Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information

Light-Triggered Reversible Disassembly of Stimuli-responsive Coordination Metallosupramolecular Pd_2L_4 Cages Mediated by Azobenzene Containing Ligand

Shuang Fu, Quan Luo, Mingsong Zang, Jun Tian, Zherui Zhang, Minghao Zeng, Yuancheng Ji, Jiayun Xu and Junqiu Liu *

E-mail: junqiuliu@jlu.edu.cn (Prof. J. Q. Liu)

Experimental Procedures

1. General materials and method

Materials:

All the solvents were purchased from Beijing chemical plant. Dichloromethane (DCM), cyclohexane, acetonitrile (MeCN), Tetrahydrofuran (THF), chloroform ($CHCl_3$) and ethyl acetate were used with further purification. All the reagents were purchased from Energy Chemical plant.

Instruments and methods:

^{1}H-NMR spectra was measured by Bruker 510 spectrometer (500 MHz) using $CDCl_3$ or DMSO-d or CD_3CN as solvent with tetramethylsilane (TMS) as reference.

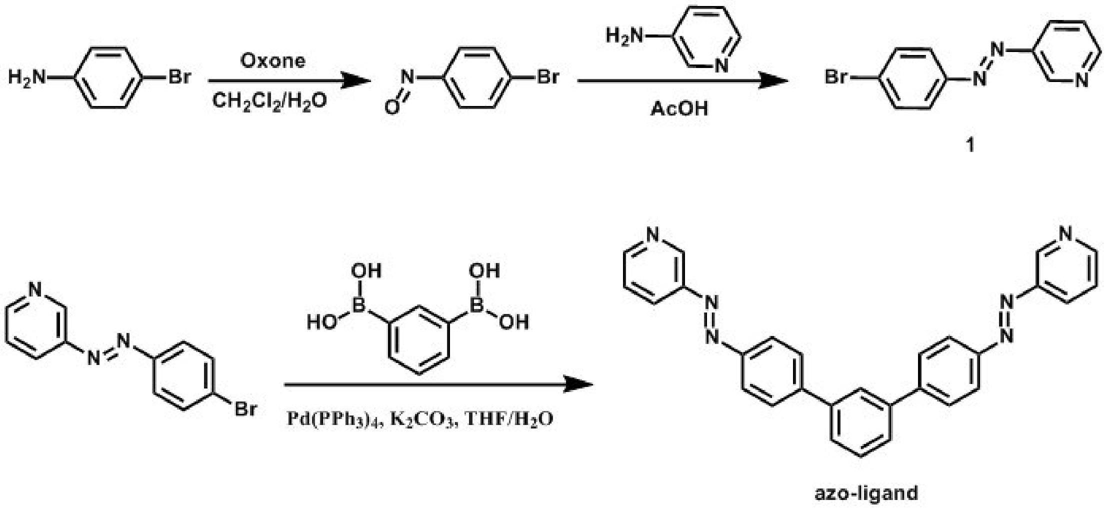
^{13}C-NMR spectra was measured by Bruker 510 spectrometer (500 MHz) using $CDCl_3$ or DMSO-d or CD_3CN as solvent with tetramethylsilane (TMS) as reference.

Diffusion-ordered NMR spectroscopy (DOSY) was measured by Bruker 510 spectrometer (500 MHz) using DMSO-d as solvent.

Mass spectrometry analyses were performed using liquid chromatograph-mass spectrometer (LC-MS, Agilent1290-micrOTOF-Q Ⅱ) using methanol or MeCN or H_2O as solvent.

UV–Vis spectrums were obtained with a Shimadzu 3100 UV-VISNIR Recording Spectrophotometer interfaced with a personal computer.

Design and synthesis of azo-ligand



Scheme S1. Design and Synthesis of substituted azobenzenes 1 and azo-ligand.

Synthesis of substituted azobenzenes 1.

The molecule 1 is synthesized according to previous work.[1] 4-bromoaniline (5.0 g, 19.8 mmol) was dissolved in 60 mL of DCM. Then a solution of Oxone (36 g, 60 mmol) dissolved in 140 mL water was added. The solution was stirred under nitrogen at room temperature until TLC monitoring indicated complete consumption of the starting material (36 h). After separation of the layers, the aqueous layer was extracted with DCM twice. The combined organic layers were washed with 1N HCl, saturated sodium bicarbonate solution, water, brine and dried (magnesium sulfate).

Removal of the solvent in vacuo yielded 5.2 g of 1-bromo-4-nitrosobenzene as a green solid. The 1-bromo-4-nitrosobenzene (5.90 g, 32.3 mmol) was dissolved in 300 ml of acetic acid. To this solution was added 3-aminopyridine (3.04 g, 32.4 mmol). The resulting mixture was stirred at room temperature for 6 d (TLC monitoring). The precipitate was separated by filtration, washed with water and dried in a desiccator over sicacide. The crude product was purified by Column chromatography on silica gel (cyclohexane/ethyl acetate 4:1) resulted in 4.3g of molecular 1. (500MHz, chloroform-d, 25℃, TMS) (Figure S1) δ: 9.22 (d, $J = 2$Hz, 1H_1), 8.75 (dd, $J = 1.5$, 4.5Hz, 1H_2), 8.18 (dd, $J = 1.5$, 6.5Hz, 1H_4), 7.86 (d, $J =$ 8.5Hz, 2H_5), 7.70 (d, $J = 8.5$Hz, 2H_6), 7.49 (dd, $J = 5$, 8Hz, 1H_3). ^{13}C-NMR(500MHz, chloroform-d, 25℃, TMS) (Figure S2) δ: 152.0, 151.4, 147.9, 147.6, 132.2, 126.8, 126.2, 124.2, 123.8. ESI-MS: calculated for $C_{11}H_8BrN_3$, m/z 260.7; found, m/z (261.7, $[M+H]^+$) (Figure S3).

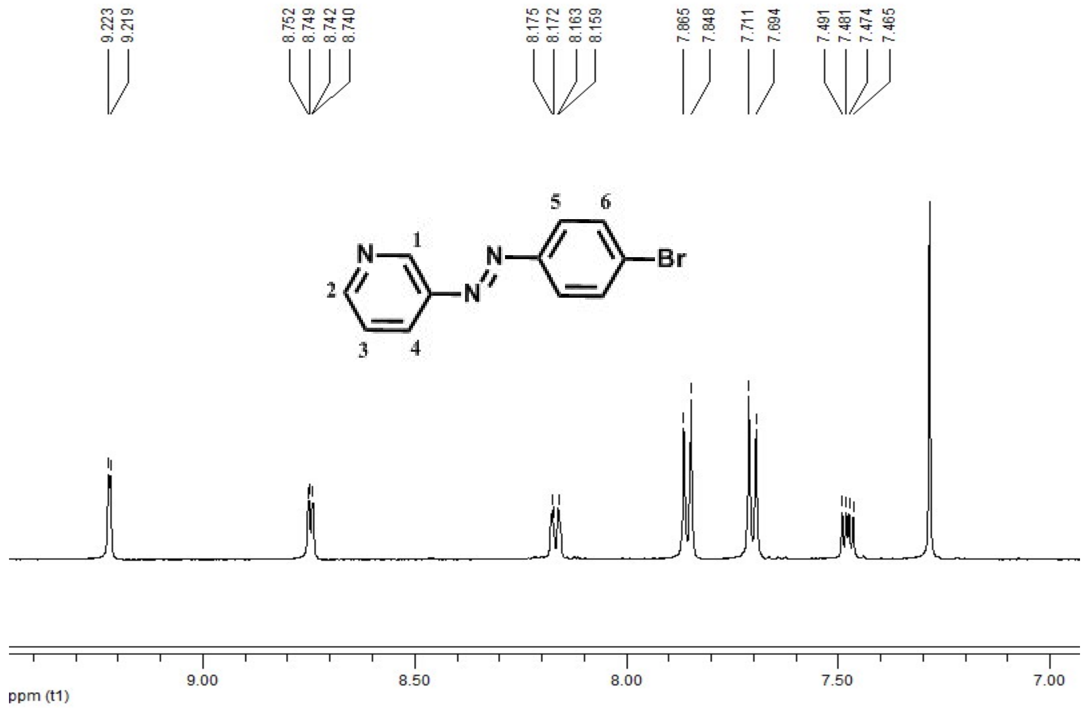


Figure S1. The ^{1}H-NMR(500MHz, chloroform-d, 25℃, TMS) spectrum of **azobenzenes 1**.

