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Chemical Synthesis

Supplementary Material

Coordination-driven [2+2] metallo-macrocycles isomers: conformational control and photophysical properties

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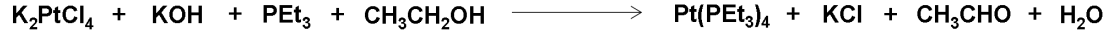
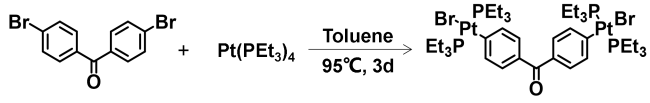
1. Materials and methods

All reagents were purchased from Sigma-Aldrich, Matrix Scientific, Alfa Aesar and used without further purification. Compound **1**[1] was prepared according the reported literature. Column chromatography was conducted using basic SiO_2 (VWR, 40-60 μm, 60 Å) and the separated products were visualized by UV light. NMR spectra data was recorded on Bruker Avance 400-MHz and 500-MHz NMR spectrometer in $CDCl_3$ and DMSO-d_6 with TMS standard as reference. ESI-MS was recorded with a Waters Synapt G2 tandem mass spectrometer, using solutions of 0.5 mg sample in 1 mL of DMSO/MeOH/Acetone (1:1:3, v/v) for complex. The UV-Vis spectra of solution samples were recorded with a Shimadzu UV2550 spectrophotometer. The emission spectra of solution samples were measured on a Shimadzu RF-5301 PC spectrometer (CCD) and Maya2000Pro optical fiber spectrophotometer. The UV-Vis spectra of solid samples were recorded with a PerkinElmer Lambda1050+ spectrophotometer. The emission spectra of solid samples were determined by Edinburgh FLS920 Steady State and Transient State Fluorescence Spectrometer. The solid-state quantum yields were recorded by Edinburgh FLS980-S2S2-stm Steady State and Transient State Fluorescence Spectrometer. X-ray diffraction data for metallacycle **SB** were collected using synchrotron radiation and MAR325 CCD detector at Shanghai Synchrotron Radiation BL17B Beamline.

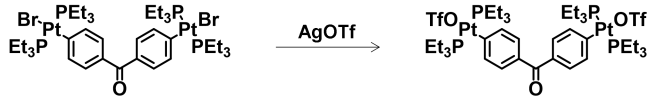
2. Synthetic procedures, ^{1}H NMR, ^{31}P{^{1}H} NMR spectra and ESI-MS of organoplatinum(II) acceptor 1



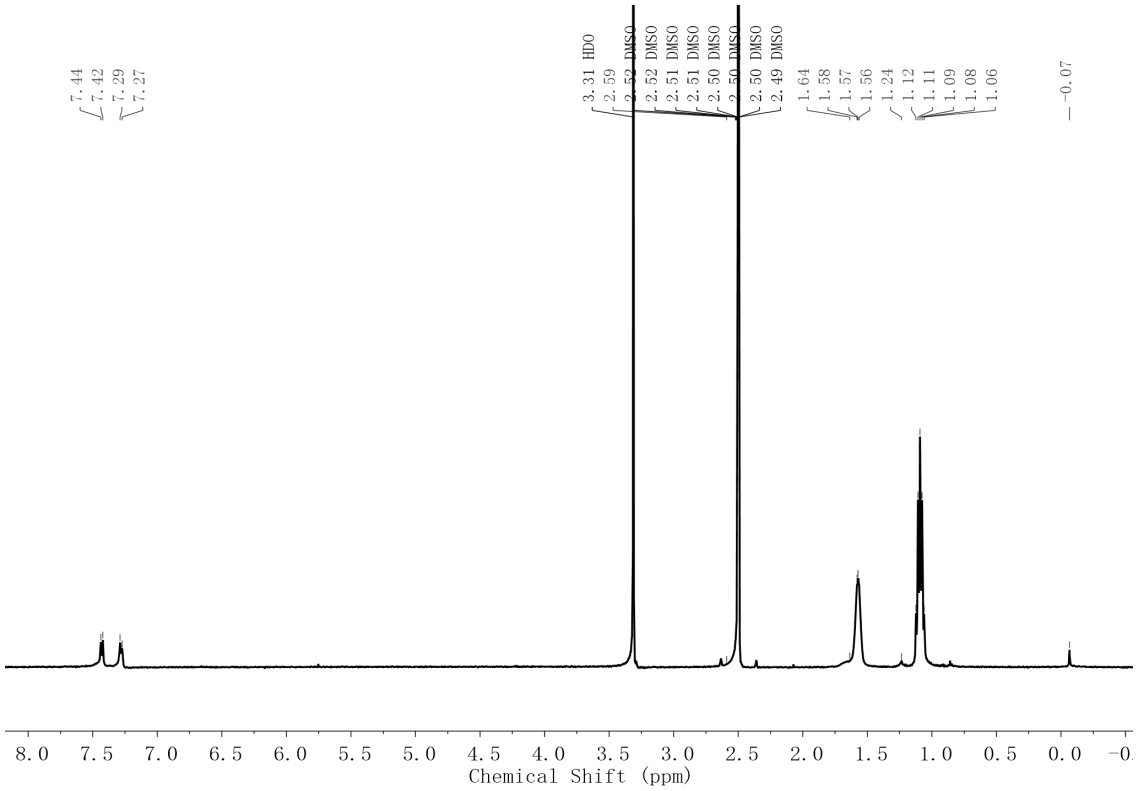
Dissolved 0.56 g (1.35 mmol) of K_2PtCl_4 with 5ml of water and added it into a Schlenk flask No. 1. Dissolved 0.305 g (5.45 mmol) of KOH with 1ml of water and 15 ml of ethanol and added it into a Schlenk flask No. 2. After the two Schlenk flasks were both evacuated in liquid nitrogen and flushed with nitrogen for three times, added triethylphosphine (1.5 ml) into the No. 2 Schlenk flask. Used a double-ended needle to transfer the liquid from Shrek flask No.1 to flask No.2. The mixture was stirred at 25 ºC for 1 h and then stirred at 60 ºC for 3 h. After cooling to room temperature, the mixture was evacuated under vacuum for 1 h and then evacuated under vacuum at 60°C for 5 h.



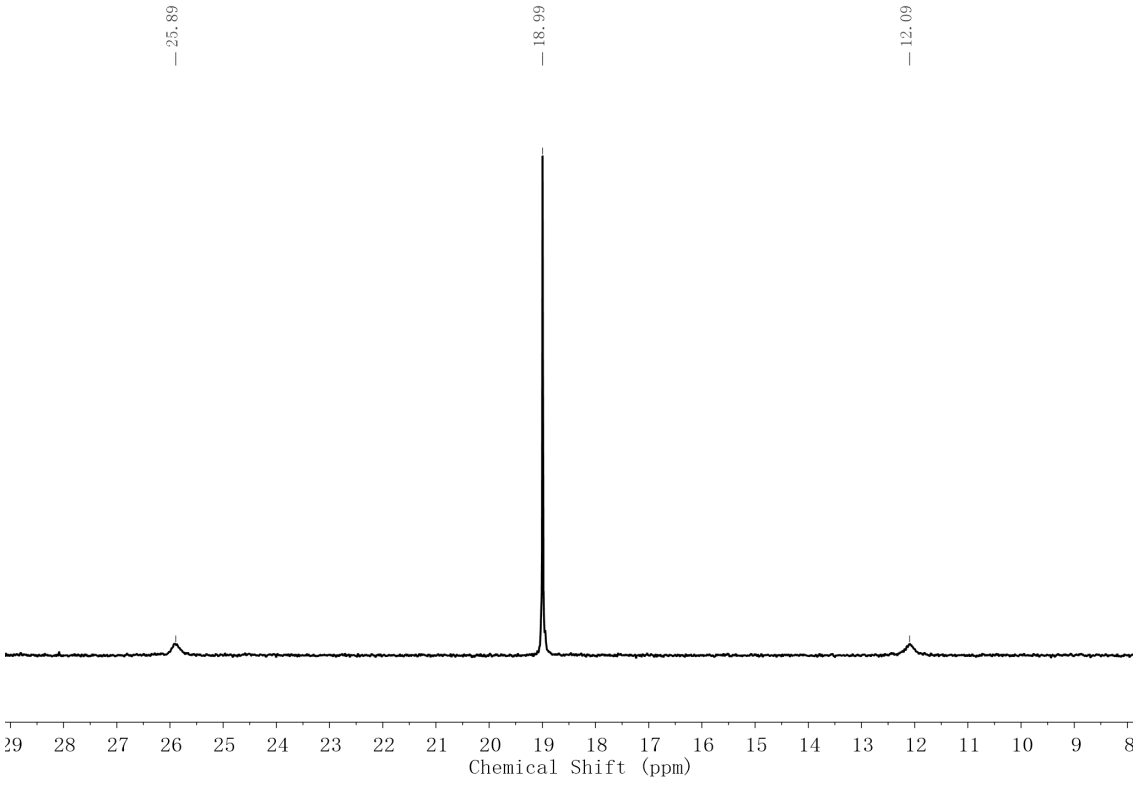
4,4'-Dibromobenzophenone (0.148 g, 0.439 mmol) was added into a Schlenk flask No. 3, and then evacuated under vacuum and flushed with nitrogen for three times. Added the toluene (25 ml) into the No. 2 Schlenk flask under nitrogen, and used a double needle to transfer the liquid in the No. 2 Schlenk flask to the No. 3 Schlenk flask. The mixture was stirred at 95 ºC for 3 days. After cooling to room temperature, the reactant evaporated in vacuo to dryness. The crude product was purified by flash column chromatography with dichloromethane: ethanol (100: 1, v/v) and was given as a white solid (0.32 g, 60%).



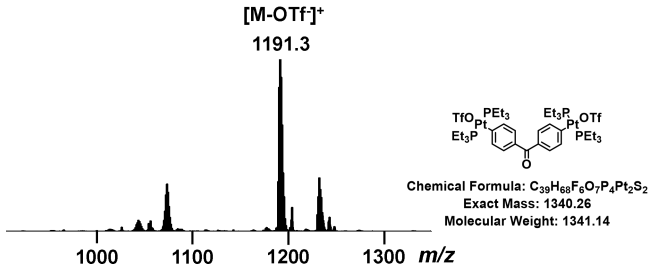
The above product (50 mg, 0.042 mmol) and silver trifluoromethanesulfonate (106 mg, 0.42 mmol) in the solvent of 15 ml dichloromethane was stirred at 25 ºC for night. Then the reactant was filtered and the filtrate evaporated in vacuo to dryness to yield a yellow product (50 mg, 90%).



