Supporting Information

1. General Procedure

Materials

3,6-dibromocarbazole (Adamas, 98.5%), 4-pyridylboronic acid (J&K, 97%), tetrakis(triphenylphosphine) palladium (J&K, 98%), sodium hydride (NaH, Adamas, 60 wt% in mineral oil), sodium trifluomethanesulfonate (CF_3NaO_3S, Adamas, 98%), dimethylaminoethanol (Adamas, 98%), 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC, TCI, 99%), potassium iodide (KI, J&K, 98%), 4-dimethylaminopyridine (DMAP, Sigma-Aldrich, 99%) and N-isopropyl acrylamide (NIPAM, 98%, Sigma-Aldrich, recrystallized twice before used) were purchased and used. Water was purified with a Millipore system, combining inverse osmosis membrane (Milli-R) and ion-exchange resins (Milli-Q). Solvents and reagents were purchased from Adamas, J&K co. Ltd., and Sigma-Aldrich Co. All the chemicals were of reagent grade and used without any further purification.

Instrumentation and measurements

Nuclear magnetic resonance (NMR). ^{1}H NMR spectra were performed on AVANCE III HD-400 (400 MHz) Bruker spectrometer**.**

Dynamic light scattering (DLS). Dynamic light scattering (DLS) was performed on a Malvern Zetasizer-Nano equipped with a 633 nm He-Ne laser and an avalanche photodiode detector. The scattering light at 90° angle was detected and used to analyze the size and distribution.

Size-exclusion chromatography (SEC). Molecular weights and dispersity (*Đ*) of the polymer samples were determined in tetrahydrofuran (THF) at a flow rate of 1.0 mL/min using an Agilent 1260 Infinity system with a variable-wavelength diode array (254, 450 and 530 nm) and a refractive index detector. Samples were filtered using regenerated cellulose membranes (0.45 μm) prior to injecting.

UV-Vis spectroscopy (UV-Vis). The UV-Vis absorption spectra of the polymer samples at different conditions were recorded by using an Agilent Cary-60 UV-Vis spectroscopy.

Electrospray ionization mass spectrometry (ESI-MS) ESI-MS experiments were performed on Waters Synapt G2 mass spectrometer under the following conditions: ESI capillary voltage, 3.5 kV; sample cone voltage, 35 V; extraction cone voltage, 3.5 V; cone gas flow, 10 L/h; desolvation gas flow, 700 L/h (N_2); source gas control, 0 mL/min; trap gas control, 2 mL/min; Helium cell gas control, 100 mL/min; sample flow rate, 5 μL/min. Source temperature and desolvation temperature were either used at 25 °C/30 °C or 125 °C/150 °C.

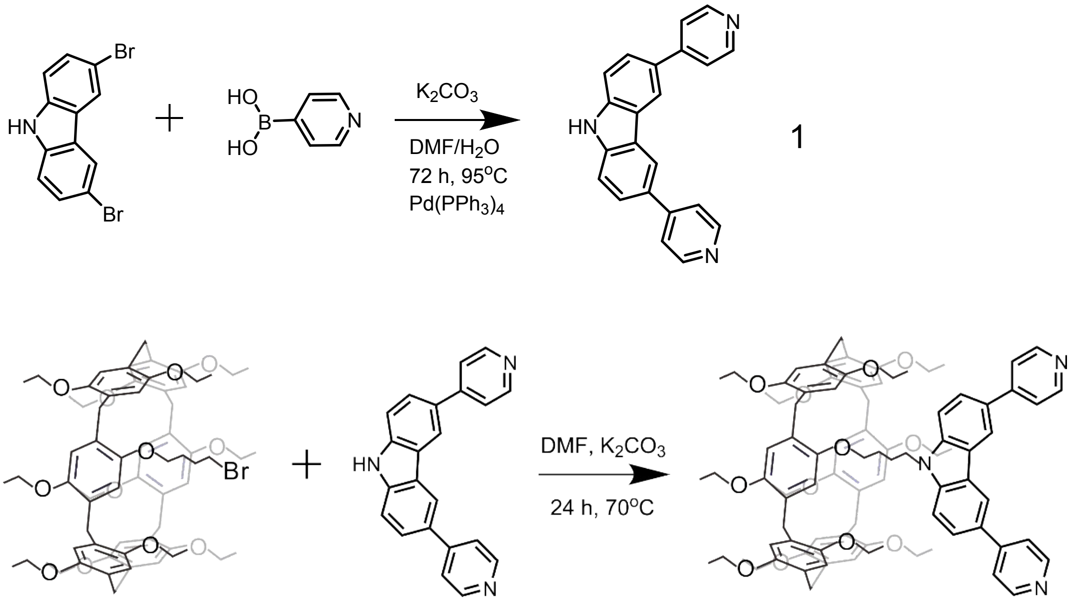
Transmission electron microscopy (TEM) TEM images were measured on a FEI Tecnai G2-F20 S-TWIN instrument at a voltage of 120 kV. The specimen was prepared by drop-casting solution onto carbon-coated grid.

Atomic force microscopy (AFM) The AFM investigation was performed on Bruker Dimension Icon. For the AFM investigation, the sample was dissolved in $CHCl_3$:CH_3COCH_3 = 5:1 at a concentration within the range 10^{-6} to 10^{-8} M. After dropping onto mica surface for 30 seconds, the surface was washed slightly with water for three times and totally dried in R.T. in air

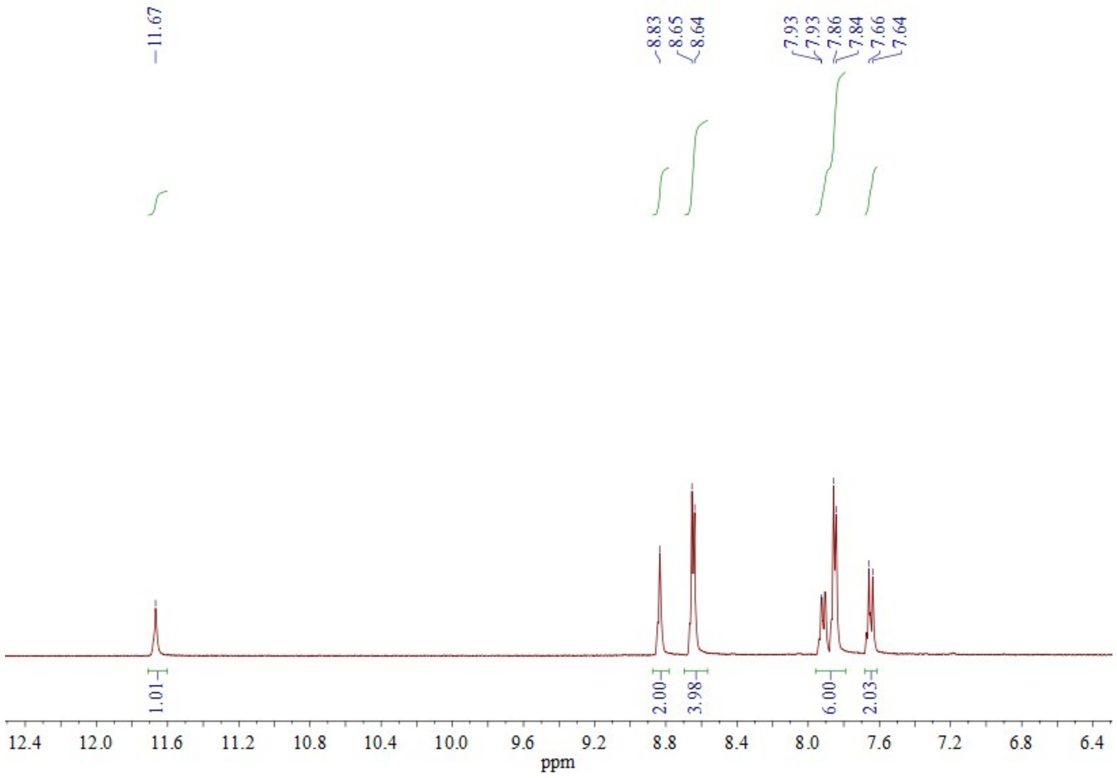
UV irradiation The photo-controllable samples were isomerized by photoirradiation using a 400 W Xe lamp equipped with a cutoff filter and a band-pass filter (360 nm UV light or 435 nm visible light, 10min). The distance between the sample cell and the lamp was fixed at 50 cm.

