Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Terpyridinyl Dibenzo[b,d]furan and Dibenzo[b,d]thiophene based Tetrameric *Bis*metallo-macrocycles

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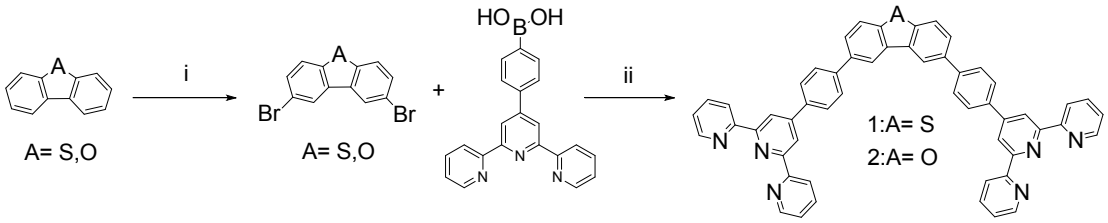
General Procedures: All the chemicals and solvents were purchased from Sigma Aldrich, MERCK or Energy-chemical, and used without further purification. 2,8-dibromodibenzo[b,d]thiophene,[1] 2,8-dibromodibenzo[b,d]furan[1] and (4-([2,2':6',2''-terpyridin]-4'-yl)phenyl) boronic acid[2] and was prepared as described in the literature. Normal phase purifications were carried out using neutral aluminum oxide (200-300 mesh). TLC was carried out using Merck Aluminium Oxide 150 F254, neutral. ^{1}H-NMR spectra was 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.



Scheme 1. Synthetic Route of the ligand (i): AcOH, Br_2; (ii) $Pd^0(PPh_3)_4$, NaOH (aqueous, 1 M), THF.

General Suzuki-Coupling Procedure: To a 3-necked round bottom flask, the initial aryl halide, 4′–(4-boronatophenyl)-2,2′:6′2″-terpyridine (1.1 equiv. per halide), NaOH (aqueous, 1M) (3 equiv. per halide), and THF were added. The system was freeze-pump-thawed and backfilled with argon or nitrogen, after which $Pd(PPh_3)_4$ (6 mol% per halide) was added. The biphasic system was refluxed for 24 h resulting in a green solution. The solvent was removed under vacuum, then washed with water. The queous layer was extracted with $CHCl_3$ (3 times), the combined extract was dried ($MgSO_4$), and concentrated in vacuo to give a residue, which was column chromatographed (Al_2O_3) eluting with CH_2Cl_2 to give pure bis(terpyridine) ligand, as white solid.

Compound L1: Using the general Suzuki-Coupling procedure, the following were used in specified quantities: 2,8-dibromodibenzo[b,d]thiophene (513 mg, 1.5 mmol), 4′–(4-boronatophenyl)-2,2′:6′2″-terpyridine (1.16 g, 3.3 mmol), NaOH (aqueous, 1M) (360 mg, 9 mmol), $Pd(PPh_3)_4$ (207 mg, 0.18 mmol), THF (80 mL); Yield: 778 mg (65%); ^{1}H-NMR(500MHz, ppm, $CDCl_3$): δ 8.82 (s, 4H, Tpy-$H^{3',5'}$), 8.76-8.75 (d, J = 5.0 Hz, 4H, Tpy-$H^{6,6''}$), 8.70-8.69 (d, J = 5.0 Hz, 4H, Tpy-$H^{3,3''}$), 8.53-8.52 (d, 2H, J = 5.0, H^c), 8.08-8.06 (d, 4H, J = 10.0, Ar-H^f), 7.98-7.97 (d, 2H, 2H, H^a), 7.91-7.89 (m, 8H, Tpy-$H^{4,4''}$, Ar-H^e), 7.82-7.80(m, 2H, H^b), 7.41-7.38(m, 4H, Tpy-$H^{5,5''}$); ^{13}C-NMR(125MHz, ppm, $CDCl_3$): 156.52, 156.32, 156.03, 149.80, 149.17, 141.90, 137.14, 136.69, 135.80, 127.89, 127.84, 126.88, 124.88, 123.85, 121.42, 119.35, 118.73, 112.07; LC-MS: 801.6 [M+H] (Calcd. 800.0). m.p. 126-130 °C.

Compound L2: 2,8-dibromodibenzo[b,d]furan (489 mg, 1.5 mmol), 4′–(4-boronatophenyl)-2,2′:6′2″-terpyridine (1.16 g, 3.3 mmol), NaOH (aqueous, 1M) (360 mg, 9 mmol), $Pd(PPh_3)_4$ (207 mg, 0.18 mmol), THF (80 mL); Yield: 857 mg (73%); ^{1}H-NMR(500MHz, ppm, $CDCl_3$): δ 8.85 (s, 4H, Tpy-$H^{3',5'}$), 8.79-8.78 (d, J = 5.0 Hz, 4H, Tpy-$H^{6,6''}$), 8.73-8.71 (d, J = 10.0 Hz, 4H, Tpy-$H^{3,3''}$), 8.34-8.33 (d, 2H, J = 5.0, H^c), 8.09-8.07 (d, 4H, J = 10.0, Ar-H^f), 7.94-7.90 (m, 4H, Tpy-$H^{4,4''}$), 7.89-7.87 (d, 4H, J = 10.0, Ar-H^e), 7.83-7.81(d, 2H, J = 10.0, H^a), 7.72-8.71 (d, 2H, J = 5.0, H^b), 7.41-7.38(m, 4H, Tpy-$H^{5,5''}$); ^{13}C-NMR(125MHz, ppm, $CDCl_3$): 156.35, 156.05, 149.80, 149.18, 141.75, 139.40, 138.60, 137.40, 137.25, 136.75, 136.20, 127.90, 126.36, 123.84, 123.30, 121.42, 120.17, 118,77; LC-MS: 783.6 [M+H] (Calcd. 783.9). m.p. 147-150 °C.

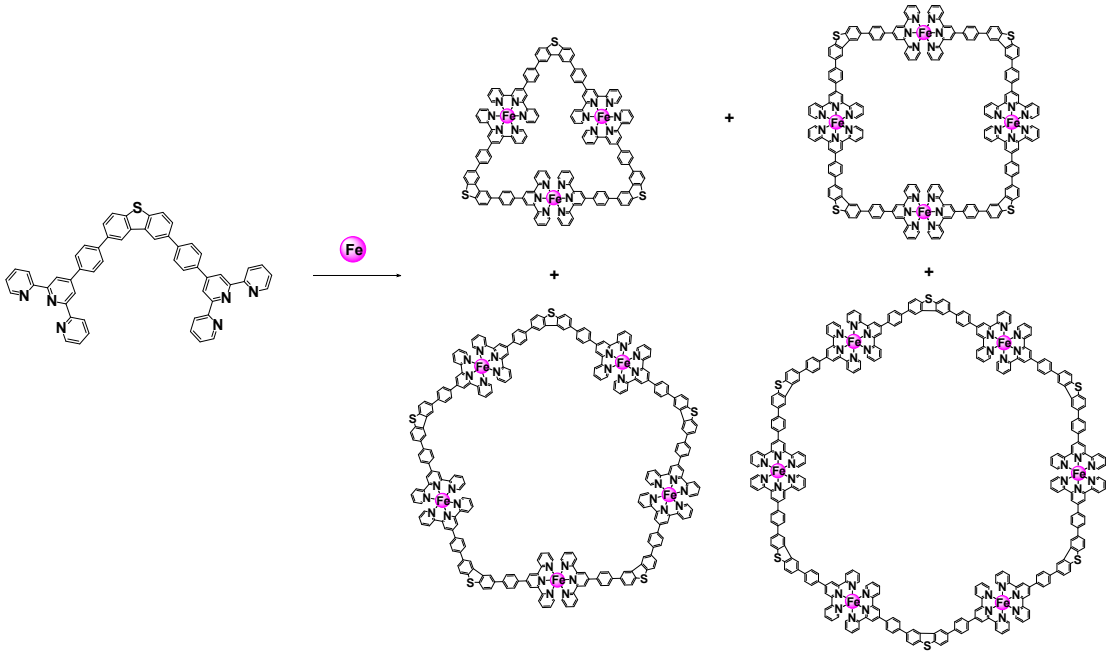
[Ru(1)$_2$Cl$_2$] (D3): To a stirred solution of **L1** (487 mg, 0.61 mmol) in $CHCl_3$ (80 mL), a solution of $RuCl_3 \cdot 3H_2O$ (78.4 mg, 0.3 mmol) in MeOH (80 mL) was added by dropwise. After refluxing for 48 h, the solvent was evaporated *in vacuo* and the residue was column chromatographed (Al_2O_3) eluting with CH_2Cl_2/MeOH to give the **D3**, as a red powder; Yield: 106 mg (20%); ^{1}H-NMR(500MHz, ppm, $CDCl_3$: MeOH= 1:1): δ 9.29 (s, 4H, Tpy-$H_A^{3',5'}$), 8.92-8.90 (d, J = 10.0 Hz, 4H, Tpy-$H_A^{3,3'}$), 8.75 (s, 4H, Tpy-$H_B^{3',5'}$), 8.72-8.66 (m, 12H, H^c, H^g, Tpy-$H_B^{3,3''}$, Tpy-$H_B^{6,6''}$), 8.43-8.42 (d, J = 5.0 Hz, 4H, Ar-H^i), 8.20-8.18 (d, J = 10.0 Hz, 4H, Ar-H^h), 8.10-8.04 (m, 8H,Tpy-$H^{4,4''}$), 7.96-7.94 (d, J = 10.0 Hz, 2H, H^e), 7.90-7.89 (d, J = 5.0 Hz, 2H, H^f), 7.51-7.50 (d, J = 5.0 Hz, 4H, Tpy-$H_A^{6,6''}$), 7.49-7.47 (t, J = 10.0 Hz, 4H, Tpy-$H_B^{5,5''}$), 7.36-7.33 (d, J = 15.0 Hz, 4H, Tpy-$H_A^{5,5''}$); ^{13}C-NMR of **3** cannot get due to its poor solubility. m.p. > 300 °C. ESI-TOF-MS (m/z): +3(m/z 566.5 $[M\text{-}2Cl^- + H]^{3+}$) (Calcd. 566.5), +2(m/z 849.2 $[M\text{-}2Cl^-]^{2+}$) (Calcd. 849.2).