Supplementary Figure 1. ^{1}H NMR (500 MHz, DMSO-d_6, 300 K) spectrum of **1**.



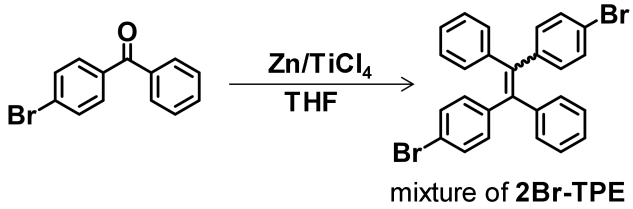
Supplementary Figure 2. ^{31}P{^{1}H} NMR (500 MHz, DMSO-d_6, 300 K) spectrum of **1**.



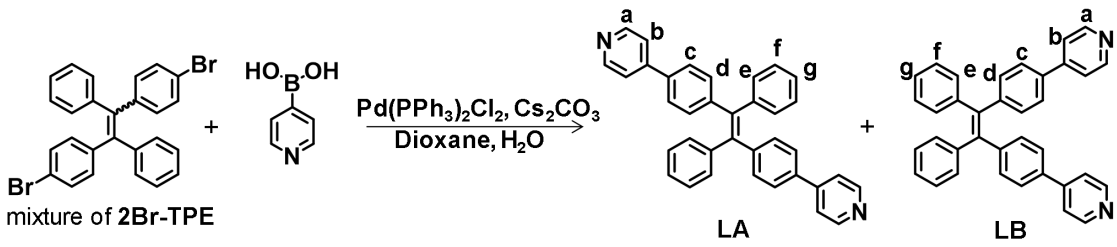
Supplementary Figure 3. HR ESI-MS spectrum of **1**.

3. Synthetic procedures and characterization data

3.1 Synthesis of ligands **LA** and **LB**.

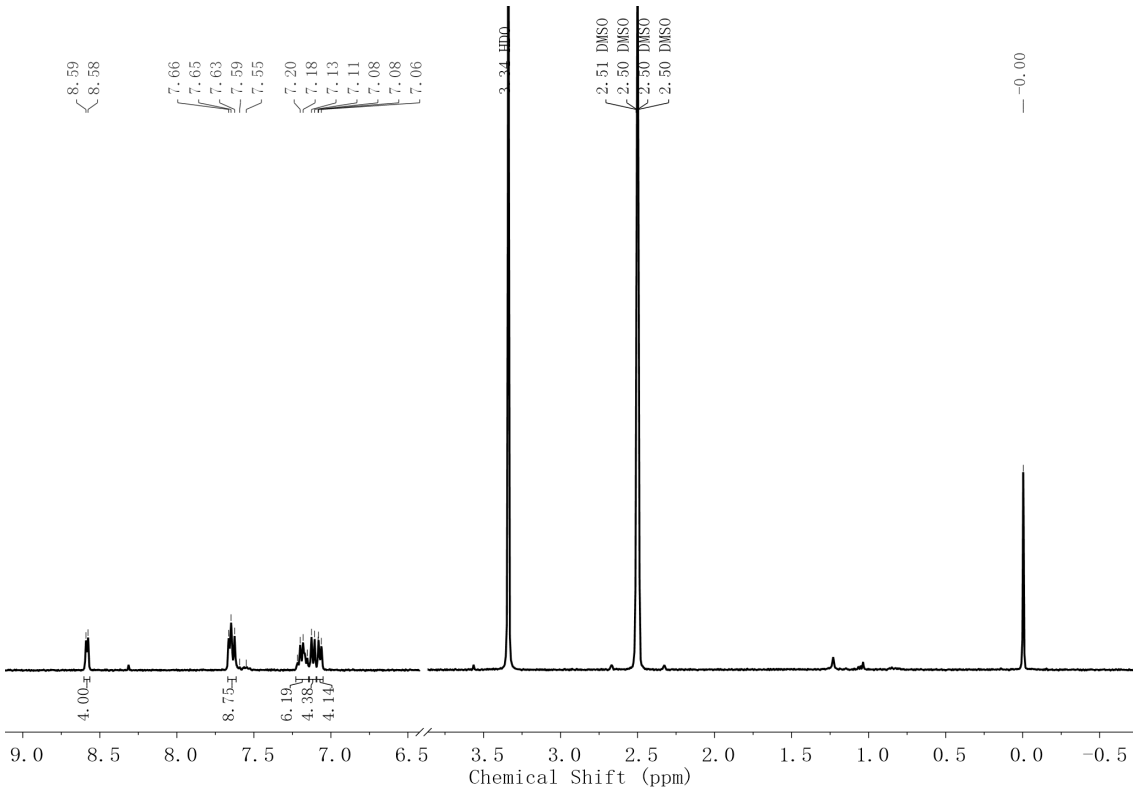


A mixture of 4-Bromobenzophenone (1.82 g, 7 mmol) and zinc dust (1.79 g, 28 mmol) was added to a dried three-neck flask, and then injected 60 ml THF at ice bath under nitrogen atmosphere. After stirred for 30 min, $TiCl_4$ (1.5 ml, 14 mmol) was drop-wise added into the flask and kept stirring for half an hour. The mixture was then refluxed overnight at 70 ºC under nitrogen atmosphere. After cooling to room temperature, the reactant was extracted with dichloromethane and the crude product was further purified by recrystallization of dichloromethane and methanol to yield a mixture of cis-trans isomers at a ratio of approximately 1:1 as pale powder (2.08 g, 61%).

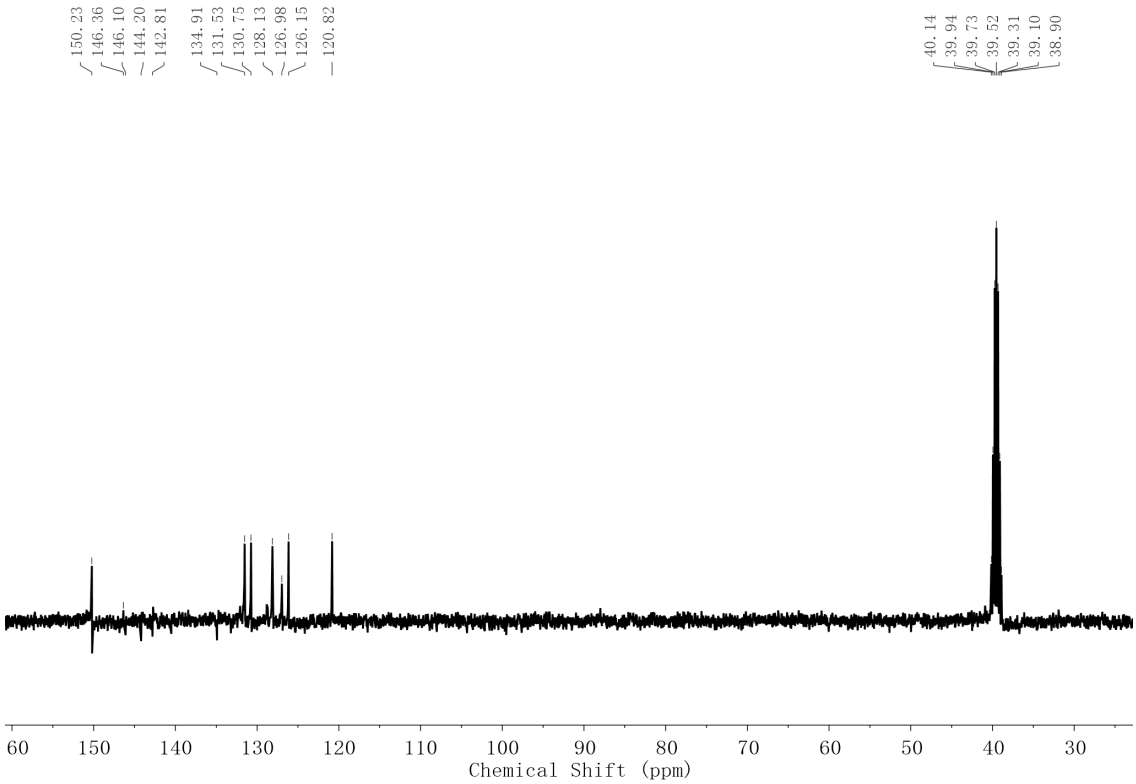


2Br-TPE (1.0 g, 2.05 mmol), 4-pyridylboronic acid (1.26 g, 10.24 mmol), $Pd(PPh_3)_2Cl_2$ (143.5 mg, 0.205 mmol) and Cs_2CO_3 (2.671 g, 8.2 mmol) were added into a 200 ml Schlenk flask. After evacuated under vacuum and flushed with nitrogen for three times, added the dioxane (80 ml) and H_2O (20 ml) into Schlenk flask. Then the mixture was stirred at 88 ºC for 48 h. After cooling to room temperature, the mixture was extracted with dichloromethane and the final products of **LA** and **LB** were purified

