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Azobenzene-functionalized iridium(III) triscyclometalated complexes†

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Twelve Ir(III) triscyclometalated compounds containing up to three azobenzene fragments on their structure have been synthesized based on photochromic 2-phenylpyridyl type ligands **1–4**. These complexes are intended to study the possibility of transferring the photochromicity of the azobenzene fragment to the organometallic compound, and the effect of the substitution pattern, relative distance of the azobenzene to the metal centre, and number of azobenzenes on their properties.

Introduction

In the last few decades, the development of photo-responsive materials has become an intensive area of research. These substances are intended for the production of "smart chemical systems", whose properties—and eventually functionality—are controlled by changes of the environment (light irradiation). These systems have been already implemented in a wide range of modern materials and devices for daily applications such as sunglass lenses, memory devices, photochromic inks, *etc.*[1,2]

In spite of the importance and versatility of transition-metal complexes, smart photo-responsive examples remain rather unexplored in comparison with the large number of well known light-triggered organic switches. In principle, photo-responsive metal complexes can be obtained by incorporation of organic photochromic units in the structure of their ligands.[3–6] These photo-sensitive ligands, rather than acting as conventional spectators that tune the properties of their complexes, transform them into dynamic smart entities able to offer a functional response to an external stimulus.[7] Azobenzene is the photochromic fragment most frequently used for this purpose. It does experience a reversible *trans*-to-*cis* photoisomerization which induces not only structural changes but also important electronic modifications in the ligands.[8] In the early examples of photochromic metallocomplexes, efforts concentrated on how metal coordination could affect the photochromism of the organic switch located at the organic ligand.[9] More recently, the focus shifted toward the modification of the properties and eventually the functionality of the metal complex upon isomerization of the photochromic fragment present in the ligands.

There is a considerable amount of examples of azobenzene-containing coordination compounds, mainly based on neutral nitrogen or phosphorus based ligands: phosphine,[10–13] pyridine,[5,14] 2,2′-bipyridine,[15–24] terpyridine,[6,24–27] or bridging azobis(4-pyridine)[28–34] ligands. Despite the fact that organometallic complexes (containing a C–metal bond) are used in a wide number of important applications—setting aside ferrocene derivatives[5,35–37]—only a handful of examples of azobenzene based organometallics are known. From these, just the most recent ones are intended for the construction of photo-sensitive organometallics.[38–43]

Cyclometalated phenylpyridine ligands are among the most popular ligands for the construction of organometallic complexes for many applications. Nevertheless, to the best of our knowledge, there are no examples of photochromic phenylpyridine azobenzenes.

We report here the synthesis of a series of phenylpyridine ligands that incorporate a photochromic azobenzene fragment at different positions of the phenyl ring. The synthesis, characterization and photochromism of their heteroleptic iridium(III) complexes formed by cyclometalation of the ligand are also presented. *A posteriori* modification of the complexes by Suzuki cross-coupling was assayed to generate complexes containing more than one azobenzene fragment per complex.

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Results and discussion

We designed a series of 2-phenylpyridyl type ligands that incorporate an azobenzene fragment in their structure (**1–3** Scheme 1). In these ligands, the phenyl moiety intended for cyclometalation is also part of the azobenzene. They respond to the three possible substitution patterns (*ortho*, *meta* and *para*). Ligand **4** (2-phenyl(4-azophenyl)pyridine) was constructed *a posteriori* by palladium-catalyzed cross-coupling on (5-bromo-2-pyridyl)phenyl iridium(III) cyclometalated complexes with 4-azophenylboronic acid pinacol ester (**f**). It was designed to introduce more than one azobenzene photochromic unit per complex. Altogether this set of azobenzene-containing phenylpyridyl ligands was used to study the photochromism of a series of azobenzene-containing iridium(III) cyclometalated complexes. The goal was to analyze the effect that the substitution pattern, the distance from the azobenzene to the metal centre, and the number of azobenzenes per complex has on the photochromism of the corresponding iridium derivatives.

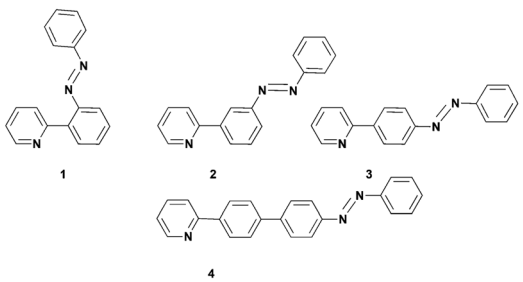
Ligands synthesis

Synthetic routes towards ligands **1–3** are shown in Scheme 2. Azophenylboronic acids **d** and **e**, were obtained by reacting Et_2O solutions of the corresponding 2-iodoazobenzene or 3-iodoazobenzene sequentially with *n*-BuLi and trimethyl borate at −112 °C, and diluted sulfuric acid at 0 °C, as previously reported for compound **d**.[44] 4-Azophenylboronic acid pinacol ester **f** was synthesized *via* condensation of aniline boronic acid pinacol ester with nitrosobenzene, as reported elsewhere.[45]

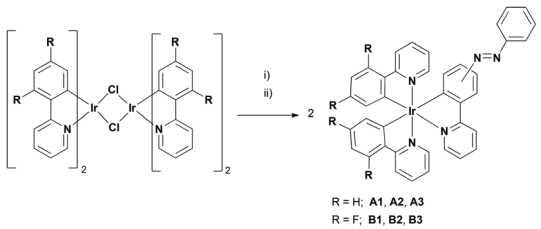
Ligands 2-(*o*-phenylazobenzene)pyridine (**1**), 2-(*m*-phenylazobenzene)pyridine (**2**), and 2-(*p*-phenylazobenzene)pyridine (**3**) were obtained by palladium-catalyzed cross-coupling between 2-bromopyridine and the corresponding (*E*)-2-azophenylboronic acid, (*E*)-3-azophenylboronic acid or (*E*)-4-azophenylboronic acid pinacol ester respectively (yields 70–80%). Alternatively, ligand **2** was also obtained by Suzuki cross-coupling between 2-bromopyridine and 3-aminophenylboronic acid, and subsequent condensation of the formed 3-aminophenyl-2-pyridine with nitrosobenzene in acetic acid at 90 °C for 3.5 h (overall yield 32%).

Iridium(III) complexes

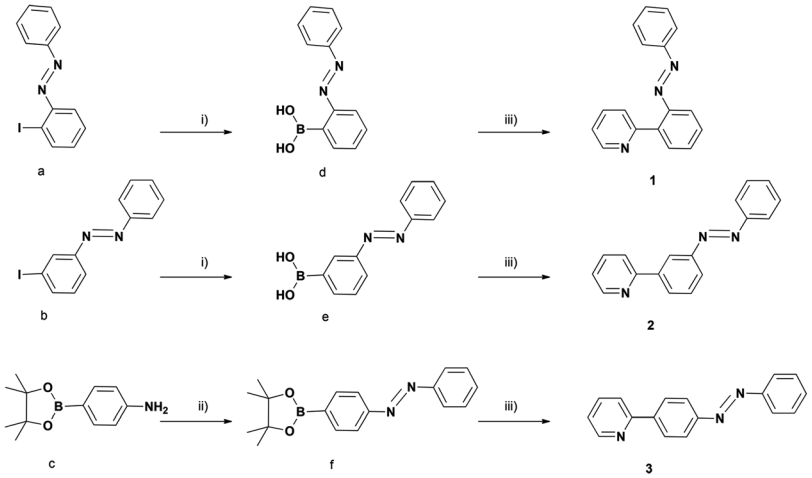
Heteroleptic meridional iridium(III) complexes of general formula $[Ir(ppy)_2(L)]$ (**A**) and $[Ir(Fppy)_2(L)]$ (**B**) (ppy = 2-phenylpyridyl, Fppy = 2-(2,4-difluorophenyl)pyridyl, L = cyclometalated ligands **1–3**) were synthesized by cleavage of the corresponding chloro-bridged dimers $[Ir(Fppy)_2Cl]_2$ or $[Ir(ppy)_2Cl]_2$ in acetone using a chloride abstractor (AgOTf), excess of ligand and NEt_3 as base, as shown in Scheme 3.



Scheme 1 Azobenzene-containing ligands used in this work.



Scheme 3 (i) AgOTf, acetone (55 °C, 2 h). (ii) **1–3** (4 equiv.), NEt_3 (7.5 equiv.), acetone (55 °C, 15 h).



Scheme 2 (i) *n*-BuLi (1.1 equiv.), Et_2O, −112 °C; $B(OMe_3)$ (1.1 equiv.), Et_2O, −112 °C; dil. H_2SO_4, 0 °C. (ii) Nitrosobenzene (1.5 equiv.), CH_3CO_2H, 90 °C, 3.5 h. (iii) 2-Bromopyridine (1.1 equiv.), $Pd(PPh_3)_4$ (2 mol%), THF, Na_2CO_3 (1 M aq., 1.6 equiv.), 80 °C, overnight.

Following the aforementioned synthetic protocol, heteroleptic complexes derived from ligands **2** and **3**, containing two additional cyclometalated ligands: either 2-phenylpyridyl (**A2** and **A3**) or 2-(2,4-difluorophenyl)pyridyl (**B2**, **B3**) were obtained as pure compounds after purification by column chromatography (R_f = 0.8, CH_2Cl_2). Complexes **A3** and **B3** were obtained with considerably better yields (56% and 70% respectively) compared to the analogous compounds derived from ligand **2** (yields 15–20%). These meridional complexes are chiral, but were obtained as racemates. The lack of any element of symmetry in their structure is evidenced by the complexity of their ^{1}H-NMR and ^{13}C-NMR spectra. Complexes derived from [Ir(ppy)$_2$Cl]$_2$ (**A2** and **A3**) present 39 different aromatic carbon signals in their ^{13}C-NMR, and 28 aromatic resonances in the corresponding ^{1}H-NMR spectra. The ^{1}H-NMR spectroscopic patterns of compounds **B2** and **B3**, derived from the fluorinated dimer [Ir(Fppy)$_2$Cl]$_2$, are slightly more simple; "only" 24 aromatic signals are expected, but ^{13}C-NMR spectra are rather complicated due to the splitting of some of the 39 aromatic signals expected due to F–C coupling. A comparative analysis of the different ^{1}H-NMR and ^{13}C-NMR spectra, combined with COSY and HSQC experiments, allowed us to identify the number of signals expected in all the cases. Although an unambiguous assignment of all the signals could not be accomplished, the spectra are consistent with the expected compounds (see ESI†). Their purity was also confirmed by elemental analysis and HR-MS spectroscopy.

When the same procedure as that described before for the synthesis of complexes of type **A** and **B** was conducted using 2-(*o*-phenylazobenzene)pyridine (ligand **1**), the properties of the obtained compounds (labelled **A1′** and **B1′**) were rather different compared to the ones of the complexes derived from ligands **2** and **3**. The residues of these reactions were dark crystalline solids that were purified by column chromatography using ethyl acetate–acetone as eluents. A first fraction (eluted with ethyl acetate) was identified as unreacted ligand (R_f **1** = 0.8; R_f **A1′**$_{\text{ethyl acetate}}$ = R_f **B1′**$_{\text{ethyl acetae}}$ = 0), the eluent polarity was gradually increased with acetone to collect a second fraction containing the metallic complexes (R_f **A1′**$_{\text{acetone}}$ = R_f **B1′**$_{\text{acetone}}$ = 0.7). ^{1}H-NMR spectra of these compounds are concentration dependent, indicative of some aggregation process in solution (see ESI†). Complexes **A1′** and **B1′** were fully characterized by NMR spectroscopy ($CDCl_3$, 0.075 M and 0.1 M, respectively). Elemental analysis and HR-MS spectroscopy were in agreement with the cationic structures [Ir(ppy)$_2$(**1**)]OTf (**A1′**) and [Ir(Fppy)$_2$(**1**)]OTf (**B1′**) for both complexes. This molecular structure, in which the ligand acts as a neutral *N*,*N*-bidentate through the pyridine and one of the azobenzene nitrogen atoms, could be confirmed in the case of complex **A1′** by X-ray diffraction analysis of a crystalline sample (Fig. 1). Crystals were obtained by slow diffusion of diethyl ether into a saturated CH_2Cl_2 solution of the complex.

In the case of ligand **1**, the coordination of the ligand as a neutral chelate is favoured over cyclometalation, probably due to the close disposition of the azo group to the metal centre. Coordination of the nitrogen atom of an azoaromatic ligand to a metal centre has been a recurring topic for many years. From the early reports that proposed such a coordination mode,[46,47] many X-ray structures have been obtained for cyclometalated azobenzenes,[48–54] 2-(arylazo)pyridines,[55–60] 2,2′-azobis(pyridine),[61–63] and 2-(arylazo)phenol[64] ligands in which a five- or six-membered chelate ring was formed. All of them are well known redox-active ligands. The N–N distance is indicative of the charge on the azo function, being longer for one-electron (*i.e.*, anion radical) and two-electron (hydrazido) reduced ligands compared to unreduced N=N bonds. The N4–N5 distance measured in the molecular structure of [Ir(ppy)$_2$(**1**)]$^+$ (1.250(5) Å) corresponds to an unreduced coordinated azoaromatic ligand. In order to gain more insight into the properties of this molecule, DFT geometry optimizations were performed. The computed N–N distance in compound [Ir(ppy)$_2$(**1**)]$^+$ is 1.268 Å with a Wiberg bond index of 1.71. Moreover, analysis of the orbital population by CASSCF(4,4) single point calculations on the optimized structure showed that the molecule does not present radical character (see Fig. S7 in ESI†).

