Supporting Information

A supermolecular from Crown Ether and arylpyridinium-substituted terpyridine Fe(II) complexes by two combination Supramolecular Coupling methods

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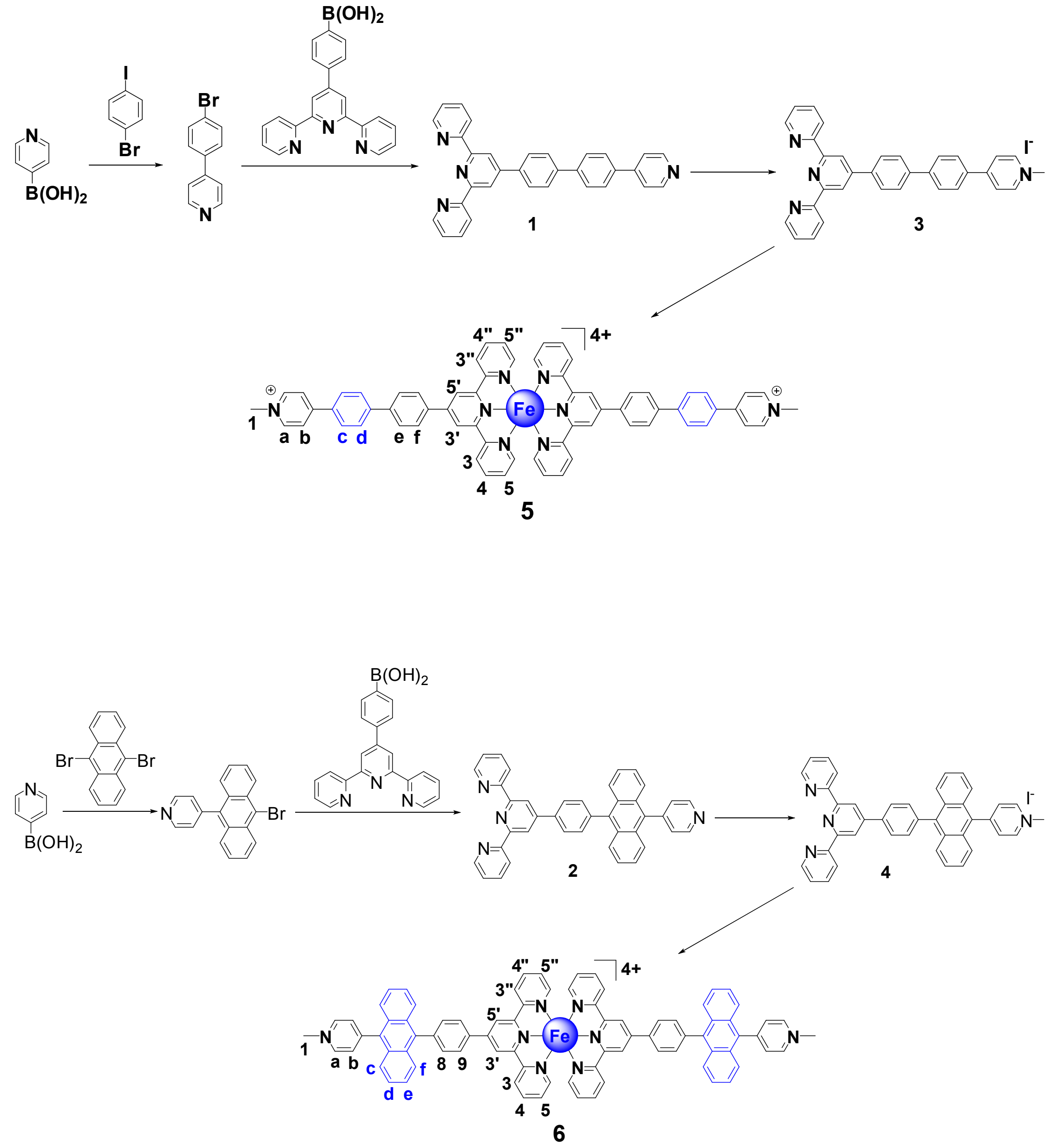
General Procedures: All the chemicals and solvents were purchased from Sigma Aldrich, MERCK or Energy-chemical, and used without further purification. 4-(4-bromophenyl)pyridine, (4-([2,2':6',2''-terpyridin]-4'-yl)phenyl) boronic acid were prepared as described in the literature.[1-2] Normal phase purifications were carried out using neutral aluminum oxide(200-300 mesh). TLC was carried out using Merck Aluminium oxide 150 F_{254}, neutral. ^{1}H-NMR spectra were recorded on Bruker Avance 400Hz and 500 Hz NMR spectrometers, and chemical shifts were reported in parts per million (ppm) relative to $Si(CH_3)_4$ as external standard. Analytical characterization was performed on a Q-TOF mass spectrometer with an ESI probe which produced by Xevo.

1. **Synthesis section**



Scheme S1. Synthetic Route.

1: Compound **1** has been prepared earlier[3] via Suzuki Coupling. In this work, the synthetic procedure had been modified as following：To a single-necked round bottom flask, 4-(4-bromophenyl)-pyridine (468mg, 2mmol), 4′–(4-boronatophenyl)-2,2′:6′2″-terpyridine (777 mg, 2.1 mmol), NaOH (aqueous, 1M) (6 mL), and THF were added. The system was degased with argon or nitrogen, after which tetrakis(triphenylphosphine) palladium(0) as catalyst was added. The biphasic system was refluxed for 12 h resulting in a green solution. The solvent was removed under vacuum, and extracted with $CHCl_3$ (3 times), to give a residue, which was column chromatographed (Al_2O_3) eluting with CH_2Cl_2 to give pure ligand, as white solid (740 mg, 80 %).

3: Iodomethane (0.125mL, 2mmol) was added to a solution of compound **1** (115mg, 0.25mmol) in 20mL CH_3CN. Then the reaction mixture was heated to reflux overnight. Then the solvent was removed by rotary evaporation, and purified by a short neutral alumina column with eluent of methylene chloride:methanol=20:1 to afford 120 mg yellow solid. ^{1}H-NMR (400MHz, d-DMSO): δ=9.05-9.03 (d, 2H, H^{a}, J= 8), 8.80-8.79 (m, 4H, tpy$H^{3,3''}$, tpy$H^{3',5'}$), 8.71-8.69 (d, 2H, tpy$H^{6,6''}$, J= 8), 8.61-8.59 (d, 2H, H^{b}, J= 8), 8.26-8.03 (m, 10H, Ar$H^{c,d,e,f}$, tpy$H^{5,5''}$), 7.58-7.54 (t, 2H, tpy$H^{4,4''}$, J= 16), 4.35(s, 3H, H^{1}). MS (ESI-MS)= Exact mass calcd for $[M-I]^+$: 477.2, found 477.1.

