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Supporting Information for

Sunlight induced photocycloaddition and host-guest property of self-assembled organometallic macrocycles based on a versatile building block

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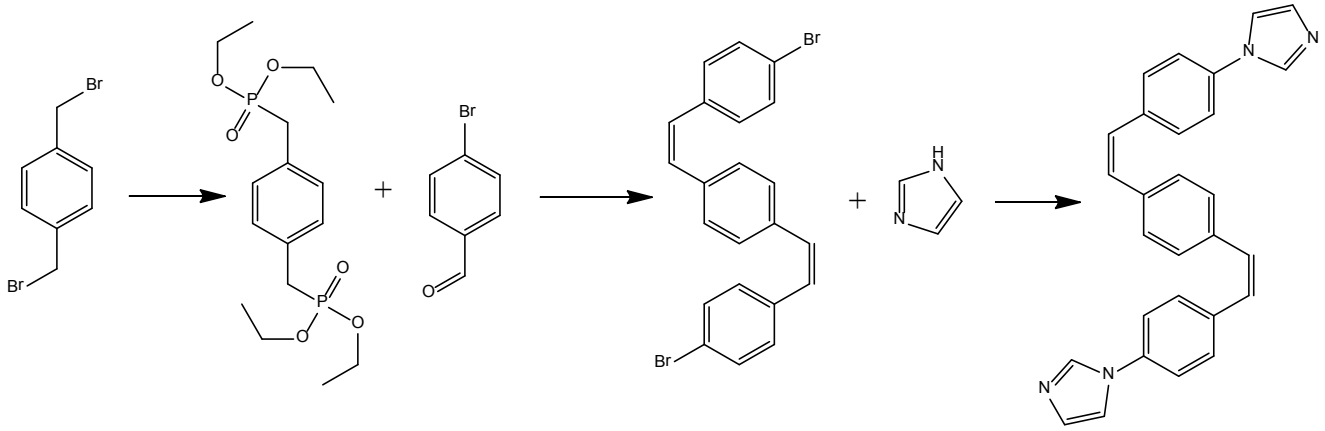
S1.

Table 1. Crystal data and structure refinement of **2b, 3a, 3b and 4b**

	2b	**3a**	**3b**	**4b**
Formula	$C_{98}H_{104}F_{12}N_{16}O_{14}Rh_4S_4$	$C_{84}H_{116}F_6N_8O_{14}Ir_2S_2$	$C_{84}H_{116}F_6N_8O_{14}Rh_2S_2$	$C_{68}H_{70}F_6N_8O_7Rh_2S_2$
F_w	2497.85	2024.36	1845.78	1421.12
Crystal system	Triclinic	Monoclinic	Monoclinic	Orthorhombic
space group	P-1	C2/c	C2/c	Fdd2
a (Å)	9.1607(8)	36.2926(8)	36.307(3)	31.441(5)
b (Å)	13.0306(11)	16.2805(4)	16.2368(14)	17.427(3)
c (Å)	22.4758(18)	28.4835(6)	28.488(2)	23.221(4)
α (°)	91.9670(10)	90	90	90
β (°)	96.5700(10)	123.0740(10)	123.1350(10)	90
γ (°)	102.4650(10)	90	90	90
V (Å ^{3})	2597.7(4)	14102.8(6)	14063(2)	12723(3)
Z	1	8	8	8
D_c (Mg / m^3)	1.597	1.907	1.744	1.484
μ(Mo-Kα)(mm^{-1})	0.796	8.565	0.626	0.664
F(000)	1268	8224	7712	5824
θ range (°)	0.914 ~ 27.678	2.906 ~ 67.997	1.486 ~ 27.544	1.60 ~ 26.10
Limiting indices (hkl)	-11, 11; -14, 17; -28, 29	-42, 39; -19, 16; -30, 33	-47, 44; -21, 16; -31, 36	-33, 38; -21, 21; -28, 27
Reflections collected	19301	35496	51385	20655
Independent reflections	11935	12189	16108	6209
R_{int}	0.0162	0.0504	0.0887	0.1020
Completeness to θ (°)	98.6 %	95.0 %	99.6 %	99.8 %
Data / restraints / parameters	11935 / 28 / 735	12189 / 42 / 872	16108 / 16 / 835	32977 / 254 / 1515
Goodness-of-fit on F^2	1.047	1.010	0.933	0.963
R_1[a],wR_2[a] [I > 2σ(I)]	0.0338, 0.0942	0.0870, 0.2003	0.0599, 0.1364	0.0696, 0.1527
R_1, wR_2 (all data)	0.0435, 0.1076	0.0976, 0.2103	0.1218, 0.1599	0.1212, 0.1740

