Electronic Supplementary Material (ESI) for Dalton Transactions.

Contents

Figure S1. Simplified wireframe view of complex **1bs** (gray for C, blue for N, red for O, orange for Ir).

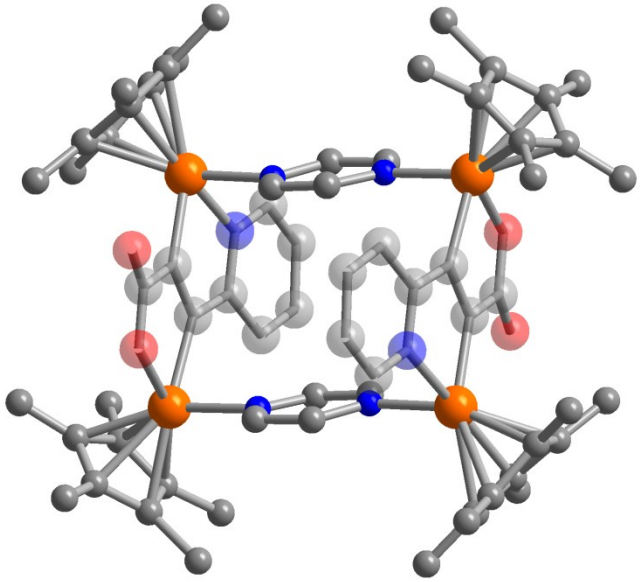

Figure S2. (a) Hydrogen bonds between the OTf anions and carbon atoms of complex **1c**; (b) The two-dimension hydrogen function (Gray for C, Blue for N, Red for O, Pink for Rh, Yellow for S, Green for F, Dark green for H.).