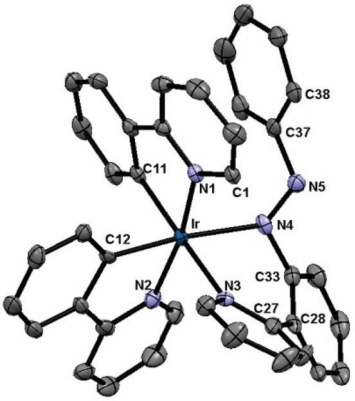


Fig. 1 ORTEP representation of the molecular structure of the cation [Ir(ppy)$_2$(**1**)]$^+$ obtained by X-ray diffraction. Ellipsoids are drawn at the 50% probability level. Relevant distances (Å): N4–N5 = 1.250(5), N1–Ir = 2.050(3), N2–Ir = 2.070(3), N3–Ir = 2.209(3), N4–Ir = 2.166(3).

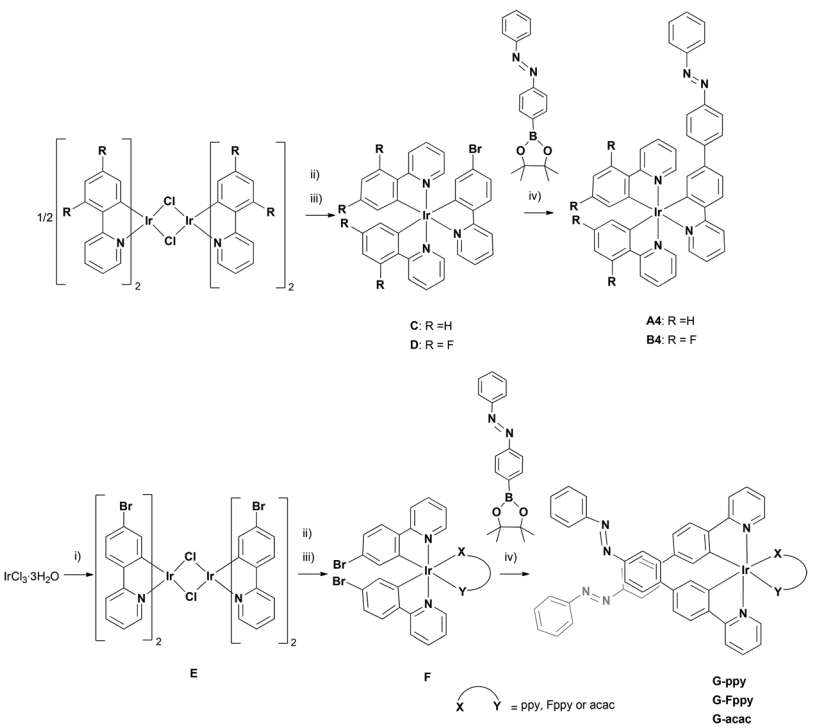
As observed frequently in other complexes containing chelating azoaromatics, in the molecular structure of complex [Ir(ppy)$_2$(**1**)]$^+$ the "free" phenyl ring is twisted with respect to the phenyl involved in the chelate ring (the angle between the phenyl planes defined as the torsion angle C33–N4–N5–C37 is 167.3(3)°). This twist produces a rupture in the conjugation within the azobenzene fragment. In this case, there is also an aromaticity loss between the phenyl and pyridyl fragments that form the chelate to permit the formation of the six-membered chelate ring (the angle between these planes defined as the torsion angle N3–C27–C28–C33 is 40.9(7)°).

In an effort to include more than one photochromic azobenzene unit per complex, we explored the possibility to synthesize chloride-bridged iridium dimers using the azobenzene-containing ligand **3**, [Ir(**3**)$_2$Cl]$_2$. Such a complex was intended as the starting material for the synthesis of triscyclometalated compounds incorporating at least two azobenzene units. We explore this strategy using 2-(*p*-phenylazobenzene)pyridine (**3**) because

this ligand is the one that rendered better yields in the cyclometalation reaction described above for the synthesis of derivatives **A** and **B**. $IrCl_3{\cdot}3H_2O$ was refluxed in a mixture of 3 : 1 2-ethoxyethanol–H_2O overnight in the presence of 2.2 equivalents of ligand **3** (as described for the synthesis of the known precursors $[Ir(ppy)_2Cl]_2$ and $[Ir(Fppy)_2Cl]_2$).[65] At the end of the reaction period, unreacted starting compounds were recovered as the only reaction product. As an alternative, we considered the possibility of synthesizing directly the triscyclometalated complex *fac*-[Ir(**3**)$_3$]. A known methodology for the synthesis of facial homoleptic triscyclometalated Ir(III) complexes (*i.e. fac*-[Ir(ppy)$_3$]) consists of introducing Ir(acac)$_3$ (acac = acetylacetonate) and the corresponding ligand (3 equiv.) in a closed digestion bomb for 24 h at 240 °C.[66] This synthetic methodology was previously tested for the synthesis of *fac*-[Ir(ppy)$_3$]. In our hands it rendered a pure compound after column chromatography (silica/CH_2Cl_2) with 50% yield. When this synthetic procedure was tested with ligand **3**, in an attempt to synthesize *fac*-[Ir(**3**)$_3$], an unidentified insoluble black material was obtained at the end of the reaction.

In view of the lack of reactivity of ligand **3** for the synthesis of bis or triscyclometalated iridium(III) compounds when commonly applied methodologies were used, we considered the possibility to introduce the photochromic azobenzene units *a posteriori* on preformed cyclometalated complexes. To make use of the formerly described azobenzene boronic acids, we designed a synthetic route based on a Suzuki cross-coupling of azobenzene boronic acids with bromo-containing iridium cyclometalated complexes. Initially, to confirm the viability of this methodology, we synthesized meridional [Ir(ppy)$_2$((5-bromo-2-pyridyl)phenyl)] **C** and [Ir(Fppy)$_2$((5-bromo-2-pyridyl)-phenyl)] **D**, both containing a bromine atom in one of the cyclometalated ligands. Complexes **C** and **D** were synthesized by cleavage of the corresponding iridium chloride-dimers in acetone with an excess of 2-(4-bromophenyl)pyridine, following a procedure analogous to the one described for complexes **A** and **B**. The monobrominated compounds **C** and **D** were obtained with yields of 40% and 30%, respectively (Scheme 4). These complexes were assayed in the Suzuki cross-coupling with (*E*)-4-azophenylboronic acid pinacol ester (**f**). We chose (*E*)-4-azophenylboronic acid pinacol ester (**f**) as the azobenzene source to avoid conformational mixtures of products that could be obtained with *meta* and *ortho* boronic acid derivatives **d** and **e**. Iridium complexes **C** and **D** were refluxed with 1.1 equiv. of (*E*)-4-azophenylboronic acid pinacol ester (**f**) in a mixture of 2 : 1 THF–H_2O using 2 mol% of $Pd(PPh_3)_4$ and Na_2CO_3 as a base. This synthetic procedure rendered azobenzene containing complexes **A4** and **B4** with yields of 85% and 88% respectively after purification by column chromatography (Scheme 4).

The high yields obtained in the coupling reaction for the synthesis of compounds **A4** and **B4** prompted us to assay the same reaction conditions on iridium complexes containing two bromine-containing cyclometalated ligands. For this purpose, a biscyclometalated iridium dimer based on 2-(4-bromophenyl)pyridine **E** was synthesized according to a published



Scheme 4 (i) 2-(4-Bromophenyl)pyridine (2.5 equiv.), 3 : 1 mixture of 2-ethoxyethanol–H_2O, 120 °C, 24 h. (ii) AgOTf, acetone (55 °C, 2 h). (iii) 2-(4-Bromophenyl)pyridine, 2-phenylpyridine, 2-(2,4-difluorophenyl)pyridine or acetylacetone (4 equiv.), NEt_3 (7.5 equiv.), acetone (55 °C, 15 h). (iv) (*E*)-4-Azophenylboronic acid pinacol ester (**C**, **D**: 1.1 equiv. and **F**: 2.1 equiv.), solvent 2 : 1 THF–Na_2CO_3aq. (1 M), $Pd(PPh_3)_4$ (2 mol%), 80 °C, overnight.

methodology.[67] Dimeric complex **E** was then cleaved by using AgOTf, an excess of ligand, and NEt_3 in refluxing acetone to form mononuclear heteroleptic bromine containing complexes **F**. The ligands used for this reaction were commercially available 2-phenylpyridine (**F-ppy**), 2-(2,4-difluorophenyl)pyridine (**F-Fppy**) and acetylacetone (**F-acac**). These complexes were obtained as pure compounds after column chromatography with 60–80% yield.

Catalytic cross-coupling of iridium complexes **F** with boronic acid azobenzenes should render compounds **G** containing two photochromic units per complex (Scheme 4). Iridium complexes **F** were refluxed with 2.1 equiv. of (*E*)-4-azophenylboronic acid pinacol ester (**f**) using the same conditions as those described above for compounds **A4** and **B4**. Complex **G-acac** was obtained with a yield of 80% after purification by column chromatography (alumina) using dichloromethane as the eluent. Due to the low solubility of compounds **G-ppy** and **G-Fppy** in all the solvents assayed, only a small quantity of the full sample was purified by column chromatography (alumina). Their low solubility hampered a full characterization of these compounds by ^{13}C-NMR, COSY or HSQC spectroscopy. Their ^{1}H-NMR spectra, EA and HRMS are consistent with the proposed formulation. The molecular structure of complex **G-acac**, containing two azobenzene fragments on different phenylpyridyl ligands, was obtained by X-ray diffraction of a crystalline sample obtained by evaporation of saturated CH_3CN solutions. The obtained molecular structure is shown in Fig. 2.

The molecular structure of **G-acac** confirms the expected octahedral coordination environment of the iridium centre, with the two phenylpyridyl ligands coordinating in a transoid manner (N1 and N4 occupy relative *trans* positions). The molecule is C_2-symmetric in solution, as observed by NMR spectroscopy. This symmetry is broken in the solid state due to slight distortions and the co-crystallization of acetonitrile molecules. The four aromatic rings of each phenylpyridyl ligand are not completely coplanar, but a slight torsion angle is observed, being more pronounced in one ligand than in the other (twist angles of 8(2)° and 40.3(19)° respectively).

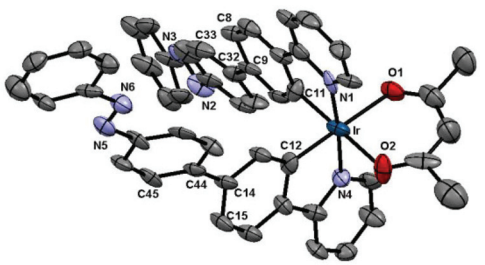
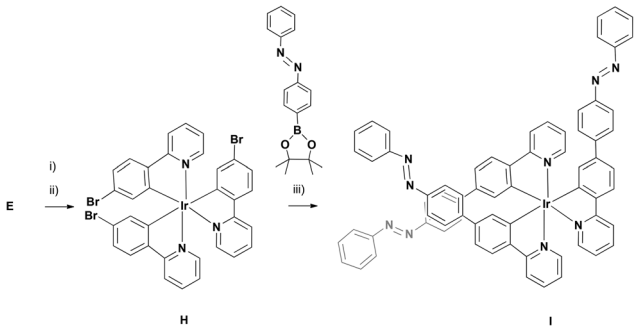


Fig. 2 Molecular structure of the complex **G-acac** obtained by X-ray diffraction. ORTEP ellipsoids at the 50% probability level. Solvent molecules (CH_3CN) and hydrogen atoms have been omitted for clarity. Relevant distances (Å): N2–N3 = 1.252(18), N5–N6 = 1.259(15) N1–Ir = 2.016(10), N4–Ir = 2.043(10), C11–Ir = 2.012(14), C12–Ir = 1.965(14), O1–Ir = 2.1682(10), O2–Ir = 2.141(11).



Scheme 5 (i) AgOTf, acetone (55 °C, 2 h). (ii) 2-(4-Bromophenyl)pyridine (4 equiv.), NEt_3 (7.5 equiv.), acetone (55 °C, 15 h). (iii) Solvent 2 : 1 THF–$Na_2CO_{3aq.}$ (1 M), 2 mol% of $Pd(PPh_3)_4$, 80 °C, 15 h.

In view of the good yields obtained in the Suzuki couplings of brominated complexes with (*E*)-4-azophenylboronic acid pinacol ester (**f**), we decided to explore the possibility to introduce three azobenzene units per metal centre (Scheme 5). For that purpose, we synthesized the triscyclometalated complex **H** [Ir(5-bromo-2-pyridyl)phenyl)$_3$]. Dimeric iridium complex **E** was cleaved using an excess of 2-(4-bromophenyl)pyridine, to form tris-brominated homoleptic meridional complex **H**. Crystals suitable for X-ray diffraction were obtained for mono-, bis- and tris-brominated complexes **C**, **F-Fppy** and **H**. **C** was obtained by slow diffusion of hexane into saturated CH_2Cl_2–$CDCl_3$ solutions of the complex, **F-Fppy** was obtained by evaporation of saturated $CDCl_3$–CH_2Cl_2 solutions and **H** was obtained by evaporation of $CDCl_3$–acetone solutions (see ESI†).