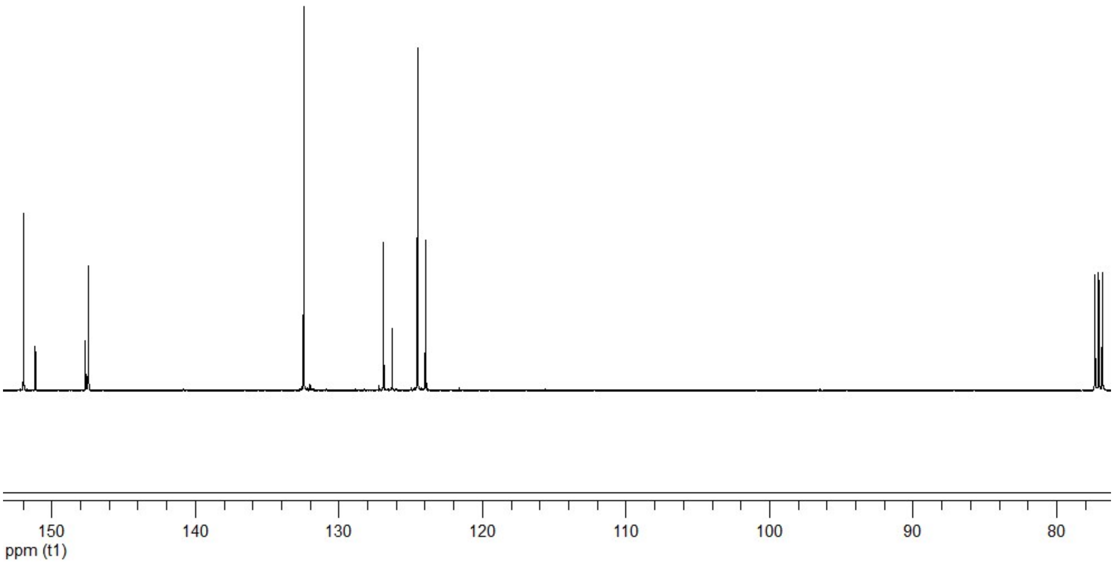


Figure S2. The ^{13}C-NMR(500MHz, chloroform-d, 25℃, TMS) spectrum of **azobenzenes 1**.

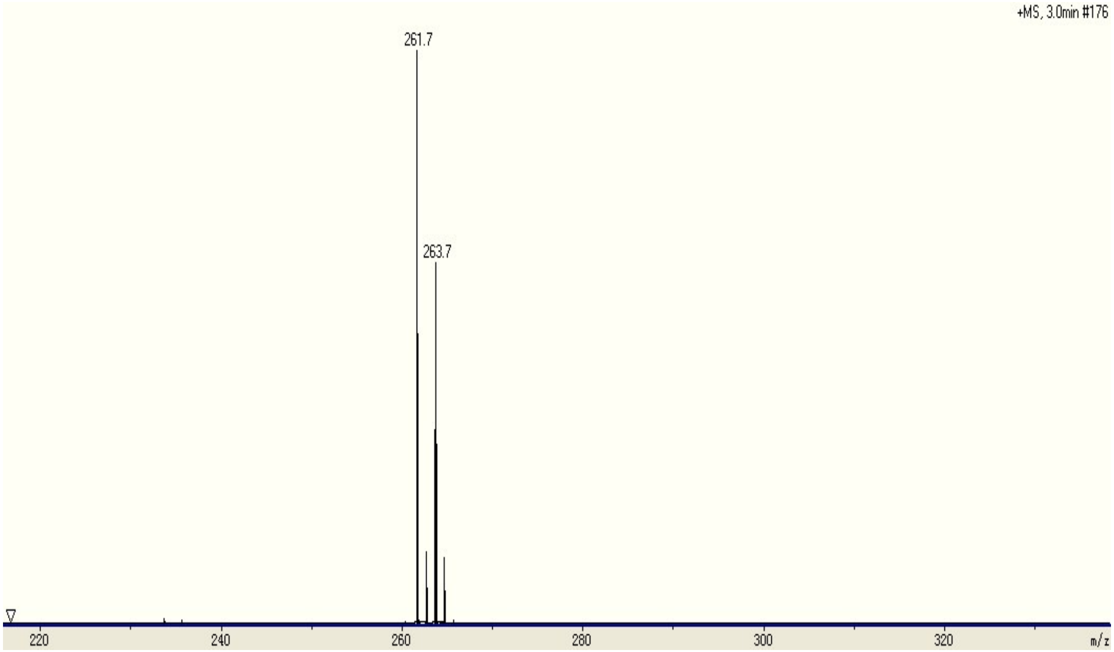


Figure S3. ESI-tof of the **azobenzenes 1**. Assignment of the main peak: m/z 261.7，[M+H]$^+$.

Synthesis of azo-ligand.

The azo-ligand was synthesized by uzuki–Miyaura cross coupling.[2] Benzene-1,3-diboronic acid (0.250 g, 1.507 mmol), 1 (1.04 g, 4 mmol), sodium carbonate solution (1.70 g, 16 mmol) and Pd(PPh$_3$)$_4$ (57.8 mg, 0.05 mmol) were suspended in a mixture of THF/H$_2$O(13 mL / 5 mL). The solution was stirred under nitrogen at reflux for 17 h. After cooling to room temperature, water (50 mL) was added, and the product extracted into ethyl acetate (50 mL). After that, the combined extracts were dried over anhydrous MgSO$_4$, filtered, and the solvent removed under reduced pressure to yield a translucent oily solid. Purification was carried out via column chromatography (silica, cyclohexane/ethyl acetate, 3:1) to yield a yellow solid (0.518 g, 77.9%).^{1}H-NMR (500MHz, chloroform-d, 25℃, TMS) (figure S4) δ: 9.27 (d, *J* = 2Hz, 2H$_7$), 8.72 (dd, *J* =1.5, 4.5Hz, 2H$_6$), 8.21 (dt, *J* = 2.0, 10.0Hz, 2H$_5$), 8.10 (d, *J* = 8Hz, 4H$_3$), 7.98(s, 1H$_9$), 7.89 (d, *J* = 8.5Hz, 4H$_2$), 7.72(dt, *J* =1.5, 7.5Hz, 2H$_8$), 7.62 (m, 1H$_1$), 7.50 (dd, *J* = 4.5, 8Hz, 2H$_4$). ^{13}C-NMR(500 MHz, chloroform-d, 25℃, TMS) (Figure S5) δ: 151.9, 148.0, 147.7, 144, 140.4, 132.0, 129.8, 128.3, 127.9, 127.0, 126.0, 124.0, 122.7. ESI-MS (Figure S6): calculated for $C_{28}H_{20}N_6$, m/z 440.17; found, 441.5, [M+H]$^+$; 221.3, [M+2H]$^{2+}$.

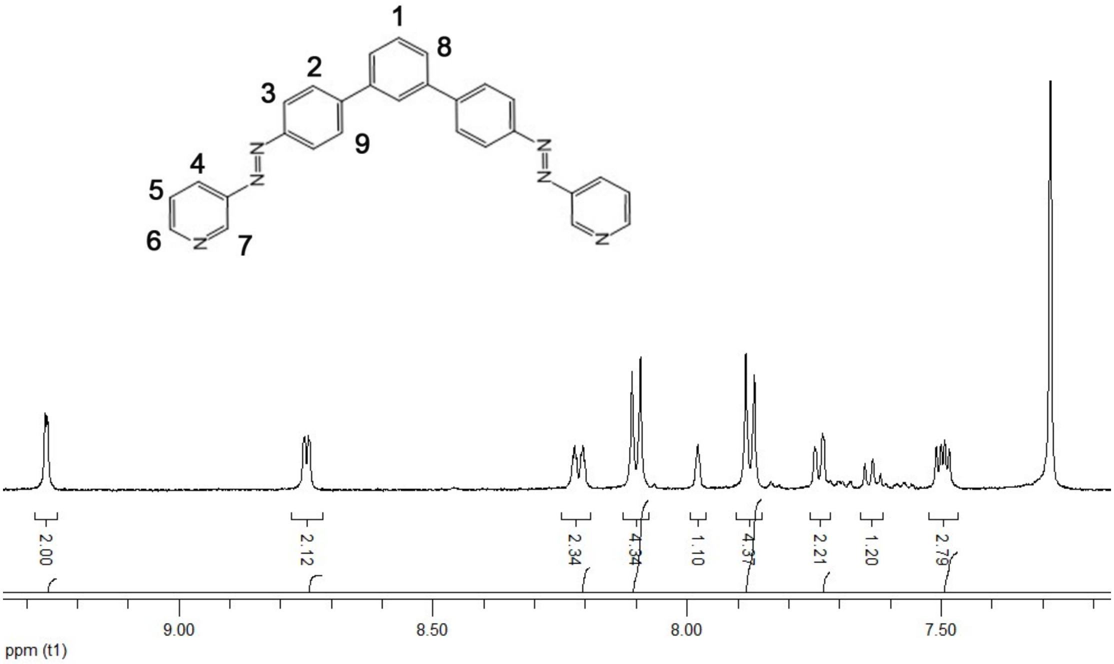


Figure S4. The ^{1}H-NMR(500MHz, chloroform-d, 25℃, TMS) spectrum of azo-ligand.

