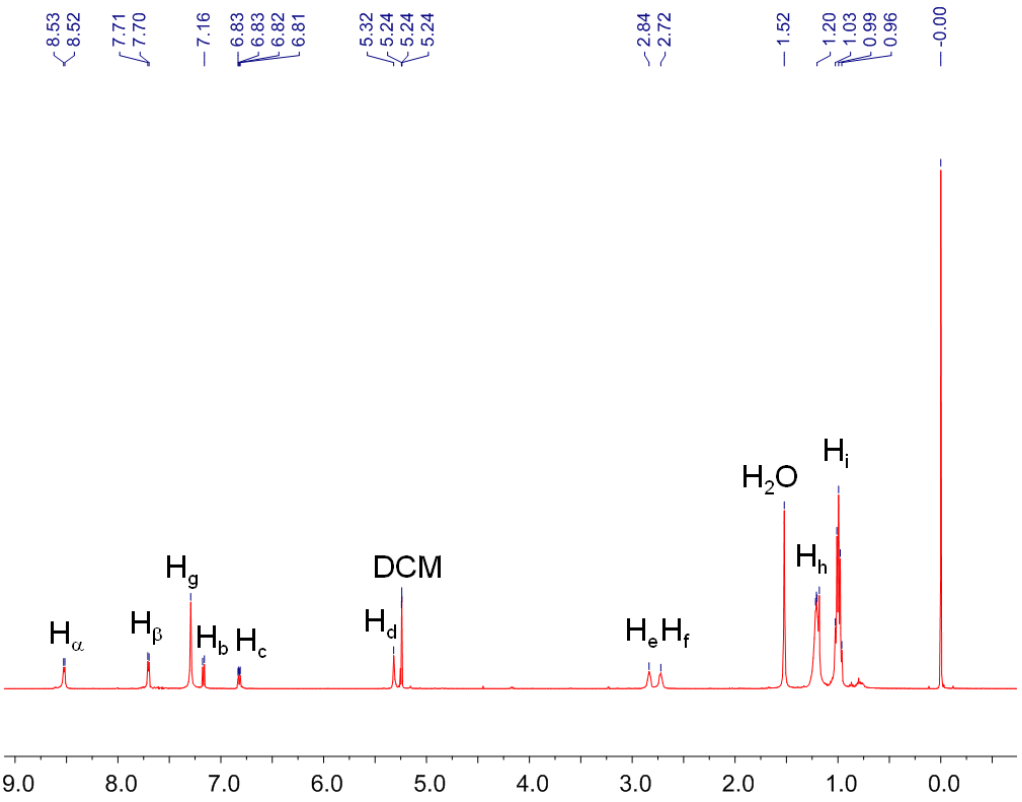


Figure S7. ^{1}H NMR spectrum (CD_2Cl_2, room temperature, 500 MHz) of metallacycle **5**.

