

Supplementary Information

Self-assembled [2]Catenane from Cp*Ir-cornered Trapezoidal Metallacycles

Naifang Liu,^{ab} Sheng-Li Huang,^{*a} Xiaogang Liu,^{ab} He-Kuan Luo^{*a} and T. S. Andy Hor,^{*abc}

^aInstitute of Materials Research & Engineering (IMRE), Agency of Science, Technology, and Research (A*STAR), 2 Fusionopolis Way 138634, Singapore

^bDepartment of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, Singapore

^cDepartment of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, China.

* to whom correspondence should be addressed

Experimental Section

Materials and physical measurements

All reactions and manipulations were performed under a nitrogen atmosphere, using standard Schlenk techniques. Solvents were purified by standard methods prior to use. $[\text{Cp}^*\text{IrCl}_2]_2$ ¹, Tetrapyrido[3,2-*a*:2',3'-*c*:3'',2''-*h*:2''',3'''-*j*]phenazine (tpphz) $\text{L}_1^{\text{I}2}$ and 9,11,20,22-tetraaza-tetrapyridopentacene (TATPP) $\text{L}_2^{\text{I}3}$ were prepared according to the reported procedures.

Elemental analysis was performed on an Elementar vario EL III analyzer, and the complexes were heated at 50 °C under vacuum for 12 h before analysis. ESI-MS spectra were recorded on a Micro TOF II mass spectrometer using electrospray ionization.

Synthesis of L_1^{II} :

The 30 ml thionyl chloride (1mmol/ml in dichloromethane) was added to the compound Isonicotinic Acid (10 mmol), then the solution was refluxed three days under N_2 atmosphere. After that, the unreacted thionyl chloride was removed. The mixture of 1,4-Benzenedimethanol (5 mmol) and triethylamine (10 mmol) in dichloromethane (30 ml) was added dropwise to the dichloromethane solution of Isonicotinoyl Chloride at room temperature with stirring. Then the reaction mixture was refluxed for 8 h under N_2 atmosphere. After cooling to room temperature, the mixture was slowly poured to ice water (50 mL). The solution was extracted with dichloromethane and the organic phase was washed two times with water and one time with brine, then dried over with sodium sulfate anhydrous. After removal of the dichloromethane, the solid residue was purified by re-crystallization with dichloromethane/ether to give compound L_1^{II} . ¹H NMR (CDCl_3 , 400 MHz, 298 K): δ = 8.78 (d, *J* = 4.8 Hz, 4 H), 7.88 (d, *J* = 4.8 Hz, 4 H), 7.48 (s, 4 H), 5.40 (s, 4 H). MS (ESI): *m/z* 348 (M^+). Elemental analysis calc. for $\text{C}_{20}\text{H}_{16}\text{N}_2\text{O}_4$: C, 68.96; H, 4.63; N, 8.04. Found: C, 68.83; H, 4.68; N, 7.83.

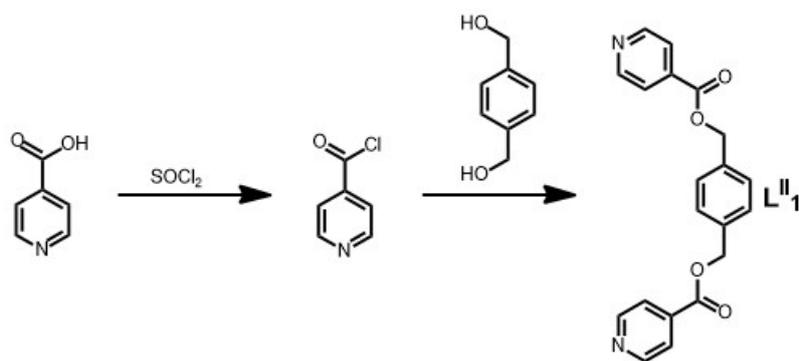


Figure 1. Synthesis of L^{II}_1 .

Synthesis of L^{II}_2 :

The 30 ml thionyl chloride (1mmol/ml in dichloromethane) was added to the compound Isonicotinic Acid (10 mmol), then the solution was refluxed three days under N_2 atmosphere. After that, the unreacted thionyl chloride was removed. The mixture of 4,4'-Bis(hydroxymethyl)biphenyl (5 mmol) and triethylamine (10 mmol) in dichloromethane (30 ml) was added dropwise to the dichloromethane solution of Isonicotinoyl Chloride at room temperature with stirring. Then the reaction mixture was refluxed for 8 h under N_2 atmosphere. After cooling to room temperature, the mixture was slowly poured to ice water (50 mL). The solution was extracted with dichloromethane and the organic phase was washed two times with water and one time with brine, then dried over with sodium sulfate anhydrous. After removal of the dichloromethane, the solid residue was purified by re-crystallization with dichloromethane/ether to give compound L^{II}_2 . 1H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 8.85 (d, J = 5.4 Hz, 4 H), 8.13 (d, J = 5.4 Hz, 4 H), 7.63 (d, J = 8.1 Hz, 4 H), 7.55 (d, J = 8.1 Hz, 4 H), 5.47 (s, 4 H). MS (ESI): m/z 424 (M^+). Elemental analysis calc. for $C_{26}H_{20}N_2O_4$: C, 73.57; H, 4.75; N, 6.60. Found: C, 73.38; H, 4.91; N, 6.44.

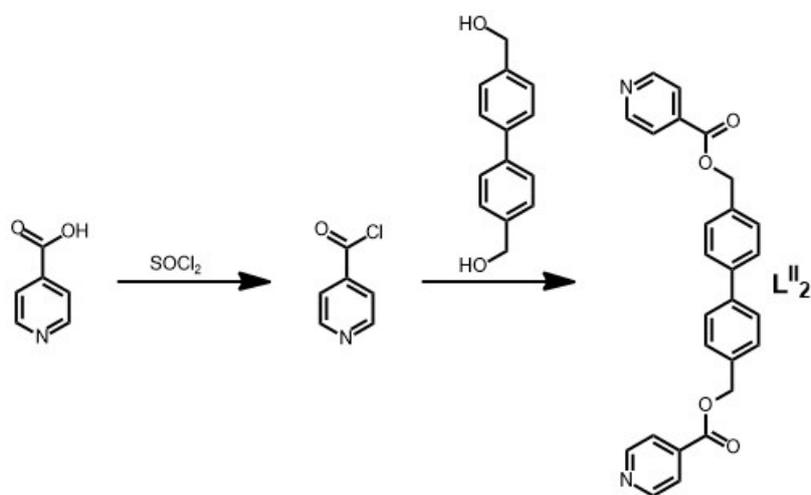


Figure 2. Synthesis of L^{II}_2 .