[a] $R_1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$; $wR_2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

S2. Synthetize of the ligand $\mathbf{L_2}$:



1 **2** **3**

The mixture of 1,4-bis(bromomethyl)benzene 6 (1.3 g, 4.93 mmol) and triethylphosphite (20 mL) was heated to reflux for 5 h. Afterwards, access triethylphosphite was removed under the reduced pressure. The remaining white slurry was poured into a large amount of hexanes to extract residual remains of triethylphosphite. A white solid of compound **1** was obtained by filtration (1.79 g, 4.73 mmol, 96%).

The solution of compound **1** (0.76 g, 2.0 mmol), and 4-Bromobenzaldehyde (0.82 g, 4.4 mmol) in THF (10 mL) was stirred at room temperature overnight after the slow addition of potassium tert-butoxide (1 M in THF, 4.2 mL, 4.2 mmol) under nitrogen atmosphere. The reaction was quenched with sat. NH4Cl aq. and was extracted with ethyl acetate three times. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, concentrated in vacuo. The residue was purified by silica gel column chromatography to give **2** as a white crystal.

The imidazole (0.14g, 2.1 mmol) was added into the toluene solution of compound **2** (0.44g, 1.0 mmol) then stirred for 24 h under reflux. The green yellow powder of compound **3** was obtain after wash and recrystallization..

S3. The characterization data of complex **2a~4b:**

Data of complex **2a**: IR (KBr disk): ν = 3123.3, 1602.8, 1532.1, 1448.4, 1354.1, 1262.4, 1223.6, 1153.4, 1075.2, 1030.1, 822.3, 759.3, 638.42 cm^{-1}. ^{1}H-NMR (400 MHz, [D_6]-DMSO, 25 °C, TMS): δ = 7.96 (q, 8H, Ar(BiBzIm)-H), 7.62 (s, 4H, imidazolyl(N-C*-N)-H), 7.36 (q, 8H, Ar(BiBzIm)-H), 7.13 (s, 4H, imidazolyl(Rh-N-C*-C)-H), 6.67 (s, 8H, phenyl(DiBzIm)-H), 5.73 (s, 4H, imidazolyl(Rh-N-C-C*)-H), 1.82 (s, 60H; Cp*-H) ppm. Elemental analysis (%) calcd. for $C_{98}H_{104}F_{12}N_{16}O_{14}Ir_4S_4$: C 41.23; H 3.67; N 7.85; Found (%): C 41.28, H 3.75, N 7.69.

Data of complex **2b**: IR (KBr disk): ν = 3123.1, 1602.6, 1533.1, 1448.4, 1354.0, 1262.8, 1223.6, 1153.4, 1075.0, 1030.1, 822.3, 759.3, 638.42 cm^{-1}. ^{1}H-NMR (400 MHz, [D_6]-DMSO, 25 °C, TMS): δ = 8.01 (q, 8H, Ar(BiBzIm)-H), 7.60 (s, 4H, imidazolyl(N-C*-N)-H), 7.43 (q, 8H, Ar(BiBzIm)-H), 7.17 (s, 4H, imidazolyl(Rh-N-C*-C)-H), 6.67 (s, 8H, phenyl(DiBzIm)-H), 5.71 (s, 4H, imidazolyl(Rh-N-C-C*)-H), 1.87 (s, 60H; Cp*-H) ppm. Elemental analysis (%) calcd. For $C_{98}H_{104}F_{12}N_{16}O_{14}Rh_4S_4$: C 47.12; H 4.20; N 8.97; Found (%): C 47.25, H 4.14, N 8.87.

