Supporting Information for

Efficient Formation of Organoiridium Macrocycles via C-H Activation Directed Self-Assembly

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Materials and instrumentations

All reactions and manipulations were performed under a nitrogen atmosphere, using standard Schlenk techniques. However, once the reactions were completed, subsequent workups were done without precaution, as the compounds are air-stable. Solvents were purified by standard methods prior to use. [Cp*IrCl₂]₂ was prepared according to the reported procedures.¹ The ¹H-NMR spectra were measured on a VAVCE-DMX 400 Spectrometer in CD₃OD, CDCl₃ or CD₃CN. Elemental analysis was performed on Elementar vario EL III Analyzer. IR (KBr) spectra were recorded on the Nicolet FT-IR spectrophotometer.

The terephthal-bis-imine ligands L₁-L₄ were prepared by the reactions of terephthalaldehyde with two equivalents of the corresponding amines in methanol overnight at room temperature according to known procedures.² N,N'-bisbenzylidenebenzene-1,4-diamines ligands L₅-L₆ were prepared by the reactions of 1,4-phenylenediamine with two equivalents of the corresponding benzaldehydes in methanol overnight at room temperature according to known procedures.³

Preparation of dinuclear complexes 3a-d

Preparation of 3a: A mixture of [Cp*IrCl₂]₂ (80 mg, 0.1 mmol), NaOAc (49 mg, 0.6 mmol), L₁ (28 mg, 0.1 mmol), and benzaldehyde (trace) was stirred at 50°C in 20 mL of dichloromethane for 6 h. The mixture was filtered through Celite and evaporated to afford dark solid which was further purified by silica gel column chromatography to afford pure cyclometalated compound 3a (77 mg, 76%). Anal. Calcd for C₄₀H₄₄Cl₂Ir₂N₂: C 47.66, H 4.40, N 2.78; found: C 47.58, H 4.37, N 2.83. ¹H-NMR (400MHz, CDCl₃, ppm): δ = 8.42 (s, 2H, HC=N); 8.10 (s, 2H); 7.58 (d, 4H); 7.42 (m, 4H); 7.31 (m, 2H); 1.45 (s, 30H, C₅Me₅). ¹³C-NMR (CDCl₃, ppm): δ = 175.78 (Ir-C), 159.60 (HC=N), 152.03, 151.50, 135.38, 128.97, 127.35, 122.60, 88.97 (C₅Me₅), 8.85 (C₅Me₅). IR(KBr): νC=N = 1551 cm⁻¹.

Preparation of 3b: A mixture of [Cp*IrCl₂]₂ (80 mg, 0.1 mmol), NaOAc (49 mg, 0.6 mmol), L₂ (34 mg, 0.1 mmol), and benzaldehyde (trace) was stirred at 50°C in 20 mL of dichloromethane for 6 h. The mixture was filtered through Celite and evaporated to afford dark solid which was further purified by
silica gel column chromatography to afford pure cyclometalated compound 3b (80 mg, 75%). Anal. Calcd for C_{42}H_{48}Cl_{2}Ir_{2}N_{2}O_{2}: C 47.23, H 4.53, N 2.62; found: C 47.16, H 4.24, N 2.72. ¹H-NMR (400MHz, CDCl₃, ppm): δ = 8.36 (s, 2H, HC=N); 8.06 (s, 2H); 7.52 (d, 4H); 6.92 (d, 4H); 3.86 (s, 6H, OMe); 1.46 (s, 30H, C₅Me₅). ¹³C-NMR (400 MHz, CDCl₃/CD₃OD 4:1, 50°C): δ = 174.86 (Ir-C), 158.99 (HC=N), 158.74, 151.37, 145.28, 135.03, 123.46, 113.85, 88.88 (C₅Me₅), 55.39 (OMe), 8.58 (C₅Me₅). IR(KBr): ν_{C=N} = 1534 cm⁻¹.