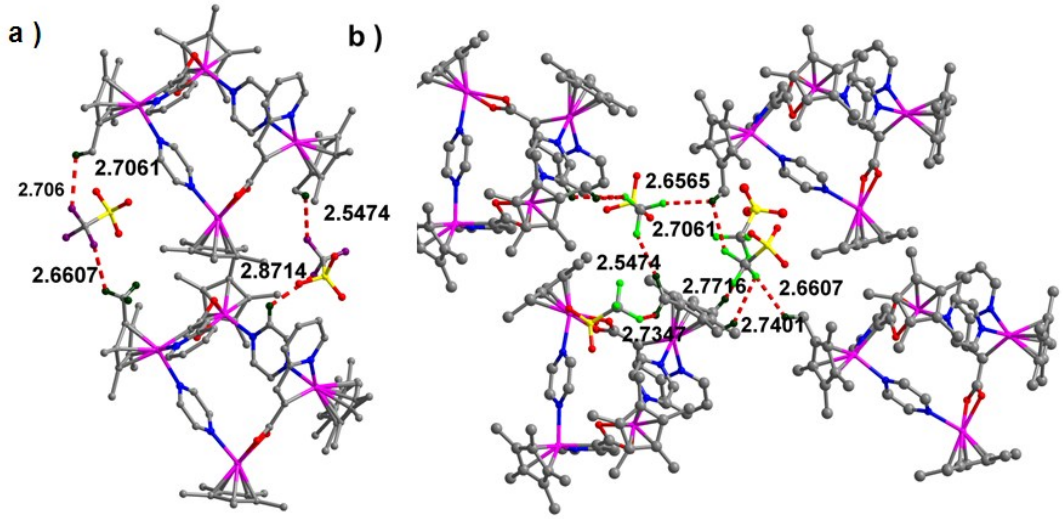

Figure S3. The ^{1}H NMR spectra of complex **1a-1b.**

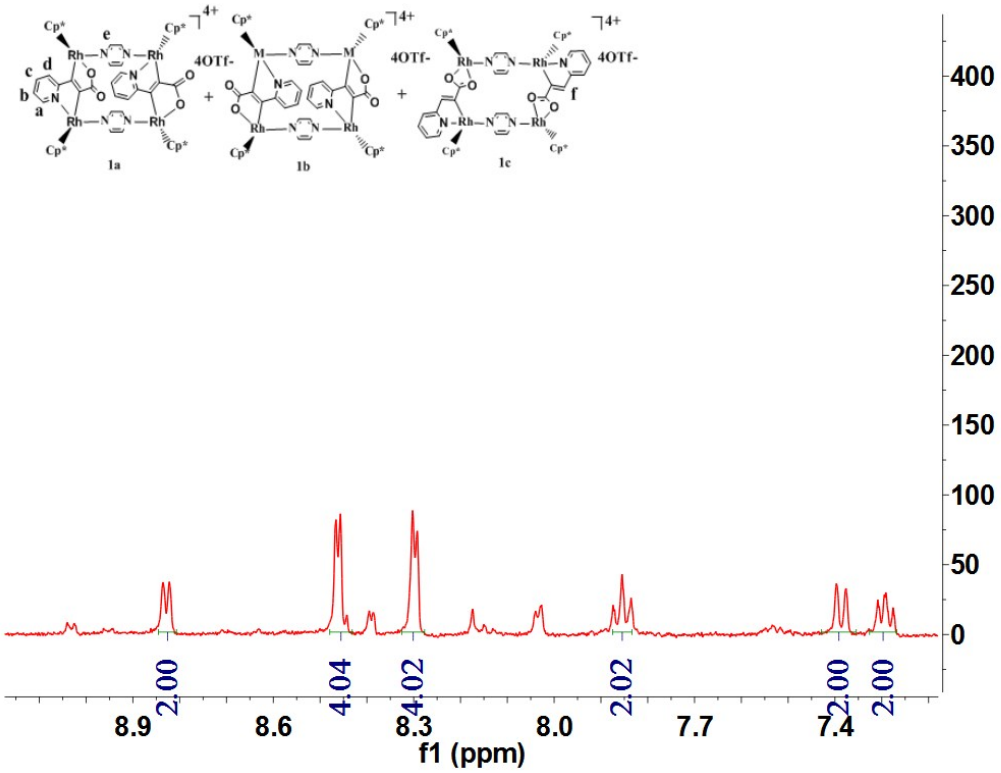

Figure S4. The ^{1}H-^{1}H COSY spectra of the complex **1a-1b.**