1. Synthesis and Characterization of Pillar[6] arene Containing Donor Ligand.

Scheme S1. Synthesis of 90° pillar[6]arene ligand L.



Synthesis of 1: 3,6-di(4-pyridylethynyl) carbazole was produced according to the previously reported[S1]. Briefly, 3,6-dibromocarbazole (1.95 g, 6.02 mmol), 4 - pyridylboronic acid (1.63 g, 13.26 mmol), tetrakis(triphenylphosphine) palladium (695.3 mg, 0.6 mmol), and potassium carbonate (8.32 g, 60.20 mmol) were added into a 100 mL single-neck flask. Under argon atmosphere, DMF-H_2O (50 mL, v/v = 50/1) was added to the flask, and the mixture was stirred for 72 h at 95 °C. After cooling down to room temperature, the residue was diluted with chloroform and filtered. The filtrate was extracted with water, brine, dried over $MgSO_4$, and concentrated in vacuum. The crude product was purified by column chromatography on silica gel (dichloromethane/methanol = 98/2, v/v) to give 1 as a yellow solid (1.1 g, yield: 60%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.67 (s, 1H), 8.83 (s, 2H), 8.65 (d, J = 6.0 Hz, 4H), 7.96-7.79 (m, 6H), 7.65 (d, J = 8.5 Hz, 2H). ^{13}C NMR (400 MHz, DMSO-d_6): δ 150.61, 148.32, 141.39, 128.36, 125.29, 123.85, 121.38, 119.77, 112.36. ESI-MS(m/z): calcd for $[M + H]^+$:322.31; found :322.48.



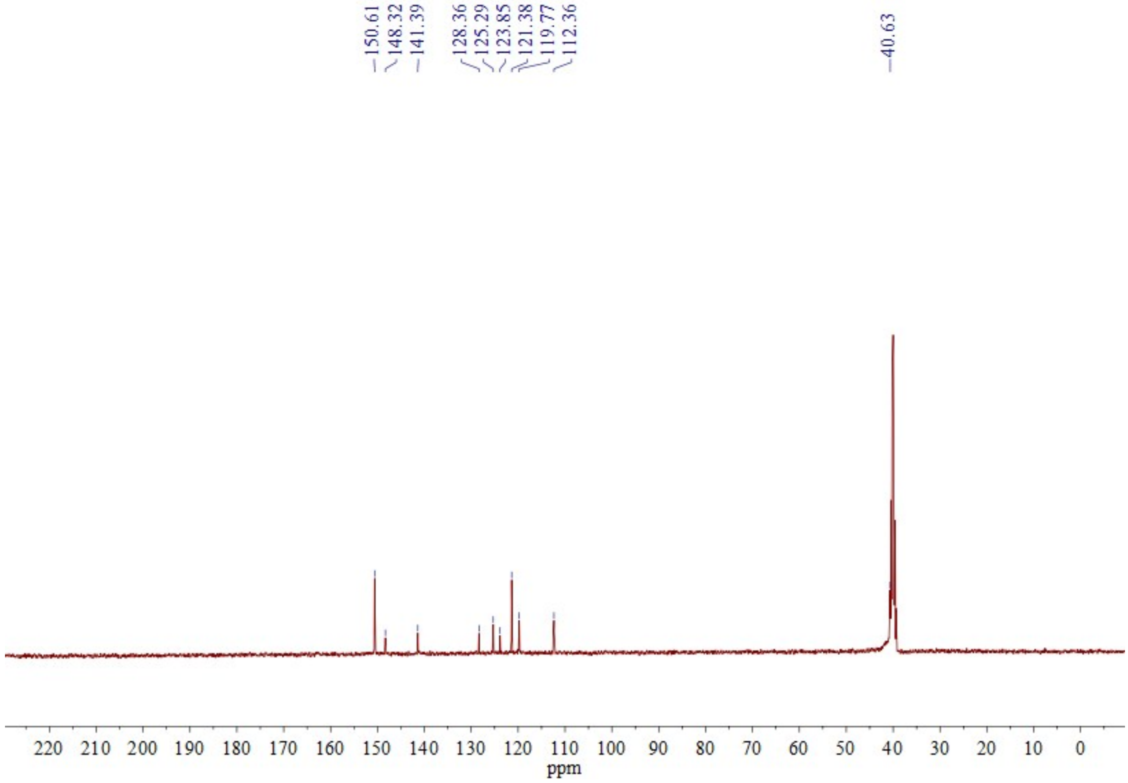
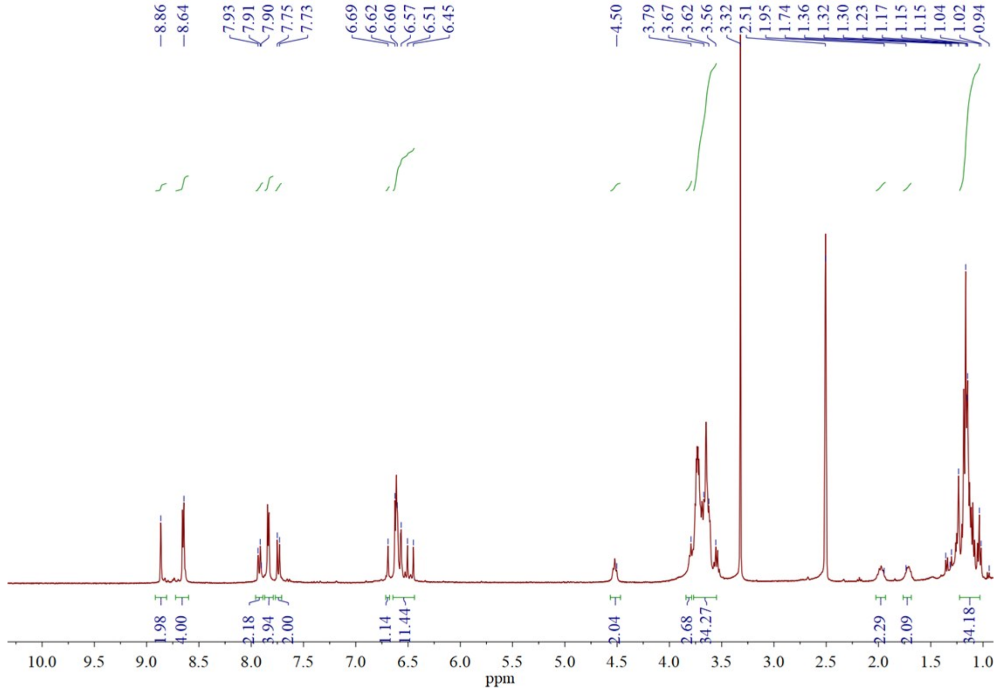


Figure S1. ^{1}H NMR and ^{13}C NMR spectrum (400 MHz, DMSO-d_6, 298 K) of 1, respectively.