Preparation of 3c: A mixture of [Cp*IrCl₂]₂ (80 mg, 0.1 mmol), NaOAc (49 mg, 0.6 mmol), L₃ (31 mg, 0.1 mmol), and benzaldehyde (trace) was stirred at 50°C in 20 mL of dichloromethane for 6 h. The mixture was filtered through Celite and evaporated to afford dark solid which was further purified by silica gel column chromatography to afford pure cyclometalated compound 3c (81 mg, 78%). Anal. Calcd for C_{42}H_{48}Cl_{2}Ir_{2}N₂: C 48.68, H 4.67, N 2.70; found: C 48.45, H 4.39, N 2.83. ¹H-NMR (400MHz, CDCl₃, ppm): δ = 8.37 (s, 2H, HC=N); 8.07 (s, 2H); 7.45 (d, 4H); 7.20 (d, 4H); 2.41 (s, 6H, Me); 1.48 (s, 30H, C₅Me₅). IR(KBr): ν_{C=N} = 1560 cm⁻¹.

Preparation of 3d: A mixture of [Cp*IrCl₂]₂ (80 mg, 0.1 mmol), NaOAc (49 mg, 0.6 mmol), L₄ (35 mg, 0.1 mmol), and benzaldehyde (trace) was stirred at 50°C in 20 mL of dichloromethane for 6 h. The mixture was filtered through Celite and evaporated to afford dark solid which was further purified by silica gel column chromatography to afford pure cyclometalated compound 3d (75 mg, 70%). Anal. Calcd for C_{40}H_{42}Cl_{4}Ir_{2}N₂: C 44.61, H 3.93, N 2.60; found: C 44.29, H 3.57, N 2.66. ¹H-NMR (400MHz, CDCl₃, ppm): δ = 8.39 (s, 2H, HC=N); 8.10 (s, 2H); 7.54 (d, 4H); 7.40 (d, 4H); 1.50 (s, 30H, C₅Me₅). ¹³C-NMR (CDCl₃, ppm): δ = 176.07 (Ir-C), 160.09 (HC=N), 151.48, 150.56, 135.62, 132.93, 129.11, 123.93, 89.10 (C₅Me₅), 8.92 (C₅Me₅). IR(KBr): ν_{C=N} = 1556 cm⁻¹.

Preparation of dinuclear complexes 4a,b

Preparation of 4a: A mixture of [Cp*IrCl₂]₂ (80 mg, 0.1 mmol), NaOAc (49 mg, 0.6 mmol), L₅ (28 mg, 0.1 mmol), and benzaldehyde (trace) was stirred at 50°C in 20 mL of dichloromethane for 6 h. The
mixture was filtered through Celite and evaporated to afford dark solid which was further purified by silica gel column chromatography to afford pure cyclometalated compound 4a (82 mg, 82%). Anal. Calcd for C₄₀H₄₄Cl₂Ir₂N₂: C 47.66, H 4.40, N 2.78; found: C 47.37, H 4.25, N 2.71. ¹H-NMR (400MHz, CDCl₃, ppm): δ = 8.52 (s, 2H, HC=N); 8.28 (d, 2H); 7.92 (d, 2H); 7.53-7.73 (m, 4H); 7.29 (m, 2H); 7.10 (m, 2H); 1.44 (s, 30H, C₅Me₅). IR(KBr): νC=N = 1586 cm⁻¹.

Preparation of 4b: A mixture of [Cp*IrCl₂]₂ (80 mg, 0.1 mmol), NaOAc (49 mg, 0.6 mmol), L₆ (34 mg, 0.1 mmol), and benzaldehyde (trace) was stirred at 50°C in 20 mL of dichloromethane for 6 h. The mixture was filtered through Celite and evaporated to afford dark solid which was further purified by silica gel column chromatography to afford pure cyclometalated compound 4b (98 mg, 92%). Anal. Calcd for C₄₂H₄₈Cl₂Ir₂N₂O₂: C 47.23, H 4.53, N 2.62; found: C 47.36, H 4.26, N 2.52. ¹H-NMR (400MHz, CDCl₃, ppm): δ = 8.25 (s, 2H, HC=N); 7.60-7.63 (m, 6H); 7.39 (d, 2H); 6.61-6.64 (m, 2H); 3.93 (s, 6H, OMe); 1.51 (s, 30H, C₅Me₅). ¹³C-NMR (CDCl₃, ppm): δ = 174.00, 173.68 (Ir-C); 162.77, 162.73 (HC=N); 150.56, 150.53; 140.54, 140.47; 131.54, 131.47; 123.25, 123.22; 108.96, 108.94; 89.15, 89.04 (C₅Me₅); 55.17 (OMe); 9.01, 8.94 (C₅Me₅). IR(KBr): νC=N = 1588 cm⁻¹.