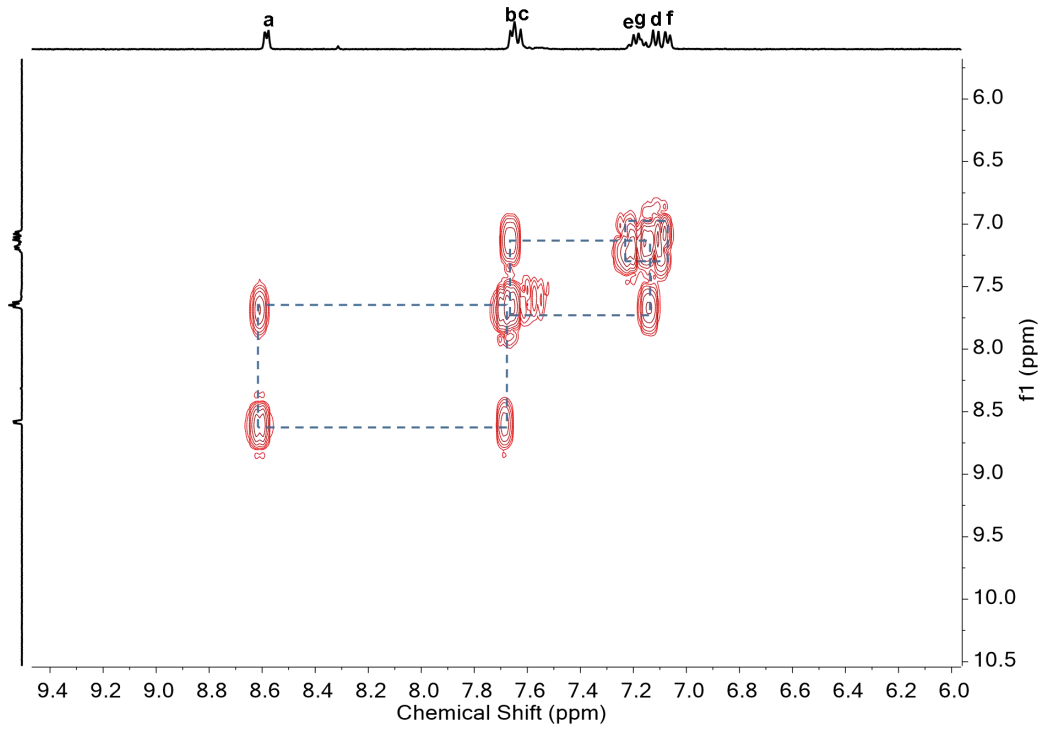
by column chromatography with dichloromethane: ethanol (100: 1, v/v) and dichloromethane: ethanol (25: 1, v/v), respectively. The product ratio of these ligands was 1:1 as yellow powder. **LA**: ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 8.58 (d, J = 5.2 Hz, 4H, Ph-H^{a}), 7.65 (t, J = 7.8 Hz, 8H, Ph-H^{b}, Ph-H^{c}), 7.23 – 7.14 (m, 6H, Ph-H^{e}, Ph-H^{g}), 7.12 (d, J = 8.1 Hz, 4H, Ph-H^{d}), 7.07 (d, J = 7.1 Hz, 4H, Ph-H^{f}). ^{13}C NMR (100 MHz, DMSO-d_6) δ(ppm): 150.23, 146.36, 146.10, 144.20, 142.81, 134.91, 131.53, 130.75, 128.13, 126.98, 126.15, 120.82. **LB**: ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 8.57 (d, J = 5.2 Hz, 4H, Ph-H^{a}), 7.66 (d, J = 3.5 Hz, 8H, Ph-H^{b}, Ph-H^{c}), 7.16 (d, J = 8.2 Hz, 10H, Ph-H^{d}, Ph-H^{e}, Ph-H^{g}), 7.02 (d, J = 7.1 Hz, 4H, Ph-H^{f}). ^{13}C NMR (100 MHz, DMSO-d_6) δ(ppm): 150.22, 146.47, 146.06, 144.12, 142.89, 135.04, 131.57, 130.72, 127.97, 126.82, 126.32, 120.85.



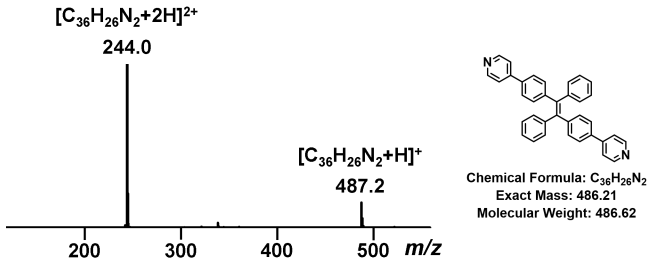
Supplementary Figure 4. ^{1}H NMR (400 MHz, DMSO-d_6, 300 K) spectrum of **LA**.



Supplementary Figure 5. ^{13}C DEPTQ NMR (100 MHz, DMSO-d_6, 300 K) spectrum of **LA**.

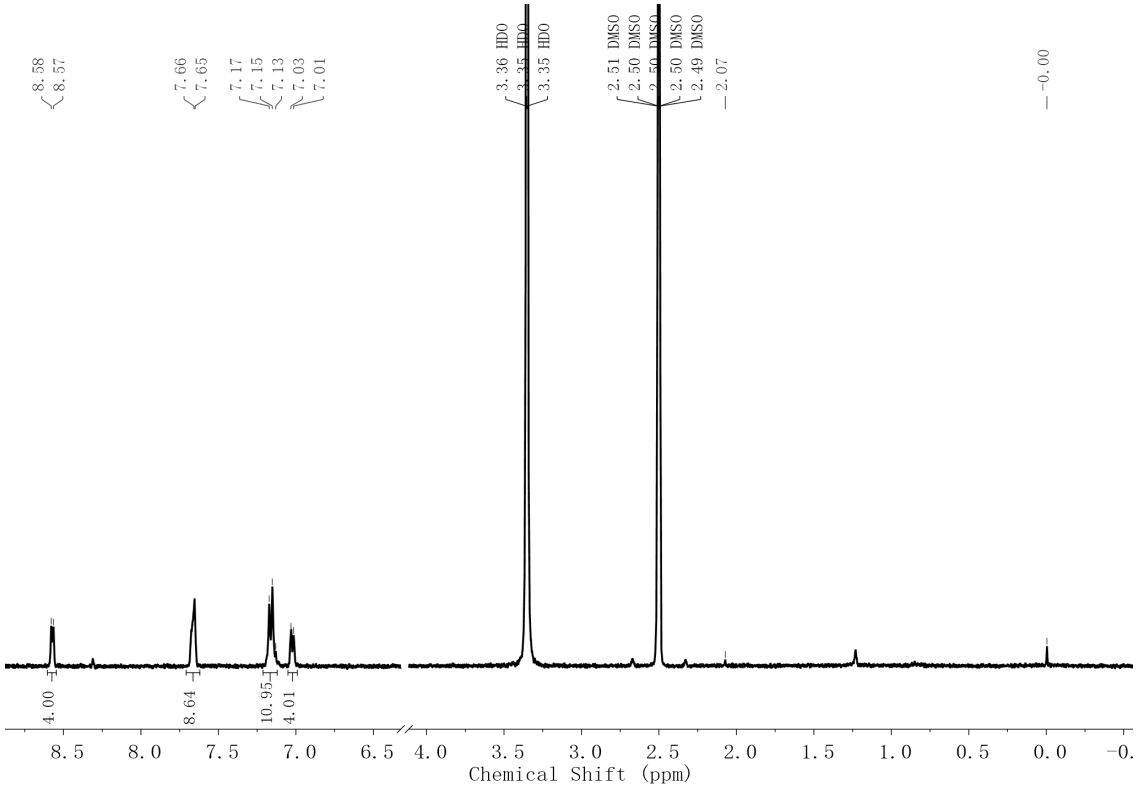


Supplementary Figure 6. 2D COSY NMR (400 MHz, DMSO-d_6, 300 K) spectrum of **LA** (aromatic region).



125

126 **Supplementary Figure 7.** HR ESI-MS spectrum of Ligand **LA**.



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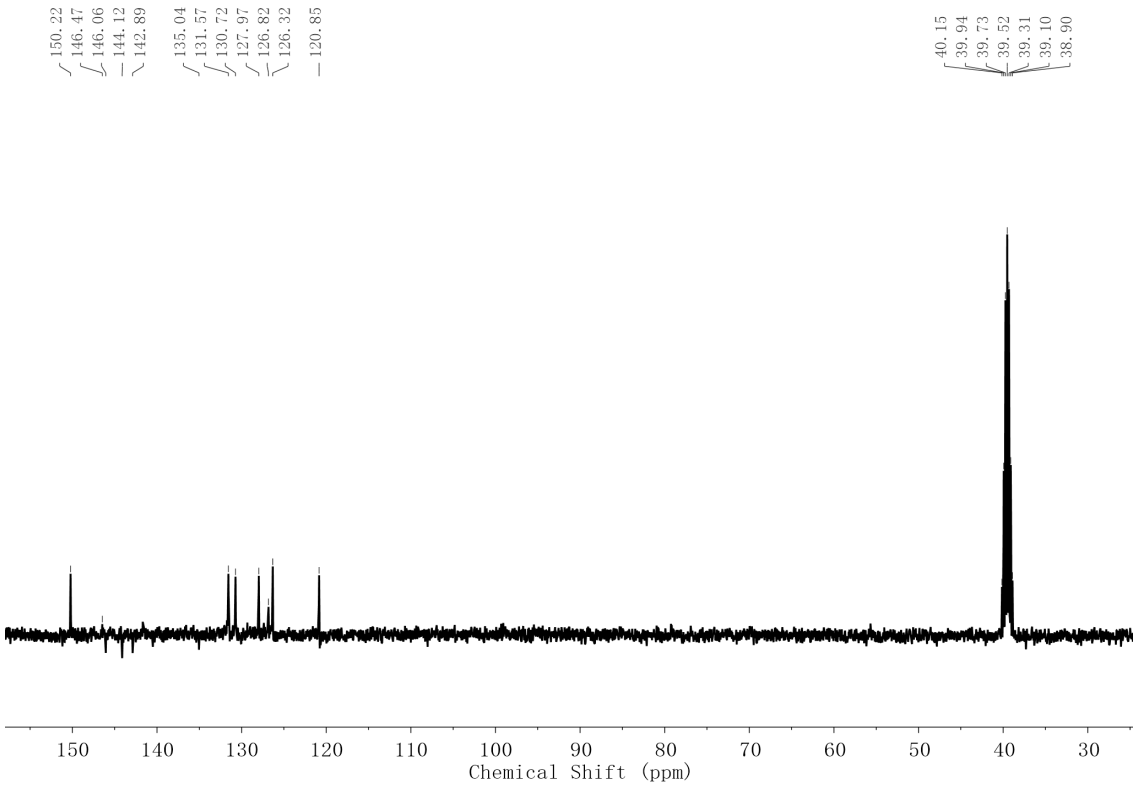
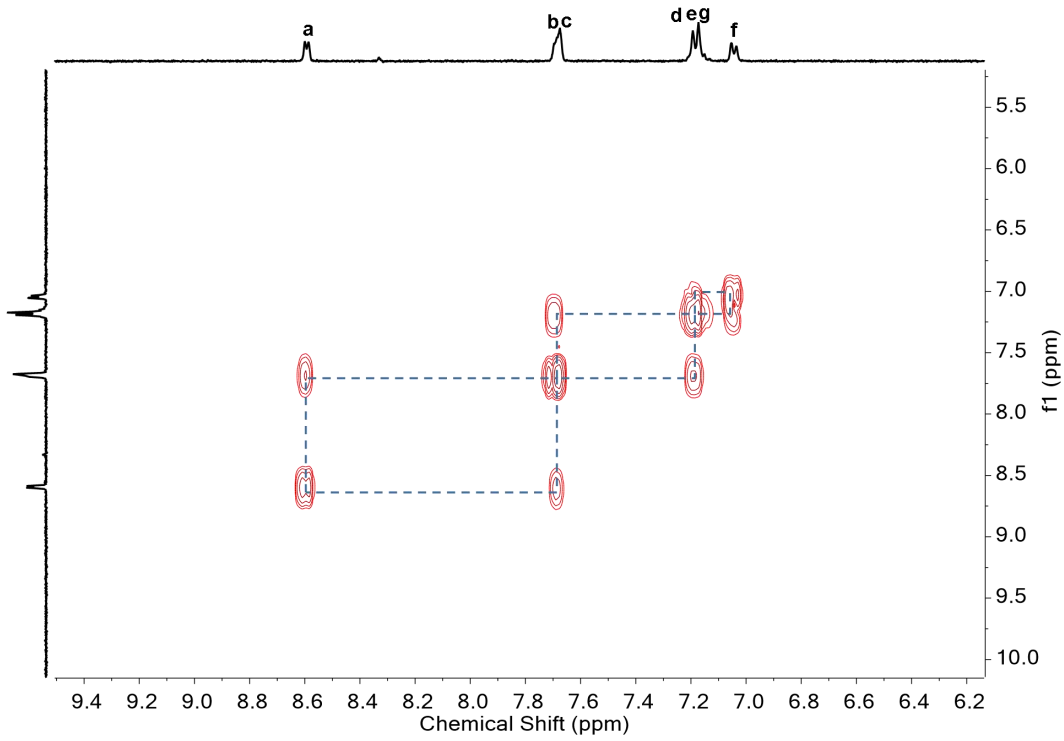
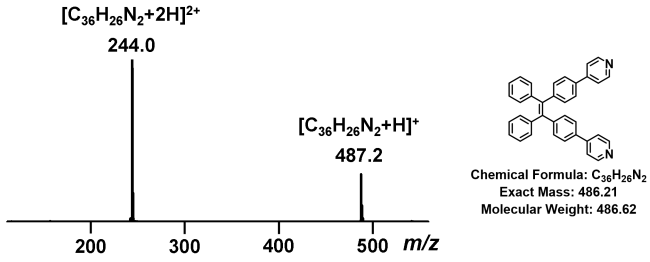
128 **Supplementary Figure 8.** ^{1}H NMR (400 MHz, DMSO-d_6, 300 K) spectrum of **LB**.



