Supporting Information

Photoswitchable azobenzene-appended iridium(III) complexes


\(^a\)Department of Applied Chemistry, Faculty of Chemistry, University of the Basque Country (UPV-EHU), San Sebastián, Spain. E-mail: Zoraida_freixa@ehu.eus
\(^b\)Surfaces Division, IK4-CIDETEC, San Sebastián, Spain.
\(^c\)Institut des Sciences Moléculaires, CNRS UMR 5255, University of Bordeaux, 33405 Talence, France.
\(^d\)IKERBASQUE, Basque Foundation for Science, Bilbao, Spain.
Synthesis, characterization and UV/Vis photoisomerization studies of new compounds. 3–55

Compound d (Fig. S1–Fig. S4)
Ligand 1 (Fig. S5–Fig. S10) 6
(6-Phenyl-3-pyridyl)-boronic acid (Fig. S11–Fig. S14)
Ligand 2 (Fig. S15–Fig. S20) 13
Ligand 3 (Fig. S21–Fig. S27) 17
Ligand 5 (Fig. S28–Fig. S34)

[Ir(ppyBr)2Cl]2 25
[Ir(ppyBr)2(acac)] (Fig. S35–Fig. S39) 26
[Ir(5)2(acac)] (Fig. S40–Fig. S46) 29
[Ir(ppy)2(1)] (Fig. S47–Fig. S53) 33
[Ir(ppy)2(2)] (Fig. S54–Fig. S59) 38
[Ir(ppy)2(3)] (Fig. S60–Fig. S66) 42
[Ir(Fppy)2(1)] (Fig. S67–Fig. S73) 46
[Ir(Brppy)2(1)] (Fig. S74–Fig. S80) 51
[Ir(4)2(1)] (Fig. S81) 55

1H-NMR photoisomerization studies 56–61
Fig. S82. 1H-NMR spectra of ligand 1 56
Fig. S82. 1H-NMR spectra of ligand 2 56
Fig. S82. 1H-NMR spectra of ligand 3 57
Fig. S82. 1H-NMR spectra of ligand 4 57
Fig. S82. 1H-NMR spectra of ligand 5 58
Fig. S82. 1H-NMR spectra of [Ir(4)2(acac)] 58
Fig. S82. 1H-NMR spectra of [Ir(5)2(acac)] 59
Fig. S82. 1H-NMR spectra of [Ir(ppy)2(2)] 59
Fig. S82. 1H-NMR spectra of [Ir(ppy)2(1)] 60
Fig. S82. 1H-NMR spectra of [Ir(Fppy)2(1)] 60
Fig. S82. 1H-NMR spectra of [Ir(Brppy)2(1)] 61
Fig. S82. 1H-NMR spectra of [Ir(ppy)2(3)] 61

Cyclic-voltammograms 62–64
Fig. S94. Cyclic voltammograms of [Ir(ppy)2(1)], [Ir(Fppy)2(1)] and [Ir(Brppy)2(1)] 62
Fig. S95. Cyclic voltammograms of [Ir(ppy)2(4)] and [Ir(Fppy)2(4)] 62
Fig. S96. Cyclic voltammograms of [Ir(4)2(acac)] and [Ir(5)2(acac)] 63
Fig. S97. Cyclic voltammograms of [Ir(ppy)2(2)] 63
Fig. S98. Cyclic voltammograms of [Ir(ppy)2(3)] 64

NMR simulation 64
Fig. S99. 1H-NMR spectra of compounds [Ir(Fppy)2(1)] and [Ir(Brppy)2(1)] 64
**Compound d. Synthesis and characterization.**

**SYNTHESIS**

4-(Phenylazo)phenol (2.00 g, 10.1 mmol), (4-bromomethylphenyl)boronic acid pinacol ester (3.58 g, 12.1 mmol) and NaOH (0.80 g, 20.0 mmol) were dissolved in 170 mL of a degassed mixture of CH3CN/CH2Cl2 (20:3, v/v). The solution was then stirred and refluxed (95 °C) for 2 days under N2. The solution was cooled to room temperature and gravity-filtered to remove NaBr. After concentrating *in vacuo*, the resulting solid was purified by column chromatography (silica, CH2Cl2, RF = 0.7). The title compound was obtained as an orange solid (2.70 g, 65%).

**Elemental Analysis:** calculated for C25H27F3BN2O3: C, 72.48; H, 6.57; N, 6.76. Found: C, 72.52; H, 6.73; N, 6.41.

**Exact mass (MALDI) - m/z:** 415.2186 for [M + H]+.

**1H NMR (300 MHz, CDCl3):** δ 7.97-7.88 (m, 6H), 7.57-7.47 (m, 5H), 7.12 (d, J = 9.0, 2H, C6H4 (C12H9N2)), 5.22 (s, 2H, CH2), 1.40 (s, 12H, CH3).

**13C NMR (75 MHz, CDCl3):** δ 161.12 (1C, Cquat.), 152.75 (1C, Cquat.), 147.15 (1C, Cquat.), 139.54 (1C, Cquat.), 135.10 (2C, CH), 130.35 (1C, CH, C6H4 (C12H9N2)), 129.00 (2C, CH), 126.52 (2C, CH), 124.72 (2C, CH), 122.55 (2C, CH), 115.13 (2C, CH), 83.84 (2C, Cquat.), 70.14 (1C, CH2), 24.85 (4C, CH3), (C-B not seen)

![Fig. S1. 1H NMR spectrum of compound d in CDCl3, 300 MHz.](image-url)
Supporting Information

Fig. S2. $^{13}$C NMR spectrum of compound $d$ in CDCl$_3$, 75 MHz.

Fig. S3. HSQC spectrum of compound $d$ in CDCl$_3$. 
Fig. S4. COSY spectrum of compound d in CDCl₃.
Supporting Information

**Ligand 1. Synthesis, characterization and photoisomerization studies.**

**SYNTHESIS**
The compound d (2.65 g, 6.3 mmol) was dissolved in 38 mL of degassed THF. To this mixture, 2-bromopyridine (1.11 g, 0.67 mL, 7.0 mmol), Pd(PPh₃)₄ (2 mol%, 0.15 g, 1.3 mmol), and Na₂CO₃ (1 M aq., 19 mL) were added successively under nitrogen, and heated overnight at 80 °C. The reaction was cooled to room temperature and 60 mL of water was added. The resulting mixture was extracted with ethyl acetate (5 × 10 mL), dried (MgSO₄), filtered and evaporated *in vacuo*. The resulting solid was washed with ethanol and dried *in vacuo*; the product was obtained as an orange powder (2.22 g, 95%).

**Elemental Analysis**: calculated for C₂₄H₁₉N₃O · 0.9CH₂Cl₂: C, 67.51; H, 4.74; N, 9.48. Found: C, 67.51; H, 4.69; N, 8.98.

**Exact mass (EI) - m/z**: 366.1603 for [M + H]+.

**¹H NMR (300 MHz, CDCl₃)**: δ 8.74 (d, J = 4.6, 1H, C₅H₄N), 8.08 (d, J = 8.3, 2H, C₆H₄(C₁₁H₈N)), 7.96 (d, J = 9.0, 2H, C₆H₄(C₁₂H₉N₂)), 7.93 – 7.90 (m, 2H, C₆H₄), 7.82 – 7.78 (m, 2H, C₆H₄), 7.60 (d, J = 8.4, 2H, C₆H₄(C₁₁H₈N)), 7.57 – 7.44 (m, 3H, C₆H₅), 7.29 – 7.26 (m, 1H, C₅H₄N), 7.15 (d, J = 9.0, 2H, C₆H₄(C₁₂H₉N₂)), 5.26 (s, 2H, CH₂).

**¹³C NMR (75 MHz, CDCl₃)**: δ 161.10 (1C, C quat.), 156.96 (1C, C quat.), 152.71 (1C, C quat.), 149.62 (1C, CH, C₅H₄N), 147.15 (1C, C quat.), 139.18 (1C, C quat.), 137.22 (1C, C quat.), 136.85 (1C, CH, C₆H₄), 130.36 (1C, CH, C₅H₄N), 128.98 (2C, CH, C₆H₄), 127.76 (2C, CH, C₆H₄), 127.20 (2C, CH, C₆H₄), 124.72 (2C, CH, C₆H₄), 122.52 (2C, CH, C₆H₄), 122.44 (1C, CH, C₆H₄), 120.63 (1C, CH, C₆H₄), 115.13 (2C, CH, C₆H₄), 69.92 (1C, CH₂).

**UV/Vis (CH₃CN, λ, nm (ε, L mol⁻¹ cm⁻³))**: 345 (1.7 · 10⁴), 444 (0.6 · 10³).

![Fig. S5. ¹H NMR spectrum of ligand 1 in CDCl₃, 300 MHz.](image-url)
Fig. S6. $^{13}$C NMR spectrum of ligand 1 in CDCl$_3$, 75 MHz.