Preparation of tetra-nuclear complexes 1a-d

Preparation of 1a: The first method: Pyrazine (8 mg, 0.1 mmol) was added to a suspension of [Cp*IrCl₂]₂ (80 mg, 0.1 mmol) in CH₃OH at room temperature and stirred for 5 h. Ag(CF₃SO₃) (102 mg, 0.4 mmol) was added to the resulting yellow precipitate and stirred for 2 h. NaOAc (49 mg, 0.6 mmol) and L₁ (28 mg, 0.1 mmol) were added and keep stirring for additional 12 h. The solvent was removed and the residue was extracted with CH₂Cl₂, followed by filtration through a glass filter (G5) to remove insoluble compounds. The filtrate was concentrated to about 3 mL and diethyl ether was added, to give 1a as a red solid in 56% yield.

The second method: Ag(CF₃SO₃) (51 mg, 0.2 mmol) was added to a solution of 3a (101 mg, 0.1 mmol) in CH₃OH (20 mL) at room temperature and stirred for 3 h, followed by filtration to remove insoluble materials. Pyrazine (8 mg, 0.1 mmol) was added to the filtrate and stirred for 12 h. The solvent was
removed and the residue was extracted with CH$_2$Cl$_2$, followed by filtration through a glass filter (G5) to remove insoluble compounds. The filtrate was concentrated to about 3 mL and diethyl ether was added, to give 1a as a red solid in 72% yield. Anal. Calcd. for C$_{92}$H$_{96}$F$_{12}$Ir$_4$N$_8$O$_{12}$S$_4$: C 42.00, H 3.68, N 4.26; found: C 41.82, H 3.63, N 4.09. $^1$H-NMR (400MHz, CD$_3$OD, ppm): $\delta$ = 8.86, 8.84 (s, 4H, HC=N); 8.31, 8.28 (s, 8H, pyrazine); 8.24 (d, 4H, Ar-H); 7.49-7.58 (m, 12H, Ar-H); 7.28-7.30 (m, 8H, Ar-H); 1.52, 1.63 (s, 60H, C$_5$Me$_5$). IR(KBr): $\nu_{C-N}$ = 1555 cm$^{-1}$.

**Preparation of 1b:** This complex was obtained in 58% yield by a procedure similar to that the first method described for 1a when L2 used. And this complex also could be obtained from 3b and pyrazine by a procedure similar to that the second method described for 1a as a red solid in 75% yield. Anal. Calcd. for C$_{96}$H$_{104}$F$_{12}$Ir$_4$N$_8$O$_{16}$S$_4$: C 41.91, H 3.81, N 4.07; found: C 41.78, H 3.54, N 4.33. $^1$H-NMR (400MHz, CDCl$_3$, ppm): $\delta$ = 8.62 (s, 4H, HC=N); 8.40 (s, 8H, pyrazine); 8.14 (s, 4H, Ar-H); 7.36 (d, 8H, Ar-H); 7.14 (d, 8H, Ar-H); 3.91 (s, 12H, OCH$_3$); 1.57 (s, 60H, C$_5$Me$_5$). IR(KBr): $\nu_{C-N}$ = 1556 cm$^{-1}$.

**Preparation of 1c:** This complex was obtained in 54% yield by a procedure similar to that the first method described for 1a when L3 used. And this complex also could be obtained from 3c and pyrazine by a procedure similar to that the second method described for 1a as a red solid in 63% yield. Anal. Calcd. for C$_{96}$H$_{104}$F$_{12}$Ir$_4$N$_8$O$_{12}$S$_4$: C 42.91, H 3.90, N 4.17; found: C 42.73, H 3.71, N 4.26. $^1$H-NMR (400MHz, CDCl$_3$, ppm): $\delta$ = 8.69 (s, 4H, HC=N); 8.43 (s, 8H, pyrazine); 8.28 (s, 4H, Ar-H); 7.39 (d, 8H, Ar-H); 7.06 (d, 8H, Ar-H); 2.42 (s, 12H, CH$_3$); 1.54 (s, 60H, C$_5$Me$_5$). IR(KBr): $\nu_{C-N}$ = 1555 cm$^{-1}$.