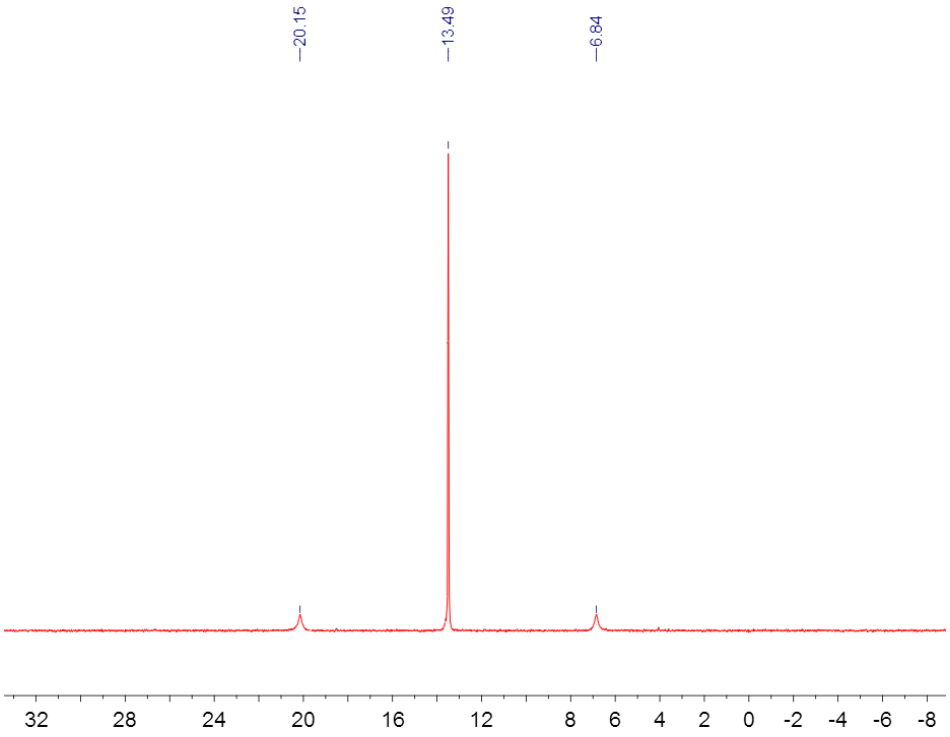
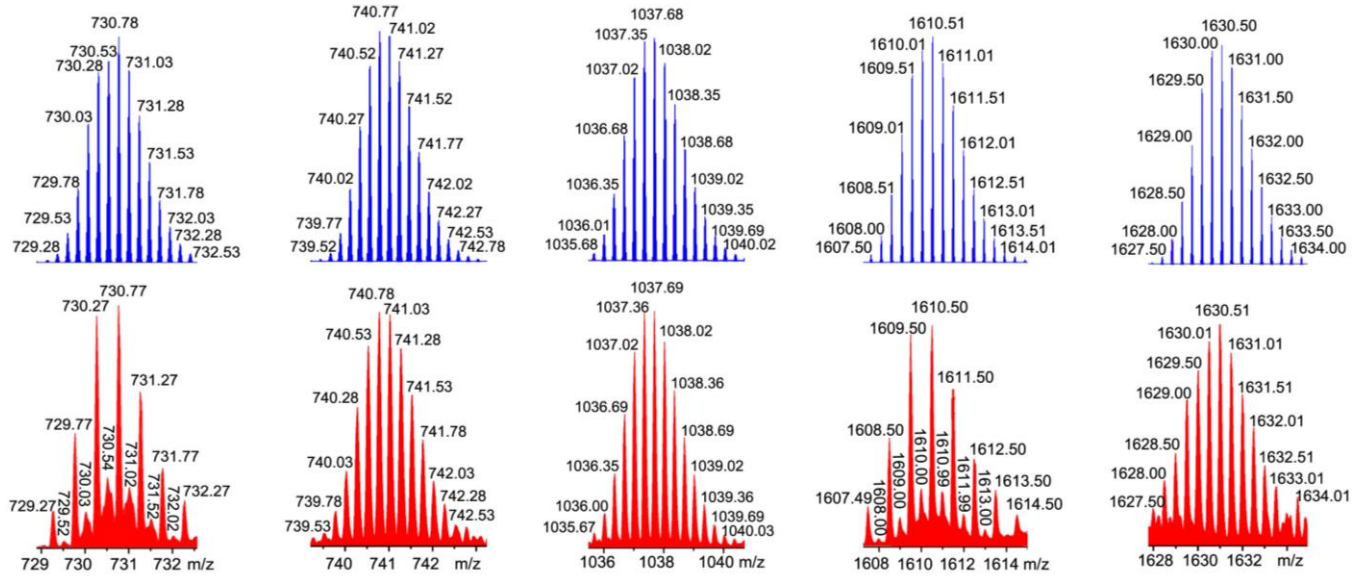


Figure S8. ^{31}P {^{1}H} NMR spectrum (CD_2Cl_2, room temperature, 202.3 MHz) of metallacycle **5**.