Synthesis of L^{II}_3 :

The 30 ml thionyl chloride (1mmol/ml in dichloromethane) was added to the compound 4-(4-Pyridyl)Benzoic Acid (2 mmol), then the solution was refluxed three days under N_2 atmosphere. After that, the unreacted thionyl chloride was removed. The mixture of 4,4'-Bis(hydroxymethyl)biphenyl (1 mmol) and triethylamine (2 mmol) in dichloromethane (30 ml) was added dropwise to the dichloromethane solution of 4-(4-Pyridyl)Benzoyl Chloride at room temperature with stirring. Then the reaction mixture was refluxed for 8 h under N_2 atmosphere. After cooling to room temperature, the mixture was slowly poured to ice water (20 mL). The solution was extracted with dichloromethane and the organic phase was washed two times with water and one time with brine, then dried over with sodium sulfate anhydrous. After removal of the dichloromethane, the solid residue was purified by re-crystallization with dichloromethane/ether to give compound L^{II}_3 . 1H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 8.80 (d, J = 4.4 Hz, 4 H), 8.29 (d, J = 6.8 Hz, 4 H), 8.00 (d, J = 4.4 Hz, 4 H), 7.81 (d, J = 6.8 Hz, 4 H), 7.63 (d, J = 8.1 Hz, 4 H), 7.57 (d, J = 8.1 Hz, 4 H), 5.47 (s, 4 H). MS (ESI): m/z 576 (M^+). Elemental analysis calc. for $C_{38}H_{28}N_2O_4$: C, 79.15; H, 4.89; N, 4.86. Found: C, 79.01; H, 4.99; N, 4.71.

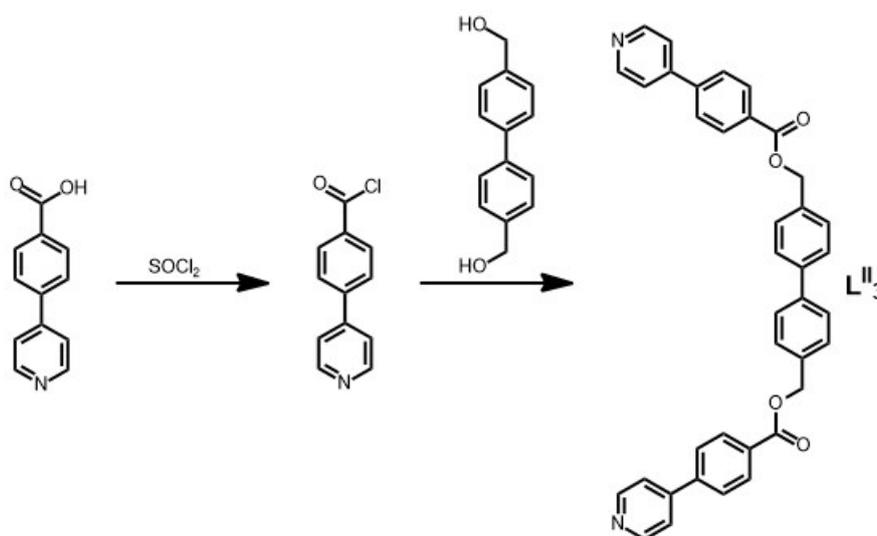


Figure 3. Synthesis of L^{II}_3 .

Synthesis of L^{II}_4 :

4,4'-Bis(chloromethyl)biphenyl (1.0 mmol, 0.25g), 4-Pyridylboronic Acid (2.5 mmol, 0.30g), K_2CO_3 (15 mmol, 2.05g) and Bis(triphenylphosphine)palladium Dichloride (0.05 mmol, 0.035g) were dissolved in a mixture of dioxane (28 ml) and H_2O (12 ml). After the mixture had been degassed by bubbling through a nitrogen flow for 1 h, it was heated to reflux for 2 days. Then, the mixture was cooled and H_2O (50 ml) was added. The solution was extracted with dichloromethane and the organic phase was washed two times with water and one time with brine, then dried over with sodium sulfate anhydrous. After removal of the dichloromethane, the solid residue was purified by re-crystallization with dichloromethane/hexane to give compound L^{II}_4 . 1H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 8.43 (d, J = 4.0 Hz, 4 H), 7.54 (d, J = 6.4 Hz, 4 H), 7.29 (d, J = 6.4 Hz, 4 H), 7.24 (d, J = 4.0 Hz, 4 H), 3.95 (s, 4 H). MS (ESI): m/z 336 (M^+). Elemental analysis calc. for $C_{24}H_{20}N_2$: C, 85.68; H, 5.99; N, 8.33. Found: C, 85.41; H, 6.11; N, 8.16.

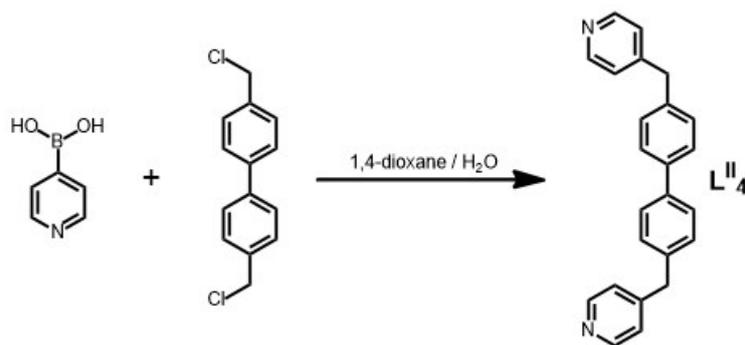


Figure 4. Synthesis of L^{II}_4 .