**Preparation of 1d:** This complex was obtained in 54% yield by a procedure similar to that the first method described for 1a when L4 used. And this complex also could be obtained from 3d and pyrazine by a procedure similar to that the second method described for 1a as a red solid in 60% yield. Anal. Calcd. for C$_{92}$H$_{92}$Cl$_4$F$_{12}$Ir$_4$N$_8$O$_{12}$S$_4$: C 39.91, H 3.35, N 4.05; found: C 39.65, H 3.04, N 4.02. $^1$H-NMR (400MHz, CD$_3$OD, ppm): $\delta$ = 8.85 (s, 4H, HC=N); 8.23-8.25 (m, 12H, pyrazine and Ar-H); 7.59 (d, 8H, Ar-H); 7.32 (d, 8H, Ar-H); 1.67 (s, 60H, C$_5$Me$_5$). IR(KBr): $\nu_{C-N}$ = 1551 cm$^{-1}$. 
Preparation of tetra-nuclear complexes 2a and 2b

Preparation of 2a:

The first method: Pyrazine (8 mg, 0.1 mmol) was added to a suspension of \([\text{Cp}^*\text{IrCl}_2]_2\) (80 mg, 0.1 mmol) in \(\text{CH}_3\text{OH}\) at room temperature and stirred for 5 h. \(\text{Ag(CF}_3\text{SO}_3)\) (102 mg, 0.4 mmol) was added to the resulting yellow precipitate and stirred for 2 h. \(\text{NaOAc}\) (49 mg, 0.6 mmol) and L5 (28 mg, 0.1 mmol) were added and kept stirring for additional 12 h. The solvent was removed and the residue was extracted with \(\text{CH}_2\text{Cl}_2\), followed by filtration through a glass filter (G5) to remove insoluble compounds. The filtrate was concentrated to about 3 mL and diethyl ether was added, to give 2a as a red solid in 68% yield.

The second method: \(\text{Ag(CF}_3\text{SO}_3)\) (51 mg, 0.2 mmol) was added to a solution of 4a (101 mg, 0.1 mmol) in \(\text{CH}_3\text{OH}\) (20 mL) at room temperature and stirred for 3 h, followed by filtration to remove insoluble materials. Pyrazine (8 mg, 0.1 mmol) was added to the filtrate and stirred for 12 h. The solvent was removed and the residue was extracted with \(\text{CH}_2\text{Cl}_2\), followed by filtration through a glass filter (G5) to remove insoluble compounds. The filtrate was concentrated to about 3 mL and diethyl ether was added, to give 2a as a red solid in 75% yield. Anal. Calcd. for \(\text{C}_{92}\text{H}_{96}\text{F}_{12}\text{Ir}_4\text{N}_8\text{O}_{12}\text{S}_4\): C 42.00, H 3.68, N 4.26; found: C 41.79, H 3.31, N 4.17. \(^1\text{H-NMR}\) (400MHz, \(\text{CD}_3\text{OD}\), ppm): \(\delta = 8.56\) (s, 4H, HC=N); 8.44 (s, 8H, pyrazine); 7.89 (m, 4H, Ar-H); 7.89 (s, 8H, Ar-H); 7.56 (d, 4H, Ar-H); 7.37 (m, 4H, Ar-H); 7.00-7.05 (m, 4H, Ar-H); 1.59 (s, 60H, C\(_5\)Me\(_5\)). IR(KBr): \(\nu_{\text{C-N}} = 1584\ \text{cm}^{-1}\).