Supplementary Figure 9. ^{13}C DEPTQ NMR (100 MHz, DMSO-d_6, 300 K) spectrum of **LB**.

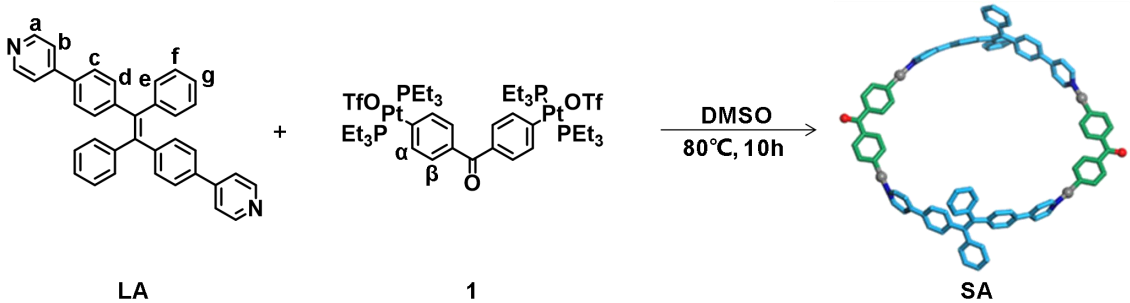


Supplementary Figure 10. 2D COSY NMR (400 MHz, DMSO-d_6, 300 K) spectrum of **LB** (aromatic region).

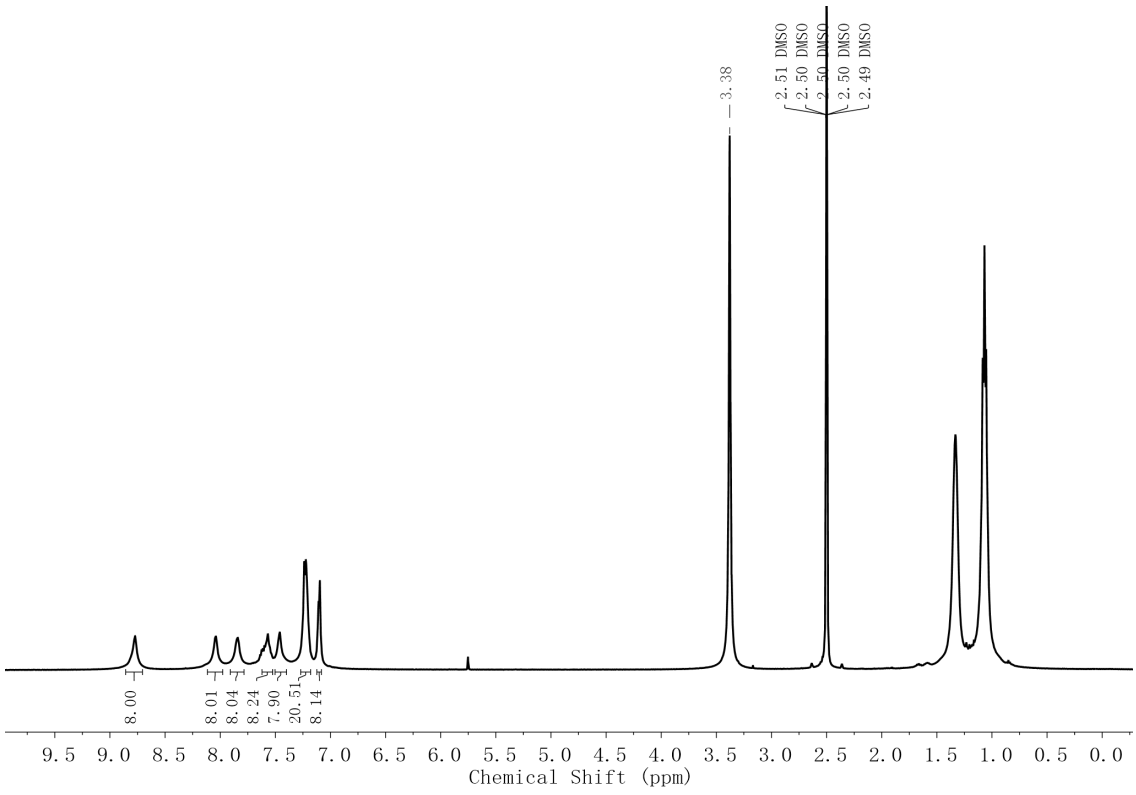


Supplementary Figure 11. HR ESI-MS spectrum of Ligand **LB**.

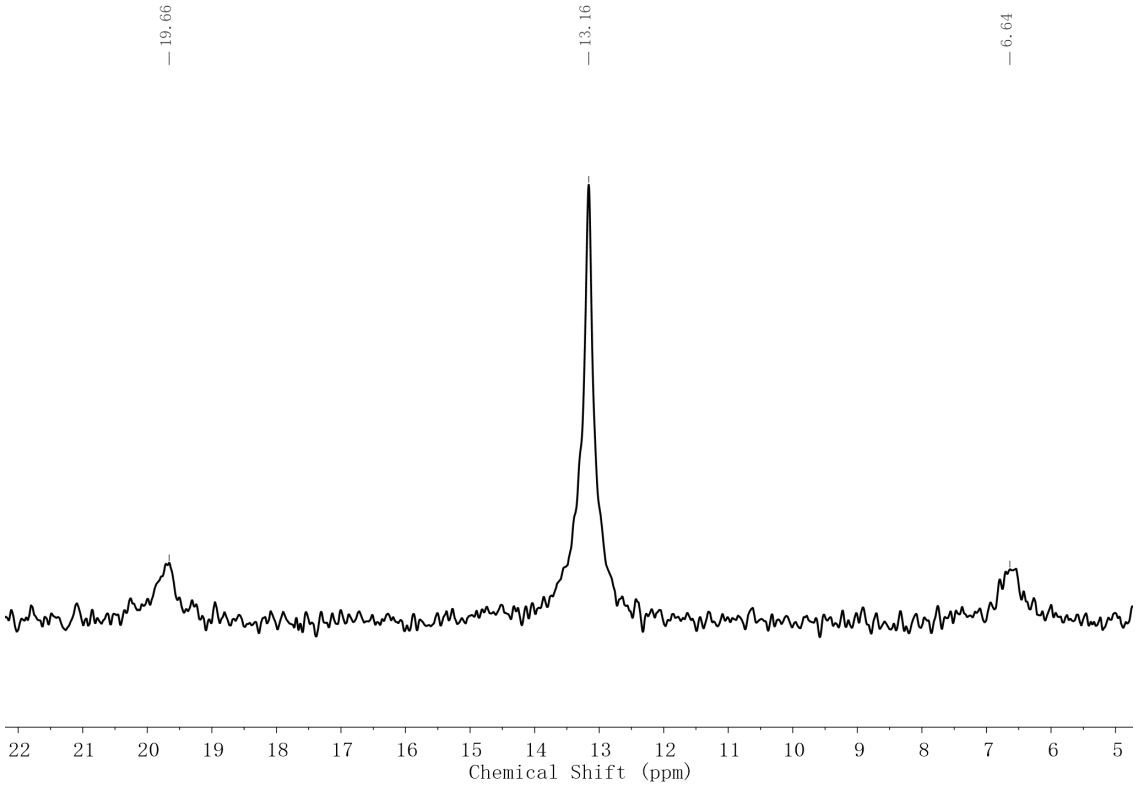
3.2 Synthesis and NMR spectra of metallacycle **SA**.