[Ru(2)$_2$Cl$_2$] (D4): The synthesis of compound 4 is the same as compound 3. **L1** (477 mg, 0.61 mmol) in $CHCl_3$ (80 mL), $RuCl_3 \cdot 3H_2O$ (78.4 mg, 0.3 mmol) in MeOH (80 mL); Yield: 120 mg (23%); ^{1}H-NMR(500MHz, ppm, $CDCl_3$): δ 9.54 (s, 4H, Tpy-$H_A^{3',5'}$), 9.29-9.27 (d, J = 10.0 Hz, 4H, Tpy-$H_A^{3,3'}$), 8.87 (s, 4H, Tpy-$H_B^{3',5'}$), 8.79-8.78 (d, J = 5.0 Hz, 4H, Tpy-$H_B^{6,6''}$), 8.74-8.72 (d, J = 10.0 Hz, 4H, Tpy-$H_B^{3,3''}$), 8.70-8.67 (d, J = 15.0 Hz, 4H, Ar-H^i), 8.39 (s, 2H, H^c), 8.35 (s, 2H, H^g), 8.12-8.10 (m, 8H, Ar-H^h , Ar-H^k), 8.03-8.01 (t, J = 10.0 Hz, 4H, $H_A^{4,4''}$), 7.95-7.85 (m, 12H, Ar-H^j, Tpy-$H_B^{4,4''}$, H^a, H^e), 7.76 (s, 2H, H^b), 7.74 (s, 2H, H^f), 7.46-7.45 (d, J = 5.0 Hz, 4H, Tpy-$H_A^{6,6''}$), 7.40-7.39 (t, J = 5.0 Hz, 4H, Tpy-$H_B^{5,5''}$), 7.33-7.31 (t, J = 10.0 Hz, 4H, Tpy-$H_A^{5,5''}$); ^{13}C-NMR of **4** cannot get due to its poor solubility. m.p. > 300 °C. ESI-TOF-MS (m/z): +4(m/z 417.1 $[M\text{-}2Cl^- + 2H]^{4+}$) (Calcd. 417.1), +3(m/z 555.8 $[M\text{-}2Cl^- + H]^{3+}$) (Calcd. 555.8), +2(m/z 833.2 $[M\text{-}2Cl^-]^{2+}$) (Calcd. 833.2).

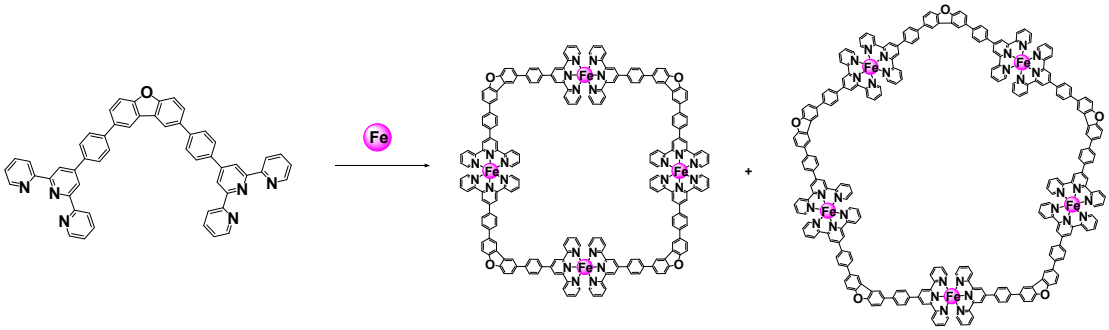
([Ru$_2$Fe$_2$(1)$_4$(PF$_6$)$_8$]) (T5): To a stirred solution of **D3** (17.4 mg, 10 μmol) in MeOH (100 mL), a solution of $FeCl_2 \cdot 4H_2O$ (2 mg, 10 μmol) in MeOH (10 mL) was slowly added. After refluxing for 18 h, excess NH_4PF_6 was added, generating a red precipitate, which was filtered and washed with MeOH and then water to give the desired **T5** possessing PF_6^- as counterions; Yield: 22 mg (96%); ^{1}H-NMR(500MHz,

ppm, CD_3CN): δ 9.35 (s, 8H, Tpy-$H_B^{3',5'}$), 9.18 (s, 8H, Tpy-$H_A^{3',5'}$), 8.59-8.57 (d, J = 10.0 Hz, 8H, Ar-H^i), 8.48-8.47 (d, J = 5.0 Hz, 8H, Ar-H^k), 8.39-8.37 (d, J = 10.0 Hz, 8H, Ar-H^j), 8.35-8.33 (d, J = 10.0 Hz, 8H, Ar-H^j), 8.27-8.24 (m, 8H, H^a, H^b), 8.15-8.12 (m, 8H, H^e, H^f), 8.01-7.96 (m, 16H, Tpy-$H_A^{4,4''}$, Tpy-$H_B^{4,4''}$), 7.53-7.52 (d, 8H, Tpy-$H_A^{6,6''}$), 7.28-7.25 (m, 16H, Tpy-$H_B^{6,6''}$, Tpy-$H_A^{6,6''}$), 7.15 (s, 8H, Tpy-$H_B^{5,5''}$). ESI-TOF-MS(m/z): +8 (m/z 438.21), +7 (m/z 521.9673), +6 (m/z 633.2730), +5 (m/z 788.92), +4 (m/z 1022.39) and +3 (m/z 1401.22).

[$Ru_2Fe_2(2)_4(PF_6)_8$]) (T6): To a stirred solution of **D4** (17.7 mg, 10 μmol) in MeOH (100 mL), a solution of $FeCl_2{\cdot}4H_2O$ (2 mg, 10 μmol) in MeOH (10 mL) was slowly added. After refluxing for 18 h, excess NH_4PF_6 was added, generating a red precipitate, which was filtered and washed with MeOH and then water to give the desired **T6** possessing PF_6^- as counterions; Yield: 21.7 mg (94%); ^{1}H-NMR(500MHz, ppm, CD_3CN) of: δ 9.33 (s, 8H, Tpy-$H_B^{3',5'}$), 9.16 (s, 8H, Tpy-$H_A^{3',5'}$), 8.76-8.71 (m, 24H, Tpy-$H_A^{3',5'}$, Tpy-$H_A^{3',5'}$, H^c, H^g), 8.56-8.54 (d, J = 10.0 Hz, 8H, Ar-H^i), 8.45-8.43 (d, J = 10.0 Hz, 8H, Ar-H^k), 8.30-8.28 (d, J = 10.0 Hz, 8H, Ar-H^h), 8.26-8.24 (d, J = 10.0 Hz, 8H, Ar-H^j), 8.15-8.11 (t, 8H, H^a, H^e), 8.03-7.93 (m, 24H, Tpy-$H_A^{4,4''}$, Tpy-$H_B^{4,4''}$, H^b, H^f), 7.53-7.52 (d, J = 10.0 Hz, 8H, Tpy-$H_A^{6,6''}$), 7.29-7.28 (d, 8H, Tpy-$H_B^{6,6''}$), 7.27-7.24 (t, 8H, Tpy-$H_A^{5,5''}$), 7.17-7.14 (t, 8H, Tpy-$H_B^{5,5''}$). ESI-TOF-MS(m/z): +8(m/z 430.72), +7(m/z 512.97), +6(m/z 622.62), +5(m/z 776.14) +4(m/z 1006.41), +3(m/z 1390.21).



L1+ Fe^{2+}: To a stirred solution of **L1** (8 mg, 10 μmol) in $CHCl_3$ (3 mL), a solution of $FeCl_2{\cdot}4H_2O$ (2 mg, 10 μmol) in MeOH (3 mL) was added. After refluxing for 18 h, excess NH_4PF_6 was added, generating a purple precipitate, which was filtered and washed with MeOH and then water to give purple solid.



L2+ Fe^{2+}: To a stirred solution of **L2** (7.8 mg, 10 μmol) in $CHCl_3$ (3 mL), a solution of $FeCl_2 \cdot 4H_2O$ (2 mg, 10 μmol) in MeOH (3 mL) was added. After refluxing for 18 h, excess NH_4PF_6 was added, generating a purple precipitate, which was filtered and washed with MeOH and then water to give purple solid.

