Supporting Information

Homochiral Emissive $\Delta_8^-$- and $\Delta_8^+\text{[Ir}_8\text{Pd}_4]\text{[}^{16+}$ Supramolecular Cages

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Experimental section.

General Synthetic Procedures. Commercial chemicals were used as supplied. All reactions in the synthesis of the metalloligands and metallocages were performed using standard Schlenk techniques under inert (N\textsubscript{2}) atmosphere with reagent-grade solvents. Flash column chromatography was performed using silica gel (Silia-P from Silicycle, 60 Å, 40-63 μm). Analytical thin layer chromatography (TLC) was performed with silica plates with aluminum backings (250 μm with indicator F-254). Compounds were visualized under UV light. $^1$H (including $^1$H DOSY), $^{13}$C and $^{19}$F solution-phase NMR spectra were recorded on a Bruker Avance spectrometer operating at 11.7 T (Larmor frequencies of 500, 126 and 471 MHz, respectively). The following abbreviations have been used for multiplicity assignments: “s” for singlet, “d” for doublet, “t” for triplet, “m” for multiplet and “br” for broad. Melting points (Mps) were recorded using open-ended capillaries on an Electrothermal melting point apparatus and are uncorrected. High-resolution mass spectra of rac-, Λ- and Δ-1, rac-, Λ- and Δ-2 and Irdmbpy were recorded at the EPSRC UK National Mass Spectrometry Facility at Swansea University on a quadrupole time-of-flight (ESI-Q-TOF), model ABSciex 5600 Triple TOF in positive electrospray or nanospray ionization mode and spectra were recorded using sodium formate solution as the calibrant. HR-ESI mass spectra of supramolecular cages rac-, Λ- and Δ-C1 and rac-, Λ- and Δ-C2 and mixed-metalloligand cages were recorded at the University of Leeds on a Bruker MaXis Impact instrument in positive ion mode. The HR-ESI mass spectra of IrCN was recorded at the University of Leeds on a Bruker MaXis Impact instrument in negative ion mode. The samples were injected by direct infusion from DMSO solutions of concentration of ca. 1×10\textsuperscript{-4} M. The syntheses of 2-(2,4-difluorophenyl)-4-phenylpyridine (dFppy),\textsuperscript{1} 2-chloro-4-(2,4,6-trimethylphenyl)pyridine,\textsuperscript{1} 2-phenyl-4-(2,4,6-trimethylphenyl)pyridine (mesppy),\textsuperscript{1} 2-(2,4-difluorophenyl)-4-(2,4,6-trimethylphenyl)pyridine (dFmesppy),\textsuperscript{1} and 4,4’:2’,2’’:4’’,4’’’-quaterpyridine (qpy)\textsuperscript{2} follow previously reported methods.
Synthesis of rac-, Λ-, Δ-[Ir(C^N)_{2}(qpy)]X; X = PF$_6$, BF$_4$ or SbF$_6$.

Scheme S1. Synthesis of [Ir(C^N)$_2$(qpy)]X (X = PF$_6$, BF$_4$ or SbF$_6$) complexes rac-1, rac-2, Δ-1, Λ-1, Δ-2, Δ-2. Reagents and conditions: $^{a,d,g}$ i. 2-MeOC$_2$H$_4$OH, 110 °C, 19 h; ii. Excess solid NH$_4$PF$_6$ or KBF$_4$ or KSbF$_6$, $^{b,e}$ CH$_2$Cl$_2$/MeOH (2:1 v/v), 1.2 equiv. C$_2$H$_5$ONa, 55 °C, 19 h, $^{c,f}$ MeOH/2M HCl$_{aq}$ (2:1 v/v), 20 °C, 30 min. All reactions were conducted under an N$_2$ atmosphere.

The syntheses of both the rac- and Λ- and Δ-enantiopure iridium(III) complexes 1 and 2 are shown in Scheme S1. The mesppy and dMesppy C^N ligands were reacted with IrCl$_3$3H$_2$O and the resulting the μ-dichloro-bridged iridium dimers rac-[Ir(mesppy)$_2$Cl]$_2$, rac-D1 and rac-[Ir(dMesppy)$_2$Cl]$_2$, rac-D2 were formed in good yield under standard conditions.$^2$ Complexes rac-1 and rac-2 were isolated in moderate yield through cleavage of rac-D1 and rac-D2 with qpy and subsequent anion metathesis with aqueous NH$_4$PF$_6$ or a methanol solution of KBF$_4$ or a methanol solution of KSbF$_6$. Following a previously reported protocol,$^3$ treatment of rac-D1 and rac-D2 with
L-serine afforded diastereomers $\Lambda-[\text{Ir}(C^\text{N})_2(\text{L-serine})]$ and $\Delta-[\text{Ir}(C^\text{N})_2(\text{L-serine})]$ (respectively, $\Delta$-Lser and $\Lambda$-Lser in Scheme S1). Chromatographic purification on silica gel permitted only isolation of analytically pure $\Delta-[\text{Ir}(C^\text{N})_2(\text{L-serine})]$, which was the first eluting diastereomer; the second, lower mobility diastereomer, corresponding to $\Lambda-[\text{Ir}(C^\text{N})_2(\text{L-serine})]$ was found to be contaminated with traces of the $\Delta$-LSer complex. Fortunately, following chromatographic resolution of the corresponding D-serine complexes, we obtained analytically pure $\Lambda-[\text{Ir}(C^\text{N})_2(\text{D-serine})]$ as the first eluting band ($\Lambda$-DSer in Scheme S1). The $^1$H NMR of the rac-[Ir(C^N)_2(L-serine)], $\Delta-[\text{Ir}(C^\text{N})_2(\text{L-serine})]$ and $\Lambda-[\text{Ir}(C^\text{N})_2(\text{D-serine})]$ complexes are reported in Figures S1 and S2. Addition of a solution of 1M HCl to the $\Lambda$- and $\Delta-[\text{Ir}(C^\text{N})_2(\text{serine})]$ complexes yielded the enantiopure $\Lambda,\Lambda$ and $\Delta,\Delta-[\text{Ir}(C^\text{N})_2\text{Cl}]_2$ dimers. Finally, the enantiopure $\Lambda$-1 and $\Delta$-1 were obtained, respectively, upon reaction of $\Lambda,\Lambda$ and $\Delta,\Delta-[\text{Ir(}\text{mesppy})_2\text{Cl}]_2$ dimers with qpy following standard conditions, while the enantiopure $\Lambda$-2 and $\Delta$-2 were obtained, respectively, by reacting the $\Lambda,\Lambda$- and $\Delta,\Delta-[\text{Ir(dFmesppy)}_2\text{Cl}]_2$ dimers with qpy. All complexes were purified by column chromatography and isolated as their PF$_6^-$, BF$_4^-$ or SbF$_6^-$ salts following an anion metathesis reaction using NH$_4$PF$_6$ or KBF$_4$ or KSbF$_6$. The purity of the complexes was confirmed by $^1$H, $^{19}$F, $^{13}$C NMR, HRMS and melting point analyses. The degree of enantiopurity and $\Delta$-1, $\Lambda$-1, $\Delta$-2 and $\Lambda$-2 was confirmed by circular dichroism (CD) spectroscopy. In addition, X-ray single crystal structures of the enantiopure $\Lambda,\Lambda$- and $\Delta,\Delta-[\text{Ir(dFmesppy)}_2\text{Cl}]_2$ dimers ($\Lambda,\Lambda$-D2 and $\Delta,\Delta$-D2) and of the racemate rac-2 were also obtained (Figure S59 and S60). The crystal structures of the enantiopure $\Lambda,\Lambda$- and $\Delta,\Delta-[\text{Ir(mesppy)}_2\text{Cl}]_2$ dimers and of the racemate rac-1 were previously reported by our group.$^{2,3}$
General procedure for the synthesis of rac-\([Ir(C^N)_2]_2Cl_2\) dimers. The iridium (III) dimers, \([Ir\text{mesppy})_2(\mu-Cl)]_2\) and \([Ir\text{dFmesppy})_2(\mu-Cl)]_2\) were prepared according to the procedure described by Nonoyama.\(^4\) Briefly, to \(\text{IrCl}_3\cdot3\text{H}_2\text{O}\) (1.0 equiv.) and \(C^N\) ligand (2.2 equiv.) was added 2-ethoxyethanol to give a concentration of 0.02 M of iridium dimer. The reaction mixture was degassed by multiple vacuum and \(N_2\) purging cycles and the mixture was heated to reflux for 19 h. The solution was cooled to room temperature and the yellow precipitate was filtered, washed with water, hexane and ether and finally dried under vacuum to afford the desired material, which was used without further purification.

Tetrakis[2-(phenyl)-4-(2,4,6-trimethylphenyl)pyridinato-\(N,C^2\)]-bis(\(\mu\)-chloro)diiridium(III)\([Ir\text{mesppy})_2(\mu-Cl)]_2\) (rac-D1). Yield: 70%. \(^1\)H NMR (500 MHz, \(\text{CD}_2\text{Cl}_2\)) \(\delta\) (ppm): 9.69 (d, \(J = 6.4\) Hz, 2H), 7.77 (s, 4H), 7.55 (d, \(J = 9.0\) Hz, 4H), 7.05 (d, \(J = 10.9\) Hz, 8H), 6.86 (m, 7H), 6.72 (dt, \(J = 8.1\) Hz, 4H), 5.95 (d, \(J = 8.1\) Hz, 4H), 2.42 (s, 12H), 2.16 (s, 24H). The characterization matches that reported.\(^1\)

Tetrakis[2-(4’,6’-difluorophenyl)-4-(2,4,6-trimethylphenyl)pyridinato-\(N,C^2\)]-bis(\(\mu\)-chloro)diiridium(III)\([Ir\text{dFmesppy})_2(\mu-Cl)]_2\) (rac-D2). Yield: 81%. \(^1\)H \{\(^{19}\)F\} NMR (400 MHz, \(\text{CD}_2\text{Cl}_2\)) \(\delta\) (ppm): 9.57 (d, \(J = 6.0\) Hz, 4H), 8.13 (s, 4H), 7.02 (d, \(J = 10.4\) Hz, 8H), 6.89 (dd, \(J = 6.0, 2.0\) Hz, 4H), 5.29 (m, 4H) 2.38 (s, 12H), 2.12 (s, 24H). \(^{19}\)F \{\(^1\)H\} NMR (471 MHz, \(\text{CD}_2\text{Cl}_2\)) \(\delta\) (ppm): −108.1 (d, \(J = 11.1\) Hz, 4F), −110.2 (d, \(J = 10.8\) Hz, 4F). The characterization matches that reported.\(^1\)

General procedure for the synthesis of \(\Lambda,\Lambda-\) and \(\Delta,\Delta-\)[Ir\(C^N\)]\(_2\)\(_2\)Cl\(_2\) dimers. The enantiopure iridium (III) dimers, \(\Lambda,\Lambda-\) and \(\Delta,\Delta-\)[Ir\(\text{mesppy})_2(\mu-Cl)]_2\) (\(\Lambda,\Lambda\text{-D1}\) and \(\Delta,\Delta\text{-D1}\) in Scheme S1) \(\Lambda,\Lambda-\) and \(\Delta,\Delta-\)[Ir\(\text{dFmesppy})_2(\mu-Cl)]_2\) (\(\Lambda,\Lambda\text{-D2}\) and \(\Delta,\Delta\text{-D2}\) in Scheme S1) were prepared according to the procedure previously reported for \(\Lambda,\Lambda-\) and \(\Delta,\Delta-\)[Ir\(\text{mesppy})_2(\mu-Cl)]_2.\(^3\) To a Schlenk tube
containing rac-[(Ir(C^N)2Cl)2] (rac-D1 or rac-D2 in Scheme S1) (0.30 mmol, 1 equiv.), L or D-serine (0.63 mmol, 2.1 equiv.) and NaOEt (0.63 mmol, 2.1 equiv.) were added. DCM and MeOH (1:1 v/v) were added to give a concentration of 0.03 M of iridium dimer. The reaction mixture was degassed by multiple vacuum and N2 purging cycles and the mixture was heated to 50 °C for 19 h under nitrogen atmosphere. The solvent was removed in vacuo and the crude product purified using silica-gel flash column chromatography (CH2Cl2/CH3OH/NEt3 (96:3:1) as eluent). The pure fractions of the higher mobility diastereoisomers, Δ-[Ir(C^N)2(L-serine)] (Δ-Lser in Scheme S1) and Λ-[Ir(C^N)2(D-serine)] (Λ-Dser in Scheme S1) were obtained analytically pure, whereas the slower eluting compounds, Λ-[Ir(C^N)2(L-serine)] (Λ-Lser in Scheme S1) and Δ-[Ir(C^N)2(D-serine)], (Δ-Dser in Scheme S1) were always contaminated with the other isomer. The pure Δ-Lser and Λ-Dser complexes isolated from the column were dissolved in CH3OH and CH2Cl2 (5:1 v/v) and to this was added 1M HCl solution (2 mL). A precipitate was formed after stirring the solutions for 10 min at room temperature. The solids were filtered, washed with hexane and diethyl ether (1:1 v/v) and air dried to give yellow powders.