Fig. S7. HSQC NMR spectrum of ligand 1 in CDCl$_3$. 
Fig. S8. COSY NMR spectrum of ligand 1 in CDCl₃.

Fig. S9. UV/Vis spectra of ligand 1 in CH₃CN. Before (pink line) and after (blue line) irradiation at 347nm, 2.50 · 10⁻⁵ M.
Fig. S10. *Cis* to *trans* thermal isomerization kinetics of ligand 1. All k values were calculated from the first-order plots of absorption change of the band 345 nm at 328 K in CH$_3$CN after irradiation at 347 nm (2.50 · 10$^{-5}$M). *Cis* to *trans* thermal isomerization of this complex is slow, and the $A_\infty$ (1.200) value obtained in the kinetic measure does not correspond to $A_\infty$ value (1.256) obtained as maximum of absorbance before the photoisomerization. We have used $A_\infty = 1.256$ as maximum of absorbance corresponding to *trans* isomer. $k$ (s$^{-1}$) = 0.9 · 10$^{-4}$. Half-life (s) = 7600.
**Supporting Information**

**(6-Phenyl-3-pyridyl)-boronic acid. Synthesis and characterization.**

**SYNTHESIS**

5-Bromo-2-phenylpyridine (2.00 g, 8.6 mmol) was dissolved in 13 mL of distilled toluene and 4 mL of distilled THF: Triisopropyl borate (2.30 mL, 10.2 mmol) and n-BuLi (1.6 M in hexane, 6.40 mL, 10.2 mmol) were added at -40 °C under N₂ atmosphere, and the reaction mixture was stirred for 1 hour at this temperature. The reaction mixture was allowed to warm up to -20 °C and 10 mL of HCl (aq.) (2 M) were added. When the reaction mixture reached r.t., it was quenched with water and treated with a NaOH aqueous solution (5 M) until a neutral pH was reached. The mixture was saturated with NaCl and it was extracted with THF (3 × 50 mL). The combined organic layers were dried over MgSO₄. The solvent was removed *in vacuo* and the residue was washed with ether and dichloromethane. The product was obtained as a white solid (1.60 g, 95%).

**Elemental Analysis:** calculated for C₁₁H₁₀BNO₂ · 1.75CH₂Cl₂: C, 44.05; H, 3.91; N, 4.03. Found: C, 43.80; H, 3.47; N, 4.42.

**Exact mass (EI) - m/z:** 200.0884 for [M + H]⁺.

**¹H NMR (300 MHz, MeOD):** \( \delta \) 8.82 (s, 1H, C₅H₃N), 8.38 (d, \( J = 7.9 \), 1H, C₅H₃N), 8.03 – 7.95 (m, 3H), 7.60 – 7.55 (m, 3H, C₆H₅).

**¹³C NMR (75 MHz, MeOD):** \( \delta \) 157.00 (1C, Cquat.), 152.02 (1C, CH, C₅H₃N), 147.08 (1C, CH, C₅H₃N), 137.99 (1C, Cquat.), 131.23 (1C, CH, C₆H₅), 130.20 (2C, CH, C₆H₅), 128.73 (2C, CH, C₆H₅), 122.88 (1C, CH, C₅H₃N), (C-B not seen).

![Fig. S11. ¹H NMR spectrum of (6-phenyl-3-pyridyl)-boronic acid in MeOD, 300 MHz.](image-url)
Fig. S12. $^{13}$C NMR spectrum of (6-phenyl-3-pyridyl)-boronic acid in MeOD, 75 MHz.

Fig. S13. HSQC NMR spectrum of (6-phenyl-3-pyridyl)-boronic acid in MeOD.
Fig. S14. COSY NMR spectrum of (6-phenyl-3-pyridyl)-boronic acid in MeOD.

SYNTHESIS.

(6-Phenyl-3-pyridyl)-boronic acid (300 mg, 1.50 mmol) and Pd(PPh₃)₄ (3 mol%, 35 mg, 0.03 mmol) were dissolved in 10 mL of DME. The mixture was stirred under N₂ at 50 °C for 10 min. To this solution, 4-(phenylazo)benzyl bromide (280 mg, 1.00 mmol) dissolved in 3mL of DME/ethanol (2:1, v/v) and Na₂CO₃ (2 M aq., 2.0 mL) were added successively under nitrogen, and heated overnight at 110 °C with continuous stirring. The reaction was cooled to room temperature and 50 mL of water were added. The resulting mixture was extracted with ethyl acetate (5 × 10 mL), dried (MgSO₄), filtered and the solvent removed in vacuo. The resulting solid was purified on by column chromatography (silica, CH₂Cl₂, Rf = 0.4); the product was obtained as a red crystalline solid (140 mg, 40%).

Elemental Analysis: calculated for C₂₄H₁₉N₃: C, 82.49; H, 5.48; N, 12.03. Found: C, 82.63; H, 5.22; N, 11.94.

Exact mass (MALDI) - m/z: 350.1646 for [M + H]+.

¹H NMR (300 MHz, CDCl₃): δ 8.66 (d, J = 1.8, 1H, C₅H₃N), 8.03 (d, J = 6.9, 2H), 7.98 – 7.91 (m, 4H), 7.71 (dd, J = 8.1, 0.4, 1H, C₅H₃N), 7.61 – 7.44 (m, 7H), 7.40 (d, J = 8.5, 2H, C₆H₄), 4.14 (s, 2H, CH₂).

¹³C NMR (75 MHz, CDCl₃): δ 155.68 (1C, C quat.), 152.64 (1C, C quat.), 151.37 (1C, C quat.), 149.95 (1C, CH, C₅H₃N), 143.11 (1C, C quat.), 139.10 (1C, C quat.), 137.13 (1C, CH), 134.30 (1C, C quat.), 130.90 (1C, CH), 129.57 (2C, CH), 129.05 (2C, CH), 128.80 (1C, CH), 128.71 (2C, CH), 126.75 (2C, CH), 125.73 (2C, CH), 122.78 (2C, CH), 120.35 (1C, CH, C₅H₃N), 38.57 (1C, CH₂).

UV/Vis (CH₃CN, λ, nm (ε, L mol⁻¹ cm⁻¹)): 326 (2.2 · 10⁴), 435 (0.9 · 10³).

Fig. S15. ¹H NMR spectrum of ligand 2 in CDCl₃, 300 MHz.
Supporting Information

Fig. S16. $^{13}$C APT NMR spectrum of ligand 2 in CDCl$_3$, 75 MHz.

Fig. S17. HSQC NMR spectrum of ligand 2 in CDCl$_3$. 
Fig. S18. COSY NMR spectrum of ligand 2 in CDCl₃.

Fig. S19. UV/Vis spectra of ligand 2 in CH₃CN. Before (pink line) and after (blue line) irradiation at 326 nm, 2.50 · 10⁻⁵ M.
Fig. S20. Cis to trans thermal isomerization kinetics of ligand 2. All k values were calculated from the first-order plots of absorption change of the band 326 nm at 328 K in CH₃CN after irradiation at 327 nm (2.50 \times 10^{-5} \text{ M}). Cis to trans thermal isomerization of this complex is slow, and the $A_{\infty}$ (1.339) value obtained in the kinetic measure does not correspond to $A_{\infty}$ value (1.616) obtained as maximum of absorbance before the photoisomerization. We have used $A_{\infty} = 1.616$ as maximum of absorbance corresponding to trans isomer. $k (\text{s}^{-1}) = 0.4 \times 10^{-4}$. Half-life (s) = 16000.
**Ligand 3. Synthesis, characterization and photoisomerization studies.**

**SYNTHESIS**

4-(phenylazo)iodobenzene (0.77 g, 2.5 mmol) was dissolved in 10 mL of DMSO. To this mixture, acetylacetone (0.75 g, 0.77 mL, 7.50 mmol), K₂CO₃ (1.38 g, 10.0 mmol), CuI (0.05 g, 0.3 mmol) and L-proline (0.06 g, 0.5 mmol) were added successively under nitrogen, and heated at 90 °C for 6 h. The reaction mixture was quenched with HCl (1 M, 100 mL) and it was extracted with EtOAc (3 × 25 mL). MgSO₄ was added to the organic fraction, filtered and evaporated in vacuo. The resulting solid was purified by column chromatography (silica) eluting with hexane/dichloromethane (5:1, v/v) (RF = 0.3); the product was obtained as a red crystalline solid (0.25 g, 36%).