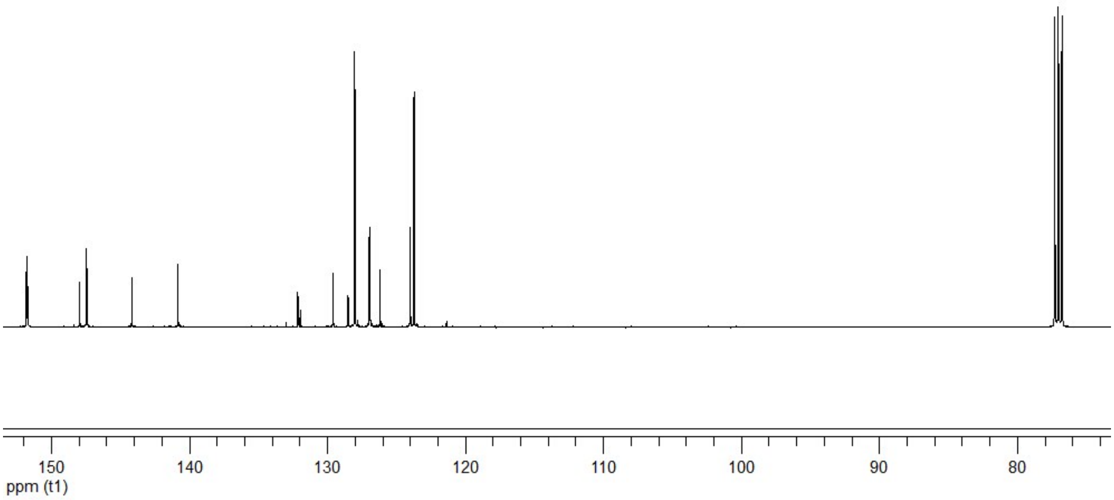


Figure S5. The ^{13}C-NMR (500MHz, chloroform-d, 25℃, TMS) spectrum of azo-ligand.

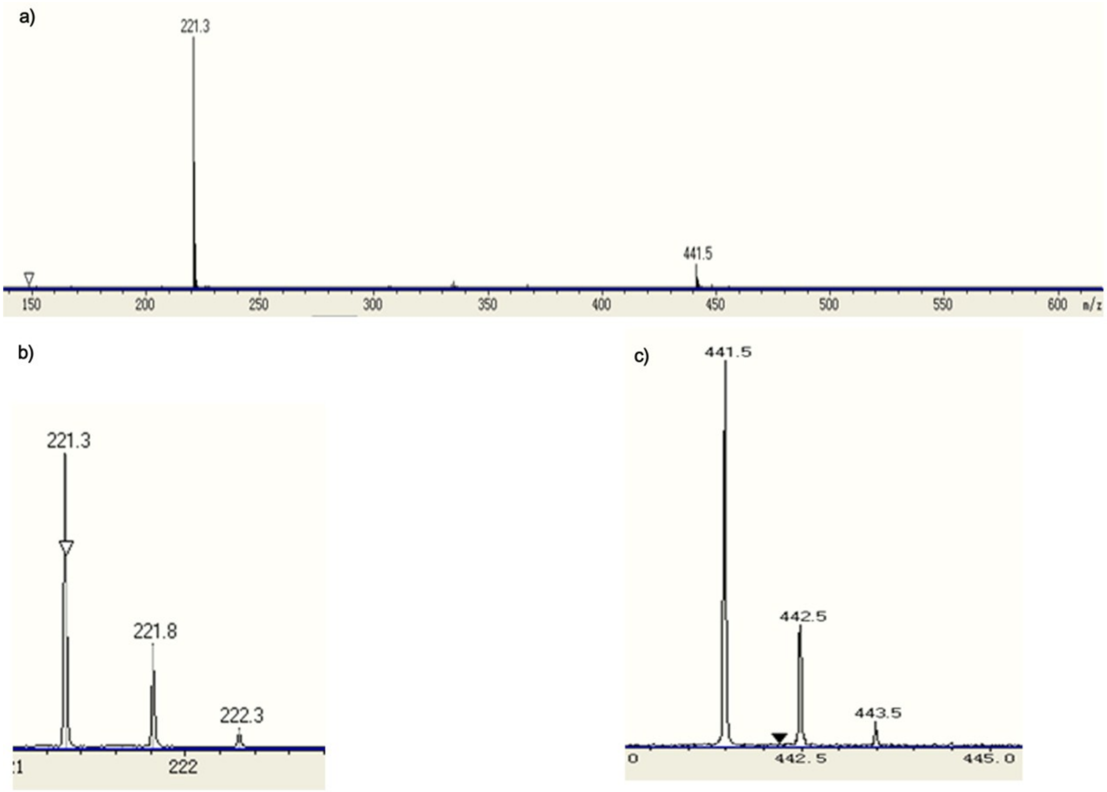


Figure S6. a) The main spectrum of ESI-tof of the azo-ligand (found, 441.5, 221.3); b) and c) the amplified spectrum the m/z 440.17[M+H]$^+$ and 221.3, [M+2H]$^{2+}$.

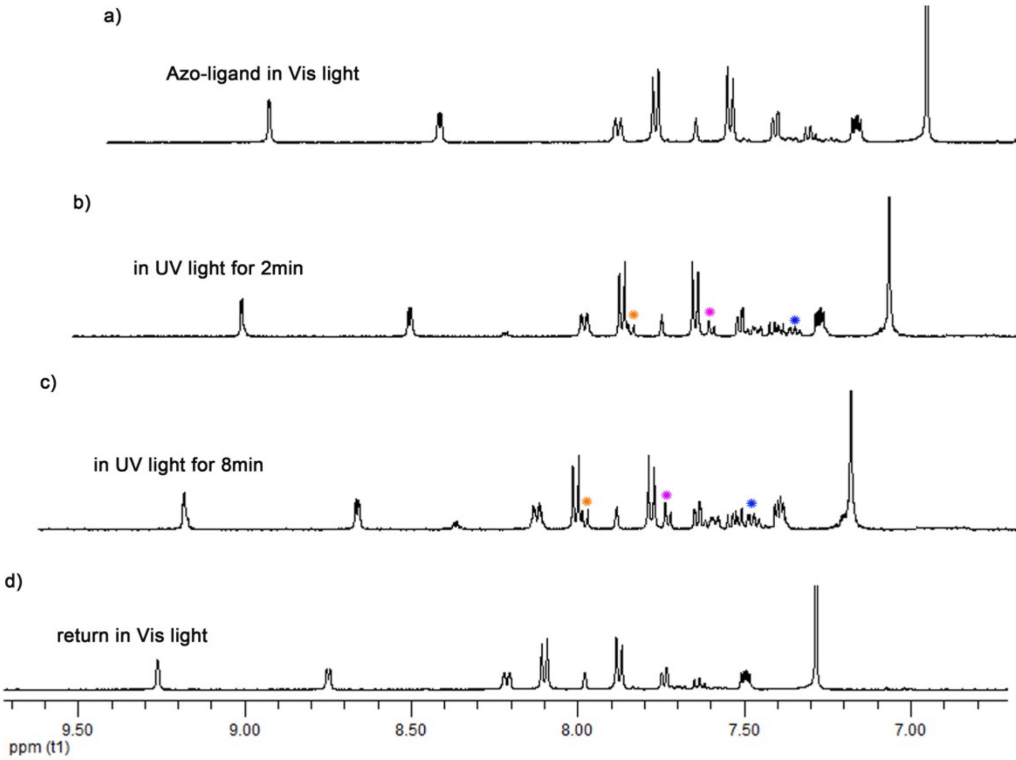


Figure S7. ^{1}**H NMR spectra monitoring the isomerization of Azo-ligand (500 MHz) in** $CDCl_3$**. a) initial spectrum of Azo-ligand in Visible light (450nm); b) after irradiation with 365 nm laser for 2min; c) after irradiation with 365 nm laser for 8min to cis-rich form; d) after irradiation with 450 nm light to return to trans state. The orange stars in the b) and c) represent the doublet of** H_3, pink **stars in the b) and c) represent the doublet of** H_2**, blue stars in the b) and c) represent the doublet of** H_1.