Complex **H** was subjected to Suzuki cross-coupling with 3.2 equiv. of (*E*)-4-azophenylboronic acid pinacol ester (**f**) following the procedure described above for derivatives **A4**, **B4** and **G**, rendering meridional homoleptic compound **I** which contains three photochromic azobenzene units. The lack of symmetry of this compound hampers full assignment of its NMR spectra. Nevertheless, the ^{1}H-NMR spectra showed aromatic signals which could fit 48 protons integration. More revealing is the ^{13}C-APT-NMR spectra. It presented, as expected, 69 carbon signals, 21 of which are quaternary.

UV-vis absorption data

UV-vis spectra of ligands **1–4**‡ and their complexes **A–I** were measured in order to evaluate the effect of the ligand coordination on the electronic structure of the azobenzene fragments. Their band maxima and molar extinction coefficient are presented in Table 1.

Ligands **1–4** present two absorption bands in the region 300–500 nm (λ_{max} and λ_2) characteristic of azobenzene derivatives.[8] The more intense and energetic absorption (λ_{max}) is attributed to a $\pi\rightarrow\pi^*$ transition, and the less intense red-shifted λ_2 to the symmetry-forbidden $n\rightarrow\pi^*$ transition. Cationic complexes **A1′** and **B1′**, in which azobenzene is coordinated to

‡Ligand **4** was synthesized *a posteriori* by Suzuki cross-coupling of **f** and 2-bromopyridine and was used only for comparative purposes.

Table 1 UV/Vis spectroscopic data of ligands **1–4** and complexes **A–I** measured in CH_3CN

Compound	λ_{max} [nm] (ε [M^{-1} cm^{-1}])	$\Delta\lambda_{max}$ [b] [nm] ([cm^{-1}])	λ_2 [nm] (ε [M^{-1} cm^{-1}])
1	323 (1.6×10^4)	—	454 (0.4×10^3)
2	319 (1.8×10^4)	—	429 (0.4×10^3)
3	339 (2.8×10^4)	—	439 (0.9×10^3)
4	348 (3.8×10^4)	—	441 (1.4×10^3)
A1′	304 (2.2×10^4)	−19 (1935)	—
B1′	310 (2.5×10^4)	−13 (1928)	—
A2	398 (1.9×10^4)	79 (−6222)	466 (9.5×10^3)
B2	387 (1.8×10^4)	68 (−5508)	436 (9.0×10^3)
A3	346 (2.9×10^4)	7 (−597)	454 (6.0×10^3)
B3	348 (2.8×10^4)	9 (−763)	433 (5.5×10^3)
A4	356 (3.7×10^4)	8 (−646)	464 (5.4×10^3)
B4	352 (3.8×10^4)	4 (−327)	449 (5.6×10^3)
G-ppy[a]	354 (6.5×10^4)	6 (−487)	481 (7.1×10^3)
G-Fppy[a]	350 (6.4×10^4)	2 (−164)	469 (8.7×10^3)
G-acac	353 (6.8×10^4)	5 (−407)	470 (8.4×10^3)
I	355 (8.9×10^4)	7 (−567)	476 (9.2×10^3)

[a] Measured in CH_2Cl_2 due to their low solubility in CH_3CN. [b] $\Delta\lambda_{max} = \lambda_{max(complex)} - \lambda_{max(ligand)}$.

the metal through one of the nitrogen atoms, do not present any intense band in the region assigned to a π→π* transition, but only a shoulder at shorter light wavelengths compared to the parent ligand. In the case of derivatives of ligands **2–4**, metal coordination produces a bathochromic shift in the band attributed to the π→π* transition. This shift is larger in the case of complexes **A2** and **B2** (79 and 68 nm respectively) compared to the ones derived from ligands **3** or **4** ($\Delta\lambda_{max}$ < 10 nm). See Fig. 3 for representative absorption spectra of ligand **2** and complex **A2**. This observation suggests that a *para* relative position of the metal coordination and the azobenzene group establishes stronger electronic communication between them, compared to the *meta* substitution. Extending the aromaticity on the phenylpyridyl ligand (see **A3**, **B3** *vs*. **A4**, **B4**) produces a slight increase in the molar absorptivity and in λ_{max}, as observed for fluorenyl tethered Ir(ppy) complexes.[68] The presence of fluorine substituents in derivatives **B** does not produce any systematic change in the UV-vis absorption spectra of their complexes. By comparing the molar absorptivity at λ_{max} in all the complexes analyzed, as expected, it is proportional to the number of azobenzenes in the complex. This trend has already been observed for cobalt complexes containing bipyridine–azobenzene ligands.[18]

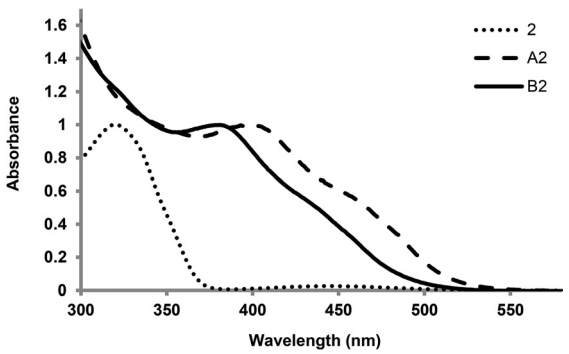


Fig. 3 Normalized UV-vis spectra of ligand **2** and complexes **A2** and **B2**, CH_3CN.

Cyclic voltammetry

The electrochemical properties of azobenzene-containing iridium complexes were studied in dimethylformamide (DMF) solutions. The corresponding half-wave potentials are summarized in Table 2. The HOMO and LUMO levels of all complexes have been deduced by the equation[69–71] E_{HOMO}/E_{LUMO} (eV) = −(4.8 + E_{onset}) and ΔE has been obtained as the difference LUMO–HOMO.

The obtained voltammograms (Fig. S1–S6 in ESI†) and redox potential values were compared to the well-known *mer*-Ir(ppy)$_3$.[69–71] According to the literature, the voltammogram of *mer*-Ir(ppy)$_3$ exhibits two reversible reduction peaks assigned to the reduction of the phenylpyridine ligands.[72] It also presents a reversible oxidation wave attributed to the Ir^{IV}/Ir^{III} redox couple.[73,74]

As has been reported before, the values of the redox potentials of iridium complexes containing ppy derivatives depend on the electron-donating or electron-withdrawing nature of their substituents.[75] The azobenzene-containing complexes analyzed in this work exhibit their first oxidation peak at potentials between 0.53 and 1.27 V *vs.* Fc/Fc^+ and their first reduction peak potentials between −1.81 and −1.60 V. These values are all anodically shifted with respect to those corresponding to Ir(ppy)$_3$. The lower reduction and higher oxidation potentials observed, compared to those of Ir(ppy)$_3$, could be attributed to the presence of the low-lying π* orbital of the azobenzene.[76] This trend is more pronounced for derivatives of ligand **1** (within **A** and **B** series of compounds), probably due to the cationic nature of complexes **A1′** and **B1′**, and the loss of aromaticity (and thus thermodynamic stability towards the reduction process) observed in the ligands upon chelation.

Comparing the values of the oxidation potentials measured for molecules of series **A** (ppy derivatives) to **B** (Fppy derivatives), it can be observed that the presence of 2 electron-withdrawing F atoms on each ligand leads to an anodic shift of the corresponding oxidation peaks. The reduction wave is affected to a lesser extent. Consequently, fluorine-containing complexes show larger ΔE values than their fluorine-free counterparts (see Fig. 4 for a representative example). This observation is in agreement with the published data for other iridium and ruthenium polypyridyl complexes.[77,78]

The reduction and oxidation peak potentials found for complex **A4** compared to **A3** indicate that the incorporation of an additional benzene ring in the structure of the phenylpyridine ligand has a slight effect on the redox behaviour of the complex.

The influence of the replacement of a second ppy ligand by an azobenzene-containing ppy on complex **A4** (to form complex **G-ppy**) is almost negligible. However, a similar substitution on Fppy derivative **B3** rendering complex **G-Fppy** produces a notable cathodic shift on the oxidation potential. This

Table 2 Electrochemical properties of the Ir complexes

	E_{red}[a] [V]	E_{ox}[a] [V]	$E_{onsetred}$[a] [V]	LUMO[b] [eV]	$E_{onsetox}$[a] [V]	HOMO[c] [eV]	ΔE [eV]
$Ir(ppy)_3$	−2.64	0.49	−2.41	−2.39	0.33	−5.13	2.75
A1′	−1.63	0.86	−1.47	−3.33	0.72	−5.52	2.19
A2	−1.81	0.55	−1.64	−3.16	0.43	−5.23	2.07
A3	−1.68	0.55	−1.50	−3.30	0.39	−5.19	1.89
B1′	−1.62	1.27	−1.47	−3.33	1.02	−5.82	2.49
B2	−1.77	0.91	−1.61	−3.19	0.76	−5.56	2.37
B3	−1.62	0.90	−1.43	−3.37	0.71	−5.51	2.14
A4	−1.61	0.53	−1.44	−3.36	0.38	−5.18	1.82
B4	−1.65	0.85	−1.46	−3.34	0.72	−5.52	2.18
G-ppy	−1.64	0.56	−1.44	−3.36	0.39	−5.19	1.83
G-Fppy	−1.60	0.67	−1.47	−3.33	0.55	−5.35	2.02
G-acac	−1.63	0.77	−1.43	−3.37	0.60	−5.40	2.03
I	−1.71	0.53	−1.45	−3.35	0.40	−5.20	1.85

[a] Potential values are reported *versus* Fc/Fc^+. [b] Determined from the onset reduction potential. [c] Determined from the onset oxidation potential.

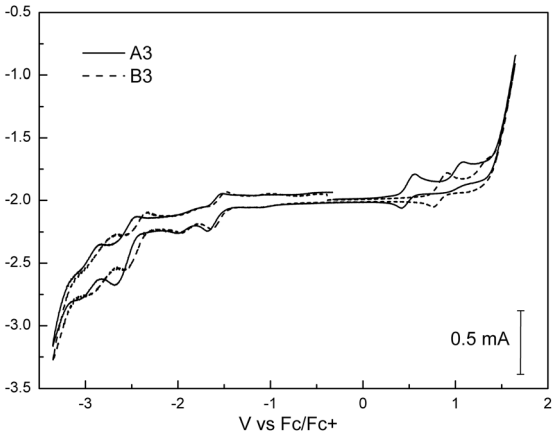


Fig. 4 Cyclo-voltammograms (10^{-3} M, dry DMF) of **A3** and **B3** containing 0.1 M $TBAPF_6$ as the supporting electrolyte, scan rate of 100 mV s^{-1}.

Table 3 Main transitions computed at TD-CAM-B3LYP(pcm)/6-31G* & LANL2DZ level from geometries optimized at B3LYP(pcm)/6-31G* & LANL2DZ level

	λ_{max} [nm] (E [eV])	f	Transition	$\Delta E_{HOMO-LUMO}$[a] [eV]
2	317.9 (3.90)	0.97	HOMO → LUMO (65%)	—
3	340.6 (3.64)	1.39	HOMO → LUMO (68%)	—
4	346.1 (3.58)	1.77	HOMO → LUMO (64%)	—
A2	368.7 (3.36)	1.25	HOMO−1 → LUMO (64%)	2.88
A3	372.6 (3.29)	0.47	HOMO−1 → LUMO (65%)	2.69
B2	351.6 (3.52)	1.28	HOMO−1 → LUMO (62%)	3.56
B3	367.2 (3.37)	0.66	HOMO−1 → LUMO (65%)	3.28
A4	358.9 (3.45)	1.67	HOMO−2 → LUMO (36%) HOMO−1 → LUMO (50%)	2.62
B4	356.8 (3.47)	1.74	HOMO−2 → LUMO (32%) HOMO−1 → LUMO (54%)	3.25

[a] Computed at B3LYP(pcm)/6-31G* & LANL2DZ level.

is probably due to the substitution of one of the F-containing ppy ligands for a less electron-withdrawing ligand **4**.

The oxidation potentials of complexes **G** are affected by the chemical nature of the ancillary L–X ligand. This is revealed by the results concerning the substitution of the ppy ligand of complex **G-ppy** by the more electron-withdrawing Fppy and acac ligands. The presence of those ligands markedly increases the oxidation potential from 0.56 (**G-ppy**) to 0.67 (**G-Fppy**) and 0.77 V (**G-acac**). It should be noted that minor changes in the reduction potential are also observed.

Concerning the homoleptic complex **I**, the oxidation potential of **I** is anodically shifted from 0.49 to 0.53 V, compared to the reference compound $Ir(ppy)_3$. According to this value, it seems that the presence of the azobenzene on the phenylpyridine ligands stabilizes the iridium(III) state towards oxidation.[76] As can be expected, this complex is also easily reduced. It shows a low ΔE value (1.85 eV).

TD-DFT calculations

Electronic energies and oscillator strengths of ligands **2**, **3**, and **4** and compounds **A2**, **A3**, **A4**, **B2**, **B3** and **B4** were computed by means of time dependent DFT calculations at the CAM-B3LYP(pcm)/6-31G* & LANL2DZ level of theory. The data associated with the main transitions computed for selected compounds are presented in Table 3, and the shape of the involved frontier molecular orbitals is depicted in Fig. 5.

As is shown in Table 3, the absorption bands are mainly associated with the HOMO → LUMO transition in the isolated ligands (**2**, **3** and **4**) and to the HOMO−1 → LUMO transition in compounds **A2,3** or **B2,3**. Moreover, a second transition (HOMO−2 → LUMO) appears to be relevant when an additional phenyl group is included in the azobenzene ligands (compounds **A4** and **B4**).