**Elemental Analysis:** calculated for C₁₇H₁₆N₂O₂: C, 72.84; H, 5.75; N, 9.99. Found: C, 72.76; H, 5.52; N, 9.88.

**Exact mass (MALDI) - m/z:** 281.1277 for [M + H]+.

**¹H NMR (300 MHz, CDCl₃):** δ 16.76 (s, 1H, CH*), 8.01–7.96 (m, 4H), 7.61–7.52 (m, 3H, C₆H₅), 7.40–7.36 (m, 2H, C₆H₄), 1.98 (s, 6H, CH₃).

**¹³C NMR (75 MHz, CDCl₃):** δ 190.78 (2C, C_quat.C=O*), 152.60 (1C, C_quat.), 151.87 (1C, C_quat.), 139.78 (1C, C_quat.), 131.94 (2C, CH, C₆H₅), 131.17 (1C, CH, C₆H₄), 129.12 (2C, CH, C₆H₅), 123.21 (2C, CH), 122.87 (2C, CH), 114.59 (1C, C_quat.), 24.20 (2C, CH₃).

**UV/Vis (CH₃CN, λ, nm (ε, L mol⁻¹ cm⁻¹)):** 326 (2.0 · 10⁴, 439 (0.8 · 10⁴).

---

![Fig. S21. ¹H NMR spectrum of ligand 3 in CDCl₃, 300 MHz.](image-url)
Supporting Information

Fig. S22. $^{13}$C APT NMR spectrum of ligand 3 in CDCl$_3$, 75 MHz.

Fig. S23. HSQC NMR spectrum of ligand 3 in CDCl$_3$. 
Fig. S24. COSY NMR spectrum of ligand 3 in CDCl₃.

Fig. S25. UV/Vis spectra of ligand 3 in CH₃CN. Before (pink line) and after (blue line) irradiation at 332 nm, 2.50 × 10⁻⁵ M.
Fig. S26. *Cis* to *trans* thermal isomerization kinetics of ligand 3. Absorption change of the band 326 nm at 328 K in CH$_3$CN after irradiation at 332 nm ($2.50 \cdot 10^{-5}$ M).

Fig. S27. *Cis* to *trans* thermal isomerization kinetics of ligand 3. First-order plot. $k$ (s$^{-1}$) = 1.2 $\cdot$ 10$^{-3}$. Half-life (s) = 530.

SYNTHESIS
5-Bromo-2-phenylpyridine (300 mg, 0.130 mmol) was dissolved in 4 mL of degassed THF. To this mixture, 4-(phenylazo)phenyl boronic acid pinacol ester (430 mg, 0.140 mmol), Pd(PPh3)4 (2 mol%, 3 mg, 0.003 mmol), Na2CO3 (1 M aq., 2 mL) were added successively under nitrogen, and heated overnight at 80 °C with continuous stirring. The reaction mixture was heated overnight at 80 °C with continuous stirring. The reaction was cooled to room temperature and 50 mL of water was added. The resulting mixture was extracted with CH2Cl2 (5 × 20 mL), dried over MgSO4, filtered and evaporated in vacuo. The product was washed with dichloromethane (2 mL) and dried in vacuo. The product was obtained as an orange powder (380 mg, 88%).

Elemental Analysis: calculated for C23H17N3 · 0.5CH2Cl2: C, 74.70; H, 4.80; N, 11.12. Found: C, 74.83; H, 4.77; N, 11.04.

Exact mass (MALDI) - m/z: 336.1495 for [M+H]+.

1H NMR (300 MHz, CDCl3): \(\delta\) 9.06 (d, \(J = 1.9\), 1H, C5H3N), 8.13 – 8.06 (m, 5H), 8.00 (d, \(J = 8.0\), 1.4, 2H), 7.89 (d, \(J = 8.3\), 1H, C6H4N), 7.85 (d, \(J = 8.5\), 2H, C6H4), 7.61 – 7.50 (m, 6H).

13C NMR (75 MHz, CDCl3): \(\delta\) 156.27 (1C, C quat.), 152.28 (1C, C quat.), 151.79 (1C, C quat.), 147.66 (1C, CH, C5H3N), 139.64 (1C, C quat.), 138.41 (1C, C quat.), 134.67 (1C, CH, C6H4N), 133.54 (1C, C quat.), 130.75 (1C, CH, C6H4), 128.74 (1C, CH, C6H4), 128.71 (2C, CH, C6H4), 128.42 (2C, CH, C6H4), 127.20 (2C, CH, C6H4), 126.47 (2C, CH), 123.25 (2C, CH), 122.52 (2C, CH, C6H4), 119.99 (1C, CH, C5H3N).

UV/Vis (CH3CN, \(\lambda\), nm (\(\varepsilon\), L mol\(^{-1}\) cm\(^{-1}\))): 347 (3.3 · 10\(^4\)), 436 (1.5 · 10\(^4\)).

Fig. S28. \(^1\)H NMR spectrum of ligand 5 in CDCl\(_3\), 300 MHz.
Fig. S29. $^{13}$C APT NMR spectrum of ligand 5 in CDCl$_3$, 75 MHz.

Fig. S30. HSQC NMR spectrum of ligand 5 in CDCl$_3$. 

S22
Fig. S31. COSY NMR spectrum of ligand 5 in CDCl₃.

Fig. S32. UV/Vis spectra of ligand 5 in CH₃CN. Before (pink line) and after (blue line) irradiation at 353 nm, 2.50 × 10⁻⁵ M.
Fig. S33. Cis to trans thermal isomerization kinetics of ligand 5. Absorption change of the band 347 nm at 328 K in CH$_3$CN after irradiation at 353 nm (2.50 × 10$^{-5}$ M).

Fig. S34. Cis to trans thermal isomerization kinetics of ligand 5. First-order plot. k (s$^{-1}$) = 1.1 × 10$^{-4}$. Half-life (s) = 6500.
**Supporting Information**

**[Ir(ppyBr)₂Cl]₂: Synthesis and characterization.**

**SYNTHESIS**

To a solution of 5-bromo-2-phenylpyridine (3.00 g, 12.8 mmol) in 2-ethoxyethanol : H₂O (3:1, v/v; 60 mL) was added IrCl₃·3H₂O (1.80 g, 5.10 mmol) and the reaction mixture was heated to 120 °C for 24 h. The reaction was cooled to room temperature and 50 mL of water were added to precipitate the formed compound. The solution was gravity filtered and the solid was washed with 20 mL of hexane, 20 mL of ethanol and 50 mL of diethyl ether. The product obtained was rather insoluble in all the solvents assayed (i.e. solubility is less than 0.1 mg in 10 mL of CDCl₃), it was a light-orange powder (3.40 g, 96%). Low solubility hampered a complete NMR characterization.

**Elemental Analysis:** calculated for C₄₄H₂₈Br₄Cl₂Ir₂N₄: C, 38.08; H, 2.03; N, 4.04. Found: C, 38.29; H, 2.44; N, 3.92.
Supporting Information

\[\text{[Ir(ppyBr)\(_2\)(acac)]}. \text{Synthesis and characterization.}\]

**SYNTHESIS**

\[\text{[Ir(ppyBr)\(_2\)Cl\(_2\)}, (150 \text{ mg, 0.11 mmol}) \text{ and AgOTf (84 mg, 0.32 mmol)} \text{ were dissolved in deamdegassed acetone (8 mL) and refluxed (55 °C) under nitrogen for 2 h. The solution was cooled to room temperature and gravity-filtered to remove AgCl. The filtrate was refluxed (55 °C) under nitrogen for 1 h and added to a 1 h refluxed solution of acetylacetone (45 \text{ µL, 0.43 mmol}) \text{ and triethylamine (113 \text{ µL, 0.81 mmol}) dissolved in deamdegassed acetone (4 mL). The resulting solution was refluxed overnight under nitrogen. After removing the solvent, the residue was purified by column chromatography: silica/CH\(_2\)Cl\(_2\) (Rf \text{ = 0.8). It was obtained as a light-orange powder (106 mg, 65%).}}\]

**Elemental Analysis:** calculated for C\(_{27}\)H\(_{21}\)Br\(_2\)IrN\(_2\)O\(_2\) \cdot 2 C\(_3\)H\(_6\)O: C, 45.37; H, 3.81; N, 3.21. Found: C, 45.52; H, 4.14; N, 3.29.