Synthesis of 90° pillar[6]arene ligand L:. For preparing L, in a 250 mL round–bottom flask, monofunctionalized pillar[6]arene[s2] (1.5 g, 1.12 mmol), sodium hydride (0.5 g, 60 wt% in mineral oil), 3,6-di(4-pyridylethynyl) carbazole (1.6 g, 5 mmol) and DMF (40 mL) were added. The reaction mixture was stirred at 50 ℃ for 24 hours. A large amount of water was added, and then the mixture was extracted with CH_2Cl_2 three times. The organic layer was further washed twice with 200 mL saturated NaCl solution. The organic layer was dried over anhydrous Na_2SO_4 and evaporated to afford the crude product, which was isolated by column chromatography using dichloromethane/methanol/triethylamine (97:2:1) (R_f = 0.3). The product was obtained as yellow solid (yield: 75%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.86 (s, 2H), 8.64 (s, 4H), 7.96-7.89 (m, 2H), 7.87-7.79 (m, 4H), 7.74 (d, J = 8.7 Hz, 2H), 6.69 (s, 1H), 6.64-6.44 (m, 11H), 4.50 (s, 2H), 3.79 (s, 3H), 3.77-3.55 (m, 34H), 1.95 (s, 2H), 1.74 (s, 2H), 1.22-1.03 (m, 34H). ESI-MS (m/z) :calcd for $[M + H]^+$:1416.42; found 1416.36.



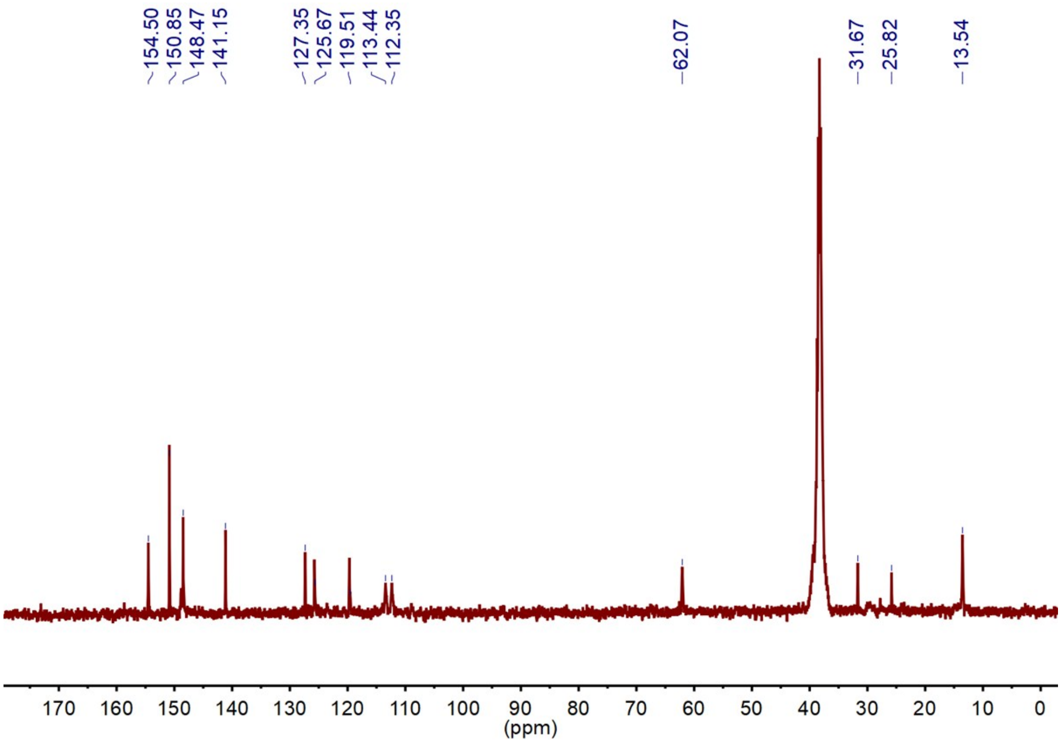
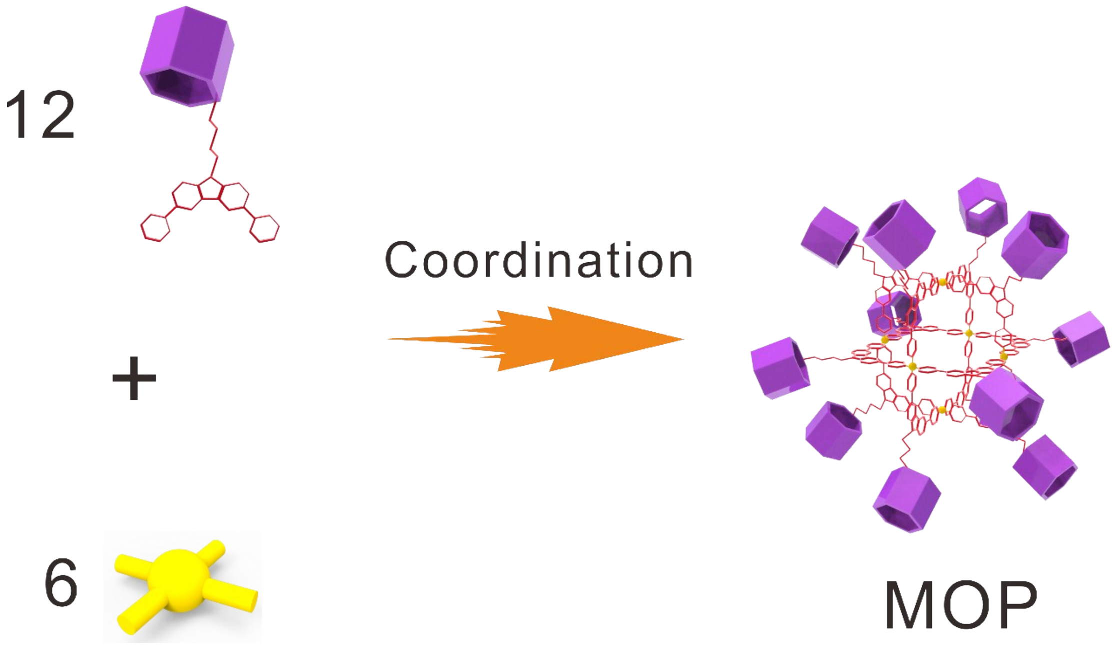


Figure S2. ^{1}H NMR and ^{13}C NMR spectrum (400 MHz, DMSO-d_6, 298 K) of L, respectively.