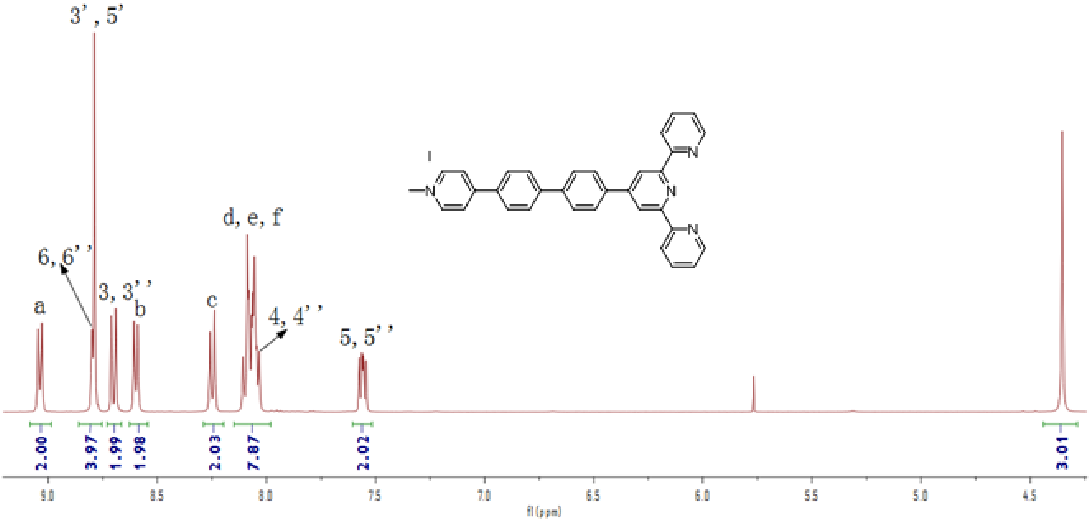


Fig S1-a. ^{1}H-NMR of Compound **3**.

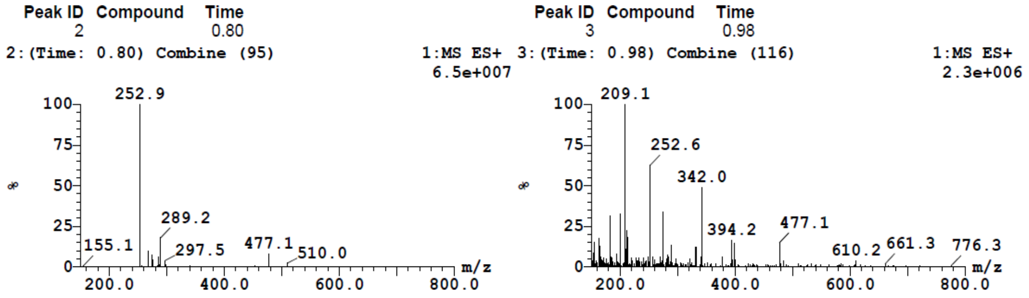


Fig S1-b. ESI-MS of Compound **3**.

5: Compound **3** (30mg, 0.05mmol) and ferrous chloride (5mg, 0.025mmol) was added to methanol (1mL), and stirred at room temperature for 2h. The reaction mixture was filtered, and washed with methanol. Solvent in the filtrate was removed by rotary evaporation. It was dried in vacuum to afford a dark purple solid. ^{1}H NMR (MeOD): δ=9.47 (s, 4H, tpy$H^{3',5'}$)， 8.86-8.84(d, 4H, H^a), 8.83-8.81 (d, 4H, tpy$H^{3,3''}$), 8.53-8.52 (d, 4H, ArH^f), 8.43-8.41 (d, 4H, ArH^b), 8.16-8.05 (m, 12H, Ar$H^{c,d,e}$), 7.93-7.90 (t, 4H, tpy$H^{4,4''}$), 7.27-7.26 (d, 4H, tpy$H^{6,6''}$), 7.14-7.11 (t, 4H, tpy$H^{5,5''}$), 4.35(s, 6H, H^1). ESI-MS= Exact mass calcd for [M-(2I$^-$+2Cl$^-$)]$^{4+}$: 252.75, found 252.9.

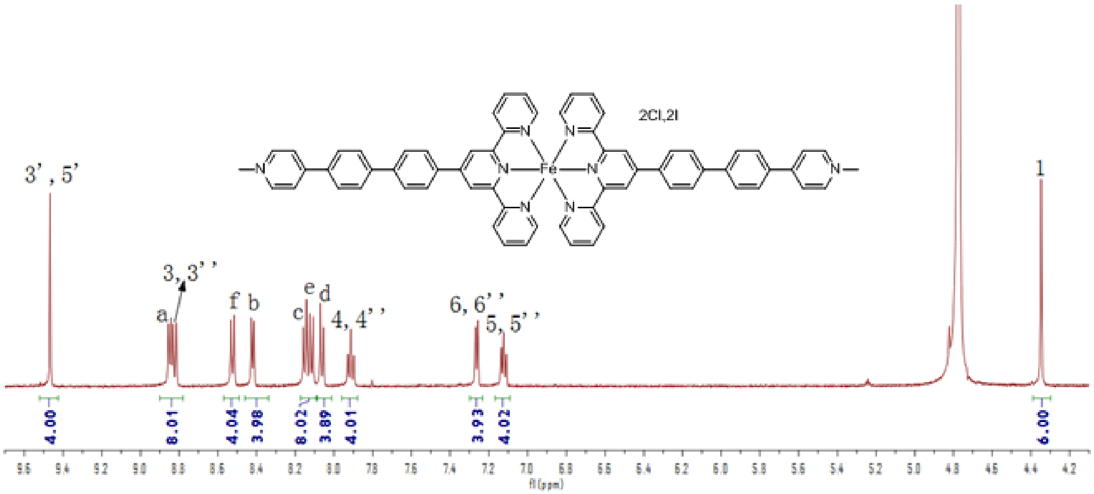


Fig S2-a. ^{1}H-NMR of Compound **5**.

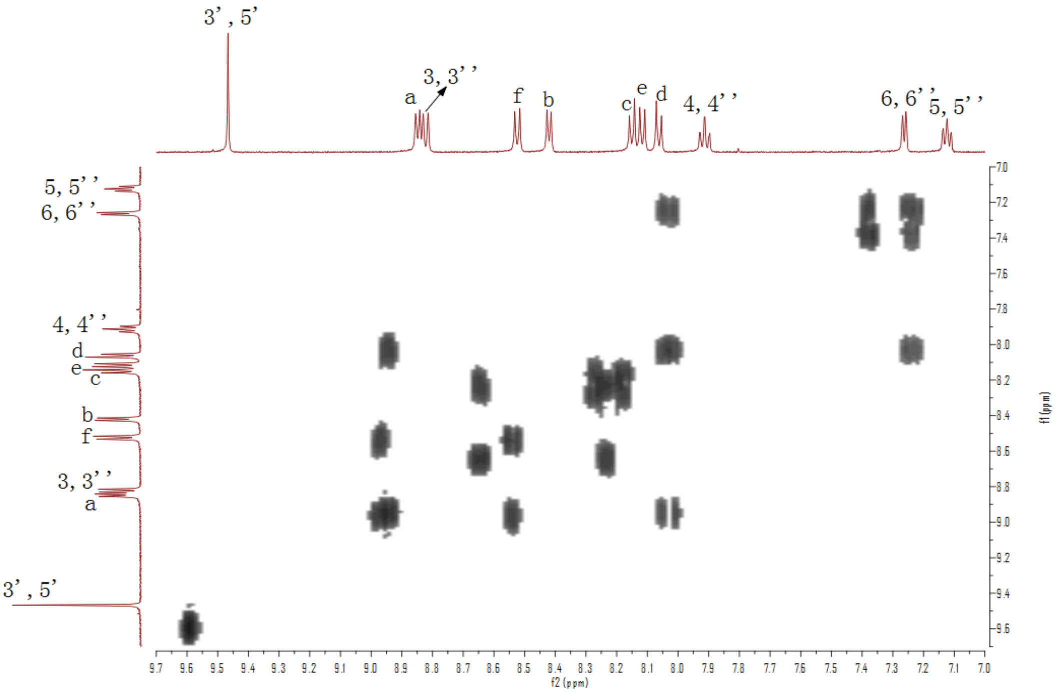


Fig S2-b. 2D-COSY-NMR of Compound **5**.

