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Iridium(III) Complexes with Sulfonyl and Fluorine Substituents: Synthesis, Stereochemistry and Effect of Functionalisation on their Photophysical Properties

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This paper is dedicated to Professor Jan Reedijk on the occasion of his 65th birthday

Abstract: The synthesis and photophysical and electrochemical characterisation of new heteroleptic iridium complexes with electron-withdrawing sulfonyl groups and fluorine atoms bound to phenylpyridine ligands are reported. The emission energy of these materials strongly depends on the position of the sulfonyl groups and on the number of fluorine substituents. A 90 nm wide tuning range of photoluminescence from the blue-green ($\lambda_{em}=468$ nm) of iridium(III)bis[2-(4′-benzylsulfonyl)-phenylpyridinato-N,C2′][3-(pentafluorophenyl)-pyridin-2-yl-1,2,4-triazolate] to the orange ($\lambda_{em}=558$ nm) of iridium(III)bis[2-(3′-benzylsulfonyl)phenylpyridinato-N,C2′](2,4-decanedionate) has been achieved. Emission quantum yields ranging from 47 to 71% have also been found for degassed solutions of the complexes, and a surprisingly high value of 16% was recorded for iridium(III)bis[2-(5′-benzylsulfonyl-3′,6′-difluoro)phenylpyridinato-*N*,*C2*′](2,4-decanedionate) in air-equilibrated dichloromethane. A unusual stereochemistry of the benzylsulfonyl-substituted dimer and heteroleptic complexes has been detected by ^{1}H NMR spectroscopy, and is characterised by the mutual *cis* disposition of the pyridyl nitrogen atoms of the phenylpyridine ligands, which differs from the most common *trans* arrangement reported in the literature.

Keywords: fluorine · iridium · luminescence · phenylpyridines · stereochemistry · sulfonyl derivatives

Introduction

Recently, cyclometalated iridium(III) complexes have emerged as a very interesting class of compounds for various applications. They can be used as biological labelling reagents,[1] photoreductants,[2] singlet oxygen sensitisers[3] and metal-cation sensing phosphorescent agents,[4] and they represent, up to now, the most promising phosphorescent dopants for organic light-emitting diodes (OLEDs)[5] because of their relatively short excited-state lifetime, high photoluminescence efficiency and excellent colour tunability. The tunability of the emission colour is particularly interesting for applications in photonics and optoelectronics, such as flat-panel displays and lighting sources. In this context, heteroleptic iridium complexes [Ir(C^N)$_2$(LX)] are very promising phosphors because, in addition to their easy synthetic accessibility compared with the corresponding homoleptic [Ir(C^N)$_3$] materials, they allow fine-tuning of the emission colour by appropriate design of the chemical structure[6] of

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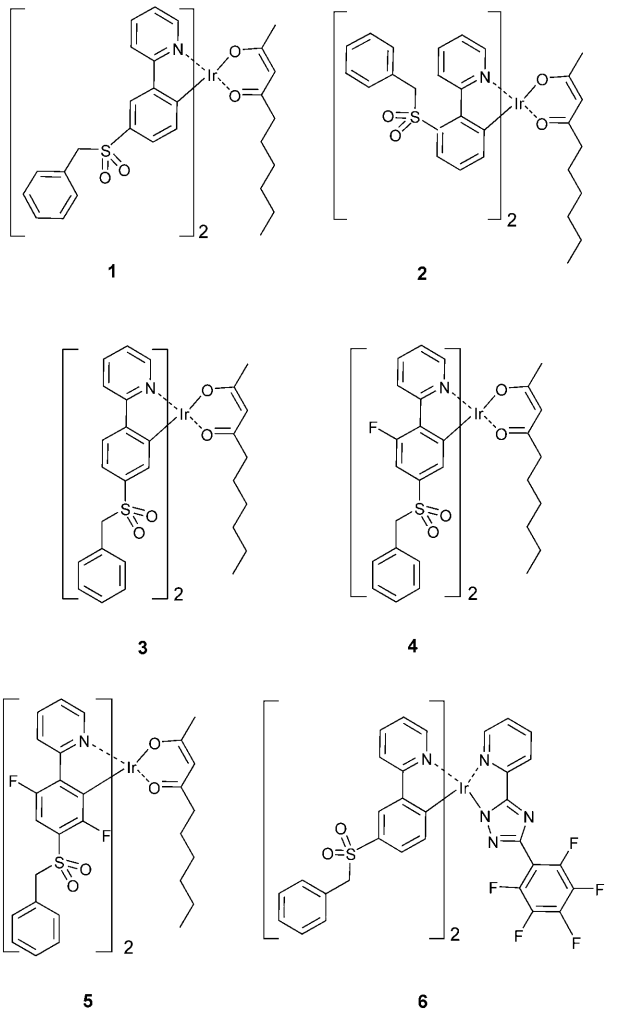
the cyclometalating ligands C^N, the most common being 2-phenylpyridine (ppy), or by systematic control of the nature[7] and position[8] of substituents on these ligands. The emission energies of $[Ir(C^N)_2(LX)]$ complexes are mainly determined by both C^N ligand- and metal-based orbitals, whereas the nature of the ancillary LX ligand plays, with few exceptions,[9] a secondary role in tuning the photophysical properties.

In the case of heteroleptic complexes that contain the 2-phenylpyridine ligand, $[Ir(LX)(ppy)_2]$, the highest occupied molecular orbital (HOMO) mainly comprises the iridium d orbitals and the phenyl π orbitals on the 2-phenylpyridines, and the lowest unoccupied molecular orbital (LUMO) is mainly comprised of the π* orbitals on the pyridyl rings.[6e] Therefore, the functionalisation of phenylpyridine ligands with electron-donating or -withdrawing groups results in significant changes in the HOMO–LUMO energy gap and, as a consequence, fine-tuning of the emission energy of iridium complexes in the visible spectral region. In particular, much effort has been devoted to the design and synthesis of blue-emitting iridium phosphors that also have high emission quantum yields and good stability for applications in phosphorescent organic light-emitting devices (PHOLEDs).[10] Moreover, the synthesis of efficient "deep blue" emitters represents a very important step towards the creation of white-light-emitting diodes (WOLEDs).[11]

The introduction of electron-withdrawing substituents to the phenyl rings of ppy ligands represents a convenient structural modification that leads to $[Ir(LX)(ppy)_2]$ complexes with blueshifted emissions (increased HOMO–LUMO energy gap) by decreasing the HOMO energy while keeping the LUMO level relatively unchanged. The electron-withdrawing groups used so far have been fluorine atoms[7,10] and, in few cases, trifluoromethyl[7f–h] or pentafluorophenyl,[8c] acetyl or cyano[12] groups, whereas the effect of alternative substituents, such as sulfonyl groups, still remains almost completely unexplored.[13]

Herein, we report the synthesis, photophysical and electrochemical characterisation of a new series of heteroleptic $[Ir(C^N)_2(LX)]$ complexes with an electron-withdrawing benzylsulfonyl group on the C^N ligands and 2,4-decandionate as the third ancillary ligand LX, which was introduced in place of the more common acetylacetonate to improve the solubility of these compounds. In particular, we have developed a straightforward and general synthetic protocol for the preparation of 2-phenylpyridines with a benzylsulfonyl group in different positions on the phenyl rings. This methodology has also been extended to the simultaneous functionalisation of the ligands with sulfonyl and fluorine substituents, to evaluate the combined effect of these electron-withdrawing groups on the photophysical properties of the resulting iridium complexes. We found that the emission energy of these compounds strongly depends on both the position of sulfonyl groups and the number of fluorine atoms in the ligands, and this resulted in a wide tuning of photoluminescence from blue-green ($\lambda_{em}=498$ nm for iridium(III)bis[2-(4′-benzylsulfonyl)phenylpyridinato-N,C2′](2,4-decanedionate) **1**, Scheme 1) to orange ($\lambda_{max}=558$ nm for iridium(III)bis[2-(3′-benzylsulfonyl)phenylpyridinato-N,C2′](2,4-decanedionate) **2**, Scheme 1).



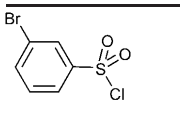
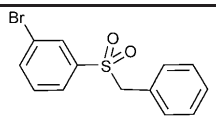
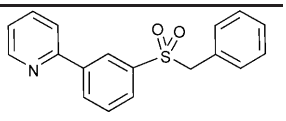
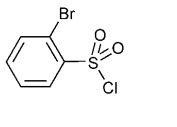
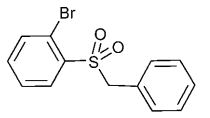
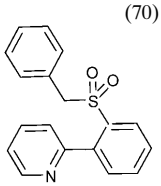
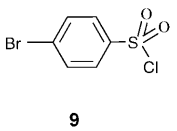
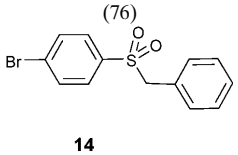
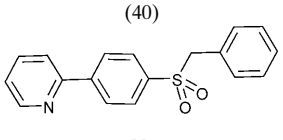
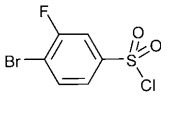
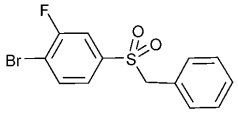
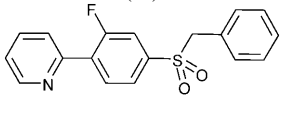
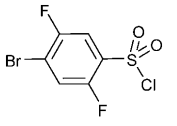
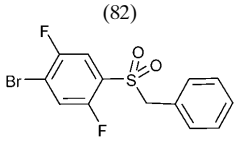
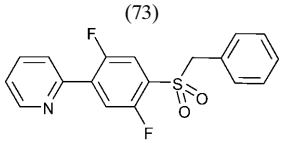
Scheme 1. Schematic formulas and numbering of the synthesised iridium complexes.

To the best of our knowledge, such a wide shift in the emission energy that is solely due to the position of the electron-withdrawing benzylsulfonyl substituent on the cyclometalating ligand has never been observed before. The functionalisation of phenylpyridines with other substituents, such as fluorine atoms,[8a] pentafluorophenyl rings[8c] or methyl groups[8d] in different positions in the cyclometalating ligands, has been reported to tune photoluminescence wavelength, but only to a lesser extent. Moreover, we have shown that by replacing the 2,4-decandionate ancillary ligand with the 2-[5-(perfluorophenyl)-2*H*-1,2,4-triazol-3-yl]-pyridine ligand,[10a] a further blueshift in the emission energy can be attained.

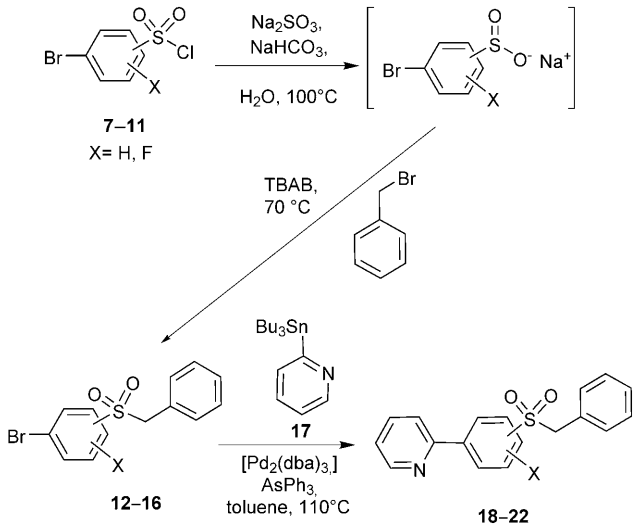
Results and Discussion

Synthesis of ligands and complexes: Cyclometalating ligands **18–22** (Table 1) were synthesised by using the general procedure shown in Scheme 2. Following a synthetic route for

Table 1. Cyclometalating ligands **18–22** with the corresponding benzylphenyl sulfones (**12–16**) and sulfonyl chlorides (**7–11**).