2. Synthesis and characterization of metal-organic polyhedron

Scheme S2. Synthesis of metal-organic polyhedron (MOP)



Synthesis of sphere MOP (NO_3^- salt): Ligand L1 (20.2 mg) was treated with $Pd(NO_3)_2$ (8.80 mg, 38.2 μmol) in DMSO (3.0 mL) at 75 °C for 8 h. ^{1}H NMR confirmed the quantitative formation of sphere MOP. An excess amount of diethyl ether was added to the solution of spheres, and the precipitate was collected by centrifugation and dried in vacuum to give sphere MOP as a light grey solid (20.1 mg, 85% isolated yield). The structure formation was further confirmed by 2D DOSY, TEM, SEM, and AFM.

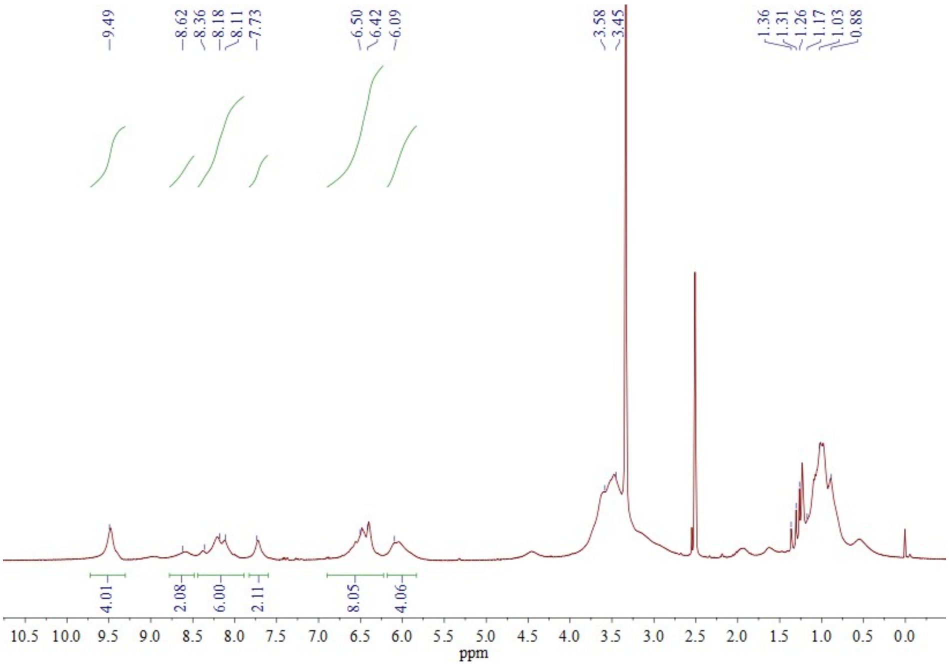


Figure S3. ^{1}H NMR spectrum (400 MHz, DMSO-d_6, 298 K) of MOP.

Synthesis of sphere MOP ($CF_3SO_3^-$ salt): A saturated $NaCF_3SO_3$ solution was added to the resultant MOP (NO_3^-) solution, and the precipitate was collected by centrifugation, washed with a large amount of water and dried in vacuum to give sphere MOP ($CF_3SO_3^-$ salt) as a light grey solid.

3. Diameter calculated by theoretical estimation

The MOP's hydrodynamic radius was estimated according to the Stokes-Einstein equation:

$$D = \frac{kT}{6\pi\mu R} \quad \text{.............(1)}$$

where D is the diffusion constant, k is the Boltzmann's constant, T is the temperature, μ is the viscosity of solvents, and R is the radius.

For molecular simulations, all counterions are omitted. An initially energy-minimized structure was subjected to 70 -100 annealing cycles with initial and mid-cycle temperatures of 300 and 1500 K, respectively, twenty heating ramps per cycle, one thousand dynamic steps per ramp, and one femtosecond per dynamic step. A constant volume/constant energy (NVE) ensemble was used and the geometry was optimized after each cycle. Geometry optimization used a universal force field with atom-based summation and cubic spline truncation for both the electrostatic and Van der Waals parameters.

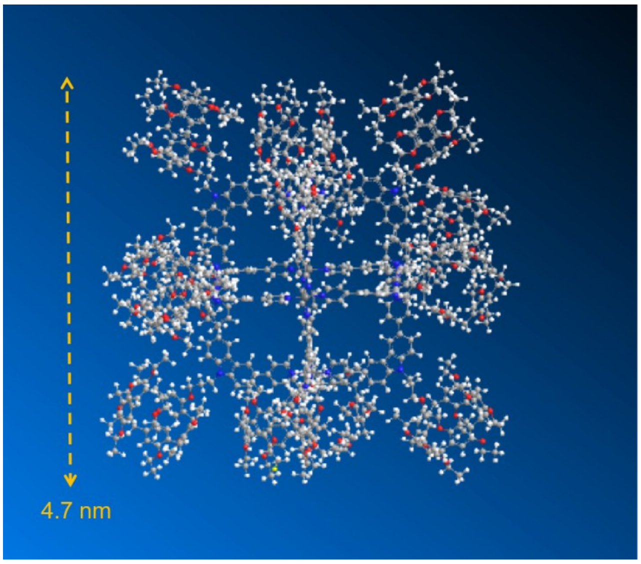


Figure S4. Representative theoretical structure of pillar[6]arene-coated MOP.

4. Determination of the molecular weight of MOP.

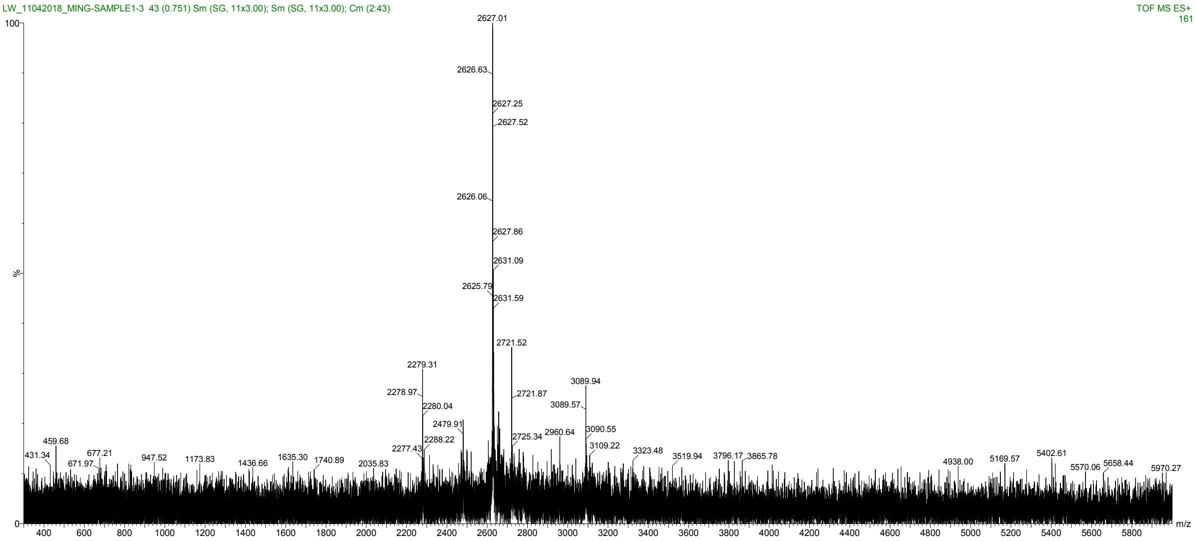
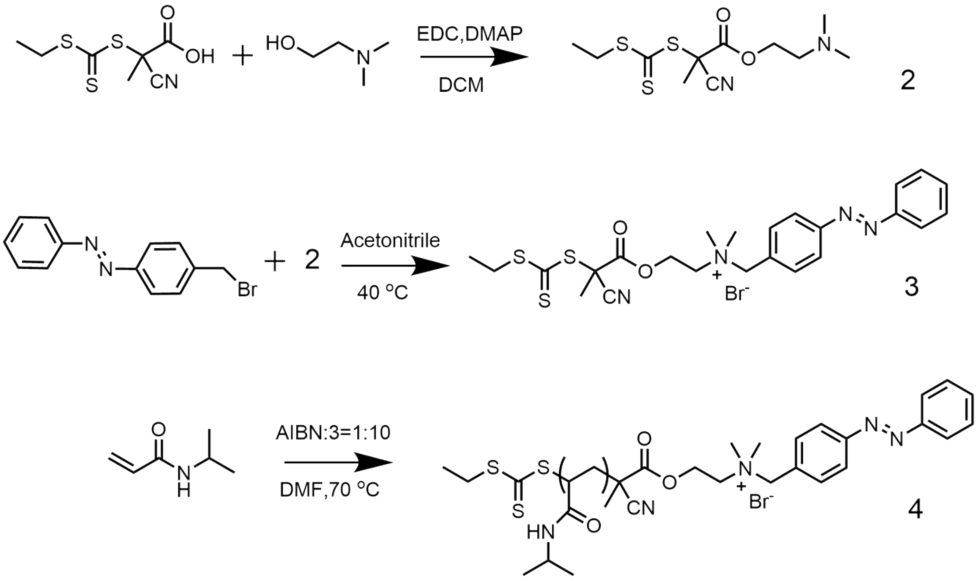