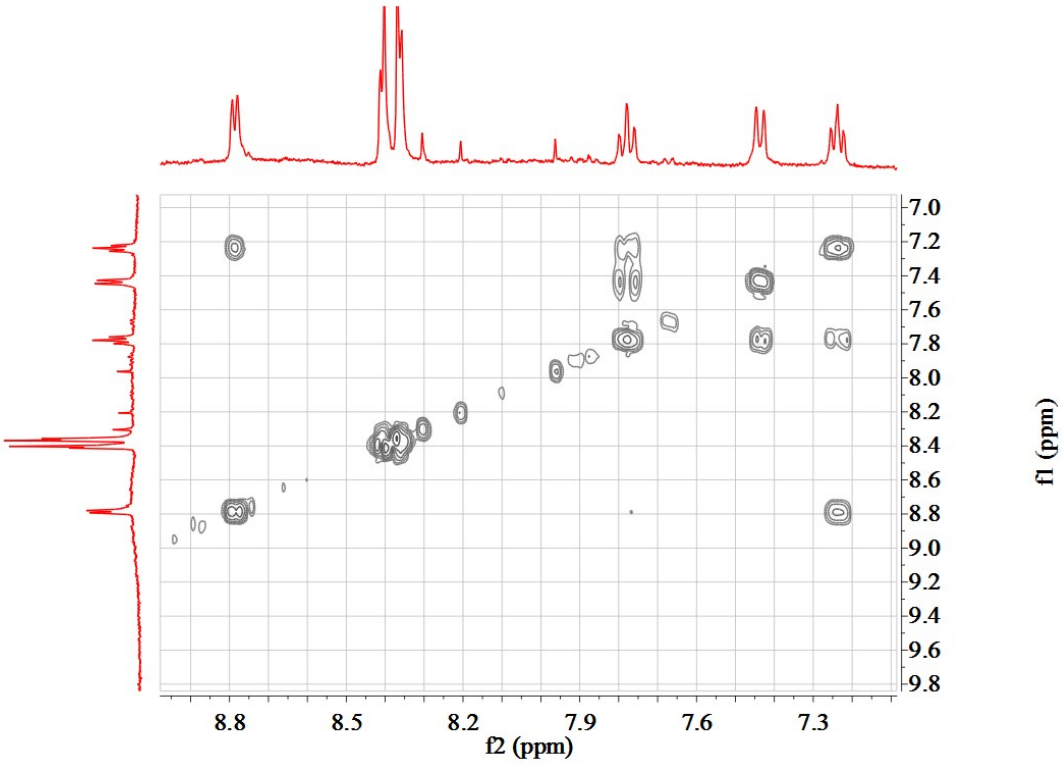

Figure S5. The ^{1}H NMR spectra of complex **1c.**

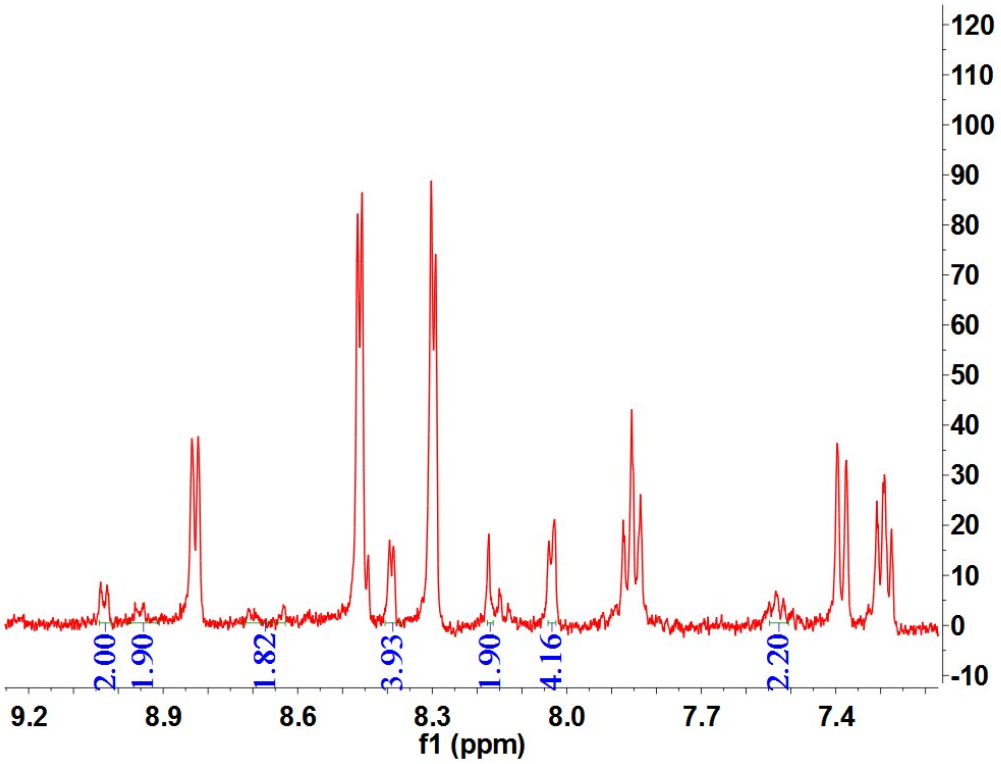

Figure S6. The ^{1}H-^{1}H COSY spectra of the complex **2a-2c**;