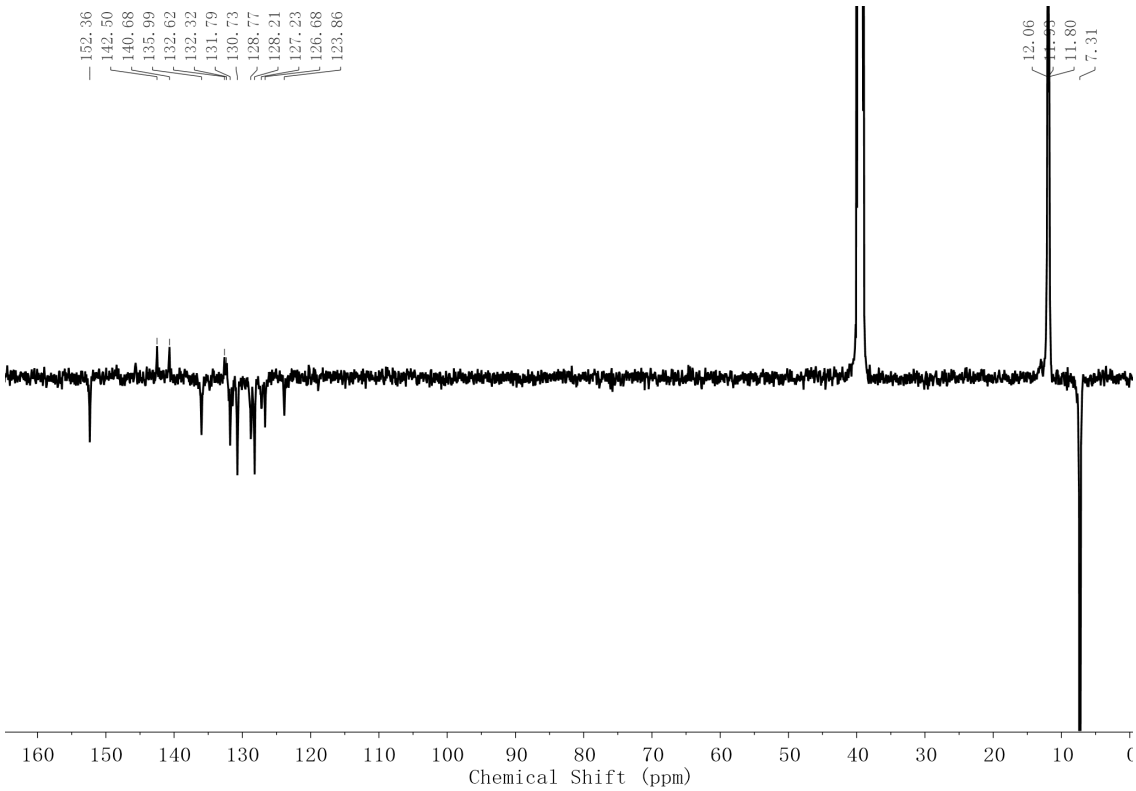
Ligand **LA** (3.0 mg, 6.2 μmol) and compound **1** (8.3 mg, 6.2 μmol) were dissolved in 0.8 mL DMSO. The mixture was heated to 80°C for 10 h. After cooling to room temperature, 5.0 mL of ethyl ether was used to precipitate the product. After filtering and washing with diethyl ether, pure **SA** was obtained as a yellow solid. (10.9 mg, 96.6%). ^{1}H NMR (500 MHz, DMSO-d_6, 300 K) δ (ppm): 8.77 (s, 8H, Ph-H^{a}), 8.14 – 7.96 (m, 8H, Ph-H^{b}), 7.94 – 7.77 (m, 8H, Ph-H^{c}), 7.66 – 7.53 (m, 8H, Ph-H^{β}), 7.50 – 7.42 (m, 8H, Ph-H^{α}), 7.23 (q, J = 7.1, 6.5 Hz, 20H, Ph-H^{d}, Ph-H^{e}, Ph-H^{g}), 7.10 (d, J = 6.9 Hz, 8H, Ph-H^{f}). ^{13}C NMR (125 MHz, DMSO-d_6) δ (ppm): 152.36, 142.50, 140.68, 135.99, 132.62, 132.32, 131.79, 130.73, 128.77, 128.21, 127.23, 126.68, 123.86, 12.06, 11.93, 11.80, 7.31. ESI-MS (*m/z*): 1068.7 [M-3OTf^{-}]$^{3+}$ (calcd *m/z*: 1068.7).



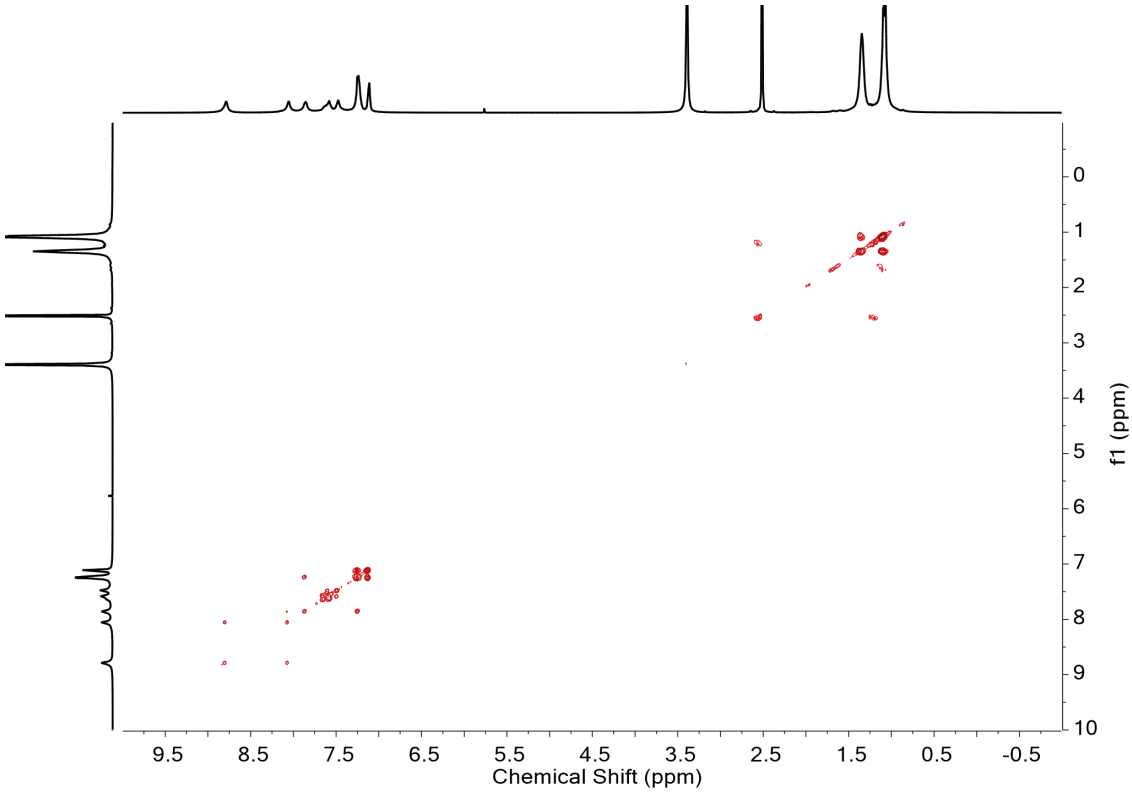
Supplementary Figure 12. ^{1}H NMR (500 MHz, DMSO-d_6, 300 K) spectrum of **SA**.



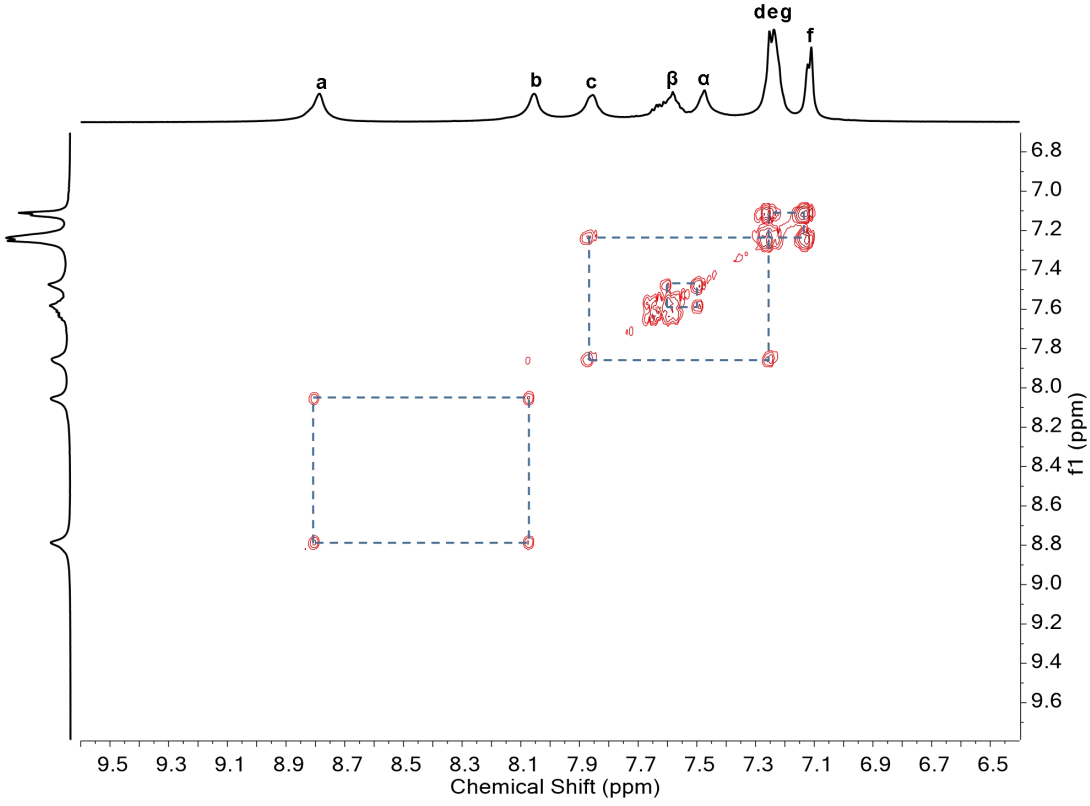
Supplementary Figure 13. ^{31}P{^{1}H} NMR (500 MHz, DMSO-d_6, 300 K) spectrum of **SA**.



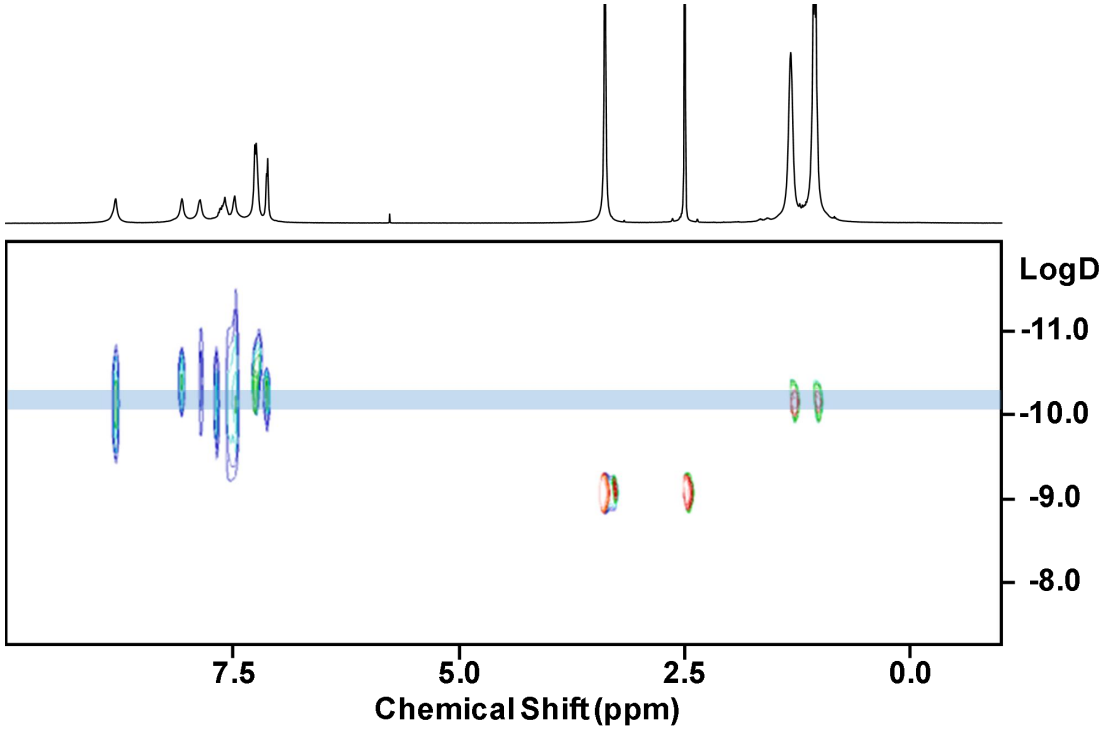
Supplementary Figure 14. ^{13}C DEPTQ NMR (125 MHz, DMSO-d_6, 300 K) spectrum of **SA**.