Synthesis of L^{II}_5 :

1,1'-bis(2,4-dinitrophenyl-4,4'-bipyridinium) dichloride (2 mmol, 1.12g) and 4-aminomethylpyridine (4.05 mmol, 0.44g) were combined in ethanol (50 mL). The mixture was stirred at 110 °C for 48 h under N_2 atmosphere. A greenish brown precipitate was filtered out, rinsed with ethanol, and dried in a vacuum oven to give $L^{II}_5 \cdot 2Cl$ as a greenish brown powder. A portion of $L^{II}_5 \cdot 2Cl$ (51.9 mg, 126 μ mol) was dissolved in 20 ml H_2O and filtered to remove the un-dissolved purity, then the filtration was added slowly to the saturated aqueous solution of NH_4PF_6 (20 mL) and stirred for 3 h. The resulting precipitate was filtered and rinsed with water to give $L^{II}_5 \cdot 2PF_6$ as a brown powder (1.0g, 80%). 1H NMR (DMSO- D_6 , 400 MHz, 298 K): δ = 9.52 (d, J = 6.5 Hz, 4 H), 8.81 (d, J = 6.5 Hz, 4 H), 8.65 (d, J = 5.7 Hz, 4 H), 7.47 (d, J = 5.7 Hz, 4 H), 6.01 (s, 4 H); MS (ESI): 170.0 $[M - 2PF_6]^{2+}$, 485.0 $[M - PF_6]^+$. Elemental analysis calc. for $C_{22}H_{20}N_4$: C, 41.92; H, 3.20; N, 8.89. Found: C, 41.76; H, 3.31; N, 8.77.

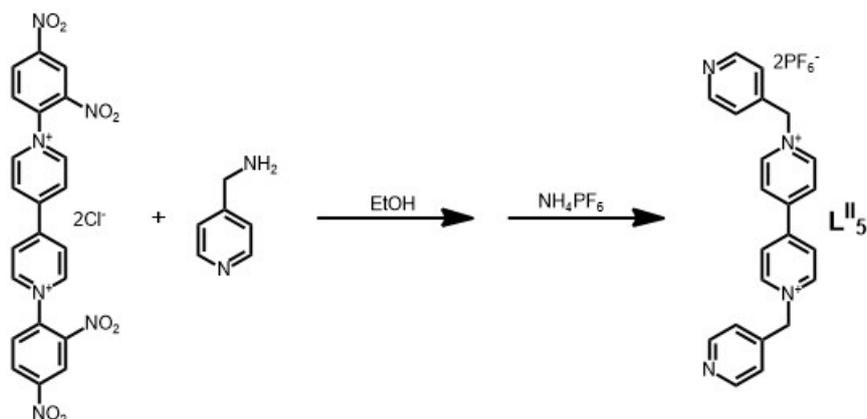


Figure 5. Synthesis of L^{II}_5 .

Synthesis of complex 1:

$[\text{Cp}^*\text{IrCl}_2]_2$ (0.2 mmol, 160 mg) was dissolved in 10 ml dry dichloromethane, then AgOTf (0.8 mmol, 205 mg) was added to it and stirred at room temperature for 6 h. Followed by filtration to remove insoluble AgCl, the L^{I}_1 (0.2 mmol, 76.4 mg) was added to the filtrate and heated at 60 °C for 6 h. Then, the solvent was evaporated and the solid was dissolved in 10 ml methanol. Then, L^{II}_1 (0.2 mmol, 69.6 mg) in 6 ml mixed solution of dichloromethane and methanol (1:2) was added. After the solution was stirred at room temperature for 12 h, the solvent was concentrated to about 5 mL and diethyl ether was added, giving **1** as yellow solid. Yield: 205 mg, 93%; ^1H NMR (DMSO- D_6 , 400 MHz, 298 K): δ = 10.23 (d, J = 8.0 Hz, 4 H), 9.81 (d, J = 5.2 Hz, 4 H), 8.59 (dd, J = 8.0 Hz, 5.2 Hz, 4 H), 8.23 (d, J = 6.4 Hz, 4 H), 7.47 (d, J = 6.4 Hz, 4 H), 7.10 (s, 4 H), 5.17 (s, 4 H); MS (ESI): 512.5 [**1** – 3OTf] $^{3+}$, 842.7 [**1** – 2OTf] $^{2+}$, 1834.3 [**1** – OTf] $^+$. Elemental analysis calc. for $\text{C}_{68}\text{H}_{58}\text{F}_{12}\text{N}_8\text{O}_{16}\text{Ir}_2\text{S}_4$ (M = 1983.91): C, 41.17; H, 2.95; N, 5.65. Found: C, 41.33; H, 3.11; N, 5.46 %.

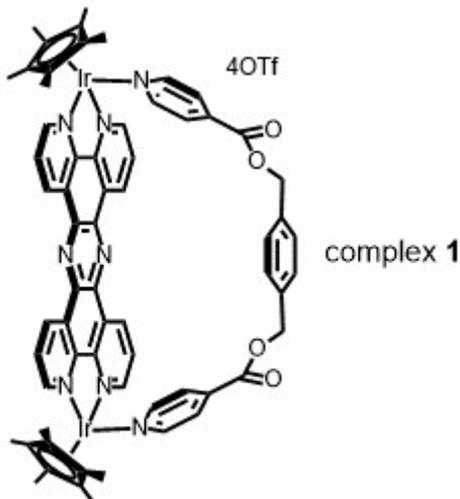


Figure 6. Chemical structure of complex 1.

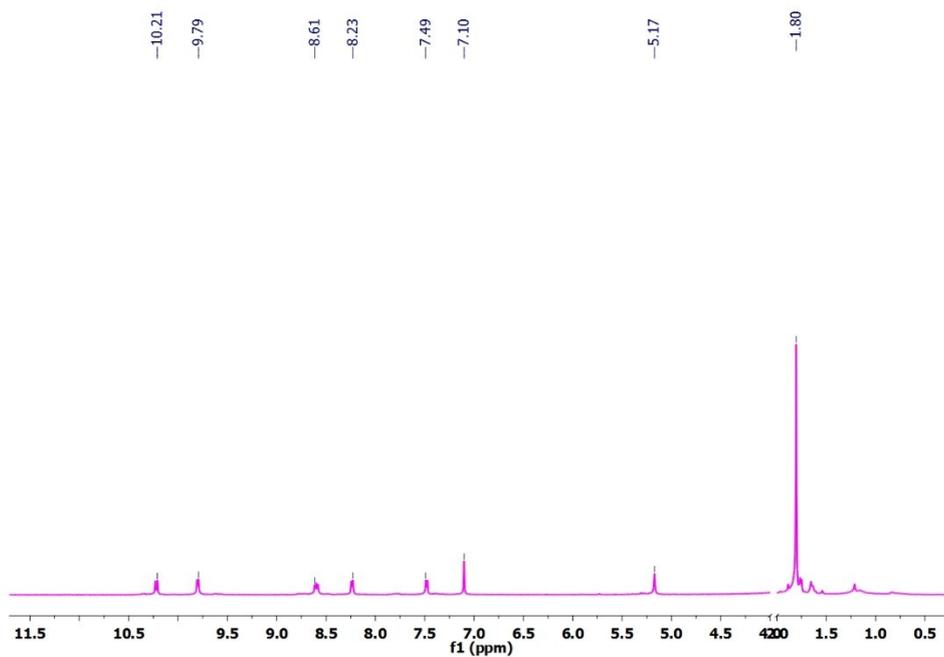


Figure 7. ^1H NMR spectra (400 MHz, $[\text{D}_6]\text{DMSO}$, 25 °C, TMS as an external standard) of **1**.