Data of complex **3a**: IR (KBr disk, cm-1): *v* = 3123.5, 1604.1, 1523.4, 1451.2, 1353.9, 1256.1, 1224.6, 1158.5, 1125.4, 1068.7, 1031.5, 741.0 cm^{-1}. ^{1}H NMR (400 MHz, [D_6]-DMSO, 25 °C, TMS): 8.45 (s, 2H, imidazolyl(N-C*-N)-H), 7.92 (q, 4H, Ar(BiBzIm)-H), 7.39 (s, 2H, imidazolyl(Rh-N-C*-C)-H), 7.37 (q, 4H, Ar(BiBzIm)-H), 7.27 (d, 4H, *J* = 8.0 Hz, side-phenyl-H), 7.20 (d, 4H, *J* = 12.0 Hz, side-phenyl-H), 7.12 (s, 4H, centra-phenyl-H), 6.65 (d, 2H, *J* = 12.0 Hz, olefin-H), 6.57 (d, 2H, *J* = 12.0 Hz, olefin-H), 5.72 (s, 2H, imidazolyl (Rh-N-C-C*)-H) 1.82 (s, 30H, Cp*-H) ppm. Elemental analysis calcd (%) for $C_{68}H_{70}F_6N_8O_7Ir_2S_2$: C 48.79; H 4.22; N 6.69. Found: C 48.84; H 4.31; N 6.68.

Data of complex **3b**: IR (KBr disk, cm^{-1}): *v* = 3123.9, 1604.9, 1523.4, 1451.1, 1353.9, 1256.1, 1224.2, 1158.7, 1125.4, 1069.7, 1031.5, 741.4 cm^{-1}. ^{1}H NMR (400 MHz, [D_6]-DMSO, 25 °C, TMS): 8.33 (s, 2H, imidazolyl(N-C*-N)-H), 7.96 (q, 4H, Ar(BiBzIm)-H), 7.37 (s, 2H, imidazolyl(Rh-N-C*-C)-H), 7.35 (q, 4H, Ar(BiBzIm)-H), 7.31 (d, 4H, *J* = 8.0 Hz, side-phenyl-H), 7.22 (d, 4H, *J* = 12.0 Hz, side-phenyl-H), 7.02 (s, 4H, centra-phenyl-H), 6.69 (d, 2H, *J* = 12.0 Hz, olefin-H), 6.59 (d, 2H, *J* = 12.0 Hz, olefin-H), 5.77 (s, 2H, imidazolyl (Rh-N-C-C*)-H) 1.87 (s, 30H, Cp*-H) ppm. Elemental analysis calcd (%) for $C_{68}H_{70}F_6N_8O_7Rh_2S_2$: C 54.62; H 4.72; N 7.49. Found(%): C 54.71; H 4.70; N 7.45.

Data of complex **4a**: IR (KBr disk, cm^{-1}): *v* = 1595.8 (s, C=O), 3007.2, 2965.7 and 2926.3 (m, Me). ^{1}H NMR (400 MHz, [D_6]-DMSO, 25 °C, TMS): 8.20 (s, 2H, imidazolyl(N-C*-N)-H), 7.76 (s, 2H, imidazolyl(Rh-N-C*-C)-H), 7.55 (s, 2H, imidazolyl (Rh-N-C-C*)-H), 7.40 (d, 4H, side-phenyl-H), 7.40 (d, 4H, side-phenyl-H), 7.12 (s, 4H, centra-phenyl-H), 6.88 (d, 2H, olefin-H), 6.85 (d, 2H, olefin-H), 1.97 (s, 6H, Me-H) 1.70 (s, 30H, Cp*-H) ppm. Elemental analysis calcd (%) for $C_{60}H_{64}F_6N_4O_{10}Ir_2S_2$: C 46.08; H 4.13; N 3.58. Found(%): C 46.10; H 4.26; N 3.54.