In the complexes, these bands are assigned to the spin allowed π→π* transition of molecular orbitals mainly located in the azobenzene moiety and the iridium atom (Fig. 5). Nevertheless, there is a small but non-negligible contribution of the phenylpyridyl ligands on the occupied orbitals. Therefore, an effect in the absorption bands will be expected when electron-withdrawing groups or electron-donating groups are included in the phenylpyridyl ligands. Our results showed that the effect would be higher on the compounds that incorporate the azobenzene in the *para* position (with respect to the metal)

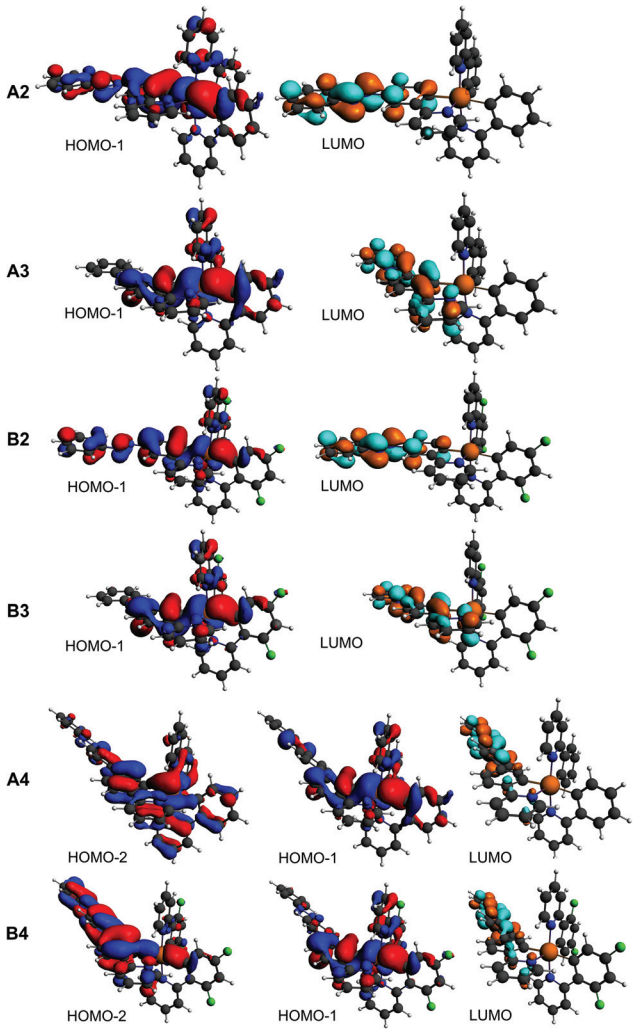


Fig. 5 Most relevant MO associated with the vertical excitations shown in Table 3. Occupied and unoccupied orbitals are represented by red & blue or yellow & green surfaces respectively.

(**A2** or **B2**), compared to the *meta* substituted ones (**A3**, **B3**, **A4** or **B4**) due to the different participation of these ligands on the involved molecular orbitals (see ESI† for further details of the expansion of molecular coefficients). Our results also show a hypsochromic shift in the absorption wavelength maxima of **A2** compared to its fluorinated counterpart **B2** of $\Delta\Lambda_{max(A2-B2)}$ = 17.1 nm (in good agreement with the experimental shift of 11 nm, Table 1). In the case of ligand **3** derivatives these calculated shifts are smaller ($\Delta\Lambda_{max(A3-B3)}$ = 5.4 nm and $\Delta\Lambda_{max(A4-B4)}$ = 2 nm). Comparative values of −2 nm and 4 nm were found experimentally, respectively. The anomalous behaviour of the pair **A3–B3** (small bathochromic effect due to fluorination) cannot be explained by means of TD-DFT calculations.

The substitution pattern has also an important effect on the computed HOMO–LUMO gaps. Our results show that the *para* substituted compounds (**A2** or **B2**) present a gap of about 0.2 eV higher than its *meta* counterpart compounds (**A3** or **B3**). Moreover, inclusion of an additional phenyl spacer in the *para* position has almost no effect on these computed gaps (**A3**, **B3** *vs.* **A4** and **B4**).

The fluorination effect was also observed on the computed HOMO–LUMO gaps. In all cases there was found a widening of the gap due to fluorination (**A2**, **A3** and **A4** *vs.* **B2**, **B3** and **B4** respectively, see ESI†). These results are in good agreement with the experimental values obtained *via* cyclic voltammetry (*vide infra*).

Photoisomerization

It is well known that azobenzenes experience a $E \rightarrow Z$ isomerization by irradiation at a light wavelength close to their absorption maxima.[8] As described by Monkowius *et al.* this process is more effective when the irradiation wavelength is individually optimized for every compound.[42] This process and the reverse thermal *cis*-to-*trans* isomerization can be easily followed by UV-vis absorption spectroscopy due to the smaller extinction coefficient of the band associated with the absorptivity of the $\pi \rightarrow \pi^*$ transition in the *cis* complex compared to the *trans* form. Following Monkowius' procedure, to maximize the population of the *cis* form in the PSS, kinetic data (first order rate constants and half-life times) on the reverse $Z \rightarrow E$ thermal isomerization of ligands **1–3** and their complexes **A–I** were obtained (see Table 4). As this process is temperature-dependent,[8] the measurements were performed in CH_3CN at 55 °C to reduce the analysis time which otherwise was taking several days.

Complexes derived from ligands **1** and **2** showed no spectral changes upon irradiation. In the case of **A1′** and **B1′** the lack of photoisomerization is probably caused by a strong coordination of the nitrogen atom of the azobenzene to the metal centre, as weakly coordinating azobenzenes or azopyridines showed an active photoisomerization process.[54,63,79] In the case of **A2** and **B2** the low degree of isomerization could be attributed to steric reasons or to a stabilizing effect of the *trans* form upon metal coordination. Complexes derived from ligands **3** and **4** presented thermally induced back isomerization processes with similar reaction rates (see Fig. 6 for a representative example of the isomerization process monitored by UV-vis absorption spectroscopy). Compared with other

Table 4 Kinetic data of the $Z \rightarrow E$ isomerization in CH_3CN at 55 °C

Compound	λ_{irrad} [a] [nm]	k [s^{-1}]	$\tau_{1/2}$ [s]
1	327	0.7×10^{-4}	9500
2	321	0.2×10^{-4}	33 000
3	343	0.9×10^{-4}	8100
4	354	1.3×10^{-4}	5500
A3	351	1.1×10^{-4}	6600
B3	355	1.0×10^{-4}	6700
A4	367	1.2×10^{-4}	6000
B4	359	1.3×10^{-4}	5500
G-acac	366	1.2×10^{-4}	5900
I	358	1.3×10^{-4}	5200

[a] Optimized wavelength for the $E \rightarrow Z$ photoisomerization. Complexes **G-Fppy** and **G-Fppy** could not be analysed due to their poor solubility in CH_3CN.

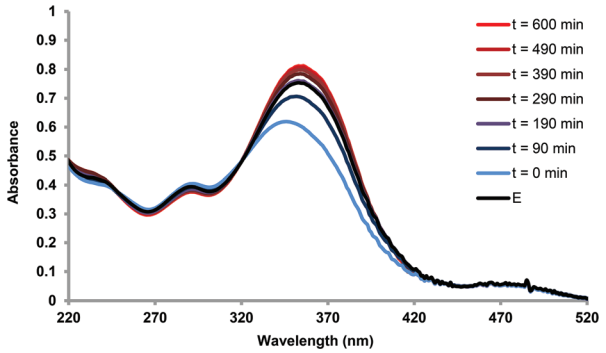


Fig. 6 UV-vis spectral changes before (black line) and after photo-irradiation at 366 nm (blue line), and thermal *cis* to *trans* isomerization of complex **G-acac**, 9 μM solution in CH_3CN (55 °C).

azobenzene-containing organometallic compounds, the kinetic data obtained locate the stability of the *cis* form of these complexes between the one of NHC–azobenzene containing complexes of gold ($k_{40\ °C} \sim 8 \times 10^{-4}\ s^{-1}$)[42] and the one of organoplatinum azobenzenes described by Puddephatt ($k_{40\ °C} = 4.5 \times 10^{-5}\ s^{-1}$).[41] An attempt to measure the degree of photoisomerization by ^{1}H-NMR was unsuccessful due to the overlap of signals.

Experimental

General considerations

$IrCl_3{\cdot}3H_2O$, $Pd(PPh_3)_4$, 2-phenylpyridine, 2-(2,4-difluorophenyl)-pyridine and other general chemicals were obtained from commercial sources and used without further purification. 2-Azophenylboronic acid **d**,[44] 4-azophenylboronic acid pinacol ester **f**,[45] $[Ir(ppy)_2Cl]_2$,[65,80,81] $[Ir(Fppy)_2Cl]_2$,[65,82] 4-bromophenylboronic acid pinacol ester,[83] 2-(4-bromophenyl)pyridine,[84] and $[Ir((5\text{-bromo-2-pyridyl})phenyl)_2Cl]_2$ **E**[67,85] were synthesized following published methodologies.

Solvents were dried and purified by known procedures and freshly distilled under nitrogen from appropriate drying agents prior to use. All manipulations and reactions involving air and/or moisture-sensitive organometallic compounds were performed under an atmosphere of dry nitrogen using standard Schlenk techniques.

Characterization methods

All electrochemical measurements were carried out in a sealed glass cell under a N_2 atmosphere on 10^{-3} M solutions of **A–I** in anhydrous DMF (containing 0.1 M $TBAPF_6$ as the supporting electrolyte) at a scan rate of 100 mV s^{-1}. The working electrode was a glassy-carbon rod (5 mm diameter) and a Pt wire encapsulated on a porous glass tube was used as the counter electrode. The potentials were controlled using a Metrohm Ag/AgCl reference electrode. On the other hand a ferrocene/ferrocenium couple (+0.352 V *vs.* Ag/AgCl) was used as the internal standard (1×10^{-3} M) and all potentials are related to it. The measurements were performed using a Bio-Logic VMP3 potentiostat–galvanostat.

UV-vis absorption measurements were performed with an Agilent 8453 diode-array spectrophotometer utilizing 10 mm cell-path quartz cuvettes (110 QS). Measurements of thermal *cis* to *trans* isomerization rates were performed using a 25 μM solution of **A–F** and **H** in acetonitrile and a 9 μM solution of **G-acac**, **G-Fppy**, **G-ppy** and **I** in acetonitrile. To maximize the initial population of *Z* derivatives on the PSS, we followed the procedure described by Monkowius:[42] using a Shimadzu RF-540 fluorimeter, a 3 mL portion of each sample was irradiated at the corresponding λ_{max} (associated with its π–π* transition band) until no further change in the UV-vis absorption spectra was observed. The λ of the maximum observed after subtracting the first and last spectra of the series was considered as the optimal light wave-length to promote the *Z–E* photoisomerization (λ_{opt}). Fresh samples were irradiated at (λ_{opt}) for 60 min, and then placed in a UV-vis spectrophotometer. Their absorbance spectral changes were measured as a function of time for 10 hours. The temperature was maintained at 55 °C controlled with a HP 89090A Peltier temperature control accessory.

Synthetic procedures

3-Azophenylboronic acid e. The title compound was obtained following a procedure analogous to the one reported for 2-azophenylboronic acid **d**.[44] 3-Iodoazobenzene (3.08 g, 10.0 mmol) was dissolved in 80 mL of distilled Et_2O, *n*-BuLi (1.60 M in hexane, 6.9 mL, 11.0 mmol) was added at −112 °C, and the reaction mixture was stirred for 30 minutes keeping the solution at −112 °C. This solution containing lithiated 3-azobenzene was added to an Et_2O solution (10 mL) of trimethyl borate (1.25 mL, 11.2 mmol) at −112 °C. The reaction temperature was gradually raised overnight to r.t. The mixture was quenched with water at 0 °C, and treated with dilute sulfuric acid (100 mL, 1 M). The reaction mixture was extracted with Et_2O (3 × 40 mL). The organic layer was treated with aq. NaOH (100 mL, 1 M), and the aqueous layer was separated and washed with Et_2O (3 × 40 mL) to remove organic side-products. The aqueous layer was neutralized with diluted sulfuric acid. The product precipitated as an insoluble yellow solid. Spectroscopic data are in agreement with the ones previously published for this compound.[86]

General procedure for the synthesis of compounds 1, 2 and 3

4.424 mmol of the corresponding azobenzene boronic acid (**d**, **e** or **f**) were dissolved in 15 mL of degassed THF. To this mixture, 2-bromopyridine (0.762 g, 0.462 mL, 4.822 mmol), $Pd(PPh_3)_4$ (2 mol%, 0.102 g, 0.088 mmol), and Na_2CO_3 (1 M aq., 7.5 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 was added. The resulting mixture was extracted with ethyl acetate (5 × 10 mL), dried ($MgSO_4$), filtered and evaporated *in vacuo*. The resulting solid was purified on a silica gel column.

2-(*o*-Phenylazobenzene)pyridine, 1. Purification by column chromatography: silica/eluent CH_2Cl_2 (R_f **1** = 0.2). It was obtained as a red oil. 0.917 g, 80% yield.