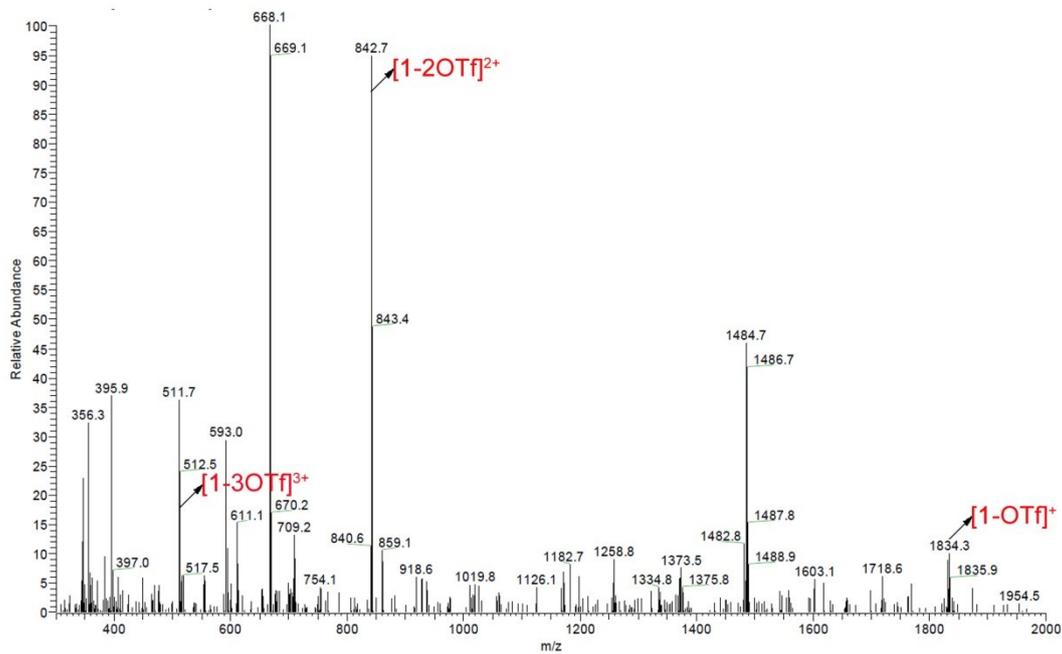


Figure 8. The experimental ESI-MS spectra of complex **1**.

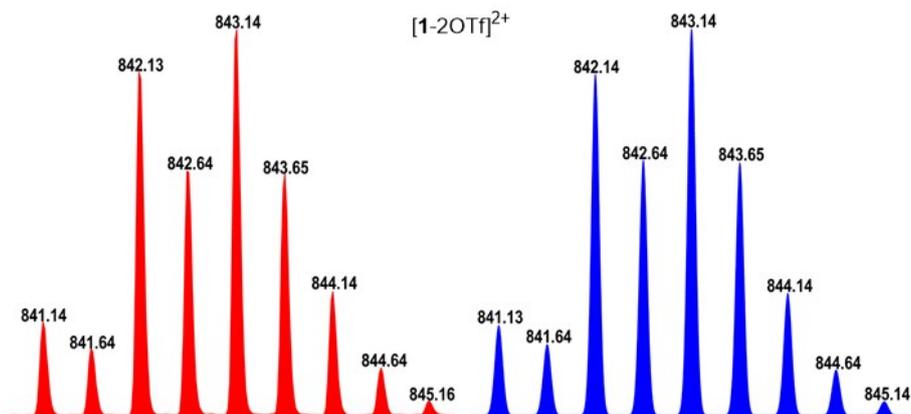


Figure 9. Experimental (left, red) and calculated (right, blue) ESI-MS spectra (2+) of **1**.

Synthesis of complex **2**:

The synthetic method of **2** is similar to **1**, just changed L^{II}_1 as L^{II}_2 . 1H NMR (DMSO- D_6 , 400 MHz, 298 K): δ = 10.21 (d, J = 8.0 Hz, 4 H), 9.75 (d, J = 5.2 Hz, 4 H), 8.64 (d, J = 6.4 Hz, 4 H), 8.57 (dd, J = 8.0 Hz, 5.2 Hz, 4 H), 7.68 (d, J = 6.4 Hz, 4 H), 7.31 (d, J = 8.4 Hz, 4 H), 7.26 (d, J = 8.4 Hz, 4 H), 5.33 (s, 4 H); MS (ESI): 537.8 [**2** - 3OTf] $^{3+}$, 880.5 [**2** - 2OTf] $^{2+}$, 1910.3 [**2** - OTf] $^{+}$. The complex **2** consisted of a cationic macrocyclic backbone and four $CF_3SO_3^-$ anions with an overall chemical formula: $C_{74}H_{62}F_{12}N_8O_{16}Ir_2S_4$ ($M = 2060.00$). C, 43.15; H, 3.03; N, 5.44. Found: C, 43.33; H, 3.22; N, 5.27 %.

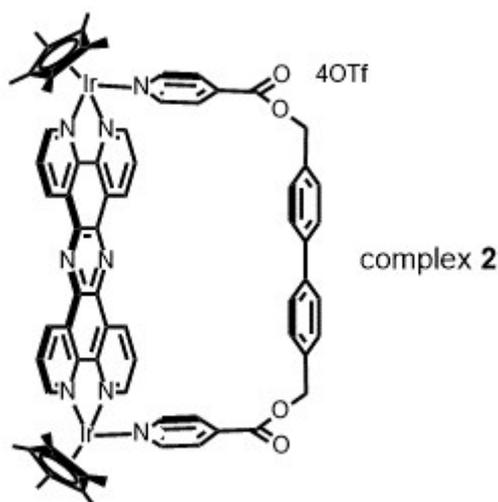


Figure 10. Chemical structure of complex **2**.