Figure S5. The HR-ESI spectrum of MOP ($CF_3SO_3^-$).

5. Synthesis and characterization of guest motifs.

Scheme S3. Synthesis of a series of guest motifs.



Synthesis of 2: DDAT (1.0 g, 4.25 mmol), excessive dimethylaminoethanol (0.76 g, 8.5 mmol), EDC (1.5 g, 7.8 mmol) and DMAP (0.2 g, 1.64 mmol) were dissolved in anhydrous CH_2Cl_2 (150 mL). The mixture was stirred for 24 h at room temperature. After washed by saturated NaCl solution, the mixture was concentrated and further purified by silica gel column chromatography using dichloromethane, and a yellow oil was obtained (79%, yield). ^1H NMR (400 MHz, $CDCl_3$): δ 4.21 (t, J = 5.7 Hz，2H), 3.40-3.30 (m, 2H), 2.72-2.63 (m, 2H), 2.61-2.56 (m, 2H), 2.29(s, 6H), 1.87(s, 3H), 1.36 (t, J = 7.4 Hz). ESI-MS (m/z) : calcd for $[M + Na]^+$: 329.12; found 329.26.

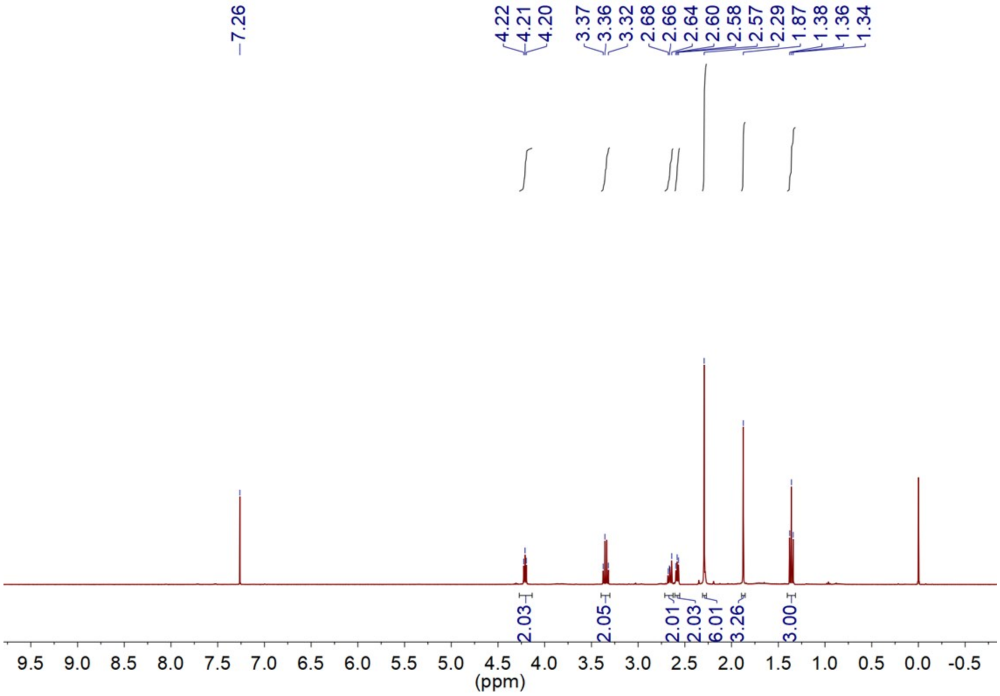
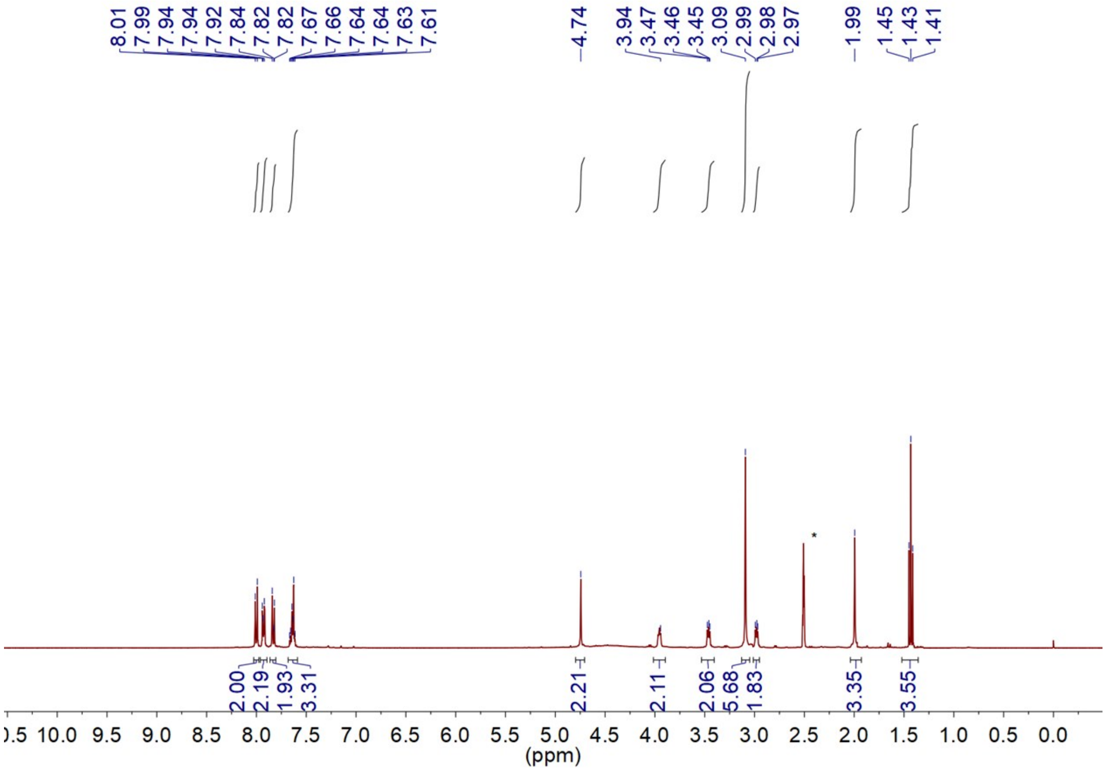


Figure S6. ^1H NMR spectrum (400 MHz, DMSO-d_6, 298 K) of 2.