^{1}H NMR (500 MHz, acetone-D6): δ 8.73 (d, J = 4.0, 1H), 8.36 (d, J = 8.6, 2H), 8.07–8.04 (m, 3H), 7.98 (d, J = 7.2, 2H), 7.92 (td, J = 7.8, 1.7, 1H), 7.64–7.55 (m, 3H), 7.38 (ddd, J = 7.4, 4.8, 0.7, 1H). ^{13}C NMR (126 MHz, acetone-D6): δ 156.50 (1C, $C_{quat.}$), 153.60 (1C, $C_{quat.}$), 153.56 (1C, $C_{quat.}$), 150.71 (1C, CH), 142.68 (1C, $C_{quat.}$), 137.90 (1C, CH), 132.23 (1C, CH), 130.17 (2C, CH), 128.42 (2C, CH), 123.90 (2C, CH), 123.75 (1C, CH), 123.61 (2C, CH), 121.38 (1C, CH). Elemental analysis: calculated for $C_{17}H_{13}N_3 \cdot 0.1CH_2Cl_2$: C, 76.47; H, 4.96; N, 15.64. Found: C, 77.00; H, 4.80; N, 15.06. Exact mass (MALDI) – m/z: 260.1178 for $[M + H]^+$.

2-(*m*-Phenylazobenzene)pyridine, 2. Purification by column chromatography: silica/eluent CH_2Cl_2 (R_f **2** = 0.2). It was obtained as a dark-red oil. 0.906 g, 79% yield.

^{1}H NMR (500 MHz, acetone-D6): δ 8.74 (d, J = 4.1, 1H), 8.71 (t, J = 1.6, 1H), 8.31 (d, J = 7.7, 1H), 8.07 (d, J = 8.0, 1H), 8.01–7.98 (m, 3H), 7.93 (td, J = 7.7, 1.8, 1H), 7.72 (t, J = 7.8, 1H), 7.64–7.58 (m, 3H), 7.39 (ddd, J = 7.6, 4.7, 0.9, 1H). ^{13}C NMR (126 MHz, acetone-D6): δ 156.20 (1C, $C_{quat.}$), 153.45 (1C, $C_{quat.}$), 152.99 (1C, $C_{quat.}$), 150.16 (1C, CH), 140.96 (1C, $C_{quat.}$), 137.46 (1C, CH), 131.74 (1C, CH), 129.99 (1C, CH), 129.67 (2C, CH), 129.59 (1C, CH), 123.28 (1C, CH), 123.21 (1C, CH), 123.12 (2C, CH), 121.43 (1C, CH), 120.67 (1C, CH). Elemental analysis: calculated for $C_{17}H_{13}N_3$ $0.7CH_2Cl_2$: C, 67.16; H, 4.57; N, 13.30. Found: C, 67.41; H, 4.15; N, 13.79. Exact mass (MALDI) – m/z: 260.1175 for $[M + H]^+$.

2-(*p*-Phenylazobenzene)pyridine, 3. Purification by column chromatography: silica/eluent CH_2Cl_2 (R_f **3** = 0.2). It was obtained as an orange powder. 0.803 g, 70% yield.

^{1}H NMR (500 MHz, acetone-D6): δ 8.73 (d, J = 4.0, 1H), 8.36 (d, J = 8.6, 2H), 8.07–8.04 (m, 3H), 7.98 (d, J = 7.2, 2H), 7.92 (td, J = 7.8, 1.7, 1H), 7.64–7.55 (m, 3H), 7.38 (ddd, J = 7.4, 4.8, 0.7, 1H). ^{13}C NMR (126 MHz, acetone-D6): δ 156.50 (1C, $C_{quat.}$), 153.60 (1C, $C_{quat.}$), 153.56 (1C, $C_{quat.}$), 150.71 (1C, CH), 142.68 (1C, Cquat.), 137.90 (1C, CH), 132.23 (1C, CH), 130.17 (2C, CH), 128.42 (2C, CH), 123.90 (2C, CH), 123.75 (1C, CH), 123.61 (2C, CH), 121.38 (1C, CH). Elemental analysis: calculated for C17H13N3: C, 78.74; H, 5.05; N, 16.20. Found: C, 78.78; H, 5.04; N, 15.94. Exact mass (MALDI) – m/z: 260.1178 for [M + H]+.

2-Phenyl(4-azophenyl)pyridine, 4‡. 2-(4-Bromophenyl)pyridine (0.300 g, 0.128 mmol) was dissolved in 4 mL of degassed THF. To this mixture, 4-azophenylboronic acid pinacol ester, **f** (0.434 mg, 0.141 mmol), $Pd(PPh_3)_4$ (2 mol%, 2.958 mg, 0.003 mmol), and Na_2CO_3 (1 M aq., 2 mL) were added successively under nitrogen, and 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 ethyl acetate (5 × 10 mL). The organic phase was dried ($MgSO_4$), and filtered. After evaporation of the solvent from the filtrate, the resulting solid was purified by column chromatography eluting with dichloromethane (R_f = 0.2). The product was obtained as a light orange powder (0.260 g, 60%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.77 (ddd, J = 4.8, 1.3, 1.3, 1H), 8.16 (d, J = 8.5, 2H), 8.07 (d, J = 8.6, 2H), 8.00 (dd, J = 8.2, 1.5, 2H), 7.88–7.81 (m, 6H), 7.61–7.50 (m, 3H), 7.33–7.28 (ddd, J = 5.0, 5.0, 3.2, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.85 (1C, $C_{quat.}$), 152.76 (1C, $C_{quat.}$), 151.91 (1C, $C_{quat.}$), 149.72 (1C, CH), 143.03 (1C, $C_{quat.}$), 140.64 (1C, $C_{quat.}$), 138.80 (1C, $C_{quat.}$), 136.86 (1C, CH), 130.99 (1C, CH), 129.09 (2C, CH), 127.71 (2C, CH), 127.51 (2C, CH), 127.43 (2C, CH), 123.43 (2C, CH), 122.87 (2C, CH), 122.28 (1C, CH), 120.58 (1C, CH). Elemental analysis: calculated for $C_{23}H_{17}N_3$: C, 82.36; H, 5.11; N, 12.53. Found: C, 82.17; H, 5.03; N, 12.53. Exact mass (MALDI) – m/z: 336.1485 for $[M + H]^+$.

General procedure for the synthesis of compounds B and C

$[Ir(ppy)_2Cl]_2$ (0.150 g, 0.140 mmol) and AgOTf (0.108 g, 0.420 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 the corresponding ligand **1–3** or 2-(4-bromophenyl)pyridine (0.560 mmol) and NEt_3 (0.147 mL, 1.054 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.

$[Ir(ppy)_2$1$][OTf]$, A1′. Purification by column chromatography: silica/eluent EtOAc (R_f **1** = 0.8; R_f **A1′** = 0), when the ligand is eluted the polarity is gradually increased to pure acetone ($R_{f\,acetone}$ **A1′** = 0.7). It was obtained as a dark-red crystalline solid. 0.178 g, 70% yield.

^{1}H NMR (300 MHz, $CDCl_3$, 0.075 M) δ 8.37 (d, J = 8.0, 1H), 8.25–8.20 (m, 2H), 8.16 (d, J = 8.3, 1H), 8.03 (d, J = 8.0, 1H), 8.00–7.97 (td, J = 7.5, 1.4, 1H), 7.93 (d, J = 5.7, 1H), 7.85 (d, J = 7.8, 1H), 7.71–7.66 (m, 2H), 7.59 (dd, J = 5.6, 1.1, 1H), 7.50 (dd, J = 7.6, 1.7, 1H), 7.40 (td, J = 7.6, 1.1 1H), 7.33–7.25 (m, 3H), 7.20–7.10 (m, 2H), 7.04 (td, J = 7.4, 1.1, 1H), 6.95–6.78 (m, 7H), 6.23 (d, J = 7.6, 1H), 6.14 (dd, J = 7.3, 1.3, 1H), 5.77 (dd, J = 8.0, 0.9, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, 0.075 M): δ 166.85 (1C, $C_{quat.}$), 166.37 (1C, $C_{quat.}$), 153.40 (1C, $C_{quat.}$), 152.15 (1C, $C_{quat.}$), 149.96 (1C, CH), 149.69 (1C, CH), 148.85 (1C, $C_{quat.}$), 148.59 (1C, $C_{quat.}$), 147.82 (1C, CH), 143.66 (1C, $C_{quat.}$), 143.31 (1C, $C_{quat.}$), 143.25 (1C, $C_{quat.}$), 140.33 (1C, CH), 138.26 (1C, CH), 137.85 (1C, CH), 132.83 (1C, CH), 132.67 (1C, $C_{quat.}$), 132.22 (1C, CH), 132.00 (1C, CH), 130.44 (1C, CH), 129.87 (1C, CH), 129.84 (1C, CH), 129.64 (1C, CH), 129.52 (1C, CH), 128.99 (2C, CH), 126.63 (1C, CH), 125.35 (1C, CH), 124.43 (1C, CH), 123.26 (1C, CH), 123.09 (1C, CH), 122.87 (1C, CH), 122.27 (2C, CH), 120.88 (2C, CH), 119.86 (1C, CH), 118.22 (1C, CH), 117.63 (1C, CH). Elemental analysis: calculated for $C_{40}H_{29}F_3IrN_5O_3S$: C, 52.85; H, 3.22; N, 7.70; S, 3.53. Found: C, 52.47; H, 3.62; N, 7.69; S, 3.54. Exact mass (EI) – m/z: 760.2070 for $[M]^+$ with (^{193}Ir).

$[Ir(ppy)_2$2$]$, A2. Purification by column chromatography: silica/CH_2Cl_2 (R_f **A2** = 0.8). It was obtained as a light-orange solid. 0.042 g, 20% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.31 (s, 1H), 8.12 (m, 2H), 7.96 (d, J = 4.8, 1H), 7.86 (d, J = 7.5, 2H), 7.83 (d, J = 8.1, 2H),

7.72–7.67 (m, 3H), 7.60 (d, J = 5.4, 1H), 7.56 (t, J = 7.9, 1H), 7.53–7.47 (m, 4H), 7.43 (d, J = 7.1, 1H), 7.14 (d, J = 7.7, 1H), 6.99–6.95 (m, 3H), 6.92 (t, J = 7.5, 1H), 6.87 (t, J = 7.0, 1H), 6.74 (t, J = 6.2, 2H), 6.62 (d, J = 5.9, 1H), 6.48 (d, J = 7.4, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 187.58 (1C, $C_{quat.}$), 174.60 (1C, $C_{quat.}$), 170.51 (1C, $C_{quat.}$), 167.98 (1C, $C_{quat.}$), 167.78 (1C, $C_{quat.}$), 158.62 (1C, $C_{quat.}$), 153.41 (1C, $C_{quat.}$), 153.31 (1C, CH), 151.35 (1C, CH), 148.80 (1C, $C_{quat.}$), 147.88 (1C, CH), 146.57 (1C, $C_{quat.}$), 144.71 (1C, $C_{quat.}$), 142.40 (1C, $C_{quat.}$), 138.57 (1C, CH), 136.86 (1C, CH), 135.85 (1C, CH), 134.48 (1C, CH), 132.81 (1C, CH), 130.70 (1C, CH), 130.14 (1C, CH), 129.82 (1C, CH), 129.80 (1C, CH), 129.11 (2C, CH), 124.73 (1C, CH), 124.26 (1C, CH), 124.11 (1C, CH), 122.94 (1C, CH), 122.34 (2C, CH), 122.20 (1C, CH), 121.38 (1C, CH), 121.18 (1C, CH), 119.65 (1C, CH), 119.23 (1C, CH), 118.80 (1C, CH), 118.59 (1C, CH), 117.84 (1C, CH). Elemental analysis: calculated for $C_{39}H_{28}IrN_5$: C, 61.72; H, 3.72; N, 9.23. Found: C, 61.57; H, 3.59; N, 8.94. Exact mass (MALDI) – m/z: 759.1978 for $[M]^+$ with (^{193}Ir).

[Ir(ppy)$_2$3], A3. Purification by column chromatography: silica/CH_2Cl_2 (R_f **A3** = 0.8). It was obtained as a dark-orange solid. 0.119 g, 56% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.22 (d, J = 5.7, 1H), 8.00 (d, J = 8.1, 1H), 7.97 (d, J = 5.3, 1H), 7.87 (d, J = 8.4, 1H), 7.81 (d, J = 7.9, 4H), 7.70 (d, J = 6.9, 1H), 7.65 (t, J = 7.2, 2H), 7.60 (d, J = 5.9, 1H), 7.57 (d, J = 1.8, 1H), 7.53 (t, J = 7.2, 1H), 7.49–7.37 (m, 5H), 6.98–6.89 (m, 4H), 6.85 (t, J = 7.3, 1H), 6.73 (t, J = 6.1, 1H), 6.72 (t, J = 6.1, 1H), 6.63 (d, J = 6.2, 1H), 6.51 (d, J = 7.5, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 179.60 (1C, $C_{quat.}$), 174.90 (1C, $C_{quat.}$), 170.78 (1C, $C_{quat.}$), 168.36 (1C, $C_{quat.}$), 167.73 (1C, $C_{quat.}$), 158.73 (1C, $C_{quat.}$), 153.75 (1C, CH), 153.48 (1C, $C_{quat.}$), 153.26 (1C, $C_{quat.}$), 151.71 (1C, CH), 148.73 (1C, $C_{quat.}$), 147.99 (1C, CH), 145.00 (1C, $C_{quat.}$), 142.44 (1C, $C_{quat.}$), 136.79 (1C, CH), 136.33 (1C, CH), 135.82 (1C, CH), 134.40 (1C, CH), 132.96 (1C, CH), 130.90 (1C, CH), 130.59 (1C, CH), 130.26 (1C, CH), 130.05 (1C, CH), 129.08 (2C, CH), 125.12 (1C, CH), 124.39 (2C, CH), 123.03 (1C, CH), 122.99 (2C, CH), 122.28 (1C, CH), 121.32 (1C, CH), 121.21 (1C, CH), 120.02 (1C, CH), 119.35 (1C, CH), 118.85 (1C, CH), 118.73 (1C, CH), 112.40 (1C, CH). Elemental analysis: calculated for $C_{39}H_{28}IrN_5$: C, 61.72; H, 3.72; N, 9.23. Found: C, 61.43; H, 3.33; N, 9.61. Exact mass (MALDI) – m/z: 759.1971 for $[M]^+$ with (^{193}Ir).