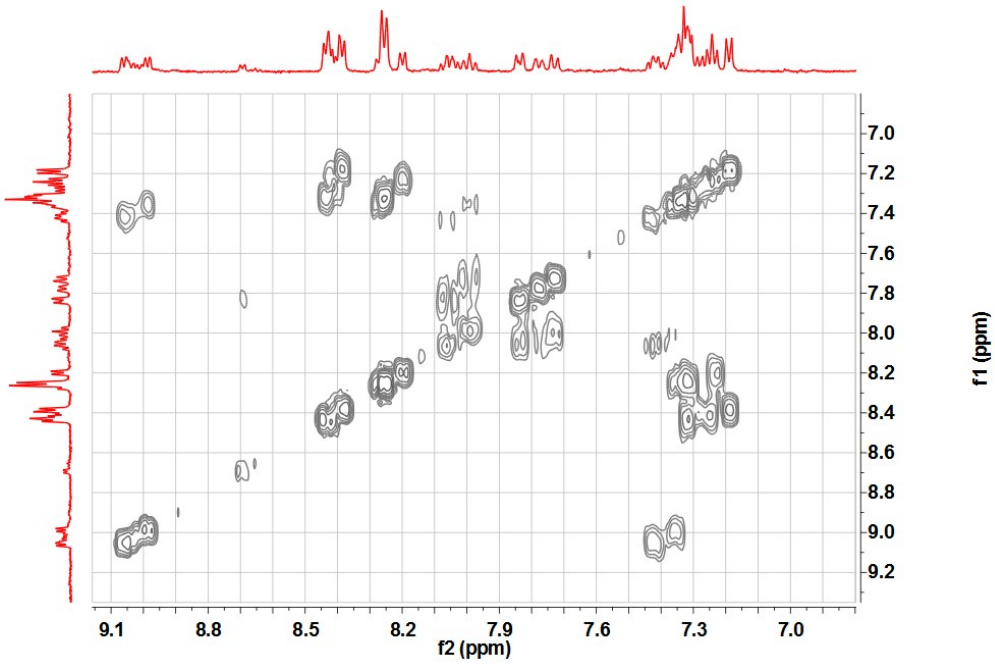

Figure S7. (a) Hydrogen bonds between the OTf anions and carbon atoms of complex **2b**; (b) The two-dimension hydrogen function (Gray for C, Blue for N, Red for O, Pink for Rh, Yellow for S, Green for F, Dark green for H.).

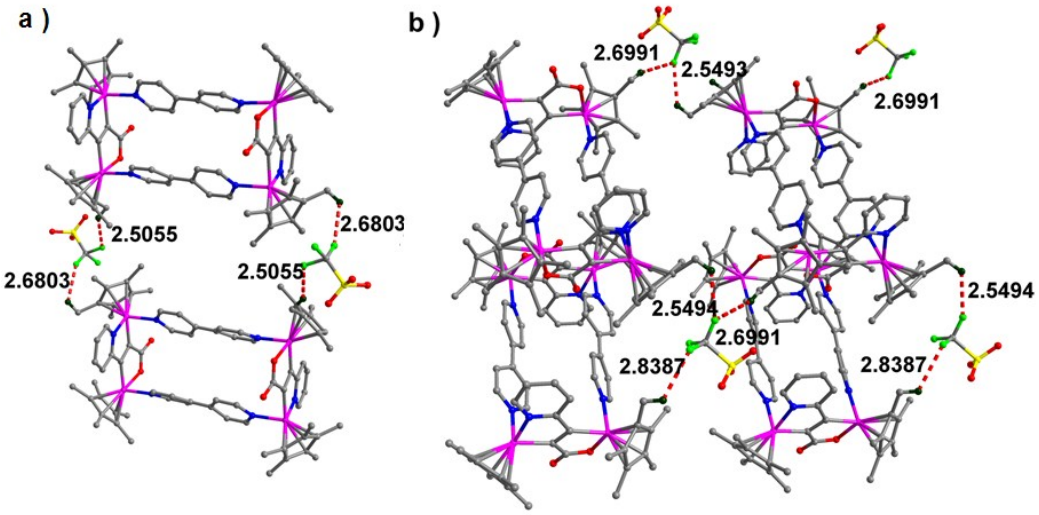

Figure S8. (a) Hydrogen bonds between the OTf anions and carbon atoms of complex **2c**; (b) The two-dimension hydrogen function (Gray for C, Blue for N, Red for O, Pink for Rh, Yellow for S, Green for F, Dark green for H.).

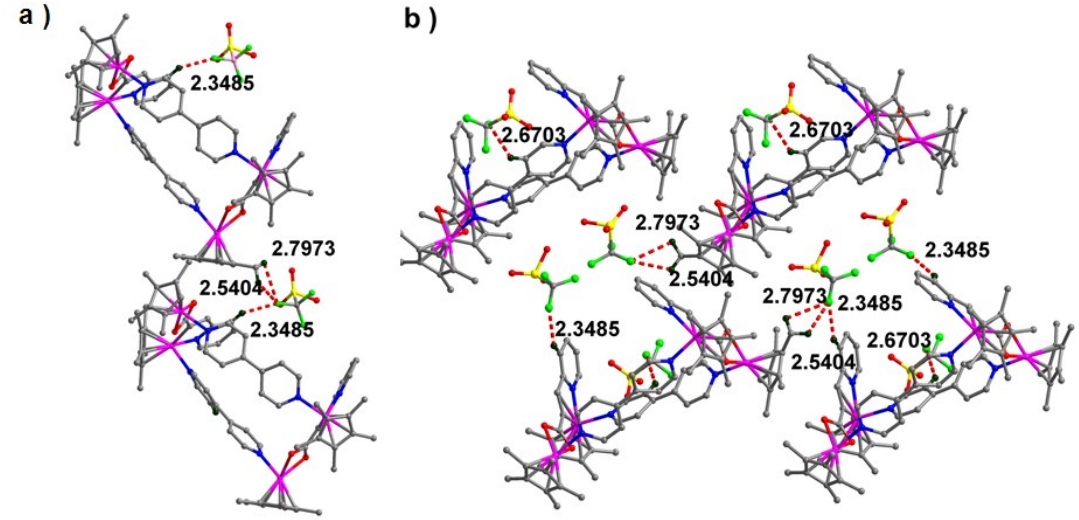

Figure S9. The ^{1}H NMR spectra of complex **2a-2c**;