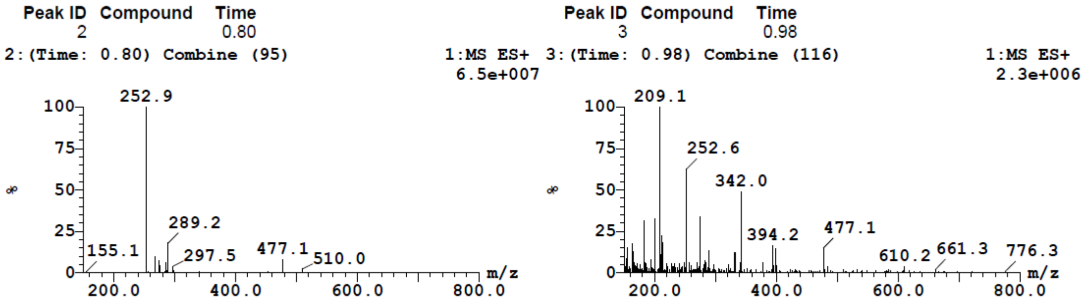


Fig S2-c. ESI-MS of Compound **5**.

4-(10-bromoanthracen-9-yl)pyridine: To a solution of 9,10-dibromoanthracene (672mg, 2mmol) in 30 mL toluene was added pyridinyl-4-ylboronic acid (246mg, 2mmol), followed by the addition of a solution of K_2CO_3 (560mg, 4mmol) in 4 mL of water. The mixture was degassed for 10 min, and tetrakis(triphenylphosphine) palladium(0) as the catalyst was added. The resulting mixture was stirred at 90℃ under nitrogen for 1d. The solvent was removed using rotary evaporation; the residue was dissolved in CH_2Cl_2 and washed with brine and water. The organic layer was dried over anhydrous sodium sulfate. Filtered, concerntrated and purified by silica gel column chromatograph to afford compound as a yellow solid (107mg, 32%). ^{1}H-NMR (400MHz, $CDCl_3$): δ= 8.89-8.87 (d, 2H, H1, J= 8), 8.67-8.65 (d, 2H, H6, J= 8), 7.66-7.62 (t, 2H, H5, J= 16), 7.58-7.55 (d, 2H, H2, J= 12), 7.46-7.42 (m, 2H, H4), 7.41-7.40 (d, 2H, H3, J=4). ESI-MS (m/z)= 335.21 $[M+H]^+$ (Calcd. m/z= 337.0388).

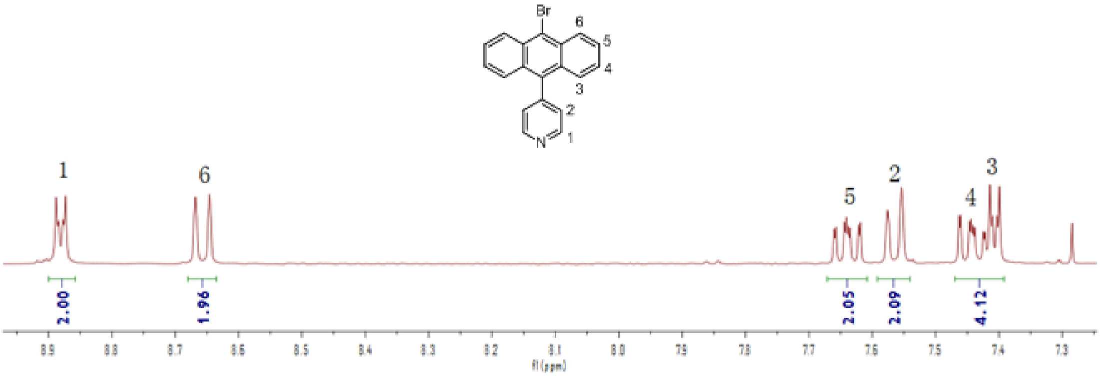


Fig S3-a. ^{1}H-NMR of 4-(10-bromoanthracen-9-yl)pyridine.

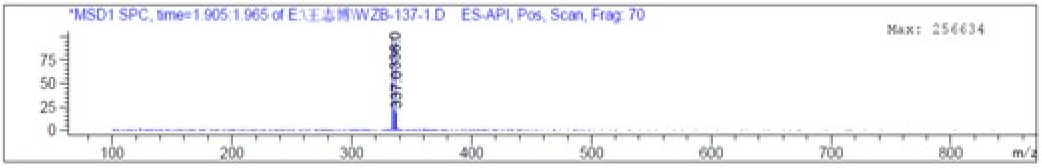


Fig S3-b. LC-MS of 4-(10-bromoanthracen-9-yl)pyridine.

2： The synthesis of compound **2** is the same as compound **1**. ^{1}H-NMR (400MHz, CDCl$_3$): δ=8.94 (s, 2H, tpy$H^{3',5'}$), 8.91-8.90 (d, 2H, tpy$H^{3,3''}$, J= 4), 8.80-8.78 (d, 2H, H^a, J= 8), 8.77-8.75 (d, 2H, tpy$H^{5,5''}$, J= 8), 8.20-8.18 (d, 2H, H^b, J= 8), 7.97-7.93 (t, 2H, tpy$H^{4,4''}$, J= 16), 7.83-7.79 (m, 2H, ArH^h), 7.65-7.62 (m, 4H, Ar$H^{d,g}$), 7.52-7.49 (d, 2H, ArH^c, J= 12), 7.45-7.40(m, 6H, Ar$H^{e,f}$, tpy$H^{5',5''}$). MS(LC-MS)= Exact mass calcd for $C_{40}H_{26}N_4$:562.66, found:558.2.