[Ir(ppy)$_2$((5-bromo-2-pyridyl)phenyl)], C. Purification by column chromatography: silica/CH_2Cl_2–hexane 5 : 1 (R_f **C** = 0.7). It was obtained as a yellow powder. 0.082 g, 40% yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.14 (dd, J = 5.8, 0.9, 1H), 7.95–7.89 (m, 2H), 7.86–7.82 (m, 2H), 7.73–7.51 (m, 7H), 7.14 (dd, J = 8.3, 2.2, 1H), 7.04 (d, J = 2.1, 1H), 7.02–6.83 (m, 5H), 6.80 (ddd, J = 7.3, 5.9, 1.4, 2H), 6.76 (ddd, J = 7.3, 5.9, 1.4, 2H), 6.62–6.58 (m, 1H), 6.45 (dd, J = 7.4, 1.1, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 181.42 (1C, $C_{quat.}$), 173.94 (1C, $C_{quat.}$), 170.39 (1C, $C_{quat.}$), 167.99 (1C, $C_{quat.}$), 167.50 (1C, $C_{quat.}$), 158.09 (1C, $C_{quat.}$), 153.26 (1C, CH), 151.23 (1C, CH), 147.72 (1C, CH), 144.65 (1C, $C_{quat.}$), 144.09 (1C, $C_{quat.}$), 142.12 (1C, $C_{quat.}$), 140.03 (1C, CH), 136.55 (1C, CH), 135.65 (1C, CH), 134.29 (1C, CH), 132.61 (1C, CH), 130.48 (1C, CH), 130.01 (1C, CH), 129.81 (1C, CH), 126.71 (1C, $C_{quat.}$), 125.80 (1C, CH), 124.36 (1C, CH), 124.12 (2C, CH), 122.54 (1C, CH), 122.08 (1C, CH), 121.15 (1C, CH), 121.00 (1C, CH), 119.23 (1C, CH), 119.13 (1C, CH), 118.62 (1C, CH), 118.52 (1C, CH). Elemental analysis: calculated for $C_{33}H_{23}BrIrN_3 \cdot C_6H_{14}$: C, 57.13; H, 4.55; N, 5.13. Found: C, 57.02; H, 4.50; N, 5.20. Exact mass (MALDI) – m/z: 733.0684 for $[M]^+$ with (^{193}Ir)(^{79}Br).

General procedure for the synthesis of compounds A and D

$[Ir(Fppy)_2Cl]_2$ (0.150 g, 0.123 mmol) and AgOTf (0.095 g, 0.370 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 the corresponding ligand **1–3** or 2-(4-bromophenyl)pyridine (0.492 mmol) and NEt_3 (0.130 mL, 0.932 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.

[Ir(Fppy)$_2$1][OTf], B1′. Purification by column chromatography: silica/eluent EtOAc (R_f **1** = 0.8; R_f **B1′** = 0) and when the ligand is eluted the polarity is gradually increased to pure acetone ($R_{facetone}$ **B1′** = 0.7). It was obtained as a red crystalline solid. 0.190 g, 79% yield.

^{1}H NMR (300 MHz, $CDCl_3$, 0.1 M): δ 8.52 (dd, J = 7.8, 2.2, 1H), 8.45 (d, J = 7.9, 1H), 8.25 (td, J = 7.8, 1.6, 1H), 8.15–7.98 (m, 5H), 7.71 (t, J = 7.7, 1H), 7.56 (dd, J = 5.6, 1.3, 1H), 7.45 (td, J = 7.7, 0.9, 1H), 7.36–7.31 (m, 3H), 7.26–7.19 (m, 2H), 6.93–6.86 (m, 4H), 6.60–6.44 (m, 2H), 5.83 (d, J = 8.0, 1H), 5.65 (dd, J = 8.5, 2.3, 1H), 5.56 (dd, J = 8.4, 2.3, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, 0.1 M): δ 163.25 (d, J = 7.2, 1C, $C_{quat.}$), 162.89 (d, J = 6.6, 1C, $C_{quat.}$), 162.22 (dd, J = 257, 12.4, 2C, $C_{quat.}$), 160.70 (d, J = 260, 12.4, 1C, $C_{quat.}$), 159.51 (d, J = 259, 12.5, 1C, $C_{quat.}$), 153.30 (1C, C_{quat}), 152.38 (d, J = 6.5, 1C, $C_{quat.}$), 151.87 (1C, $C_{quat.}$), 149.96 (2C, CH), 148.23 (1C, CH), 147.97 (1C, $C_{quat.}$), 147.60 (d, J = 7.3, 1C, $C_{quat.}$), 140.97 (1C, CH), 139.16 (1C, CH), 138.74 (1C, CH), 133.42 (1C, CH), 132.63 (1C, $C_{quat.}$), 131.00 (1C, CH), 130.69 (1C, CH), 129.96 (1C, CH), 129.12 (2C, CH.), 127.32 (1C, CH), 127.19 (1C, $C_{quat.}$), 127.16 (1C, $C_{quat.}$), 125.66 (1C, CH), 123.77 (d, J = 21.1, 1C, CH), 122.73 (1C, CH), 122.66 (1C, CH), 122.14 (d, J = 19.6, 1C, CH), 121.45 (2C, CH), 117.53 (1C, CH), 114.45 (d, J = 18.4, 2C, CH), 99.58 (pst, J = 27.0, 1C, CH), 99.23 (pst, J = 27.0, 1C, CH). Elemental analysis: calculated for $C_{40}H_{25}F_7IrN_5O_3S$: C, 48.98; H, 2.57; N, 7.14; S, 3.27. Found: C, 49.40; H, 2.62; N, 6.99; S, 3.41. Exact mass (EI) – m/z: 832.1658 for $[M]^+$ with (^{193}Ir).

[Ir(Fppy)$_2$2], B2. Purification by column chromatography: silica/CH_2Cl_2 (R_f **B2** = 0.8). It was obtained as a light-orange solid. 0.031 g, 15% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.31 (s, 1H), 8.24 (t, J = 8.6, 2H), 8.15 (d, J = 8.0, 1H), 8.09 (d, J = 5.3, 1H), 7.92 (d, J = 5.0, 1H), 7.88 (d, J = 7.5, 2H), 7.76 (t, J = 7.4, 1H), 7.62 (t, J = 7.7, 1H), 7.58–7.54 (m, 3H), 7.52–7.49 (m, 2H), 7.45 (d, J = 7.1, 1H), 7.10 (d, J = 7.7, 1H), 7.04 (t, J = 6.1, 1H), 6.78 (t, J = 6.3, 2H), 6.47 (t, J = 9.4, 1H), 6.45 (t, J = 9.4, 1H), 6.03 (d, J = 5.6, 1H), 5.84 (d, J = 8.1, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 183.67 (1C, $C_{quat.}$), 180.10 (1C, $C_{quat.}$), 167.50 (1C, $C_{quat.}$), 166.90 (d, J = 8.1,

1C, $C_{quat.}$), 164.68 (d, J = 6.9, 1C, $C_{quat.}$), 164.62 (dd, J = 10.1, J = 259, 1C, $C_{quat.}$), 163.93 (dd, J = 12.5, J = 254, 1C, $C_{quat.}$), 162.38 (dd, J = 10.9, J = 263, 1C, $C_{quat.}$), 162.36 (d, J = 6.4, 1C, $C_{quat.}$), 161.78 (dd, J = 13.4, J = 259, 1C, $C_{quat.}$), 153.25 (1C, $C_{quat.}$), 153.20 (1C, CH), 151.04 (1C, CH), 149.17 (1C, $C_{quat.}$), 147.78 (1C, CH), 146.13 (1C, $C_{quat.}$), 138.13 (1C, CH), 137.49 (1C, CH) 136.91 (1C, CH), 135.64 (1C, CH), 130.13 (1C, CH), 129.16 (2C, CH), 127.90 (1C, $C_{quat.}$), 126.58 (1C, $C_{quat.}$), 125.02 (1C, CH), 123.29 (1C, CH), 123.04 (d, J = 20.8, 1C, CH), 122.78 (d, J = 19.7, 1C, CH), 122.49 (1C, CH), 122.44 (2C, CH), 121.69 (1C, CH), 120.02 (1C, CH), 118.12 (1C, CH), 113.85 (d, J = 13.0, 1C, CH), 112.14 (d, J = 16.8, 1C, CH), 97.72 (pst, J = 27.2, 1C, CH), 95.79 (pst, J = 27.2, 1C, CH). Elemental analysis: calculated for $C_{39}H_{24}F_4IrN_5{\cdot}C_3H_6O$: C, 56.75; H, 3.40; N, 7.88. Found: C, 56.46; H, 3.43; N, 7.43. Exact mass (EI) – 832.1677 for $[M + H]^+$ with (^{193}Ir).

[Ir(Fppy)$_2$3], B3. Purification by column chromatography: silica/CH_2Cl_2 (R_f **B3** = 0.8). It was obtained as a dark-orange solid. 0.143 g, 70% yield.

^{1}H NMR (500 MHz, CD_2Cl_2): δ 8.27 (t, J = 7.1, 2H), 8.21 (d, J = 5.0, 1H), 8.08 (d, J = 8.2, 1H), 7.96–7.94 (m, 2H), 7.83 (d, J = 7.3, 2H), 7.78 (td, J = 8.1, J = 1.4, 1H), 7.68–7.61 (m, 3H), 7.53–7.45 (m, 5H), 7.06 (t, J = 6.0, 1H), 6.86 (ddd, J = 7.4, 6.0, 1.4, 1H), 6.83 (ddd, J = 7.3, 6.0, 1.3, 1H), 6.53–6.49 (m, 2H), 6.08 (dd, J = 7.4, 2.3, 1H), 5.92 (dd, J = 9.1, 2.2, 1H). ^{13}C NMR (126 MHz, CD_2Cl_2): δ 180.09 (1C, $C_{quat.}$), 175.72 (1C, $C_{quat.}$), 166.92 (1C, $C_{quat.}$), 166.74 (d, J = 7.9, 1C, $C_{quat.}$), 164.54 (dd, J = 10.0, J = 260, 1C, $C_{quat.}$), 164.48 (d, J = 7.2, 1C, $C_{quat.}$), 163.90 (dd, J = 12.7, J = 254, 1C, $C_{quat.}$), 162.86 (d, J = 7.6, 1C, $C_{quat.}$), 162.39 (dd, J = 10.9, J = 263, 1C, C_{quat}), 161.80 (dd, J = 12.9, J = 260, 1C, $C_{quat.}$), 153.35 (1C, CH), 153.16 (1C, $C_{quat.}$), 152.93 (1C, $C_{quat.}$), 151.25 (1C, CH), 148.38 (1C, $C_{quat.}$), 148.01 (1C, CH), 137.52 (1C, CH), 136.99 (1C, CH), 135.73 (1C, CH), 134.71 (1C, CH), 130.76 (1C, CH), 129.07 (2C, CH), 128.15 (1C, $C_{quat.}$), 126.73 (1C, $C_{quat.}$), 125.32 (1C, CH), 123.47 (1C, CH), 123.04 (d, J = 21.4, 1C, CH), 122.74 (d, J = 20.2, 1C, CH), 122.70 (2C, CH), 122.66 (1C, CH) 121.90 (1C, CH), 120.41 (1C, CH), 113.74 (dd, J = 13.8, 2.0 1C, CH), 113.49 (1C, CH), 112.11 (dd, J = 16.2, 2.0, 1C, CH), 97.43 (pst, J = 27.2, 1C, CH), 95.48 (pst, J = 27.2, 1C, CH). Elemental analysis: calculated for $C_{39}H_{24}F_4IrN_5$: C, 56.38; H, 2.91; N, 8.43. Found: C, 56.84; H, 2.64; N, 8.25. Exact mass (EI) – m/z: 832.1656 for $[M + H]^+$ with (^{193}Ir).