Δ-Iridium(III)bis[2-phenyl-4-(2,4,6-trimethylphenyl)pyridinato]-L-serine, Δ-[Ir(mesppy)2(L-serine)] (Δ-Lser1). Yield: 52%. Rf: 0.35 (CH2Cl2/CH3OH/NEt3 (96:3:1)). Mp: 282 - 286 °C. 1H NMR (500 MHz, CD2Cl2) δ(ppm) 9.56 (d, J = 6.2 Hz, 2H), 8.73 (d, J = 6.1 Hz, 2H), 7.77 (dd, J = 0.9, 23.5 Hz, 4H), 7.57 (dt, J = 0.4, 5.9 Hz, 4H), 7.22 (dd, J = 1.7, 5.7 Hz, 2H), 7.15 (dd, J = 1.7, 5.9 Hz, 2H), 7.07 (m, 8H), 6.87 (m, 4H), 6.75 (m, 4H), 6.42 (dd, J = 1.0, 8.1 Hz, 2H), 6.31 (dd, J = 0.7, 6.7 Hz, 2H), 4.08 (dd, J = 5.6 Hz, 2H), 3.89 (dd, J = 3.2, 8.5 Hz, 1H), 2.21 (s, 6H), 2.21 (s, 6H), 2.19 (s, 6H).

Δ-Iridium(III)bis[2-phenyl-4-(2,4,6-trimethylphenyl)pyridinato]-D-serine, Δ-[Ir(mesppy)2(D-serine)] (Δ-Dser1). Yield: 52%. Rf: 0.35 (CH2Cl2/CH3OH/NEt3 (96:3:1)). Mp: 282 - 286 °C. 1H
NMR (500 MHz, CD₂Cl₂) δ(ppm) 9.62 (d, J = 6.5 Hz, 2H), 8.77 (d, J = 5.3 Hz, 2H), 7.72 (dd, J = 1.6, 17.8 Hz, 4H), 7.55 (dt, J = 1.1, 5.8 Hz, 4H), 7.15 (ddd, J = 1.5, 5.5, 9.5 Hz, 2H), 7.04 (m, 8H), 6.84 (m, 4H), 6.73 (m, 4H), 6.47 (dd, J = 0.6, 8.0 Hz, 2H), 6.28 (dd, J = 0.6, 7.4 Hz, 2H), 3.90 (dd, J = 3.7, 11.0 Hz, 2H), 3.82 (dd, J = 5.3, 10.8 Hz 1H), 2.21 (s, 6H), 2.21 (s, 6H), 2.19 (s, 6H).

Δ-Iridium(III)bis[2-(4',6'-difluorophenyl)-4-(2,4,6-trimethylphenyl)pyridinato]-L-serine, Δ-[Ir(dfesppy)₂(L-serine)] (Δ-Lser2). Yield: 55%. Rf: 0.30 (CH₂Cl₂/CH₃OH/NEt₃ (96:3:1)). Mp: 292 - 296 °C. ¹H NMR (500 MHz, CD₂Cl₂) δ(ppm) 8.90 (d, J = 5.2 Hz, 2H), 8.78 (d, J = 5.9 Hz, 2H), 8.18 (dd, J = 0.8, 9.6 Hz, 4H), 7.26 (dd, J = 1.5, 6.0 Hz, 2H), 7.21 (dd, J = 1.7, 5.8 Hz, 2H), 7.08 (bm, 2H), 6.43 (m, 6H), 5.80 (dd, J = 2.6, 8.8 Hz, 2H), 5.65 (m, J = 2.2, 8.8 Hz, 2H), 5.53 (t, J = 1.0 Hz, 2H), 5.18 (t, J = 1.1 Hz, 2H), 4.36 (dd, J = 2.0, 10.0 Hz, 2H), 3.89 (dd, J = 10.1 Hz, 2H), 2.40 (s, 6H), 2.22 (s, 6H), 2.19 (s, 6H). ¹⁹F NMR (471 MHz, CD₂Cl₂) δ (ppm): −108.3 (q, J = 10.0 Hz, 2F), −108.8 (q, J = 10.1 Hz, 2F).

Δ-Iridium(III)bis[2-(4',6'-difluorophenyl)-4-(2,4,6-trimethylphenyl)pyridinato]-D-serine, Δ-[Ir(dfesppy)₂(D-serine)] (Δ-Dser2). Yield: 55%. Rf: 0.35 (CH₂Cl₂/CH₃OH/NEt₃ (96:3:1)). Mp: 292 - 296 °C. ¹H NMR (500 MHz, CD₂Cl₂) δ(ppm) 8.93 (d, J = 6.0 Hz, 2H), 8.69 (d, J = 6.8 Hz, 2H), 8.15 (dd, J = 1.0, 15.6 Hz, 4H), 7.19 (dd, J = 1.7, 5.7 Hz, 2H), 7.05 (m, 4H), 6.41 (dt, J = 2.4, 8.8 Hz, 2H), 6.29 (dt, J = 2.7, 10.2 Hz, 2H), 5.85 (dd, J = 2.6, 9.2 Hz, 2H), 5.53 (t, J = 1.2 Hz, 2H), 5.18 (t, J = 1.1 Hz, 2H), 4.26 (dd, J = 2.2, 10.4 Hz, 2H), 3.84 (m, 2H), 2.40 (s, 6H), 2.39 (s, 6H), 2.20 (s, 6H). ¹⁹F NMR (471 MHz, CD₂Cl₂) δ (ppm): −108.4 (q, J = 10.0 Hz, 2F), −108.0 (q, J = 10.1 Hz, 2F).

Δ, Δ- a.1 Λ, Λ-Tetrakis[2-(phenyl)-4-(2,4,6-trimethylphenyl)pyridinato-η₂C₂]-bis(µ-chloro)diiridium(III)[Ir(mesppy)₂(µ-Cl)]₂ (Δ,Δ-D1 and Λ,Λ-D1). Yield: Δ,Δ-D1: 5%; Λ,Λ-D1: 45%. ¹H NMR (500 MHz, CD₂Cl₂) δ(ppm): 9.69 (d, J = 6.4 Hz, 2H), 7.77 (s, 4H), 7.55 (d, J = 9.0
Hz, 4H), 7.05 (d, \( J = 10.9 \) Hz, 8H), 6.86 (m, 7H), 6.72 (dt, \( J = 8.1 \) Hz, 4H), 5.95 (d, \( J = 8.1 \) Hz, 4H), 2.42 (s, 12H), 2.16 (s, 12H), 2.15 (s, 12H). The characterization matches that reported.3

Δ, Δ- and Λ, Λ-Tetrakis[2-(4',6'-difluorophenyl)-4-(2,4,6-trimethylphenyl)pyridinato-N,C^2]-bis(μ-chloro)diiridium(III), \([Ir(dFmesppy)_2(μ-Cl)]_2 \ (Δ,Δ-D2 \ and \ Λ,Λ-D2)\). Yield: Δ,Δ-D2: 60%; Δ,Λ-D2: 50%. \(^1\)H \{\(^{19}\)F\} NMR (400 MHz, CD\(_2\)Cl\(_2\)) \( δ \) (ppm): 9.57 (d, \( J = 6.0 \) Hz, 4H), 8.13 (s, 4H), 7.02 (d, \( J = 10.4 \) Hz, 8H), 6.89 (dd, \( J = 6.0, 2.0 \) Hz, 4H), 5.29 (m, 4H) 2.38 (s, 12H), 2,12 (s, 24H). \(^{19}\)F \{\(^1\)H\} NMR (471 MHz, CD\(_2\)Cl\(_2\)) \( δ \) (ppm): −108.1 (d, \( J = 11.1 \) Hz, 4F), −110.2 (d, \( J = 10.8 \) Hz, 4F). The characterization matches that reported.1

**General procedure for the synthesis of rac-, Δ- and Δ-[Ir(C^N)_2(qpy)]PF\(_6\), BF\(_4\) or SbF\(_6\) complexes.**

To a Schlenk tube containing one of rac-[Ir(mesppy)_2Cl]\(_2\) (rac-D1), rac-[Ir(dFmesppy)_2Cl]\(_2\), (rac-D2), Λ, Λ-[Ir(mesppy)_2Cl]\(_2\), (Λ,Λ-D1), Δ, Δ-[Ir(mesppy)_2Cl]\(_2\), (Δ,Δ-D1), Λ, Λ-[Ir(dFppymes)_2Cl]\(_2\), (Λ,Λ-D2) or Δ, Δ-[Ir(dFppymes)_2Cl]\(_2\), (Δ,Δ-D2) (1.0 equiv.), and qpy ligand (2.5 equiv.), was added 2-methoxyethanol to give a concentration of 0.03 M of iridium dimer. The reaction mixture was degassed by multiple vacuum and N\(_2\) purging cycles and the mixture was heated to 55 °C for 19 h under nitrogen atmosphere. For preparing the PF\(_6\) salts: the solution was cooled to room temperature and solid NH\(_4\)PF\(_6\) (10.0 equiv.) was added and the reaction mixture was left to stir for a further 1 h. For preparing the BF\(_4\) salts: a 2 M solution of KBF\(_4\) in MeOH (10 mL) was added at room temperature to the reaction mixture and the resulting suspension was stirred at room temperature for 4 h. For preparing SbF\(_6\) salts: a 2 M solution of KSbF\(_6\) in MeOH (10 mL) was added at room temperature to the reaction mixture and the resulting suspension stirred at room temperature for 4 h. For all three anions, the resulting suspensions were evaporated to dryness, with the residue then copiously washed with Et\(_2\)O and distilled water. This crude product was purified by
flash column chromatography (silica, DCM/MeOH/NEt₃ gradient 100:0:0 to 60:40:10). Fractions containing the desired complex were combined and solid NH₄PF₆ (10.0 equiv.) or KBF₄ (10.0 equiv.) or SbF₆ (10.0 equiv.) was added. The suspension was stirred at room temperature for 0.5 h. This mixture was then evaporated to dryness, washed vigorously with distilled water and diethyl ether and dried to afford the pure material.

\[ \text{rac-}, \Delta-, \Lambda-\text{Iridium(III)bis[2-phenyl-4-(2,4,6-trimethylphenyl)pyridinato]-4,4':2',2'':4'',4'''-quaterpyridine hexafluorophosphate, } \Delta-, \Lambda-[\text{Ir(mesppy)}_2(qpy)](PF₆) \] (\text{rac-}, \Delta-, \Lambda-1): Yield: \text{rac-1}: 55%; \Delta-1: 45%; \Lambda-1 50%. \text{Rf: } 0.20 \text{ (DCM: MeOH: NEt₃ = 100:3:2)}. \text{Mp: } \text{rac-1}: 350 - 353 °C \text{ (decomposed); } \Delta-1: 351 - 354 °C \text{ (decomposed); } \Lambda-1: 348 - 352 °C \text{ (decomposed).} \text{¹H NMR (500 MHz, CDCl₃) } \delta(\text{ppm}): \text{9.51 (s, 2H), 8.88 (d, } J = 5.7 \text{ Hz, 4H), 8.25 (dd, } J = 6.1, 2.1 \text{ Hz, 2H), 8.17 (s, 2H), 8.12 (d, } J = 5.6 \text{ Hz, 2H), 8.08 (d, } J = 6.7 \text{ Hz, 3H), 8.03 (d, } J = 7.8 \text{ Hz, 2H), 7.78 (d, } J = 5.6 \text{ Hz, 2H), 7.05 - 6.98 \text{ (m, 10H), 6.30 (d, } J = 6.3 \text{ Hz, 2H), 2.29 (s, 6H), 2.10 (s, 6H), 1.90 (s, 6H).} \text{¹³C NMR (126 MHz, CDCl₃) } \delta(\text{ppm}): 167.8, 165.5, 152.4, 151.5, 150.9, 149.8, 149.0, 148.6, 143.9, 143.0, 138.3, 134.9, 133.2, 131.5, 130.8, 128.5, 126.2, 125.1, 124.9, 122.9, 122.3, 121.3, 29.7, 20.8, 20.3. \text{HR NSI⁺ MS: [M-PF₆]⁺ Calculated: (C₆₀H₅₀IrN₆): 1047.3726 Found: } \Delta-1: 1047.3719; \Lambda-1: 1047.3718. \text{The characterization of } \text{rac-1 matches that previously reported.}^2