7–11	12–16 (Yield [%])	18–22 (Yield [%])
		
7	**12** (63)	**18** (70)
		
8	**13** (76)	**19** (40)
		
9	**14** (74)	**20** (71)
		
10	**15** (82)	**21** (73)
		
11	**16** (70)	**22** (78)

chloromethylsulfones reported in the literature,[14] functionalised phenylbenzylsulfones **12–16** were prepared by using a one-pot procedure that involved the reaction of a series of commercially available sulfonyl chlorides **7–11** (Table 1) with sodium sulfite and sodium hydrogen carbonate in water at 100 °C for three hours. This was followed by nucleophilic substitution of the resulting sulfinate intermediate salts with benzylbromide in the presence of tetra-*N*-butyl ammonium bromide as the phase-transfer catalyst. Finally, cyclometalating ligands **18–22** were synthesised in good yields by a Stille cross-coupling reaction of the isolated bromophenyl benzyl sulfones **12–16** with tributyl(pyridin-2-yl)-stannane **17** in toluene with $[Pd(AsPh_3)_4]$ as the catalyst, generated in situ.[15]



Scheme 2. General procedure for the synthesis of ligands **18–22**; dba = dibenzylideneacetone, TBAB = tetra-*N*-butyl ammonium bromide.

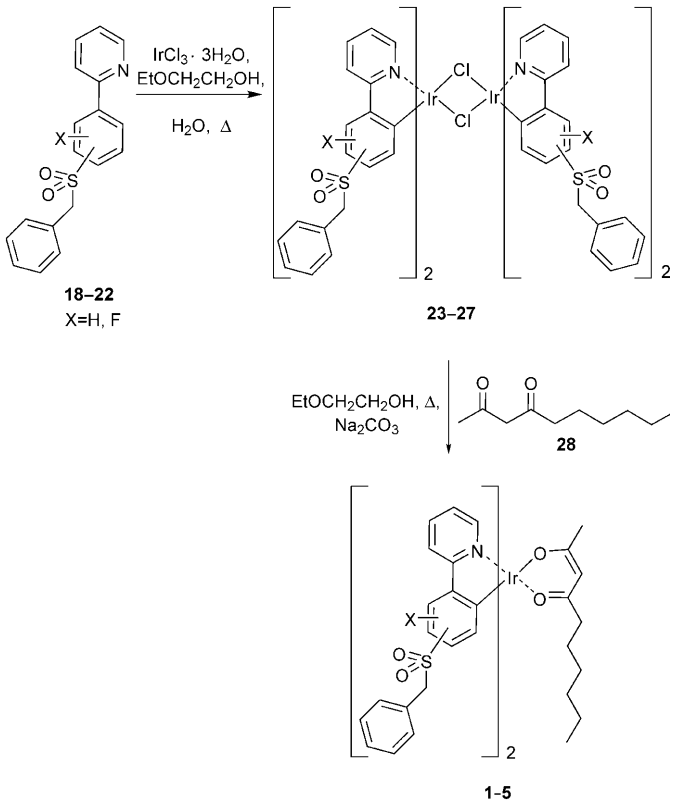
Substituted 2-phenylpyridines **18–22** were used in the synthesis of the novel heteroleptic iridium complexes **1–5** with the 2,4-decandione anion as the third ancillary ligand (Scheme 1). Complexes **1–5** were prepared by a two-step synthetic protocol that involved the preliminary synthesis of the corresponding dichloro-bridged dimer complexes **23–27**, and subsequent reaction of these intermediates with the anionic diketonate ligand derived from the deprotonation of 2,4-decandione **28** by sodium carbonate in ethoxyethanol (Scheme 3).

2,4-Decandione **28** was prepared by Claisen-type condensation of 2-octanone with ethyl acetate in the presence of sodium (Scheme 4) and it was selected as the ancillary ligand in place of the commonly used acetylacetone[6a] to improve the solubility of the resulting complexes. The synthesis of isomeric complexes **1**, **2** and **3**, characterised by the same β-diketonate ancillary ligand, allows the study of the effect of the position of the electron-withdrawing benzylsulfonyl substituent on the phenylpyridine ligands on the photophysical properties.

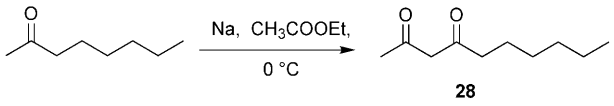
Furthermore, the synthesis of complexes **4** and **5**, enabled the photophysical investigation of the combined effects of the functionalisation of phenylpyridine ligands with two electron-withdrawing moieties, that is, benzylsulfonyl groups and fluorine atoms. In these complexes the β-diketonate ancillary ligand and the position of the benzylsulfonyl moiety were kept unchanged.

In the case of complex **6** (Scheme 1), 2-[5-(perfluorophenyl)-2*H*-1,2,4-triazol-3-yl]pyridine was used as the third ancillary ligand, which was synthesised according to the literature procedure.[10a] The reaction of 2-[5-(perfluorophenyl)-2*H*-1,2,4-triazol-3-yl]pyridine with iridium dimer complex **23** was performed under mild conditions and led to heteroleptic complex **6** in 60% yield (Scheme 5).

The synthesis of **6** allowed us to study the effect of the change of the ancillary ligand on the photophysical proper-



Scheme 3. General procedure for the synthesis of the iridium complexes **1**–**5**.



Scheme 4. Synthetic route to 2,4-decandione (**28**).

ties aiming to a further blue shift in photoluminescence and to more efficient emission colour tuning.

^{1}H NMR spectroscopic characterisation of iridium dimer complexes 23–27: Information on the stereochemistry of iridium dimer complexes **23–27** can be derived from the interpretation of their ^{1}H NMR spectra and from the comparison of these spectra with those recorded for the corresponding ligands **18–22**. Figure 1 shows the comparison between ligand **20** and the corresponding dimer complex **25**.

The ^{1}H NMR spectrum of **25** shows two distinct sets of resonances that correspond to two non-equivalent pairs of cyclometalated ligands present in the complex. This observation is quite unusual because the ^{1}H NMR spectra of all iridium dichloro-bridged dimer complexes reported in the literature[6a,b,16] show only one set of protonic resonances, due to the equivalence of the four ligands in their structure.

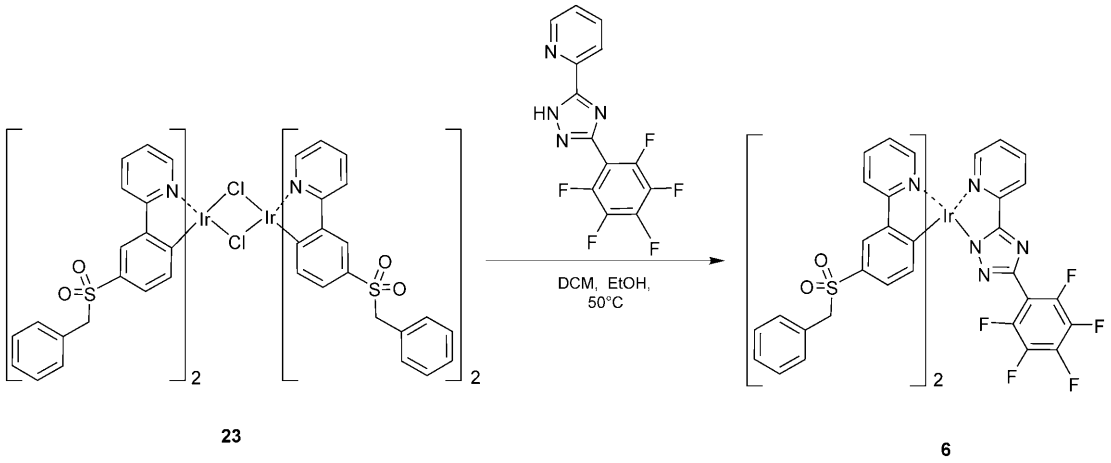
The presence of two sets of protonic signals here observed can be explained by assuming that the two cyclometalated ligands bound to each iridium ion are in a mutually *cis* disposition with respect to the nitrogen atoms, contrary to the *trans* arrangement reported in the literature (Scheme 6a).[6a,b,16] Furthermore, the ^{1}H NMR spectrum of **25** (Figure 1b) reveals that the two benzyl protons belonging to each non-equivalent ligand are diastereotopic because they have two distinct AB signals in the spectral range $\delta =$ 4.14–4.46 ppm.

This observation implies that dimer complex **25** is chiral and that it has been obtained as a racemic mixture of two enantiomers, which thus excludes any achiral *cis* arrangement and is in accordance with the two alternative chiral *cis* structures shown in Scheme 6b and c, and described in detail in Scheme 7.

As confirmed by the ^{1}H NMR spectra of **23–27** in the Experimental Section, the conclusion drawn from the spectroscopic analysis of **25** can be extended to the other iridium dimer complexes reported herein.

In agreement with their NMR spectra, the mutual *cis* disposition of the two phenylpyridine ligands is maintained in heteroleptic complexes **1–6** (Scheme 1).

Absorption and emission spectroscopy: Figure 2 shows the absorption spectra of all the complexes measured at



Scheme 5. Synthetic route for complex **6**.

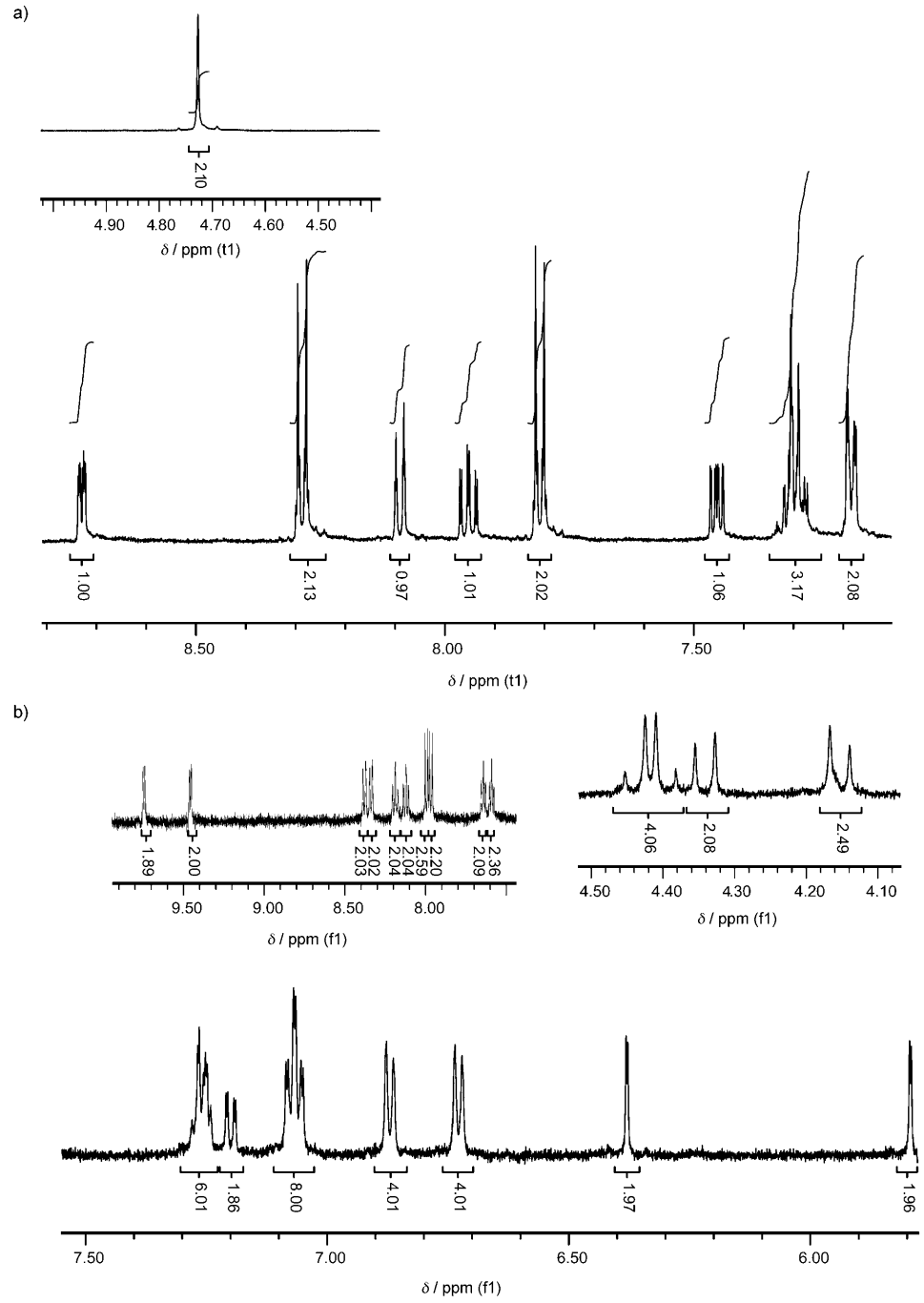


Figure 1. a) ^{1}H NMR spectrum of cyclometalating ligand **20** in [D$_6$]DMSO; b) ^{1}H NMR spectrum of dichloro-bridged dimer **25** in [D$_6$]DMSO.