**Exact mass (MALDI) - m/z:** 755.9575 for \([\text{M}]+\) with \((^{193}\text{Ir})(^{79}\text{Br})\).

\(^1\text{H NMR (300 MHz, CDCl}_3\text{):} \ \delta 8.60 \text{ (d, } J = 1.9, 2\text{H, C}_5\text{H}_3\text{NBr}), 7.87 \text{ (dd, } J = 8.7, \text{ 2.1, 2H, C}_6\text{H}_4\text{NBr), 7.75 \text{ (d, } J = 8.7, 2\text{H, C}_6\text{H}_4\text{NBr), 7.54 \text{ (dd, } J = 7.6, 1.2, 2\text{H, C}_6\text{H}_4\text{), 6.87 \text{ (td, } J = 7.5, 1.3, 2\text{H, C}_6\text{H}_4\text{), 6.77 (td, 7.4, 1.4, 2\text{H, C}_6\text{H}_4\text{), 6.30 (d, } J = 7.5, 2\text{H, C}_6\text{H}_4\text{), 5.31 (s, 1\text{H, HAcac)}, 1.87 (s, 6\text{H, HAcac).}}\]

\(^{13}\text{C NMR (75 MHz, CDCl}_3\text{):} \ \delta 185.11 \text{ (2C, C quat.), 167.58 (2C, Ciquat.), 148.75 (2C, CH, C}_6\text{H}_4\text{NBr), 147.31 (2C, Cquart.), 143.49 (2C, Ciquat.), 139.68 (2C, CH, C}_6\text{H}_4\text{NBr), 132.99 (2C, CH, C}_6\text{H}_4\text{), 129.61 (2C, CH, C}_6\text{H}_4\text{), 124.22 (2C, CH, C}_6\text{H}_4\text{), 121.10 (2C, CH, C}_6\text{H}_4\text{), 119.16 (2C, CH, C}_6\text{H}_4\text{NBr), 115.78 (2C, Cquart.), 100.78 (1C, CH, HAcac), 28.77 (2C, CH, HAcac).}}\]

**UV/Vis (CH\(_3\)CN, \(\lambda, \text{ nm (} \epsilon, \text{ L mol}^{-1} \text{ cm}^{-1})\):** 265 (4.5 \cdot 10\(^4\)), 312 (1.9 \cdot 10\(^4\)), 347 (8.6 \cdot 10\(^3\)), 380 (5.3 \cdot 10\(^3\)), 416 (3.9 \cdot 10\(^3\)), 470 (2.5 \cdot 10\(^3\)), 503 (1.0 \cdot 10\(^3\)).

![Fig. S35. \(^1\text{H NMR spectrum of [Ir(ppyBr)\(_2\)(acac)] in CDCl}_3, 300 MHz.}\]
Fig. S36. $^{13}$C NMR spectrum of $\text{[Ir(ppyBr)₂(acac)]}$ in CDCl$_3$, 75 MHz.

Fig. S37. HSQC spectrum of $\text{[Ir(ppyBr)₂(acac)]}$ in CDCl$_3$. 

Supporting Information

**Fig. S38.** COSY spectrum of [Ir(ppyBr)₂(acac)] in CDCl₃.

**Fig. S39.** UV/Vis spectra of [Ir(ppyBr)₂(acac)] in CH₃CN, 2.50·10⁻⁵M.
Supporting Information

[Ir(5)$_2$(acac)]. Synthesis, characterization and photoisomerization studies.

SYNTHESIS
[Ir(ppyBr)$_2$(acac)] (60 mg, 0.079 mmol) was dissolved in 4 mL of degassed THF. To this mixture, 4-(phenylazo)phenyl boronic acid pinacol ester (54 mg, 0.174 mmol), Pd(PPh$_3$)$_4$ (2 mol%, 3 mg, 0.002 mmol), and Na$_2$CO$_3$ (1 M aq., 2 mL) were added successively under nitrogen. The reaction mixture was heated overnight at 80 °C with continuous stirring. The reaction was cooled to room temperature and 50 mL of water were added to precipitate the formed compound. The solution was gravity filtered and the solid was washed with hexane (20 mL). The resulting solid was purified by column chromatography (silica) eluting with dichloromethane (Rf = 0.7), obtaining 65 mg of the title compound (86% yield) as a red powder.

Elemental Analysis: calculated for C$_{51}$H$_{39}$IrN$_6$O$_2$ · 1C$_6$H$_{14}$: C, 65.43; H, 5.11; N, 8.03. Found: C, 65.10; H, 4.89; N, 7.91.

Exact mass (MALDI) - m/z: 960.2776 for [M]$^+$ with ($^{193}$Ir).

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.93 (d, $J = 1.9$, 2H, C$_6$H$_3$N), 8.12 – 8.08 (m, 6H), 8.00 (m, 6H), 7.84 (d, $J = 8.6$, 4H, C$_6$H$_4$(C$_{12}$H$_9$N$_2$)), 7.66 (dd, $J = 8.1$, 1.2, 2H, C$_6$H$_4$(C$_{11}$H$_7$)), 7.59 – 7.53 (m, 6H, C$_6$H$_5$), 6.91 (dt, $J = 7.4$, 1.1, 2H, C$_6$H$_4$(C$_{11}$H$_7$)), 6.78 (dt, $J = 7.5$, 1.3, 2H, C$_6$H$_4$(C$_{11}$H$_7$)), 6.43 (dd, $J = 7.5$, 0.8, 2H, C$_6$H$_4$(C$_{11}$H$_7$)), 5.37 (s, 1H, HAcac), 1.89 (s, 6H, HAcac).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 184.55 (2C, C quat.), 167.33 (2C, C quat.), 152.25 (2C, C quat.), 151.88 (2C, C quat.), 147.45 (2C, C quat.), 145.87 (2C, CH, C$_6$H$_3$N), 143.87 (2C, C quat.), 138.55 (2C, C quat.), 134.76 (2C, CH, C$_6$H$_3$N), 133.04 (2C, C quat.), 132.86 (2C, CH, C$_6$H$_4$(C$_{11}$H$_7$)), 130.83 (2C, CH, C$_6$H$_5$), 128.93 (2C, CH, C$_6$H$_4$(C$_{11}$H$_7$)), 128.72 (4C, CH, C$_6$H$_5$), 126.89 (4C, CH, C$_6$H$_4$(C$_{12}$H$_9$N$_2$)), 123.76 (2C, CH, C$_6$H$_4$(C$_{11}$H$_7$)), 123.37 (4C, CH, C$_6$H$_4$(C$_{12}$H$_9$N$_2$)), 122.54, (4C, CH, C$_6$H$_5$) 120.60 (2C, CH, C$_6$H$_4$(C$_{11}$H$_7$)), 117.97 (2C, CH, C$_6$H$_3$N), 100.34 (1C, CH, HAcac), 28.34 (2C, CH$_3$, HAcac).

UV/Vis (CH$_3$CN, $\lambda$, nm (ε, L mol$^{-1}$ cm$^{-1}$)): 349 ($7.9 \times 10^4$), 486 ($6.9 \times 10^3$).

Fig. S40. $^1$H NMR spectrum of [Ir(5)$_2$(acac)] in CDCl$_3$, 300 MHz.
Fig. S41. $^{13}$C APT NMR spectrum of [Ir(5)$_2$(acac)] in CDCl$_3$, 75 MHz.

Fig. S42. HSQC NMR spectrum of [Ir(5)$_2$(acac)] in CDCl$_3$. 

S30
Fig. S43. COSY NMR spectrum of [Ir(5)₂(acac)] in CDCl₃.

Fig. S44. UV/Vis spectra of [Ir(5)₂(acac)] in CH₃CN. Before (pink line) and after (blue line) irradiation at 359 nm, 2.50 × 10⁻⁵ M.
Fig. S45. *Cis* to *trans* thermal isomerization kinetics of [Ir(5)$_2$(acac)]. Absorption change of the band 349 nm at 328 K in CH$_3$CN after irradiation at 359 nm (2.50 $\times$ 10$^{-5}$ M).

Fig. S46. *Cis* to *trans* thermal isomerization kinetics of [Ir(5)$_2$(acac)]. First-order plot. $k$ (s$^{-1}$) = 1.1 $\times$ 10$^{-4}$. Half-life (s) = 6500.
[Ir(ppy)$_2$(1)]. Synthesis, characterization and photoisomerization studies.

**SYNTHESIS**

[Ir(ppy)$_2$(Cl)$_2$]$_2$ (150 mg, 0.14 mmol) and AgOTf (108 mg, 0.42 mmol) were dissolved in degassed acetone (8 mL) and refluxed under nitrogen for 2 h. The solution was cooled to room temperature and gravity-filtered to remove AgCl. The filtrate was refluxed under nitrogen (55 °C) for 1 h and added to a 1 h refluxed solution of ligand I (205 mg, 0.56 mmol) and NEt$_3$ (147 µL, 1.05 mmol) in degassed acetone (4 mL). The resulting solution was refluxed overnight (55 °C) under nitrogen. After removing the solvent, the residue was purified by column chromatography: silica/CH$_2$Cl$_2$ (Rf = 0.8). It was obtained as an orange powder (120 mg, 50%).