Data of complex **4b**: IR (KBr disk, cm^{-1}): *v* = 1596.5 (s, C=O), 3007.0, 2965.7 and 2926.4 (m, C-CH_3). ^{1}H NMR (400 MHz, [D_6]-DMSO, 25 °C, TMS): 8.18 (s, 2H, imidazolyl(N-C*-N)-H), 7.88 (s, 2H, imidazolyl(Rh-N-C*-C)-H), 7.68 (s, 2H, imidazolyl (Rh-N-C-C*)-H), 7.43 (d, 4H, *J* = 8.0 Hz, side-phenyl-H), 7.37 (d, 4H, *J* = 8.0 Hz, side-phenyl-H), 7.06 (s, 4H, centra-phenyl-H), 6.79 (d, 2H, *J* = 12.0 Hz, olefin-H), 6.73 (d, 2H, *J* = 12.0 Hz, olefin-H), 1.97 (s, 6H, Me-H) 1.74 (s, 30H, Cp*-H) ppm. Elemental analysis calcd (%) for $C_{60}H_{64}F_6N_4O_{10}Rh_2S_2$: C, 52.03; H, 4.66; N, 4.04 Found(%): C 51.97; H 4.71; N 3.99.

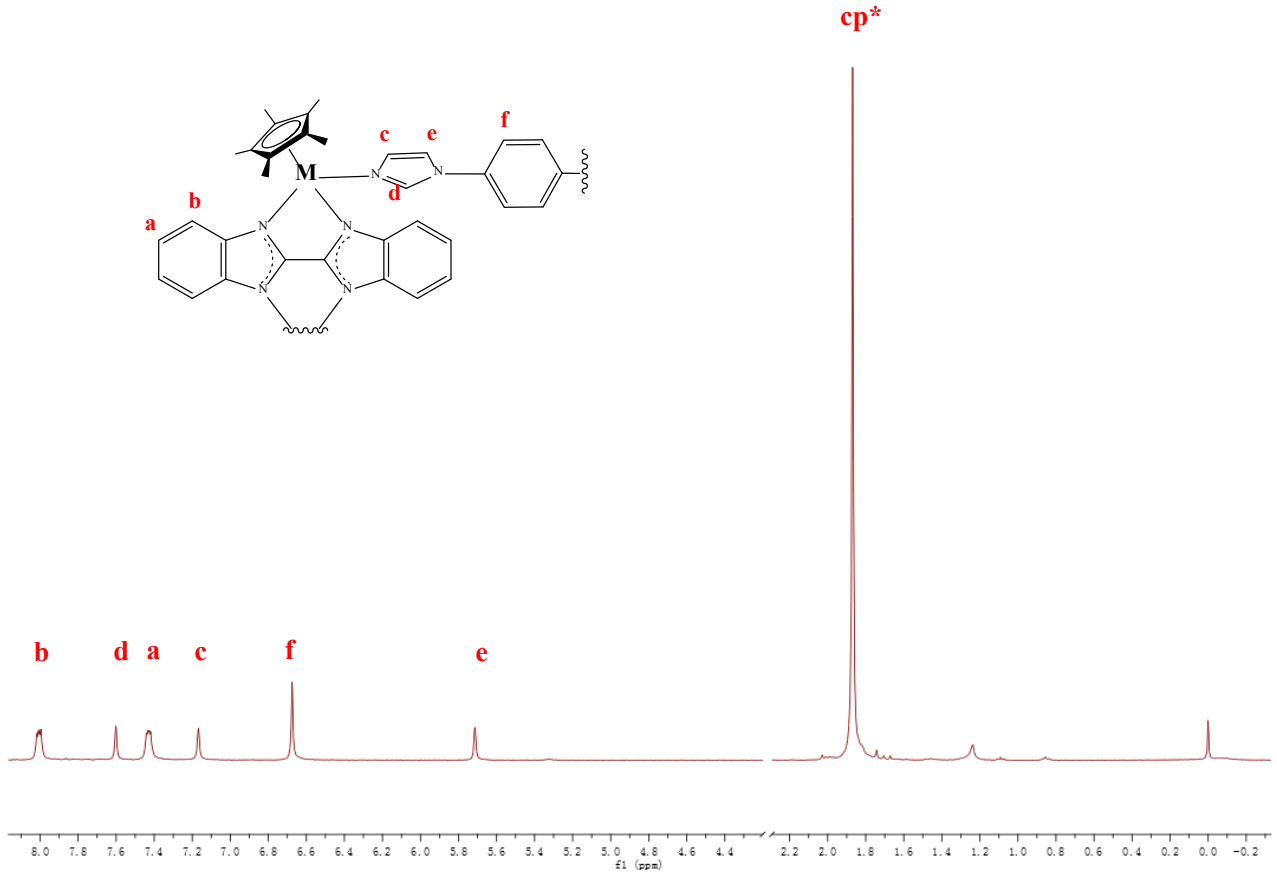


Figure 1. ^{1}H NMR (*400 MHz, DMSO*) spectrum of complex **2b**.