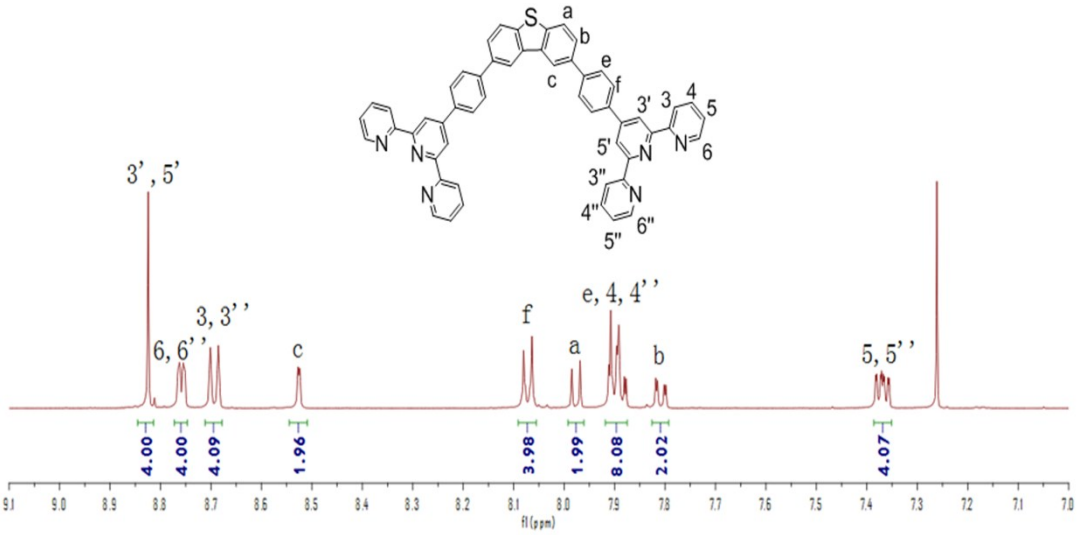


Fig *S1.* ^{1}H-NMR of L1.

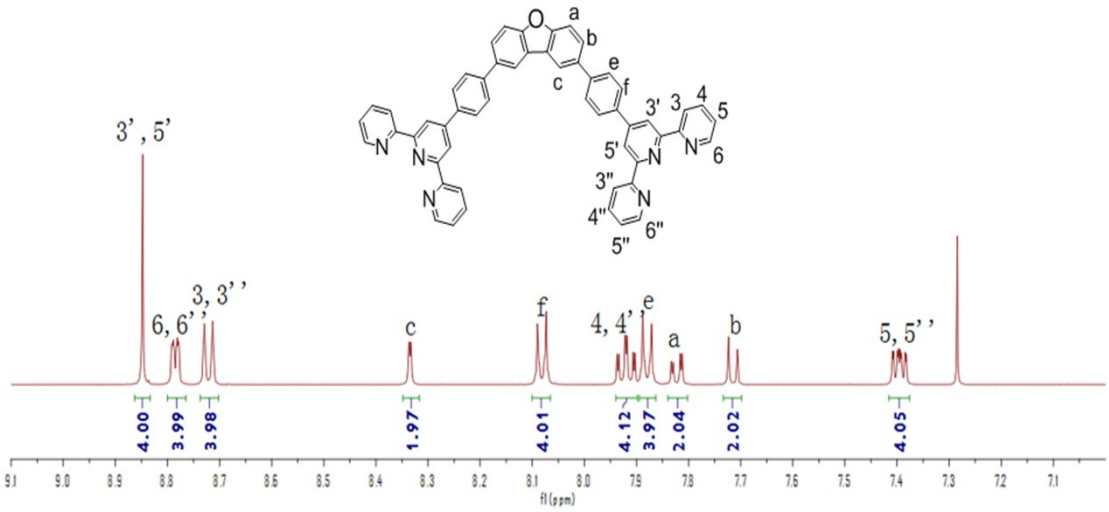


Fig *S2.* ^{1}H-NMR of L2.

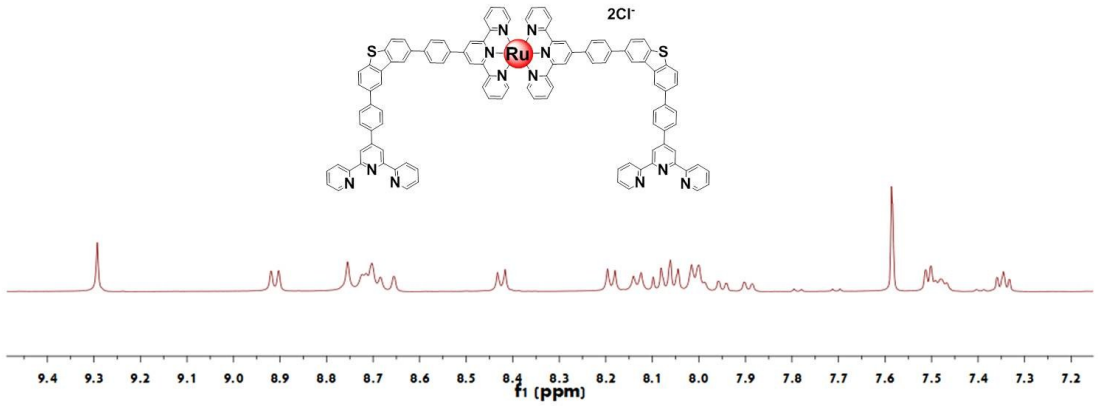


Fig *S3.* ^{1}H-NMR of D3.

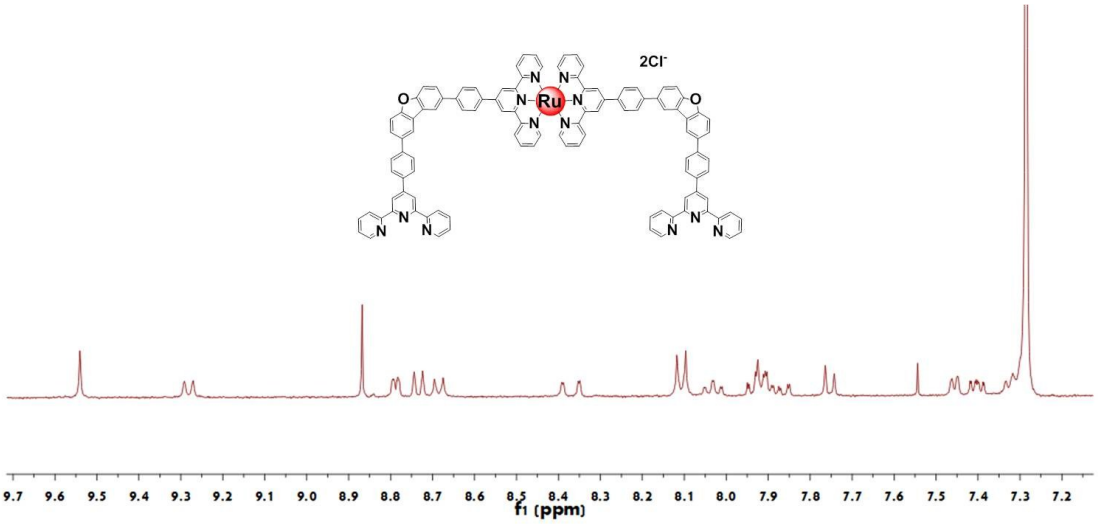


Fig *S4.* ^{1}H-NMR of D4.

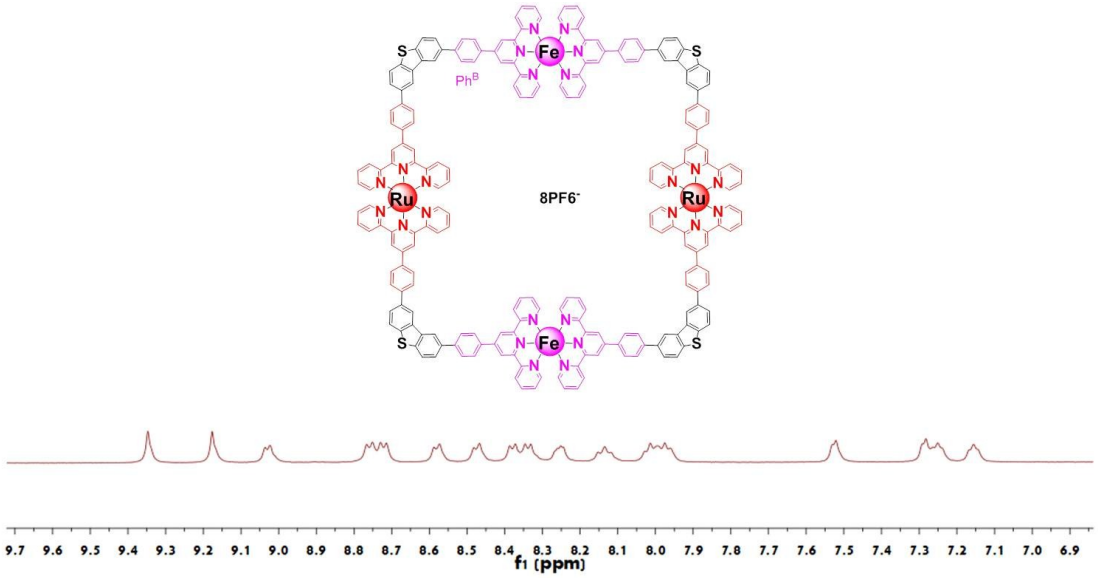


Fig *S5.* ^{1}H-NMR of T5.