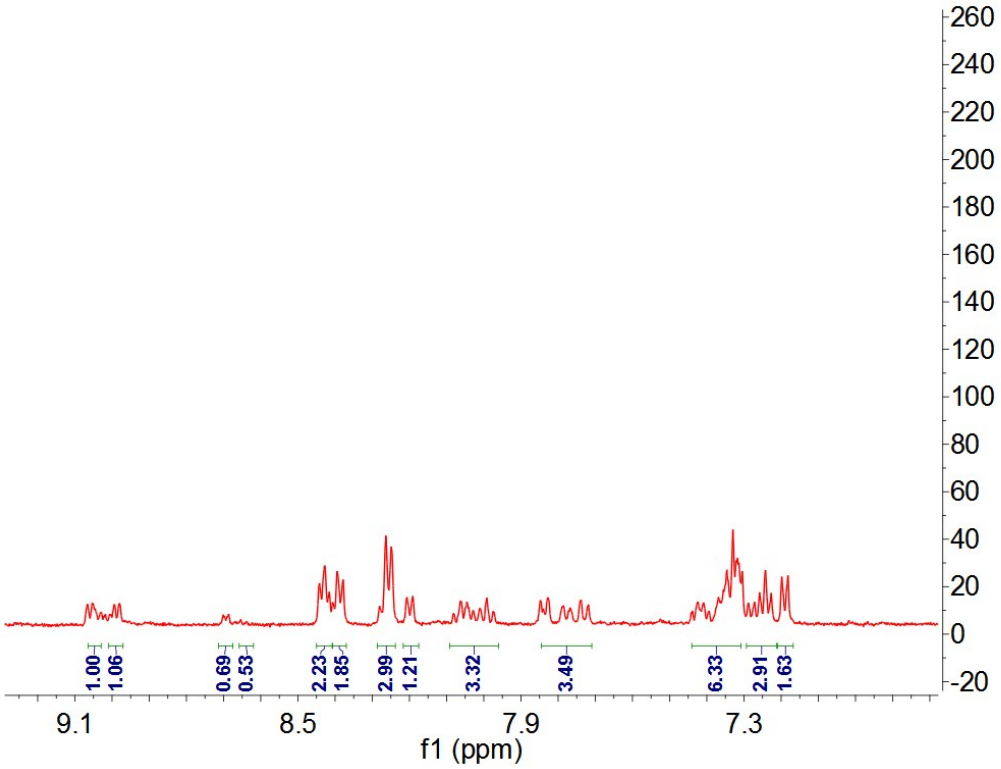

Figure S10. Simplified wireframe view of complex **3cs** (gray for C, blue for N, red for O, orange for Ir).