[Ir(Fppy)$_2$((5-bromo-2-pyridyl)phenyl)], D. Purification by column chromatography: silica/CH_2Cl_2 (R_f **D** = 0.9). It was obtained as a light-orange solid. 0.060 g, 30% yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.29–8.23 (d, J = 8.3, 2H), 8.11 (dd, J = 5.9, 1.1, 1H), 7.92 (d, J = 8.22, 1H), 7.88 (dd, J = 5.6, 0.9, 1H), 7.72 (t, J = 7.4, 1.7, 1H C_5H_5N), 7.66–7.58 (m, 3H), 7.51 (dd, J = 5.9, 0.9, 1H, C_5H_5N), 7.19 (dd, J = 8.3, 2.1, 1H), 7.02 (ddd, J = 7.2, 5.6, 1.3, 1H), 7.01 (d, J = 2.19, 1H), 6.84 (ddd, J = 7.3, 5.9, 1.4, 1H), 6.82 (ddd, J = 7.3, 5.9, 1.4, 1H), 6.53–6.41 (m, 2H), 5.99 (dd, J = 7.5, 2.4, 1H), 5.81 (dd, J = 9.1, 2.4, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 179.38 (1C, $C_{quat.}$), 178.16 (1C, C_{quat}), 167.20 (1C, C_{quat}), 166.77 (d, J = 7.9, 1C, C_{quat}), 164.65 (d, J = 7.1, 1C, C_{quat}), 164.49 (dd, J = 10.0, J = 257, 1C, C_{quat}), 163.85 (dd, J = 12.5, J = 252, 1C, $C_{quat.}$), 162.23 (dd, J = 10.8, J = 261, 1C, $C_{quat.}$), 161.87 (d, J = 6.4, 1C, C_{quat}), 161.69 (dd, J = 13.1, J = 257, 1C, $C_{quat.}$), 153.14 (1C, CH), 150.91 (1C, CH), 147.64 (1C, CH), 143.71 (1C, C_{quat}), 139.61 (1C, CH), 137.21 (1C, CH), 136.73 (1C, CH), 135.49 (1C, CH), 127.84 (1C, C_{quat}), 126.84 (1C, $C_{quat.}$), 126.37 (1C, $C_{quat.}$), 126.04 (1C, CH), 125.08 (1C, CH), 122.89 (1C, CH), 122.87 (d, J = 20.3, 1C, CH), 122.8 (d, J = 21, 1C, CH), 122.38 (1C, CH), 121.50 (1C, CH), 119.51 (1C, CH), 113.65 (d, J = 14.1, 1.9, 1C, CH), 111.99 (d, J = 16.5, 2.1, 1C, CH), 97.56 (pst, J = 27.2, 1C, CH), 95.80 (pst, J = 27.1, 1C, CH). Elemental analysis: calculated for $C_{33}H_{19}BrF_4IrN_3{\cdot}3C_3H_6O$: C, 51.48; H, 3.81; N, 4.29. Found: C, 51.57; H, 3.55; N, 4.52. Exact mass (EI) – 806.0393 for $[M + H]^+$ with (^{193}Ir)(^{79}Br).

[Ir((5-bromo-2-pyridyl)phenyl)$_2$(L)] L = acac (F-acac); ppy (F-ppy); Fppy (F-Fppy); (5-bromo-2-pyridyl)phenyl (J). [Ir((5-bromo-2-pyridyl)phenyl)$_2$Cl]$_2$, **E** (0.150 g, 0.108 mmol) and AgOTf (0.084 g, 0.324 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 the corresponding ligand acetylacetone, 2-phenylpyridine, 2-(2,4-difluorophenyl)-pyridine or 2-(4-bromophenyl)pyridine (0.432 mmol) and triethylamine (0.113 mL, 0.810 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.

[Ir((5-bromo-2-pyridyl)phenyl)$_2$(acac)] F-acac. Purification by column chromatography: alumina/CH_2Cl_2 (R_f **F-acac** = 0.6). It was obtained as a yellow powder. 0.131 g, 80% yield.

Spectroscopic data are in agreement with the ones previously published for this compound.[67,85]

[Ir((5-bromo-2-pyridyl)phenyl)$_2$(ppy)], F-ppy. Purification by column chromatography: silica/CH_2Cl_2–hexane 5 : 1 (R_f **F-ppy** = 0.7). It was obtained as a yellow powder. 0.105 g, 60% yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.08 (dd, J = 5.8, 0.9, 1H), 7.98–7.92 (m, 2H), 7.78 (m, 3H), 7.71–7.50 (m, 6H), 7.17 (dd, J = 8.3, 2.1, 1H), 7.10 (dd, J = 8.3, 2.0, 1H), 7.04–6.92 (m, 4H), 6.81 (ddd, J = 7.4, 1.4, 2H), 6.79 (ddd, J = 7.4, 1.4, 2H), 6.69 (d, J = 2.0, 1H), 6.52 (d, J = 2.0, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 178.34 (1C, $C_{quat.}$), 175.75 (1C, $C_{quat.}$), 169.74 (1C, $C_{quat.}$), 168.76 (1C, $C_{quat.}$), 167.23 (1C, $C_{quat.}$), 161.56 (1C, $C_{quat.}$), 153.57 (1C, CH), 151.58 (1C, CH), 148.24 (1C, CH), 145.50 (1C, $C_{quat.}$), 144.00 (1C, $C_{quat.}$), 141.89 (1C, $C_{quat.}$), 138.23 (1C, CH), 137.26 (1C, CH), 136.43 (1C, CH), 135.57 (1C, CH), 135.05 (1C, CH), 133.28 (1C, CH), 130.58 (1C, CH), 127.20 (1C, C_{quat}), 126.26 (1C, CH), 125.56 (1C, $C_{quat.}$), 125.85 (1C, CH), 124.72 (1C, CH), 124.69 (1C, CH), 122.99 (1C, CH), 122.86 (1C, CH), 122.66 (1C, CH), 122.24 (1C, CH), 122.07 (1C, CH), 119.58 (1C, CH), 119.40 (1C, CH), 119.17 (1C, CH). Elemental analysis: calculated for $C_{33}H_{22}Br_2IrN_3{\cdot}C_6H_{14}$: C, 57.19; H, 6.02; N, 3.92. Found: C, 57.20; H, 6.11; N, 3.77. Exact mass (MALDI) – m/z: 810.9785 for $[M]^+$ with (^{193}Ir)(^{79}Br).

[Ir((5-bromo-2-pyridyl)phenyl)$_2$(Fppy)], F-Fppy. Purification by column chromatography: silica/CH_2Cl_2 (R_f **F-Fppy** = 0.9). It was obtained as a yellow powder. 0.110 g, 60% yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.36 (ddd, $^5J_{F-H}$ = 1.7, J = 8.3, 1.0, 1H), 8.04 (brdd, J = 5.8, 1.4, 1H), 7.98 (brdd, J = 5.5, 1.6, 1H), 7.82 (d, J = 8.1, 2H), 7.74–7.68 (brddd, J = 8.3, 7.3, 1.6, 1H), 7.67–7.51 (m, 5H), 7.18 (dd, J = 8.3, 2.1, 1H), 7.11 (dd, J = 8.3, 2.0, 1H), 6.97 (ddd, J = 7.1, 5.6, 1.2, 1H), 6.88 (ddd, J = 7.3, 5.9, 1.4, 1H), 6.84 (ddd, J = 7.3, 5.9, 1.4, 1H), 6.63 (d, J = 2.0, 1H), 6.49–6.37 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 182.15 (1C, $C_{quat.}$), 176.10 (1C, $C_{quat.}$), 169.15 (1C, $C_{quat.}$), 166.89 (1C, $C_{quat.}$), 164.94 (d, J = 7.6, 1C, $C_{quat.}$), 164.16 (dd, J = 9.1, J = 258, 1C, $C_{quat.}$), 162.48 (dd, J = 10.6, J = 262, 1C, $C_{quat.}$), 160.19 (1C, $C_{quat.}$), 153.04 (1C, CH), 151.33 (1C, CH), 147.85 (1C, CH), 143.43 (1C, $C_{quat.}$), 141.52 (1C, $C_{quat.}$), 137.42 (1C, CH), 136.42 (1C, CH), 135.24 (1C, CH), 135.06 (1C, CH), 132.95 (1C, CH), 128.42 (1C, $C_{quat.}$), 126.80 (1C, $C_{quat.}$), 126.00 (1C, CH), 125.67 (1C, CH), 125.40 (1C, $C_{quat.}$), 124.62 (1C, CH), 123.38 (d, J = 21.7, 1C, CH), 122.93 (1C, CH), 122.85 (1C, CH), 122.48 (1C, CH), 122.02 (1C, CH), 119.27 (1C, CH), 119.04 (1C, CH), 118.63 (d, J = 13.7, 2.0, 1C, CH), 97.85 (pst, J = 27.5, 1C, CH, $C_6H_2F_2$). Elemental analysis: calculated for $C_{33}H_{20}Br_2F_2IrN_3{\cdot}CH_2Cl_2$: C, 43.75; H, 2.38; N, 4.50. Found: C, 43.92; H, 1.98; N, 4.28. Exact mass (MALDI) – m/z: 846.9603 for $[M]^+$ with (^{193}Ir)(^{79}Br).

[Ir((5-bromo-2-pyridyl)phenyl)$_3$], H. Purification by column chromatography: silica/CH_2Cl_2 (R_f **H** = 0.9). It was obtained as a yellow powder. 0.116 g, 60% yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.09 (dd, J = 5.8, 0.9, 1H), 7.91 (m, 2H), 7.81 (m, 2H), 7.71–7.50 (m, 7H), 7.16 (dd, J = 8.3, 2.0, 2H), 7.10 (dd, J = 8.3, 1.9, 1H), 7.00 (d, J = 2.0, 1H), 6.98 (ddd, J = 7.1, J = 5.4, J = 1.4, 1H), 6.86 (ddd, J = 7.3, 5.9, 1.4, 1H), 6.80 (ddd, J = 7.3, 5.9, 1.4, 1H), 6.64 (d, J = 2.0, 1H), 6.46 (d, J = 1.9, 1H).^{13}C NMR (75 MHz, $CDCl_3$): δ 178.82 (1C, $C_{quat.}$), 176.43 (1C, $C_{quat.}$), 169.09 (1C, $C_{quat.}$), 167.31 (1C, $C_{quat.}$), 166.82 (1C, $C_{quat.}$), 159.86 (1C, $C_{quat.}$), 153.22 (1C, CH), 151.16 (1C, CH), 147.72 (1C, CH), 143.87 (1C, $C_{quat.}$), 143.47 (1C, $C_{quat.}$), 141.33 (1C, $C_{quat.}$), 139.79 (1C, CH), 136.98 (1C, CH), 136.22 (1C, CH), 135.02 (1C, CH), 134.96 (1C, CH), 132.79 (1C, CH), 126.73 (1C, $C_{quat.}$), 126.69 (1C, $C_{quat.}$), 125.27 (1C, $C_{quat.}$), 125.92 (1C, CH), 125.87 (1C, CH), 125.62 (1C, CH), 125.28 (1C, 1C$_{quat.}$), 124.87 (1C, CH), 124.46 (1C, CH), 122.75 (2C, CH), 122.71 (1C, CH), 121.83 (1C, CH), 119.33 (1C, CH), 119.08 (1C, CH), 118.96 (1C, CH). Elemental analysis: calculated for $C_{33}H_{21}Br_3IrN_3{\cdot}3C_3H_6O$: C, 47.33; H, 3.69; N, 3.94. Found: C, 47.26; H, 3.36; N, 4.04. Exact mass (EI) – m/z: 889.8982 for $[M + H]^+$ with (^{193}Ir)(^{79}Br).

[Ir(ppy)$_2$4], A4. [Ir(ppy)$_2$((5-bromo-2-pyridyl)phenyl)], **C** (0.100 g, 0.136 mmol) was dissolved in 4 mL of degassed THF. To this mixture, (*E*)-4-azophenylboronic acid pinacol ester (**f**) (0.046 mg, 0.150 mmol), $Pd(PPh_3)_4$ (2 mol%, 3.143 mg, 0.003 mmol), and Na_2CO_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 (R_f = 0.8), obtaining 0.097 g (yield 85%) as an orange powder. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.22 (dd, J = 5.7, 0.8, 1H), 8.01–7.83 (m, 9H), 7.76–7.67 (m, 4H), 7.62–7.49 (m, 7H), 7.36 (dd, J = 8.1, 2.0, 1H), 7.31 (d, J = 1.9, 1H), 7.00–6.99 (m, 2H), 6.97–6.86 (m, 3H), 6.80–6.74 (m, 2H), 6.71–6.69 (m, 1H), 6.53 (dd, J = 7.1, 1.4 1H). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 177.29 (1C, $C_{quat.}$), 173.91 (1C, $C_{quat.}$), 169.67 (1C, $C_{quat.}$), 167.09 (1C, $C_{quat.}$), 167.04 (1C, $C_{quat.}$), 158.34 (1C, $C_{quat.}$), 152.45 (1C, CH), 152.03 (1C, $C_{quat.}$), 150.65 (1C, $C_{quat.}$), 150.53 (1C, CH), 147.15 (1C, CH), 145.15 (1C, $C_{quat.}$), 144.19 (1C, $C_{quat.}$), 144.05 (1C, $C_{quat.}$), 141.67 (1C, $C_{quat.}$), 139.37 (1C, $C_{quat.}$), 135.99 (1C, CH), 135.15 (1C, CH) 135.02 (1C, CH), 133.62 (1C, CH), 131.89 (1C, CH), 130.07 (1C, CH), 129.73 (1C, CH), 129.11 (1C, CH), 128.90 (1C, CH), 128.32 (2C, CH), 126.75 (2C, CH), 123.84 (1C, CH), 123.47 (1C, CH), 123.33 (1C, CH), 122.28 (2C, CH), 121.94 (2C, CH), 121.83 (1C, CH), 121.44 (1C, CH), 120.68 (1C, CH), 120.25 (1C, CH), 119.71 (1C, CH), 118.69 (1C, CH), 118.31 (1C, CH), 118.01 (1C, CH), 117.79 (1C, CH). Elemental analysis: calculated for $C_{45}H_{32}IrN_5{\cdot}1.5C_3H_6O$: C, 64.48; H, 4.48; N, 7.59. Found: C, 63.97; H, 4.08; N, 7.72 Exact mass (MALDI) – m/z: 835.2299 for $[M]^+$ with (^{193}Ir).