Supplementary Figure 15. 2D COSY NMR (500 MHz, DMSO-d_6, 300 K) spectrum of **SA**.

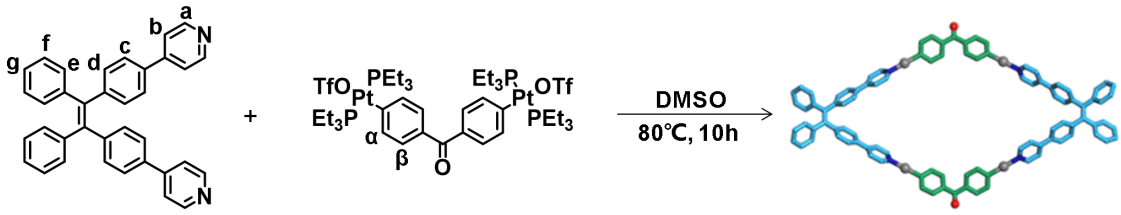


Supplementary Figure 16. 2D COSY NMR (500 MHz, DMSO-d_6, 300 K) spectrum of **SA** (aromatic region).



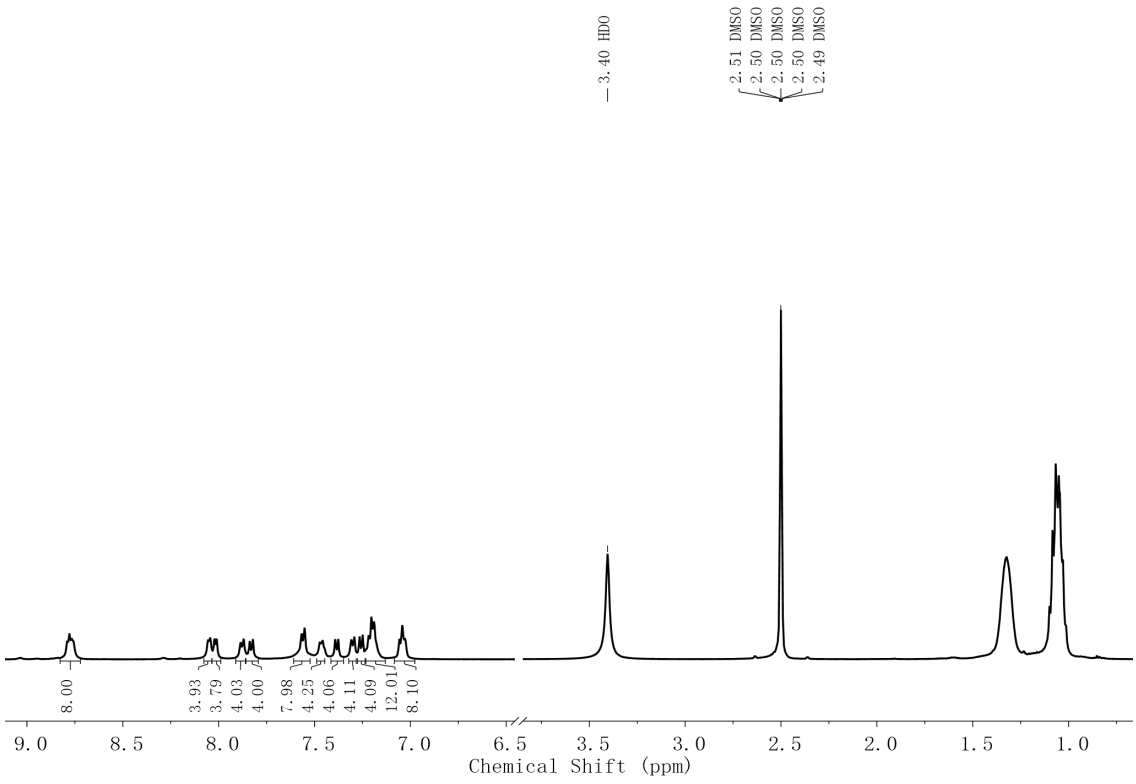
Supplementary Figure 17. 2D DOSY (500 MHz, DMSO-d_6, 300 K) spectrum of **SA**.