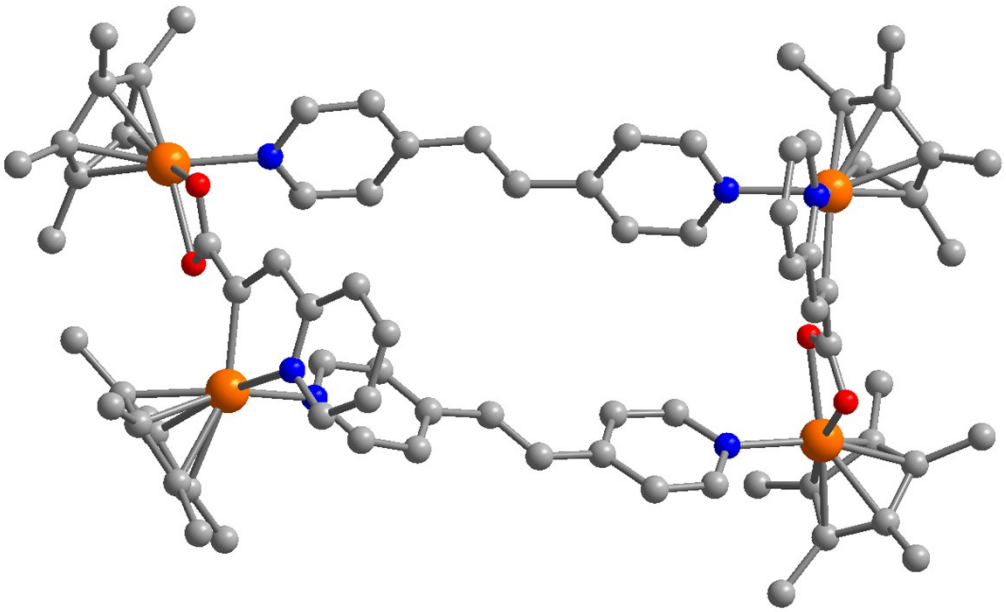

Figure S11. (a) Hydrogen bonds between the OTf anions and carbon atoms of complex **3c**; (b) The two-dimension hydrogen function (Gray for C, Blue for N, Red for O, Pink for Rh, Yellow for S, Green for F, Dark green for H.).