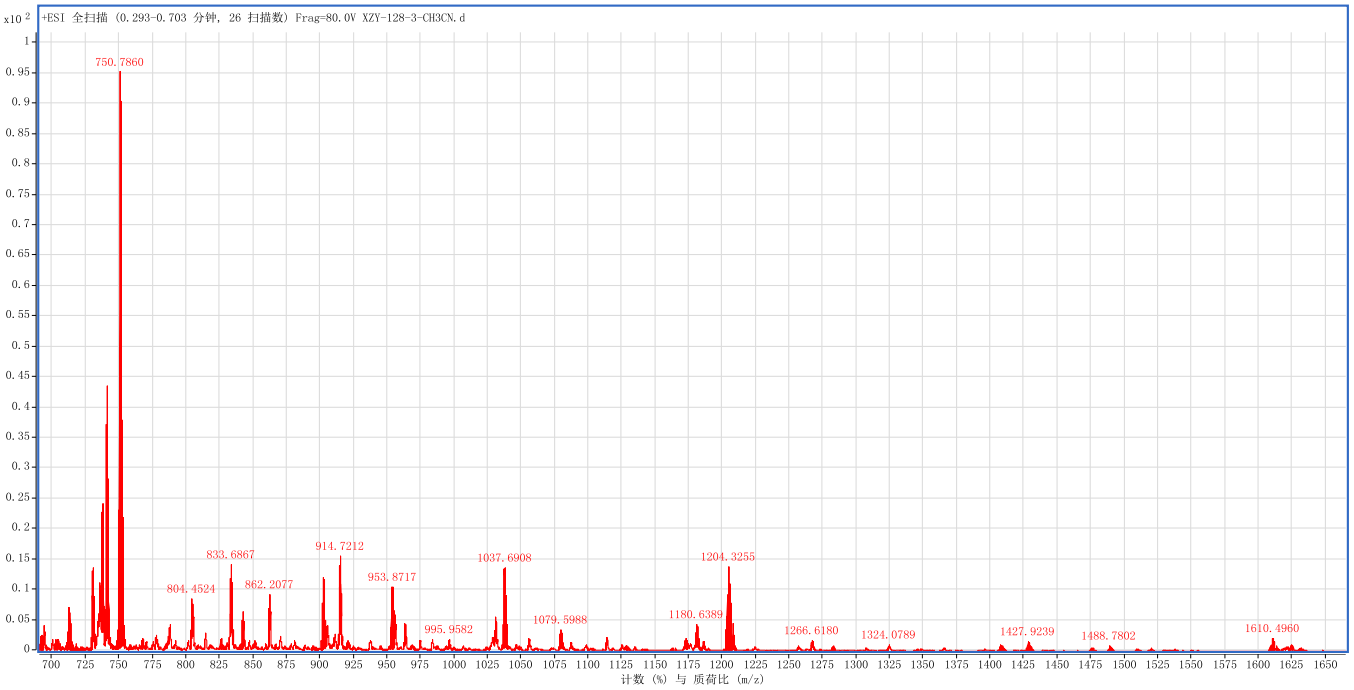


Figure S9. Experimental (red) and calculated (blue) electrospray ionization mass spectra of metallacycle **5**.

Section C. Characterization of Metallosupramolecules

*1. $^{31}P\{^{1}H\}$ NMR spectra of DMCs **4** and **5** and MSPs **6** and **7***

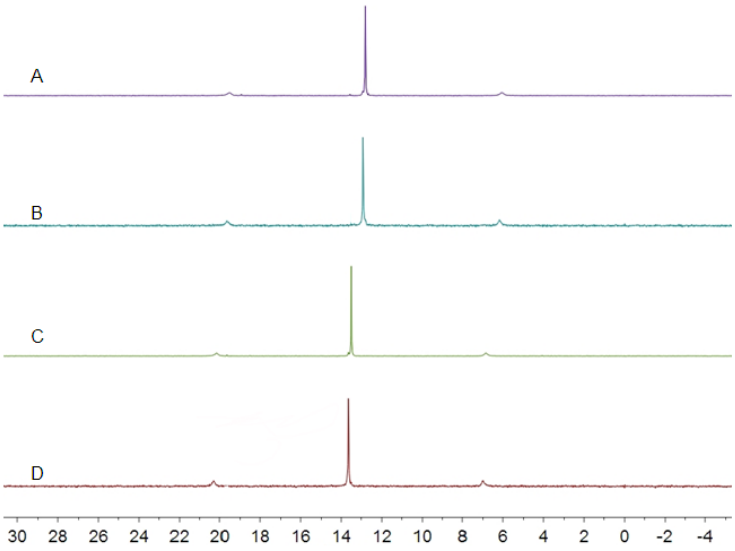


Figure S10. $^{31}P\{^{1}H\}$ NMR spectra (CD_2Cl_2, 293 K, 500 MHz): (*A*) discrete metallacycle **4**; (*B*) metallosupramolecular polymer **6**; (*C*) discrete metallacycle **5**; (*D*) metallosupramolecular polymer **7**. *c* = 5.00 mM.