Synthesis of 3 (Azo-R): 2 (0.9 g, 2.9 mmol), 4-bromomethylazobenzene[s3] (0.96 g, 3.5 mmol), and KI (0.05 g, 0.3 mmol) were dissolved in anhydrous acetonitrile (25 mL).The mixture was stirred for 24 h under reflux. After cooled to temperature, a large amount of solid was obtained. The crude product was recrystallized from ethanol and a dark brown solid was obtained. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.00 (d, J = 8.5 Hz,2H), 7.96-7.89 (m, 2H), 7.86-7.81 (m, 2H), 7.68-7.59 (m, 3H), 4.74(s, 2H), 3.94(s, 2H), 3.53 -3.41 (m, 2H), 3.09(s, 6H), 3.01-2.95 (m, 2H), 1.99(s, 3H), 1.43 (t, J = 7.4 Hz, 3H). ^{13}C NMR (400 MHz, DMSO-d_6): δ 215.70, 173.41, 152.76, 134.88, 135.33, 123.18, 66.45, 54.32, 50.47, 15.48. ESI-MS(m/z): calcd for [M + H]$^+$: 503.03; found 503.17.



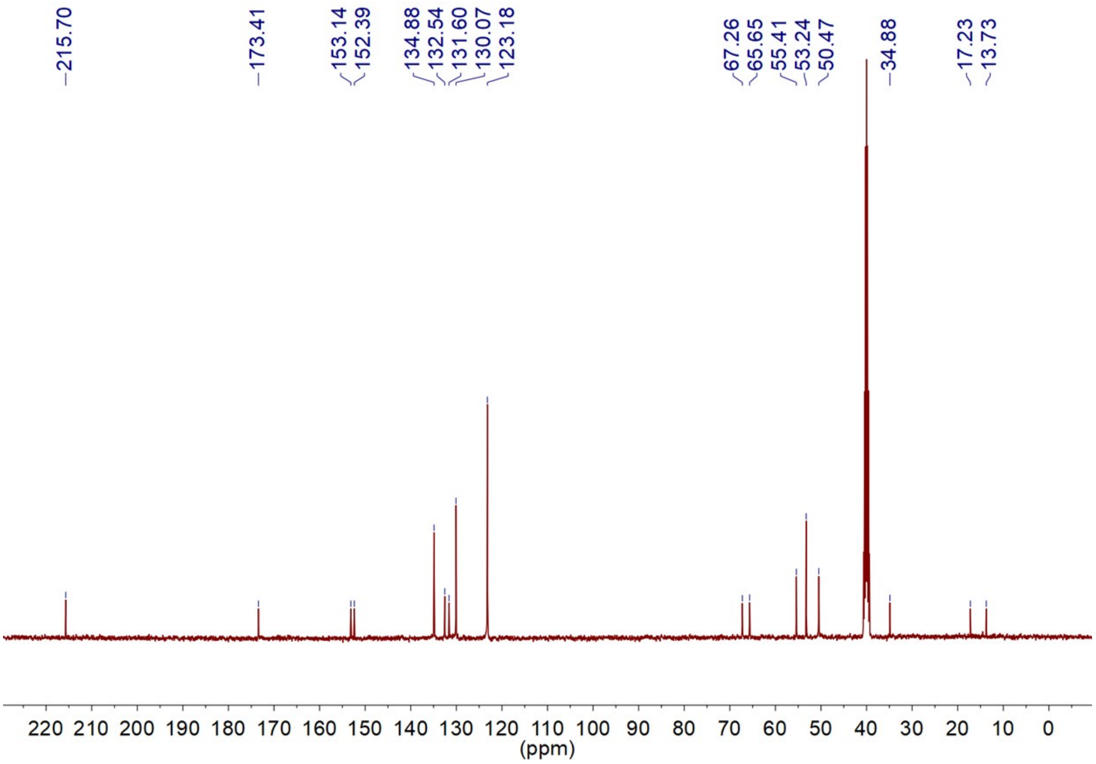


Figure S7. ^{1}H NMR and ^{13}C NMR spectrum (400 MHz, DMSO-d_6, 298K) of 3, respectively.

Synthesis of Azo-PNIPAM (AZO-P): NIPAM (1.3 g, 7.87 mmol), 3 (19.6 mg, 0.039 mmol), and AIBN (2.0 mg, 0.004 mmol) were dissolved in anhydrous dimethylformamide (5 mL). The solution was thoroughly degassed using three freeze-pump-thaw cycles. The schlenk flask was placed in an oil bath at 70 °C and heated for two hours. After quenching in liquid nitrogen and diluting with THF, the polymer was precipitated into a cold solution of diethyl ether. After filtration, the filtrate was further redissolved in THF and precipitated again. Such a process was repeated three times, and the yellow solid was obtained. (M_n = 10500, $Đ$ = 1.12, SEC-RI calibrated using PSTY Standards)