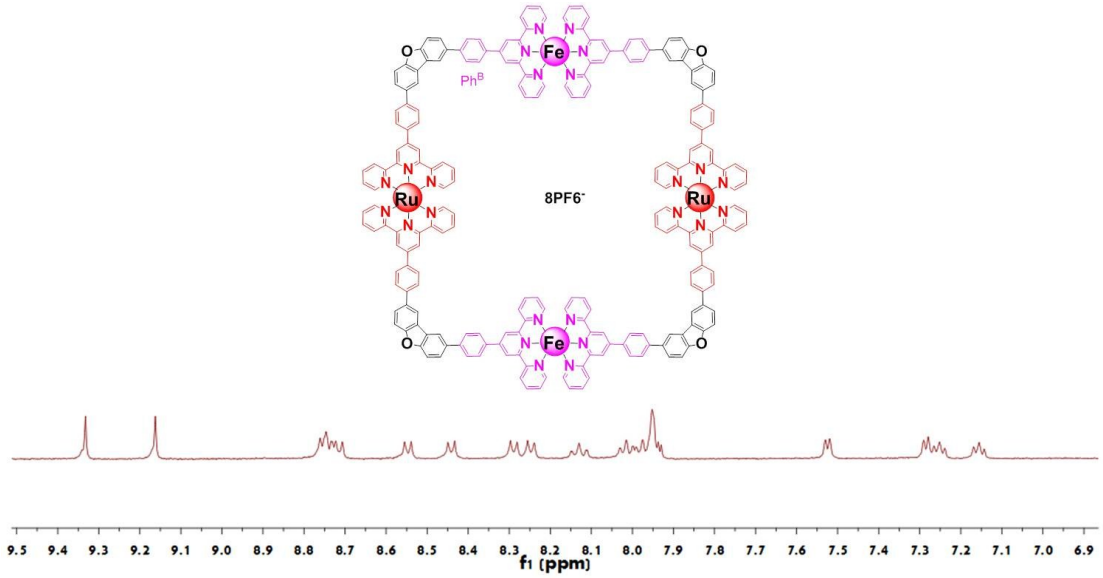


Fig *S6.* ^{1}H-NMR of T6.

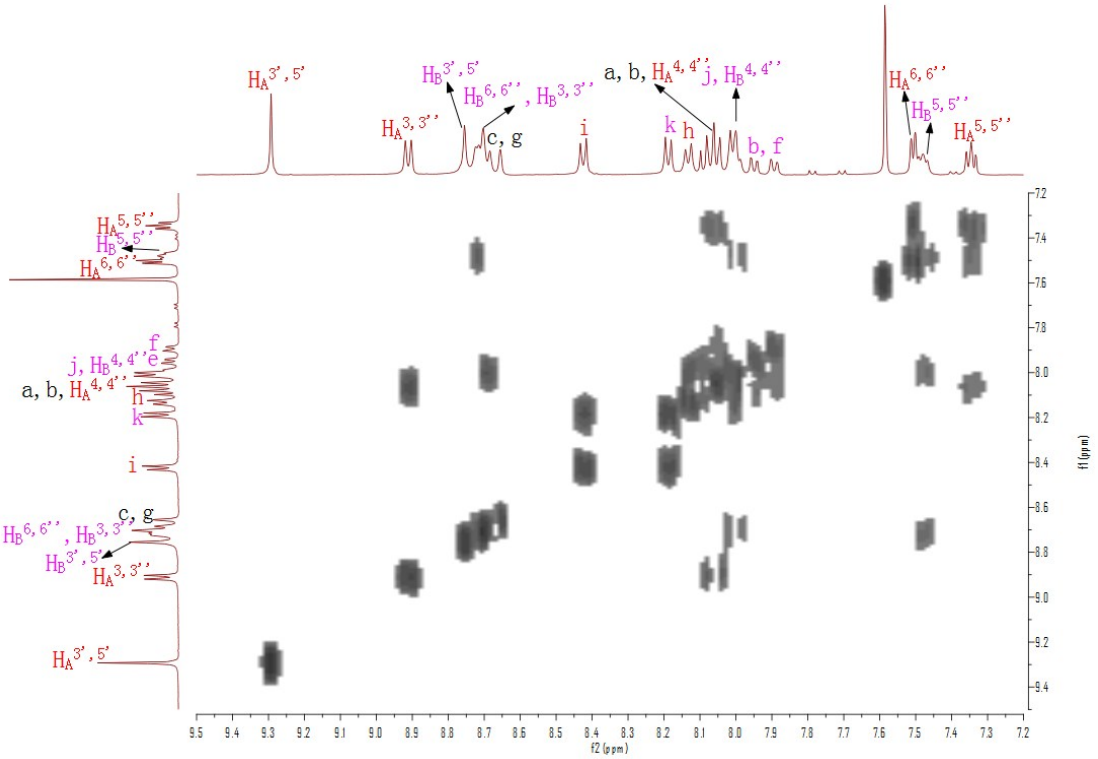


Fig *S7.* COSY-NMR of D3.

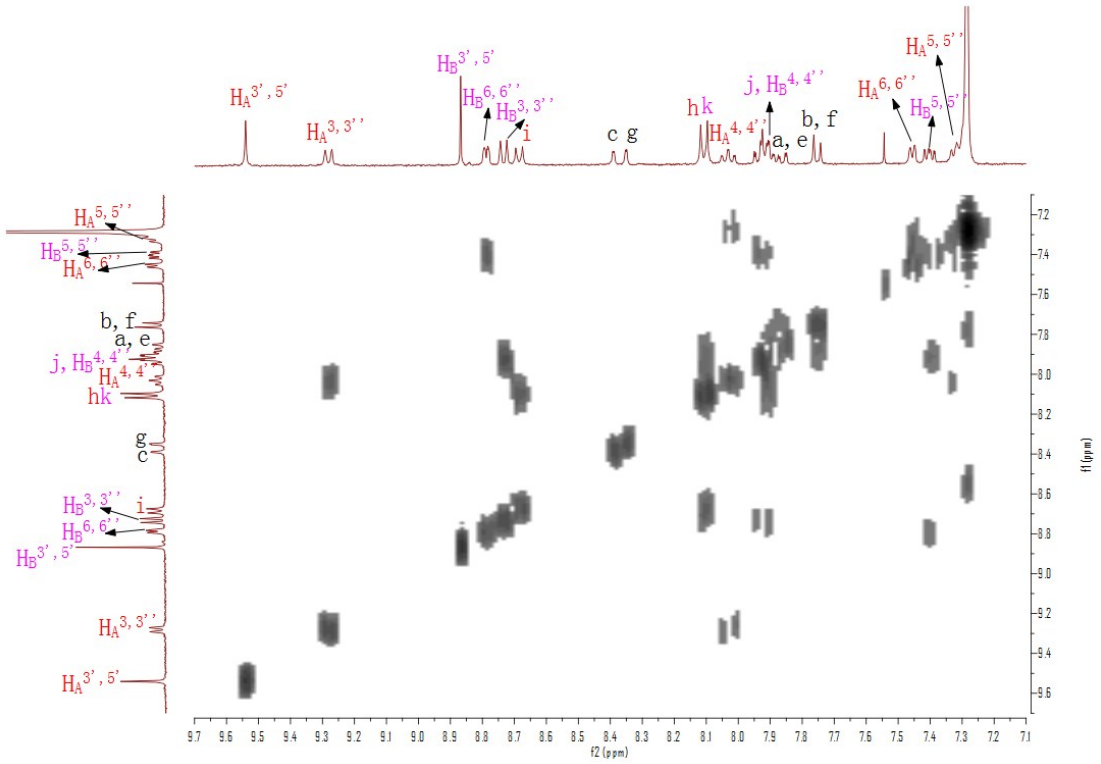


Fig *S8.* COSY-NMR of D4.

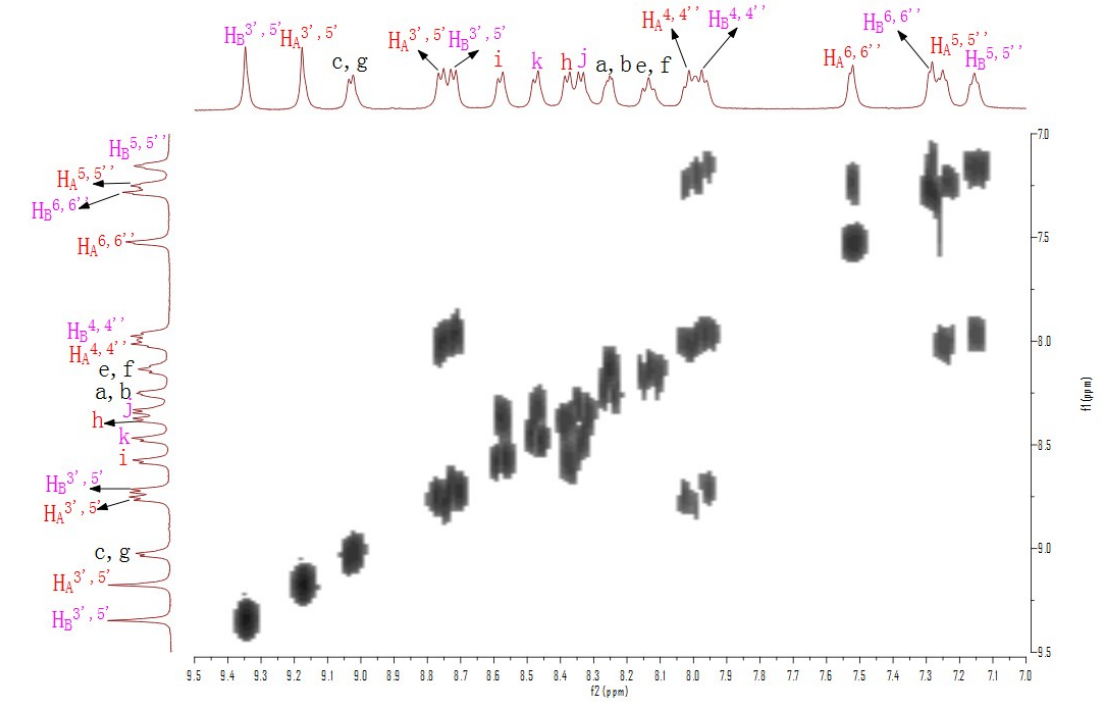


Fig *S9.* COSY-NMR of T5.