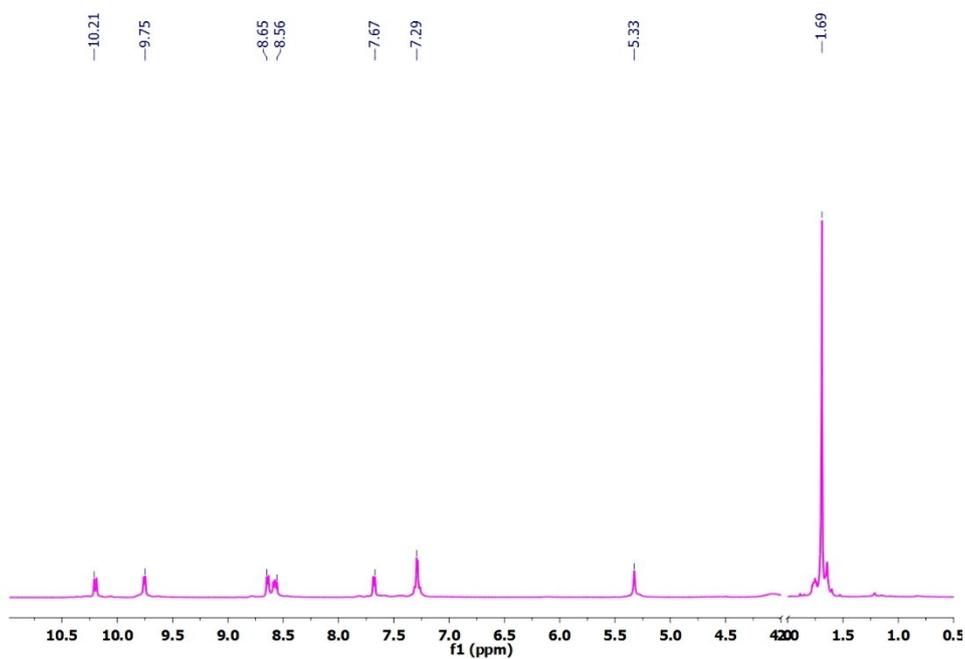


Figure 11. ^1H NMR spectra (400 MHz, $[\text{D}_6]\text{DMSO}$, 25 $^\circ\text{C}$, TMS as an external standard) of **2**.

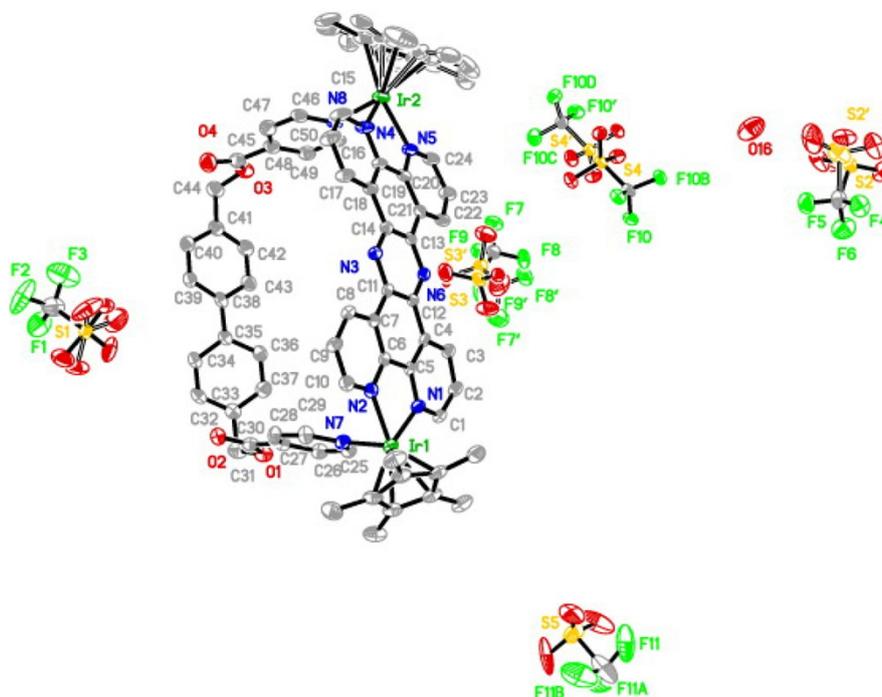


Figure 12. Single-crystal X-ray structure of complex **2**·2MeOH·H₂O with thermal ellipsoids drawn at the 30% level (MeOH molecules were omitted due to disorder).

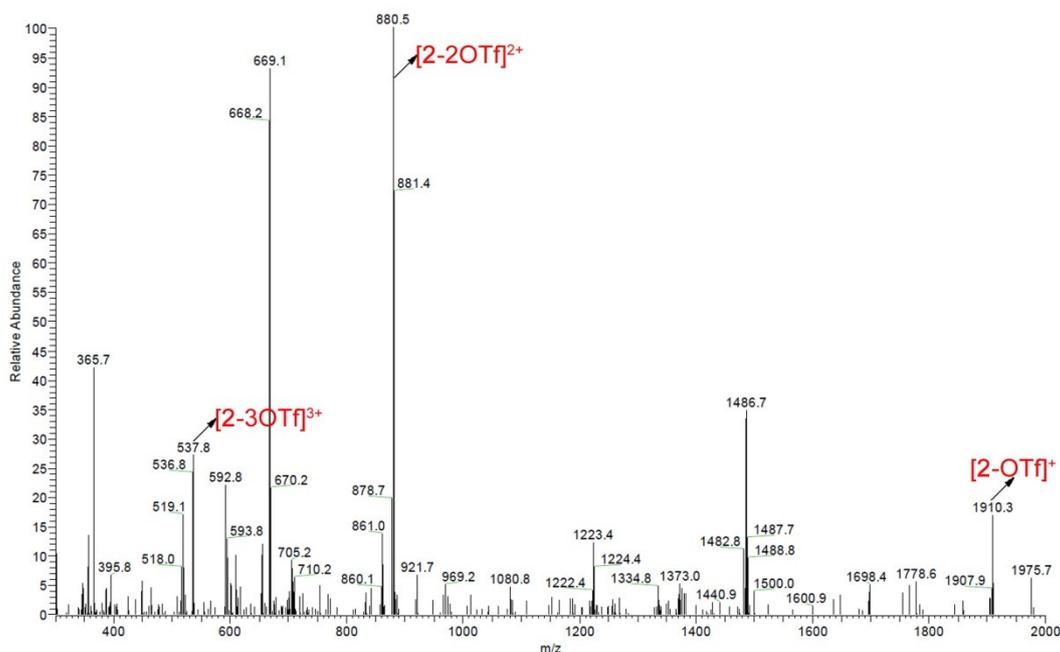


Figure 13. The experimental ESI-MS spectra of complex **2**.