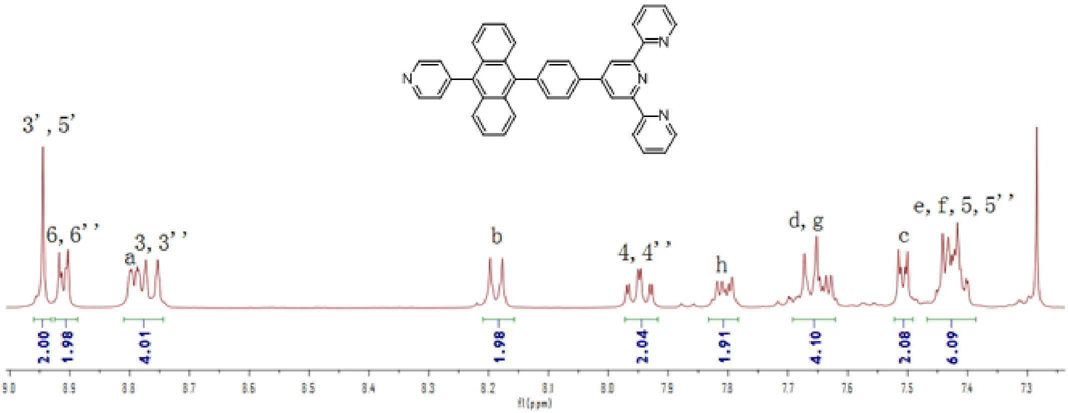


Fig S4-a. ^{1}H-NMR of compound **2**.

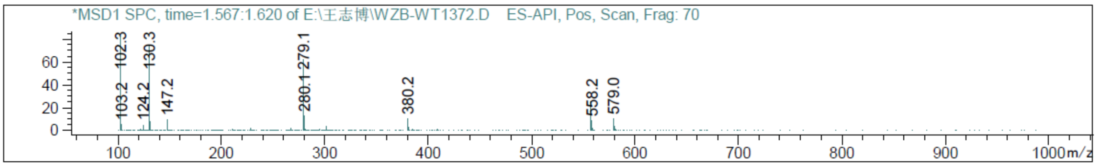


Fig S4-b LC-MS spectrum of compound **2**.

4: The synthesis of compound **4** is the same as compound **3**. ^{1}H-NMR (400MHz, d-DMSO): δ= 9.30-9.28 (d, 2H, tpy$H^{3,3''}$, J= 8), 8.93 (s, 2H, tpy$H^{3',5'}$), 8.82-8.81 (d, 2H, H^a, J= 4), 8.76-8.74(d, 2H, tpy$H^{6,6''}$, J= 8), 8.40-8.38(d, 2H, ArH^h, J= 8), 8.29-8.27 (d, 2H, H^b, J= 8), 8.12-8.08(t, 2H, tpy$H^{4,4''}$, J= 16), 7.79-7.76 (m, 2H, ArH^d), 7.72-7.70 (d, 2H, ArH^g, J= 8), 7.59-7.56 (m, 8H, Ar$H^{c,e,f}$, tpy$H^{5,5''}$), 4.54 (s, 3H, H^1). ESI-MS= Exact mass calcd for [M-I]$^+$: 577.2, found 577.2.

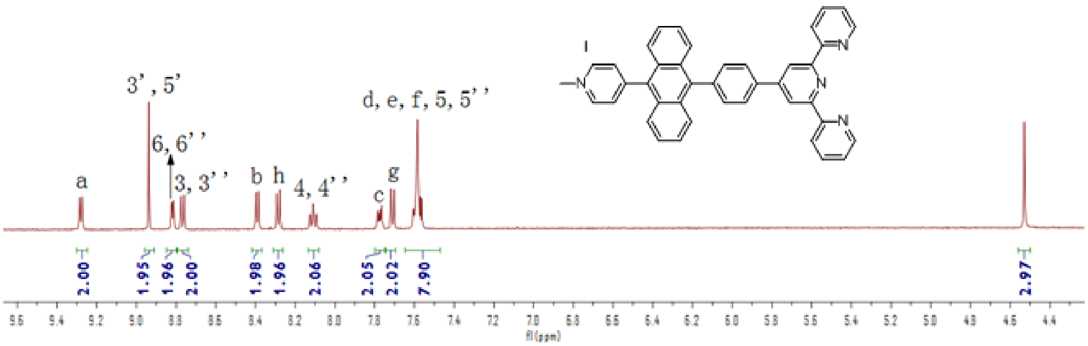


Fig S5-a. ^{1}H-NMR of Compound 4.

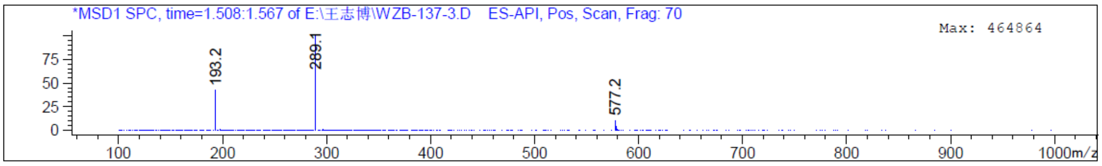


Fig S5-b. ESI-MS of Compound **4**.

6: The synthesis of compound **6** is the same as compound **5**. ^{1}H-NMR (MeOD): δ=9.71 (s, 4H, H tpy$H^{3',5'}$), 9.24-9.22 (d, 4H, H^a), 9.0-8.99 (d, 4H, tpy$H^{3,3''}$), 8.80-8.79 (d, 4H, ArH^h), 8.34-8.33 (d, 4H, ArH^b), 8.07 (t, 4H, tpy$H^{4,4''}$), 7.93-7.92 (d, 8H, Ar$H^{d,g}$), 7.72-7.70(d, 4H, ArH^c), 7.63-7.56 (n, 8H, Ar$H^{e,f}$), 7.46 (s, 4H, tpy$H^{6,6''}$), 7.29 (s, 4H, tpy$H^{5',5''}$), 4.67 (s, 6H, H^1). MS(ESI-MS)= Exact mass calcd for [M-(2I$^-$+2Cl$^-$)]$^{4+}$: 302.81, found 303.2.

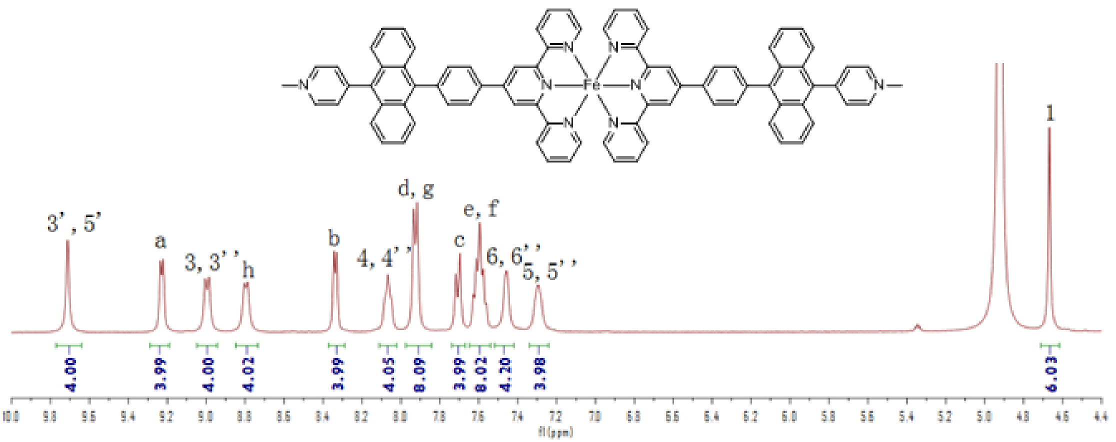


Fig S6-a. ^{1}H-NMR of Compound **6**.