[Ir(Fppy)$_2$4], B4. [Ir(Fppy)$_2$((5-bromo-2-pyridyl)phenyl)], **D** (0.100 g, 0.124 mmol) was dissolved in 4 mL of degassed THF. To this mixture, (*E*)-4-azophenylboronic acid pinacol ester (**f**) (0.042 mg, 0.137 mmol), $Pd(PPh_3)_4$ (2 mol%, 2.867 mg, 0.002 mmol), and Na_2CO_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 (R_f = 0.8), obtaining 0.099 g (yield 88%) as an orange powder.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.30–8.24 (m, 2H), 8.21 (dd, J = 5.8, 1.1, 1H), 8.03 (d, J = 8.1, 1H), 7.98–7.92 (m, 5H), 7.87 (d, J = 8.2, 1H), 7.74 (td, J = 7.6, 1.7, 1H), 7.65–7.52 (m, 8H), 7.39 (dd, J = 8.1, 2.0, 1H), 7.26 (d, J = 1.9, 1H), 7.02 (ddd, J = 7.1, 5.6, 1.1, 1H), 6.83 (ddd, J = 7.2, 5.7, 1.4, 1H), 6.81 (ddd, J = 7.2, 5.7, 1.4, 1H), 6.53–6.43 (m, 2H), 6.07 (dd, J = 7.5, 2.3, 1H), 5.90 (dd, J = 9.2, 2.3, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 180.48 (1C, J = 3.1, $C_{quat.}$), 175.49 (1C, $C_{quat.}$), 167.73 (1C, $C_{quat.}$), 166.99 (d, J = 8.0, 1C, $C_{quat.}$), 164.74 (d, J = 7.2, 1C, $C_{quat.}$), 164.57 (dd, J = 9.6, J = 257, 1C, $C_{quat.}$), 163.93 (dd, J = 12.6, J = 253, 1C, $C_{quat.}$), 162.82 (d, J = 5.9, 1C, $C_{quat.}$), 162.67 (dd, J = 10.8, J = 262, 1C, $C_{quat.}$), 161.75 (dd, J = 13.1, J = 257, 1C, $C_{quat.}$), 153.23 (1C, CH), 152.84 (1C, $C_{quat.}$), 151.61 (1C, $C_{quat.}$), 150.99 (1C, CH), 147.76 (1C, CH), 145.10 (1C, $C_{quat.}$), 144.40 (1C, $C_{quat.}$), 140.85 (1C, $C_{quat.}$), 137.12 (1C, CH), 136.60 (1C, CH) 135.72 (1C, CH), 135.30 (1C, CH), 130.78 (1C, CH), 129.05 (2C, CH), 127.93 (1C, $C_{quat.}$), 127.65 (2C, CH), 126.46 (1C, $C_{quat.}$), 124.72 (1C, CH), 123.21 (2C, CH), 122.84 (d, J = 20.3, 1C, CH), 122.81 (2C, CH), 122.68 (1C, CH), 122.65 (d, J = 21, 1C, CH), 122.30 (1C, CH), 121.53 (1C, CH), 121.11 (1C, CH), 119.56 (1C, CH), 113.74 (d, J = 14.0, 1.6, 1C, CH), 111.98 (d, J = 16.0, 1.7, 1C, CH), 97.46 (pst, J = 27.4, 1C, CH), 95.52 (pst, J = 27.2, 1C, CH). Elemental analysis: calculated for $C_{45}H_{28}F_4IrN_5{\cdot}2CH_2Cl_2$: C, 52.42; H,

3.00; N, 6.50. Found: C, 52.18; H, 2.49; N, 6.43. Exact mass (MALDI) – *m*/*z*: 907.1906 for $[M]^+$ with (^{193}Ir).

[Ir(4)$_2$(ppy)], G-ppy. [Ir((5-bromo-2-pyridyl)phenyl)$_2$(ppy)], **F-ppy** (0.100 g, 0.123 mmol) was dissolved in 4 mL of degassed THF. To this mixture, (*E*)-4-azophenylboronic acid pinacol ester (**f**) (0.080 mg, 0.258 mmol), $Pd(PPh_3)_4$ (2 mol%, 2.843 mg, 0.002 mmol), and Na_2CO_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 dark-orange powder (0.110 g, 80%) is highly insoluble in all the solvents assayed (*i.e.* solubility is less than 3 mg in 10 mL of $CDCl_3$). A small sample (5 mg) was purified by column chromatography (alumina) eluting with dichloromethane (R_f = 0.8). The ^{1}H-NMR of the eluted compound is virtually identical to the one of unpurified sample, the colour being much brighter tough. The low solubility hampered complete NMR characterization. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.24 (dd, *J* = 5.8, 1.1, 1H), 8.06 (dd, *J* = 5.7, 1.1, 1H), 8.00 (dd, *J* = 8.3, 1.2, 1H), 7.96–7.89 (m, 7H), 7.85–7.78 (m, 3H), 7.75–7.48 (m, 16H), 7.36 (dd, *J* = 8.1, 2.0, 1H), 7.27 (dd, *J* = 8.1, 1.9, 1H), 7.09–6.94 (m, 6H), 6.86–6.79 (m, 3H). Elemental analysis: calculated for $C_{57}H_{40}IrN_7{\cdot}2C_3H_6O$: C, 66.88; H, 4.63; N, 8.67. Found: C, 66.20; H, 4.06; N, 8.28. Exact mass (MALDI) – *m*/*z*: 1015.2990 for $[M]^+$ with (^{193}Ir).

[Ir(4)$_2$(Fppy)], G-Fppy. [Ir((5-bromo-2-pyridyl)phenyl)$_2$(Fppy)], **F-Fppy** (0.100 g, 0.118 mmol) was dissolved in 4 mL of degassed THF. To this mixture, (*E*)-4-azophenylboronic acid pinacol ester (**f**) (0.076 mg, 0.247 mmol), $Pd(PPh_3)_4$ (2 mol%, 2.727 mg, 0.002 mmol), and Na_2CO_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 orange powder (0.111 g, 90%) is highly insoluble in all the solvents assayed (*i.e.* solubility is less than 1.5 mg in 10 mL of $CDCl_3$). A small sample (5 mg) was purified by column chromatography (alumina) eluting with dichloromethane (R_f = 0.8). The ^{1}H-NMR of the eluted compound is virtually identical to the one of impure sample, the colour being much brighter tough. Its low solubility hampered ^{13}C-NMR characterization. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.42–8.38 (m, 1H), 8.19 (dd, *J* = 5.6, 0.7, 1H), 8.12–8.09 (m, 1H), 7.95–7.89 (m, 7H), 7.83 (d, *J* = 8.1, 1H), 7.78 (d, *J* = 8.8, 1H), 7.74–7.46 (m, 14H), 7.36 (dd, *J* = 8.2, 2.0, 1H), 7.27 (dd, *J* = 8.1, 1.9, 1H, 1H), 6.99–6.83 (m, 5H), 6.75 (d, *J* = 1.7, 1H), 6.55–6.41 (m, 4H). Elemental analysis: calculated for $C_{57}H_{38}F_2IrN_7$: C, 65.13; H, 3.64; N, 9.33. Found: C, 64.75; H, 3.456; N, 8.816. Exact mass (MALDI) – *m*/*z*: 1051.2782 for $[M]^+$ with (^{193}Ir).

[Ir(4)$_2$(acac)], G-acac. [Ir((5-bromo-2-pyridyl)phenyl)$_2$(acac)], **F-acac** (0.100 g, 0.132 mmol) was dissolved in 4 mL of degassed THF. To this mixture, (*E*)-4-azophenylboronic acid pinacol ester (**f**) (0.085 mg, 0.277 mmol), $Pd(PPh_3)_4$ (2 mol%, 3.051 mg, 0.003 mmol), and Na_2CO_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 (alumina) eluting with dichloromethane (R_f = 0.4), obtaining 0.101 g (yield 80%) as an orange powder.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.64 (dd, *J* = 5.7, 0.8, 2H), 7.97–7.79 (m, 12H), 7.67 (d, *J* = 8.1, 2H), 7.58–7.49 (m, 10H), 7.24 (ddd, *J* = 7.2, 5.8, 1.4, 2H), 7.18 (dd, *J* = 8.1, 1.7, 2H), 6.60 (d, *J* = 1.7, 2H), 5.31 (s, 1H), 1.87 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 184.76 (2C, $C_{quat.}$), 168.16 (2C, $C_{quat.}$), 152.80 (2C, $C_{quat.}$), 151.45 (2C, $C_{quat.}$), 148.32 (2C, CH), 147.76 (2C, $C_{quat.}$), 144.99 (2C, $C_{quat.}$), 144.46 (2C, $C_{quat.}$), 140.00 (2C, $C_{quat.}$), 137.02 (2C, CH), 131.43 (2C, CH), 130.75 (2C, CH), 129.04 (4C, CH), 127.74 (4C, CH), 124.10 (2C, CH), 122.94 (4C, CH), 122.75 (4C, CH), 121.62 (2C, CH), 120.27 (2C, CH), 118.71 (2C, CH), 100.54 (1C, CH, H), 28.77 (2C, CH_3, H). Elemental analysis: calculated for $C_{51}H_{39}IrN_6O_2$: C, 63.80; H, 4.09; N, 8.75. Found: C, 63.67; H, 4.11; N, 8.23. Exact mass (EI) – *m*/*z*: 960.2753 $(M)^+$ with (^{193}Ir).

[Ir(4)$_3$], I. [Ir((5-bromo-2-pyridyl)phenyl)$_3$], **H** (0.100 g, 0.112 mmol) was dissolved in 4 mL of degassed THF. To this mixture, (*E*)-4-azophenylboronic acid pinacol ester (**f**) (0.110 mg, 0.359 mmol), $Pd(PPh_3)_4$ (2 mol%, 2.588 mg, 0.002 mmol), and Na_2CO_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 (R_f = 0.8), obtaining 0.123 g (yield 82%) as an orange powder.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.31 (dd, *J* = 5.8, 0.9, 1H), 8.10 (dd, *J* = 5.4, 0.9, 1H), 8.03 (d, *J* = 8.3, 1H), 7.97–7.86 (m, 15H), 7.83 (d, *J* = 5.4, 1H), 7.79–7.77 (m, 2H), 7.70 (td, *J* = 7.32, 1.56, 1H), 7.65–7.49 (m, 17H), 7.41–7.35 (m, 3H), 7.30 (dd, *J* = 8.0, 1.8, 1H), 7.05 (d, *J* = 1.8, 1H), 6.99 (ddd, *J* = 6.9, 5.6, 0.9, 1H), 6.89 (d, *J* = 1.8, 1H), 6.88–6.81 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 177.69 (1C, $C_{quat.}$), 175.33 (1C, $C_{quat.}$), 170.09 (1C, $C_{quat.}$), 167.98 (1C, $C_{quat.}$), 167.58 (1C, $C_{quat.}$), 159.12 (1C, $C_{quat.}$), 153.43 (1C, CH), 152.81 (3C, $C_{quat.}$), 151.42 (3C, $C_{quat.}$), 151.42 (1C, CH), 148.00 (1C, CH), 145.62 (1C, $C_{quat.}$), 145.28 (1C, $C_{quat.}$), 145.18 (1C, $C_{quat.}$), 145.02 (1C, $C_{quat.}$), 144.59 (1C, $C_{quat.}$), 142.73 (1C, $C_{quat.}$), 140.79 (1C, $C_{quat.}$), 140.70 (1C, $C_{quat.}$), 140.23 (1C, $C_{quat.}$), 136.65 (1C, CH), 136.16 (1C, CH), 135.79 (1C, CH), 134.40 (1C, CH), 131.10 (1C, CH), 130.76 (1C, CH), 130.69 (2C, CH), 129.05 (1C, CH), 129.01 (6C, CH), 127.80 (2C, CH), 127.72 (2C, CH), 127.53 (2C, CH), 124.53 (1C, CH), 124.48 (1C, CH), 124.41 (1C, CH), 123.13 (2C, CH), 123.07 (2C, CH), 123.02 (2C, CH), 122.76 (6C, CH), 122.51 (1C, CH), 122.30 (1C, CH), 121.53 (1C, CH), 120.53 (1C, CH), 120.50 (1C, CH), 119.32 (1C, CH), 118.96 (1C, CH), 118.80 (2C, CH). Elemental

analysis: calculated for $C_{69}H_{48}IrN_9 \cdot 2C_3H_6O$: C, 68.68; H, 4.61; N, 9.61. Found: C, 68.88; H, 4.16; N, 9.68. Exact mass (MALDI) – *m*/*z*: 1195.3662 for $[M]^+$ with (^{193}Ir).

Conclusions

Twelve new triscyclometalated Ir(III) organometallic complexes containing up to three photoswitchable azobenzene units have been synthesized. In complexes derived from ligand **1**, the ligand acts as a neutral N–N donor coordinating through the pyridinic nitrogen and one of the nitrogen atoms of the azobenzene. Consequently, derivatives **B1′** and **A1′** are cationic compounds, containing twisted azobenzene units, in which the photoisomerization process of the azobenzene is inhibited. Analysis of the spectroscopic and electronic properties of complexes derived from ligands **2**, **3** and **4** compared to the well known $[Ir(ppy)_3]$ showed that in derivatives of ligand **2**, a strong electronic communication between the metal centre and the azobenzene unit is established. Probably this produces an additional stabilization of the *trans* form of the azobenzene responsible of the nearly undetectable photoisomerization process for derivatives **B2** and **A2**. Complexes incorporating ligands **3** or **4** behave as photochromic compounds with isomerization rates comparable to those reported for other azobenzene-containing organometallic complexes.[41,42] Currently, other photochromic derivatives of these ligands are being synthesized in our laboratory.

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Notes and references

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