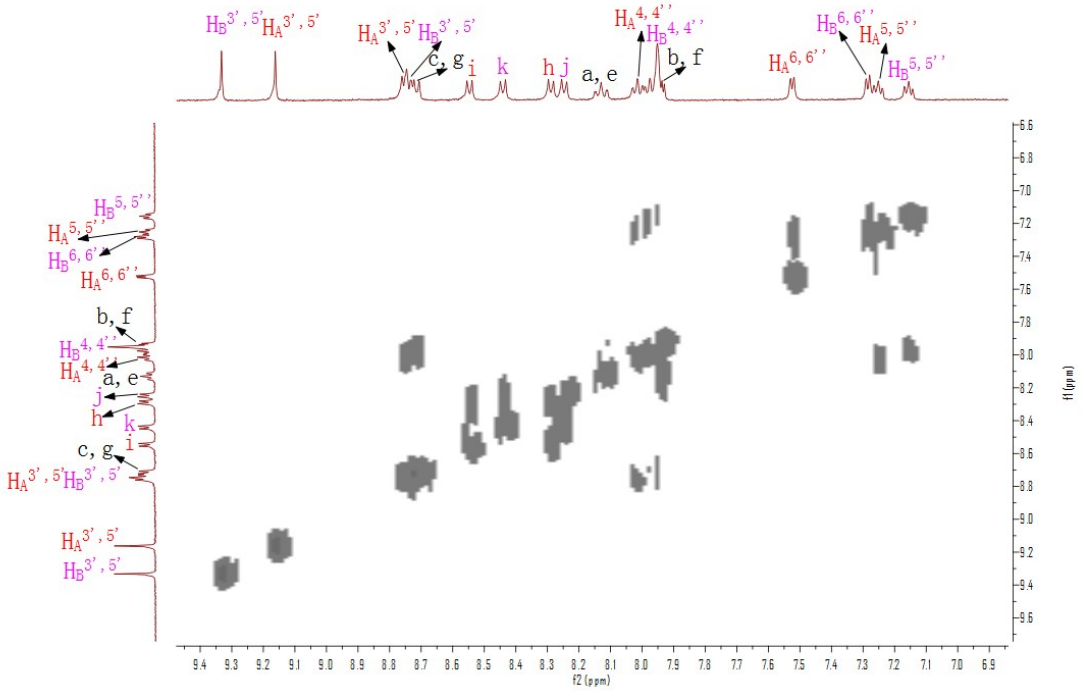


Fig *S10.* COSY-NMR of T6.

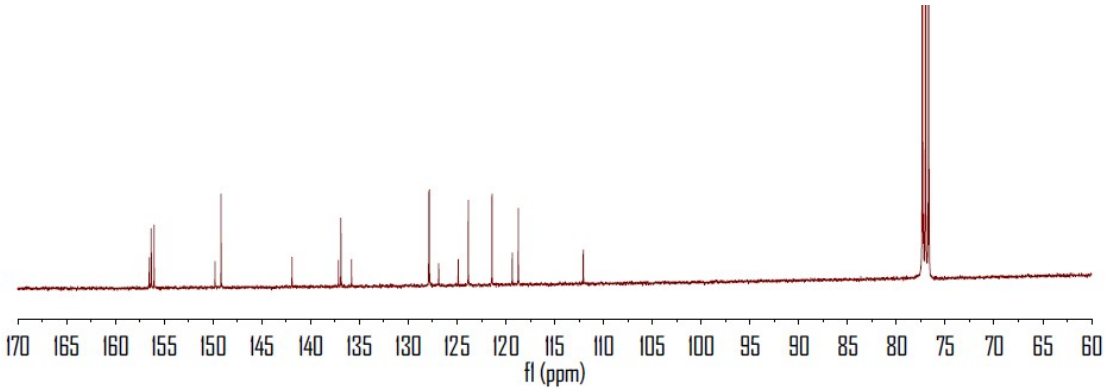


Fig *S11.* ^{13}C-NMR of L1.

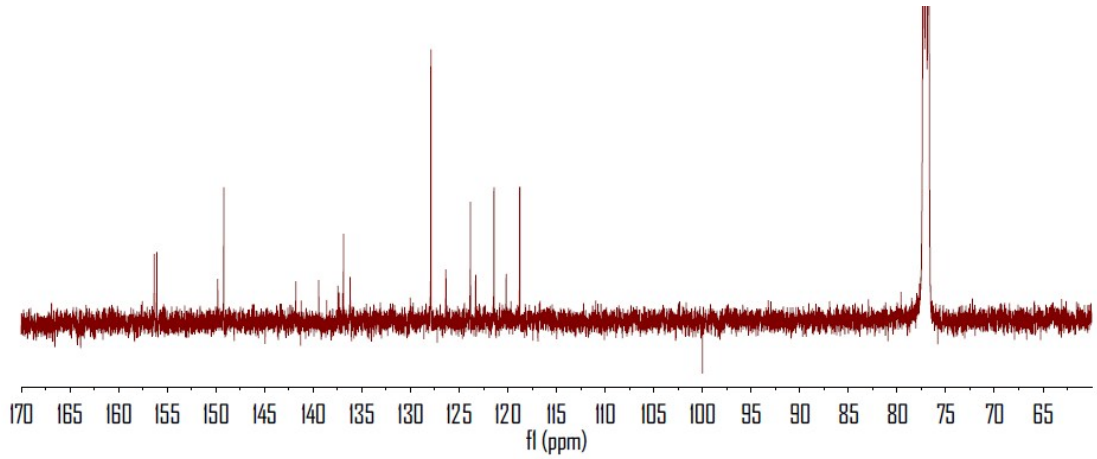


Fig *S12.* ^{13}C-NMR of L2.

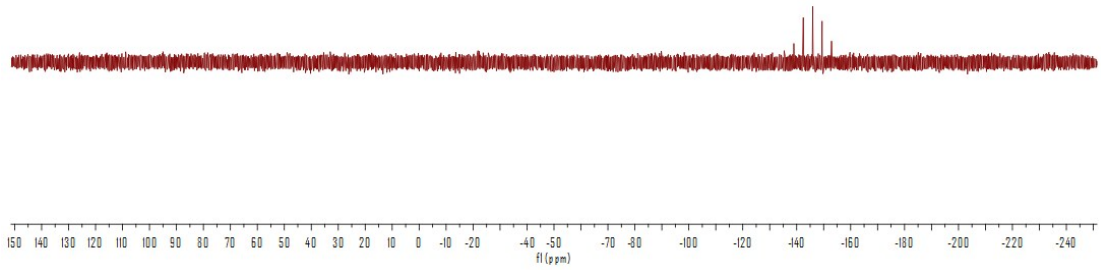


Fig *S13.* 31P-NMR of T5.

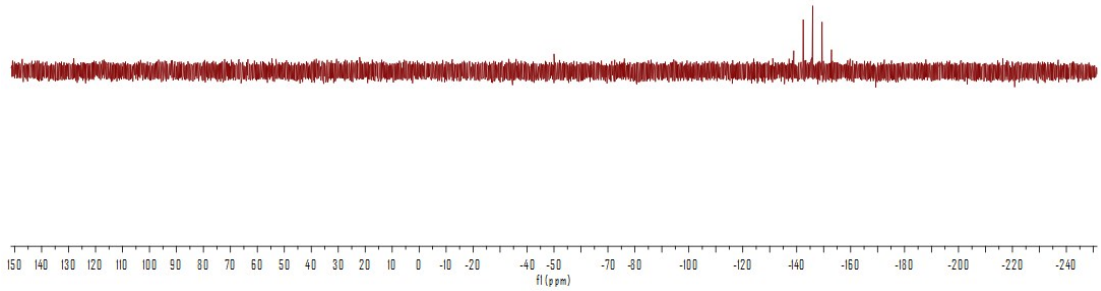


Fig *S14.* 31P-NMR of T6.

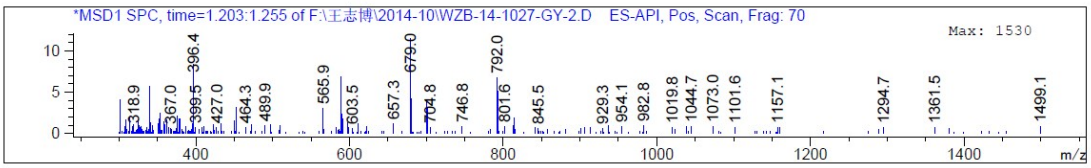


Fig *S15*. LC-MS of L1.