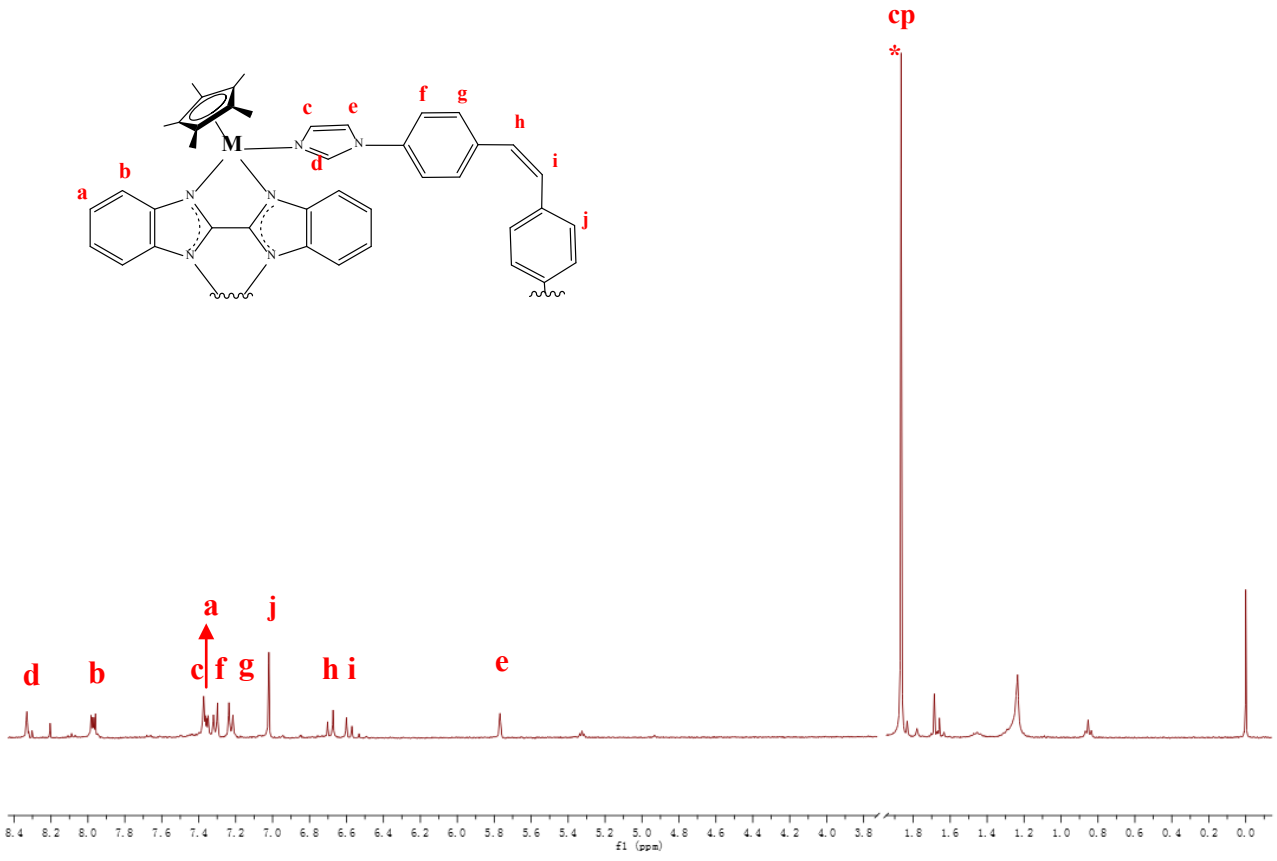


Figure 2. ^{1}H NMR (*400 MHz, DMSO*) spectrum of complex **3b**.