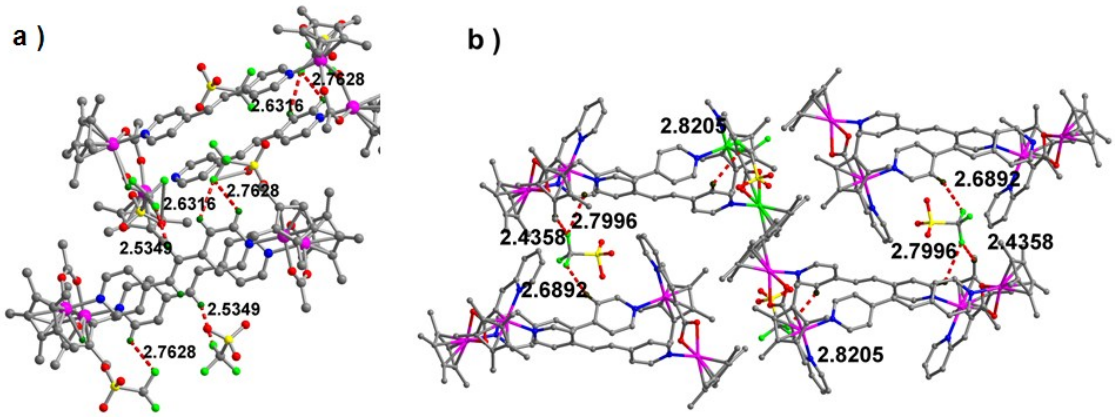

Figure S12. The ^{1}H NMR spectra of complex **3a-3c.**

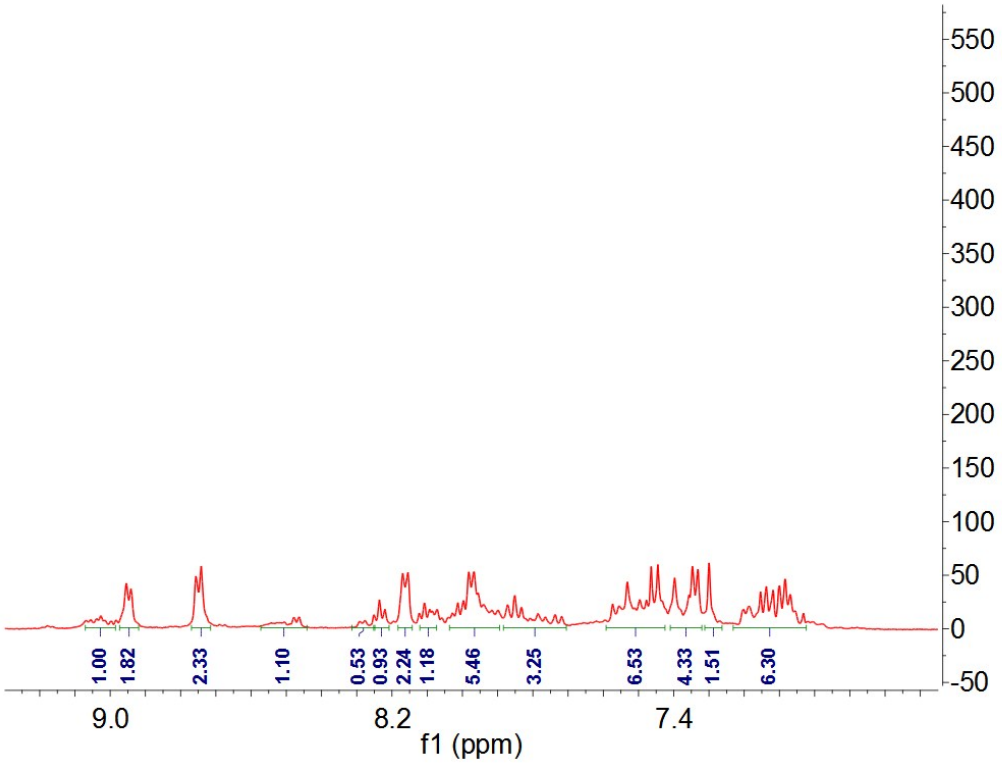

Figure S13. The ^{1}H-^{1}H COSY spectra of the complex **3a-3c.**

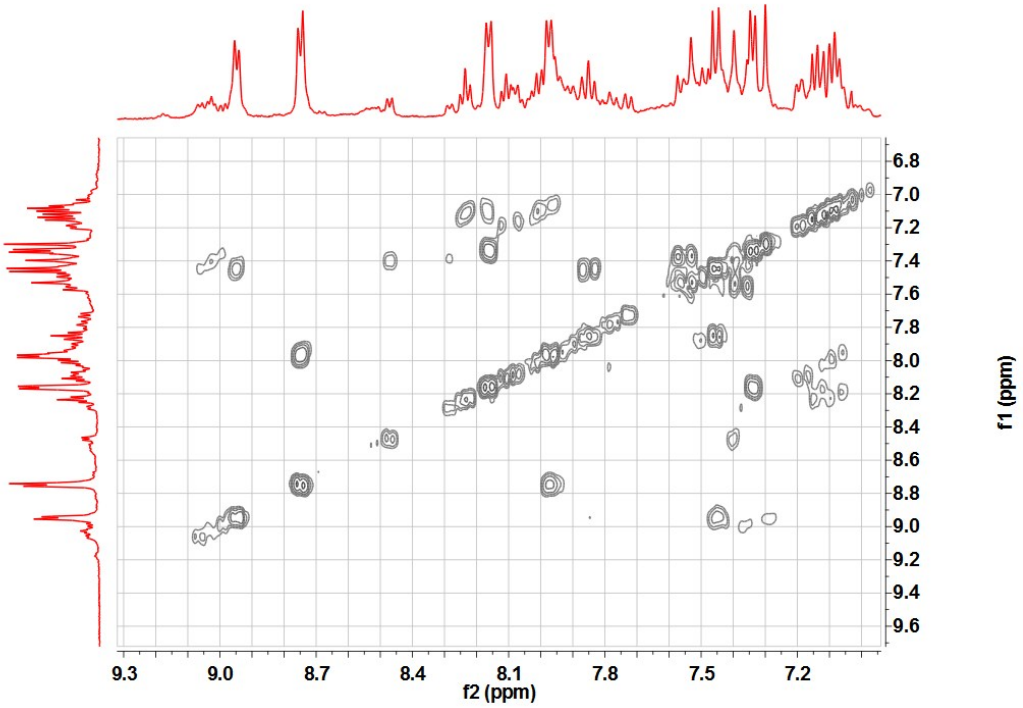

Figure S14. CO_2 adsorption-desorption isotherms with complex **3a,b** and **4**.

