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;

Figure S3. The ¹H NMR spectra of complex **1a-1b**;

Figure S4. The ¹H-¹H COSY spectra of the complex **1a-1b**;

Figure S5. The ¹H NMR spectra of complex **1c**;

Figure S6. The ¹H-¹H 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;

Figure S8. (a) Hydrogen bonds between the OTf anions and carbon atoms of complex **2c**; (b) The two-dimension hydrogen function;

Figure S9. The ¹H 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;

Figure S12. The ¹H NMR spectra of complex **3a-3b**;

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

Figure S14. CO₂ adsorption-desorption isotherms with complex **3a,b** and **4**;

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

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

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 ¹H NMR spectra of complex 1a-1b.

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







Figure S6. The ¹H-¹H 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 S10. Simplified wireframe view of complex **3cs** (gray for C, blue for N, red for O, orange for Ir).



Figure S9. The ¹H NMR spectra of complex 2a-2c;

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 ¹H NMR spectra of complex **3a-3c.**



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



Figure S14. CO₂ adsorption-desorption isotherms with complex **3a,b** and **4**.



f1 (ppm)

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	$0.210 \times 0.160 \times 0.110 \text{ mm}^3$		
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		

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 γ = 90 deg. γ = 90 deg. Volume 11131(3) A^3 γ = 90 deg. γ = 90 deg. Volume 11131(3) A^3 γ = 90 deg. γ = 90 deg. Volume 11131(3) A^3 γ = 90 deg. γ = 90 deg. Volume 11131(3) A^3 γ = 90 deg. γ = 90 deg. Volume 11131(3) A^3 γ = 90 deg. γ = 90 deg. Volume 11131(3) A^3 γ = 90 deg. γ = 90 deg. Volume 11131(3) A^3 γ = 90 deg. γ = 90 deg. Volume 1.154 to 26.999 deg. γ = 90 deg. γ = 90 deg. Limiting indices -26<-19<<=k<17, -46<<=l<43 γ = 90 deg. γ = 90 deg. <t< th=""><th>Complex</th><th>3cs</th><th></th></t<>	Complex	3cs	
Formula weight 3032.53 Temperature 173(2) K Wavelength 0.71073 A Crystal system, space group Monoclinic, C 2/c Unit cell dimensions $a = 20.973(3) A$ $\alpha = 90 deg.$ $b = 15.042(2) A$ $\beta = 101.963(2) deg.$ $c = 36.067(5) A$ $\gamma = 90 deg.$ 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<<="k<=43</td"> 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 =</k<<17,>	Empirical formula	C92 H114 Cl8 F12 Ir4 N6 O20 S4	
Temperature173(2) KWavelength0.71073 ACrystal system, space groupMonoclinic, C 2/cUnit cell dimensions $a = 20.973(3) A$ $\alpha = 90 deg.$ $b = 15.042(2) A$ $\beta = 101.963(2) deg.$ $c = 36.067(5) A$ $\gamma = 90 deg.$ Volume11131(3) A^3Z, Calculated density4, 1.810 Mg/m^3Absorption coefficient5.120 mm^-1F(000)5936Crystal size0.090 x 0.040 x 0.030 mmTheta range for data collection1.154 to 26.999 deg.Limiting indices-26<=h<26, -19<=k<=17, -46<=l<43	Formula weight	3032.53	
Wavelength 0.71073 A Crystal system, space group Monoclinic, C 2/c Unit cell dimensions $a = 20.973(3) A$ $\alpha = 90 deg.$ $b = 15.042(2) A$ $\beta = 101.963(2) deg.$ $c = 36.067(5) A$ $\gamma = 90 deg.$ 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 $0.090 \times 0.040 \times 0.030 \text{ mm}$ Theta range for data collection $1.154 \text{ to } 26.999 deg.$ Limiting indices $-26<=h<=26, -19<<=k<=17, -46<<= <=43]$ Reflections collected / unique $37332 / 12104$ [R(int) = 0.551] Completeness to theta = 25.242 99.5% Absorption correction $0.746 \text{ and } 0.380$ 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 = $0.0028, wR2 = 0.1945$ R indices (all data) R1 = $0.1009, wR2 = 0.2021$ Extinction coefficient n/a	Temperature	173(2) К	
Crystal system, space groupMonoclinic, C 2/cUnit cell dimensions $a = 20.973(3) A$ $\alpha = 90 deg.$ $b = 15.042(2) A$ $\beta = 101.963(2) deg.$ $c = 36.067(5) A$ $\gamma = 90 deg.$ Volume11131(3) A^3Z, Calculated density4, 1.810 Mg/m^3Absorption coefficient $5.120 mm^{-1}$ F(000)5936Crystal size $0.090 \times 0.040 \times 0.030 mm$ 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 $0.746 and 0.380$ Refinement method $0.746 and 0.380$ Refinement method 1.096 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	Wavelength	0.71073 A	