3.3 Synthesis and NMR spectra of metallacycle **SB**.

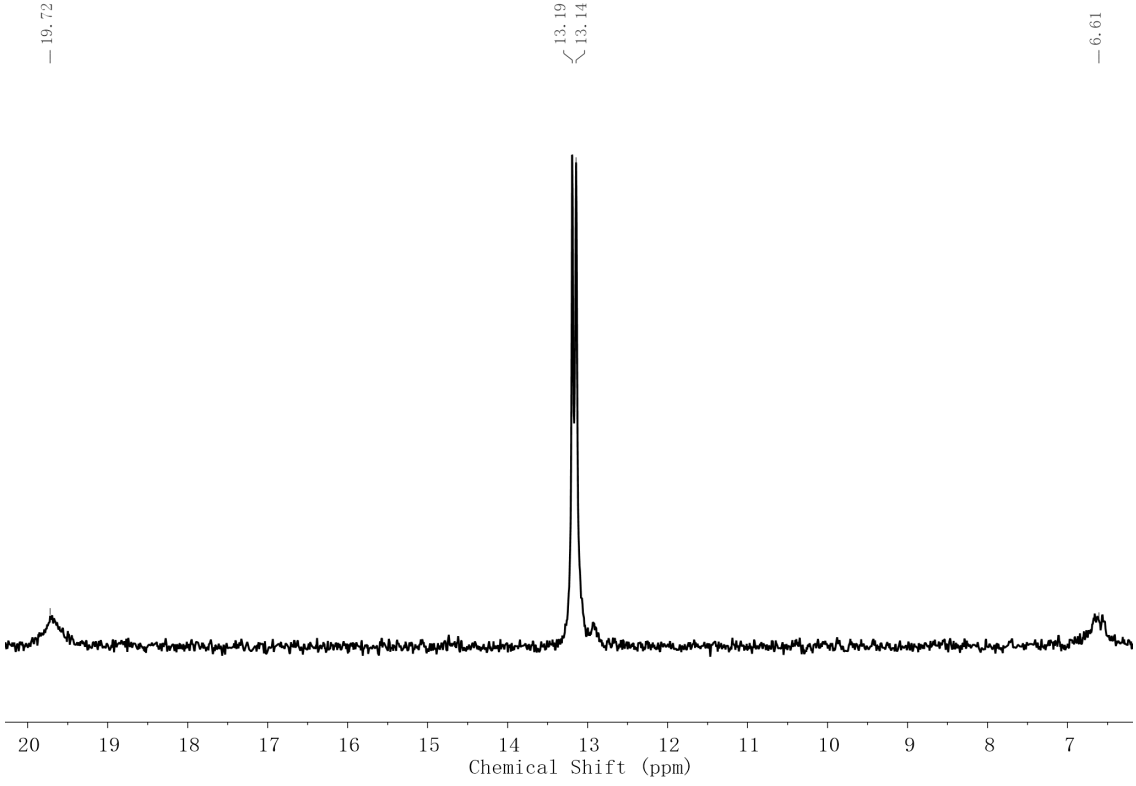


LB **1** **SB**

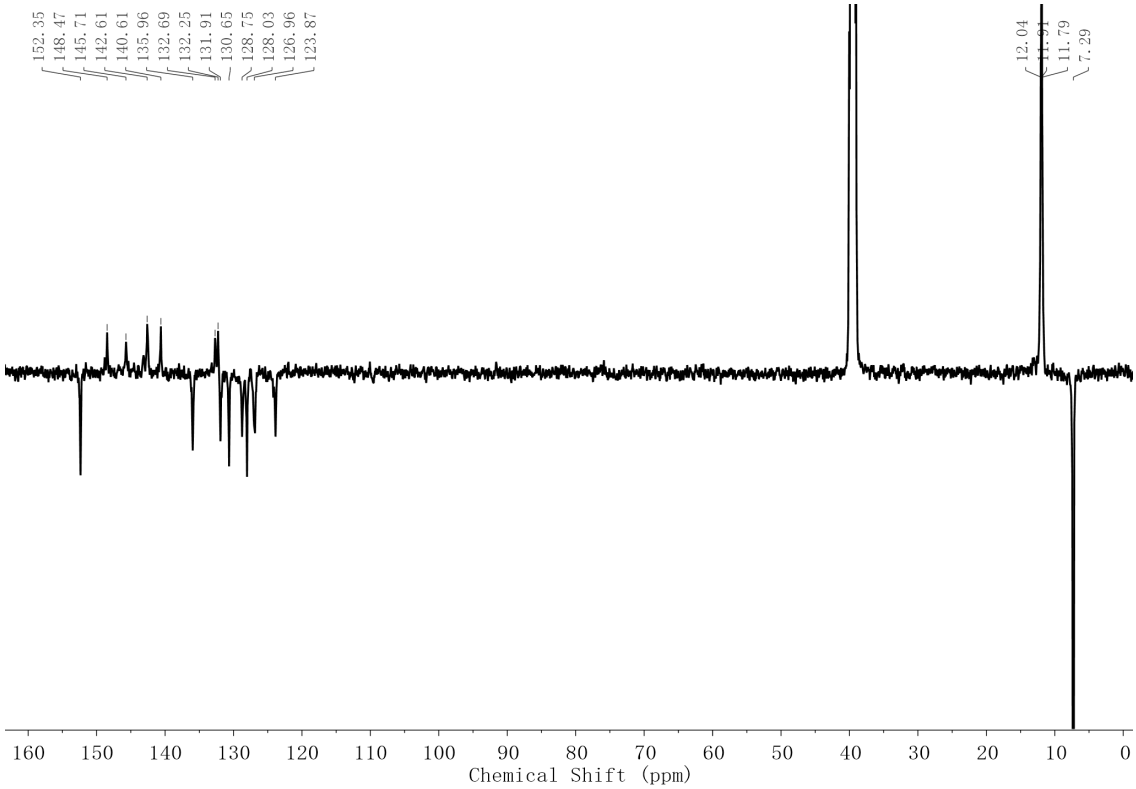
Ligand **LB** (2.6 mg, 5.3 μmol) and compound **1** (7.2 mg, 5.3 μmol) were dissolved in 0.8 mL DMSO. The mixture was heated to 80°C for 10 h. After cooling to room temperature, 5.0 mL of ethyl ether was used to precipitate the product. After filtering and washing with diethyl ether, pure **SB** was obtained as a yellow solid. (9.3 mg, 95.2%). ^{1}H NMR (500 MHz, DMSO-d_6, 300 K) δ (ppm): 8.77 (dd, J = 11.9, 5.6 Hz, 8H, Ph-H^{a}), 8.05 (d, J = 6.1 Hz, 4H, Ph-H^{b}), 8.02 (d, J = 6.2 Hz, 4H, Ph-H^{b}), 7.88 (d, J = 8.1 Hz, 4H, Ph-H^{c}), 7.83 (d, J = 8.1 Hz, 4H, Ph-H^{c}), 7.56 (d, J = 7.9 Hz, 8H, Ph-H^{β}), 7.46 (d, J = 7.6 Hz, 4H, Ph-H^{α}), 7.38 (d, J = 7.8 Hz, 4H, Ph-H^{α}), 7.30 (d, J = 8.0 Hz, 4H, Ph-H^{d}), 7.26 (d, J = 8.2 Hz, 4H, Ph-H^{d}), 7.20 (q, J = 7.3 Hz, 12H, Ph-H^{e}, Ph-H^{g}), 7.04 (t, J = 7.0 Hz, 8H, Ph-H^{f}). ^{13}C NMR (125 MHz, DMSO-d_6) δ (ppm): 152.35, 148.47, 145.71, 142.61, 140.61, 135.96, 132.69, 132.25, 131.91, 130.65, 128.75, 128.03, 126.96, 123.87, 12.04, 11.91, 11.79, 7.29. ESI-MS (*m/z*): 1677.5 $[M\text{-}2OTf^{-}]^{2+}$ (calcd *m/z*: 1677.5), 1068.7 $[M\text{-}3OTf^{-}]^{3+}$ (calcd *m/z*: 1068.7).



Supplementary Figure 18. ^{1}H NMR (500 MHz, DMSO-d_6, 300 K) spectrum of **SB**.



Supplementary Figure 19. ^{31}P{^{1}H} NMR (500 MHz, DMSO-d_6, 300 K) spectrum of **SB**.



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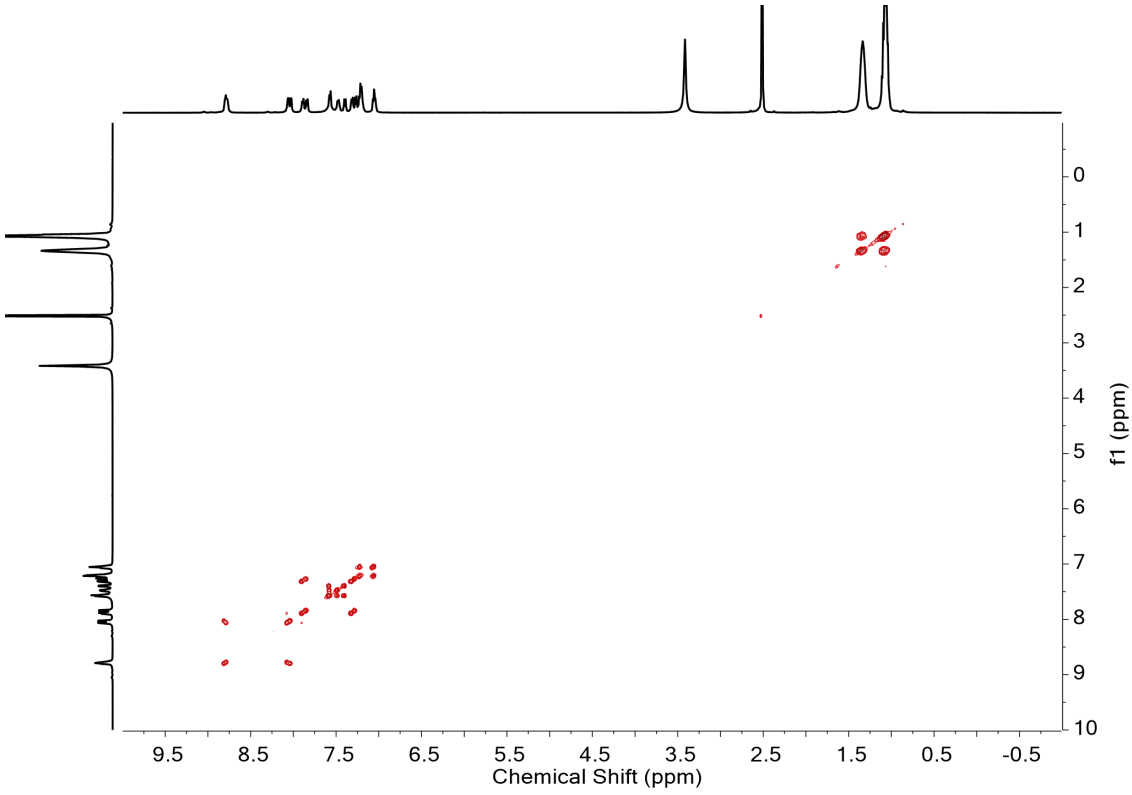
187 **Supplementary Figure 20.** ^{13}C DEPTQ NMR (125 MHz, DMSO-d_6, 300 K) spectrum

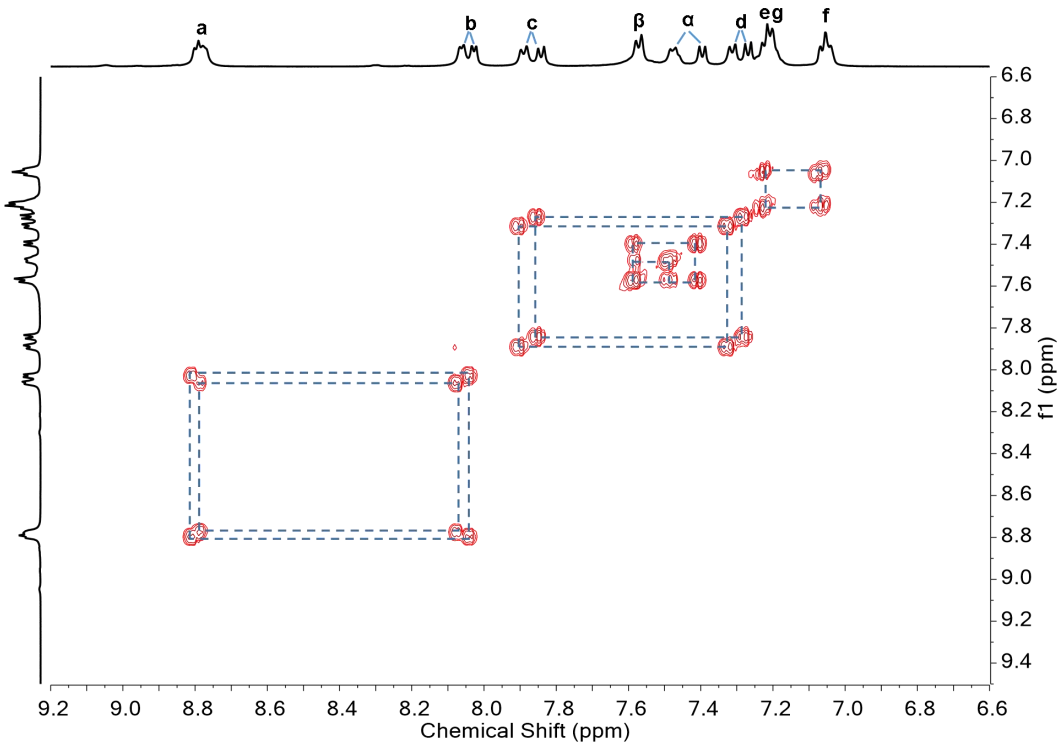
188 of **SB**.



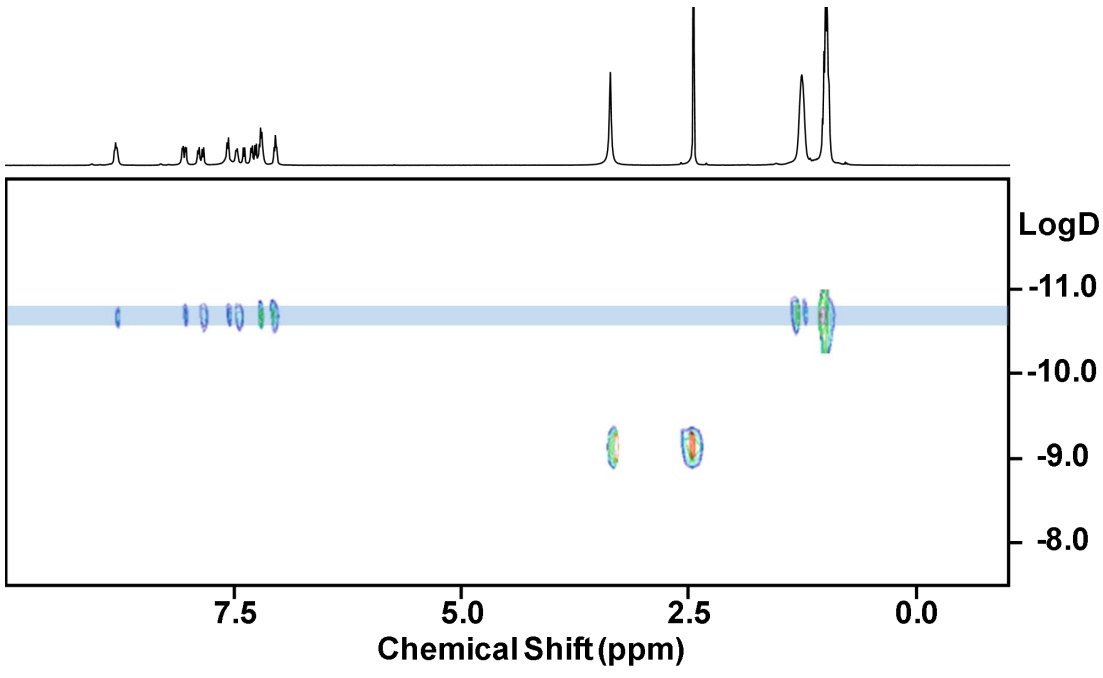
189

190 **Supplementary Figure 21.** 2D COSY NMR (500 MHz, DMSO-d_6, 300 K) spectrum

191 of **SB**.