\[ \text{rac-}, \Delta-, \Lambda-\text{Iridium(III)bis[2-(2,4-difluoro)-phenyl-4-(2,4,6-trimethylphenyl)pyridinato]-4,4':2',2'':4'',4'''-quaterpyridine hexafluorophosphate, } \Delta-, \Lambda-[\text{Ir(dFmesppy)}_2(qpy)](PF₆) \] (\text{rac-}, \Delta-, \Lambda-2). Yield: \text{rac-2}: 40%; \Delta-2: 38%; \Lambda-2: 30%. \text{Rf: } 0.20 \text{ (DCM: MeOH: NEt₃ = 100:3:2)}. \text{Mp: } \text{rac-2}: 342 - 346 °C \text{ (decomposed); } \Delta-2: 340 - 344 °C \text{ (decomposed); } \Lambda-2: 348 - 352 °C \text{ (decomposed).} \text{¹H NMR (500 MHz, CD₂Cl₂) } \delta(\text{ppm}): 8.83 (m, 5H), 8.31 (d, } J = 5.4 \text{ Hz, 1H), 8.22 (bs, 2H), 7.85 (d, } J = 5.9 \text{ Hz, 1H), 7.80 (d, } J = 5.3 \text{ Hz, 2H), 7.69 (d, } J = 5.8 \text{ Hz, 2H), 7.04 (m, 6H), 6.68 (m, 3H), 5.81 (m, 3H), 2.35 (s, 6H), 2.16 (s, 6H), 1.99 (s, 6H).} \text{¹⁹F NMR (417 MHz, CD₂Cl₂) } \delta
(ppm): –72.5 (d, J = 707.5 Hz, 6F), –106.0 (d, J = 10.3 Hz, 2F), –108.3 (d, J = 10.3 Hz, 2F). HR NSI$^+$ MS: [M-PF$_6$]$^+$ Calculated: (C$_{60}$H$_{46}$F$_4$IrN$_6$): 1119.3349 Found: Δ-2; 1119.3326; Λ-2; 1119.3324. The characterization of rac-2 matches that reported.$^2$

**rac-**  
Δ-, $\Lambda$-Iridium(III)bis[2-phenyl-4-(2,4,6-trimethylphenyl)pyridinato]-4,4’:2’,2’’:4”,4’’’-quaterpyridine tetrafluoroborate, Δ-, Λ-[Ir(mesppy)$_2$(qpy)](BF$_4$) (rac-, Δ-, Δ-1): Yield: rac-1; 55%; Δ-1; 52%; Λ-1; 50%. R$_f$: 0.20 (DCM + 3% MeOH + 2% NEt$_3$). Mp: rac-1: 348 - 352 °C (decomposed); Δ-1: 351 - 354 °C (decomposed); Λ-1: 355 - 358 °C (decomposed). $^1$H NMR (500 MHz, CDCl$_3$) δ(ppm): 9.20 (s, 2H), 8.86 (d, J = 5.7 Hz, 4H), 8.30 (d, J = 5.3 Hz, 2H), 7.91 (m, 4H), 7.84 (s, 2H), 7.81 (dd, J = 1.5, 6.1 Hz, 2H), 7.76 (d, J = 7.8 Hz, 2H), 7.69 (d, J = 6.8 Hz, 2H), 7.14 (dt, J = 1.0, 6.9 Hz, 2H), 7.05 (m, 7H), 6.93 (dd, J = 0.5, 6.4 Hz, 2H), 6.46 (d, J = 6.4 Hz, 2H), 2.36 (s, 6H), 2.17 (s, 6H), 1.99 (s, 6H). HR NSI$^+$ MS: [M-BF$_4$]$^+$ Calculated: (C$_{60}$H$_{50}$IrN$_6$): 1047.3726 Found: rac-1; 1047.3719; Δ-1 ; 1047.3719; Λ-1: 1047.3715.

**rac-**  
Δ-, $\Lambda$-Iridium(III)bis[2-(2,4-difluoro)-phenyl-4-(2,4,6-trimethylphenyl)pyridinato]-4,4’:2’,2’’:4”,4’’’-quaterpyridine tetrafluoroborate, Δ-, Λ-[Ir(dFmesppy)$_2$(qpy)](BF$_4$) (rac-, Δ-, Δ-, Δ-2). Yield: rac-2; 40%; Δ-2: 38%; Λ-2: 35%. R$_f$: 0.20 (DCM : MeOH :NEt$_3$ = 100 : 3 : 2). Mp: rac-2: 344 - 348 °C (decomposed); Δ-2: 340 - 344 °C (decomposed); Λ-2: 341 - 345 °C (decomposed). $^1$H NMR (500 MHz, CD$_2$Cl$_2$) δ(ppm): 9.27 (s, 2H), 8.86 (s, 4H), 8.25 (m, 4H), 7.90 (m, 6H), 7.70 (d, J = 5.6 Hz, 2H), 7.01 (m, 2H), 6.68 (t, J = 11.1 Hz, 2H), 6.68 (m, 3H), 5.83 (d, J = 6.5 Hz, 2H), 2.35 (s, 6H), 2.16 (s, 6H), 1.99 (s, 6H). $^{19}$F NMR (417 MHz, CD$_2$Cl$_2$) δ(ppm): –106.2 (d, J = 10.3 Hz, 2F), –108.4 (d, J = 10.3 Hz, 2F), –150.9 (d, J = 10 Hz, 4F). HR NSI$^+$ MS: [M-BF$_4$]$^+$ Calculated: (C$_{60}$H$_{46}$F$_4$IrN$_6$): 1119.3349 Found: rac-2; 1119.3326; Δ-2; 1119.3326, Λ-2; 1119.3325.
Δ-Iridium(III)bis[2-phenyl-4-(2,4,6-trimethylphenyl)pyridinato]-4,4':2',2'':4'',4'''-
quaterpyridine hexafluoroantimonate, Δ-[Ir(mesppy)(qpy)](SbF₆) (Δ–1): Yield: 55%. Rᵢ: 0.20 (DCM : MeOH : NEt₃ = 100 : 3 : 2). Mp: 358 - 360 °C (decomposed). ¹H NMR (500 MHz, CDCl₃) δ(ppm): δ 9.51 (d, J = 2.0 Hz, 2H), 8.99 – 8.81 (m, 4H), 8.25 (dd, J = 5.8, 1.8 Hz, 2H), 8.17 (d, J = 1.9 Hz, 2H), 8.11 (d, J = 5.8 Hz, 2H), 8.08 (d, J = 6.3 Hz, 4H), 8.03 (dd, J = 7.7, 1.5 Hz, 2H), 7.78 (d, J = 6.0 Hz, 2H), 7.09 – 6.90 (m, 10H), 6.33 – 6.25 (m, 2H), 2.28 (s, 6H), 2.09 (s, 6H). HR NSI⁺ MS: [M – SbF₆]⁺ Calculated: (C₆₀H₅₀IrN₆): 1047.3726 Found: 1047.3719.

The general procedures for the synthesis of rac-TBA[Ir(dFppy)₂(CN)₂] (IrCN)⁵ and [Ir(dFppy)₂(dmbpy)](PF₆) (Irdmbpy)⁶ are according to those previously reported.

rac-Tetrabutyl ammonium bis(cyanide)-bis[2-(2,4-difluoro)-phenylpyridinato]-iridium(III), rac-TBA[Ir(dFppy)₂(CN)₂] (IrCN). The synthesis of this complex follows a previously reported method.⁵ Yield: 70%. ¹H NMR (500 MHz, CD₂Cl₂) δ(ppm): δ 9.54 (d, J = 5.8 Hz, 2H), 8.36 – 7.86 (m, 5H), 7.45 (t, J = 6.8 Hz, 2H), 6.61 (t, J = 11.3 Hz, 3H), 5.53 (d, J = 8.1 Hz, 2H). ¹⁹F NMR (417 MHz, CD₂Cl₂) δ (ppm): −109.9 (d, J = 11.3 Hz, 2F), −111.0 (d, J = 11.3 Hz, 2F). HR ESI⁺ MS: [TBA-M]⁺ Calculated: (C₂₄H₁₂F₄IrN₄): 625.0627 Found: 625.0925. The characterization matches that reported.⁵

rac-Iridium(III)bis[2-(2,4-difluoro)-phenylpyridinato]-4,4'-dimethyl-2,2'-bypiridine hexafluorophosphate, [Ir(dFppy)₂(dmbpy)](PF₆) (Irdmbpy). The synthesis of this complex follows a previously reported method.⁶ Yield: 80%. Rᵢ: 0.20 (DCM + 3% MeOH). Mp: 290 - 300 °C. ¹H NMR (500 MHz, CD₂Cl₂) δ(ppm): δ 8.47 – 8.26 (m, 2H), 7.92 – 7.78 (m, 2H), 7.60 – 7.48 (m, 1H), 7.33 (d, J = 5.2 Hz, 1H), 7.09 (ddd, J = 7.4, 5.8, 1.5 Hz, 1H), 6.64 (ddd, J = 12.1, 9.2, 2.4
Hz, 1H), 5.78 (dd, $J = 8.4, 2.4$ Hz, 1H). $^{19}$F NMR (417 MHz, CD$_2$Cl$_2$) $\delta$ (ppm): –109.0 (d, $J = 13.4$ Hz, 2F), –106.6 (d, $J = 13.2$ Hz, 2F), –74.0 (s, 3F), –72.2 (s, 3F). HR NSI$^+$ MS: [M-PF$_6$]$^+$

**Calculated:** (C$_{34}$H$_{24}$F$_4$IrN$_4$): 757.1549 **Found:** 757.1562. The characterization matches that reported.$^6$

**General procedure for the synthesis of cages rac-, $\Lambda$- and $\Delta$-C1 and rac-, $\Lambda$- and $\Delta$-C2.** In a dry 10 mL Schlenk vial, one of the complexes rac-, $\Lambda$- or $\Delta$-1 or rac-, $\Lambda$- or $\Delta$-2 (2 equiv.) and [Pd(NCMe)$_4$](BF$_4$)$_2$ (1 equiv.) were dissolved in DMSO-$d_6$ (1 mL) to give a concentration of the iridium metallo-ligands of approximately 0.05 M. The solution was degassed for five minutes by bubbling nitrogen and heated at 85 °C for 12 h under a nitrogen atmosphere. The solution was cooled to room temperature and the black solid was filtered through celite. A 2 M aqueous solution of NH$_4$PF$_6$ (5 mL) or a 2M MeOH/H$_2$O solution (1:1 v/v) of KBF$_4$ (5 mL) or a 2M MeOH/H$_2$O solution (1:1 v/v) of SbF$_6$ (5 mL) was added to the resulting DMSO solution and the mixture was stirred at room temperature for 4h. The solution was cooled in an ice bath for 30 minutes and the obtained precipitate was filtered, washed with water and diethyl ether to yield a dark red solid (rac-, $\Lambda$- or $\Delta$-C1) or a dark yellow solid (rac-, $\Lambda$- or $\Delta$-C2).