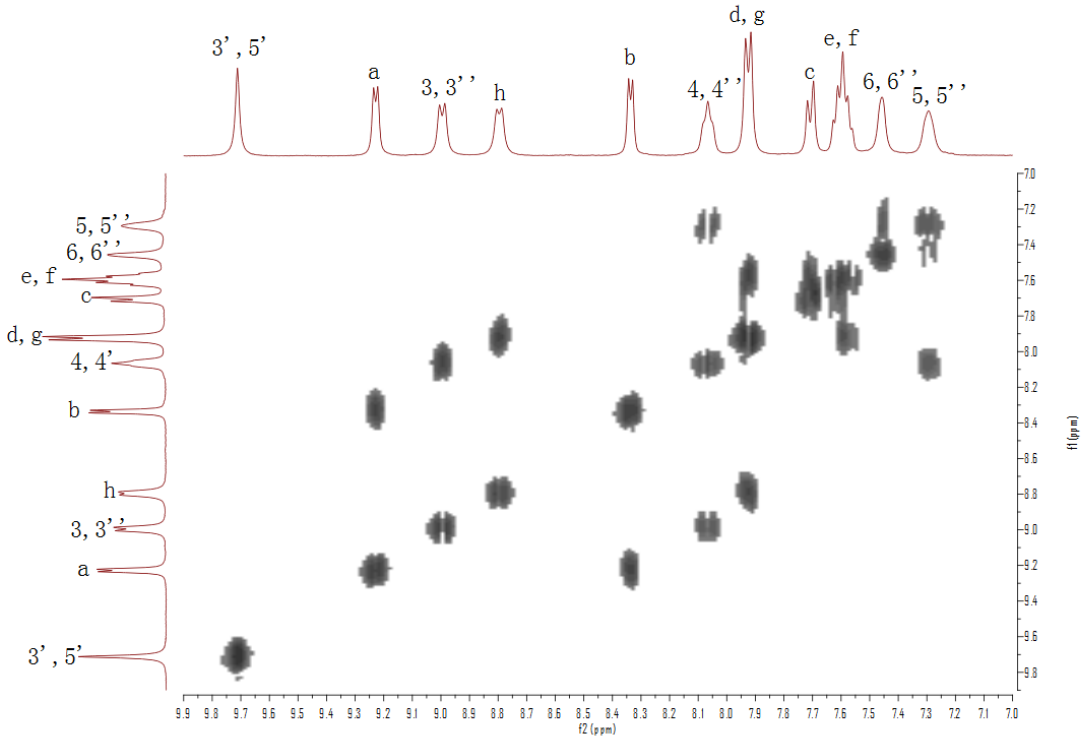
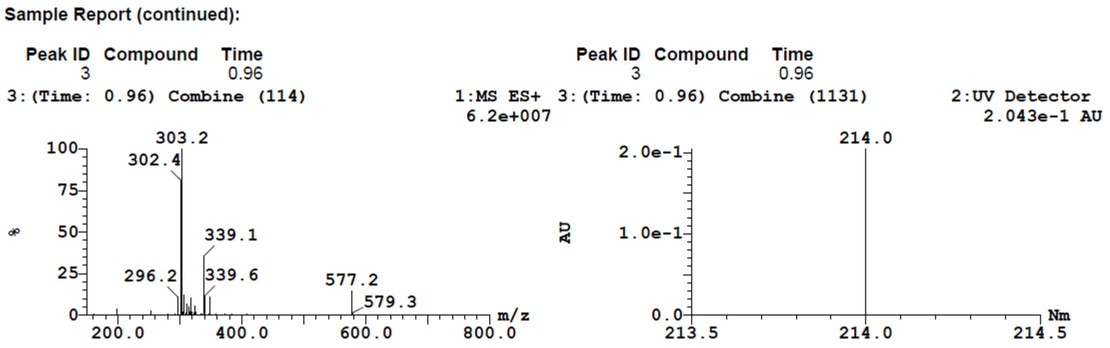


Fig S6-b. 2D COSY-NMR of Compound **6**.



Sample Report (continued):

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3: (Time: 0.96) Combine (114)

Peak ID Compound Time
3 0.96
1:MS ES+ 3: (Time: 0.96) Combine (1131)
6.2e+007

2:UV Detector
2.043e-1 AU

Fig S6-c. ESI-MS of Compound **6**.

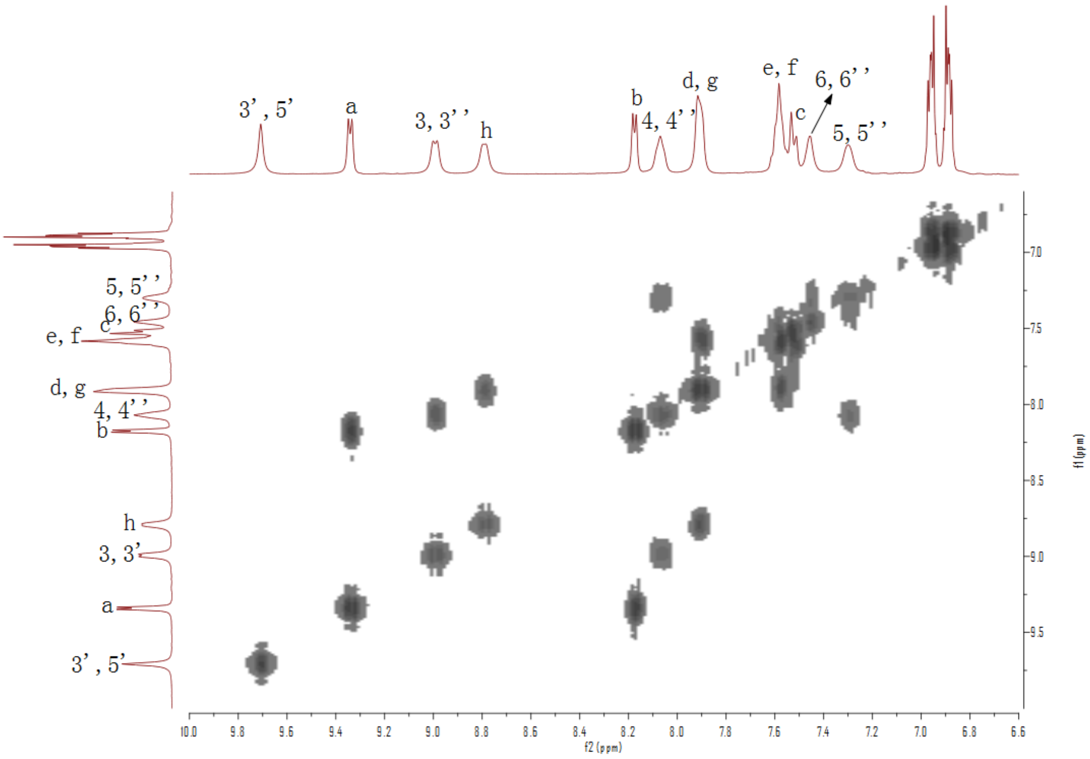

Fig S7. 2D COSY-NMR of the Rotaxane **9**.