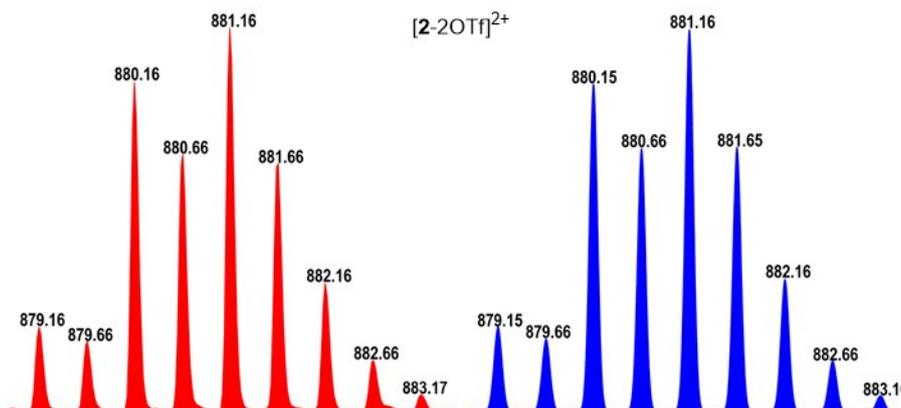


Figure 14. Experimental (left, red) and calculated (right, blue) ESI-MS spectra (2+) of

2.

Synthesis of complex **3**:

The synthetic method of **3** is similar to **1**, just changed L^{II}_1 as L^{II}_2 . 1H NMR (DMSO- D_6 , 400 MHz, 298 K): δ = 9.71 (d, J = 5.2 Hz, 4 H), 9.49 (d, J = 8.4 Hz, 4 H), 8.44 (dd, J = 8.4 Hz, 5.2 Hz, 4 H), 8.40 (d, J = 6.0 Hz, 4 H), 7.44 (d, J = 6.0 Hz, 4 H), 5.18 (d, J = 7.6 Hz, 4 H), 3.55 (s, 4 H), 3.09 (d, J = 7.6 Hz, 4 H); MS (ESI): 507.8 [**3** – 6OTf] $^{6+}$, 836.5 [**3** – 4OTf] $^{4+}$, 1165.6 [**3** – 3OTf] $^{3+}$, 1822.2 [**3** – 2OTf] $^{2+}$. Elemental analysis calc. for $C_{144}H_{124}F_{24}N_{16}O_{24}Ir_4S_8$ (M = 3943.97): C, 43.85; H, 3.17; N, 5.68.

(DMSO-D₆, 400 MHz, 298 K): δ = 10.22 (d, J = 8.0 Hz, 4 H), 9.44 (d, J = 5.2 Hz, 4 H), 8.95 (dd, J = 8.0 Hz, 5.2 Hz, 4 H), 8.71 (d, J = 5.6 Hz, 4 H), 7.47 (m, 8 H), 7.62 (d, J = 5.6 Hz, 4 H), 5.96 (s, 4 H); MS (ESI): 419.5 [**4** - 2PF₆ - 2OTf]⁴⁺, 985.1 [**4** - PF₆ - OTf]²⁺. Elemental analysis calc. for C₇₀H₆₂F₂₄N₁₀O₁₂Ir₂P₂S₄ (M = 2265.90): C, 37.10; H, 2.76; N, 6.18. Found: C, 37.22; H, 2.88; N, 6.06 %.

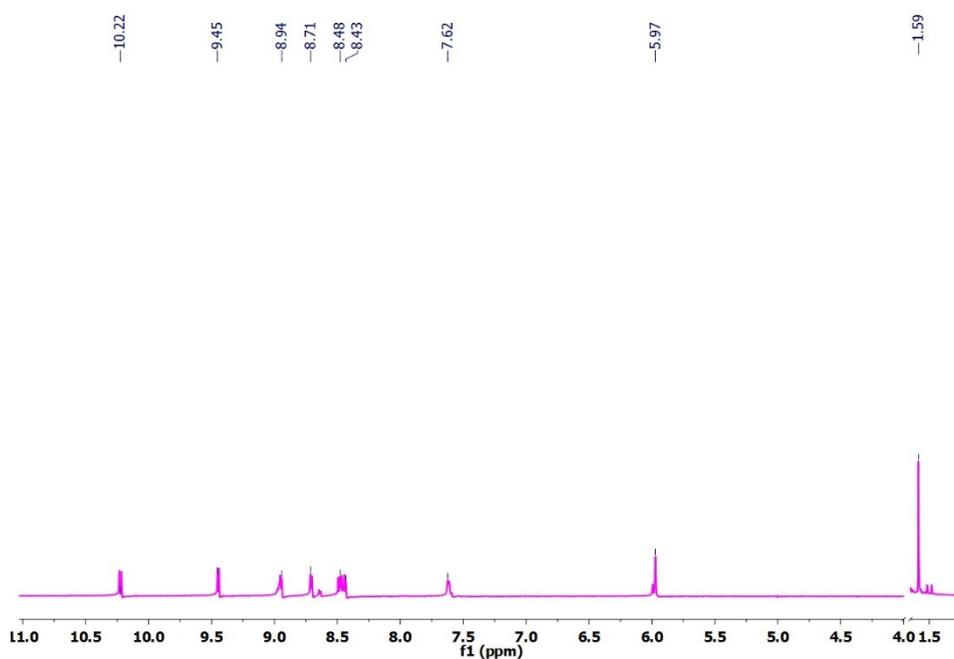
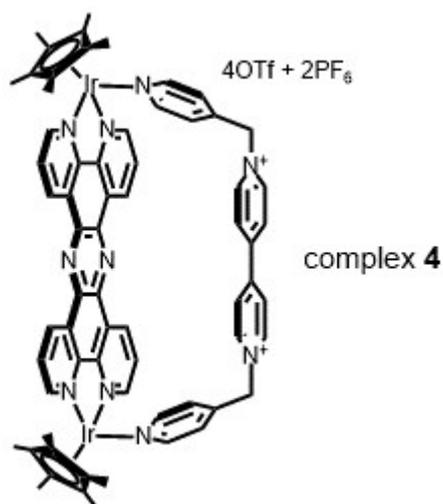


Figure 19. ¹H NMR spectra (400 MHz, [D₆]DMSO, 25 °C, TMS as an external standard) of **4**.