Preparation of 2b: This complex was obtained in 71% yield by a procedure similar to that of the first method described for 2a when L6 used. And this complex also could be obtained from 4b and pyrazine by a procedure similar to that the second method described for 1a as a red solid in 78% yield. Anal. Calcd. for \(\text{C}_{96}\text{H}_{104}\text{F}_{12}\text{Ir}_4\text{N}_8\text{O}_{16}\text{S}_4\): C 41.91, H 3.81, N 4.07; found: C 41.63, H 3.66, N 3.98. \(^1\text{H-NMR}\) (400MHz, \(\text{CD}_3\text{OD}\), ppm): \(\delta = 8.64\) (s, 4H, HC=N); 8.21 (s, 8H, pyrazine); 7.68 (s, 8H, Ar-H); 7.67 (s, 4H, Ar-H); 7.15 (d, 4H, Ar-H); 6.65-6.67 (dd, 4H, Ar-H); 3.87 (s, 12H, OCH\(_3\)); 1.61 (s, 60H, C\(_5\)Me\(_3\)). IR(KBr): \(\nu_{\text{C-N}} = 1586\ \text{cm}^{-1}\).
Preparation of tetra-nuclear complexes 5a and 5b

Preparation of 5a: A mixture of 1a (132 mg, 0.05 mmol) and DMAD (28 μL, 0.22 mmol) in 20 mL methanol was stirred at room temperature for 12 h. The solution was evaporated to dryness, and the solid was washed with hexane and dimethyl ether to remove excess DMAD. 5a was obtained as a red solid (125 mg, 78%). Anal. Calcd. for C_{116}H_{120}F_{12}Ir_{4}N_{8}O_{28}S_{4}: C 43.55, H 3.78, N 3.50; found: C 43.39, H 3.66, N 3.21. \(^1\)H-NMR (400MHz, CD\(_3\)CN, ppm): \(\delta = 8.93\) (s, 4H, HC=N); 7.62 (s, 8H, pyrazine); 7.53-7.58 (m, 12H, Ar-H); 7.43 (m, 4H, Ar-H); 7.09 (d, 8H, Ar-H); 3.70 (s, 12H, COOCH\(_3\)); 3.64 (s, 12H, COOCH\(_3\)); 1.52 (s, 60H, C\(_5\)Me\(_5\)). IR(KBr): \(\nu = 1556\) (C=N), 1710 (C=O) cm\(^{-1}\).

Preparation of 5b: A mixture of 1b (138 mg, 0.05 mmol) and DMAD (28 μL, 0.22 mmol) in 20 mL methanol was stirred at room temperature for 12 h. The solution was evaporated to dryness, and the solid was washed with hexane and dimethyl ether to remove excess DMAD. 5b was obtained as a red solid (134 mg, 81%). Anal. Calcd. for C_{120}H_{128}F_{12}Ir_{4}N_{8}O_{32}S_{4}: C 43.42, H 3.89, N 3.38; found: C 43.25, H 3.57, N 3.16. \(^1\)H-NMR (400MHz, CD\(_3\)CN, ppm): \(\delta = 8.63\) (s, 4H, HC=N); 8.40 (d, 8H, pyrazine); 8.14 (d, 4H, Ar-H); 7.35 (d, 8H, Ar-H); 7.14 (d, 8H, Ar-H); 3.91 (s, 12H, OCH\(_3\)); 3.89 (s, 12H, COOCH\(_3\)); 3.85 (s, 12H, COOCH\(_3\)); 1.57 (s, 60H, C\(_5\)Me\(_5\)). IR(KBr): 1553 (C=N), 1732 (C=O) cm\(^{-1}\).
**Single-Crystal Structure Determination.**

All the determinations of unit cell and intensity data were performed with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). All the data were collected at room temperature using the ω scan technique. These structures were solved by direct methods, using Fourier techniques, and refined on F² by a full-matrix least-squares method. All the calculations were carried out with the SHELXTL⁴ program. In complex 1b, 1c, 2a, 3a, 3b, 4a and 4b, all non-hydrogen atoms were refined anisotropically.

In complex 1a, all atoms of two triflate anions were refined isotropically because of non-positive definition and other non-hydrogen atoms were refined anisotropically. Two of the four triflate anions and some unknown solvents are strongly disordered and cannot be refined properly, as a result, the SQUEEZE⁵ algorithm was used to omit all of these disordered fragments. Three pair of atoms (O2, S1, F2, and O2’ S1’, F2’) with C45/S1 triflate anion and all O and F atoms with C46/S2 were treated using disorder mode. All 67 restraints were used to restrain the geometry of both triflate anions (C45/S1, C45’/S1’, and C46/S2) to get the better result.