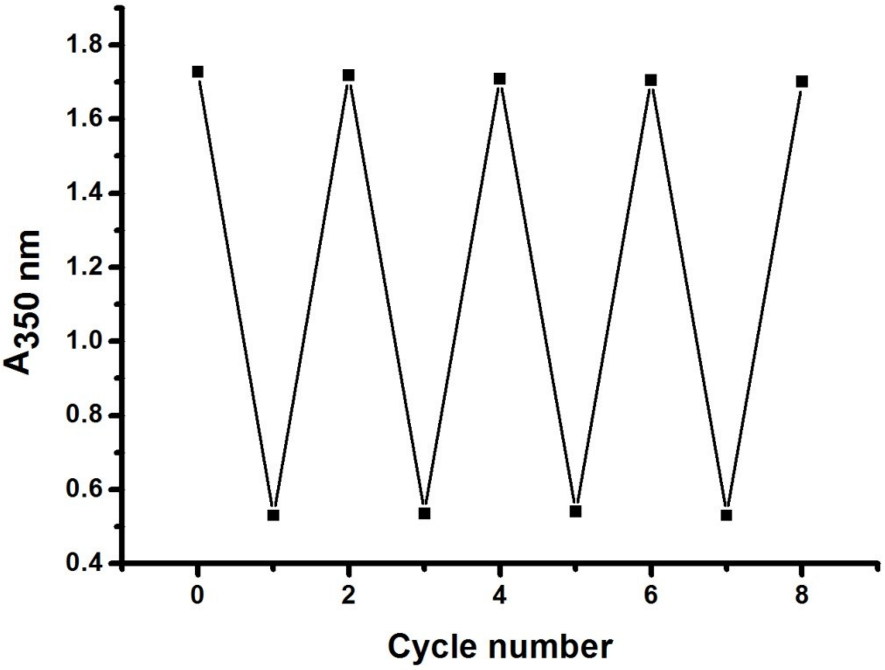
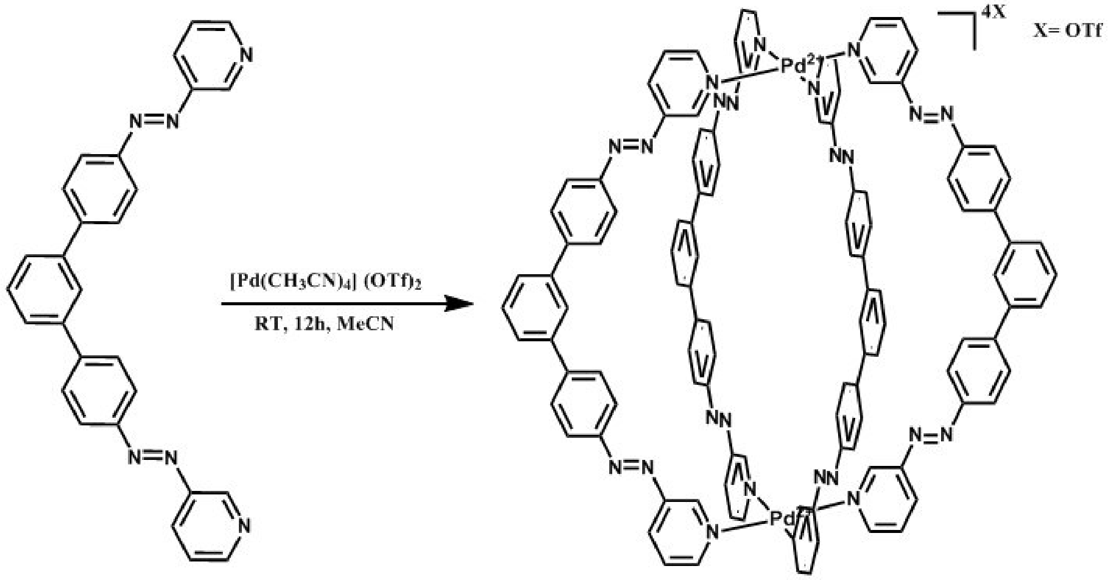


Figure S8. The absorption at 350 nm of the azo-ligand with alternative UV light and Vis light irradiation (in $CHCl_3$ solvent).

Synthesis of Azo-cage.



Scheme S2. Design and Synthesis of Azo-cage.

The design and synthesis of Azo-cage is shown in scheme S2. In visible light, by simply addition of $[Pd(CH_3CN)_4]$ $(OTf)_2$ (1 eq. 0.089 mmol) in 500 μL MeCN to a solution of azo-ligand (2 eq. 0.179 mmol) in MeCN (5 mL) solution, and then stirring in room temperature for 2h, the self-assembled coordination cage complex Azo-cage is prepared. A solid was isolated by concentration of the solution under vacuum followed by precipitation with Et_2O. The solid was filtered, washed with Et_2O and dried under vacuum to yield the product as a yellow powder (yield 67%). ^1H-NMR (500 MHz, DMSO-d, 25°C, TMS) (Figure S8) δ: 12.2 (s, $8H_{7'}$), 9.58 (d, *J* = 5Hz, $8H_{6'}$), 8.53 (d, *J* = 8Hz $8H_{5'}$), 8.28 (s, $4H_{9'}$), 8.22 (d, *J* = 8.5Hz, $16H_{3'}$), 8.17 (d, *J* = 8.5Hz, $16H_{2'}$), 8.02 (m, $8H_{8'}$), 7.90 (d, *J* = 7.5Hz, $8H_{4'}$), 7.64 (d, *J* = 8Hz, $4H_{1'}$). ^{13}C-NMR (500 MHz, DMSO-d,, 25°C, TMS)

(Figure S9) δ: 153.1, 151.3, 149.4, 147.2, 144.3, 139.5, 133.5, 132.5, 131.9, 129.2, 128.5, 127.7, 124.4. ^{19}F-NMR (500 MHz, DMSO-d,, 25℃, TMS) (Figure S10) δ: -78. The ESI-MS is shown in Figure S6 and Figure 2. signals were observed in the mass spectrum at m/z 493.6, 708.2, 1136.2 and 2422.1, indicative of $[Pd_2(L)_4]^{4+}$, $[Pd_2(L)_4(OTf)_1]^{3+}$, $[Pd_2(L)_4(OTf)_2]^{2+}$ and $[Pd_2(L)_4(OTf)_3]^{+}$ ions, respectively.

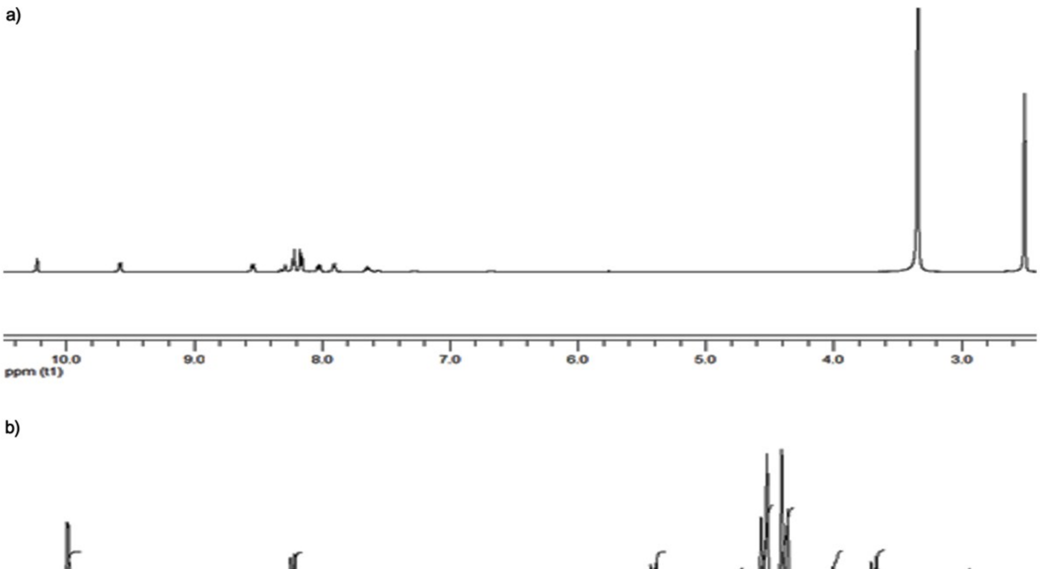


Figure S9. a) The main spectrum of ^{1}H-NMR (500 MHz, DMSO-d, 25℃, TMS) of Azo-cage.; b) The amplified ^{1}H-NMR.