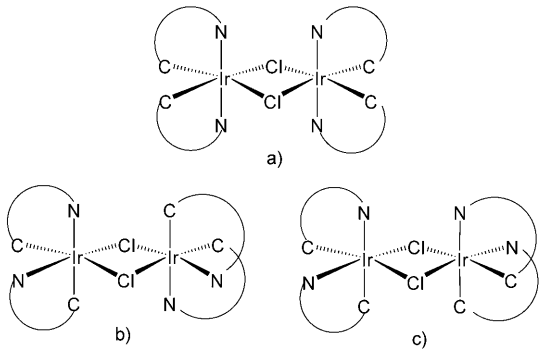
room temperature in dichloromethane solutions. All complexes display intense absorption bands in the UV ($\varepsilon =$ 20000–50000 $M^{-1}cm^{-1}$) and weaker absorption structures in the visible region ($\varepsilon = 700$–$6000\ M^{-1}cm^{-1}$), similar to those reported for other iridium complexes.[17,18]

The strong absorption bands in the UV region between $\lambda = 240$ and 340 nm are attributed to π–π* ligand-centred (LC) transitions. The weaker transitions observed at lower energies between $\lambda = 340$ and 530 nm can be ascribed to singlet and triplet metal-to-ligand charge transfer transitions (^{1,3}MLCT). All complexes with benzylsulfonyl substituents show similar features, with maxima at around $\lambda = 250$ and 280 nm and a shoulder at lower energy. Small shifts in the spectral shape can be attributed to the substitution pattern on the phenylpyridine. The absorption spectrum of complex **6** is similar to those previously reported for iridium complexes with triazole ligands.[10a]

Figure 3 shows the normalised emission spectra of complexes **1**–**6**, and all emission data are summarised in Table 2. All complexes are highly luminescent at room temperature in dichloromethane solutions, and their emission intensities are strongly affected by the presence of oxygen, which is known to be responsible for triplet-excited-state emission quenching.[18] The emission maxima cover a wide window of the visible spectrum between $\lambda =$ 468 and 560 nm, and the emission colours vary from blue to green and orange.

In addition, complexes that emit at lower energies, such as **2** and **3**, show broader and less structured bands if compared with, for example, **1** and **6**, which show more structured bands. According to previously reported work,[6a,19] ^{3}LC states normally give emission spectra with vibronic progressions, whereas ^{3}MLCT states give broader, featureless bands. In our case, the emission spectra measured at 298 K indicate that for complexes emitting at low energy, the emitting triplet excited state has a substantial ^{3}MLCT character, whereas on going to "bluer" emitting complexes, the contribution from the ^{3}MLCT state is diminished, as confirmed by the vibronic structures of **3** and **6**. The substitution of the phenylpyridine moiety with sulfonyl groups in different positions noticeably affects the emission colours.

For isomers **1**–**3**, a remarkable shift that depends on the substitution position of the sulfonyl group on the ppy ligand

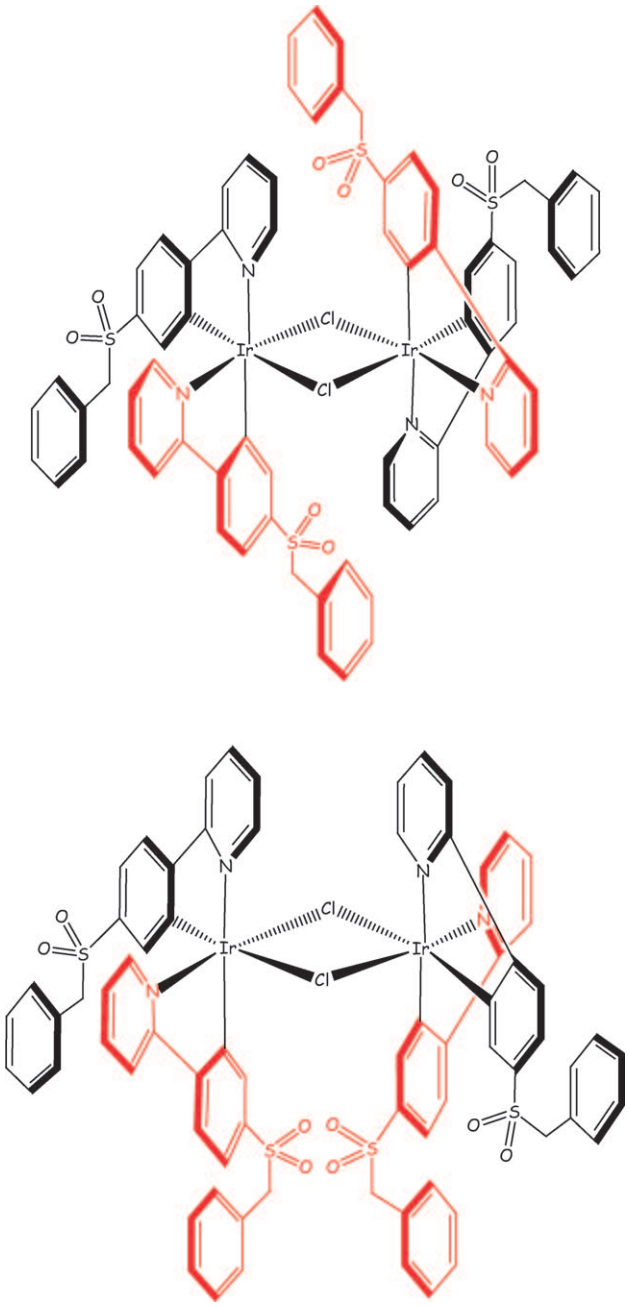


Scheme 6. Schematic representation of the stereochemistry of the dichloro-bridged iridium dimer complexes: a) *trans* arrangement reported in the literature;[6a,b,16] b and c) *cis* chiral arrangements.

is noted, with a trend that can be summarised as follows: If the benzylsulfonyl substituent is *ortho* to the pyridine ring, the complex shows the lowest energy emission ($\lambda = 558$ nm) of the whole series, which is also lower than that of [Ir(acac)(ppy)$_2$] ($\lambda_{max} = 516$ nm);[6b] if the sulfonyl moiety is *para* to the pyridine ring, a blueshift to $\lambda = 546$ nm is observed; and finally, if the benzylsulfonyl group is *meta* to the pyridine (*para* to the iridium), the bluest emission is observed at $\lambda = 498$ nm. Clearly, the sulfonyl unit has a destabilizing effect on the HOMO when it is *meta* to the iridium ion (causing a redshift), whereas a stabilizing effect is observed when the sulfonyl moiety is *para* to the iridium ion (blueshift). This was previously observed in similar systems with electron-withdrawing pentafluorophenyl (F_5Ph-) substituents.[8c]

This trend can be rationalised by taking into account the charge delocalisation on the SO_2-substituted phenyl ring. As reported earlier for similar compounds,[13b,d] the electron-withdrawing character of SO_2 manifests itself by reducing the electron density on the iridium centre, which induces a partial positive charge in the phenyl ring. For complexes **2** and **3**, the formal positive charge is mainly localised at the *ortho* and *para* positions with respect to the iridium core, and never resides on the carbon covalently bound to the iridium atom, whereas for **1** the charge mainly resides on the carbon directly bound to the iridium and on the *meta* position. This likely lowers the energy of the HOMO, and thus enhances the HOMO–LUMO gap and shifts the emission towards the blue region. This is supported by the oxidation potential measured for these complexes (see Table 2), as discussed later. It is worth noting that the emission maximum of **2** is blueshifted by 12 nm with respect to **3**, although for both these complexes the sulfonyl group is in the *meta* position; this difference can be attributed to a steric effect of the pyridine ring in the ppy ligand.

Addition of one (**4**) or two (**5**) fluorine atoms to the sulfonyl-substituted ppy ligands leads to a further blueshift compared with non-fluorinated analogue **3**. However, in comparison with the parent [Ir(acac)(ppy)$_2$], the hypsochromic shift induced by the electron-withdrawing fluorine atoms is negated by the bathochromic shift imposed by having the benzylsulfonyl group *meta* to the iridium, so the emission maximum of complex **5** ($\lambda_{max} = 515$ nm) is identical to that of [Ir(acac)(ppy)$_2$] ($\lambda_{max} = 516$ nm).[6b]



Scheme 7. Alternative *cis* chiral arrangements of the dichloro-bridged dimer **25**.

Finally, the emission of complex **1** could be further blueshifted by substituting the 2,4-decandionate ancillary ligand by a 2-[5-(perfluorophenyl)-2*H*-1,2,4-triazol-3-yl]pyridine to give complex **6**. This ligand was previously reported for other blue-emitting iridium complexes that displayed intense blue emission.[10a] In particular, **6** shows a 30 nm hypsochromic shift with respect to analogue **1**. This increase in emission energy on going from 2,4-decandionate to a triazole

Table 2. Emission spectral data and redox potentials for complexes **1–6**.[a]

		De-aerated		Aerated							
	λ_{max}[b] [nm]	Φ[c]	τ [μs]	Φ[c]	τ [μs]	k_r [10^5 s^{-1}]	k_{nr} [10^5 s^{-1}]	λ_{max}[b,d] [nm]	τ[d] [μs]	$E_{1/2}$(Red)[e,d] [V]	$E_{1/2}$(Ox)[e] [V]
1	498	0.68	1.5	0.05	0.11	4.53	2.13	484	4.8	−1.50[f]	0.76
2	558	0.47	2.3	0.07	0.29	2.04	2.30	535	8.7	−1.41[f]	0.69
3	546	0.71	2.7	0.08	0.26	2.62	1.07	533	7.6	−1.33[f]	0.67
4	533	0.62	2.7	0.09	0.37	2.29	1.40	523	7.2	−1.26[f]	0.77
5	515	0.65	3.0	0.16	0.56	2.16	1.16	502	6.9	−1.42[f]	0.98
6	468	0.55	2.0	0.08	0.28	2.75	2.25	460	3.6	−2.33[f]	1.04

[a] All data for complexes in CH_2Cl_2. [b] $\lambda_{ex}=350$ nm. [c] Quantum yields (Φ) are measured versus quinine bisulfate in 1 N H_2SO_4 ($\Phi=0.546$). [d] Recorded at 77 K in a butyronitrile matrix. [e] Recorded in nitrogen-equilibrated acetonitrile at RT. All data are displayed versus Fc/Fc^+. Scan rate: 100 mV s^{-1}. [f] Irreversible.

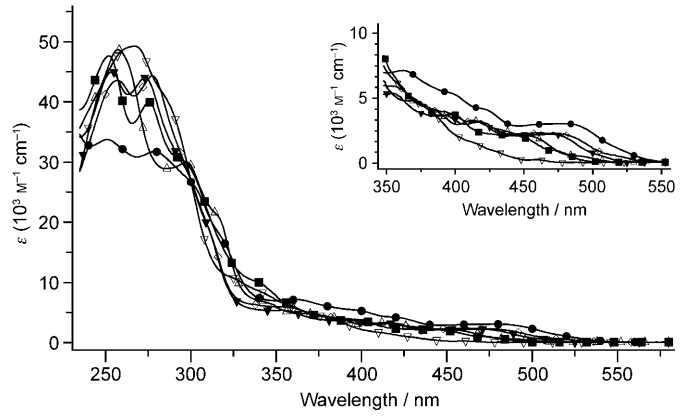


Figure 2. Absorption spectra of complexes **1–6** recorded in CH_2Cl_2 at RT. The inset shows a magnified view of the spectra between $\lambda=350$ and 550 nm. ◇: **1**, ■: **2**, ●: **3**, ▼: **4**, △: **5**, ▽: **6**.