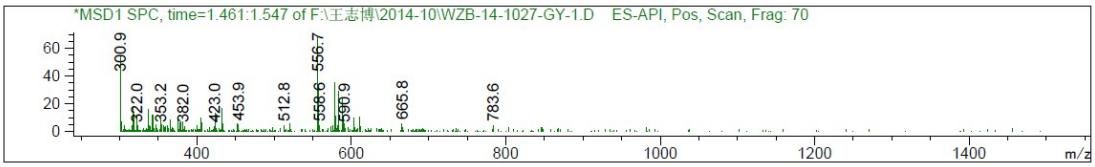


Fig *S16*. LC-MS of L2.

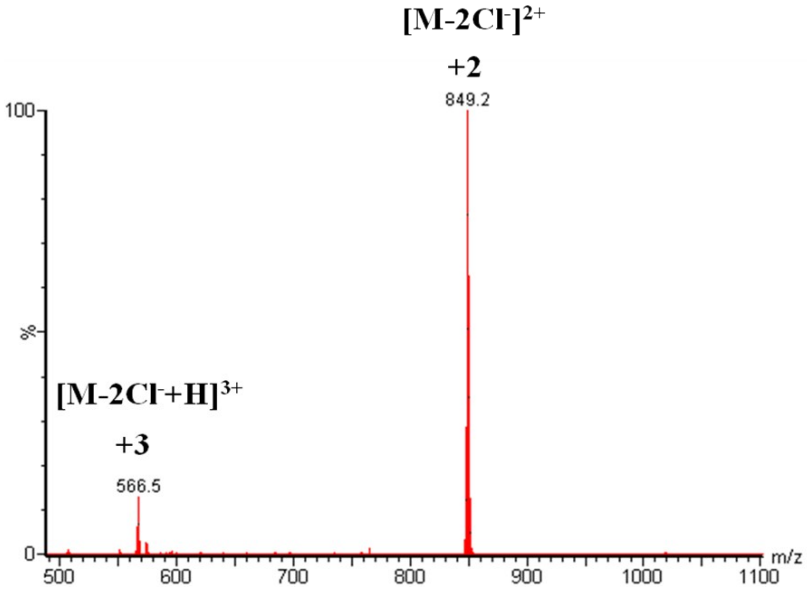


Fig *S17*. ESI-TOF-MS of D3.

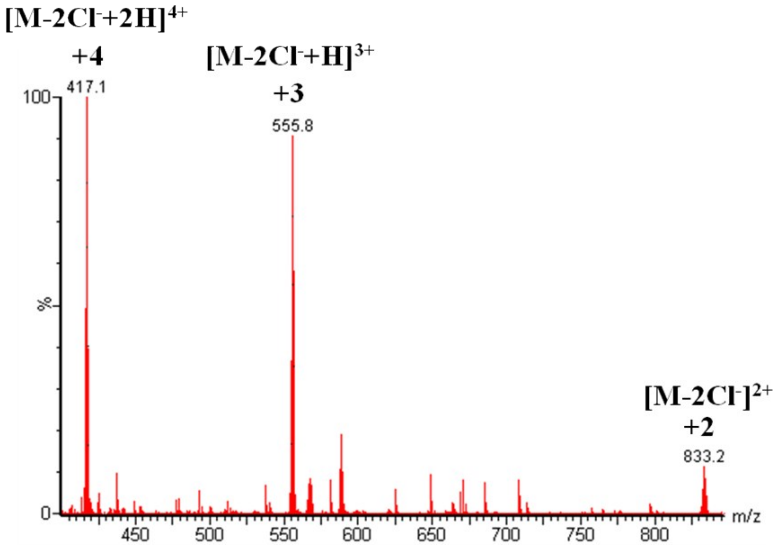
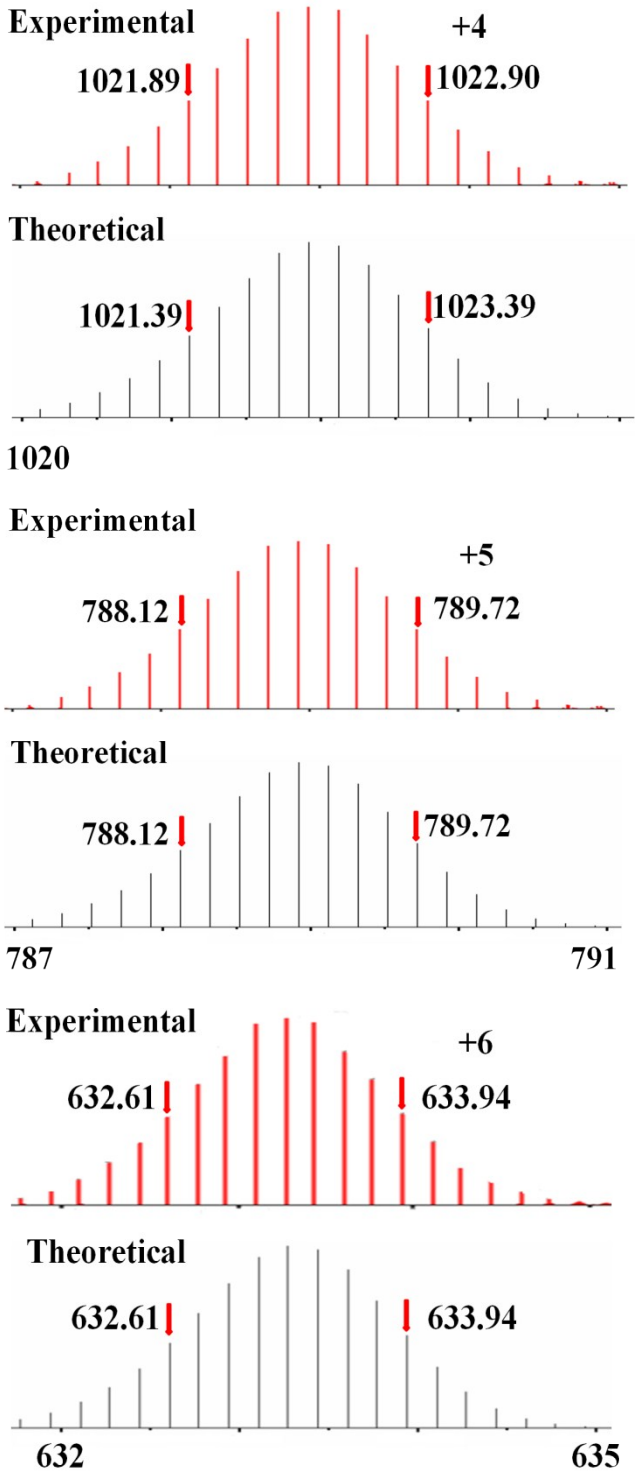


Fig *S18*. ESI-TOF-MS of D4.

Isotopic Patterns (ESI-TOF-MS)



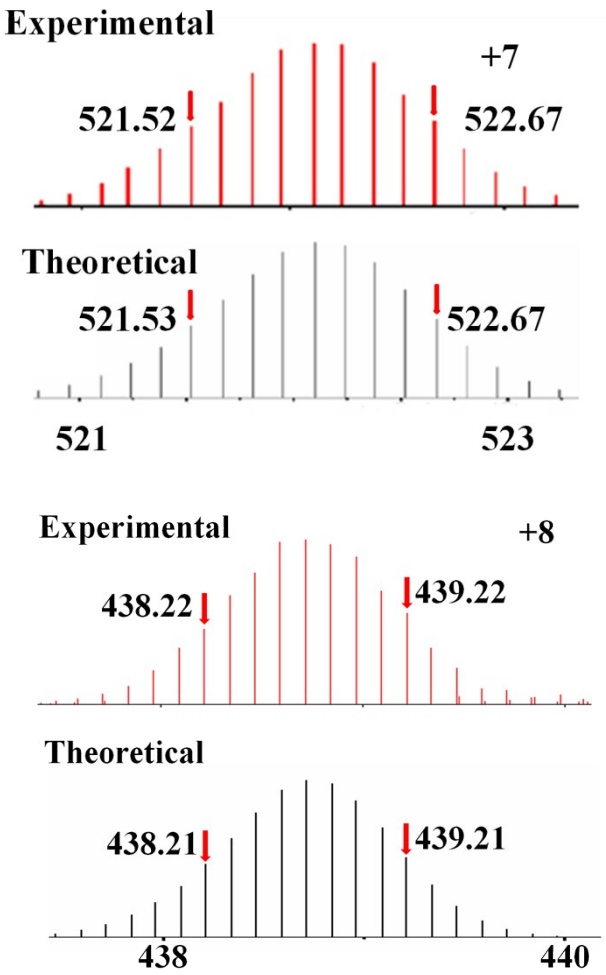
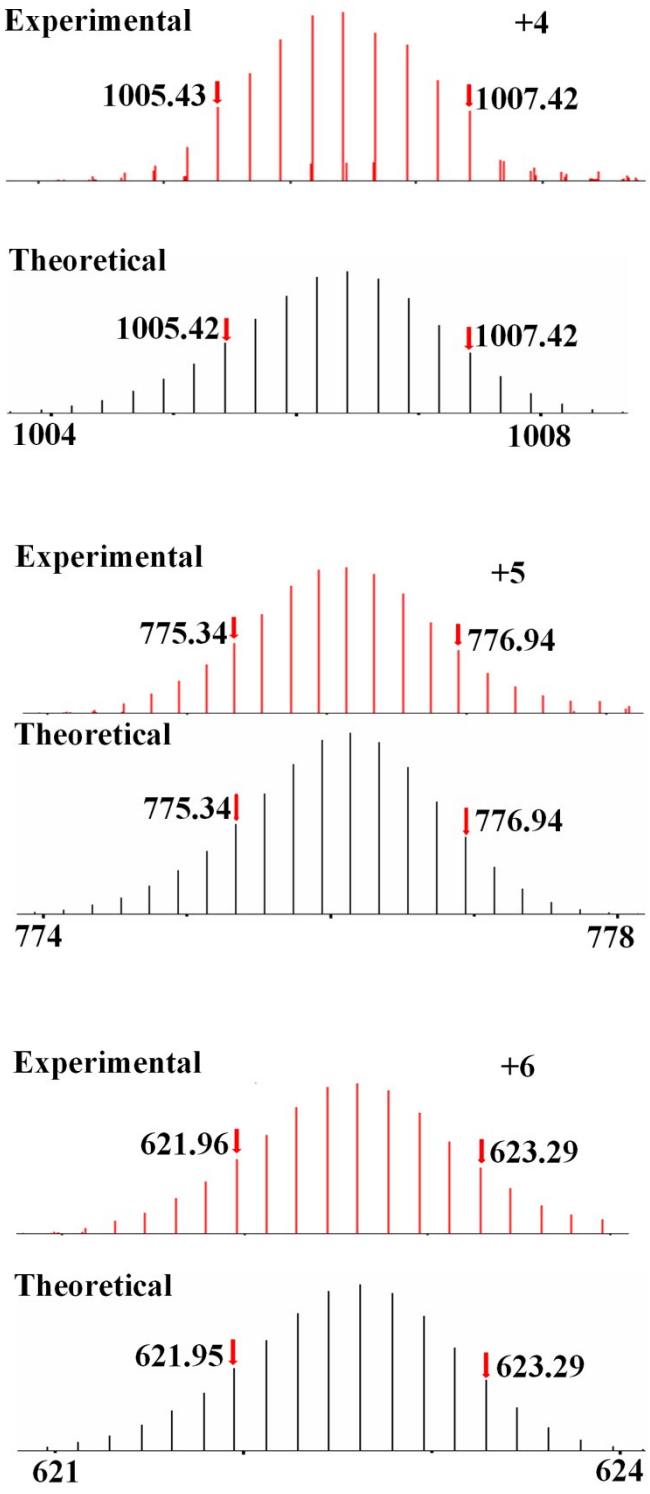