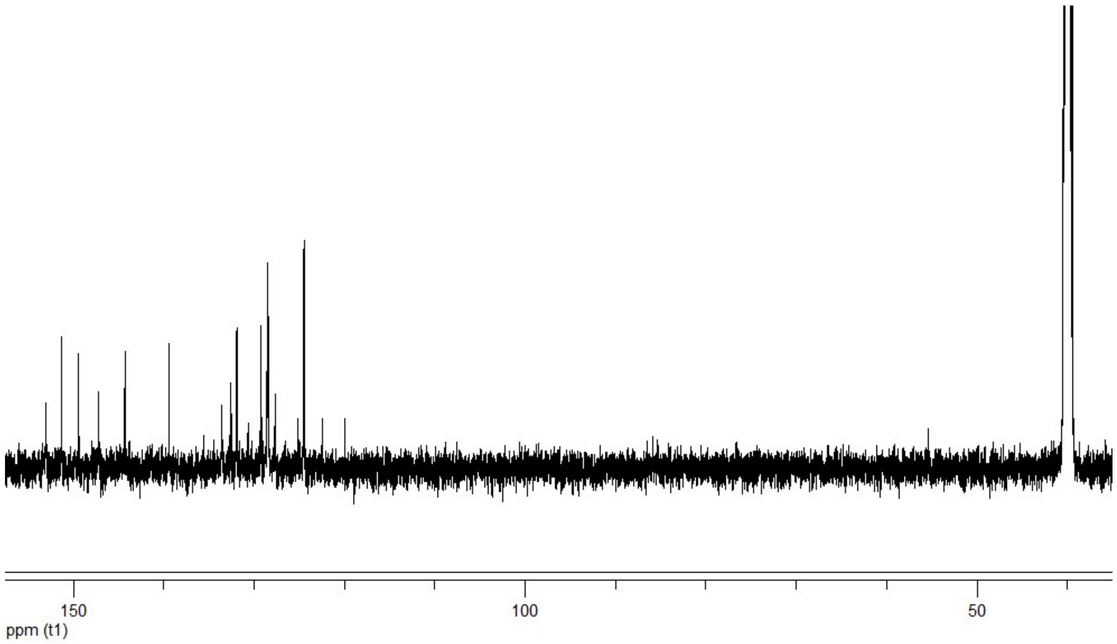


Figure S10. The ^{13}C-NMR (500MHz, DMSO-d, 25℃, TMS) spectrum of Azo-cage.

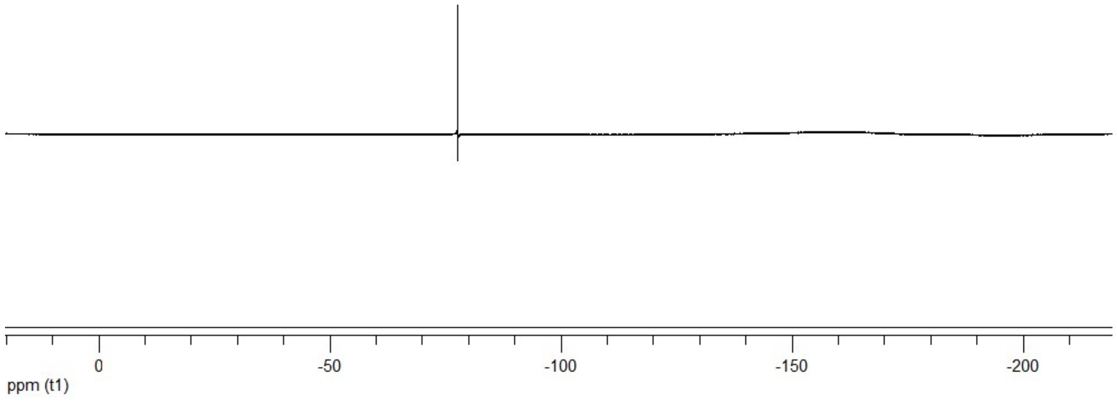


Figure S11. The ^{19}F-NMR(500MHz, DMSO-d, 25℃, TMS) spectrum of Azo-cage.

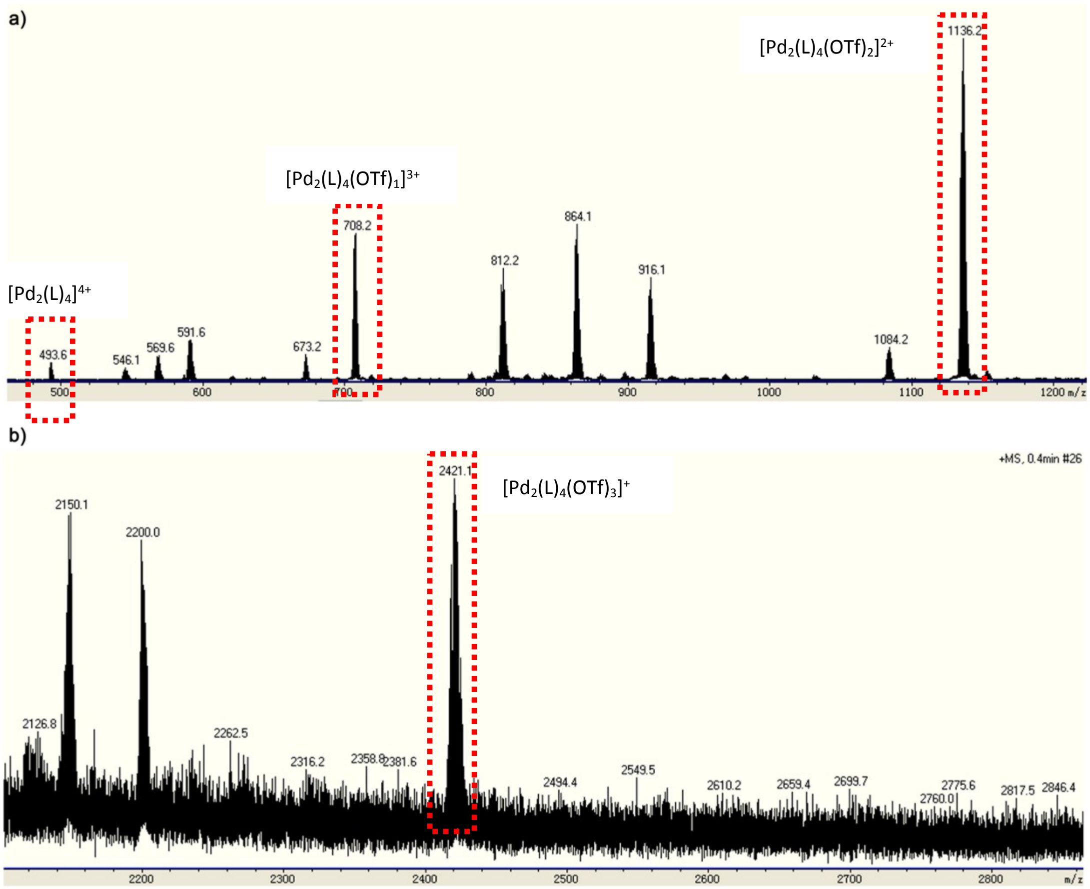


Figure S12. The main spectrum of ESI-tof of the Azo-cage for a) and for b).

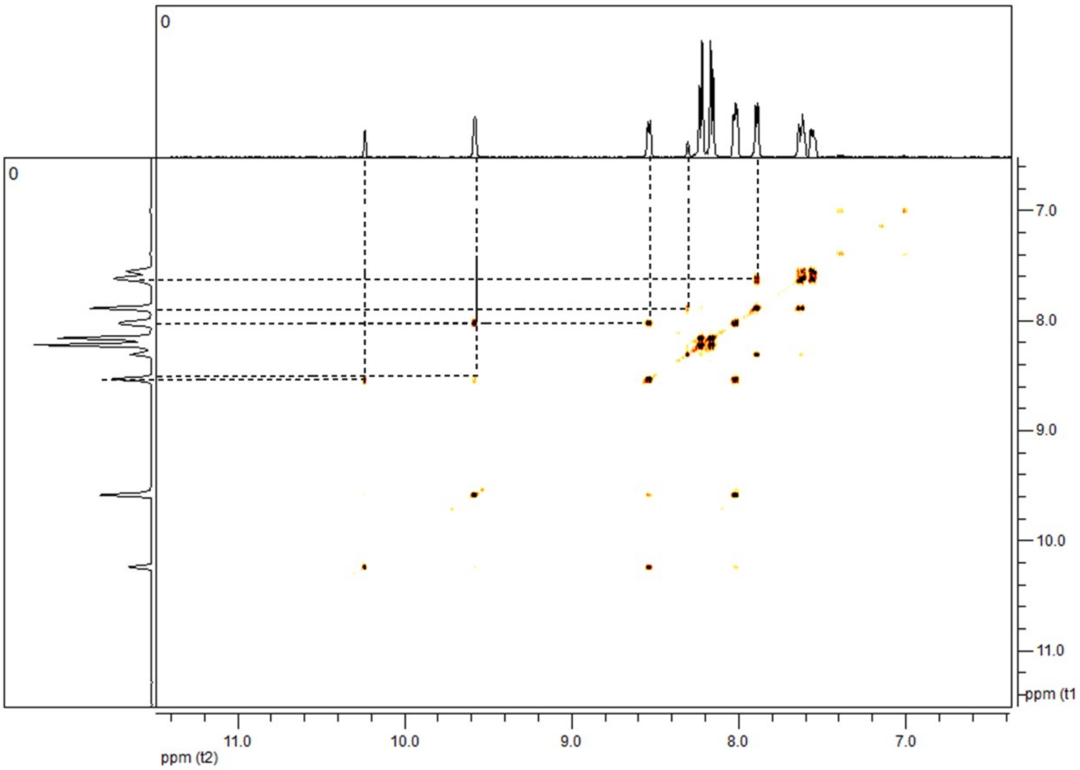


Figure S13. ^{1}H-2D COSY spectrum (500 MHz, DMSO-d) of **Azo-cage**.