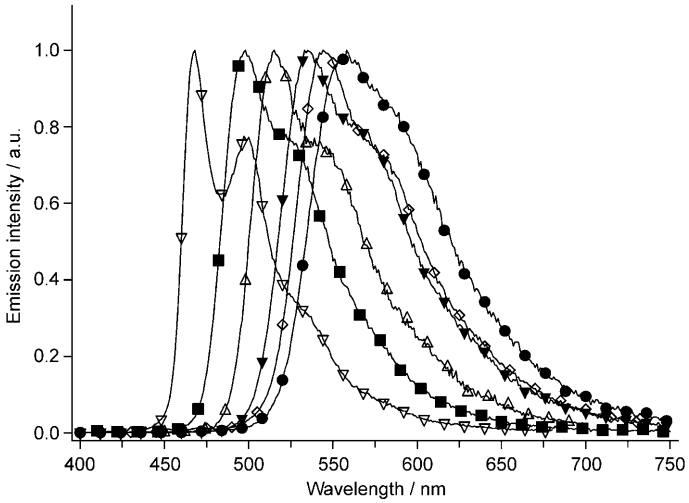


Figure 3. Normalised RT emission spectra of complexes **1–6** recorded in CH_2Cl_2 ($\lambda_{ex}=350$ nm). ◇: **1**, ■: **2**, ●: **3**, ▼: **4**, △: **5**, ▽: **6**.

ligand can be attributed to the higher σ-donating capability of the triazole,[20] which mainly results in increased stability of the HOMO, pushing it to lower energies and increasing the HOMO–LUMO gap. As already reported,[9b] this electron-donating effect induced by the ancillary ligand usually destabilises the ^{1}MLCT state and results in less ^{1}MLCT character mixed into the lowest-energy excited triplet state and leading to higher emission energies. This statement is in agreement with the fact that, as mentioned above, the emission spectra of **6** indicates an admixture of MLCT and LC states, with the latter being predominant.

All complexes also exhibit very high quantum yield values (Φ) between 40 and 70% in de-aerated conditions (Table 2). Interestingly, emission quantum yields measured for air-equilibrated solutions also show remarkably high values along the series. All complexes display values that are in general higher than those reported in the literature, which are typically below 5%.[18] Complex **5** has a quantum yield of 16% in aerated conditions, a value almost three times higher than expected, and, to the best of our knowledge, the highest reported in the literature for iridium complexes in the presence of oxygen. We believe that this unexpected behaviour could be related to a combination of several factors that more efficiently prevent oxygen quenching, such as steric hindrance around the iridium core, the presence of two F atoms known to have hydrophobic character,[10c] an electronic effect due to the simultaneous presence of two F atoms and a sulfonyl group, the position of the substituents on the ppy ligand or, more important, the lack of a thermally activated state responsible for the quenching of the emission at room temperature.

The excited-state lifetimes measured in de-aerated samples are in the microsecond range between 1.5 and 3 μs, and they are shortened in the presence of oxygen. However, we also observed abnormally long lifetimes for several of the complexes in the aerated solution. For example, complex **5** has an excited-state lifetime of 0.56 μs in air-equilibrated solutions, which is extraordinarily long for iridium emitters in the presence of dioxygen.

When frozen at 77 K in a butyronitrile glass matrix, the emission spectra of complexes **1–6** exhibit a typical rigidochromic shift toward higher energies (see Table 2 and Figure 4), which further indicates the partial ^{3}MLCT character of the excited state together with ^{3}LC character, as suggested by the structure of both emission spectra at 298 and 77 K (vide supra). The lifetimes for the complexes in the frozen matrices range between 3.6 and 8.7 μs and emission maxima span from $\lambda=460$ (**6**) to 535 nm (**2**).

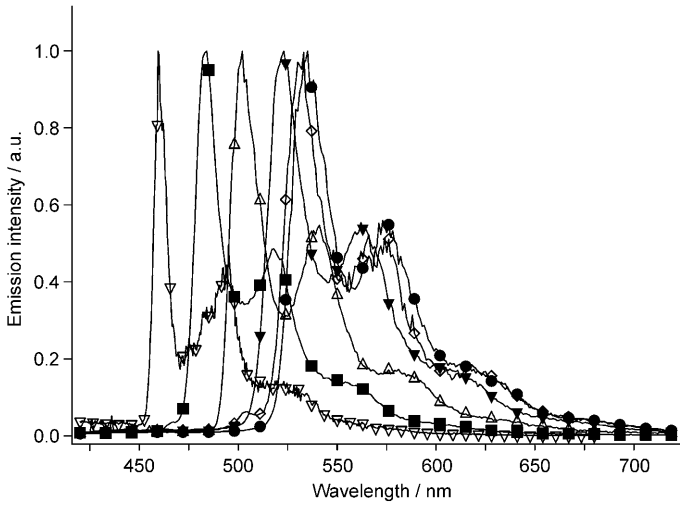


Figure 4. Normalised emission spectra of complexes **1**–**6** measured at 77 K ($\lambda_{ex}=350$ nm) in butyronitrile glass matrix. ◇: **1**, ■: **2**, ●: **3**, ▼: **4**, △: **5**, ▽: **6**.

Electrochemistry: The redox properties of complexes **1**–**6** were studied by cyclic voltammetry (CV) in acetonitrile solutions at room temperature. All the data were measured relative to an internal ferrocenium/ferrocene (Fc^+/Fc) reference. The results obtained are collected in Table 2. At a scan rate of 100 mV s^{-1}, all reduction processes are irreversible and the reported values are thus approximate, whereas the oxidation processes are all reversible and span a relatively wide potential range (0.67–1.04 V).

As anticipated above, the electron-withdrawing capabilities of the sulfonyl group likely manifest themselves in the oxidation potential values; in particular, looking at isomers **1**, **2** and **3**, the former exhibits an oxidation potential that is 70 and 90 mV higher than those of **2** and **3**, respectively. This is in agreement with the emission spectral shifts seen for these complexes, which were examined by considering the charge delocalisation on the SO_2-substituted phenyl (vide supra). Considering the chemical structure of **3** as the basic unit for **4** and **5** can be useful for understanding the electrochemical and photophysical data measured for such complexes. For **3**, the oxidation potential is 0.67 V, whereas for **4** and **5** it is 0.77 and 0.98 V, respectively, which implies that addition of one and two fluorine atoms onto the ppy phenyl ring further lowers the energy of the HOMO level of the iridium complex.

Finally, as expected, by replacing 2,4-decanedionate (**28**) with 2-[5-(perfluorophenyl)-2*H*-1,2,4-triazol-3-yl]pyridine, and thus increasing the ancillary ligand field strength, the oxidation potential on going from **1** to **6** is enhanced by about 300 mV. This once more clearly indicates that the ancillary triazole ligand has the effect of lowering the HOMO energy, which results in a more blue-emitting complex (Figure 3).

Conclusion

In summary, we have synthesised and characterised a new series of heteroleptic iridium complexes with benzylsulfonyl and fluorine substituents on the phenylpyridine ligands and 2,4-decandionate or perfluorophenylpyridinetriazolate as the ancillary ligand. We have demonstrated that functionalisation with two electron-withdrawing moieties, that is, the fluorine and benzylsulfonyl groups, leads to the ability to widely tune the photoluminescence from blue to orange, depending on the position in which these substituents are bound to the phenylpyridines. A further blueshift in emission is also induced by the choice of the third ancillary ligand. Surprisingly, a high emission quantum yield and lifetime have also been found in air-equilibrated solutions for heteroleptic complex **5**, which make it a good candidate for use in biomedical applications.[21]

Experimental Section

Spectroscopy: Absorption spectra were measured by using a Varian Cary 5000 double-beam UV/Vis/NIR spectrometer and baseline corrected. Steady-state emission spectra were recorded by using a HORIBA Jobin–Yvon IBH FL-322 Fluorolog 3 spectrometer equipped with a 450 W xenon arc lamp, double grating excitation and emission monochromators (2.1 nm mm^{-1} dispersion; 1200 grooves mm^{-1}) and a Hamamatsu R928 photomultiplier tube or a TBX-4-X single-photon-counting detector. Emission and excitation spectra were corrected for source intensity (lamp and grating) and emission spectral response (detector and grating) by standard correction curves. Time-resolved measurements were performed by using the time-correlated single-photon counting (TCSPC) option on the Fluorolog 3. NanoLEDs ($\lambda=295$, 402 or 431 nm; full width at half maximum <750 ps) with repetition rates between 10 kHz and 1 MHz were used to excite the sample. The excitation sources were mounted directly in the sample chamber at 90° to a double grating emission monochromator (2.1 nm mm^{-1} dispersion; 1200 grooves mm^{-1}) and collected by a TBX-4-X single-photon-counting detector. The photons collected at the detector are correlated by a time-to-amplitude converter to the excitation pulse. Signals were collected by using an IBH DataStation Hub photon-counting module and data analysis was performed by using the commercially available DAS6 software (HORIBA, Jobin Yvon IBH). The goodness of fit was assessed by minimizing the reduced chi-squared function (χ^2) and visual inspection of the weighted residuals. The error on the excited-state lifetimes is estimated to be $<8\%$. Emission quantum yields were measured by using the method of Demas and Crosby[22] with quinine bisulfate in 1.0 N sulfuric acid as the standard ($\Phi=0.546$). The error on the calculated emission quantum yields is about 15%. All solvents were spectrometric grade and all solutions were filtered through a 0.2 μmL syringe filter before measurement. De-aerated samples were prepared by the freeze-pump-thaw technique. Low-temperature (77 K) emission spectra for glasses and solid-state samples were recorded in 5 mm diameter quartz tubes that were placed in a liquid nitrogen Dewar with quartz walls.

CV studies: CV was performed by using a Voltalab 40 system from Radiometer Analytical, which consists of a PGZ301 potentiostat and Voltamaster 4 software.[26] The working and counter electrodes were a Pt-disc and a Pt wire, respectively, and Ag wire was used as a pseudoreference electrode. All glassware was dried prior to use. The dry electrolyte tetrabutyl ammonium hexafluorophosphate (>99.0% purity), the analyte and ferrocene ($FeCp_2$; used as the reference) were dried and degassed at high temperature and at reduced pressure in a Schlenk flask to eliminate any moisture and oxygen. The flask was then evacuated and filled three times with N_2. Acetonitrile, freshly distilled from P_2O_5, was added directly to

the sealed Schlenk flask by syringe, the solution was sonicated if necessary and then degassed for ten minutes with a gentle stream of nitrogen. The degassed solution was injected into the electrochemical cell and, after the introduction of electrodes, measurements were performed under a nitrogen atmosphere.

Synthesis of ligands and complexes: $IrCl_3 \cdot 3H_2O$ was purchased from Alpha Aesar. Arylsulfonyl chlorides **7**–**11** and all reagents used in the syntheses of ligands and complexes were purchased from Aldrich. Tributyl(pyridin-2-yl)stannane[23] **17** and 2-(5-(perfluorophenyl)-2*H*-1,2,4-triazol-3-yl)pyridine[10a] were synthesised according to the literature procedures and **17** was also purified by distillation in a Büchi GKR-51 apparatus (10^{-3} mbar, 115 °C). Toluene, used as the solvent for the Stille cross-coupling reactions, was freshly distilled from sodium and benzophenone under a nitrogen atmosphere immediately prior to use. As noted in the literature,[6,24,25] all reactions involving $IrCl_3 \cdot 3H_2O$ were carried out under a nitrogen atmosphere and with previously degassed solvents. Column chromatography was performed by using silica gel 60, (40–63 μm) from Merck, and Merck silica gel 60 F254 aluminium sheets were used for analytical TLC. FTIR spectra were measured by using a Perkin–Elmer Spectrum BX spectrophotometer with dry KBr pellets. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded at 400, 100 and 376 MHz, respectively, by using a Varian Inova 400 spectrometer. ^{1}H and ^{13}C NMR were also recorded at 500 and 125 MHz, respectively, by using a Bruker AM 500 spectrometer. The residual proton signals of $CDCl_3$, CD_2Cl_2 and [D_6]DMSO at $\delta = 7.26$, 5.36 and 2.50 ppm, respectively, were used as references for the ^{1}H NMR spectra, and the signals of $CDCl_3$, CD_2Cl_2 and [D_6]DMSO at $\delta = 77.0$, 53.8 and 39.43 ppm, respectively, were used as references for the ^{13}C NMR spectra. The ^{19}F signal of trichlorofluoromethane was used as an internal standard at $\delta = 0.0$ ppm for the ^{19}F NMR spectra. Melting points (uncorrected) were obtained on a capillary melting point apparatus. Elemental analyses were performed by using a Carlo Erba CHNS-O EA1108-Elemental Analyzer. Electrospray ionisation (ESI) mass spectra were recorded in methanol by using a Bruker Daltonics (Bremen, Germany) MicroTof with loop injection.

