1,2,3-Triazolyl-pyridine derivatives as chelating ligands for blue iridium(III) complexes. Photophysics and electroluminescent devices[†]

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We report on the study of a new family of neutral heteroleptic $Ir(F_2ppy)_2L$ ($F_2ppy = 2-(2,4-$ difluorophenyl)pyridine) complexes bearing different triazole derivatives (L = 2-(1,2,3-triazol-5yl)pyridine) as the third ligand. Two of these ligands were used for the first time as ancillary ligands in iridium(III) complexes. A full photophysical and electrochemical study of these complexes is reported here, together with theoretical investigations at the density functional theory (DFT) level. The complexes were also obtained as single crystals and their structures were determined by X-ray crystallography. The newly reported complexes exhibit blue emission with high quantum yields in solution. Photophysical results are also compared to those reported for their 1,2,4-triazole isomer analogues. The emitting state is a mixture between the triplet metal-to-ligand charge transfer (³MLCT) and triplet inter-ligand charge transfer (³ILCT) states, and it is more localized on the F₂ppy ligand as supported by DFT calculations. In addition, this paper reports some preliminary tests of polymer lightemitting diodes (PLEDs) doped with these iridium complexes. The results indicate that such molecules are good candidates as blue- and green-emitting dopants in LED devices.

Introduction

In the last decade, increasing attention has been focused on the preparation of a variety of metal complexes suitable to act as phosphorescent dopants in optoelectronic devices such as organic light-emitting diodes (OLEDs)1-3 and light-emitting electrochemical cells (LECs).4,5 It has been shown that the strong spinorbit coupling caused by heavy-metal ions incorporated in the complexes facilitates efficient intersystem crossing from the singlet to the triplet excited state, leading to theoretical efficiencies of ca. 100%. Some of the most promising metals were found to be ruthenium(II),^{6,7} osmium(II),^{7,8} platinum(II)^{9,10} and mainly iridium(III).^{11,12} Development of such molecules showing all the three primary colors (red, green and blue) is the key factor which needs to be taken into account for their application in full-color displays and lighting devices. After the discovery of very efficient green-13 and red-emitting¹⁴ iridium complexes, in the last few years many research groups focused their efforts on trying to find efficient

blue-emitting complexes to use in OLED devices along with other phosphorescent dyes.^{15–18} Recent studies screened the effect of a variety of chelating ligands on the photophysical properties of iridium complexes.^{19,20} It has been shown that it is possible to tune the emission of these systems by simply changing the organic ligands coordinated to the heavy-metal center. In addition, theoretical investigations have proven to be very useful in the interpretation of photophysical data of iridium complexes. In particular, density functional theory (DFT) has been successfully applied to describe the nature of their emitting excited state.^{21–25}

A work published by our group in 2004 reports on Ir complexes having 2-phenyl-pyridine ligands that bear electron withdrawing groups such as fluorine and trifluoromethyl. The effect of these electron withdrawing substituents was discussed, as well as the influence of the substitution pattern on the spectroscopic behavior of the Ir emitter.²⁶ More recently, we tried to achieve deep-blue emission by changing the ancillary ligands in a series of Ir(F_2ppy) derivatives.²⁷ In the latter case, we screened different substituents of the 1,2,4-triazole family and have shown how the photophysical behavior of the resulting Ir emitters could be related to the electronic and sterical properties of the substituents.

In this paper we report the synthesis and characterization of two new heteroleptic $Ir(F_2ppy)_2L$ complexes bearing ligands (L) belonging to the 1,2,3-triazole family. These ligands could be prepared using "click chemistry",²⁸ which is known to be a very reliable synthesis tool in terms of high yields, selectivity and versatility.²⁹ The complexes were obtained as single crystals which were resolved by X-ray crystallography. We also report on a theoretical study of the synthesized complexes, with their photophysics being discussed also by means of DFT calculations. The complexes were tested as dopants in polymer-based OLEDs,

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[†] Electronic supplementary information (ESI) available: Low temperature emission spectra, cyclic voltammogram of complex 2. Energy levels of the molecular orbitals most contributing to the triplet emitting state calculated for complexes 1–5. Current efficiencies for devices containing complexes 1 and 3. CCDC reference numbers 678024 and 678025. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b805324c



Chart 1 The iridium complexes studied in this work.

which gave promising results for a further optimization of devices based on these materials.