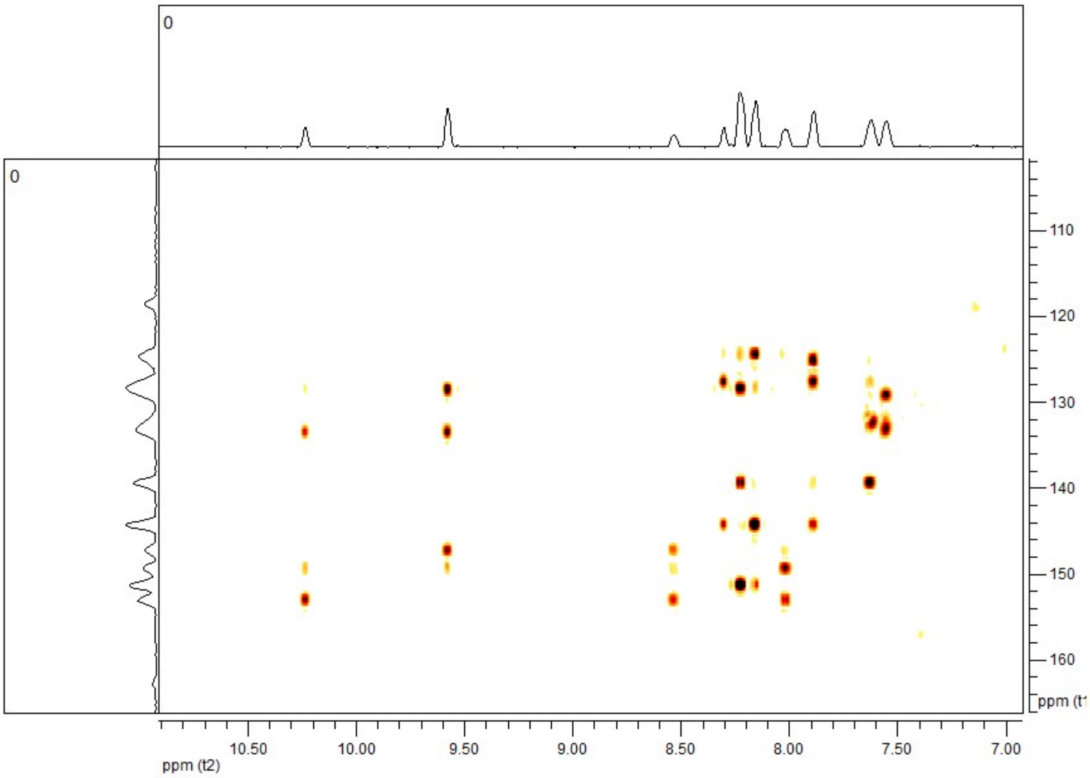


Figure S14. HSQC spectrum (500 MHz, DMSO-d) of Azo-cage.

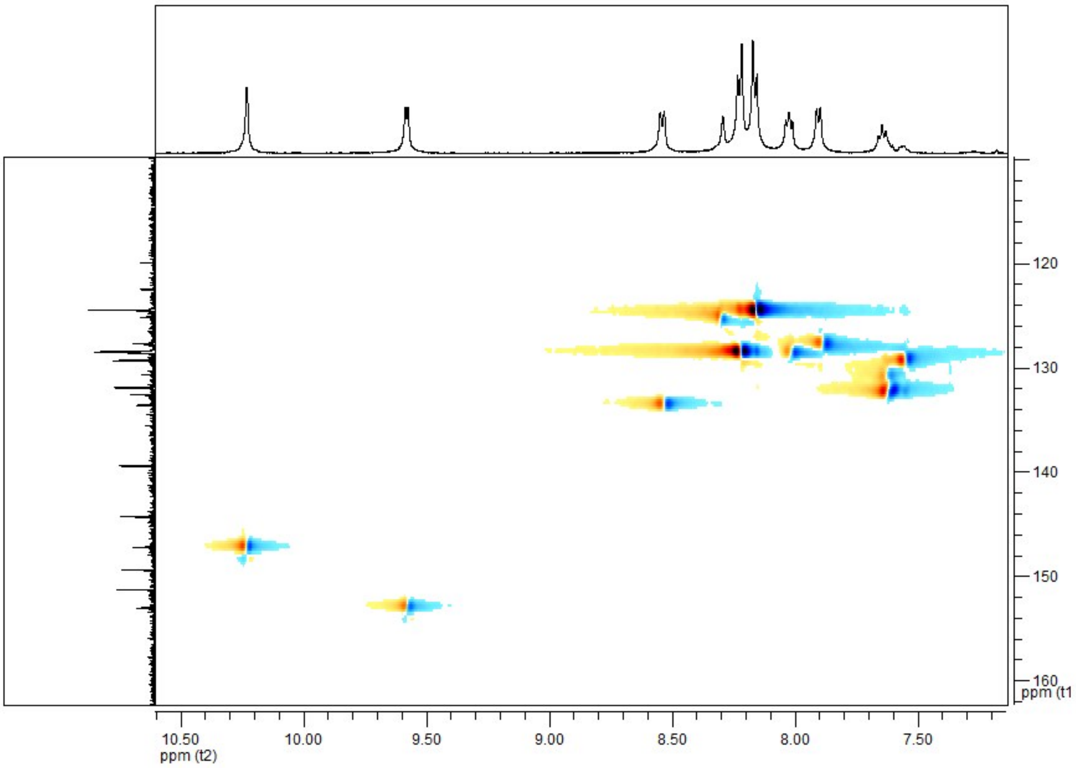


Figure S15. HMBC NMR (600 MHz, DMSO-d) spectrum of complex Azo-cage.

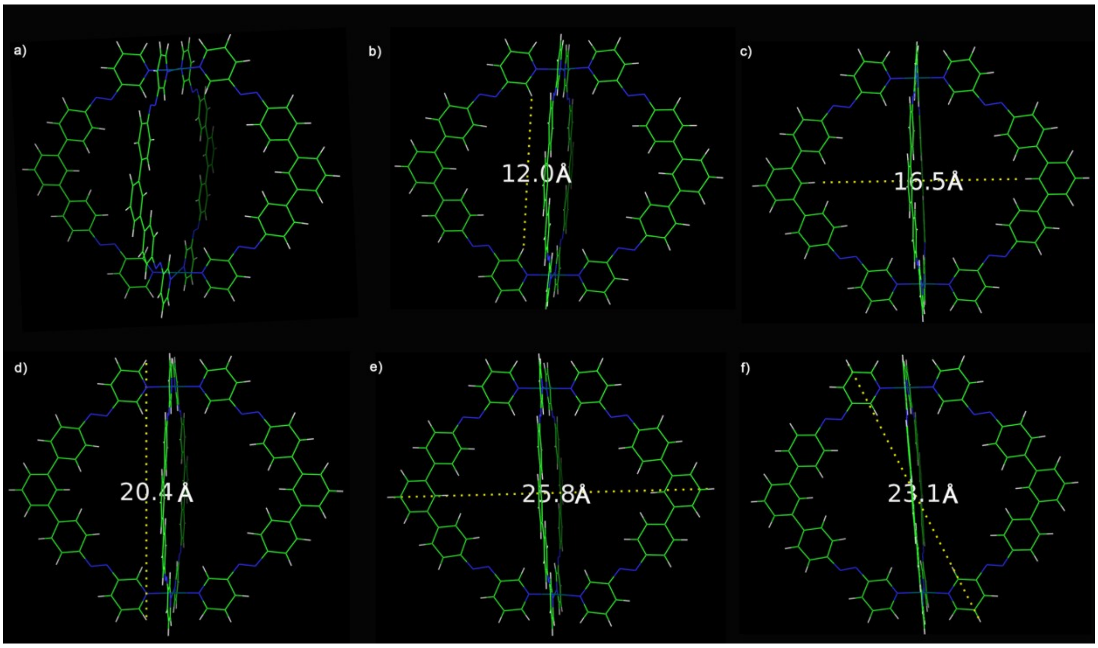


Figure S16. a) Theoretial molecular model A of Azo-cage. b) and c) show that the cage has a cavity approximately 12.0 Å deep and 16.5 Å wide; d), e) and f) show that the cage has outer diameters of 20.4 Å hight, 25.8 Å width, and 23.1 Å of diagonal, respectively. The longest outer diameter is 25.8 Å.