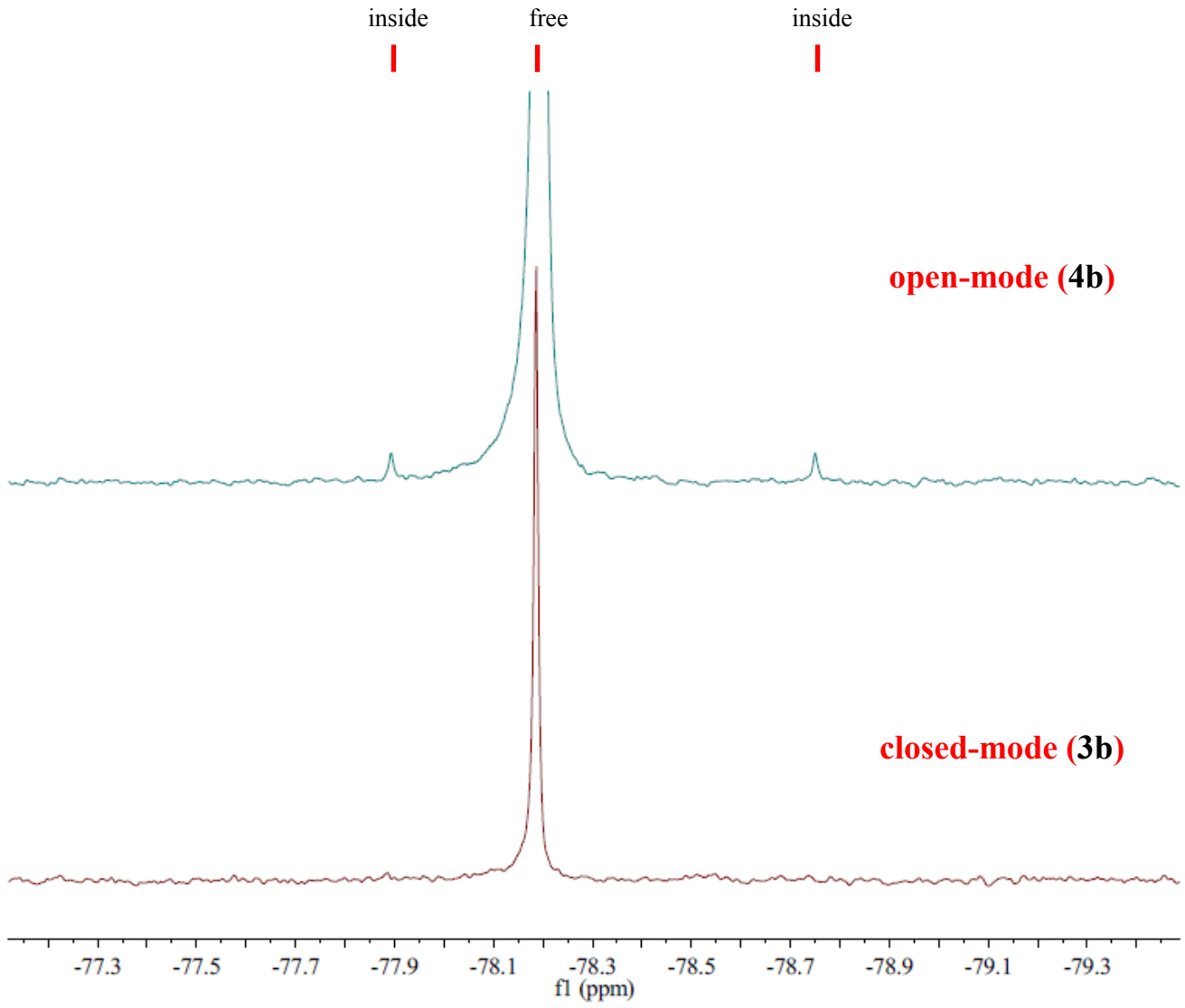


Figure 3. ^{19}F NMR spectra of **3b** and **4b**.

S4.