*2. Concentration dependence of diffusion coefficients of MSPs **6** and **7***

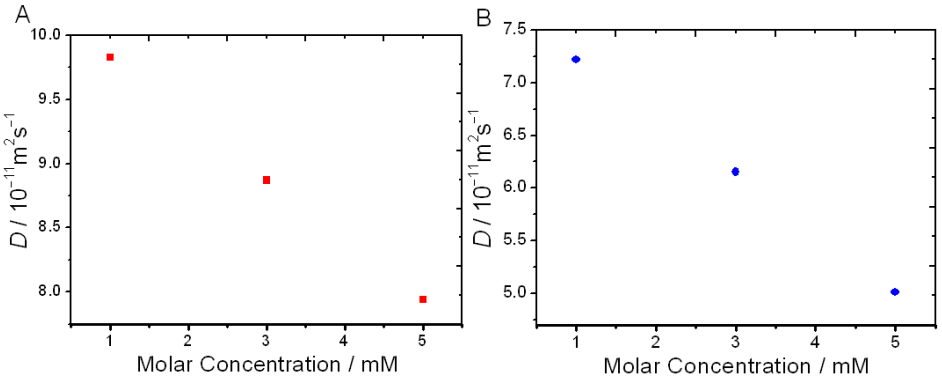


Figure S11. Concentration dependence of diffusion coefficients *D* (500 MHz, [D_3]acetonitrile, 293 K) of MSP **6** (*A*) and MSP **7** (*B*).

To further substantiate the photoinduced formation of MSPs **6** and **7**, concentration-dependent 2D DOSY experiments were performed. Upon increasing the MSPs concentration, the measured weight-average diffusion coefficients decreased from 9.83×10^{-10} to 7.94×10^{-10} m^2s^{-1} for MSP **6** and 7.21×10^{-10} to 5.01×10^{-10} m^2s^{-1} for MSP **7**.

*3. Simulated molecular models of DMCs **4** and **5***

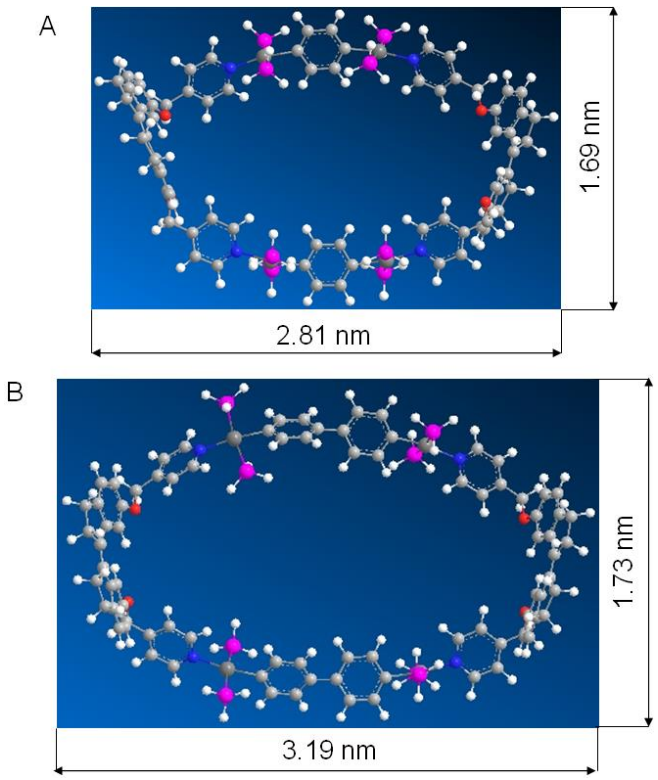


Figure S12. Simulated molecular models of DMCs **4** (*A*) and **5** (*B*) by PM6 semiempirical molecular orbital methods. To minimize computational cost, the PEt_3 ligands were modeled as PH_3.

*4. Size distributions of MSPs **6** and **7** at different concentrations*

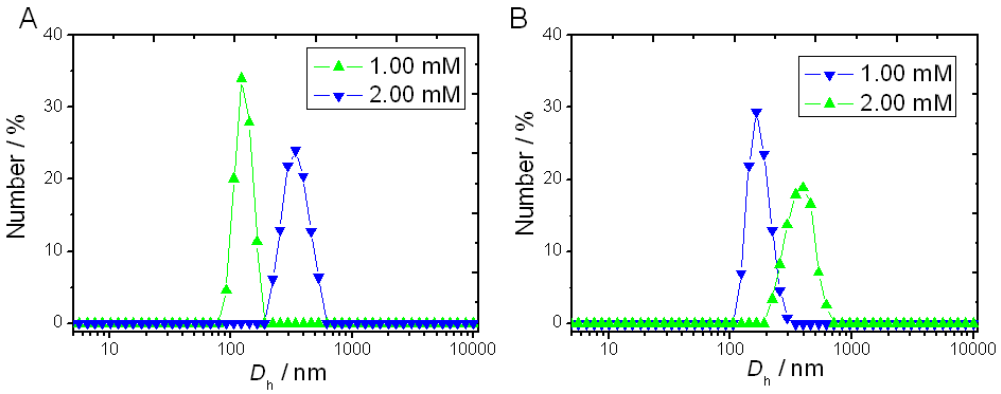


Figure S13. Size distributions of MSPs **6** (*A*) and **7** (*B*) at different concentrations.