**Elemental Analysis**: calculated for C$_{46}$H$_{34}$IrN$_5$O: C, 63.87; H, 3.96; N, 8.10. Found: C, 64.43; H, 4.23; N, 7.60.

**Exact mass (MALDI) - m/z**: 865.2393 for [M]$^+$ with ($^{191}$Ir).

**$^1$H NMR (500 MHz, CDCl$_3$):** δ 8.07 (d, $J = 5.0$, 1H), 7.93 (d, $J = 6.7$, 2H), 7.90 (d, $J = 7.7$, 2H, C$_{24}$H$_{18}$N$_3$O), 7.86 (d, $J = 8.5$, 2H, C$_{24}$H$_{18}$N$_3$O), 7.78 (m, 3H), 7.69 (d, $J = 5.9$, 1H), 7.62 (m, 3H), 7.54 – 7.44 (m, 5H), 7.12 (d, $J = 7.1$, 1H), 6.93 (m, 8H), 6.70 (d, $J = 4.5$, 2H), 6.63 (d, $J = 5.6$, 1H), 6.47 (d, $J = 7.1$, 1H), 4.98 (s, 2H, CH$_2$).

**$^{13}$C NMR (126 MHz, CDCl$_3$):** δ 178.38 (1C, C$_{quat}$), 175.06 (1C, C$_{quat}$), 170.59 (1C, C$_{quat}$), 168.12 (1C, C$_{quat}$), 167.98 (1C, C$_{quat}$), 161.55 (1C, C$_{quat}$), 159.14 (1C, C$_{quat}$), 153.35 (1C, CH), 152.91 (1C, C$_{quat}$), 151.34 (1C, CH), 147.88 (1C, CH), 146.87 (1C, C$_{quat}$), 145.49 (1C, C$_{quat}$), 144.84 (1C, C$_{quat}$), 142.32 (1C, C$_{quat}$), 137.24 (1C, CH), 137.22 (1C, C$_{quat}$), 136.62 (1C, CH), 135.61 (1C, CH), 134.15 (1C, CH), 132.81 (1C, CH), 130.59 (1C, CH), 130.36 (1C, CH), 130.07 (1C, CH), 129.76 (1C, CH), 129.13 (2C, CH, C$_{12}$H$_9$N$_2$), 124.66 (2C, CH, C$_{12}$H$_9$N$_2$), 124.50 (1C, CH), 124.21 (1C, CH), 124.11 (1C, CH), 122.60 (2C, CH, C$_{12}$H$_9$N$_2$), 122.45 (1C, CH), 122.13 (1C, CH), 121.29 (1C, CH), 120.98 (1C, CH), 120.68 (1C, CH), 119.18 (1C, CH), 119.01 (1C, CH), 118.67 (1C, CH), 118.48 (1C, CH), 115.44 (2C, CH, C$_{12}$H$_9$N$_2$), 71.04 (1C, CH$_2$).

UV/Vis (CH$_3$CN, $\lambda$, nm (ε, L mol$^{-1}$ cm$^{-1}$)): 345 (3.2 · 10$^4$), 454 (4.0 · 10$^3$).
Fig. S47. $^1$H NMR spectrum of [Ir(ppy)$_2$(1)] in CDCl$_3$, 500 MHz.

Fig. S48. $^{13}$C NMR spectrum of [Ir(ppy)$_2$(1)] in CDCl$_3$, 126 MHz.
Fig. S49. HSQC NMR spectrum of [Ir(ppy)$_2$(1)] in CDCl$_3$.

Fig. S50. COSY NMR spectrum of [Ir(ppy)$_2$(1)] in CDCl$_3$. 
Fig. S51. UV/Vis spectra of $[\text{Ir} (\text{ppy})_2(\mathbf{1})]$ in CH$_3$CN. Before (pink line) and after (blue line) irradiation at 349 nm, $2.50 \times 10^{-5}$ M.

Fig. S52. Cis to trans thermal isomerization kinetics of $[\text{Ir}(\text{ppy})_2(\mathbf{1})]$. Absorption change of the band 345 nm at 328 K in CH$_3$CN after irradiation at 349 nm ($2.50 \times 10^{-5}$ M).
Fig. S53. Cis to trans thermal isomerization kinetics of \([\text{Ir}(\text{ppy})_2(1)]\). First-order plot. \(k \ (s^{-1}) = 1.2 \times 10^{-4}\). Half-life (s) = 5600.
Supporting Information

**[Ir(ppy)$_2$(2)]. Synthesis, characterization and photoisomerization studies.**

**SYNTHESIS**

[Ir(ppy)$_2$Cl$_2$] (150 mg, 0.14 mmol) and AgOTf (108 mg, 0.42 mmol) were dissolved in degassed acetone (8 mL) and refluxed under nitrogen for 2 h. The solution was cooled to room temperature and gravity-filtered to remove AgCl. The filtrate was refluxed under nitrogen (55 °C) for 1 h and added to a 1 h refluxed solution of ligand 2 (196 mg, 0.56 mmol) and NEt$_3$ (147 µL, 1.05 mmol) in degassed acetone (4 mL). The resulting solution was refluxed overnight (55 °C) under nitrogen. After removing the solvent, the residue was purified by column chromatography: silica/CH$_2$Cl$_2$ (Rf = 0.8). It was obtained as an orange powder (100 mg, 42%).

**Elemental Analysis**: calculated for C$_{60}$H$_{34}$Ir$_5$: C, 64.88; H, 4.44; N, 7.72. Found: C, 64.75; H, 4.21; N, 7.59.

**Exact mass (MALDI) - m/z**: 849.2443 for [M]$^+$ with ($^{193}$Ir).

**$^1$H NMR (300 MHz, CDCl$_3$)**: δ 8.15 (dd, $J$ = 5.8, 0.9, 1H), 7.98 (dd, $J$ = 8.2, 1.5, 2H, C$_{12}$H$_9$N$_2$), 7.87 – 7.72 (m, 7H), 7.70 – 7.63 (m, 3H), 7.61-7.43 (m, 6H), 7.10 (d, $J$ = 8.4, 2H, C$_{12}$H$_9$N$_2$), 7.02 – 6.84 (m, 7H), 6.72 (d, $J$ = 1.3, 1H), 6.72 (dd, $J$ =7.1, 5.8, 2.4, 1.2, 1H), 6.63-6.61 (m, 1H), 6.56 (dd, $J$ = 7.4, 1.3, 1H), 3.80 (s, 2H, CH$_2$).

**$^{13}$C NMR (75 MHz, CDCl$_3$)**: δ 177.31 (1C, C$_{quat}$), 175.10 (1C, C$_{quat}$), 170.52 (1C, C$_{quat}$), 167.85 (1C, C$_{quat}$), 166.65 (1C, C$_{quat}$), 159.40 (1C, C$_{quat}$), 153.17 (1C, 1CH), 152.67 (1C, C$_{quat}$), 151.22 (1C, C$_{quat}$), 150.95 (1C, CH), 147.77 (1C, CH), 145.18 (1C, C$_{quat}$), 144.62 (1C, C$_{quat}$), 142.58 (1C, C$_{quat}$), 142.25 (1C, C$_{quat}$), 137.89 (1C, CH), 136.75 (1C, CH), 135.40 (1C, CH), 134.63 (1C, C$_{quat}$), 133.90 (1C, CH), 132.57 (1C, CH), 130.96 (1C, CH), 130.60 (1C, CH), 130.04 (1C, CH), 129.69 (1C, CH), 129.48 (1C, CH), 129.30 (2C, CH C$_{12}$H$_9$N$_2$), 129.10 (2C, CH C$_{12}$H$_9$N$_2$), 124.13 (1C, CH), 123.98 (1C, CH), 123.91 (1C, CH), 123.19 (2C, CH C$_{12}$H$_9$N$_2$), 122.77 (2C, CH C$_{12}$H$_9$N$_2$), 121.86 (1C, CH), 121.15 (1C, CH), 121.12 (1C, CH), 120.96 (1C, CH), 118.74 (1C, CH), 118.71 (1C, CH), 118.42 (1C, CH), 118.29 (1C, CH), 38.45 (1C, CH$_2$).