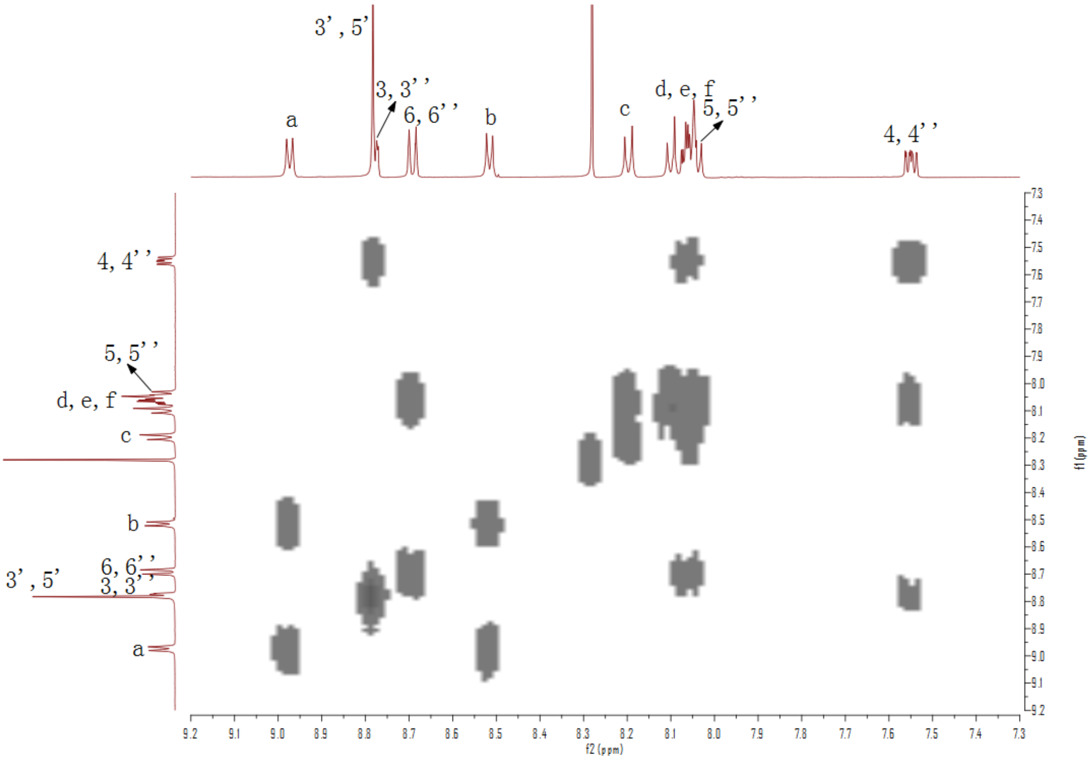

Fig S8. 2D COSY -NMR of the Rotaxane **10**.

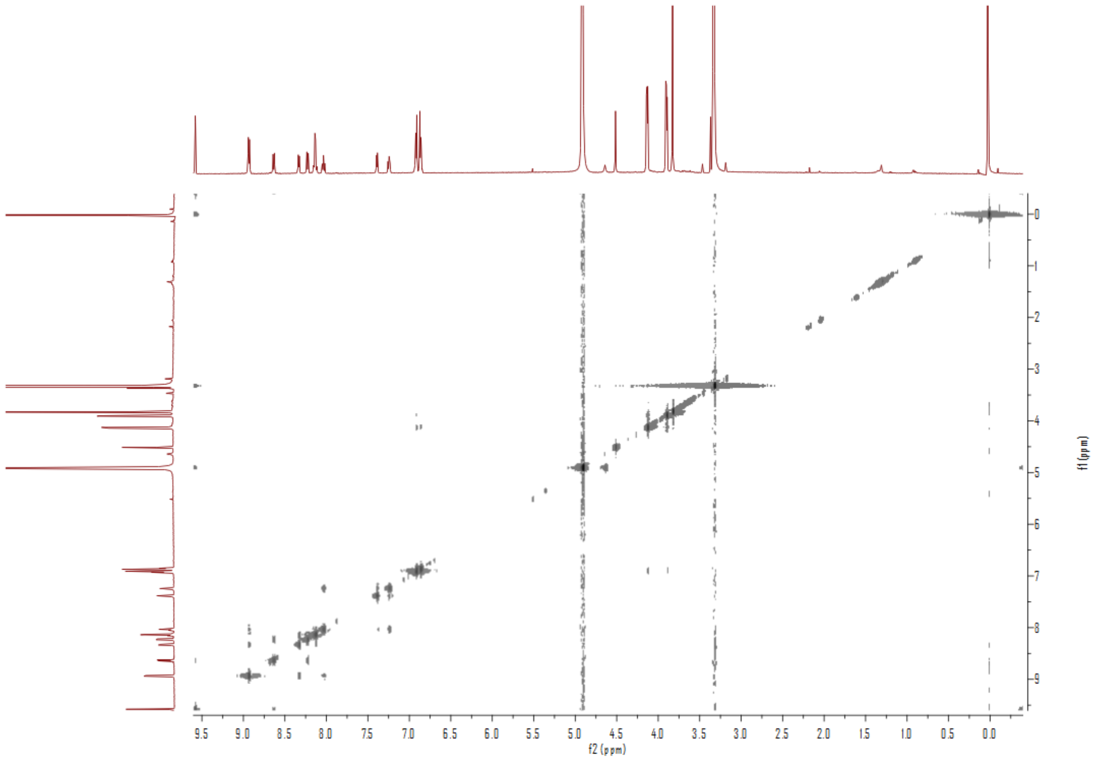

Fig S9. 2D NOESY-NMR of **8**.