General synthesis of the aryl bromides 12–16: The sulfonyl chloride (**7**–**11**; 8.0 mmol), sodium sulfite heptahydrate (4.0 g, 16.0 mmol) and sodium bicarbonate (1.3 g, 16.0 mmol) were dissolved in water (30 mL) under a nitrogen atmosphere and heated at 100 °C for three hours. After cooling the solution to RT, benzylbromide (8.3 mL, 70 mmol) and the phase-transfer catalyst tetra-*N*-butyl ammonium bromide (0.23 g, 0.7 mmol) were added under a nitrogen flow. The reaction mixture was stirred overnight at 70 °C. After cooling to RT, the solid product (**12**–**16**) slowly precipitated from solution. It was isolated by filtration and directly purified on a Büchner funnel by washing with water (5 × 10 mL) and hexane (5 × 10 mL). The product was used in the Stille cross-coupling procedure without further purification.

*3-(Phenylmethanesulfonyl)bromobenzene (**12**)*: Yield 63 %; m.p. 116–117 °C (crystallised from CH_3OH); ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): $\delta = 4.36$ (s, 2H), 7.13–7.19 (m, 2H), 7.32–7.37 (m, 2H), 7.37–7.43 (m, 2H), 7.57–7.62 (m, 1H), 7.78–7.83 ppm (m, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2, 25 °C): $\delta = 63.06$, 123.18, 127.53, 128.18, 128.95, 129.27, 130.87, 131.20, 131.74, 137.11, 140.23 ppm; FTIR (KBr): $\tilde{\nu} = 1455$, 1406, 1318, 1294, 1152, 768, 694, 673, 623, 520 cm^{-1}; elemental analysis calcd (%) for $C_{13}H_{11}BrO_2S$: C 50.17, H 3.56, S 10.30; found: C 49.83, H 3.73, S 10.15.

*2-(Phenylmethanesulfonyl)bromobenzene (**13**)*: Yield 76 %; m.p. 88–89 °C (crystallised from CH_3OH); ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): $\delta = 4.71$ (s, 2H), 7.24 (app. d, $J \approx 8$ Hz, 2H), 7.27–7.37 (m, 3H), 7.40 (td, $J = 7.6$, 1.1 Hz, 1H), 7.49 (td, $J = 7.6$, 1.7 Hz, 1H), 7.81 (dd, $J = 7.8$, 1.7 Hz, 1H), 7.84 ppm (dd, $J = 7.8$, 1.1 Hz, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2, 25 °C): $\delta = 60.09$, 121.16, 128.05, 128.18, 128.86, 129.12, 131.14, 132.83, 135.14, 135.67, 137.71 ppm; FTIR (KBr): $\tilde{\nu} = 1455$, 1429, 1317, 1250, 1200, 1155, 1120, 1024, 882, 790, 762, 705, 601, 549, 529 cm^{-1}; elemental analysis calcd (%) for $C_{13}H_{11}BrO_2S$: C 50.17, H 3.56, S 10.30; found: C 49.92, H 3.67, S 10.60.

*4-(Phenylmethanesulfonyl)bromobenzene (**14**)*: Yield 74 %; m.p. 158–159 °C (crystallised from CH_3OH); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 4.23$ (s, 2H), 7.01 (app. d, $J \approx 8$ Hz, 2H), 7.21 (app. t, $J \approx 8$ Hz, 2H), 7.27 (app. t, $J \approx 8$ Hz, 1H), 7.38 (app. d, $J \approx 8$ Hz, 2H), 7.51 ppm (app. d, $J \approx 8$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 62.84$, 127.76, 128.68, 128.92, 129.08, 130.15, 130.75, 132.14, 136.72 ppm; FTIR (KBr): $\tilde{\nu} = 1390$, 1313, 1272, 1149, 1085, 1068, 1012, 829, 774, 751, 697, 637, 549, 525 cm^{-1}; elemental analysis calcd (%) for $C_{13}H_{11}BrO_2S$: C 50.17, H 3.56, S 10.30; found: C 49.90, H 3.76, S 10.21.

*2-Fluoro-4-(phenylmethanesulfonyl)bromobenzene (**15**)*: Yield 82 %; m.p. 161–162 °C (crystallised from CH_3OH); ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): $\delta = 4.26$ (s, 2H), 7.04 (app. d, $J \approx 8.0$ Hz, 2H), 7.16–7.33 (m, 5H), 7.58 ppm (dd, $J = 8.3$, ^4J(H,F) = 6.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): $\delta = 62.84$, 116.22 (d, ^2J(C,F) = 21 Hz), 116.87 (d, ^2J(C,F) = 25.2 Hz), 125.35 (d, ^3J(C,F) = 3.8 Hz), 127.52, 128.83, 129.17, 130.77, 134.28, 138.87 (d, ^3J(C,F) = 5.5 Hz), 158.74 ppm (d, ^1J(C,F) = 253.5 Hz); ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): $\delta = -103.54$ ppm (app. t, $J \approx 7.0$ Hz, 1F); FTIR (KBr): $\tilde{\nu} = 1471$, 1399, 1315, 1284, 1233, 1149, 1039, 899, 775, 729, 700, 636, 592, 512 cm^{-1}; elemental analysis calcd (%) for $C_{13}H_{10}BrFO_2S$: C 47.43, H 3.06, S 9.74; found: C 47.17, H 3.19, S 9.92.

*2,5-Difluoro-4-(phenylmethanesulfonyl)bromobenzene (**16**)*: Yield 70 %; m.p. 118–120 °C (crystallised from CH_3OH); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 4.53$ (s, 2H), 7.19–7.21 (m, 2H), 7.27–7.36 (m, 3H), 7.38 (dd, ^3J(H,F) = 7.1, ^4J(H,F) = 6.0 Hz, 1H), 7.49 ppm (dd, ^3J(H,F) = 8.3, ^4J(H,F) = 5.0 Hz, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2, 25 °C): $\delta = 62.26$ (d, ^4J(C,F) = 2.1 Hz), 117.16 (dd, ^2J(C,F) = 23.7, ^3J(C,F) = 9.7 Hz), 118.19 (d, ^2J(C,F) = 27.3 Hz), 122.67 (d, ^2J(C,F) = 26.8 Hz), 127.06 (dd, ^2J(C,F) = 17.6, ^3J(C,F) = 5.7 Hz) 127.28, 129.20, 129.59, 131.08, 155.25 (dd, ^1J(C,F) = 255.5, ^4J(C,F) = 3.2 Hz), 155.59 ppm (dd, ^1J(C,F) = 249.0, ^4J(C,F) = 3.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): $\delta = -114.20$ (ddd, ^5J(F,F) = 17.0, ^3J(H,F) = 8.4, ^4J(H,F) = 6.0 Hz, 1F), −110.05–−109.91 ppm (m, 1F); FTIR (KBr): $\tilde{\nu} = 1471$, 1381, 1329, 1320, 1190, 1148, 960, 907, 857, 791, 777, 696, 643, 524 cm^{-1}; elemental analysis calcd (%) for $C_{13}H_9BrF_2O_2S$: C 44.97, H 2.61, S 9.24; found: C 44.79, H 2.61, S 9.34.

General synthesis of functionalised 2-phenylpyridine ligands 18–22: The catalyst [$Pd(AsPh_3)_4$] was synthesised in situ by reacting [$Pd_2(dba)_3$] (0.082 g, 0.09 mmol) and trisphenylarsine (0.21 g, 0.7 mmol) in dry toluene (7 mL) at RT under a nitrogen atmosphere. After few minutes, the aryl halide (**12**–**16**; 3.0 mmol) and a solution of tributyl(pyridin-2-yl)stannane **17** (1.18 g, 3.2 mmol) in toluene (13 mL) were added in sequence, under a nitrogen atmosphere. The resulting reaction mixture was stirred for 12 h at 110 °C. After cooling to RT, the solvent was removed under reduced pressure. H_2O (20 mL) was then added and the crude product was extracted with ethyl acetate (3 × 15 mL). The organic extracts were combined and dried with anhydrous Na_2SO_4. After filtration, the solvent was distilled in vacuo. In the case of reactions leading to the ligands **20**, **21** and **22**, a further washing with hexane and subsequent filtration of the crude products allowed the removal of the soluble organotin byproducts. Finally, the resulting ligands **18**–**22** were isolated by column chromatography over silica gel.

*2-(3-Phenylmethanesulfonylphenyl)pyridine (**18**)*: Yield 70 % (eluent: petroleum ether/ethyl acetate 2:8); m.p.: 91–92 °C (crystallised from CH_3OH); ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): $\delta = 4.41$ (s, 2H), 7.17–7.23 (m, 2H), 7.30–7.40 (m, 4H), 7.62 (t, $J = 8.0$ Hz, 1H), 7.70 (br dt, $J = 7.7$, 1.5 Hz, 1H), 7.73 (br dt, $J = 8.0$, 0.9 Hz, 1H), 7.84 (td, $J = 7.7$, 1.8 Hz, 1H), 8.32–8.34 (m, 1H), 8.36 (br dt, $J = 7.7$, 1.5 Hz, 1H), 8.74 ppm (ddd, $J = 4.8$, 1.8, 0.9 Hz, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2, 25 °C): $\delta = 63.01$, 120.80, 123.43, 127.02, 128.62, 128.87, 128.97, 129.07, 129.72, 131.27, 132.20, 137.35, 139.12, 140.68, 150.17, 155.20 ppm; FTIR (KBr): $\tilde{\nu} = 1585$, 1494, 1458, 1302, 1277, 1146, 1083, 829, 770, 701, 623, 525 cm^{-1}; elemental analysis calcd (%) for $C_{18}H_{15}NO_2S$: C 69.88, H 4.89, N 4.53, S 10.36; found: C 69.99, H 4.92, N 4.65, S 10.16.

*2-(2-Phenylmethanesulfonylphenyl)pyridine (**19**)*: Yield 40 % (eluent: petroleum ether/ethyl acetate 7:3); m.p. 169–171 °C (crystallised from CH_3OH); ^{1}H NMR (500 MHz, $CDCl_3$ 25 °C): $\delta = 4.86$ (s, 2H), 7.20–7.31 (m, 5H), 7.33–7.40 (m, 2H), 7.45 (app. t, $J \approx 8$ Hz, 2H), 7.61 (app. t, $J \approx 8$ Hz, 1H), 7.68 (app. d, $J \approx 8$ Hz, 1H), 7.80 (app. t, $J \approx 8$ Hz, 1H), 8.70–8.72 ppm (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 63.52$, 112.84, 124.34, 128.09, 128.24, 128.32, 128.49, 130.94, 131.30, 131.47, 133.13, 136.56, 136.64, 141.28, 148.12, 158.01 ppm; FTIR (KBr): $\tilde{\nu} = 1582$, 1462, 1424, 1309, 1250, 1199, 1155, 1117, 881, 794, 768, 751, 703, 600, 549, 538,

524 cm^{-1}; elemental analysis calcd (%) for $C_{18}H_{15}NO_2S$: C 69.88, H 4.89, N 4.53, S 10.36; found: C 69.89, H 5.06, N 4.50, S 10.21.