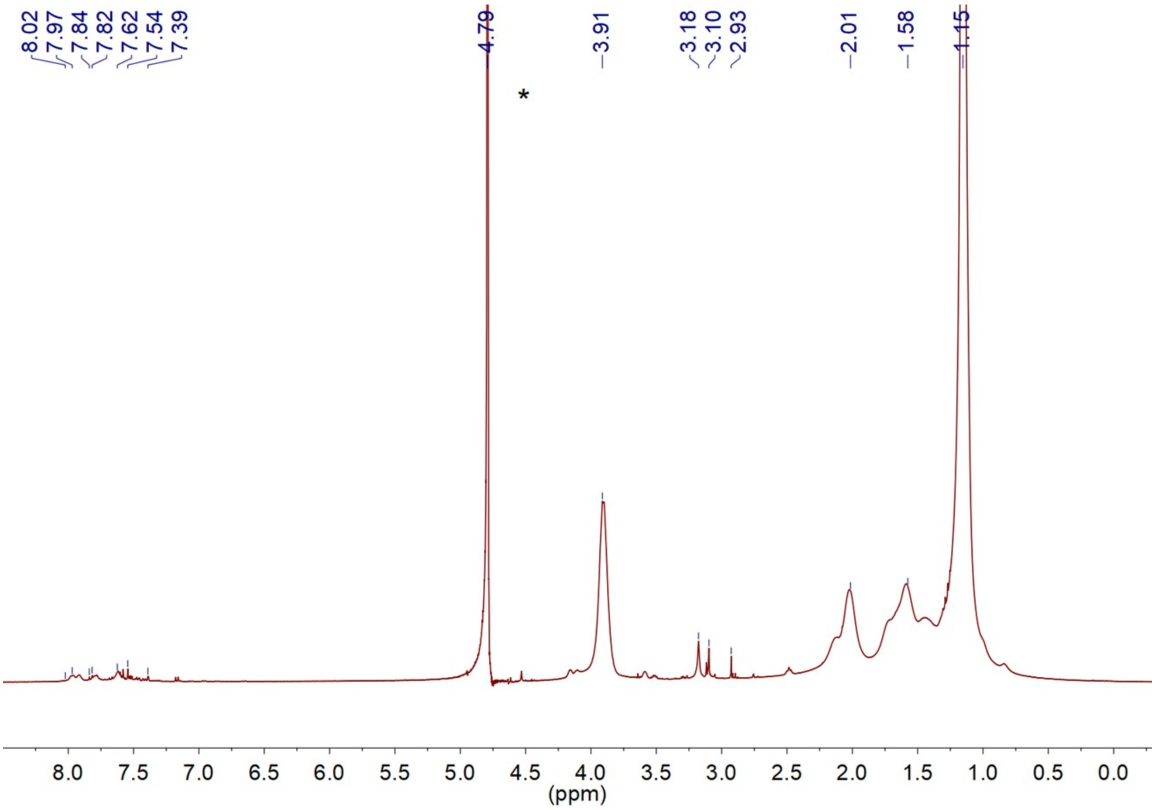


Figure S8. ^{1}H NMR spectrum (400 MHz, D_2O, 298 K) of Azo-P.

6. Job Plot of MOP and Azo-R.

The stoichiometry of the complexes was determined using the Job plot method based on the changes of UV intensities at 350 nm**.** Binding constants were determined by plotting changes in ratios (I/I_0) of the emission intensity at 350 nm versus the concentration of guest based on the following equation:

$$\frac{I}{I_0} = \frac{1 + aK_aC_{guest}}{1 + K_aC_{guest}}$$

Where I is the intensity of UV emission at 310 nm, I_0 is the fluorescent intensity of free host, "a" is a constant, K_a is the binding constant, and C_{guest} is the total concentration of guest.

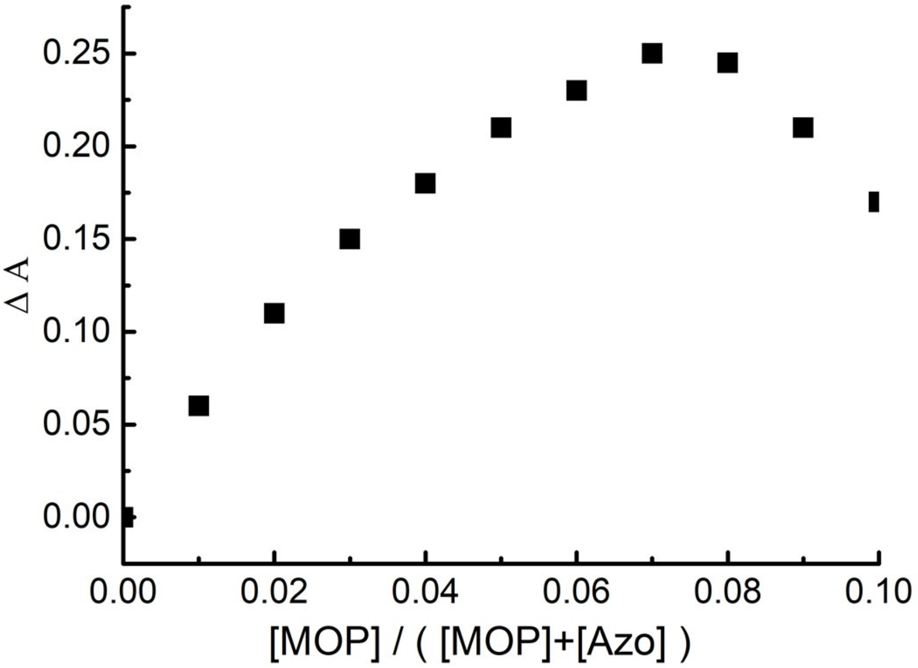


Figure S9. Job Plot of model molecules Azo-R and MOP, total concentration: 2 × 10^{-5} M.

7. UV and Vis study of Azo-R and Azo-R/MOP

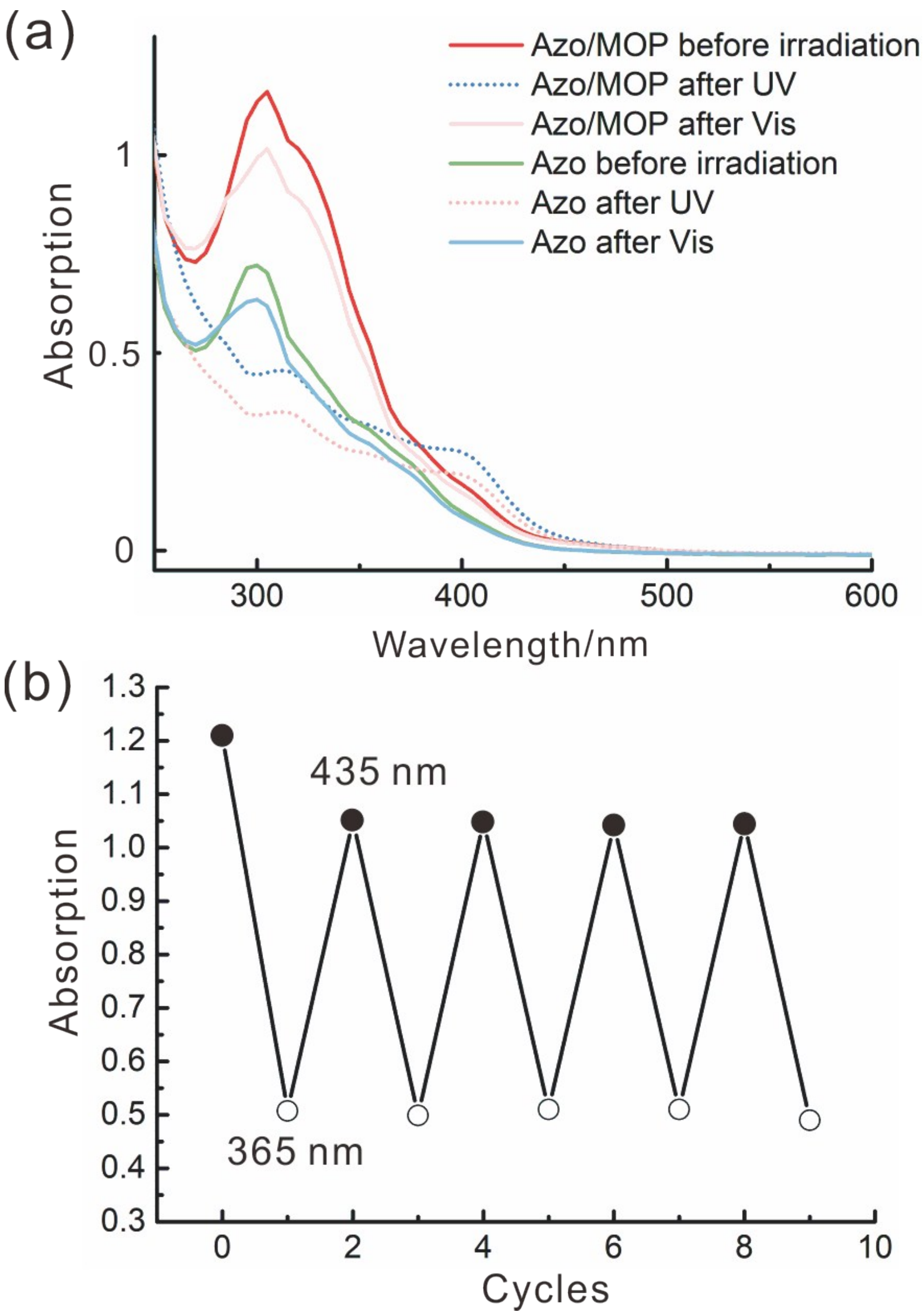


Figure S10. UV and Vis study of Azo-R and Azo-R/MOP mixture.