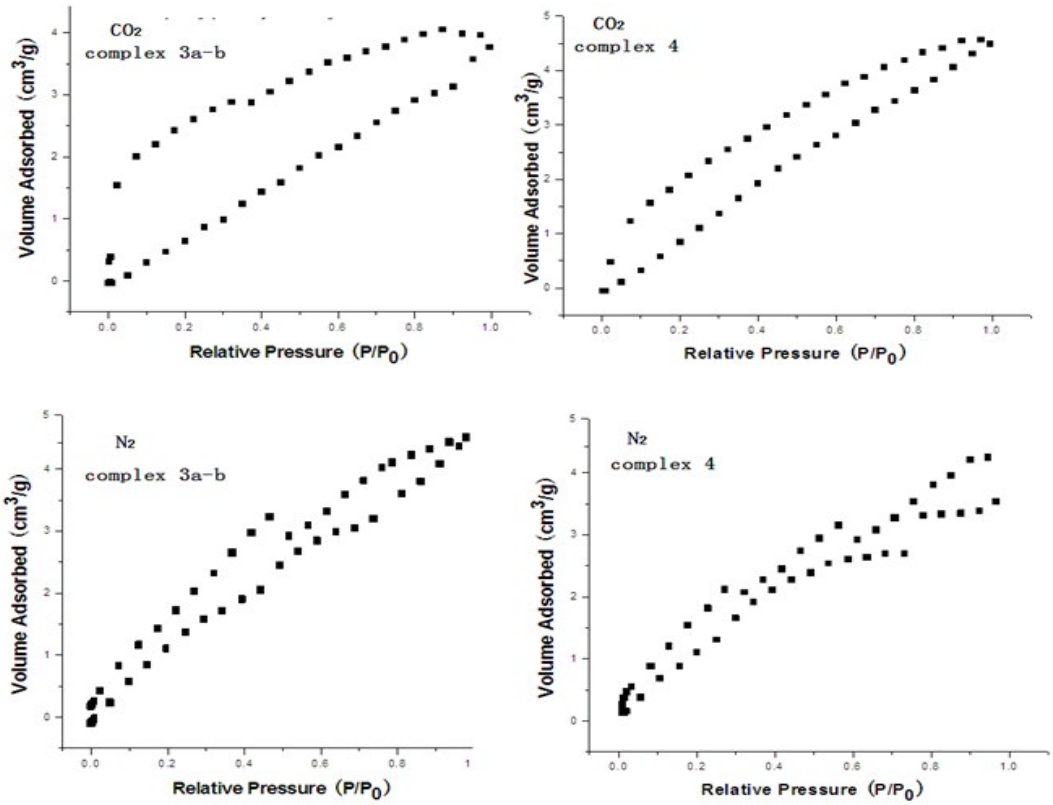

Table S1. Crystallographic data for complexes **1bs**

Complex	**1bs**	
Empirical formula	C80 H108 F12 Ir4 N8 O16 S4	
Formula weight	2562.78	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 14.728(15) Å	α = 117.078(17)°.
	b = 14.785(16) Å	β = 91.549(16)°.
	c = 15.17(3) Å	γ = 117.800(12)°.
Volume	2479(6) $Å^3$	
Z	1	
Density (calculated)	1.717 Mg/m^3	
Absorption coefficient	5.519 mm^{-1}	
F(000)	1252	
Crystal size	0.210 x 0.160 x 0.110 mm^3	
Theta range for data collection	1.673 to 25.009°.	
Index ranges	-17<=h<=14, -13<=k<=17, -17<=l<=18	
Reflections collected	11753	
Independent reflections	8403 [R(int) = 0.0314]	
Completeness to theta = 25.242°	93.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.746 and 0.481	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8403 / 62 / 556	
Goodness-of-fit on F^2	0.989	
Final R indices [I>2sigma(I)]	R1 = 0.0804, wR2 = 0.2282	
R indices (all data)	R1 = 0.1091, wR2 = 0.2633	
Extinction coefficient	n/a	
Largest diff. peak and hole	3.876 and -4.140 $e.Å^{-3}$	

Table S2. Crystallographic data for complexes **3cs**

Complex	**3cs**
Empirical formula	C92 H114 Cl8 F12 Ir4 N6 O20 S4
Formula weight	3032.53
Temperature	173(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, C 2/c
Unit cell dimensions	a = 20.973(3) A α = 90 deg.
	b = 15.042(2) A β= 101.963(2) deg.
	c = 36.067(5) A γ= 90 deg.
Volume	11131(3) A^3
Z, Calculated density	4, 1.810 Mg/m^3
Absorption coefficient	5.120 mm^-1
F(000)	5936
Crystal size	0.090 x 0.040 x 0.030 mm
Theta range for data collection	1.154 to 26.999 deg.
Limiting indices	-26<=h<=26, -19<=k<=17, -46<=l<=43
Reflections collected / unique	37332 / 12104 [R(int) = 0.0551]
Completeness to theta = 25.242	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.746 and 0.380
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	12104 / 28 / 600
Goodness-of-fit on F^2	1.096
Final R indices [I>2sigma(I)]	R1 = 0.0828, wR2 = 0.1945
R indices (all data)	R1 = 0.1009, wR2 = 0.2021
Extinction coefficient	n/a
Largest diff. peak and hole	5.875 and -4.757 e.A^-3