*2-(4-Phenylmethanesulfonylphenyl)pyridine (**20**)*: Yield 71% (eluent: petroleum ether/ethyl acetate 1:1); m.p. 173–176°C (crystallised from CH_3OH); ^1H NMR (500 MHz, [D$_6$]DMSO, 25°C): $\delta = 4.73$ (s, 2H), 7.17–7.21 (m, 2H), 7.27–7.33 (m, 3H), 7.45 (ddd, $J = 7.7$, 4.7, 1.0 Hz, 1H), 7.81 (app. d, $J \approx 9$ Hz, 2H), 7.95 (td, $J = 7.7$, 1.8 Hz, 1H), 8.09 (dt, $J = 7.7$, 1.0, 1H), 8.29 (app. d, $J \approx 9$ Hz, 2H), 8.73 ppm (ddd, $J = 4.7$, 1.8, 1.0 Hz, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2, 25°C): $\delta = 63.08$, 121.36, 123.74, 127.56, 128.64, 128.89, 129.08, 129.29, 131.23, 137.38, 138.49, 144.72, 150.33, 155.36 ppm; FTIR (KBr): $\tilde{\nu} = 1585$, 1560, 1491, 1464, 1455, 1434, 1406, 1392, 1304, 1284, 1085, 1026, 1013, 862, 825, 770, 730, 695, 635, 627, 561, 537, 521 cm^{-1}; elemental analysis calcd (%) for $C_{18}H_{15}NO_2S$: C 69.88, H 4.89, N 4.53, S 10.36; found: C 69.85, H 5.12, N 4.30, S 10.19.

*2-(2-Fluoro-4-phenylmethanesulfonylphenyl)pyridine (**21**)*: Yield 73% (eluent: petroleum ether/ethyl acetate 4:6); m.p. 151–153°C (crystallised from CH_3OH); ^1H NMR (500 MHz, $CDCl_3$ 25°C): $\delta = 4.28$ (s, 2H), 7.02–7.09 (m, 2H), 7.16–7.28 (m, 4H), 7.33 (dd, $J = 10.2$, 1.7 Hz, 1H), 7.44 (dd, $J = 8.2$, 1.7 Hz, 1H), 7.70 (td, $J = 7.2$, 1.7 Hz, 1H) 7.72–7.77 (m, 1H), 8.05 (t, $J = 7.7$ Hz, 1H), 8.66 ppm (ddd, $J = 4.8$, 1.5, 1.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, 25°C): $\delta = 62.71$, 116.91 (d, ^2J(C,F) = 26.6 Hz), 123.50, 124.46 (d, ^4J(C,F) = 3.4 Hz), 124.84 (d, ^4J(C,F) = 10.0 Hz), 127.58, 128.67, 128.93, 130.74, 131.82 (d, ^3J(C,F) = 2.0 Hz), 132.43 (d, ^2J(C,F) = 11.6 Hz), 136.64, 139.35 (d, ^3J(C,F) = 6.9 Hz), 149.98, 151.17, 159.64 ppm (d, ^1J(C,F) = 255.6 Hz); ^{19}F NMR (376 MHz, $CDCl_3$, 25°C): $\delta = -114.49$–-114.40 ppm (m, 1F); FTIR (KBr): $\tilde{\nu} = 1585$, 1458, 1437, 1398, 1306, 1200, 1146, 1120, 784, 699, 624, 530, 509 cm^{-1}; elemental analysis calcd (%) for $C_{18}H_{14}FNO_2S$: C 66.04, H 4.31, N 4.28, S 9.79; found: C 65.85, H 4.66, N 4.28, S 9.59.

*2-(2,5-difluoro-4-phenylmethanesulfonylphenyl)pyridine (**22**)*: Yield 78% (eluent: petroleum ether/ethyl acetate 7:3); m.p. 136–137°C (crystallised from CH_3OH); ^1H NMR (400 MHz, CD_2Cl_2, 25°C): $\delta = 4.62$ (s, 2H), 7.29–7.45 (m, 6H), 7.49 (dd, $J = 9.9$, 5.5 Hz, 1H), 7.87 (td, $J = 7.7$, 1.8 Hz, 1H), 7.92–7.97 (m, 1H), 8.14 (dd, $J = 10.6$, 5.7 Hz, 1H), 8.80 ppm (ddd, $J = 4.8$, 1.7, 1.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, 25°C): $\delta = 61.71$ (d, ^4J(C,F) = 1.5 Hz), 118.59 (br d, ^2J(C,F) = 29.0 Hz), 118.84 (dd, ^2J(C,F) = 25.8, ^3J(C,F) = 7.0 Hz), 124.00, 124.73 (d, ^4J(C,F) = 11.9 Hz), 126.65 (dd, ^2J(C,F) = 18.2, ^3J(C,F) = 7.4 Hz), 126.82, 128.72, 129.03, 130.58, 134.44 (dd, ^2J(C,F) = 13.6, ^3J(C,F) = 7.8 Hz), 136.82, 149.80 (app. d, ^3J(C,F) ≈ 2.0 Hz), 149.97, 155.26 (dd, ^1J(C,F) = 251.2, ^4J(C,F) = 2.4 Hz), 155.41 ppm (dd, ^1J(C,F) = 251.9, ^4J(C,F) = 2.3 Hz); ^{19}F NMR (376 MHz, CD_2Cl_2, 25°C): $\delta = -119.42$–-119.23 (m, 1F), −115.05 ppm (ddd, $J = 19.1$, 10.5, 5.5 Hz, 1F). FTIR (KBr): $\tilde{\nu} = 1484$, 1459, 1442, 1394, 1318, 1145, 895, 789, 696, 632, 527 cm^{-1}; elemental analysis calcd (%) for $C_{18}H_{13}F_2NO_2S$: C 62.60, H 3.79, N 4.06, S 9.28; found: C 62.83, H 3.97, N 4.01, S 9.57.

General synthesis of iridium dimer complexes 23–27:[16,25] Dichloro-bridged dimer complexes **23–27** were synthesised by treating $IrCl_3 \cdot 3H_2O$ (0.35 g, 1.0 mmol) with the ligand (**18–22**; 2.5 mmol) in a 2-ethoxyethanol/H_2O mixture (3:1, 25 mL) at reflux under a nitrogen atmosphere for 12 h. After cooling to RT, water (25 mL) was added to the reaction mixture and the product was filtered in a Büchner funnel and then washed with hexane (25 mL) and ethanol (5 mL). The product was dissolved in dichloromethane (100 mL), dried with anhydrous Na_2SO_4 and isolated by filtration and distillation of the solvent under reduced pressure. In the case of dimer complexes **26** and **27**, further purification by column chromatography over silica gel was carried out. In particular, the residual ligand was first recovered by using petroleum ether/ethyl acetate (1:1) as the eluent, then the iridium dimer complex was isolated by eluting with acetone/petroleum ether (6:4).

*Tetrakis[2-(4′-benzylsulfonyl)phenylpyridinato-*N,C2′*](μ-dichloro)diiridium (**23**)*: Yield 74%; ^1H NMR (400 MHz, [D$_6$]DMSO, 25°C): $\delta = 4.48$ (s, 4H), 4.49 (d, $J = 13.8$, 2H), 4.55 (d, $J = 13.8$, 2H), 5.78 (d, $J = 8.2$ Hz, 2H), 6.36 (d, $J = 8.1$ Hz, 2H), 6.90–7.25 (m, 24H), 7.57 (app. t, $J \approx 7$ Hz, 2H), 7.66 (app. t, $J \approx 7$ Hz, 2H), 7.98 (br s, 2H), 8.03 (br s, 2H), 8.09 (app. t, $J \approx 8$ Hz, 2H), 8.16 (app. t, $J \approx 8$ Hz, 2H), 8.26 (d, $J = 8.5$ Hz, 2H), 8.30 (d, $J = 8.0$ Hz, 2H), 9.50 (d, $J = 6.0$ Hz, 2H), 9.75 ppm (d, $J = 6.0$ Hz, 2H); ^{13}C NMR (100 MHz, [D$_6$] DMSO, 25°C): $\delta = 60.61$, 60.64, 120.51, 121.15, 122.60, 123.82, 124.32, 125.04, 127.42, 128.05, 128.11, 128.52, 128.59, 128.91, 129.97, 130.80, 130.95, 131.73, 132.14, 133.46, 139.06, 140.11, 144.07, 144.64, 150.89, 152.24, 154.60, 159.96, 164.85, 165.26 ppm; FTIR (KBr): $\tilde{\nu} = 1608$, 1575, 1478, 1422, 1303, 1148, 1029, 831, 779, 697, 629, 610, 531, 516 cm^{-1}; elemental analysis calcd (%) for $C_{72}H_{56}Cl_2Ir_2N_4O_8S_4$: C 51.20, H 3.34, N 3.32, S 7.59; found: C 51.07, H 3.54, N 3.19, S 7.38; ESI-MS (+ve, MeOH): m/z (%): 867.3 (100) $[M+2Na]^{2+}$.

*Tetrakis[2-(3′-benzylsulfonyl)phenylpyridinato-*N,C2′*](μ-dichloro)diiridium (**24**)*: Yield 78%; ^1H NMR (500 MHz, [D$_6$]DMSO, 25°C): $\delta = 4.70$ (d, $J = 13.8$ Hz, 2H), 4.74 (s, 2H), 4.77 (s, 2H), 4.87 (d, $J = 13.8$ Hz, 2H), 5.82 (d, $J = 7.7$ Hz, 2H), 6.66 (d, $J = 7.7$ Hz, 2H), 6.84 (t, $J = 7.8$ Hz, 2H), 6.99 (t, $J = 7.8$ Hz, 2H), 7.05 (app. d, $J \approx 7$ Hz, 4H), 7.12 (app. t, $J \approx 7$ Hz, 4H), 7.19–7.35 (m, 12H), 7.46 (d, $J = 7.6$ Hz, 2H), 7.63–7.71 (m, 4H), 7.76 (app. t, $J \approx 7$ Hz, 2H), 8.23 (app. t, $J \approx 8$ Hz, 2H), 8.31 (app. t, $J \approx 8$ Hz, 2H), 9.29 (d, $J = 8.4$ Hz, 2H), 9.33 (d, $J = 8.4$ Hz, 2H), 9.78 (d, $J = 5.6$ Hz, 2H), 9.98 ppm (d, $J = 5.6$, 2H);^{13}C NMR (125 MHz, [D$_6$]DMSO, 25°C): $\delta = 59.10$, 59.15, 124.48, 125.21, 125.33, 125.73, 126.64, 127.50, 127.72, 128.07, 128.24, 128.31, 128.50, 129.21, 131.16, 131.31, 134.59, 135.85, 136.76, 137.25, 138.47, 139.46, 140.03, 140.22, 150.13, 151.99, 153.02, 155.25, 163.21, 163.69 ppm; FTIR (KBr): $\tilde{\nu} = 1602$, 1560, 1475, 1420, 1390, 1317, 1297, 1274, 1153, 1138, 1121, 1060, 787, 769, 696, 619, 527 cm^{-1}; elemental analysis calcd (%) for $C_{72}H_{56}Cl_2Ir_2N_4O_8S_4$: C 51.20, H 3.34, N 3.32, S 7.59; found: C 51.05, H 3.20, N 3.10, S 7.46; ESI-MS (+ve, MeOH): m/z (%): 867.3 (100) $[M+2Na]^{2+}$, 1711.3 (30) $[M+Na]^+$.

*Tetrakis[2-(5′-benzylsulfonyl)phenylpyridinato-*N,C2′*](μ-dichloro)diiridium (**25**)*: Yield 80%; ^1H NMR (500 MHz, [D$_6$]DMSO, 25°C): $\delta = 4.16$ (d, $J = 13.8$ Hz, 2H), 4.34 (d, $J = 13.8$ Hz, 2H), 4.40 (d, $J = 14.0$ Hz, 2H), 4.44 (d, $J = 14.0$ Hz, 2H), 5.79 (d, $J = 1.8$ Hz, 2H), 6.38 (d, $J = 1.8$ Hz, 2H), 6.73 (d, $J = 7.3$ Hz, 4H), 6.87 (d, $J = 7.3$ Hz, 4H), 7.01–7.10 (m, 8H), 7.20 (dd, $J = 8.1$, 1.8 Hz, 2H), 7.23–7.29 (m, 6H), 7.60 (app. t, $J \approx 7$ Hz, 2H), 7.65 (app. t, $J \approx 7$ Hz, 2H), 7.97 (d, $J = 8.3$ Hz, 2H), 8.00 (d, $J = 8.3$ Hz, 2H), 8.13 (app. t, $J \approx 8$ Hz, 2H), 8.19 (app. t, $J \approx 8$ Hz, 2H), 8.34 (app. d, $J \approx 8$ Hz, 2H), 8.38 (app. d, $J \approx 8$ Hz, 2H), 9.45 (app. d, $J \approx 7$ Hz, 2H), 9.73 ppm (app. d, $J \approx 7$ Hz, 2H); ^{13}C NMR (100 MHz, [D$_6$]DMSO, 25°C): $\delta = 60.74$, 60.81, 121.26, 121.84, 121.97, 122.27, 124.08, 124.69, 125.06, 125.37, 128.06, 128.15, 128.20, 128.28, 128.53, 129.64, 130.48, 137.02, 137.88, 138.84, 139.82, 145.04, 148.16, 148.86, 151.29, 164.69, 165.05 ppm; FTIR (KBr): $\tilde{\nu} = 1608$, 1562, 1476, 1455, 1427, 1374, 1314, 1298, 1269, 1198, 1151, 1125, 1087, 873, 808, 776, 727, 697, 666, 652, 614, 541, 505 cm^{-1}; elemental analysis calcd (%) for $C_{72}H_{56}Cl_2Ir_2N_4O_8S_4$: C 51.20, H 3.34, N 3.32, S 7.59; found: C 51.03, H 3.54, N 3.47, S 7.50; ESI-MS (+ve, MeOH): m/z (%): 867.3 (100) $[M+2Na]^{2+}$, 1711.1 (20) $[M+Na]^+$.