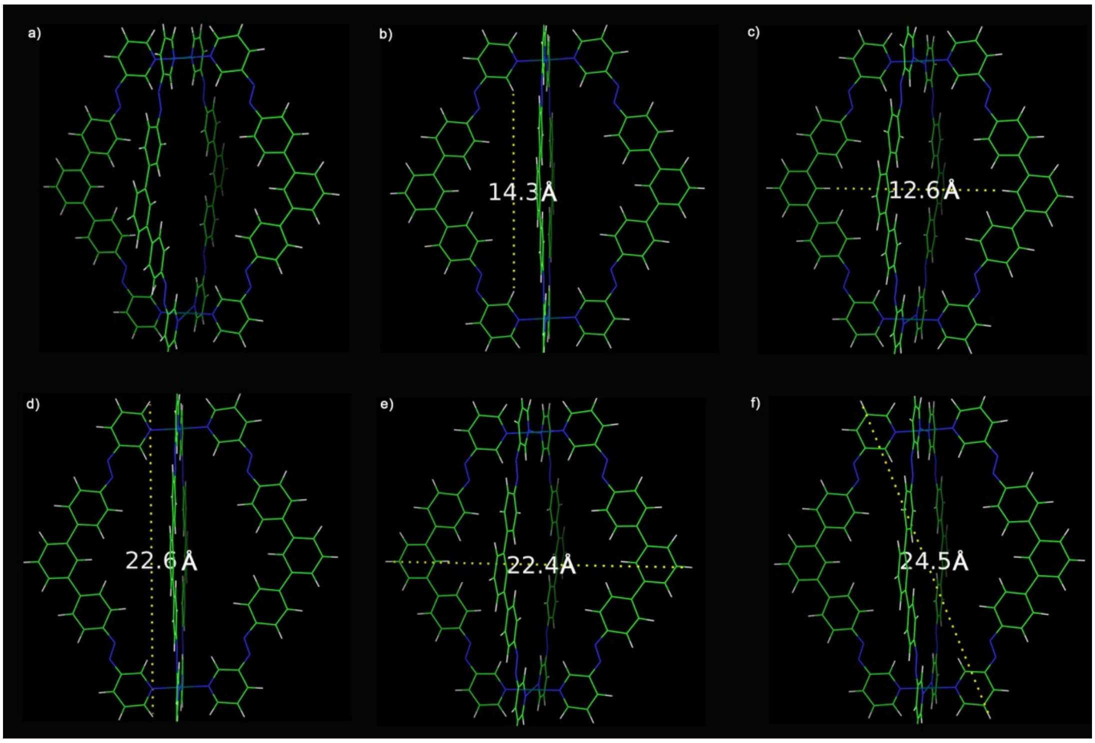


Figure S17. a) Theoretial molecular model B of Azo-cage. b) and c) show the cage has a cavity approximately 14.3 Å deep and 12.6 Å wide; d) and e) and f) show that the mode B has outer diameters of 22.6 Å hight, 22.4 Å width, and 24.5 Å of diagonal, respectively. The longest diameter is 24.5 Å.

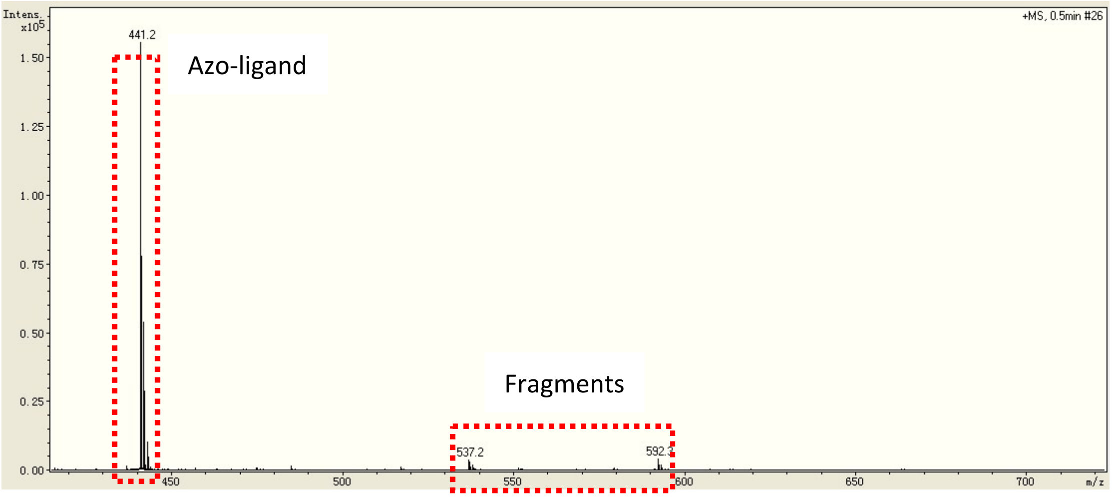


Figure S18. ESI-tof spectrum of the Azo-cage system after irradiation with UV light. The spectrum shows that the m/z 493.6, 708.8, 1136.2 indicative of $[Pd_2(L)_4]^{4+}$, $[Pd_2(L)_4(OTf)_1]^{3+}$, $[Pd_2(L)_4(OTf)_2]^{2+}$ disappear after irradiation with UV light. Only some fragments and Azo-ligand generate;

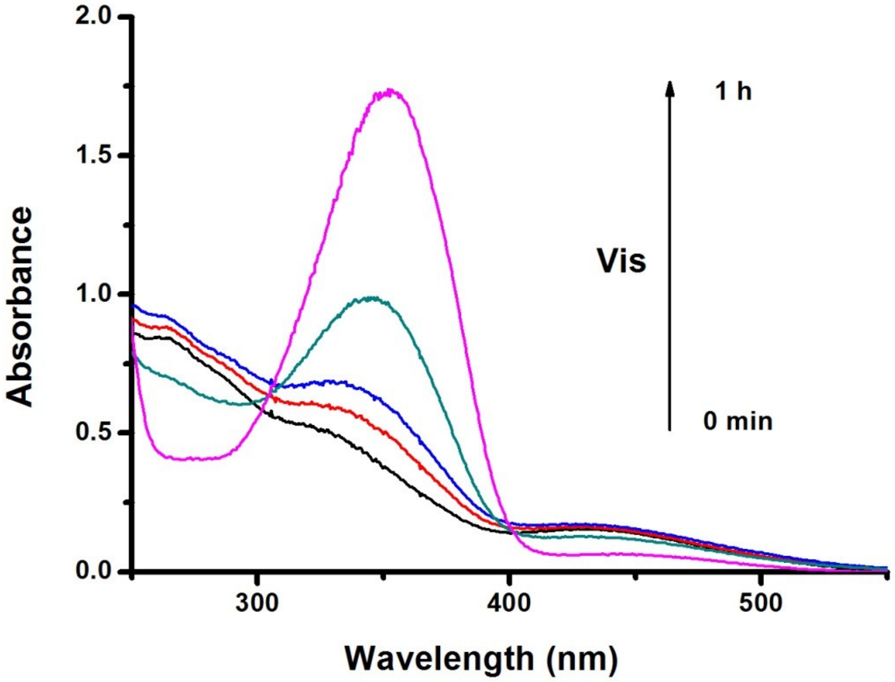


Figure S19. UV-Vis spectra of the disassembled Azo-cage system under Vis light irradiation.

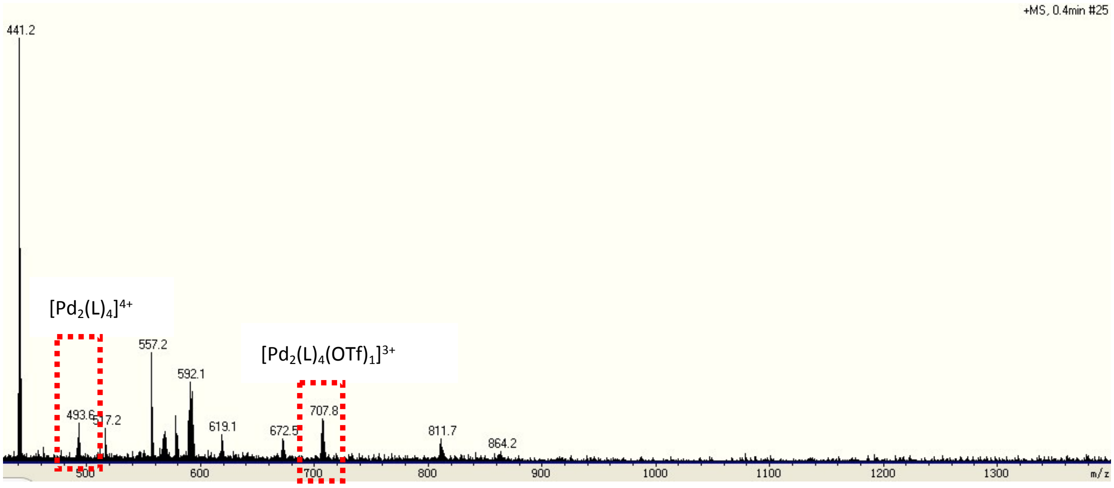


Figure S20. ESI-tof spectrum of the sample after irradiation with Vis light. The spectrum shows that the m/z 493.6, 708.8, indicative of $[Pd_2(L)_4]^{4+}$, $[Pd_2(L)_4(OTf)_1]^{3+}$ appear again after irradiation with Vis light.