**UV/Vis (CH$_3$CN, $\lambda$, nm ($\epsilon$, L mol$^{-1}$ cm$^{-1}$))**: 324 (3.5 · 10$^4$), 436 (5.0 · 10$^3$).
Fig. S54. $^1$H NMR spectrum of [Ir(ppy)$_2$(2)] in CDCl$_3$, 300 MHz.

| f1 (ppm) | 38.45 | 118.29 | 118.42 | 118.71 | 118.74 | 120.96 | 121.15 | 122.77 | 123.91 | 129.10 | 129.30 | 129.48 | 129.69 | 130.04 | 130.60 | 130.96 | 137.89 | 142.25 | 144.62 | 147.77 | 150.95 | 151.22 | 152.67 | 153.17 | 159.40 | 166.65 | 167.85 | 170.52 | 175.10 | 177.31 |
|----------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|

Fig. S55. $^{13}$C APT NMR spectrum of [Ir(ppy)$_2$(2)] in CDCl$_3$, 75 MHz.

| f1 (ppm) | 38.45 | 118.29 | 118.42 | 118.71 | 118.74 | 120.96 | 121.15 | 122.77 | 123.91 | 129.10 | 129.30 | 129.48 | 129.69 | 130.04 | 130.60 | 130.96 | 137.89 | 142.25 | 144.62 | 147.77 | 150.95 | 151.22 | 152.67 | 153.17 | 159.40 | 166.65 | 167.85 | 170.52 | 175.10 | 177.31 |
Fig. S56. HSQC NMR spectrum of [Ir(ppy)_2(2)] in CDCl₃.

Fig. S57. COSY NMR spectrum of [Ir(ppy)_2(2)] in CDCl₃.
Fig. S58. UV/Vis spectra of [Ir(ppy)$_2$(2)] in CH$_3$CN. Before (pink line) and after (blue line) irradiation at 328 nm, $2.50 \times 10^{-5}$ M.

Fig. S59. Cis to trans thermal isomerization kinetics of [Ir(ppy)$_2$(2)]. All k values were calculated from the first-order plots of absorption change of the band 324 nm at 328 K in CH$_3$CN after irradiation at 328 nm ($2.50 \times 10^{-5}$ M). Cis to trans thermal isomerization of this complex is slow, and the $A_\infty$ (0.789) value obtained in the kinetic measure does not correspond to $A_\infty$ value (0.826) obtained as maximum of absorbance before the photoisomerization. We have used $A_\infty = 0.826$ as maximum of absorbance corresponding to trans isomer. $k$ (s$^{-1}$) = $0.3 \times 10^{-4}$. Half-life (s) = 21000.
**Supporting Information**

**[Ir(ppy)$_2$(3)]. Synthesis, characterization and photoisomerization studies.**

**SYNTHESIS**

[Ir(ppy)$_2$Cl]$_2$ (150 mg, 0.14 mmol) and AgOTf (108 mg, 0.42 mmol) were dissolved in degassed acetone (8 mL) and refluxed under nitrogen for 2 h. The solution was cooled to room temperature and gravity-filtered to remove AgCl. The filtrate was refluxed under nitrogen (55 °C) for 1 h and added to a 1 h refluxed solution of ligand 3 (157 mg, 0.56 mmol) and NEt$_3$ (147 µL, 1.05 mmol) in degassed acetone (4 mL). The resulting solution was refluxed overnight (55 °C) under nitrogen. After removing the solvent, the residue was purified by column chromatography: alumina/CH$_2$Cl$_2$ (Rf = 0.7). It was obtained as an orange powder (50 mg, 23%).

**Elemental Analysis**: calculated for C$_{39}$H$_{31}$IrN$_4$O$_2$: C, 60.06; H, 4.01; N, 7.18. Found: C, 59.85; H, 3.84; N, 7.05.

**Exact mass (MALDI) - m/z**: 780.2056 for [M]$^+$ with ($^{193}$Ir).

$^1$H NMR (300 MHz, CDCl$_3$): δ 8.71 (dd, J = 5.7, 0.7, 2H, C$_{11}$H$_8$N), 7.98 – 7.89 (m, 6H), 7.83 (ddd, J = 8.1, 7.4, 1.5, 2H, C$_{11}$H$_8$N), 7.62 (dd, J = 8.7, 7.0, 2H, C$_{11}$H$_8$N), 7.59 – 7.47 (m, 3H, C$_{11}$H$_8$N$_2$), 7.33 (d, J = 8.9, 2H, C$_{11}$H$_8$N$_2$), 7.27 (ddd, J = 8.2, 5.8, 1.4, 2H, C$_{11}$H$_8$N), 7.16 (s, 6H, CH$_3$).

$^{13}$C NMR (75 MHz, CDCl$_3$): δ 182.99 (2C, C$_{quat}$), 168.35 (2C, C$_{quat}$), 152.33 (1C, C$_{quat}$), 150.74 (1C, C$_{quat}$), 147.72 (2C, CH, C$_{11}$H$_8$N), 147, 63 (2C, C$_{quat}$), 146.15 (1C, C$_{quat}$), 144.26 (2C, C$_{quat}$), 136.50 (2C, CH, C$_{11}$H$_8$N), 133.69 (4C, CH), 130.44 (1C, CH, C$_{11}$H$_8$N$_2$), 128.65 (2C, CH), 128.62 (2C, CH), 123.45 (2C, CH, C$_{11}$H$_8$N), 122.61 (2C, CH), 122.33 (2C, CH), 120.88 (2C, CH, C$_{11}$H$_8$N), 120.19 (2C, CH, C$_{11}$H$_8$N), 118.03 (2C, CH), 114.56 (1C, C$_{quat}$), 29.18 (2C, CH$_3$).

**UV/Vis (CH$_3$CN, λ, nm ($\varepsilon$, L mol$^{-1}$ cm$^{-1}$)):** 327 (3.0 ·10$^4$), 455 (3.7·10$^3$).

Fig. S60. $^1$H NMR spectrum of [Ir(ppy)$_2$(3)] in CDCl$_3$, 300 MHz.
Fig. S61. $^{13}$C NMR spectrum of $[\text{Ir}(\text{ppy})_2(3)]$ in CDCl$_3$, 75 MHz.

Fig. S62. HSQC NMR spectrum of $[\text{Ir}(\text{ppy})_2(3)]$ in CDCl$_3$. 
Fig. S63. COSY NMR spectrum of [Ir(ppy)$_2$(3)] in CDCl$_3$.

Fig. S64. UV/Vis spectra of [Ir(ppy)$_2$(3)] in CH$_3$CN. Before (pink line) and after (blue line) irradiation at 331 nm, 2.50 x 10$^{-5}$ M.
Fig. S65. *Cis* to *trans* thermal isomerization kinetics of [Ir(ppy)$_2$(3)]. Absorption change of the band 327 nm at 328 K in CH$_3$CN after irradiation at 331 nm (2.50 $\times$ 10$^{-5}$ M).

Fig. S66. *Cis* to *trans* thermal isomerization kinetics of [Ir(ppy)$_2$(3)]. First-order plot. $k$ (s$^{-1}$) = 0.8 $\times$ 10$^{-4}$. Half-life (s) = 8300.
Supporting Information

[Ir(Fppy)$_2$(1)]. Synthesis, characterization and photoisomerization studies.

SYNTHESIS

[Ir(Fppy)$_2$Cl$_2$] (150 mg, 0.12 mmol) and AgOTf (95 mg, 0.37 mmol) were dissolved in degassed acetone (8 mL) and refluxed under nitrogen for 2 h. The solution was cooled to room temperature and gravity-filtered to remove AgCl. The filtrate was refluxed under nitrogen for 1 h and added to a 1 h refluxed solution of 1 (180 mg, 0.49 mmol) and NEt$_3$ (130 µL, 0.93 mmol) in degassed acetone (4 mL). The resulting solution was refluxed overnight under nitrogen. After removing the solvent, the residue was purified by column chromatography: silica/CH$_2$Cl$_2$ (Rf = 0.8). [Ir(Fppy)$_2$(1)] was obtained as a light orange powder (92 mg, 40%).

Elemental Analysis: calculated for C$_{46}$H$_{30}$F$_4$IrN$_5$O · C$_3$H$_6$O: C, 59.15; H, 3.65; N, 7.04. Found: C, 59.17; H, 3.69; N, 6.80.

Exact mass (EI) - m/z: 938.2110 for [M+H]$^+$ with (193Ir).