Fig. *S19*. Isotopic patterns for the different charge states (4+ to 8+) observed from **T5** (PF_6^- as counterion).


Experimental
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1007.42
Theoretical
1005.42
1007.42
1004
1008
Experimental
+5
775.34
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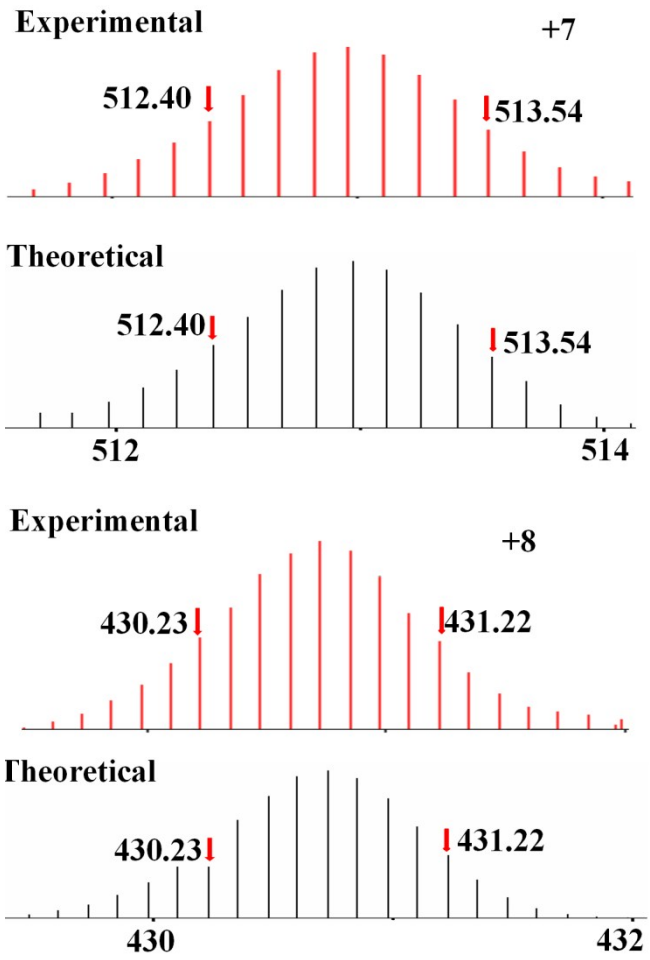

Fig. *S20*. Isotope patterns for the different charge states (4+ to 8+) observed from **T6** (PF_6^- as counterion).

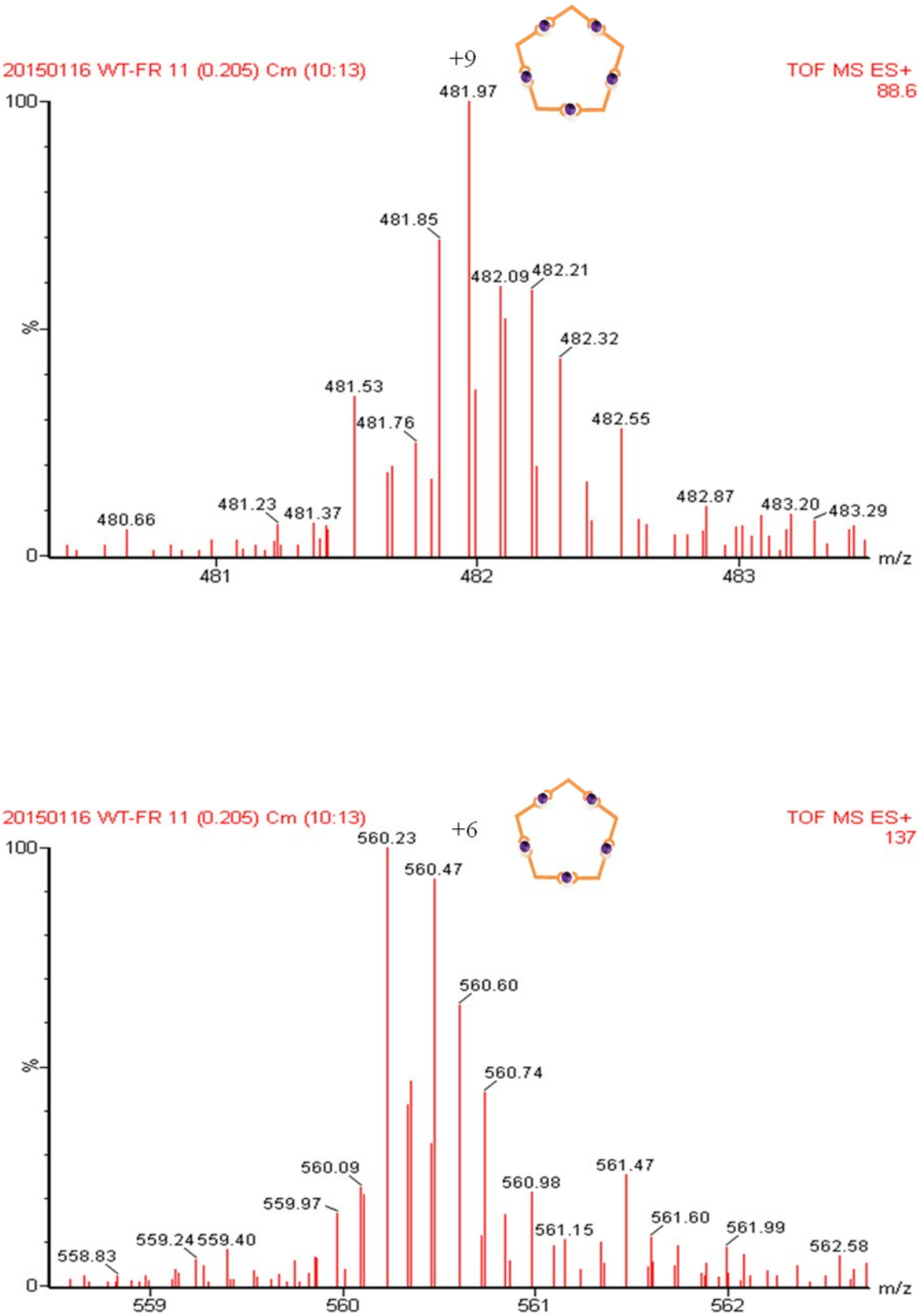

Fig *S21.* Partial isotopic patterns of ESI-TOF-MS spectra for $[(\mathbf{L2}Fe)_5]^{9+}$, top, and $[(\mathbf{L2}Fe)_5]^{6+}$, bottom, from self-assembly between **L2** and Fe^{2+}.