Results and discussion

Synthesis and characterization

Chart 1 shows the molecular structures of the iridium complexes 1–5 discussed in this work. We have previously reported the synthesis and photophysical studies of complexes 4 and 5^{27} In Scheme 1, the synthesis route to the ancillary third ligands L1–L3 that are used for the preparation of the corresponding complexes 1–3 is depicted. In the procedure, the introduction of the 1,2,3-triazole moiety relies on the conveniently applicable 'click'-type of chemistry, *i.e.* copper catalyzed 1,3-dipolar additions on acetylenes using azide building blocks, as first described by Meldal *et al.*^{30–32} The 2-(1*H*-1,2,3-triazol-5-yl)pyridine ligand L1 was synthesized according to a reported procedure.³³ Briefly,

chloromethyl pivalate is reacted with sodium azide to form azidomethyl pivalate, which is subsequently converted in a 'click' reaction with 2-pyridyl acetylene to the protected version of L1. Deprotection is achieved by hydrolysis using NaOH in an aqueous mixture of MeOH. The syntheses of the ligands 2-[4-(pentafluorophenyl)-1H-1,2,3-triazol-5-yl]pyridine (L2) and 2-[4-(3,5-difluorophenyl)-1H-1,2,3-triazol-5-yl]pyridine (L3) have never been reported. 2-Pyridyl acetylene is reacted with the corresponding (per)fluorobromobenzenes in Pd-catalyzed Sonogashira coupling reactions to give the alkyne intermediates 2-[(pentafluorophenyl)ethynyl]pyridine³⁴ and 2-[(3,5-difluorophenyl)ethynyl]pyridine. The pentafluorophenyl derivative is reacted with azidomethyl pivalate in a 1,3-dipolar addition reaction by applying a Ru catalyst.^{35,36} Next, the N-methyl pivalate group is cleaved under basic conditions to produce ligand L2. The 3,5-difluorophenyl alkyne derivative can be reacted with trimethylsilyl azide without the need for a metal catalyst.37 Deprotection of the TMS group occurs in situ or



Scheme 1 a. (i) azidomethyl pivalate, t-BuOH–H₂O, CuSO₄, sodium ascorbate, RT, (ii) NaOH, MeOH–H₂O, 85 °C; b. pentafluorobromobenzene or 3,5-difluorobromobenzene, Et₃N, PdCl₂(PPh₃)₂, CuI, 80 °C; c. (i) azidomethyl pivalate, dioxane, Cp*Ru(PPh₃)₂Cl, 100 °C, (ii) NaOH, MeOH–H₂O, RT (for L2) or TMS-N₃, DMF, 90 °C (for L3).



Fig. 1 Crystallographic structures of 2 and 3. Hydrogen atoms are omitted for clarity. Displacement ellipsoids are at the 50% probability level.

during work-up, giving ligand L3 in one preparative step from its corresponding alkyne.

The triazole ligand and the intermediate dichloro-bridged iridium complex $[(F_2ppy)_2Ir(\mu-Cl)]_2^{26}$ are refluxed in a solvent mixture of dichloromethane and ethanol affording complexes **1–3** in yields that vary from 44% to 65% after purification by column chromatography. Characterization of all the metal complexes was performed using ¹H-NMR, ¹⁹F-NMR and high-resolution mass spectrometry (HRMS).