$^1$H NMR (300 MHz, CDCl$_3$): δ 8.22 (t, J = 9.1, 2H, C$_5$H$_4$N(C$_{11}$H$_6$NF$_2$)), 8.04 (dd, J = 5.8, 1.0, 1H, C$_5$H$_2$N(C$_2$H$_4$N$_2$F$_2$)), 7.98 (d, J=8.16, 1H, C$_6$H$_7$N(C$_{24}$H$_{18}$N$_3$O)), 7.95 – 7.88 (m, 5H), 7.81 (d, J = 8.1, 1H, C$_6$H$_3$), 7.70 (dd, J = 8.0, 1.5, 1H, C$_6$H$_7$N(C$_{24}$H$_{18}$N$_3$O)), 7.62 – 7.48 (m, 6H), 7.18 (dd, J = 8.0, 1.8, 1H, C$_6$H$_3$), 7.06 – 6.97 (m, 3H), 6.93 (d, J = 1.5, 1H, C$_6$H$_3$), 6.77 (ddd, J = 6.9, 6.0, 1.3, 1H, C$_6$H$_7$N(C$_{2}$H$_4$N$_2$F$_2$)), 6.76 (ddd, J = 7.1, 5.9, 1.3, 1H, C$_6$H$_7$N(C$_{11}$H$_6$NF$_2$)) 6.52 – 6.42 (m, 2H, C$_6$H$_4$F$_2$), 6.05 (dd, J = 7.5, 2.3, 1H, C$_6$H$_4$F$_2$), 5.84 (dd, J = 9.2, 2.3, 1H, C$_6$H$_4$F$_2$), 5.06 (s, 2H, CH$_2$).

$^{13}$C NMR (75 MHz, CDCl$_3$): δ 180.51 (1C, C$_{quat.}$ C$_{11}$H$_6$NF$_2$), 175.19 (1C, C$_{quat.}$ C$_{24}$H$_{18}$N$_3$O), 167.75 (1C, C$_{quat.}$ C$_{24}$H$_{18}$N$_3$O), 166.89 (d, J=8.1, 1C, C$_{quat.}$ C$_{11}$H$_6$NF$_2$), 164.87 (dd, J=10.1, 1J=257, 1C, C$_{quat.C.F}$), 164.59 (d, J=6.8, 1C, C$_{quat.}$ C$_{11}$H$_6$NF$_2$), 163.84 (dd, J=12.4, 1J=253, 1C, C$_{quat.C.F}$), 162.78 (d, J=6.0, 1C, C$_{quat.}$ C$_{11}$H$_6$NF$_2$), 162.27 (dd, J=10.9, J=262, 1C, C$_{quat.C.F}$), 161.66 (dd, J=13.1, J=258, 1C, C$_{quat.C.F}$), 161.26 (1C, C$_{quat.}$ C$_{24}$H$_{18}$N$_3$O), 153.10 (1C, CH, C$_6$H$_7$N(C$_{2}$H$_4$N$_2$F$_2$)), 152.82 (1C, C$_{quat.}$ C$_{24}$H$_{18}$N$_3$O), 150.90 (1C, CH, C$_6$H$_7$N(C$_{24}$H$_{18}$N$_3$O)), 147.68 (1C, CH), 146.88 (1C, C$_{quat.}$ C$_{24}$H$_{18}$N$_3$O), 144.89 (1C, C$_{quat.}$ C$_{24}$H$_{18}$N$_3$O), 137.76 (1C, C$_{quat.}$ C$_{24}$H$_{18}$N$_3$O), 137.13 (1C, CH, C$_6$H$_7$N (C$_{2}$H$_4$N$_2$F$_2$)), 136.55 (1C, CH, C$_6$H$_3$), 136.45 (1C, CH), 135.22 (1C, CH), 130.27 (1C, CH, C$_6$H$_3$), 129.01 (2C, CH C$_{12}$H$_9$N$_2$), 127.88 (1C, C$_{quat.}$ C$_{11}$H$_6$NF$_2$), 126.41 (1C, C$_{quat.}$ C$_{11}$H$_6$NF$_2$), 124.63 (1C, CH, C$_6$H$_3$), 124.57 (2C, CH C$_{12}$H$_9$N$_2$), 122.80 (d, J= 21.3, 1C, CH, C$_6$H$_7$N(C$_{11}$H$_6$NF$_2$)), 122.66 (1C, CH, C$_6$H$_7$N(C$_{2}$H$_4$N$_2$F$_2$)), 122.58 (d, J=19.0, 1C, CH, C$_6$H$_7$N(C$_{11}$H$_6$NF$_2$)), 122.51 (2C, CH, C$_{12}$H$_9$N$_2$), 122.29 (1C, CH, C$_6$H$_7$N(C$_{2}$H$_4$N$_2$F$_2$)), 121.48 (1C, CH, C$_6$H$_7$N(C$_{11}$H$_6$NF$_2$)), 121.17 (1C, CH, C$_6$H$_3$), 119.43 (1C, CH, C$_6$H$_7$N(C$_{2}$H$_4$N$_2$F$_2$)), 115.32 (2C, CH C$_{12}$H$_9$N$_2$),113.71 (d, J=14.1, 1C, CH, C$_6$H$_4$F$_2$), 111.93 (d, J=16.3, 1C, CH, C$_6$H$_4$F$_2$), 97.42 (pst, J=27.2, 1C, CH, C$_6$H$_4$F$_2$), 95.47 (pst, J=27.1, 1C, CH, C$_6$H$_4$F$_2$), 70.67 (1C, CH$_2$).

UV/Vis (CH$_3$CN, λ, nm (ε, L mol$^{-1}$ cm$^{-1}$)): 346 (3.1 × 10$^4$), 436 (4.0 × 10$^3$).
Fig. S67. $^1$H NMR spectrum of [Ir(Fppy)$_2$(1)] in CDCl$_3$, 300 MHz.

Fig. S68. $^{13}$C NMR spectrum of [Ir(Fppy)$_2$(1)] in CDCl$_3$, 75 MHz.
Fig. S69. HSQC NMR spectrum of [Ir(Fppy)$_2$(I)] in CDCl$_3$.

Fig. S70. COSY NMR spectrum of [Ir(Fppy)$_2$(I)] in CDCl$_3$. 
Fig. S71. UV/Vis spectra of [Ir(Fppy)$_2$(I)] in CH$_3$CN. Before (pink line) and after (blue line) irradiation at 349 nm, 2.50 × 10$^{-5}$ M.

Fig. S72. Cis to trans thermal isomerization kinetics of [Ir(Fppy)$_2$(I)]. Absorption change of the band 346 nm at 328 K in CH$_3$CN after irradiation at 349 nm (2.50 × 10$^{-5}$ M).
Fig. S73. *Cis* to *trans* thermal isomerization kinetics of [Ir(Fppy)_2(I)]. First-order plot. $k \; (s^{-1}) = 1.1 \times 10^{-4}$. Half-life (s) = 6300.
Supporting Information

[Ir(Brppy)$_2$(I)]. Synthesis, characterization and photoisomerization studies.

SYNTHESIS

[Ir(Brppy)$_2$]Cl$_2$, (150 mg, 0.11 mmol) and AgOTf (84 mg, 0.32 mmol) were dissolved in degassed acetone (8 mL) and refluxed under nitrogen for 2 h. The solution was cooled to room temperature and gravity-filtered to remove AgCl. The filtrate was refluxed under nitrogen for 1 h and added to a 1 h refluxed solution of I (158 mg, 0.43 mmol) and triethylamine (113 µL, 0.81 mmol) dissolved in degassed acetone (4 mL). The resulting solution was refluxed overnight under nitrogen. After removing the solvent, the residue was purified by column chromatography: silica/CH$_2$Cl$_2$ (Rf = 0.9). It was obtained as an orange powder (74 mg, 35%).

Elemental Analysis: calculated for C$_{46}$H$_{32}$Br$_2$IrN$_5$O · C$_3$H$_6$O: C, 54.45; H, 3.54; N, 6.48. Found: C, 54.24; H, 3.65; N, 6.17.

Exact mass (MALDI) - m/z: 1021.0578 for [M$^+$] with ($^{193}$Ir)$({}^{79}$Br).

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.99-7.88 (m, 7H), 7.81-7.74 (m, 3H), 7.67 (td, $J = 7.7, 1.5, 1$H), 7.60 – 7.47 (m, 8H), 7.18-7.09 (m, 3H), 7.03 – 6.95 (m, 3H), 6.93 (d, $J = 1.1, 1$H, C$_6$H$_3$) 6.80 – 6.71 (m, 2H), 6.69 (d, $J = 2.0, 1$H, C$_6$H$_4$Br), 6.50 (d, $J = 1.9, 1$H, C$_6$H$_4$Br), 5.05 (d, $J = 2.2, 2$H, CH$_2$).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 177.52 (1C, C$_{quat.}$), 175.78 (1C, C$_{quat.}$), 169.23 (1C, C$_{quat.}$), 167.86 (1C, C$_{quat.}$), 166.77 (1C, C$_{quat.}$), 161.30 (1C, C$_{quat.}$), 160.77 (1C, C$_{quat.}$), 153.10 (1C, CH), 152.84 (1C, C$_{quat.}$), 151.16 (1C, CH), 147.76 (1C, CH), 146.87 (1C, C$_{quat.}$), 145.05 (1C, C$_{quat.}$), 143.56 (1C, C$_{quat.}$), 141.41 (1C, C$_{quat.}$), 137.55 (1C, C$_{quat.}$), 136.90 (1C, CH), 136.69 (1C, CH, C$_6$H$_3$), 135.12 (1C, CH, C$_6$H$_4$Br), 134.67 (1C, CH), 132.79 (1C, CH, C$_6$H$_4$Br), 130.26 (1C, CH), 129.02 (2C, CH C$_{12}$H$_9$N$_2$), 126.75 (1C, C$_{quat.}$), 125.84 (1C, CH), 125.53 (1C, CH), 125.19 (1C, C$_{quat.}$), 124.57 (2C, CH C$_{12}$H$_9$N$_2$), 124.51 (1C, CH), 124.31 (1C, CH), 122.63 (1C, CH), 122.51 (3C, 2CH C$_{12}$H$_9$N$_2$ + CH), 122.39 (1C, CH), 121.80 (1C, CH), 120.95 (1C, CH), 119.24 (1C, CH), 118.99 (1C, CH), 118.79 (1C, CH), 115.46 (2C, CH C$_{12}$H$_9$N$_2$), 70.70 (1C, CH$_2$).