*Tetrakis[2-(5′-benzylsulfonyl-3′-fluoro)phenylpyridinato-*N,C2′*](μ-dichloro)diiridium (**26**)*: Yield 90%; ^1H NMR (500 MHz, [D$_6$]DMSO, 25°C): $\delta = 4.33$ (d, $J = 14.0$ Hz, 2H), 4.49 (d, $J = 14.0$ Hz, 2H), 4.50 (d, $J = 14.0$ Hz, 2H), 4.56 (d, $J = 14.0$ Hz, 2H), 5.46 (br s, 2H), 6.12 (br s, 2H), 6.79 (br d, $J = 7.9$ Hz, 4H), 6.89 (br d, $J = 7.9$ Hz, 4H), 7.01–7.12 (m, 8H), 7.18–7.30 (m, 8H), 7.61–7.70 (m, 4H), 8.14–8.25 (m, 4H), 8.33 (br t, $J = 8.2$ Hz, 4H), 9.5 (br d, $J = 5.8$ Hz, 2H), 9.7 ppm (br d, $J = 5.8$ Hz, 2H); ^{13}C NMR (100 MHz, [D$_6$]DMSO, 25°C): $\delta = 60.48$ (br), 109.88 (d, ^2J(C,F) = 26.3 Hz), 110.26 (d, ^2J(C,F) = 27.4 Hz), 124.37, 124.68 (d, ^2J(C,F) = 20.4 Hz), 125.14, 125.31 (d, ^2J(C,F) = 19.7 Hz), 125.77, 125.87, 128.02, 128.14, 128.26, 128.30, 130.49, 135.10 (d, ^4J(C,F) = 4.0 Hz), 135.95 (d, ^4J(C,F) = 4.4 Hz), 138.00 (d, ^3J(C,F) = 6.7 Hz), 138.02 (d, ^3J(C,F) = 7.5 Hz), 139.17 (d, ^3J(C,F) = 7.4 Hz), 139.21 (d, ^3J(C,F) = 7.3 Hz), 139.63, 140.54, 148.06 (d, ^5J(C,F) = 2.8 Hz), 151.67, 152.80, 154.03, 158.43 (d, ^1J(C,F) = 260.7 Hz), 158.90 (d, ^1J(C,F) = 261.0 Hz), 161.85 (d, ^3J(C,F) = 7.7 Hz), 162.24 ppm (d, ^3J(C,F) = 6.9 Hz); ^{19}F NMR (376 MHz, [D$_6$]DMSO, 25°C): $\delta = -107.58$ (d, $J = 11.8$ Hz, 2F), −106.19 ppm (d, $J = 11.8$ Hz, 2F); FTIR (KBr): $\tilde{\nu} = 1601$, 1583, 1558, 1473, 1391, 1306, 1225, 1146, 1121, 932, 774, 697, 624, 534 cm^{-1}; elemental analysis calcd (%) for $C_{72}H_{52}Cl_2F_4Ir_2N_4O_8S_4$: C 49.11, H 2.98, N 3.18, S 7.28; found: C 49.07, H 3.21, N 3.23, S 7.53; ESI-MS (+ve, MeOH): m/z (%): 903.3 (100) $[M+2Na]^{2+}$, 1783.3 (10) $[M+Na]^+$.

*Tetrakis[2-(5′-benzylsulfonyl-3′,6′-difluoro)phenylpyridinato-*N,C2′*](μ-dichloro)diiridium (**27**)*: Yield 85%; ^1H NMR (400 MHz, CD_2Cl_2, 25°C): $\delta = 4.09$–4.25 (s, 8H), 6.87–6.97 (m, 12H), 7.02 (dd, $J = 10.8$, 4.5 Hz, 4H), 7.13 (app. t, $J \approx 7.5$ Hz, 8H), 7.19–7.25 (m, 4H), 8.02 (app. t, $J \approx 8$ Hz, 4H), 8.56 (br d, $J \approx 8$ Hz, 4H), 9.13 ppm (br d, $J = \approx 5$ Hz, 4H); ^{13}C NMR

(100 MHz, CD_2Cl_2, 25 °C): δ = 61.81, 113.00, 113.29, 116.01, 119.35, 124.61, 125.30, 125.52, 125.78–126.28 (m), 126.32, 126.69, 127.64, 128.90, 129,12, 130.78, 138.86, 141.67 (dd, ^2J(C,F) = 14.5, ^3J(C,F) = 6.5 Hz), 152.84, 155.44 (d, ^1J(C,F) = 256.1 Hz), 160.20 (d, ^1J(C,F) = 242.2 Hz), 164.25 ppm (d, ^3J(C,F) = 7.1 Hz); ^{19}F NMR (376 MHz, CD_2Cl_2, 25 °C): δ = −116.35, (dd, J = 21.1, 10.8 Hz, 2F), −108.60 ppm (dd, J = 21.1, 4.5 Hz, 2F); FTIR (KBr): $\tilde{\nu}$ = 1478, 1424, 1371, 1317, 1149, 1120, 827, 792, 698, 542, 533, 497 cm^{-1}; elemental analysis calcd (%) for $C_{72}H_{48}Cl_2F_8Ir_2N_4O_8S_4$: C 47.18, H 2.64, N 3.06, S 7.00; found: C 46.93, H 2.55, N 3.01, S 6.76; ESI-MS (+ve, MeOH): m/z (%): 939.3 (100) $[M+2Na]^{2+}$, 1855.3 (10) $[M+Na]^+$.

Synthesis of decane-2,4-dione (28): 2-Octanone (8.0 mL, 51.0 mmol) was dissolved in dry ethyl acetate (130 mL) under a nitrogen atmosphere and, after cooling to 0 °C, sodium (2.3 g, 102.0 mmol) was added. The reaction mixture was stirred at 0 °C for one hour, then allowed to warm to RT and stirred overnight. The resulting yellow solution was quenched with ice and aqueous HCl (1.2 M). The crude product was extracted with ethyl acetate (100 mL), and the organic extract dried with anhydrous Na_2SO_4, filtered and distilled under vacuo. The liquid crude product was first purified by distillation in a Büchi GKR-51 apparatus (11 torr, 115–120 °C) and then by column chromatography over silica gel, eluting with a mixture of petroleum ether and ethyl acetate (95:5) as eluent (yield 95%). This compound exists as a mixture of keto (15%) and enol (85%) forms, as determined by the integral values of proton resonance peaks at δ = 3.54 (for the keto form) and 5.46 ppm (for the enol form). ^{1}H NMR (500 MHz, $CDCl_3/D_2O$, 25 °C): δ = 0.80–0.90 (m, 3H), 1.20–1.36 (m, 6H), 1.50–1.62 (m, 2H), 2.02 (s, 3H; enol form), 2.20 (s, 3H; keto form), 2.23 (t, J = 7.6 Hz, 2H; enol form), 2.47 (t, J = 7.4 Hz, 2H; keto form), 3.54 (s, 2H; keto form), 5.46 ppm (s, 1H; enol form); ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C): δ = 13.87, 22.36, 24.80, 25.54, 28.76, 31.42, 38.10, 43.67 (keto form), 57.68 (keto form), 99.58 (enol form), 191.29 (enol form), 194.14 (enol form), 202.05 (keto form), 204.16 ppm (keto form).

General synthesis of acac-type iridium complexes 1–5: The dichloro-bridged dimer complex (0.1 mmol), decane-2,4-dione **28** (0.042 g, 0.25 mmol) and sodium carbonate (0.12 g, 1.1 mmol) were suspended in 2-ethoxyethanol (6 mL) and stirred for 12 h at 120 °C under a nitrogen atmosphere. After cooling to RT, the reaction mixture was diluted with dichloromethane and water was added. The reaction product was extracted with dichloromethane (3×15 mL) and the organic phase was dried with anhydrous Na_2SO_4. After the distillation of the solvent at reduced pressure, the heteroleptic iridium complex (**1–5**) was isolated by column chromatography over silica gel with petroleum ether/acetone (7:3) as the eluent.

Iridium(III)bis[2-(4′-benzylsulfonyl)phenylpyridinato-N,*C2′](2,4-decanedionate) (**1**)*: yield: 55%; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 0.81 (t, J = 7.2 Hz, 3H), 0.86–1.10 (m, 4H), 1.13 (q, J = 7.0 Hz, 2H), 1.21–1.35 (m, 2H), 1.82 (s, 3H), 2.01 (t, J = 7.3, 2H), 4.15–4.23 (m, 4H), 5.25 (s, 1H), 6.32 (d, J = 8.0 Hz, 1H), 6.39 (d, J = 8.0 Hz, 1H), 6.70 (t, J = 2.1 Hz, 1H), 7.00–7.05 (m, 5H), 7.15 (td, J = 7.7, 1.5 Hz, 4H), 7.21–7.32 (m, 4H), 7.59 (d, J = 1.9 Hz, 1H), 7.64 (d, J = 1.9 Hz, 1H), 7.71–7.86 (m, 4H), 8.43–8.47 ppm (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 14.07, 22.50, 26.85, 28.51, 28.65, 31.63, 41.46, 63.01, 100.35, 119.02, 119.22, 122.69, 122.78, 123.42, 123.54, 127.55, 127.67, 128.34, 128.44, 128.49, 128.59, 130.22, 130.29, 130.93, 133.48, 133.74, 137.83, 137.89, 145.62, 145.70, 148.31, 148.40, 158.72, 158.82, 166.48, 166.56, 185.13, 188.73 ppm; FTIR (KBr): $\tilde{\nu}$ = 1573, 1512, 1423, 1403, 1305, 1148, 1030, 779, 696, 629, 610, 531 cm^{-1}; elemental analysis calcd (%) for $C_{46}H_{45}IrN_2O_6S_2$: C 56.48, H 4.64, N 2.86, S 6.56; found: C 56.38, H 4.78, N 2.96, S 6.82; HRMS: m/z calcd for $C_{46}H_{45}IrN_2O_6S_2$: 1001.2240 $[M+Na]^+$; found 1001.2255.

Iridium(III)bis[2-(3′-benzylsulfonyl)phenylpyridinato-N,*C2′](2,4-decanedionate) (**2**)*: yield: 60%; ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ = 0.83 (t, J = 7.1 Hz, 3H), 1.00–1.42 (m, 8H), 1.87 (s, 3H), 2.00–2.14 (m, 2H), 4.49 (d, J = 13.7 Hz, 2H), 4.56 (d, J = 13.7 Hz, 2H), 4.56 (s, 2H), 5.37 (s, 1H), 6.58 (dd, J = 7.6, 1.3 Hz, 1H), 6.67 (dd, J = 7.6, 1.4 Hz, 1H), 6.74 (t, J = 7.7 Hz, 2H), 7.09 (app. t, J ≈ 7 Hz, 4H), 7.17 (app. t, J ≈ 7.5 Hz, 2H), 7.23–7.30 (m, 2H), 7.35–7.42 (m, 2H), 7.55 (dd, J = 5.0, 1.4 Hz, 1H), 7.57 (dd, J = 5.0, 1.4 Hz, 1H), 8.01–8.06 (m, 2H), 8.68 (dd, J = 5.7, 0.7 Hz, 1H), 8.69 (dd, J = 5.7, 0.7 Hz, 1H), 9.63–9.69 ppm (m, 2H); ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C): δ = 14.16, 22.87, 27.76, 28.70, 29.01, 32.00, 42.22, 60.31, 60.39, 100.55, 123.69, 123.74, 125.74, 125.76, 125.82, 125.96, 127.89, 127.96, 128.14, 128.26, 128.73, 128.96, 131.22, 131.26, 136.11, 136.21, 138.44, 138.49, 139.32, 139.55, 142.02, 142.08, 149.35, 149.44, 154.22, 154.34, 165.11, 165.16, 185.71, 189.39 ppm; FTIR (KBr): $\tilde{\nu}$ = 1575, 1561, 1512, 1474, 1404, 1316, 1296, 1271, 1152, 1139, 1121, 785, 768, 696, 619, 527 cm^{-1}; elemental analysis calcd (%) for $C_{46}H_{45}IrN_2O_6S_2$: C 56.48, H 4.64, N 2.86, S 6.56; found: C 56.46, H 4.45, N 2.88, S 6.58; HRMS: m/z calcd for $C_{46}H_{45}IrN_2O_6S_2$: 1001.2240 $[M+Na]^+$; found 1001.2235.