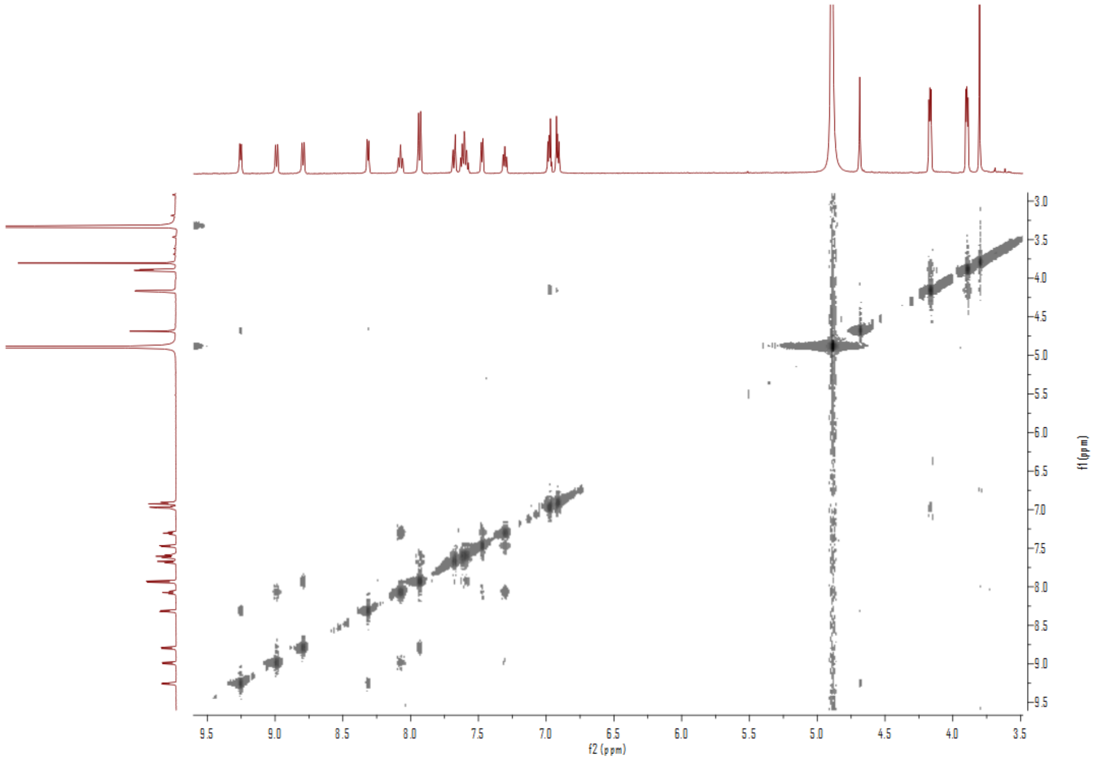

Fig S10. 2D NOESY -NMR of **9**.

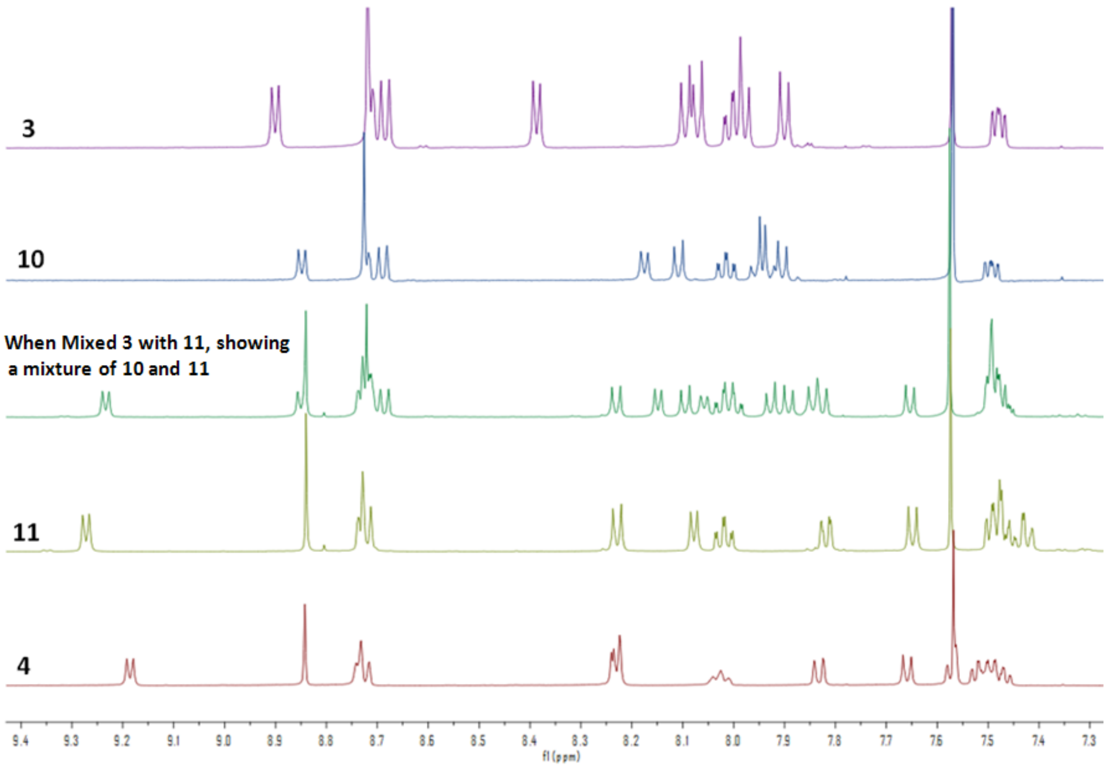

Fig ***S11.*** Conceptual diagram of exchange experiment: ^{1}H-NMR of **3** (purple), ^{1}H-NMR of **10** (**3**+DB24C8, blue), ^{1}H-NMR of adding **3** to a solution of **11** (**4**+DB24C8, cyan), ^{1}H-NMR of **11**(green) and ^{1}H-NMR of **4** (red). In CD_3OD: $CDCl_3$ =1 : 1 at 25 ºC.

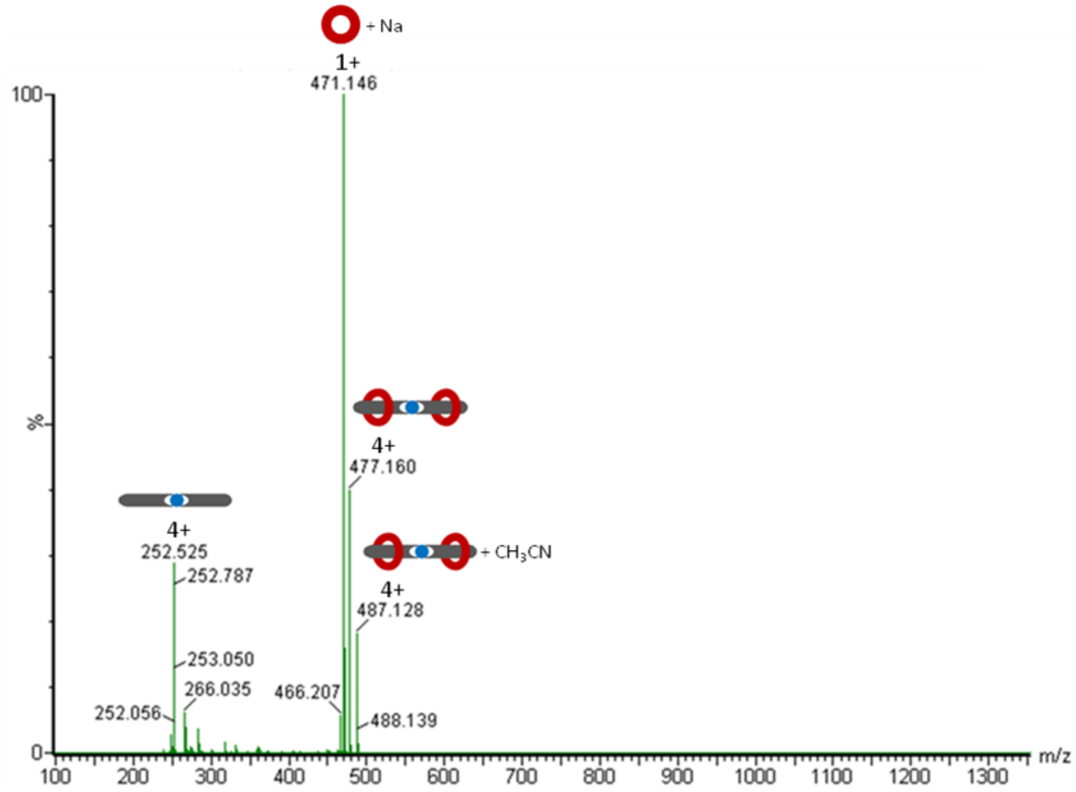

Fig S12. Q-TOF-MS spectra of **8**.