UV/Vis (CH$_3$CN, $\lambda$, nm (ε, L mol$^{-1}$ cm$^{-1}$)): 343(2.8 · 10$^4$), 448 (4.0 · 10$^3$).

Fig. S74. $^1$H NMR spectrum of [Ir(Brppy)$_2$(I)] in CDCl$_3$, 300 MHz.
Fig. S75. $^{13}$C NMR spectrum of $[\text{Ir(Brppy)}_2(1)]$ in CDCl$_3$, 75 MHz.

Fig. S76. HSQC NMR spectrum of $[\text{Ir(Brppy)}_2(1)]$ in CDCl$_3$. 
Fig. S77. COSY NMR spectrum of [Ir(Brppy)$_2$(I)] in CDCl$_3$.

Fig. S78. UV/Vis spectra of [Ir(Brppy)$_2$(I)] in CH$_3$CN. Before (pink line) and after (blue line) irradiation at 349 nm, 2.50 $\times$ 10$^{-5}$ M.
Fig. S79. **Cis** to **trans** thermal isomerization kinetics of \([\text{Ir(Brppy)}_2(1)]\). Absorption change of the band 343 nm at 328 K in CH$_3$CN after irradiation at 349 nm (2.50 \times 10^{-5}$ M).

Fig. S80. **Cis** to **trans** thermal isomerization kinetics of \([\text{Ir(Brppy)}_2(1)]\). First-order plot. $k \text{ (s}^{-1}) = 1.2 \times 10^{-4}$. Half-life (s) = 5800.
Supporting Information

[Ir(4)2(1)]. Synthesis and characterization.

SYNTHESIS

[Ir(Brppy)2(1)] (60 mg, 0.058 mmol) was dissolved in 4 mL of degassed THF. To this mixture, 4-(phenylazo)phenyl boronic acid pinacol ester (40 mg, 0.129 mmol), Pd(PPh3)4 (2 mol%, 3 mg, 0.002 mmol), and Na2CO3 (1 M aq., 2 mL) were added successively under nitrogen. The reaction mixture was heated overnight at 80 °C with continuous stirring. The reaction was cooled to room temperature and 50 mL of water were added to precipitate the formed compound. The solution was gravity filtered and the solid was washed with hexane (20 mL) and dichloromethane (10 mL). The compound was obtained as a dark-orange powder (70 mg, 92%), rather insoluble in all the solvents assayed (i.e. solubility is less than 0.8 mg in 10 mL of CDCl3). Low solubility hampered a complete NMR characterization.

Elemental Analysis: calculated for C70H50IrN9O · 2CH2Cl2 · 1C6H14: C, 63.24; H, 4.63; N, 8.51. Found: C, 63.34; H, 4.09; N, 8.55.

Exact mass (MALDI) - m/z: 1225.3766 for [M]+ with (193Ir).

UV/Vis (CH3CN, λ, nm (ε, L mol⁻¹ cm⁻¹)): 351 (6.5 · 10⁴), 465 (6.6 · 10³).

Fig. S81. UV/Vis spectra of [Ir(4)2(1)] in CH2Cl2. Before (pink line) and after (blue line) irradiation at 354 nm, 0.90 × 10⁻⁵ M.
Fig. S82. $^1$H-NMR spectra of ligand 1 in CDCl$_3$, 300 MHz. Before (red line) and after (blue line) irradiation at 365nm, $2.50 \times 10^{-3}$ M.

Fig. S83. $^1$H-NMR spectra of ligand 2 in CDCl$_3$, 300 MHz. Before (red line) and after (green line) irradiation at 365nm, $2.50 \times 10^{-3}$ M. After heating overnight at 55°C (blue line).
Fig. S84. $^1$H-NMR spectra of ligand 3 in CDCl$_3$, 300 MHz. Before (red line) and after (green line) irradiation at 365nm, $2.50 \times 10^{-3}$ M. After heating overnight at 55 °C (blue line).

Fig. S85. $^1$H-NMR spectra of ligand 4 in CDCl$_3$, 300 MHz. Before (red line) and after (blue line) irradiation at 365nm, $2.50 \times 10^{-3}$ M.
Fig. S86. $^1$H-NMR spectra of ligand $5$ in CDCl$_3$, 300 MHz. Before (red line) and after (blue line) irradiation at 365nm, $2.50 \times 10^{-3}$ M.

Fig. S87. $^1$H-NMR spectra of [Ir(4)(acac)] in CDCl$_3$, 300 MHz. Before (red line) and after (blue line) irradiation at 365nm, $2.50 \times 10^{-3}$ M.
Fig. S88. $^1$H-NMR spectra of [Ir(5)(acac)] in CDCl$_3$, 300 MHz. Before (red line) and after (blue line) irradiation at 365nm, $2.50 \times 10^{-3}$ M.

Fig. S89. $^1$H-NMR spectra of [Ir(ppy)$_2$(2)] in CDCl$_3$, 300 MHz. Before (red line) and after (blue line) irradiation at 365nm, $2.50 \times 10^{-3}$ M.
Fig. S90. $^1$H-NMR spectra of [Ir(ppy)$_2$(1)] in CDCl$_3$, 300 MHz. Before (red line) and after (blue line) irradiation at 365nm, $2.50 \times 10^{-3}$ M.

Fig. S91. $^1$H-NMR spectra of [Ir(Fppy)$_2$(1)] in CDCl$_3$, 300 MHz. Before (red line) and after (blue line) irradiation at 365nm, $2.50 \times 10^{-3}$ M.
Fig. S92. $^1$H-NMR spectra of [Ir(Brppy)$_2$(1)] in CDCl$_3$, 300 MHz. Before (red line) and after (blue line) irradiation at 365nm, $2.50 \times 10^{-3}$ M.

Fig. S93. $^1$H-NMR spectra of [Ir(ppy)$_2$(3)] in CDCl$_3$, 300 MHz. Before (red line) and after (blue line) irradiation at 365nm, $2.50 \times 10^{-3}$ M.
Figure S94. Cyclic voltammograms (10^{-3} M, dry DMF) of [Ir(ppy)_2(1)], [Ir(Fppy)_2(1)] and [Ir(Brppy)_2(1)] containing 0.1 M TBAPF_6 as the supporting electrolyte, scan rate of 100 mV s^{-1}.

Figure S95. Cyclic voltammograms (10^{-3} M, dry DMF) of [Ir(ppy)_2(4)] and [Ir(Fppy)_2(4)] containing 0.1 M TBAPF_6 as the supporting electrolyte, scan rate of 100 mV s^{-1}.
Figure S96. Cyclic voltammograms (10^{-3} M, dry DMF) of \([\text{Ir}(4)_2(\text{acac})]\) and \([\text{Ir}(5)_2(\text{acac})]\) containing 0.1 M TBAPF₆ as the supporting electrolyte, scan rate of 100 mV s⁻¹.

Figure S97. Cyclic voltammograms (10^{-3} M, dry DMF) of \([\text{Ir}(ppy)_2(2)]\) containing 0.1 M TBAPF₆ as the supporting electrolyte, scan rate of 100 mV s⁻¹.
Supporting Information

Figure S98. Cyclic voltammograms (10^{-3} M, dry DMF) of [Ir(ppy)_{2}(3)] containing 0.1 M TBAPF_{6} as the supporting electrolyte, scan rate of 100 mV s^{-1}.

Figure S99. -OCH_{2}- signal of the ¹H-NMR spectra of compounds [Ir(Fppy)_{2}(1)] and [Ir(Brppy)_{2}(1)]. Top (experimental) bottom (simulated). Chemical shift and coupling constants used for the simulation are presented in the table.