$\Delta_r$-[I$_3$Pd$_4$](PF$_6$)$_{16}$, ($\Delta_r$-C1-PF$_6$): **Yield:** 90%. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$(ppm): $\delta$ 9.67 (d, $J = 12.2$ Hz, 16H), 9.05 (d, $J = 36.6$ Hz, 11H), 8.84 (s, 15H), 8.44 – 8.22 (m, 19H), 8.06 (dd, $J = 45.9$, 31.0 Hz, 38H), 7.72 (s, 6H), 7.44 (s, 7H), 7.13 – 6.68 (m, 46H), 6.57 (s, 4H), 6.22 (d, $J = 10.4$ Hz, 12H), 2.32 (s, 48H), 2.12 (s, 48H), 1.95 (s, 48H). $^{19}$F NMR {PF$_6$} (417 MHz, CD$_2$Cl$_2$) $\delta$ (ppm): –69.348 (bs), –70.859 (bs). **HR ESI MS:** [M-PF$_6$]$^+$ **Calculated:** [(C$_{60}$H$_{50}$IrN$_6$)$_8$Pd$_4$(PF$_6$)$_{12}$]$^{4+}$: 2635.5650 Found: 2635.7938; [(C$_{60}$H$_{50}$IrN$_6$)$_8$Pd$_4$(PF$_6$)$_{11}$]$^{5+}$: 2079.6497 Found: 2079.6421; [(C$_{60}$H$_{50}$IrN$_6$)$_8$Pd$_4$(PF$_6$)$_{10}$]$^{6+}$: 1708.7120 Found: 1708.7056; [(C$_{60}$H$_{50}$IrN$_6$)$_8$Pd$_4$(PF$_6$)$_9$]$^{7+}$: 1404.1881 Found: 1404.0402; [(C$_{60}$H$_{50}$IrN$_6$)$_8$Pd$_4$(PF$_6$)$_8$]$^{8+}$: 1245.4881 Found: 1245.4146.
\( \Delta_r-[I_{8}Pd_{4}](BF_{4})_{16}, (\Delta_r-Cl-BF_{4}) \): Yield: 90%. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\)(ppm): \(^1\)H NMR (500 MHz, DMSO-\(d_6\)) \(\delta\) 9.67 (d, \(J = 11.8\) Hz, 16H), 9.58 – 9.40 (m, 11H), 9.33 (s, 7H), 9.21 – 8.77 (m, 28H), 8.61 – 7.85 (m, 104H), 7.74 (d, \(J = 16.8\) Hz, 14H), 7.44 (s, 8H), 7.14 – 6.68 (m, 82H), 6.57 (s, 7H), 6.35 – 6.12 (m, 20H), 2.31 (s, 48H), 2.12 (s, 48H), 1.95 (s, 48H). \(^{19}\)F NMR \{PF\(_6\)\} (417 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) (ppm): –69.348 (bs), –70.859 (bs). HR ESI MS: [M-PF\(_4\)]^+ Calculated: [(C\(_6\)H\(_5\)IrN\(_6\))\(_8\)Pd\(_4\)(PF\(_6\))\(_{12}\)]\(^{5+}\): 2635.5650 Found: 2635.7938; [(C\(_6\)H\(_5\)IrN\(_6\))\(_8\)Pd\(_4\)(PF\(_6\))\(_{11}\)]\(^{5+}\): 2079.6497 Found: 2079.6421; [(C\(_6\)H\(_5\)IrN\(_6\))\(_8\)Pd\(_4\)(PF\(_6\))\(_{10}\)]\(^{6+}\): 1709.0431 Found: 1708.7056; [(C\(_6\)H\(_5\)IrN\(_6\))\(_8\)Pd\(_4\)(PF\(_6\))\(_9\)]\(^{7+}\): 1404.1881 Found: 1404.0402; [(C\(_6\)H\(_5\)IrN\(_6\))\(_8\)Pd\(_4\)(PF\(_6\))\(_8\)]\(^{8+}\): 1245.2926 Found: 1245.4146.

\( \Delta_r-[I_{8}Pd_{4}](BF_{4})_{16}, (\Delta_r-Cl-BF_{4}) \): Yield: 95%. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\)(ppm): \(\delta\) 9.68 (d, \(J = 14.2\) Hz, 16H), 9.10 (d, \(J = 42.7\) Hz, 11H), 8.34 (s, 20H), 8.24 – 7.88 (m, 38H), 7.76 (s, 6H), 7.43 (s, 5H), 7.10 – 6.73 (m, 45H), 6.54 (s, 6H), 6.22 (d, \(J = 12.6\) Hz, 11H), 2.35 (s, 48H), 2.13 (s, 48H), 1.91 (s, 48H). \(^{19}\)F NMR \{BF\(_4\)\} (417 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) (ppm): –148.098 (d, \(J = 10.3\) Hz, 4F). HR ESI MS: [M-BF\(_4\)]^+ Calculated: [(C\(_6\)H\(_5\)IrN\(_6\))\(_8\)Pd\(_4\)(BF\(_4\))\(_{11}\)]\(^{5+}\): 1951.3302 Found: 1951.7289; [(C\(_6\)H\(_5\)IrN\(_6\))\(_8\)Pd\(_4\)(BF\(_4\))\(_{10}\)]\(^{6+}\): 1612.9401 Found: 1612.1035; [(C\(_6\)H\(_5\)IrN\(_6\))\(_8\)Pd\(_4\)(BF\(_4\))\(_9\)]\(^{7+}\): 1369.2538 Found: 1369.2337; [(C\(_6\)H\(_5\)IrN\(_6\))\(_8\)Pd\(_4\)(BF\(_4\))\(_8\)]\(^{8+}\): 1187.3291 Found: 1187.3267.

\( \Delta_r-[I_{8}Pd_{4}](BF_{4})_{16}, (\Delta_r-Cl-BF_{4}) \): Yield: 95%. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\)(ppm): \(^1\)H NMR (500 MHz, DMSO-\(d_6\)) \(\delta\) 9.71 (s, 16H), 9.12 (d, \(J = 40.3\) Hz, 8H), 8.94 (s, 8H), 8.35 (s, 18H), 8.22 – 7.93 (m, 49H), 7.77 (s, 9H), 7.13 – 6.77 (m, 62H), 6.55 (s, 5H), 6.37 – 6.10 (m, 15H), 2.35 (s, 48H), 2.13 (s, 48H), 1.91 (s, 48H). \(^{19}\)F NMR \{BF\(_4\)\} (417 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) (ppm): –148.098 (d, \(J = 10.3\) Hz, 4F). HR ESI MS: [M-BF\(_4\)]^+ Calculated: [(C\(_6\)H\(_5\)IrN\(_6\))\(_8\)Pd\(_4\)(BF\(_4\))\(_{11}\)]\(^{5+}\): 1951.9102 Found: 1951.7289; [(C\(_6\)H\(_5\)IrN\(_6\))\(_8\)Pd\(_4\)(BF\(_4\))\(_{10}\)]\(^{6+}\): 1610.9905 Found: 1612.1035; [(C\(_6\)H\(_5\)IrN\(_6\))\(_8\)Pd\(_4\)(BF\(_4\))\(_9\)]\(^{7+}\): 1369.2518 Found: 1369.2337; [(C\(_6\)H\(_5\)IrN\(_6\))\(_8\)Pd\(_4\)(BF\(_4\))\(_8\)]\(^{8+}\): 1187.3172 Found: 1187.3267.

S-14
rac-[1₈Pd₄](BF₄)₁₆, (rac-CI-BF₄): Yield: 90%. ¹H NMR (500 MHz, CDCl₃) δ (ppm): δ 9.67 (d, J = 14.0 Hz, 16H), 9.08 (d, J = 43.7 Hz, 11H), 8.37 (s, 20H), 8.25 – 7.84 (m, 38H), 7.76 (s, 6H), 7.41 (s, 5H), 7.09 – 6.71 (m, 44H), 6.53 (s, 6H), 6.20 (d, J = 11.4 Hz, 11H), 2.34 (s, 48H), 2.15 (s, 48H), 1.95 (s, 48H). ¹⁹F NMR {BF₄} (417 MHz, CD₂Cl₂) δ (ppm): –148.093 (d, J = 10.0 Hz, 4F). HR ESI MS: [M-BF₄]⁺ Calculated: [(C₆₀H₅₀IrN₆)₈Pd₄(BF₄)₁₁]⁵⁺: 1951.9102 Found: 1951.7289; [(C₆₀H₅₀IrN₆)₈Pd₄(BF₄)₁₀]⁶⁺: 1612.9401 Found: 1612.1056; [(C₆₀H₅₀IrN₆)₈Pd₄(BF₄)₉]⁷⁺: 1369.2538 Found: 1369.2345; [(C₆₀H₅₀IrN₆)₈Pd₄(BF₄)₈]⁸⁺: 1187.3291 Found: 1187.3294.

Δₐr-[1₈Pd₄](SbF₄)₁₆, (Δₐr-CI-SbF₄): Yield: 95%. ¹H NMR (500 MHz, CDCl₃) δ (ppm): δ 9.68 (s, 1H), 9.07 (d, J = 30.1 Hz, 1H), 8.30 (s, 1H), 8.20 – 7.87 (m, 2H), 7.71 (d, J = 17.5 Hz, 0H), 7.46 (s, 1H), 7.13 – 6.50 (m, 3H), 6.20 (d, J = 34.6 Hz, 1H), 2.34 (s, 48H), 2.11 (s, 48H), 1.95 (s, 48H). ¹⁹F NMR {SbF₄} (417 MHz, CD₂Cl₂) δ (ppm): –148.104 (d, J = 10.3 Hz, 6F). HR ESI MS: [M-PF₆]⁺ Calculated: [(C₆₀H₅₀IrN₆)₈Pd₄(BF₄)₁₁]⁵⁺: 1951.9102 Found: 1951.7289; [(C₆₀H₅₀IrN₆)₈Pd₄(BF₄)₁₀]⁶⁺: 1610.9905 Found: 1612.1035; [(C₆₀H₅₀IrN₆)₈Pd₄(BF₄)₉]⁷⁺: 1369.2518 Found: 1369.2337; [(C₆₀H₅₀IrN₆)₈Pd₄(BF₄)₈]⁸⁺: 1187.3172 Found: 1187.3267.

Δₐr-[2₈Pd₄](BF₄)₁₆, (Δₐr-C2-BF₄): Yield: 88%. ¹H NMR (500 MHz, CDCl₃) δ (ppm): ¹H NMR (400 MHz, DMSO-d₆) δ 9.72 (s, 16H), 8.27 (d, J = 75.6 Hz, 34H), 7.96 (s, 15H), 7.22 – 6.72 (m, 28H), 5.63 (s, 11H), 2.37 (s, 48H), 2.10 (s, 48H), 1.96 (s, 48H). ¹⁹F NMR (417 MHz, CD₂Cl₂) δ (ppm): –106.066 (bs, 32F), -108.331 (bs, 32F), -148.108 (bd, J = 15.3 Hz), -146.175 (bd, J = 18.1 Hz). HR ESI MS: [M-BF₄]⁺ Calculated: [(C₆₀H₄₆F₄IrN₆)₈Pd₄(BF₄)₁₁]⁵⁺: 2067.0798 Found: 2067.0646; [(C₆₀H₄₆F₄IrN₆)₈Pd₄(BF₄)₁₀]⁶⁺: 1707.9986 Found: 1708.0532; [(C₆₀H₄₆F₄IrN₆)₈Pd₄(BF₄)₉]⁷⁺: 1451.4807 Found: 1461.6165; [(C₆₀H₄₆F₄IrN₆)₈Pd₄(BF₄)₈]⁸⁺: 1259.2943 Found: 1259.2890.
$\Lambda_r$-[2$_8$Pd$_4$]($BF_4$)$_{16}$, ($\Lambda_r$-C$_2$-BF$_4$): Yield: 88%. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$(ppm): $^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$ 9.73 (s, 16H), 9.54 (s, 10H), 9.17 (d, $J$ = 29.2 Hz, 16H), 8.98 (s, 13H), 8.37 (s, 21H), 8.22 (d, $J$ = 33.3 Hz, 51H), 7.94 (d, $J$ = 60.4 Hz, 35H), 7.17 (s, 11H), 7.13 – 6.77 (m, 62H), 6.67 (s, 9H), 2.35 (s, 48H), 2.09 (s, 48H), 1.94 (s, 48H). $^{19}$F NMR (417 MHz, CD$_2$Cl$_2$) $\delta$(ppm): –106.274 (bs, 32F), -108.477 (bs, 32F), -148.103 (bd, $J$ = 15.3 Hz), -146.209 (bd, $J$ = 18.1 Hz). HR ESI MS: [M-BF$_4$]$^+$ Calculated: [(C$_60$H$_{46}$F$_4$IrN$_6$)$_8$Pd$_4$(BF$_4$)$_{11}$]$^{5+}$: 2067.1791 Found: 2067.0646; [(C$_60$H$_{46}$F$_4$IrN$_6$)$_8$Pd$_4$(BF$_4$)$_{10}$]$^{6+}$: 1707.8640 Found: 1708.0532; [(C$_60$H$_{46}$F$_4$IrN$_6$)$_8$Pd$_4$(BF$_4$)$_9$]$^{7+}$: 1451.5934 Found: 1461.6165; [(C$_60$H$_{46}$F$_4$IrN$_6$)$_8$Pd$_4$(BF$_4$)$_8$]$^{8+}$: 1259.2675 Found: 1259.2890.

rac-[2$_8$Pd$_4$]($BF_4$)$_{16}$, (rac-C$_2$-BF$_4$): Yield: 86%. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$(ppm): $^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$ 9.71 (s, 16H), 8.29 (d, $J$ = 73.6 Hz, 34H), 7.93 (s, 14H), 7.21 – 6.75 (m, 28H), 5.60 (s, 10H), 2.37 (s, 48H), 2.13 (s, 48H), 1.95 (s, 48H). $^{19}$F NMR (417 MHz, CD$_2$Cl$_2$) $\delta$(ppm): –106.064 (bs, 32F), -108.329 (bs, 32F), -148.112 (bd, $J$ = 15.3 Hz), -146.174 (bd, $J$ = 17.9 Hz). HR ESI MS: [M-BF$_4$]$^+$ Calculated: [(C$_60$H$_{46}$F$_4$IrN$_6$)$_8$Pd$_4$(BF$_4$)$_{11}$]$^{5+}$: 2067.0798 Found: 2067.0695; [(C$_60$H$_{46}$F$_4$IrN$_6$)$_8$Pd$_4$(BF$_4$)$_{10}$]$^{6+}$: 1707.9986 Found: 1708.0556; [(C$_60$H$_{46}$F$_4$IrN$_6$)$_8$Pd$_4$(BF$_4$)$_9$]$^{7+}$: 1451.4815 Found: 1451.6469; [(C$_60$H$_{46}$F$_4$IrN$_6$)$_8$Pd$_4$(BF$_4$)$_8$]$^{8+}$: 1259.2943 Found: 1259.2897.
Characterization of [Ir(C^N)₂(Serine)]PF₆

Figure S1.¹H NMR spectra (aromatic region) of a) Λ-[Ir(ppymes)₂(D-serine)] (Λ-Dser1), b) Δ-[Ir(ppymes)₂(L-serine)] (Δ-Lser1) and c) rac-[Ir(ppymes)₂(L-serine)] (rac-Lser1) in CD₂Cl₂.