Because the diffraction point is not very perfect and there some trailing, the error of refinement of complex 1b is slightly larger, as a result, the reported su parameters on the unit cell axes are also large.

In complex 1c, the bond distance of C47-F2 was restrained so that the geometry of the triflate anion looks better, the thermal ellipsoid of atom N1 was restrained, 13 least-squares restraints were used, of which 12 thermal parameters of C47 and N1, and 1 bond distance C47-F2 were restrained. Some unknown solvents are strongly disordered and cannot be refined properly, as a result, the SQUEEZE⁵ algorithm was used to omit all of these disordered fragments.

In the asymmetric unit of complex 2a, two of the four triflate anions and some unknown solvents are strongly disordered and cannot be refined properly, as a result, the SQUEEZE⁵ algorithm was used to omit all of these disordered fragments. The H atoms of the water molecule couldn’t restrained and deleted. 8 least-squares restraints were used, which are corresponding to 6 thermal parameters of C46.
and 2 bond distances of S2-C46. The cell contents (C 368, H 392, N 32, O 52, F48, S16, Ir 16) include the atoms in absence of two triflate anions.

The pentamethylcyclopentadienyl ligand of complex 4a was strongly disordered because of rotation in room temperature, and it was also refined to two idealized positions (68:32). The 120 thermal parameters of 20 atoms, which are C11 C12 C13 C14 C15 C16 C17 C18 C19 C20 C11' C12' C13' C14' C15' C16' C17' C18' C19' C20', were restrained. Some unknown solvents are strongly disordered and cannot be refined properly, as a result, the SQUEEZE algorithm was used to omit all of these disordered fragments.

In Complex 4b, the 2 restraints were used to restrain both bond distance of C22- Cl2 and angle distance of Cl2 Cl2_#1 (symmetry code #1: 2-x, y, 3/2-z).

In all complexes, hydrogen atoms which could be found were placed in the geometrically calculated positions with fixed isotropic thermal parameters.

Crystal data for 1a·unknown solvent: C92H96F12Ir4N8O12S4, M = 2630.81, monoclinic, a = 33.826(15), b = 18.632(8), c = 19.427(9) Å, β = 109.080(7)°, V = 11571(9) Å³, T = 293 K, space group C2/c, Z = 4, 23505 reflections measured, 10174 unique (R int = 0.0982) which were used in all calculations. The final wR(F2) was 0.1379 (all data).

Crystal data for 1b·2CH3OH: C98H112F12Ir4N8O18S4, M = 2815.00, monoclinic, a = 17.03(3) Å, b = 18.63(3) Å, c = 17.40(3) Å, β = 114.60(2)°, V = 5020(14) Å³, T = 293 K, space group P21/n, Z = 2, 20681 reflections measured, 8812 unique (R int = 0.1283) which were used in all calculations. The final wR(F2) was 0.1194 (all data).

Crystal data for 1c·2CH2Cl2·unknown solvent: C98H106Cl4F12Ir4N8O12S4, M = 2854.75, monoclinic, a = 16.551(10) Å, b = 34.96(2) Å, c = 21.073(13) Å, β = 106.644(9)°, V = 11684(12) Å³, T = 293 K, space group C2/c, Z = 4, 22373 reflections measured, 10252 unique (R int = 0.0775) which were used in all calculations. The final wR(F2) was 0.0908 (all data).

Crystal data for 2a·H2O·unknown solvent: C92H98F12Ir4N8O13S4, M = 2648.82, monoclinic, a =
27.719(12) Å, \( b = 22.208(12) \) Å, \( c = 20.173(10) \) Å, \( \beta = 119.209(9)^\circ \), \( V = 10840(9) \) Å\(^3\), \( T = 293 \) K, space group \( C2/m \), \( Z = 4 \), 25942 reflections measured, 11808 unique (R\(_{\text{int}}\) = 0.0699) which were used in all calculations. The final wR\(_2\) was 0.1359 (all data).