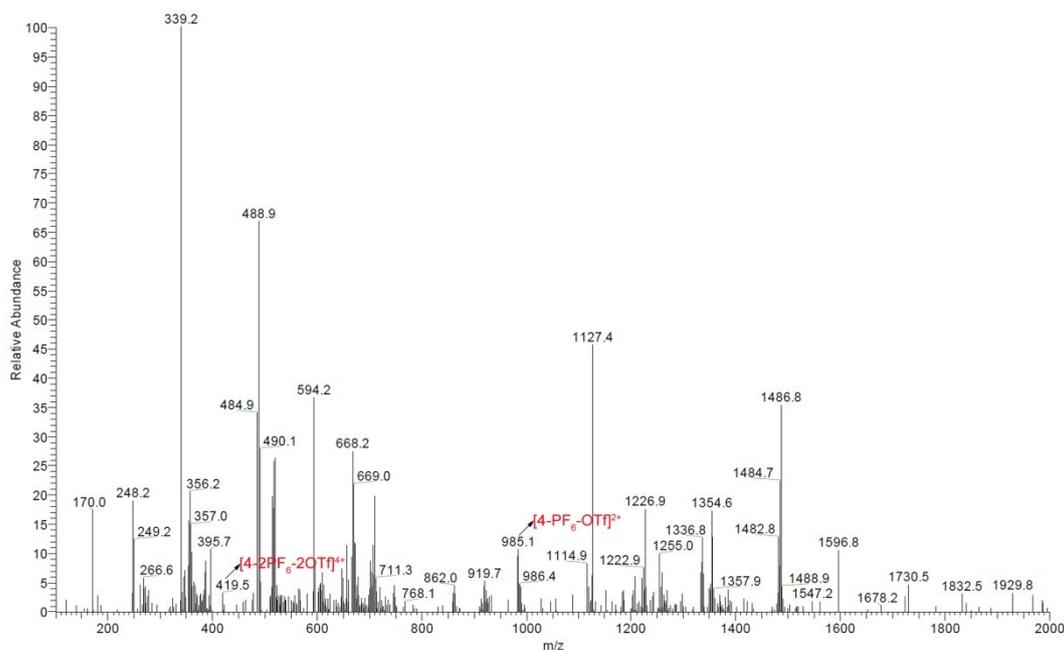


Figure 20. The experimental ESI-MS spectra of complex **4**.

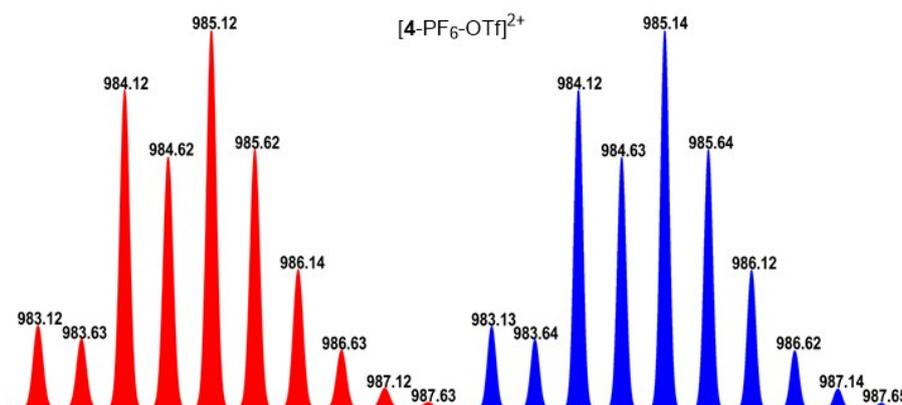


Figure 21. Experimental (left, red) and calculated (right, blue) ESI-MS spectra (2+) of **4**.

Synthesis of complex **5**:

The synthetic method of **5** is similar to **1**, just changed L^{II}_1 as L^{II}_2 . 1H NMR (DMSO- D_6 , 400 MHz, 298 K): δ = 9.85 (d, J = 8.0 Hz, 4 H), 9.69 (dd, J = 8.0 Hz, 4.0 Hz, 4 H), 9.47 (d, J = 4.0 Hz, 4 H), 8.61 (s, 4 H), 8.48 (d, J = 6.0 Hz, 4 H), 8.41 (d, J = 6.0 Hz, 4 H), 7.58 (d, J = 8.0 Hz, 4 H), 7.35 (d, J = 8.0 Hz, 4 H), 5.73 (s, 4 H); MS (ESI): 541.9 [**5** - 3OTf] $^{3+}$. Elemental analysis calc. for $C_{78}H_{64}F_{12}N_{10}O_{12}Ir_2S_4$ (M = 2074.08): C, 45.17; H, 3.11; N, 6.75. Found: C, 45.35; H, 3.28; N, 6.56 %.

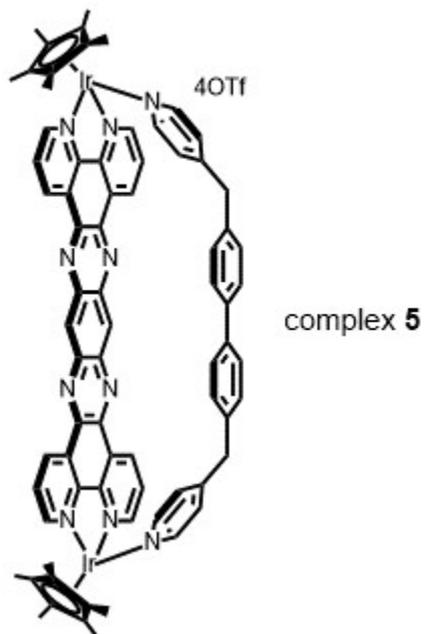


Figure 22. Chemical structure of complex 5.