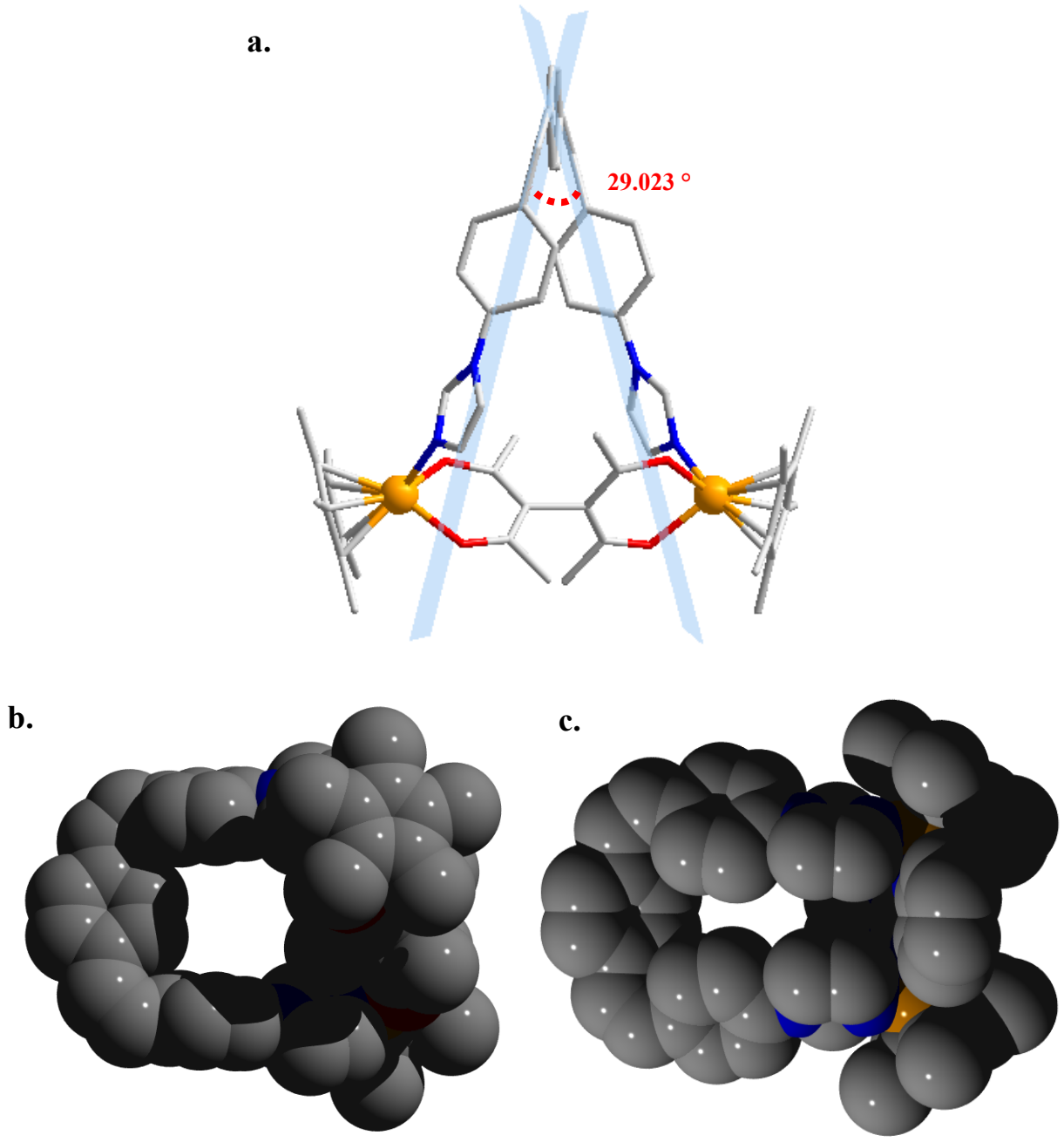


Figure 4. a) The angel between two plane (plane(C9, C10, C11, C14) and plane(C9A, C10A, C11A, C14A)) is 29.023°; b) open mode of the complex **4b** with space-filling structure; c) closed mode of the complex **3b** with space-filling structure.