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	Crystal system, space group	Monoclinic, C 2/c	
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	Unit cell dimensions	a = 20.973(3) A	α = 90 deg.
c = 36.067(5) A y= 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		b = 15.042(2) A	β= 101.963(2) 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		c = 36.067(5) A	γ= 90 deg.
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	Volume	11131(3) A^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	Z, Calculated density	4, 1.810 Mg/m^3	
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	Absorption coefficient	5.120 mm^-1	
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	F(000)	5936	
Theta range for data collection1.154 to 26.999 deg.Limiting indices-26<=h<=26, -19<=k<=17, -46<=l<=43	Crystal size	0.090 x 0.040 x 0.030 mm	
Limiting indices-26<=h<=26, -19<=k<=17, -46<=l<=43Reflections collected / unique37332 / 12104 [R(int) = 0.0551]Completeness to theta = 25.24299.5 %Absorption correctionSemi-empirical from equivalentsMax. and min. transmission0.746 and 0.380Refinement methodFull-matrix least-squares on F^2Data / restraints / parameters12104 / 28 / 600Goodness-of-fit on F^21.096Final R indices [I>2sigma(I)]R1 = 0.0828, wR2 = 0.1945R indices (all data)R1 = 0.1009, wR2 = 0.2021Extinction coefficientn/aLargest diff. peak and hole5.875 and -4.757 e.A^-3	Theta range for data collection	1.154 to 26.999 deg.	
Reflections collected / unique37332 / 12104 [R(int) = 0.0551]Completeness to theta = 25.24299.5 %Absorption correctionSemi-empirical from equivalentsMax. and min. transmission0.746 and 0.380Refinement methodFull-matrix least-squares on F^2Data / restraints / parameters12104 / 28 / 600Goodness-of-fit on F^21.096Final R indices [I>2sigma(I)]R1 = 0.0828, wR2 = 0.1945R indices (all data)R1 = 0.1009, wR2 = 0.2021Extinction coefficientn/aLargest diff. peak and hole5.875 and -4.757 e.A^-3	Limiting indices	-26<=h<=26, -19<=k<=17, -46<=l<=43	
Completeness to theta = 25.24299.5 %Absorption correctionSemi-empirical from equivalentsMax. and min. transmission0.746 and 0.380Refinement methodFull-matrix least-squares on F^2Data / restraints / parameters12104 / 28 / 600Goodness-of-fit on F^21.096Final R indices [I>2sigma(I)]R1 = 0.0828, wR2 = 0.1945R indices (all data)R1 = 0.1009, wR2 = 0.2021Extinction coefficientn/aLargest diff. peak and hole5.875 and -4.757 e.A^-3	Reflections collected / unique	37332 / 12104 [R(int) = 0.0551]	
Absorption correctionSemi-empirical from equivalentsMax. and min. transmission0.746 and 0.380Refinement methodFull-matrix least-squares on F^2Data / restraints / parameters12104 / 28 / 600Goodness-of-fit on F^21.096Final R indices [I>2sigma(I)]R1 = 0.0828, wR2 = 0.1945R indices (all data)R1 = 0.1009, wR2 = 0.2021Extinction coefficientn/aLargest diff. peak and hole5.875 and -4.757 e.A^-3	Completeness to theta = 25.242	99.5 %	
Max. and min. transmission0.746 and 0.380Refinement methodFull-matrix least-squares on F^2Data / restraints / parameters12104 / 28 / 600Goodness-of-fit on F^21.096Final R indices [I>2sigma(I)]R1 = 0.0828, wR2 = 0.1945R indices (all data)R1 = 0.1009, wR2 = 0.2021Extinction coefficientn/aLargest diff. peak and hole5.875 and -4.757 e.A^-3	Absorption correction	Semi-empirical from equivalents	
Refinement methodFull-matrix least-squares on F^2Data / restraints / parameters12104 / 28 / 600Goodness-of-fit on F^21.096Final R indices [I>2sigma(I)]R1 = 0.0828, wR2 = 0.1945R indices (all data)R1 = 0.1009, wR2 = 0.2021Extinction coefficientn/aLargest diff. peak and hole5.875 and -4.757 e.A^-3	Max. and min. transmission	0.746 and 0.380	
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	Refinement method	Full-matrix least-squares on F^2	
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	Data / restraints / parameters	12104 / 28 / 600	
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	Goodness-of-fit on F^2	1.096	
R indices (all data)R1 = 0.1009, wR2 = 0.2021Extinction coefficientn/aLargest diff. peak and hole5.875 and -4.757 e.A^-3	Final R indices [I>2sigma(I)]	R1 = 0.0828, wR2 = 0.1945	
Extinction coefficientn/aLargest diff. peak and hole5.875 and -4.757 e.A^-3	R indices (all data)	R1 = 0.1009, wR2 = 0.2021	
Largest diff. peak and hole5.875 and -4.757 e.A^-3	Extinction coefficient	n/a	
	Largest diff. peak and hole	5.875 and -4.757 e.A^-3	

Table S2. Crystallographic data for complexes 3cs