Figure S2.¹H NMR spectra (aromatic region) of a) Λ-[Ir(dMesppy)₂(D-serine)] (Λ-Dser2), b) Δ-[Ir(dMesppy)₂(L-serine)] (Δ-Lser2) and c) rac-[Ir(dMesppy)₂(L-serine)] (rac-Lser2) in CD₂Cl₂.
Characterization of [Ir(C^N)_{2}(N^N)]PF_{6} Complexes.

rac-, Δ- and Λ-Iridium(III)bis[2-phenyl-4-(2,4,6-trimethylphenyl)pyridinato]-4,4':2',2'':4'',4'''-quaterpyridine hexafluorophosphate, rac-, Δ- and Λ-[Ir(mesppy)_{2}(qpy)](PF_{6}).

Figure S3. ¹H NMR spectrum of rac-, Δ- and Δ-[Ir(mesppy)_{2}(qpy)]PF_{6} (rac-, Δ- and Δ-1-PF_{6}) in CD_{2}Cl_{2}.
Figure S4. $^{13}$C NMR spectrum of rac-, Δ− and Λ-[Ir(mesppy)$_2$(qpy)]PF$_6$ (rac-, Δ− and Λ-1-PF$_6$) in CD$_2$Cl$_2$.

Figure S5. $^1$H DOSY NMR spectrum of rac-[Ir(mesppy)$_2$(qpy)]PF$_6$ (rac-1-PF$_6$) in DMSO-$d_6$ (D = 1.3 × 10$^{-10}$ m$^2$/s).

$rac$, Δ− and Λ−Iridium(III)bis[2-phenyl-4-(2,4,6-trimethylphenyl)pyridinato]-4,4':2',2'':4'',4'''-quaterpyridine tetrafluoroborate, rac-, Δ− and Λ−[Ir(mesppy)$_2$(qpy)](BF$_4$).
Figure S6. $^1$H NMR spectrum of rac-, $\Lambda$- and $\Delta$-[Ir(mesppy)$_2$(qpy)]BF$_4$ (rac-, $\Lambda$- and $\Delta$-1-BF$_4$) in CD$_2$Cl$_2$.

Figure S7. $^1$H DOSY NMR spectrum of $\Delta$-[Ir(mesppy)$_2$(qpy)]BF$_4$ (\$\Delta$-1-BF$_4$) in DMSO-$d_6$ ($D = 1.3 \times 10^{-10}$ m$^2$/s).
Figure S8. $^1$H DOSY NMR spectrum of $\Lambda$-[Ir(mesppy)$_2$(qpy)]BF$_4$ ($\Lambda$-1-BF$_4$) in DMSO-$d_6$ (D = 1.3 × 10$^{-10}$ m$^2$/s).

Figure S9. FTMS spectra of rac-, $\Lambda$- and $\Delta$-[Ir(mesppy)$_2$(qpy)]BF$_4$ (rac-, $\Lambda$- and $\Delta$-1-BF$_4$).
Δ–Iridium(III)bis[2-phenyl-4-(2,4,6-trimethylphenyl)pyridinato]-4,4':2',2'':4'',4'''-quaterpyridine hexafluoroantimonate, Δ–[Ir(mesppy)$_2$(qpy)](SbF$_6$).

Figure S10. $^1$H NMR spectrum of Δ-[Ir(mesppy)$_2$(qpy)]SbF$_6$ (Δ-1-SbF$_6$) in CD$_2$Cl$_2$.

rac-, Δ– and Λ–Iridium(III)bis[2-(2,4-difluoro)-phenyl-4-(2,4,6-trimethylphenyl)pyridinato]-4,4':2',2'':4'',4'''-quaterpyridine tetrafluoroborate, rac-, Δ– and

Λ–[Ir(dFmesppy)$_2$(qpy)](BF$_4$).
Figure S11. $^1$H NMR spectrum of rac-, $\Delta$- and $\Lambda$-[Ir(dFmesppy)$_2$(qpy)]BF$_4$ (rac-, $\Lambda$- and $\Delta$-2-BF$_4$) in CD$_2$Cl$_2$.

Figure S12. $^{19}$F NMR spectrum of rac-, $\Delta$- and $\Lambda$-[Ir(mesppy)$_2$(qpy)]BF$_4$ (rac-, $\Lambda$- and $\Delta$-2-BF$_4$) in CD$_2$Cl$_2$. 
Figure S13. $^1$H DOSY NMR spectrum of $\text{rac-}[\text{Ir(dFmesppy)}_2(qpy)]\text{BF}_4$ ($\text{rac-2-BF}_4$) in DMSO-$d_6$ ($D = 1.2 \times 10^{-10} \text{ m}^2/\text{s}$).

Figure S14. FTMS spectra of $\text{rac-}$, $\Lambda$- and $\Delta$-[Ir(dFmesppy)$_2$(qpy)]BF$_4$ ($\text{rac-}$, $\Lambda$- and $\Delta$-2-BF$_4$).
*rac*-Tetrabutyl ammonium bis(cyanide)-bis[2-(2,4-difluoro)-phenylpyridinato]-iridium(III),

*rac*-NBu₄[Ir(dFppy)₂(CN)₂] (IrCN).

Figure S15.¹H NMR spectrum of NBu₄[Ir(dFppy)₂(CN)₂] (IrCN) in DMSO-d₆.

Figure S16.¹⁹F NMR spectrum of NBu₄[Ir(dFppy)₂(CN)₂] (IrCN) in DMSO-d₆.
Figure S17. $^1$H DOSY NMR spectrum of \textit{rac-NBu}_4[Ir(dFppy)_2(CN)] (IrCN) in DMSO-$d_6$ ($D = 1.9 \times 10^{-10}$ m$^2$/s).

Figure S18. ESI-MS spectra of \textit{rac-NBu}_4[Ir(dFppy)_2(CN)] (IrCN).
rac-Iridium(III)bis[2-(2,4-difluoro)-phenylpyridinato]-4,4'-dimethyl-2,2'-bypiridine hexafluorophosphate, [Ir(dFppy)$_2$(dmbpy)](PF$_6$) (Irdmbpy).

Figure S19.$^1$H NMR spectrum of rac-[Ir(dFppy)$_2$(dmbpy)]PF$_6$ (Irdmbpy) in CD$_2$Cl$_2$.

Figure S20.$^{19}$F NMR spectrum of rac-[Ir(dFppy)$_2$(dmbpy)]PF$_6$ (Irdmbpy) in CD$_2$Cl$_2$. 
Figure S21. $^1$H DOSY NMR spectrum of $\text{rac}\text{-}[\text{Ir}(dFppy)_2(dmbpy)]PF_6$ (Irdmbpy) in DMSO-$d_6$ ($D = 1.7 \times 10^{-10} \text{ m}^2/\text{s}$).

Figure S22. FTMS spectra of $\text{rac}\text{-}[\text{Ir}(dFppy)_2(dmbpy)]PF_6$ (Irdmbpy).
NMR Characterisation of rac-, Δ₈⁻, Λ₈⁻-[1₈Pd₄](BF₄)₁₆, (rac-, Δ₈⁻, Λ₈⁻-C1-BF₄) Cages.

NMR Spectra of Δ⁻ and Λ-[1₈Pd₄](BF₄)₁₆ Cages (Δ⁻ and Λ-C1-BF₄).

Figure S23. ¹H NMR spectrum of a) Λ₈–C1-BF₄; b) Δ₈–C1-BF₄ and c) rac--[Ir(mesppy)₂(qpy)]BF₄ (rac-1-BF₄) collected in DMSO-d₆ at 298 K.

¹H NMR of cages Δ⁻-[1₈Pd₄]¹₆⁻, (Δ⁻-C1) with BF₄⁻, PF₆⁻ and SbF₆⁻ as counterions.
Figure S24. $^1$H NMR spectra of a) $\Delta_c$-C1-SbF$_6$; b) $\Delta_c$-C1-PF$_6$ and c) $\Delta_c$-C1-BF$_4$ collected in DMSO-$d_6$ at 298 K.

Figure S25. $^1$H NMR spectra of a) rac–C1-PF$_6$ and b) rac–C1-BF$_4$ collected in DMSO-$d_6$ at 298 K.
Figure S26. $^1$H DOSY NMR spectrum of rac-C1-BF$_4$ in DMSO-$d_6$ at 298 K ($D = 5.2 \times 10^{-11}$ m$^2$/s).

Figure S27. Comparison between the $^1$H DOSY NMR spectra of $\Lambda_8$-C1-BF$_4$ (in red), and of $\Lambda$-1 (in blue) in DMSO-$d_6$ at 298 K.

NMR Spectra of rac-, $\Delta_-$ and $\Lambda_-$-[2$_8$Pd$_4$](BF$_4$)$_{16}$, (rac-, $\Delta_-$ and $\Lambda_-$-C2-BF$_4$).
Figure S28. $^1$H NMR spectra of a) $\Lambda_8$–C2-BF$_4$; b) $\Delta_8$–C2-BF$_4$ and c) rac--[Ir(dFmesppy)$_2$(qpy)]BF$_4$ (rac-2-BF$_4$) collected in DMSO-$d_6$ at 298 K.

Figure S29. $^{19}$F NMR spectra of a) rac–C2-BF$_4$ (left); and b) $\Lambda_8$–C2-BF$_4$ (right) collected in DMSO-$d_6$ at 298 K.
Figure S30. \(^1\)H DOSY NMR spectrum of \textit{rac-C2-BF}_4 in DMSO-\(d_6\) at 298 K \((D = 4.9 \times 10^{-11} \text{ m}^2/\text{s})\).

Figure S31. Comparison between the \(^1\)H DOSY NMR spectra of \(\Lambda_8\text{-C2-BF}_4\) (in red) and of \(\Delta-2\) (in blue) in DMSO-\(d_6\) at 298 K.