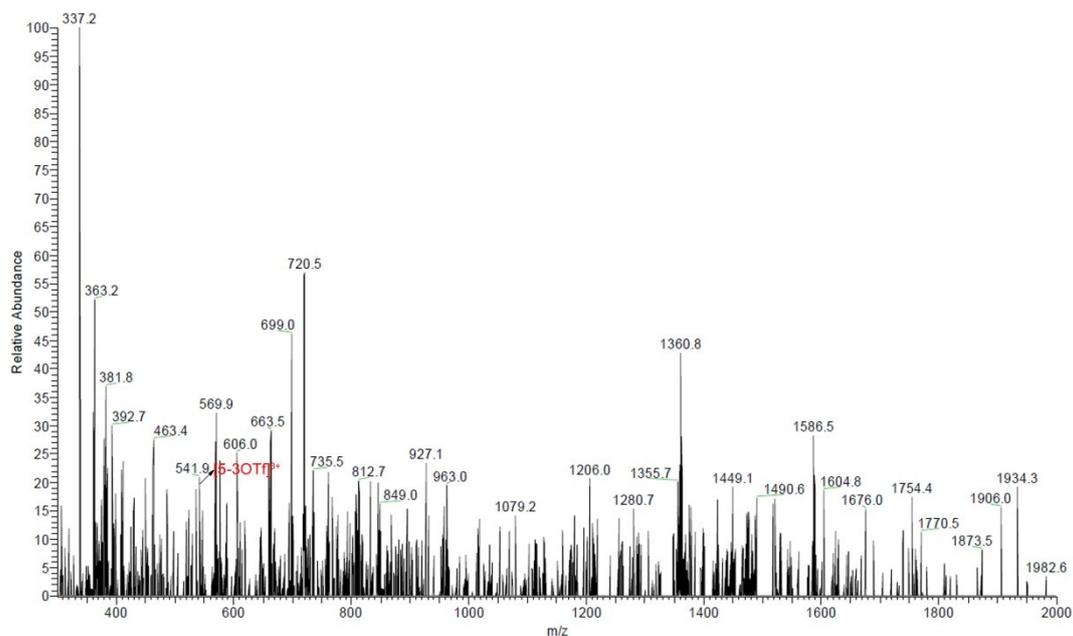


Figure 23. The experimental ESI-MS spectra of complex 5.

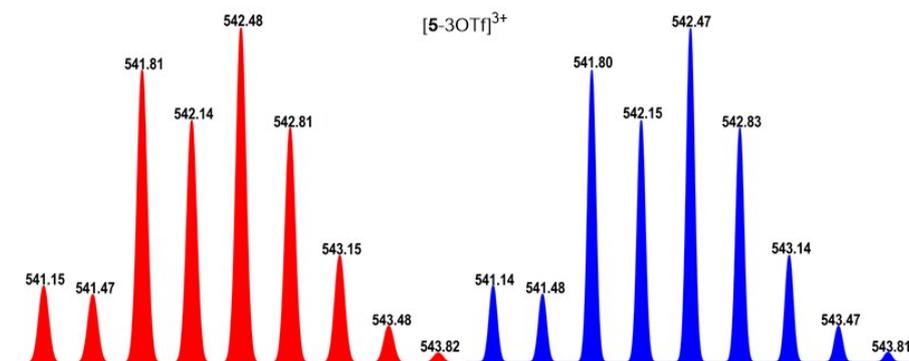


Figure 24. Experimental (left, red) and calculated (right, blue) ESI-MS spectra (3+) of **5**.

Crystal structure analysis

Diffraction data were collected on a Bruker APEX DUO diffractometer equipped with triumph-monochromated Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$) using the ρ - and ω -scan technique. The data was collected at 173 K temperature and the structure was solved by using SHELXS-97 program.⁴ SADABS⁵ absorption corrections and SQUEEZE process⁶⁻⁷ were applied to the data. Crystallographic data are summarized in Table 1.

In asymmetric unit of this data, there were disordered anions and solvents (one-third triflate anion and two methanol molecules) which could not be restrained properly. Therefore, SQUEEZE algorithm was used to omit them. The triflate anions and one pentamethylcyclopentadienyl ligand (Cp* for short) were disordered and they were divided into two parts (56:44, 65:35, 57:43, 72:28 for triflate anions and 75:25 for Cp*). 56 ISOR, 3 SIMU and 29 DFIX instructions were used to restrain anions and Cp* fragments so that there were 431 restraints in the data. Hydrogen of water molecule could not be found and others were put in calculated positions.

Table 1. Crystallographic data and structure refinement results for complex **2**·2MeOH·H₂O.

Complex	2 ·2MeOH·H ₂ O
Formula	C ₇₆ H ₇₂ F ₁₂ Ir ₂ N ₈ O ₁₉ S ₄
Mr	2142.05
Crystal system	Trigonal
Space group	R-3

a, Å	27.7386(6)
b, Å	27.7386(6)
c, Å	54.2411(13)
α , °	90
β , °	90
γ , °	120
V, Å ³	36143.3(18)
Z	18
Dc, g cm ⁻³	1.771
μ , mm ⁻¹	8.202
θ range/°	2.011 to 68.279
GOF	1.040
R1	0.0629
WR2 [I > 2 σ (I)]	0.1639
R1	0.0728
WR2 [all data]	0.1752
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$, Å ⁻³	4.942 and -2.736
$^a R1 = \sum F_o - F_c / \sum F_o , wR2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$.	

References

- (1) White, C.; Yates, A.; Maitles, P. M. *Inorg. Synth.* **1992**, *29*, 228-234.
- (2) Bolger, J.; Gourdon, A.; Ishow, E.; Launay, J. P. *Inorg. Chem.* **1996**, *35*, 2937-2944.
- (3) Kim, M. J.; Konduri, R.; Ye, H. W.; MacDonnell, F. M.; Puntoriero, F.; Serroni, S.; Campagna, S.; Holder, T.; Kinsel, G.; Rajeshwar, K. *Inorg. Chem.* **2002**, *41*, 2471-2476.
- (4) a) Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112-122; b) Sheldrick, G. M. *SHELXS-97*: Program for the Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, **2008**; c) Sheldrick, G. M. *SHELXL-2014/7*: Program for the Solution of Crystal Structures, University of Göttingen, Göttingen, Germany, **2014**.
- (5) Sheldrick, G. M. *SADABS (2.01)*, *Bruker/Siemens Area Detector Absorption Correction Program*; Bruker AXS: Madison, WI, **1998**.
- (6) Spek, A. L. *Acta Cryst.* **2009**, *D65*, 148-155.
- (7) Spek, A.L. *Acta Cryst.* **2015**, *C71*, 9-18.