8. TEM of MOPs and Stars.

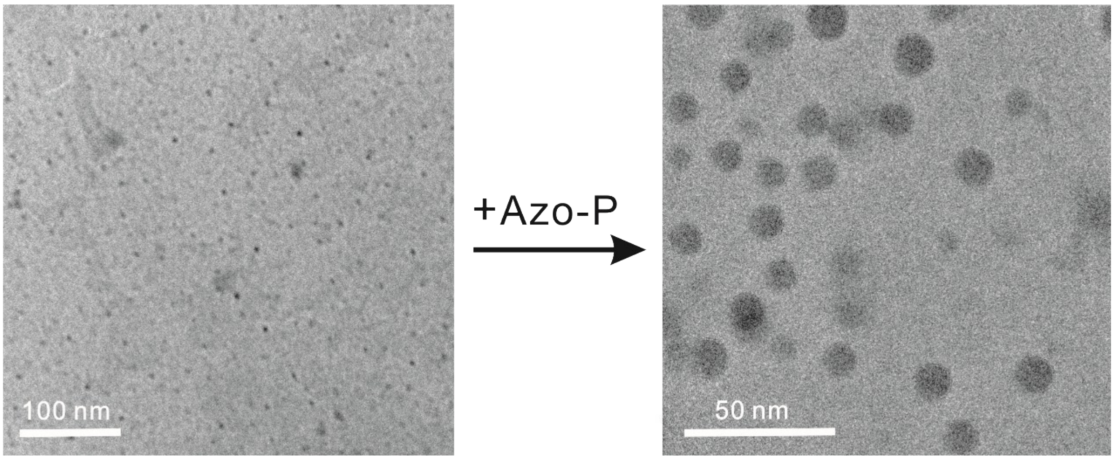
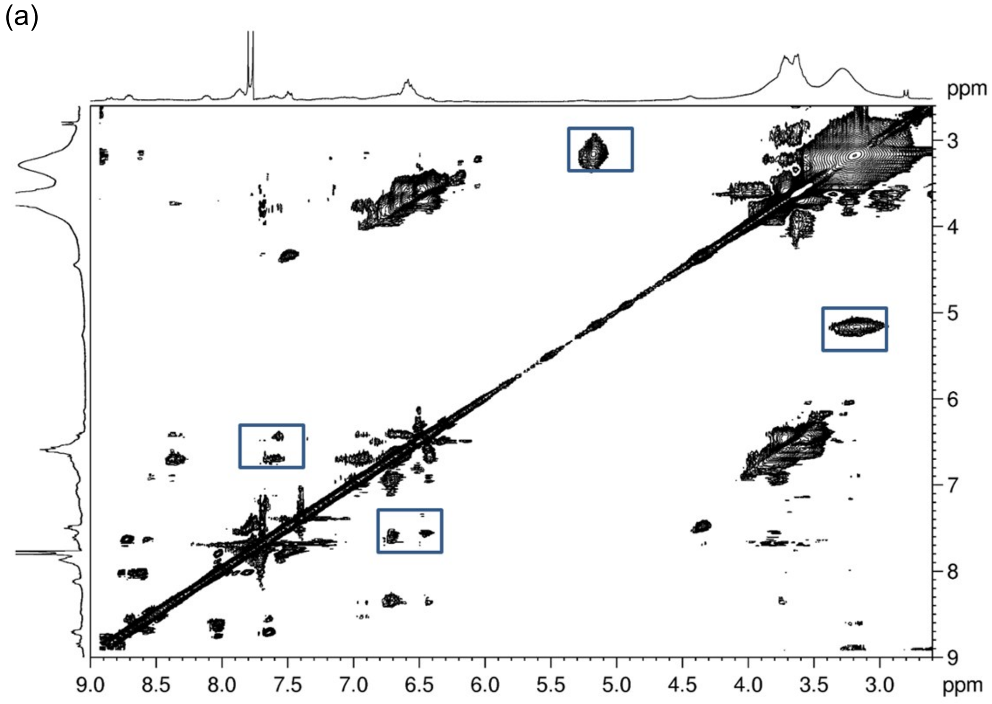


Figure S11. TEM images of MOPs and stars, respectively.

8. 2D NOESY study of Azo-P/MOP mixture.



(b)

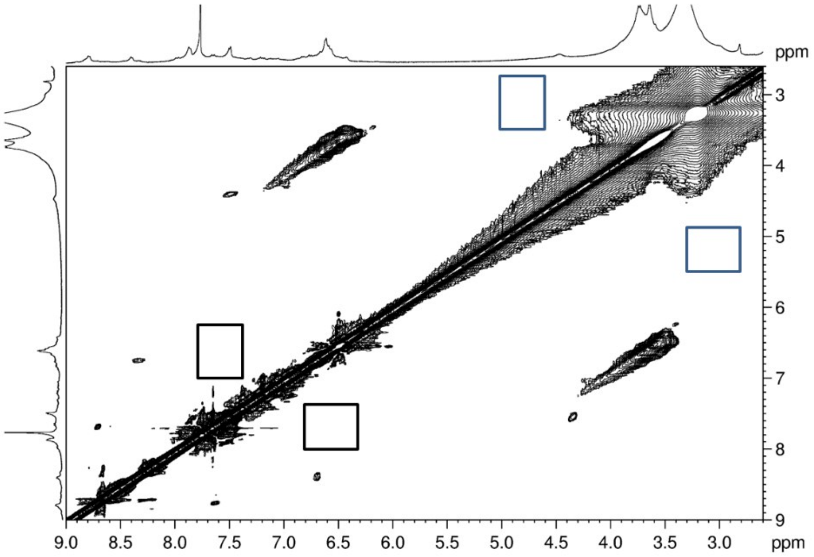


Figure S12. 2D NOESY study of Azo-P/MOP mixture in $CDCl_3$, T = 298 K.

References

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2. T. Ogoshi, H. Kayama, D. Yamafuji, T. Aoki, T.-a. Yamagishi, *Chemical Science* 2012, 3, 3221-3226.
3. G. Yu, C. Han, Z. Zhang, J. Chen, X. Yan, B. Zheng, S. Liu, F. Huang, *Journal of the American Chemical Society*, 2012, 134, 8711-8717.