Calculation of Hydrodynamic Radii \((r_s)\) of \textit{rac-}, \(\Delta\)- and \(\Lambda-1\), \textit{rac-}, \(\Delta\)-, \(\Lambda-2\) \textit{rac-}, \(\Delta_8\)- and \(\Lambda_8\)-C1 and \textit{rac-}, \(\Delta_8\)- and \(\Lambda_8\)-C2.
**Table S1.** Comparison of diffusion coefficients (D, m² s⁻¹) of ligands and cages obtained by ¹H DOSY NMR (500 MHz, DMSO-d₆).

| metalloligand | D metalloligand (m² s⁻¹) | cages | D cages (m² s⁻¹) | rₛ metalloligands (nm) | rₛ cages (nm) |
|---------------|--------------------------|-------|-----------------|------------------------|---------------|
| rac-, Δ- and Λ-1 | 1.3 x 10⁻¹⁰ | rac-, Δ- and Λ-1 | 5.2 x 10⁻¹¹ | 0.83 | 1.98 |
| rac-, Δ- and Λ-2 | 1.2 x 10⁻¹⁰ | rac-, Δ- and Λ-2 | 4.9 x 10⁻¹¹ | 0.90 | 2.00 |

In diffusion experiments, the molecular size of the metalloligands and metallocages are estimated by the Stokes Einstein equation:

\[ \text{r}_s = \frac{k_b \cdot T}{6\pi \cdot \eta \cdot D} \]

With \( r_s \) = hydrodynamic or Stokes radii of the metalloligands or metallocages, which are assumed to exhibit a spherical shape, \( k_b \) = Boltzmann constant, \( T \) = temperature (298 K), \( \eta \) = viscosity of DMSO solution (1.99 mPa s) and \( D \) = diffusion coefficient, obtained here by ¹H DOSY NMR.
Figure S32. Illustration of the qpy coordinating vector of 1 and of the diameter around the metallamacrocyclic core across long axes of C1 from one mesityl on one ‘end’ to the opposite mesityl on the other ‘end’.

ESI-MS Spectra of rac-, Δ8- and Λ8-[18Pd4]16+, (rac-, Δ- and Λ-C1) Cages.

Figure S33. ESI-MS spectra of: a) Δ8-C1-BF4 and b) Λ8-C1-BF4. Simulated MS spectra of: c) [C1-(BF4)3]5⁺; d) [C1-(BF4)6]6⁺; e) [C1-(BF4)7]7⁺ and f) [C1-(BF4)8]8⁺.
Figure S34. a) ESI-MS spectra of $\Delta_8$-C1-PF$_6$. Simulated MS spectra of: b) [C1-(PF$_6$)$_4$]$^{4+}$; c) [C1-(PF$_6$)$_3$]$^{5+}$; d) [C1-(PF$_6$)$_6$]$^{6+}$; e) [C1-(PF$_6$)$_7$]$^{7+}$ and f) [C1-(PF$_6$)$_8$]$^{8+}$.

Figure S35. a) ESI-MS spectra of the [C1-(PF$_6$)$_7$]$^{7+}$ of $\Delta_8$-C1-PF$_6$; b) Simulation of isotopic distribution pattern of [C1-(PF$_6$)$_7$]$^{7+}$.
Figure S36. a) ESI-MS spectra of the [C1-(PF₆)₆]⁶⁺ of Δ₈-C1-PF₆; b) Simulation of isotopic distribution pattern of [C1-(PF₆)₆]⁶⁺.

Figure S37. a) ESI-MS spectra of the [C1-(PF₆)₅]⁵⁺ of Δ₈-C1-PF₆; b) Simulation of isotopic distribution pattern of [C1-(PF₆)₅]⁵⁺.
ESI-MS of rac-, Δ₈- and Λ₈-[2₈Pd₄](BF₄)₁₆, (rac-, Δ- and Λ-C2).

Figure S38. ESI-MS spectra of: a) Δ₈-C₂-BF₄ and b) Λ₈-C₂-BF₄. Simulated MS spectra of: c) [C₂-(BF₄)₅]⁵⁺; d) [C₂-(BF₄)₆]⁶⁺; e) [C₂-(BF₄)₇]⁷⁺ and f) [C₂-(BF₄)₈]⁸⁺.

Figure S39. a) ESI-MS spectra of the [C₂-(BF₄)₈]⁸⁺ of Δ₈-C₂-BF₄; b) Simulation of isotopic distribution pattern of [C₂-(BF₄)₈]⁸⁺.
Figure S40. a) ESI-MS spectra of the [C2-(BF₄)₇]⁺⁺ of Δ₈-C₂-BF₄; b) Simulation of isotopic distribution pattern of [C2-(BF₄)₇]⁺⁺.

Figure S41. a) ESI-MS spectra of the [C2-(BF₄)₆]⁺⁺ of Δ₈-C₂-BF₄; b) Simulation of isotopic distribution pattern of [C2-(BF₄)₆]⁺⁺ with its simulation.
Formation of Cages By Mixing $\Lambda$- or $\Delta$-1 and $\Delta$-2 with Pd$^{2+}$ ions.

Experiment design: In a dry 10 mL Schlenk vial, one of complexes $\Lambda$- or $\Delta$-1 (1 equiv.) as well as $\Delta$-2 (1 equiv.) and $[\text{Pd(NCMe)}_4](\text{BF}_4)_2$ (1 equiv.) were dissolved in DMSO-$d_6$ (1 mL) to give a concentration of the iridium metalloligands of approximately 0.05 M. The solution was degassed for five minutes by bubbling nitrogen and then heated at 85 °C for 12 h under nitrogen atmosphere. The solution was cooled to room temperature. The black solid was filtered through celite and the resulting DMSO solution was analysed directly by ESI-MS spectrometry. The formation of statistical mixtures of cages species comprising various degrees of the two metallo-ligands $[(\Lambda$-$/\Delta$-$1)_n(\Delta$-$2)_m\text{Pd}_4](\text{BF}_4)_{16}$ ($n + m = 8$, from $\Lambda$-$/\Delta$-$1 : \Delta$-$2 = 7 : 1$ to $\Lambda$-$/\Delta$-$1 : \Delta$-$2 = 1 : 7$) has been observed.

Figure S42. ESI-MS spectra of: a) $\Delta$-1-\text{BF}_4 + \Delta$-2-\text{BF}_4 + $[\text{Pd(NCMe)}_4](\text{BF}_4)_2$; b) $\Lambda$-1-\text{BF}_4 + $[\text{Pd(NCMe)}_4](\text{BF}_4)_2$; c) $[\text{(1)}_4(\text{2})_4(\text{BF}_4)_6]$; d) $[\text{(1)}_4(\text{2})_4(\text{BF}_4)_6]^6+$; e) $[\text{(1)}_4(\text{2})_4(\text{BF}_4)_7]^7+$ and f) $[\text{(1)}_4(\text{2})_4(\text{BF}_4)_8]^8+$. 

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Figure S43. Illustration of the formation of a statistical mixture of cages species of compositions $[(\Lambda-\Delta-1)_n(\Delta-2)_m\text{Pd}_4](\text{BF}_4)_{16}$ (n + m = 8, from $\Lambda-\Delta-1 : \Delta-2 = 7 : 1$ to $\Lambda-\Delta-1 : \Delta-2 = 1 : 7$). ESI-MS spectra of the 7+ charge states $[(1)_n(2)_m-(\text{BF}_4)_7]^{7+}$ (n + m = 8, from 1 : 2 = 7 : 1 to 1 : 2 = 1 : 7) of: a) $\Delta-1-\text{BF}_4 + \Delta-2-\text{BF}_4 + [\text{Pd(NCMe)}_3](\text{BF}_4)_2$ and b) $\Delta-1-\text{BF}_4 + \Delta-2-\text{BF}_4 + [\text{Pd(NCMe)}_3](\text{BF}_4)_2$.

In red are illustrated the simulated 7+ charge states of the heteroleptic cages. The same statistical distributions are also observed for the 8+, 6+ and 5+ charge states. c) Representation of the heteroleptic cages; in red are illustrated the ppy ligands whereas in green the dFppy ligands. The mesityl substituents have been omitted for clarity.
Formation of Heteronuclear Cages by Mixing the Homonuclear Cages $\Delta_8$- or $\Lambda_8$-C1 and $\Delta_8$-C2.

Experiment design: In a dry 10 mL Schlenk vial, cages $\Delta_8$- or $\Delta_8$-I (1 equiv.) and $\Delta_8$-2 (1 equiv.) were dissolved in DMSO-$d_6$ (1 mL) to give a concentration of the iridium cages of approximately 0.05 M. The solution was degassed for few minutes by bubbling nitrogen and a) heated at 85 °C for 12 h under nitrogen atmosphere or b) stirred at room temperature for 12 h. The solution was cooled to room temperature and analysed directly by ESI-MS spectrometry. a) The formation of statistical mixtures of cages species comprising various degree of the two metalloligands $[(\Lambda-/\Delta-\mathbf{1})_n(\Lambda-/\Delta-\mathbf{2})_m\text{Pd}_4](\text{BF}_4)_{16}$ ($n + m = 8$, from $\Lambda-/\Delta-\mathbf{1} : \Lambda-/\Delta-\mathbf{2} = 7 : 1$ to $\Lambda-/\Delta-\mathbf{1} : \Lambda-/\Delta-\mathbf{2} = 1 : 7$) have been observed when the cages were mixed at 85 °C. b) No ligand exchange was observed when the cages were mixed at room temperature.

Figure S44. ESI-MS spectra of: a) $\Delta_8$-C1-BF$_4$ + $\Delta_8$-C2-BF$_4$ stirred at 85 °C for 12 h; b) $\Lambda_8$-C1-BF$_4$ + $\Delta_8$-C2-BF$_4$ stirred at 85 °C for 12 h; Simulated MS spectra of: c) $[(\mathbf{1})_4(\text{BF}_4)_4]^{5+}$; d) $[(\mathbf{1})_4(\text{BF}_4)_5]^{6+}$; e) $[(\mathbf{1})_4(\text{BF}_4)_6]^{7+}$ and f) $[(\mathbf{1})_4(\text{BF}_4)_7]^{8+}$. 
Figure S45. a) ESI mass spectrum of Δ-C1 indicating the Δ₀-[1₈-(BF₄)₇]⁺ charge state with its simulation; b) ESI mass spectrum of Δ-C1 indicating the Δ₀-[1₈-(BF₄)₇]⁺ charge state; c) ESI mass spectrum of Δ-C2 indicating the Δ₀-[2₈-(BF₄)₇]⁺ charge state with its simulation; d) ESI mass spectrum of Λ-C2 indicating the Λ₀-[2₈-(BF₄)₇]⁺ charge state; e) ESI mass spectrum of a mixture of Δ-C1 and Δ-C2 mixed at 273 K; f) ESI mass spectrum of a mixture of Δ-C1 and Δ-C2 mixed at 358 K for 16h; g) ESI mass spectrum of a mixture of Λ-C1 and Δ-C2 mixed at 358 K for 16h; h) CD spectra of Δ-C1 (red line), Λ-C1 (light-red line), Δ-C2 (green line) and mixed cages of compositions [(Δ-C1)ₙ(Δ-C2)ₙ](BF₄)₁₆ (dark-blue line) and [(Δ-C1)ₙ(Δ-C2)ₙ](BF₄)₁₆ (light-blue line).
Figure S46. ESI-MS spectra of: a) $\Delta_8$-C1-BF$_4$ + $\Delta_8$-C2-BF$_4$ stirred at RT °C for 12 h; b) $\Lambda_8$-C1-BF$_4$; c) $\Delta_8$-C2-BF$_4$. d) simulated MS spectra of [(2)$_8$-(BF$_4$)$_7$]$^7^+$; e) simulated MS spectra of [(2)$_8$-(BF$_4$)$_7$]$^7^+$.

Figure S47. a) ESI-MS spectra illustrating the 7+ charge states $\Delta_8$-[1$_8$-(BF$_4$)$_7$]$^7^+$ and $\Delta_8$-[2$_8$-(BF$_4$)$_7$]$^7^+$ of a mixture of $\Delta_8$-C1 and $\Delta_8$-C2 left at RT for 12h. b) simulated MS spectra of $\Delta_8$-[1$_8$-(BF$_4$)$_7$]$^7^+$ and c) simulated MS spectra of $\Delta_8$-[2$_8$-(BF$_4$)$_7$]$^7^+$. 
Host-Guest Assemblies Monitored by NMR Spectroscopies.

Host-Guest chemistry with small organic compounds.

Figure S48. ^1^H NMR spectra collected in DMSO-^d_6_ at 298 K of: a) i) pyrene; ii) pyrene + Δ-C1; iii) Δ-C1. b) i) pyrene-carboxylic acid; ii) pyrene carboxylic acid + Δ-C1; iii) Δ-C1. c) i) ammonium pyrene carboxylate; ii) ammonium pyrene carboxylate + Δ-C1; iii) Δ-C1. The concentration of Δ-C1 was kept constant at 3.0 mM and one equivalent of each guest was added.

Figure S49. ^1^H NMR spectra collected in DMSO-^d_6_ at 298 K of: a) i) ammonium tetraphenylborate; ii) ammonium tetraphenylborate + Δ-C1; iii) Δ-C1. b) ^1^B NMR collected in
DMSO-$d_6$ at 298 K of: i) ammonium tetraphenylborate + $\Delta$-C1; ii) ammonium tetraphenylborate. The concentration of $\Delta$-C1 was kept constant at 3.0 mM and one equivalent of each guest was added.