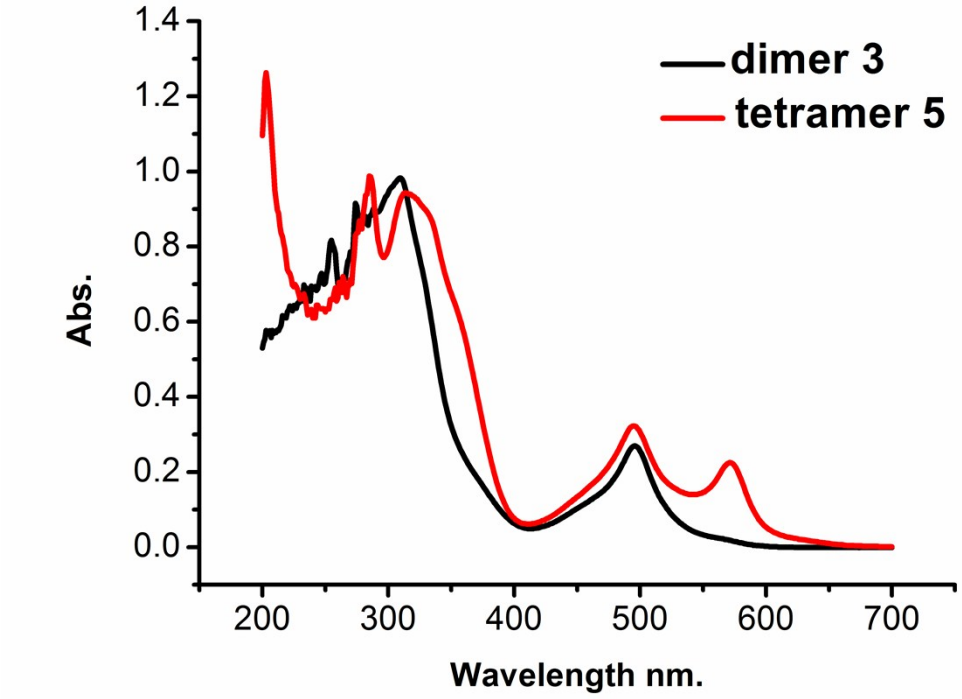

Fig *S22.* Full-figure of UV-vis spectra for dimer **3** and tertramer **5**.

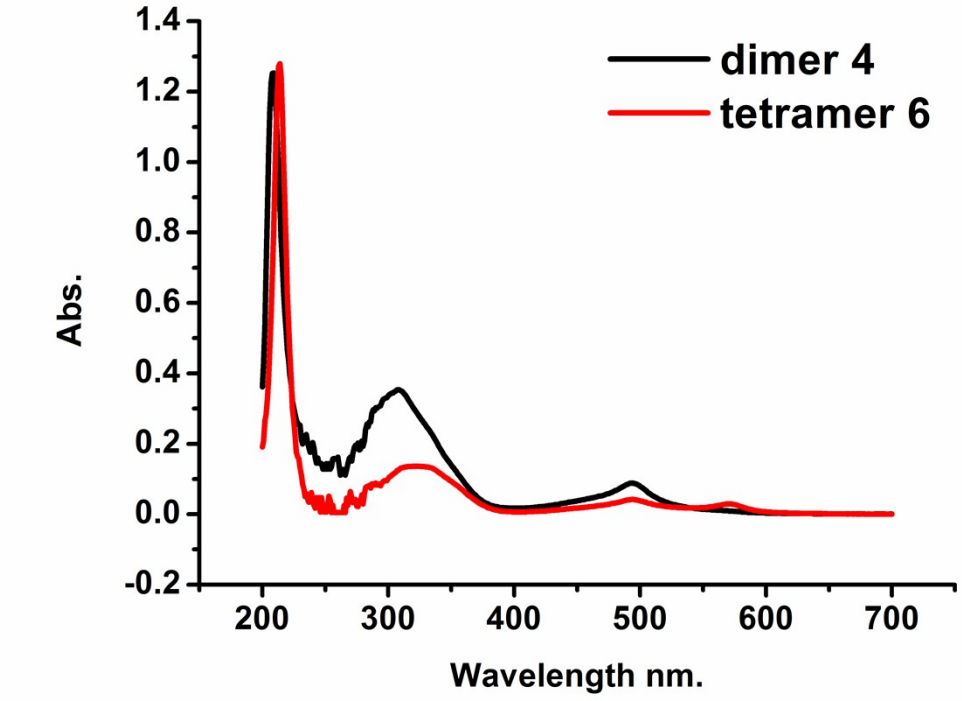

Fig *S23.* Full-figure of UV-vis spectra for dimer **4** and tertramer **6**.

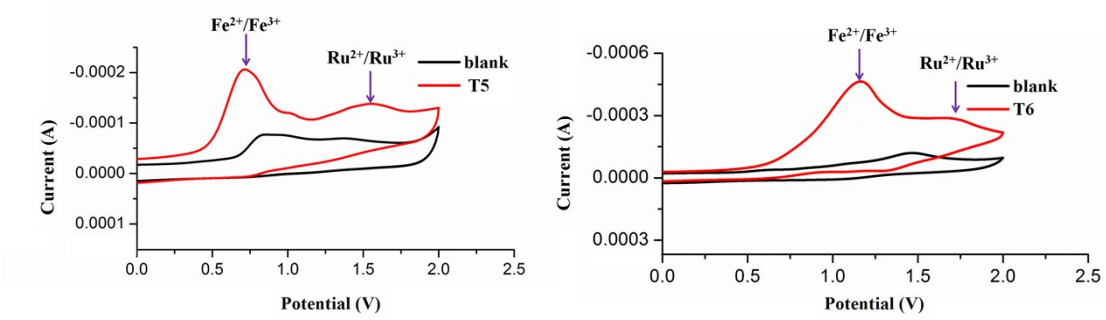

Fig. *S24.* Cyclic voltammograms of the complexes **T5** (Left), and **T6** (Right) (in 0.1 M Bu_4NPF_6, CH_3CN solution).

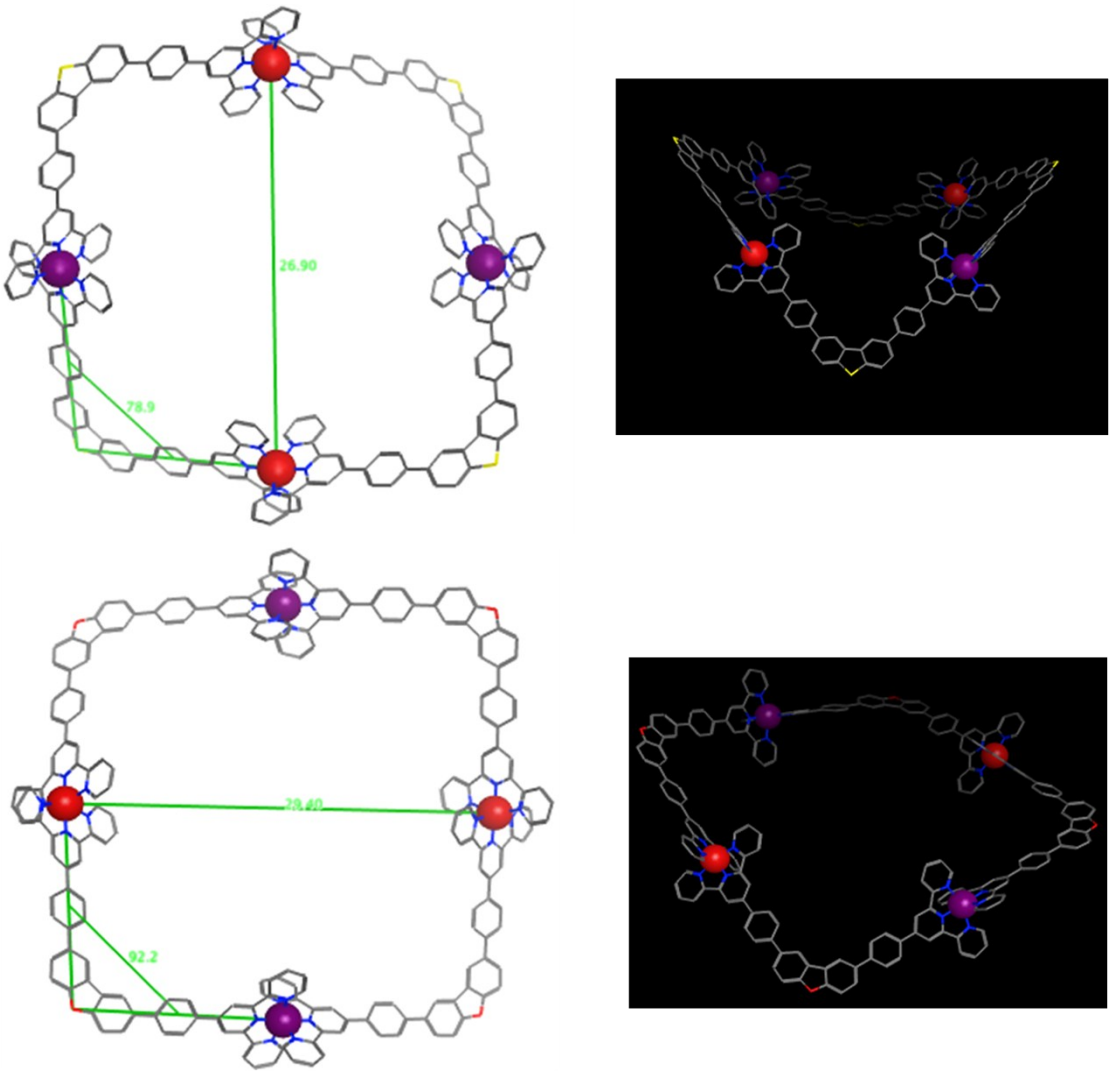

Fig *S25.* Energy-minimized structures from molecular modeling (MOE): **T5** (up), **T6** (bottom).

References:

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