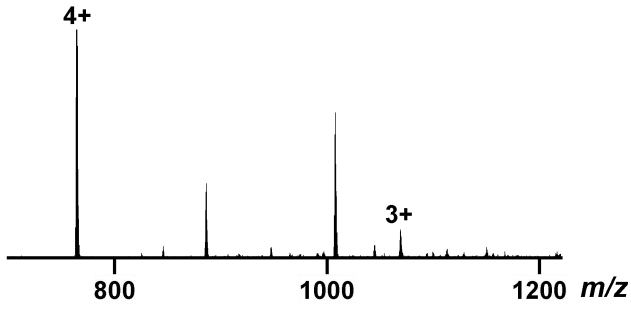


Supplementary Figure 22. 2D COSY NMR (500 MHz, DMSO-d_6, 300 K) spectrum of **SB** (aromatic region).

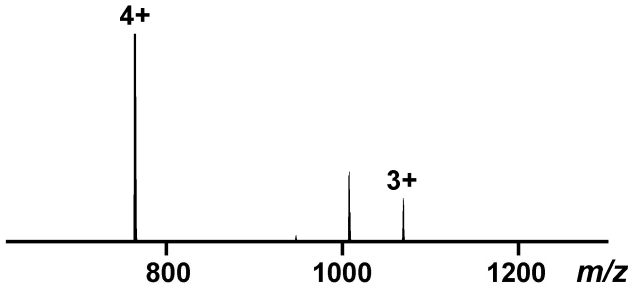


Supplementary Figure 23. 2D DOSY (500 MHz, DMSO-d_6, 300 K) spectrum of **SB**.

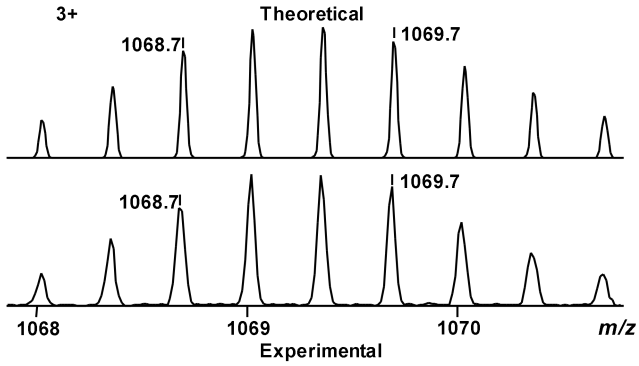
3.4 ESI-MS of metallacycles **SA** and **SB**.



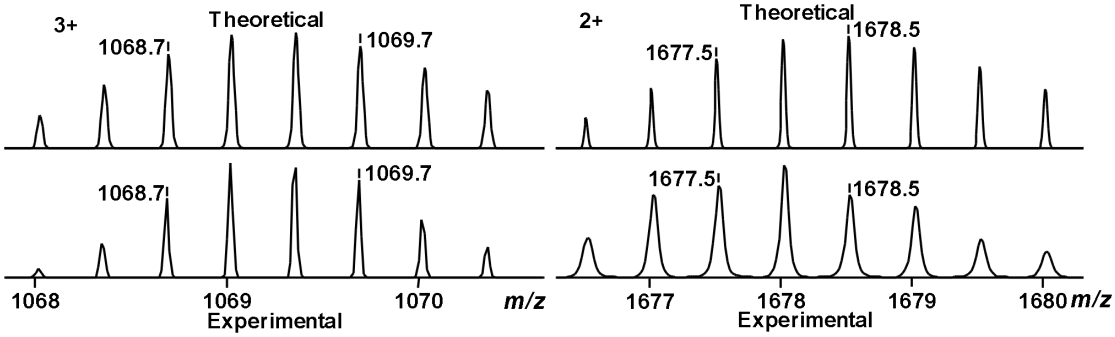
Supplementary Figure 24. The full ESI-MS spectra of **SA**.



Supplementary Figure 25. The full ESI-MS spectra of **SB**.



Supplementary Figure 26. Measured (bottom) and calculated (top) isotope patterns for the 3+ charge state observed from **SA** (OTf^- as counterion).



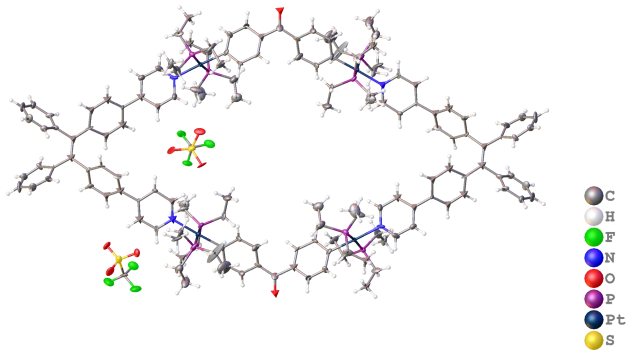
Supplementary Figure 27. Measured (bottom) and calculated (top) isotope patterns for different charge states observed from **SB** (OTf^- as counterion).

4. The formula for calculating molecular weight

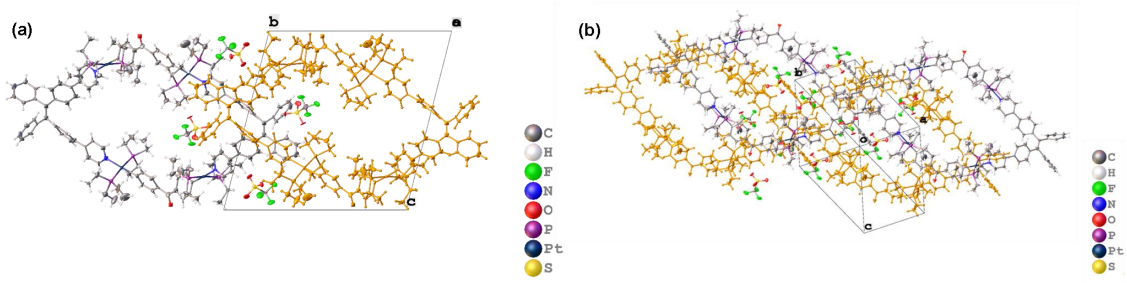
$$M = (m/z)*z + z*m'$$

(M = theoretical molecular weight, m' = the molecular weight of OTf^-, m/z = the experimental peak, z = the number of charges obtained by ESI-MS)

5. Crystal Information of SB

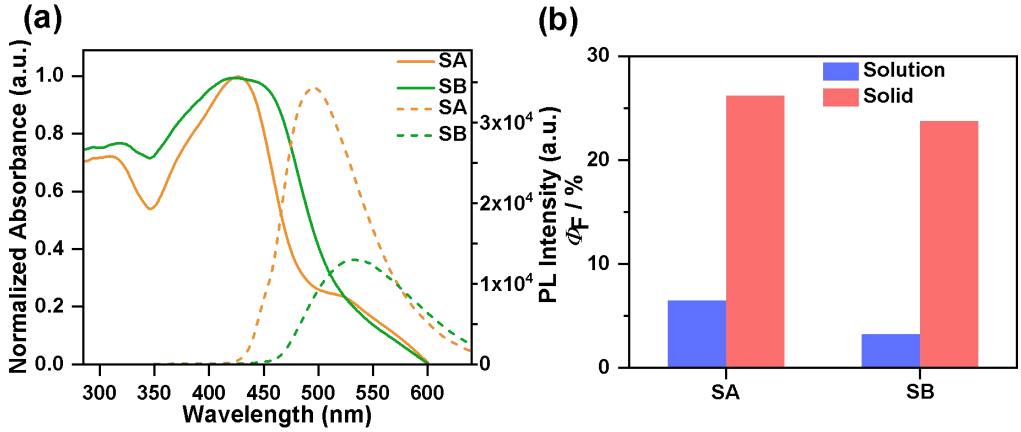


Supplementary Figure 28. The ORTEP drawing (50% probability) of structure of **SB**.



Supplementary Figure 29. The unit cell packing view from 100 (a) and 111 (b) of **SB**. Part of molecular structures were labelled orange for better visualization**.**

5. Optical characterization of SA and SB in the solid state



Supplementary Figure 30. (a) UV-Vis spectra and fluorescence emission spectra of **SA** and **SB** in the solid state (λ_{ex} = 320 nm). (b) Fluorescence quantum yields of metallacycles **SA** and **SB** in DMSO and in the solid state.

Supplementary Table 1 Crystal data and structure refinement of **SB**

Identification code	**SB**	
Empirical formula	C_{154} H_{188} F_{24} N_4 O_{26} P_8 Pt_4 S_8	
Formula weight	4251.67	
Temperature	273(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 10.2129(4) Å	a= 75.5000(10)°.
	b = 19.7946(7) Å	b= 79.3520(10)°.
	c = 20.3027(8) Å	g = 87.654(2)°.
Volume	3905.2(3) Å3	
Z	1	
Density (calculated)	1.808 Mg/m3	
Absorption coefficient	3.861 mm-1	
F(000)	2124	
Crystal size	0.120 x 0.110 x 0.100 mm3	
Theta range for data collection	1.298 to 26.433°.	
Index ranges	-12<=h<=12, -24<=k<=24, -25<=l<=25	
Reflections collected	53055	
Independent reflections	14428 [R(int) = 0.0475]	
Completeness to theta = 25.242°	90.50%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.699 and 0.654	
Refinement method	Full-matrix least-squares on F2	
Data / restraints / parameters	14428 / 0 / 895	
Goodness-of-fit on F2	3.32	
Final R indices [I>2sigma(I)]	R1 = 0.1068, wR2 = 0.3431	
R indices (all data)	R1 = 0.1216, wR2 = 0.3805	
Extinction coefficient	n/a	
Largest diff. peak and hole	9.760 and -2.698 e.Å-3	

6. Reference

1. Yang HB, Ghosh K, Northrop BH, et al. A highly efficient approach to the self-assembly of hexagonal cavity-cored tris[2]pseudorotaxanes from several components via multiple noncovalent interactions. *J Am Chem Soc* 2007;129:14187-9.[PMID:17963382 DOI:10.1021/ja073744m]