Iridium(III)bis[2-(5′-benzylsulfonyl)phenylpyridinato-N,*C2′](2,4-decanedionate) (**3**)*: Yield 52%; ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ = 0.87 (t, J = 7.0 Hz, 3H), 0.97–1.48 (m, 8H), 1.87 (s, 3H), 2.07 (t, J = 7.3 Hz, 2H), 4.06–4.22 (m, 4H), 5.33 (s, 1H), 6.40 (d, J = 1.7 Hz, 1H), 6.45 (d, J = 1.7 Hz, 1H), 6.89 (app. t, J ≈ 8 Hz, 4H), 7.13 (app. t, J ≈ 8 Hz, 4H), 7.19–7.40 (m, 6H), 7.69 (d, J = 8.1 Hz, 1H), 7.72 (d, J = 8.1 Hz, 1H), 7.86–8.10 (m, 4H), 8.43 ppm (app. t, J ≈ 6 Hz, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2, 25 °C): δ = 14.22, 22.89, 27.40, 28.63, 28.92, 31.99, 41.94, 62.73, 100.53, 120.31, 120.48, 121.28, 121.31, 123.87, 123.94, 123.98, 124.04, 128.58, 128.61, 128.75, 130.92, 130.96, 132.05, 132.40, 137.09, 137.22, 138.29, 138.33, 148.19, 148.28, 148.86, 148.98, 150.92, 166.32, 166.37, 185.37, 189.12 ppm; FTIR (KBr): $\tilde{\nu}$ = 1607, 1574, 1512, 1475, 1428, 1403, 1311, 1297, 1149, 774, 696, 540 cm^{-1}; elemental analysis calcd (%) for $C_{46}H_{45}IrN_2O_6S_2$: C 56.48, H 4.64, N 2.86, S 6.56; found: C 56.26, H 4.44, N 2.85, S 6.78; HRMS: m/z calcd for $C_{46}H_{45}IrN_2O_6S_2$: 1001.2240 $[M+Na]^+$; found 1001.2213.

Iridium(III)bis[2-(5′-benzylsulfonyl-3′-fluoro)phenylpyridinato-N,*C2′](2,4-decanedionate) (**4**)*: Yield 50%; ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C): δ = 0.88 (t, J = 7.1 Hz, 3H), 0.91–1.46 (m, 8H), 1.87 (s, 3H), 2.07 (t, J = 7.3 Hz, 2H), 4.16 (brs, 2H), 4.17 (brs, 2H), 5.32 (s, 1H), 6.09–6.13 (m, 1H), 6.15–6.18 (m, 1H), 6.93 (t, J = 7.0 Hz, 4H), 7.02 (d, J = 11.4 Hz, 1H), 7.05 (d, J = 11.2 Hz, 1H), 7.13 (t, J = 7.0 Hz, 4H), 7.27–7.39 (m, 4H), 7.91–7.99 (m, 2H), 7.36–7.46 ppm (m, 4H); ^{13}C NMR (100 MHz, CD_2Cl_2, 25 °C): δ = 14.19, 22.87, 27.26, 28.58, 28.86, 31.97, 41.77, 62.73, 100.60, 108.84 (d, ^4J(C,F) = 2.7 Hz), 108.94 (d, ^4J(C,F) = 2.7 Hz), 123.97, 124.08, 124.63 (d, ^2J(C,F) = 15.2 Hz), 124.82 (d, ^2J(C,F) = 15.1 Hz), 128.23 (d, ^2J(C,F) = 31.4 Hz), 128.25 (d, ^2J(C,F) = 31.5 Hz), 128.47, 128.57, 128.74, 128.77, 130.90, 130.94, 137.92 (d, ^3J(C,F) = 7.6 Hz), 138.06 (d, ^3J(C,F) = 7.6 Hz), 138.29 (d, ^3J(C,F) = 4.5 Hz), 138.34 (d, ^3J(C,F) = 4.5 Hz), 138.82, 138.86, 148.87, 148.97, 151.74, 151.79, 159.88 (d, ^{1}J(C,F) = 260.4 Hz), 159.92 (d, ^1J(C,F) = 260.7 Hz), 163.96 (d, ^3J(C,F) = 7.2 Hz), 164.03 (d, ^3J(C,F) = 7.3 Hz), 185.56, 189.26 ppm; ^{19}F NMR (376 MHz, CD_2Cl_2, 25 °C): δ = −112.70 (d, J = 11.2 Hz, 1F), −112.48 ppm (d, J = 11.4 Hz, 1F); FTIR (KBr): $\tilde{\nu}$ = 1576, 1513, 1473, 1390, 1307, 1221, 1143, 1121, 930, 791, 773, 696, 626, 533 cm^{-1}; elemental analysis calcd (%) for $C_{46}H_{43}F_2IrN_2O_6S_2$: C 54.48, H 4.27, N 2.76, S 6.32; found: C 54.29, H 4.49, N 2.81, S 6.15; HRMS: m/z calcd for $C_{46}H_{43}F_2IrN_2O_6S_2$: 1037.2052 $[M+Na]^+$; found 1037.2070.

Iridium(III)bis[2-(5′-benzylsulfonyl-3′,6′-difluoro)phenylpyridinato-N,*C2′](2,4-decanedionate) (**5**)*: Yield 72%; ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C): δ = 0.87 (t, J = 7.2 Hz, 3H), 0.90–1.41 (m, 8H), 1.90 (s, 3H), 2.11 (t, J = 7.0 Hz, 2H), 4.28 (s, 4H), 5.42 (s, 1H), 6.93–7.03 (m, 6H), 7.18 (app. t, J ≈ 8 Hz, 4H), 7.23–7.30 (m, 2H), 7.34–7.41 (m, 2H), 7.94–8.02 (m, 2H), 8.44 (app. t, J ≈ 8 Hz, 2H), 8.52 ppm (app. d, J ≈ 6 Hz, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 14.20, 22.85, 27.21, 28.54, 28.78, 31.96, 41.69, 61.69 (br), 100.91, 111.51, 111.74, 127.67, 123.79, 124.72 (d, ^2J(C,F) = 21.0 Hz), 124.84 (d, ^2J(C,F) = 20.9 Hz), 125.00–125.50 (m), 127.80, 127.87, 128.82, 129.10, 130.79, 130.83, 132.18 (d, ^2J(C,F) = 18.7 Hz), 132.52 (d, ^2J(C,F) = 19.74 Hz), 138.82, 138.89, 149.35, 149.57, 156.0 (d, ^1J(C,F) = 255.8 Hz), 161.45 (d, ^1J(C,F) = 237.9 Hz), 163.95 (d, ^3J(C,F) = 7.4 Hz), 164.18 (d, ^3J(C,F) = 7.0 Hz), 185.61, 189.26 ppm; ^{19}F NMR (376 MHz, CD_2Cl_2, 25 °C): δ = −117.66 (dd, J = 22.0, 11.0 Hz, 1F), −117.58 (dd, J = 22.0, 11.0 Hz, 1F), −107.26 (dd, J = 22.0, 4.5 Hz, 1F), −106.49 ppm (dd, J = 22.0, 4.7 Hz, 1F); FTIR (KBr): $\tilde{\nu}$ = 1569, 1514, 1423, 1404, 1369, 1319, 1151, 1121, 826, 791, 697, 543, 497 cm^{-1}; elemental analysis calcd (%) for $C_{46}H_{41}F_4IrN_2O_6S_2$: C 52.61, H 3.94, N 2.67, S 6.11; found: C 52.72, H 4.21, N 2.71, S 6.26; HRMS: m/z calcd for $C_{46}H_{41}F_4IrN_2O_6S_2$: 1073.1864 $[M+Na]^+$; found 1073.1849.

Synthesis of iridium(III)bis[2-(4′-benzylsulfonyl)phenylpyridinato-N,C2′] [3-(pentafluoro-phenyl)-pyridin-2-yl-1,2,4-triazolate] (6): Dimer complex **23** (0.17 g, 0.1 mmol) and 3-(2,3,4,5,6-pentafluorophenyl)-pyridin-2-yl-1,2,4-triazole (0.066 mg, 0.21 mmol) were dissolved under a nitrogen atmosphere in dichloromethane (6 mL) and ethanol (6 mL). The solution was stirred for 24 h at 40 °C under a nitrogen atmosphere. After cooling to RT, the reaction mixture was diluted with dichloromethane and water was added. The reaction product was extracted three times with dichloromethane (3×10 mL) and the organic extracts were dried with anhydrous Na_2SO_4. Then the solvent was removed by distillation under reduced pressure and complex **6** was isolated by using column chromatography over silica gel with a mixture of petroleum ether/acetone (1:1) as the eluent (60 % yield). ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C): δ = 4.27 (d, J = 13.6 Hz, 1H), 4.28 (d, J = 14.0 Hz, 1H), 4.30 (d, J = 14.0 Hz, 1H), 4.32 (d, J = 13.6 Hz, 1H), 6.50 (d, J = 8.0 Hz, 1H), 6.57 (d, J = 8.0 Hz, 1H), 7.07–7.16 (m, 6H), 7.18 (dd, J = 8.05, 1.9, 1H), 7.20–7.34 (m, 8H), 7.67 (ddd J = 5.8, 1.4, 0.7 Hz, 1H), 7.74 (ddd J = 5.5, 1.5, 0.9 Hz, 1H), 7.77–7.92 (m, 7H), 7.98 (td, J = 7.8, 1.6 Hz, 1H), 8.32 ppm (br d, J = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, CD_2Cl_2, 25 °C): δ = 63.13, 63.16, 109.95 (td, J = 16.7, 3.8 Hz), 120.25, 120.30, 122.17, 124.11, 124.22, 124.39, 124.68, 125.50, 128.46, 128.67, 128.71, 128.83, 128.92, 128.94, 129.18, 131.22, 131.37, 131.81, 132.38, 132.55, 133.09, 138.06 (dm (doublet of multiplet), ^{1}J(C,F) ≈ 251 Hz), 138.33, 138.62, 139.68, 141.05 (dm, ^1J(C,F) ≈ 253 Hz), 145.41 (dm, ^1J(C,F) ≈ 251 Hz), 145.15, 146.03, 149.23, 149.95, 150.32, 151.54, 153.70 (br), 159.40, 163.69, 164.12, 166.31, 166.53 ppm; ^{19}F NMR (376 MHz, CD_2Cl_2): δ = −163.00 (td, J = 21.0, 7.0 Hz, 2F), −155.32 (t, J = 21.0 Hz, 1F), −139.67 ppm (dd, J = 21.0, 7.0 Hz, 2F); FTIR (KBr): 1610, 1576, 1536, 1517, 1496, 1477, 1438, 1424, 1305, 1149, 1091, 1030, 990, 841, 779, 754, 697, 629, 610, 531 cm^{-1}; elemental analysis calcd (%) for $C_{49}H_{32}F_5IrN_6O_4S_2$: C 52.54, H 2.88, N 7.50, S 5.73; found: C 52.68, H 3.07, N 7.45, S 5.94; HRMS: m/z calcd for $C_{49}H_{32}F_5IrN_6O_4S_2$: 1143.1368 $[M+Na]^+$; found 1143.1474.

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