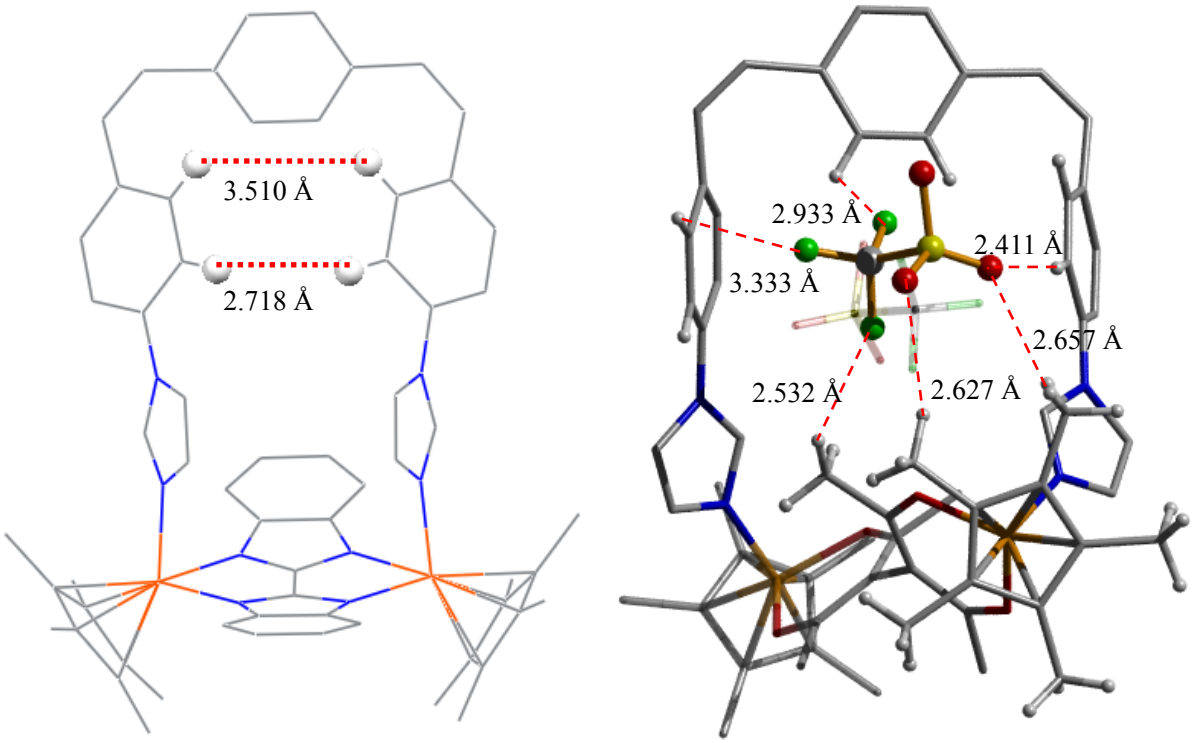


Figure 5. Left: intermolecular interaction within two benzene rings of cation **3b**; right: intramolecular interaction between anions with the host structure of cation **4b.**(white ball: H, green ball: F, red ball: O, yellow ball: S, gray: C, blue: N, orange: Rh)

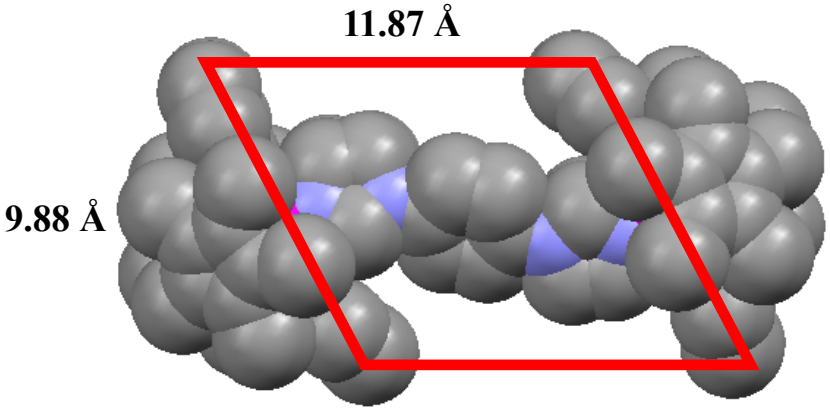


Figure 6. A standard rhombus structure for the cation **2b.**