**Host-Guest chemistry with TBA[Ir(dFppy)$_2$(CN)$_2$], IrCN.**

![Diagram of host-guest chemistry with TBA[Ir(dFppy)$_2$(CN)$_2$], IrCN.](image)

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**Figure S50.** $^1$H NMR titration spectra collected in DMSO-$d_6$ at 298 K of: a) IrCN (the concentration of IrCN was kept constant at 0.5 mM during the titration experiment); b) to m) IrCN + gradual addition of $\Delta$-C1 (from 0.10 mM to 0.8 mM); c) $\Delta$-C1.
Figure S51. $^{19}$F NMR titration spectra collected in DMSO-$d_6$ at 298 K of: a) IrCN (the concentration of IrCN was kept constant at 0.5 mM during the titration experiment); b) to m) IrCN + gradual addition of Δ-C1 (from 0.10 mM to 0.8 mM); c) Δ-C1.

Figure S52. $^{19}$F NMR titration spectra collected in DMSO-$d_6$ at 298 K of: a) IrCN; b) to d) Δ-1 cage + gradual addition of IrCN (from 0.10 mM to 0.6 mM). The concentration of Δ-1 cage was kept constant at 0.50 mM.
Figure S53. $^1$H NMR CPMGZ spectra collected in DMSO-$d_6$ at 298 K of $\Delta$-C1 + 1 equiv. of IrCN. Filter conditions: a) no filter applied; b) D21 = 0.05; c) D21 = 0.1; d) D21 = 0.2. e) $^1$H NMR of IrCN with no filter applied.

Figure S54. $^1$H DOSY NMR spectra collected in DMSO-$d_6$ at 298 K of: IrCN (in purple, D = 1.9 $\times$ 10^{-10} m^2/s); $\Delta$-C1 (in red, D = 4.9 $\times$ 10^{-10} m^2/s) and a 1:1 mixture of IrCN and $\Delta$-C1 (in blue, D = 4.9 $\times$ 10^{-10} m^2/s).
Host-Guest chemistry with \([\text{Ir}(\text{dFppy})_2(\text{dmbpy})]\)PF$_6$, Irdmbpy.

Figure S5. $^1$H NMR titration spectra collected in DMSO-$d_6$ at 298 K of: a) $\Delta$-C1 (the concentration of $\Delta$-C1 was kept constant at 0.5 mM during the titration experiment); b) to e) $\Delta$-C1 + gradual addition of Irdmbpy (from 0.10 mM to 0.80 mM); f) Irdmbpy.
Figure S56. $^{19}$F NMR titration spectra collected in DMSO-$d_6$ at 298 K of: a) Irdmbpy; b) to d) $\Delta$-C1 + gradual addition of Irdmbpy (from 0.10 mM to 0.80 mM). The concentration of $\Delta$-C1 was kept constant at 0.5 mM.

Figure S57. $^1$H DOSY NMR spectra collected in DMSO-$d_6$ at 298 K of: Irdmbpy (in purple, $D = 1.7 \times 10^{-10}$ m$^2$/s); $\Delta$-C1 (in red, $D = 5.2 \times 10^{-11}$ m$^2$/s) and a 1:1 mixture of Irdmbpy and $\Delta$-C1 (in blue, $D = 5.2 \times 10^{-11}$ m$^2$/s - $\Delta$-C1 - and $1.7 \times 10^{-10}$ m$^2$/s - Irdmbpy).
Control experiment by mixing [Ir(mesppy)$_2$(qpy)$_2$]BF$_4$, Δ-1 with TBA[Ir(dFppy)$_2$(CN)$_2$], Irdmbpy.

Figure S58. $^1$H NMR and $^{19}$F NMR spectra, respectively a) and b), collected in DMSO-$d_6$ at 298 K of: i) IrCN; ii) Δ-1 (1 equiv.) + IrCN (1 equiv.); iii) Δ-1.

Figure S59. $^1$H DOSY NMR spectra collected in DMSO-$d_6$ at 298 K of: IrCN (in purple, D = 1.9 $\times$ 10$^{-10}$ m$^2$/s); Δ-1 (in red, D = 1.3 $\times$ 10$^{-10}$ m$^2$/s) and a 1:1 mixture of IrCN and Δ-1 (in blue, D = 1.3 $\times$ 10$^{-10}$ m$^2$/s - Δ-1 - and 1.8 $\times$ 10$^{-10}$ m$^2$/s - IrCN).
Crystal Structures of Λ,Λ- and Δ,Δ-D2 and rac-2

X-ray diffraction data for compounds Λ,Λ- and Δ,Δ-D2 and rac-2 were collected at 93 K by using a Rigaku FR-X Ultrahigh brilliance Microfocus RA generator/confocal optics and Rigaku XtaLAB P200 system, with Mo Kα radiation (λ = 0.71075 Å). Intensity data were collected using ω steps accumulating area detector images spanning at least a hemisphere of reciprocal space. All data were corrected for Lorentz polarization effects. A multiscan absorption correction was applied by using either CrystalClear (Λ,Λ-D2 and rac-2)7 or CrysalisPro (Δ,Δ-D2).8 Structures were solved by Patterson methods (PATTY)9 and refined by full-matrix least-squares against F² (SHELXL-2014).10 Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined using a riding model. All calculations were performed using the CrystalStructure11 interface. CCDC 1543500-1543502 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via https://www.ccdc.cam.ac.uk/structures/ (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033). Crystallographic data are presented in Table S2. Thermal ellipsoid plots of the structures are presented in Figures S59 (Λ,Λ- and Δ,Δ-D2) and S60 (rac-2).

Repeated attempts were made at collecting X-ray diffraction data on cages C1 and C2. The best data obtained to date, for rac-C1, was collected at beamline I19, Diamond Light Source, Didcot, UK using silicon double crystal monochromated radiation (λ = 0.6889 Å, Pilatus 2M detector),12 at 100 K. A multiscan absorption correction was applied by using CrysalisPro.8 A solution was obtained using charge-flipping methods (Superflip),13 which revealed the positions of the metal centers and an approximation of the structure of the ligand (Figure S62), however it has not, as yet, been possible to refine the data. Calculations were performed using the WinGX interface.14
Table S2. Crystallographic data for complexes Λ,Λ- and Δ,Δ-D2 and rac-2.

|                | Λ,Λ-D2   | Δ,Δ-D2   | rac-2     |
|----------------|----------|----------|-----------|
| CCDC number    | 1543500  | 1543501  | 1543502   |
| Formula        | \(C_{81}H_{66}Cl_{4}F_{8}Ir_{2}N_{4}\) | \(C_{81}H_{66}Cl_{4}F_{8}Ir_{2}N_{4}\) | \(C_{64}H_{56}BF_{8}IrN_{6}O\) |
| Formula weight | 1773.68  | 1773.68  | 1280.20   |
| Crystal colour, habit | Yellow, rod | Yellow, rod | Yellow, prism |
| Crystal dimensions (\(\text{mm}^3\)) | 0.13×0.03×0.02 | 0.13×0.02×0.02 | 0.13×0.09×0.07 |
| Space group    | \(P2_12_1\) | \(P2_12_1\) | \(P\) |
| a (Å)          | 12.5492(16) | 12.496(4) | 13.320(2) |
| b (Å)          | 24.138(3)  | 24.105(7) | 14.856(2) |
| c (Å)          | 26.122(3)  | 26.041(8) | 19.963(4) |
| \(\alpha\) (°) | 70.564(17) |          |           |
| \(\beta\) (°) |            |          | 81.23(2)  |
| \(\gamma\) (°) |            |          | 67.778(18) |
| Volume (Å\(^3\)) | 7912.7(17) | 7844(4)  | 3446.9(11) |
| Z              | 4         | 4        | 2         |
| \(\rho_{\text{calc}}\) (g cm\(^{-3}\)) | 1.489     | 1.502    | 1.233     |
| Temperature (K) | 93        | 93       | 93        |
| \(\mu\) (mm\(^{-1}\)) | 3.567     | 3.598    | 2.004     |
| 2\(\theta\) range | 2.298–25.242 | 1.836–30.140 | 1.947–25.360 |
| Reflections collected | 76850     | 123445   | 86700     |
| Independent reflections \((R_{int})\) | 14268 (0.0658) | 20443 (0.1817) | 12452 (0.1317) |
| \(R_1\) \([I>2\sigma(I)]\) | 0.0488    | 0.0802   | 0.1078    |
| \(wR_2\) (all data) | 0.1368    | 0.2194   | 0.3348    |
| Goodness of fit | 1.112     | 1.033    | 1.136     |
| Data/restraints/parameters | 14268/57/904 | 20443/921/904 | 12452/44/734 |
| Residual electron peak, hole | 2.82, -0.82 | 1.74, -3.99 | 4.45, -1.36 |
Figure S60. X-ray crystal structures of a) $\Lambda,\Lambda$-[Ir(dFmesppy)$_2$(µ-Cl)]$_2$ ($\Lambda,\Lambda$-$\text{D2}$) and b) $\Delta,\Delta$-[Ir(dFmesppy)$_2$(µ-Cl)]$_2$ ($\Delta,\Delta$-$\text{D2}$). Ellipsoids are drawn at the 50 % probability level. Solvent molecules and hydrogen atoms are omitted for clarity.

Figure S61. X-ray crystal structure of $\textit{rac}$-[Ir(dFmesppy)$_2$(qpy)]BF$_4$ ($\textit{rac}$-$\textit{2}$). Ellipsoids are drawn at the 50 % probability level. Solvent molecules and hydrogen atoms are omitted for clarity.
Figure S62. Preliminary X-ray crystal structure of the cage rac-C1. The data, as yet, isn’t being amenable to further refinement due to the extremely weak diffraction exhibited by the single crystals.
Optoelectronic Characterization.

*Photophysical measurements.* All samples were prepared in HPLC grade CH$_2$Cl$_2$ or DMSO with varying concentrations on the order of $10^{-4} - 10^{-6}$ M. Absorption spectra were recorded at room temperature using a Shimadzu UV-1800 double beam spectrophotometer. Molar absorptivity determination was verified by linear least-squares fit of the values obtained from at least four independent solutions at varying concentrations with absorbance ranging from $6.05 \times 10^{-5}$ to $2.07 \times 10^{-5}$ M.

The sample solutions for the emission spectra were prepared in HPLC-grade DCM or DMSO and degassed *via* freeze-pump-thaw cycles using a quartz cuvette designed in-house. Steady-state emission and excitation spectra and time-resolved emission spectra were recorded at 298 K using an Edinburgh Instruments F980. All samples for steady-state measurements were excited at 360 nm using a xenon lamp, while samples for time-resolved measurements were excited at 378 nm using a PDL 800-D pulsed diode laser. Photoluminescence quantum yields were determined using the optically dilute method.$^{15}$ A stock solution with absorbance of ca. 0.5 was prepared and then four dilutions were prepared with dilution factors between 2 and 20 to obtain solutions with absorbances of ca. 0.095, 0.065, 0.05 and 0.018, respectively. The Beer-Lambert law was found to be linear at the concentrations of these solutions. The emission spectra were then measured after the solutions were rigorously degassed *via* three freeze-pump-thaw cycles prior to spectrum acquisition. For each sample, linearity between absorption and emission intensity was verified through linear regression analysis and additional measurements were acquired until the Pearson regression factor ($R^2$) for the linear fit of the data set surpassed 0.9. Individual relative quantum yield values were calculated for each solution and the values reported represent the slope value. The equation $\Phi_s = \Phi_r (A_s / A_r) (I_s / I_r)(n_s / n_r)^2$ was used to calculate the relative quantum yield of each of the sample, where $\Phi_r$ is the absolute quantum yield of the reference, $n$ is the refractive index of the solvent, $A$ is the
absorbance at the excitation wavelength, and \( I \) is the integrated area under the corrected emission curve. The subscripts \( s \) and \( r \) refer to the sample and reference, respectively. A solution of quinine sulfate in 0.5 M \( \text{H}_2\text{SO}_4 \) (\( \Phi_r = 54.6\% \))\(^{16}\) was used as external reference.\(^{17}\)

**UV-Vis spectroscopy (DCM solution).**

Figure **S63.** UV-Vis spectra of \( \text{rac--}[\text{Ir(mesppy)}_2(qpy)]\text{BF}_4 \) (1, in orange), \( \text{rac--}[\text{Ir(dFmesppy)}_2(qpy)]\text{PF}_6 \) (2, in blue), and cages \( \text{rac-C1} \) (in red) and \( \text{rac-C2} \) (in green) collected in \( \text{CD}_2\text{Cl}_2 \) at 298 K.