Crystal data for 3a: \( \text{C}_{40}\text{H}_{44}\text{Cl}_2\text{Ir}_2\text{N}_2 \), \( M = 1008.07 \), monoclinic, \( a = 7.468(3) \) Å, \( b = 18.049(7) \) Å, \( c = 13.623(6) \) Å, \( \beta = 101.915(5)^\circ \), \( V = 1796.8(13) \) Å\(^3\), \( T = 293 \) K, space group \( P2_1/n \), \( Z = 2 \), 8531 reflections measured, 3824 unique (R\(_{\text{int}}\) = 0.0390) which were used in all calculations. The final wR\(_2\) was 0.0471 (all data).

Crystal data for 3b·2CH\(_2\)Cl\(_2\): \( \text{C}_{44}\text{H}_{52}\text{Cl}_6\text{Ir}_2\text{N}_2\text{O}_2 \), \( M = 1237.98 \), monoclinic, \( a = 16.338(7) \) Å, \( b = 10.244(5) \) Å, \( c = 13.969(6) \) Å, \( \beta = 105.319(6)^\circ \), \( V = 2255.0(18) \) Å\(^3\), \( T = 293 \) K, space group \( P2_1/c \), \( Z = 2 \), 10451 reflections measured, 4818 unique (R\(_{\text{int}}\) = 0.0500) which were used in all calculations. The final wR\(_2\) was 0.0723 (all data).

Crystal data for 4a·unknown solvent: \( \text{C}_{40}\text{H}_{44}\text{Cl}_2\text{Ir}_2\text{N}_2 \), \( M = 1008.07 \), monoclinic, \( a = 22.261(12) \) Å, \( b = 8.705(5) \) Å, \( c = 22.589(12) \) Å, \( \beta = 90.839(7)^\circ \), \( V = 4377(4) \) Å\(^3\), \( T = 293 \) K, space group \( C2/c \), \( Z = 4 \), 10280 reflections measured, 4686 unique (R\(_{\text{int}}\) = 0.0531) which were used in all calculations. The final wR\(_2\) was 0.0705 (all data).

Crystal data for 4b·CH\(_2\)Cl\(_2\): \( \text{C}_{43}\text{H}_{50}\text{Cl}_4\text{Ir}_2\text{N}_2\text{O}_2 \), \( M = 1153.05 \), monoclinic, \( a = 27.594(9) \) Å, \( b = 12.355(4) \) Å, \( c = 12.452(4) \) Å, \( \beta = 96.464(4)^\circ \), \( V = 4218(2) \) Å\(^3\), \( T = 293 \) K, space group \( C2/c \), \( Z = 4 \), 9875 reflections measured, 4462 unique (R\(_{\text{int}}\) = 0.0337) which were used in all calculations. The final wR\(_2\) was 0.0765 (all data).
Figure S1. Left: Side view of the cation of 1a in stick mode. All hydrogen atoms, anions, and solvent molecules are omitted for clarity. Right: ORTEP view of 1a (ellipsoids at the 30% probability level). All hydrogen atoms, anions, and solvent molecules are omitted for clarity.

Figure S2. Left: Side view of the cation of 1b in stick mode. Ir (green), N (blue), C (dark gray), O (red). Right: ORTEP view of 1b (ellipsoids at the 30% probability level). All hydrogen atoms, anions, and solvent molecules are omitted for clarity.
Figure S3. (a) Side view of the cation of 1c in stick mode. (b) The crystal packing of 1c in the solid states. Ir (green), N (blue), C (dark gray). (c) ORTEP view of 1c (ellipsoids at the 30% probability level). All hydrogen atoms, anions, and solvent molecules are omitted for clarity.
Figure S4. ORTEP view of the cationic part of 2a (ellipsoids at the 30% probability level). Selected bond lengths [Å] and angles [°]: Ir(1)-C(1) 2.045(9), Ir(1)-N(1) 2.119(8), Ir(1)-N(3) 2.121(7); C(1)-Ir(1)-N(1) 77.9(3), C(1)-Ir(1)-N(3) 84.2(3), N(1)-Ir(1)-N(3) 88.6(3).

Figure S5. ORTEP view of 3b (ellipsoids at the 30% probability level). All hydrogen atoms and solvent molecules are omitted for clarity.
Figure S6. ORTEP view of 4b (ellipsoids at the 30% probability level). All hydrogen atoms and solvent molecules are omitted for clarity.

References