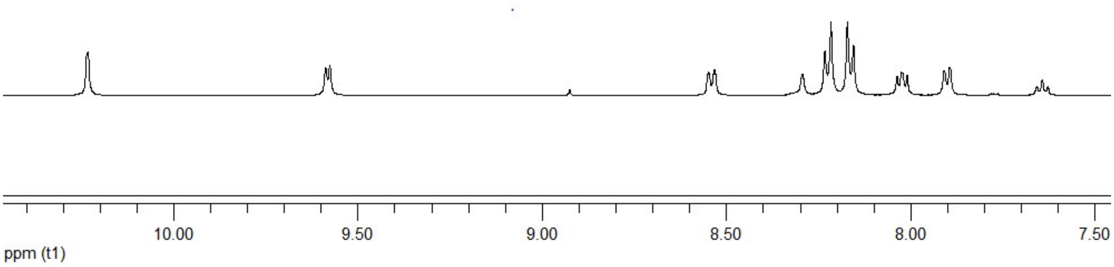


Figure S21. a) The spectrum of ^{1}H-NMR (500 MHz, CDCN, 25℃, TMS) of re self-assembly of Azo-cage.

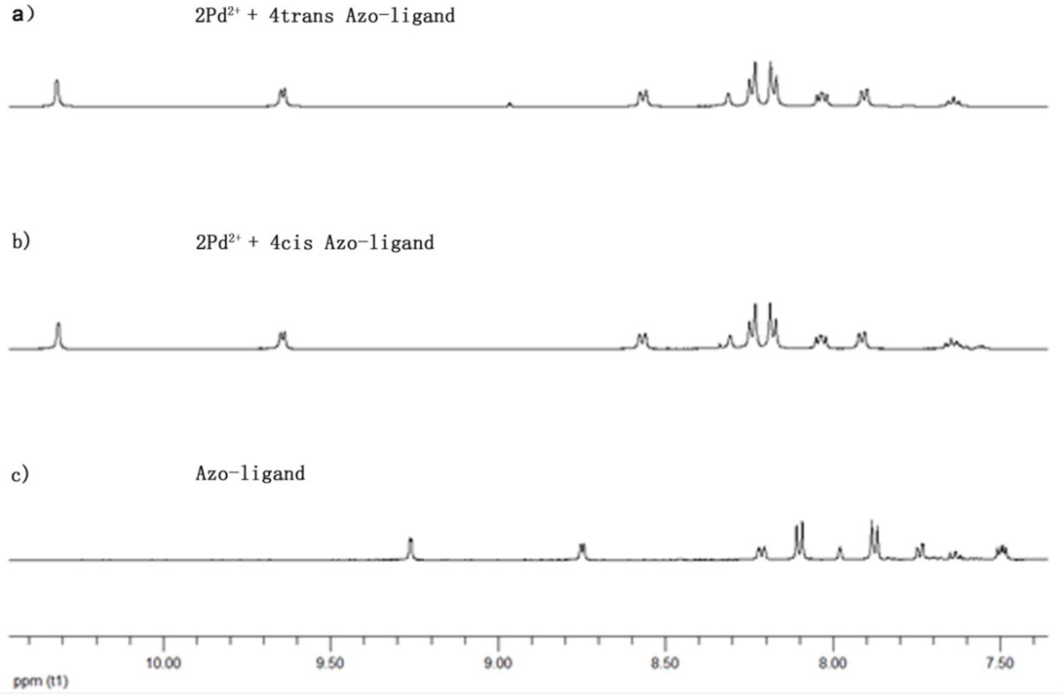


Figure 22. a) ^{1}H NMR spectra (CD_3CN, 298 K) a) Pd^{2+} coordinated with the Azo-ligand in visible light; b) Pd^{2+} coordinated with the Azo-ligand in UV light; c) the Azo-ligand before coordinate with Pd^{2+}.

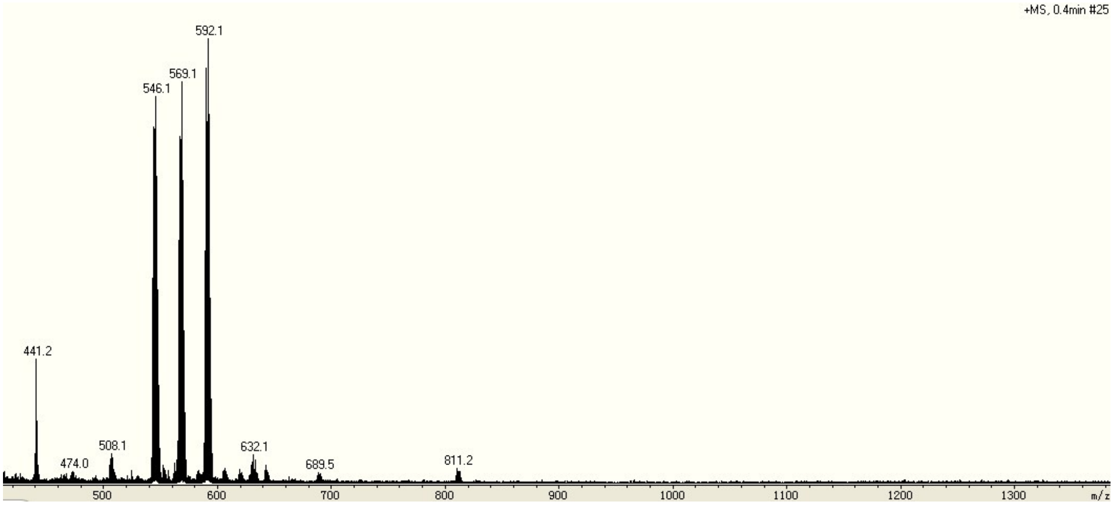


Figure S23. ESI-tof spectrum of the sample irradiation with UV light. The signals of the m/z 493.6, 708.8, 1136.2 indicative of $[Pd_2(L)_4]^{4+}$, $[Pd_2(L)_4(OTf)_1]^{3+}$, $[Pd_2(L)_4(OTf)_2]^{2+}$ do not appear.

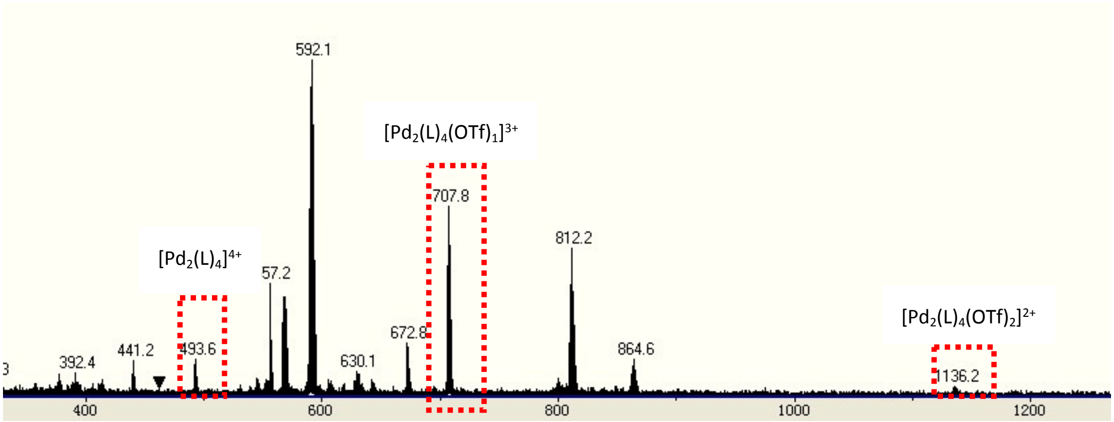


Figure S24. ESI-tof spectrum of the sample after irradiation with Vis light. The spectrum shows that the m/z The signals of the m/z 493.6, 708.8, 1136.2 indicative of [$Pd_2(L)_4$]$^{4+}$, [$Pd_2(L)_4(OTf)_1$]$^{3+}$, [$Pd_2(L)_4(OTf)_2$]$^{2+}$ appear again after irradiation with Vis light.

Reference

1. B. Priewisch and K. Rück-Braun, *J. Org. Chem.* 2005, **70**, 2350.

2. K. L. Garner, L. F. Parkes, J. D. Piper and J. A. G. Williams, *Inorg. Chem.* 2010, **49**, 476.