**Table S3.** UV-Vis absorptions of 1, 2, C1, C2

| Compound        | \( \lambda_{\text{max}} \) (nm) | \( \epsilon \) (\( \times 10^3 \text{ M}^{-1} \text{ cm}^{-1} \)) |
|-----------------|---------------------------------|-------------------------------------------------------------|
| **rac, \( \Lambda^- \) and \( \Delta^-1 \)** | 255 [50.4], 294 [37.3], 381 [9.4], 403 [7.7] | |
| **rac, \( \Lambda^- \) and \( \Delta^-2 \)** | 253 [51.0], 291 [33.7], 321 [18.9], 367 [8.2], 387 [5.2] | |
| **rac, \( \Lambda^- \) and \( \Delta^-\text{C1} \)** | 261 [56.8], 311 [21.5], 337 [16.2], 387 [11.3], 413 [10.8] | |
| **rac, \( \Lambda^- \) and \( \Delta^-\text{C2} \)** | 260 [58.9], 311 [26.5], 369 [15.1], 397 [9.3] | |
Emission spectra (DCM solution and PMMA-doped films).

Figure S64. Normalized DCM emission spectra of: rac-1, dotted violet line; Λ-1, dotted red line; rac-C1, solid orange line; Λ-C1, solid red line collected in degassed DCM at 298 K and normalized emission spectra of PMMA-doped films with 5% wt % of samples spin-coated on quartz substrates of: rac-1, dotted light-violet line; Λ-1, dotted light-blue line; rac-C1, solid blue line; Λ-C1, solid green line collected at 298 K.

\(^a\) UV-Vis absorption in DCM with a concentration in the order of \(10^{-5} \rightarrow 10^{-6}\) M collected at 298 K. \(^b\) concentration-independent extinction coefficients.
Figure S65. Normalized DCM emission spectra of: \textit{rac-2}, dotted violet line; \textit{\Lambda-2}, dotted red line; \textit{rac-C2}, solid orange line; \textit{\Lambda-C2}, solid red line collected in degassed DCM at 298 K and normalized emission spectra of PMMA-doped films with 5\% wt \% of samples spin-coated on quartz substrates of: \textit{rac-2}, dotted light-violet line; \textit{\Lambda-2}, dotted light-blue line; \textit{rac-C2}, solid blue line; \textit{\Lambda-C2}, solid green line collected at 298 K.

Emission decays (DCM solutions and PMMA-doped films).

Figure S66. Emission decay of: \textit{rac-1} (left) and \textit{\Delta-1} (right) collected in degassed DCM at 298 K ($\lambda_{exc} = 378$ nm).
Figure S67. Emission decay of: $\Lambda$-1 (left) and rac-2 (right) collected in degassed DCM at 298 K ($\lambda_{\text{exc}} = 378$ nm).

Figure S68. Emission decay of: $\Delta$-2 (left) and $\Lambda$-2 (right) collected in degassed DCM at 298 K ($\lambda_{\text{exc}} = 378$ nm).

Figure S69. Emission decay of: rac-C1 (left) and $\Delta$-C1 (right) collected in degassed DCM at 298 K ($\lambda_{\text{exc}} = 378$ nm).
Figure S70. Emission decay of: $\Lambda$-C1 (left) and rac-C2 (right) collected in degassed DCM at 298 K ($\lambda_{\text{exc}} = 378$ nm).

Figure S71. Emission decay of: $\Delta$-C2 (left) and $\Lambda$-C2 (right) collected in degassed DCM at 298 K ($\lambda_{\text{exc}} = 378$ nm).

Figure S72. Emission decay of: rac-1 (left) and $\Delta$-1 (right) collected in PMMA-doped films at 298 K ($\lambda_{\text{exc}} = 378$ nm).
Figure S73. Emission decay of: $\Lambda^{-1}$ (left) and $\text{rac-2}$ (right) collected in PMMA-doped films at 298 K ($\lambda_{exc} = 378$ nm).

Figure S74. Emission decay of: $\Delta^{-2}$ (left) and $\Lambda^{-2}$ (right) collected in PMMA-doped films at 298 K ($\lambda_{exc} = 378$ nm).

Figure S75. Emission decay of: $\text{rac-C1}$ (left) and $\Delta-C1$ (right) collected in PMMA-doped films at 298 K ($\lambda_{exc} = 378$ nm).
Figure S76. Emission decay of $\Lambda$-C1 (left) and rac-C2 (right) collected in PMMA-doped films at 298 K ($\lambda_{\text{exc}} = 378$ nm).

Figure S77. Emission decay of $\Delta$-C2 (left) and $\Lambda$-C2 (right) collected in PMMA-doped films at 298 K ($\lambda_{\text{exc}} = 378$ nm).
Energy Transfer studies between IrCN and Δ-C1.

Figure S78. Normalized emission spectra collected in DMSO at 298 K of IrCN (dark-blue line), Δ-C1 (dark red line) and of Δ-C1 after gradual addition of IrCN. The concentration of Δ-C1 was kept constant at 100 μM whereas the concentration of IrCN varied from 0 to 120 μM (μM of IrCN; titr. 1 = 10, titr. 2 = 60, titr. 3 = 120). Due to the efficient energy transfer from IrCN to Δ-C1, the emission intensity of the red-emitting cage was found to be always predominant over the emission of the blue-emitting donor.

Determination of binding constant for the formation of Δ-C1⇒IrCN

The binding constant for the host-guest structure Δ-C1⇒IrCN was determined from emission titration experiments (see Figure 7). Small aliquots of Δ-C1 were added to a 100 μM degassed solution of IrCN in DMSO such that the concentration of Δ-C1 in the sample ranged from 0 μM to 120 μM. An emission spectrum of the solution was recorded after each addition and the variation of the emission intensity of IrCN in Δ-C1⇒IrCN with respect to Δ-C1 concentration determined from this data. This data was then fitted to the sequential 1:1 binding model using an iterative fitting method.
procedure implemented within the OpenDataFit tool of the Supramolecular program (www.supramolecular.org) (see Figure S79). The best fit of the binding model to the emission data afforded a value for $K_b$ of $3.9 \times 10^6 \pm 0.2$ M$^{-1}$.

Figure S79. 1:1 Binding isotherm obtained by emission titration experiments of IrCN (donor) after gradual addition of $\Delta$-C1 (acceptor) in DMSO at 298 K, while monitoring the emission intensity of IrCN (Figure 4) by emission spectroscopy.

Figure S80. Binding model corresponding to the formation of $\Delta$-C1$\supset$IrCN. Molar fractions of guest $\Delta$-C1 (in blue) and 1:1 $\Delta$-C1:IrCN (in red) present in solution.
Stern-Volmer Quenching Studies Analysis

Emission titration in DMSO at 298 K of cage Δ-C1 (quencher) into a degassed solution of IrCN (donor). The concentration of IrCN was kept constant at 100 μM whereas the concentration of Δ-C1 was gradually varied from 0 to 120 μM. To monitor the emission quenching of IrCN due to the energy transfer to the red-emitting iridium cage, we monitored the lifetime decays in correspondence of the emission maxima of IrCN, at \( \lambda_{PL} \) 480 nm. The solutions were excited at \( \lambda_{exc} \) = 378 nm.

![Figure S81](image)

**Figure S81.** Molar absorptivity of Δ-C1 cage in DMSO at 298 K (red line) and normalized emission of IrCN (blue line) collected in degassed DMSO at 298 K.

**Table S4.** Emission lifetime as a function of concentration of quencher.

|       | [IrCN] (μM) | [Δ-C1] (μM) | \( \tau_e \) 470 nm (ns) |
|-------|-------------|-------------|--------------------------|
| IrCN  | 100         | -           | 2915                     |
| Titr. 1 | 100       | 21          | 672                      |
| Titr. 2 | 100       | 30          | 550                      |
| Titr. 3 | 100       | 48          | 383                      |
Emission decays monitored at 470 nm of IrCN and IrCN after gradual addition of Δ-C1 (quencher) in degassed DMSO at 298 K. The lifetime data combined with the concentration values have been used to calculate the Stern-Volmer constants.

Figure S82. Emission decay of TBA[Ir(dFppy)₂(CN)₂] (IrCN) collected in degassed DMSO at 298 K (λ_exc = 378 nm).

Figure S83. Emission decay of TBA[Ir(dFppy)₂(CN)₂] (IrCN) (100 μM) + Δ-C1 (21 μM) collected in degassed DMSO at 298 K (λ_exc = 378 nm).
Figure S84. Emission decay of TBA[Ir(dFppy)$_2$(CN)$_2$] (IrCN) (100 μM) + Δ-C1 (30 μM) collected in degassed DMSO at 298 K ($\lambda_{exc} = 378$ nm).

Figure S85. Emission decay of TBA[Ir(dFppy)$_2$(CN)$_2$] (IrCN) (100 μM) + Δ-C1 (48 μM) collected in degassed DMSO at 298 K ($\lambda_{exc} = 378$ nm).

Figure S86. Emission decay of TBA[Ir(dFppy)$_2$(CN)$_2$] (IrCN) (100 μM) + Δ-C1 (101 μM) collected in degassed DMSO at 298 K ($\lambda_{exc} = 378$ nm).

Figure S87. Emission decay of TBA[Ir(dFppy)$_2$(CN)$_2$] (IrCN) (100 μM) + Δ-C1 (118 μM) collected degassed DMSO at 298 K ($\lambda_{exc} = 378$ nm).
Figure S88. Emission decay of TBA[Ir(dFppy)$_2$(CN)$_2$] (IrCN) (100 μM) + Δ-C1 (118 μM) monitored at 650 nm collected in degassed DMSO at 298 K ($\lambda_{\text{exc}} = 378$ nm).

Figure S89. Emission decay of Δ-C1 monitored at 650 nm collected in degassed DMSO at 298 K ($\lambda_{\text{exc}} = 378$ nm).
Energy Transfer Studies between Irdmbpy and Δ-C1.

Figure S90. Normalized emission spectra collected in DMSO at 298 K of Irdmbpy (blue line), Δ-C1 (dark red line) and of Δ-C1 after gradual addition of Irdmbpy. The concentration of Δ-C1 was kept constant at 100 μM whereas the concentration of Irdmbpy varied from 0 to 120 μM (μM of Irdmbpy; trit. 1 = 10, trit. 2 = 30, trit. 3 = 70, trit. 4 = 90, trit. 5 = 120).

In contrast to that observed for the Δ-C1⊃IrCN assemblies, no energy transfer was observed between Irdmbpy and Δ-C1. Indeed, the emission intensity of Irdmbpy (λ_{em} = 480 nm) increases proportionally with concentration. The emission intensity of Δ-C1 is also not affected by the addition of Irdmbpy. The same conclusion can be extracted from the time-resolved emission experiments presented below.
Table S5. Lifetime decays.

|       | [Irdmbpy] (µM) | [Δ-C1] (µM) | $\tau_e$ 470 nm (ns) |
|-------|----------------|-------------|----------------------|
| Irdmbpy       | 100           | -           | 1167                 |
| Titr. 5       | 100           | 118         | 950                  |

Emission decays monitored at 520 nm of Irdmbpy and Irdmbpy after gradual addition of Δ-C1 (quencher) in degassed DMSO at 298 K.

Figure S91. Emission decay of [Ir(dFppy)$_2$(dmbpy)]PF$_6$ (Irdmbpy) monitored at 530 nm collected in degassed DMSO at 298 K ($\lambda_{ex} = 378$ nm).

Figure S92. Emission decay of [Ir(dFppy)$_2$(dmbpy)]$_2$ (Irdmbpy) (100 µM) + Δ-C1 (118 µM) monitored at 530 nm collected in degassed DMSO at 298 K ($\lambda_{ex} = 378$ nm).
Figure S93. Emission decay of $[\text{Ir(dFppy)}_2(\text{dmbpy})_2] \ (\text{Ir}dmbpy)$ (100 μM) + Δ-C1 (118 μM) monitored at 650 nm collected in degassed DMSO at 298 K ($\lambda_{\text{ex}} = 378$ nm).

**Computational details**

All calculations are based on Hartree Fock theory (HF) theory. The geometries of the host and host-guest complexes were fully optimized without symmetry restriction in the gas phase using the 6-31G(d) basis set for the light atoms. Scalar relativistic effects were included for the Ir and Pd atoms by using the LANL2DZ pseudopotentials. All calculations were carried out with the Gaussian09.D01 program package.

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