5. Partial ^{1}H NMR spectra of MSPs before and after irradiation at 360 nm

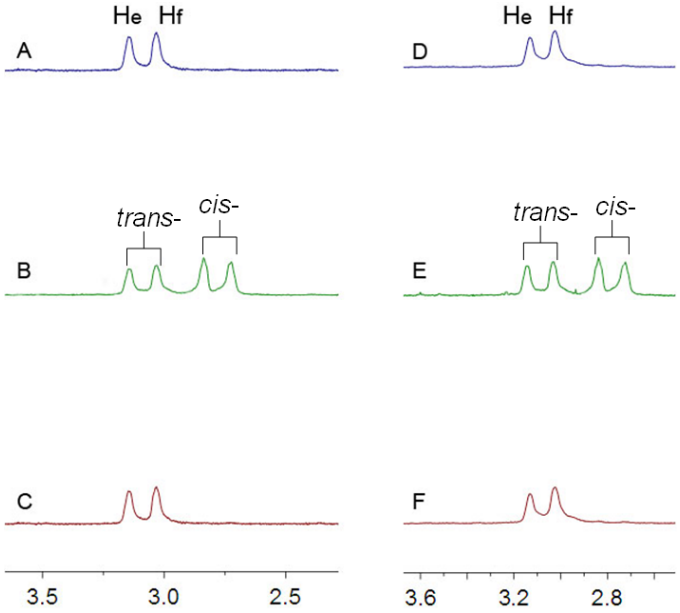


Figure S14. Partial ^{1}H NMR spectra (CD_2Cl_2, 293 K, 500 MHz): (*A*) metallosupramolecular polymer **7**; (*B*) irradiation of sample (*A*) at 360 nm; (*C*) irradiation of sample (*B*) at 387 nm; (*D*) metallosupramolecular polymer **6**; (*E*) irradiation of sample (*D*) at 360 nm; (*F*) irradiation of sample (*E*) at 387 nm. *c* = 2.00 mM.

*6. Size distributions of MSPs **6** and **7** before and after irradiation at 360 nm*

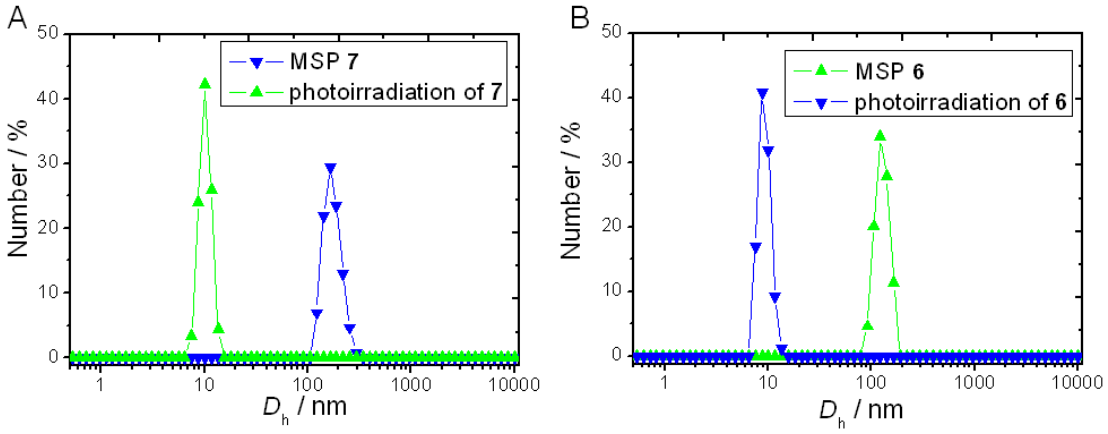


Figure S15. Size distributions of MSPs **7** (*A*) and **6** (*B*) before and after irradiation at 360 nm. *c* = 1.00 mM.

Section D. References

S1. Manna J, et al. (1997) Nanoscale tectonics: self-assembly, characterization, and chemistry of a novel class of organoplatinum square macrocycles. *J Am Chem Soc* 119: 11611–11619.

S2. Akbulatov S, Tian Y, Boulatov R (2012) Force–reactivity property of a single monomer is sufficient to predict the micromechanical behavior of its polymer. *J Am Chem Soc* 134: 7620–7623.