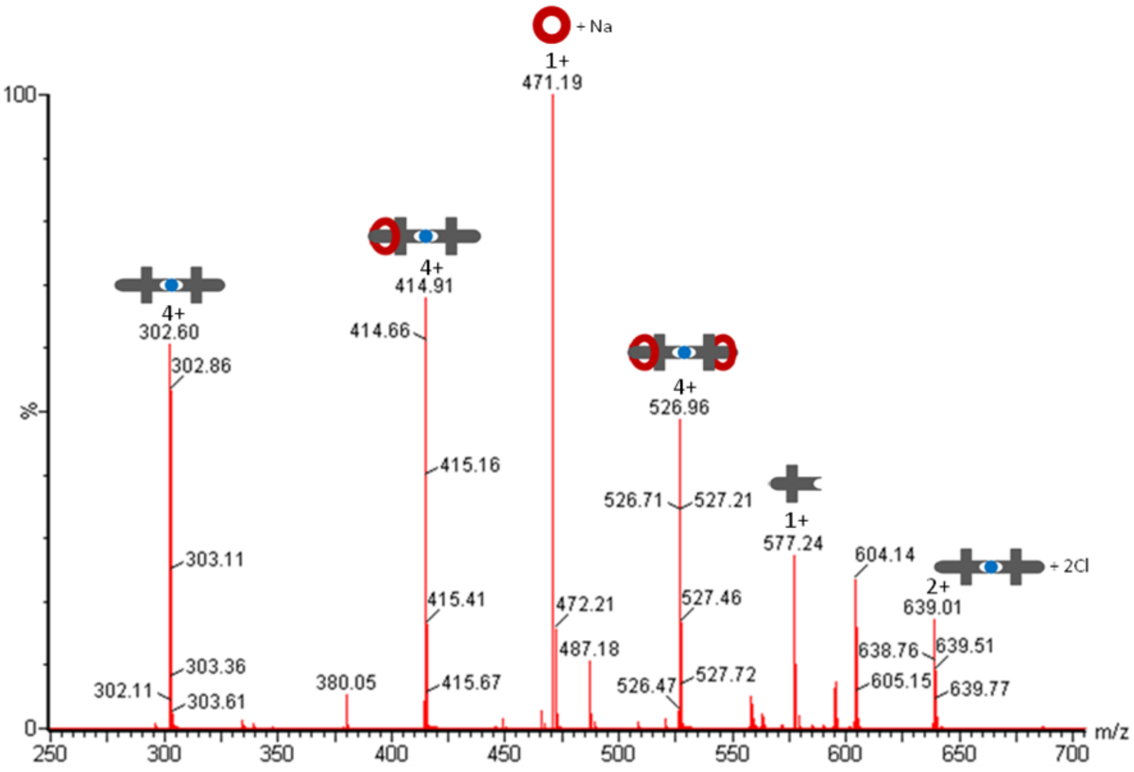

Fig S13. Q-TOF-MS spectra of **9**.

Table S1. Datas base on Scatchard Plotting Techniques for the complexation between guest **5** and DB24C8.

[G1](mM)	δ_b(ppm)	Δ^a(ppm)	$p=\Delta/\Delta_0^b$	p/[G1](M^{-1})
1.0264	8.220	0.085	0.4444	433.0
1.3214	8.223	0.110	0.4528	342.7
1.5967	8.224	0.110	0.4556	285.3
2.3950	8.225	0.120	0.4583	191.4
2.7371	8.226	0.125	0.4611	168.5
4.2578	8.228	0.140	0.4667	109.6
4.7900	8.230	0.155	0.4722	98.58

[a] δ_f= 8.56 ppm, the chemical shifts of the protons H_b, ±0.001 ppm. [b] δc=8.11 ppm, intial mole of Host (DB24C8) is 2 mM (1μmol in 0.5 mL CD_3OD). We get the data by titrating a solution of guest 1 (9.58 mM) in CD_3OD with 60, 80, 100, 150, 200, 300, 400, 500 μL.

Table S2. Datas base on Scatchard Plotting Techniques for the complexation between guest **6** and DB2C8.

[G2](mM)	δ_3(ppm)	Δ^a(ppm)	$p=\Delta/\Delta_0^b$	p/[G2](M^{-1})
1.302	8.285	0.110	0.6875	528.0
1.953	8.295	0.120	0.750	384.0
2.387	8.30	0.125	0.78125	327.3
4.774	8.305	0.13	0.8125	170.2
9.6565	8.313	0.138	0.8625	89.32
11.83	8.317	0.142	0.8875	75.02

[a] δc=8.175ppm, the chemical shifts of the protons H_b, ±0.001 ppm. [b] δf=8.335ppm, [H]0=1.858 Mm(CD_3OD).

Table S3. Datas base on Scatchard Plotting Techniques for the complexation between **3** and DB2C8.

[G3](mM)	δ_3(ppm)	Δ^a(ppm)	$p=\Delta/\Delta_0^b$	p/[G2](M^{-1})
1.875	8.200	0.025	0.1190	63.47
2.222	8.215	0.040	0.1905	85.73
2.500	8.225	0.050	0.2381	95.24
2.727	8.235	0.060	0.2857	104.8
2.917	8.250	0.075	0.3571	122.4
3.214	8.270	0.095	0.4524	140.8

[a] δc=8.175 ppm, the chemical shifts of the protons H_b, ±0.001 ppm. [b] δf=8.385 ppm, $[H]_0$=2 mM($CDCl_3$: CD_3OD= 1: 1). *K*av= 228 ± 9 M^{-1}.

Table S4. Datas base on Scatchard Plotting Techniques for the complexation between **4** and DB2C8.

[G4](mM)	δ_3(ppm)	Δ^a(ppm)	$p=\Delta/\Delta_0^b$	p/[G2](M^{-1})
1.875	8.184	0.009	0.1385	73.87
2.222	8.189	0.014	0.2154	96.94
2.500	8.193	0.018	0.2769	110.8
2.727	8.197	0.022	0.3385	124.1
2.917	8.201	0.025	0.3846	131.8
3.214	8.204	0.029	0.4462	138.8

[a] δc=8.175 ppm, the chemical shifts of the protons H_b, ±0.001 ppm. [b] δf=8.24 ppm, $[H]_0$=2 mM($CDCl_3$: CD_3OD= 1: 1). *K*av= 212 ± 16 M^{-1}.

References for the General Procedure section :

1. Wang, Y. L.; David, L. F; Tobin J. M, *J. Phys. Chem. C.* **2008**, *112*, 8005–8015.
2. Schultz, A.; Li, X. P.; Barkakaty, B.; Moorefield, C. N.; Wesdemitotis, C; Newkome, G. R. *J. Am. Chem. Soc*. **2011**, *133*, 11450-11453.
3. Emi, K.; Lee, Y. H.; Akira, F.; Satoshi, K; Jack, M. H.; Kim, Y.; Shinya, H.; *Polyhedron*. **2013,** *52*, 435–441.