The decomposition temperatures of the studied complexes were determined *via* thermogravimetric analysis (TGA) under nitrogen stream. All compounds undergo to a significant weight reduction (>5%) between 330 and 340 °C, but **1** and **2** also show a small (~3%) weight loss between 200 and 230 °C. The former values are similar to those of complexes bearing acetylacetonate (acac) ligands of the type (ppy)₂Ir(acac), which is reported to decompose at around 340 °C.¹⁴

X-Ray diffraction analyses

Single crystals of 2 and 3 were obtained by slow evaporation of a dichloromethane-hexanes solution and they were characterized by X-ray diffraction to confirm the mode of coordination of the phenylpyridine and triazole ligands. In Fig. 1 the crystallographic structures of 2 and 3 are reported, while Tables 1 and 2 contain some selected structural parameters and crystallographic data,† respectively. A comparison of these crystal structures with those of 4 and 5 is possible, since the latter have already been reported.27 The Ir-N distances involving the triazole ligand are almost identical for 3 and 5, while in 2, the iridium-triazole [Ir-N(8) =2.127(2)] and iridium-pyridine [Ir-N(1) = 2.164(2)] distances of ligand L2 are, respectively, longer and shorter if compared to those of complex 4. As already reported for their isomers, also for 2 and 3 a *trans*-effect is observable: such a statement is based on the fact that bonds opposite to C atoms [Ir-N(1) and Ir-N(8)] are longer than bonds opposite to N atoms [Ir-N(21) and Ir-N(41)]. In addition, Ir-C(52) bond distance is longer in 2 and 3 than for 4 and 5. More interestingly, the triazole ring and the F-substituted phenyl ring are highly distorted from coplanarity, having both a torsional angle quite close to 90° (83.04° for 2 and 89.89° for 3). This feature reflects the steric hindrance of the pyridine ring in the

 Table 1
 Selected structural parameters for complexes 2 and 3

	2 Selected bond lengths		
Ir(1) - N(1)	2.164(2)	2,168(3)	
Ir(1) - N(8)	2.127(2)	2.115(3)	
Ir(1) - N(21)	2.039(2)	2.036(3)	
Ir(1) - N(41)	2.043(2)	2.042(3)	
Ir(1)-C(32)	2.014(3)	2.012(4)	
Ir(1)–C(52)	2.009(3)	2.012(4)	
	Selected bond	angles/°	
N(1)–Ir(1)–N(8)	76.17(9)	76.24(13)	
N(41) - Ir(1) - N(8)	89.04(9)	89.47(14)	
N(8)-Ir(1)-C(32)	172.93(10)	172.90(14)	
N(1)-Ir(1)-N(21)	88.76(9)	89.14(12)	
N(21)-Ir(1)-N(41)	172.09(9)	172.07(12)	
N(8)–Ir(1)–C(52)	100.15(10)	99.34(14)	
C(32)-Ir(1)-C(52)	86.83(11)	87.53(16)	
	Selected torsi	onal angles/°	
N(10)-C(11)-C(12)-C(13)	83.04	89.89	

pyridine-1,2,3-triazole ligand, which forces the F-substituted phenyl ring into a perpendicular conformation.

Absorption and emission spectroscopy

The absorption spectra of complexes 1–3 are presented in Fig. 2 and were recorded at room temperature in dichloromethane solutions. The compounds show absorption features similar to those reported for other Ir(ppy) complexes^{16,21} with typical strong π – π * transitions in the UV region localized on the F₂ppy ligands (~260 nm) and on the triazole ligand (~300 nm) and weak singlet and triplet metal-to-ligand charge transfer (^{1,3}MLCT) bands at lower energies between 350 and 450 nm. In comparison with complex 1, complexes 2 and 3 exhibit more intense absorption bands due to the additional presence of the chromophoric (per)fluorinated phenyl ring in the chemical structure.

In Fig. 2 the normalized emission spectra of complexes 1-5 are reported. The vibronic structure of the emission bands indicates a certain degree of mixing between the ligand centered (³LC)

Table 2Crystallographic data and refinement parameters for complexes2 and 3

	2	3
Formula	C ₃₅ H ₁₆ F ₉ IrN ₆ •C ₄ H ₈ O	C ₃₅ H ₁₉ F ₆ IrN ₆ •CH ₂ Cl ₂
M_r	955.84	914.69
Crystal size/mm	$0.30 \times 0.20 \times 0.10$	$0.25 \times 0.20 \times 0.10$
Crystal system	monoclinic	monoclinic
a/Å	25.9847(2)	26.1732(2)
b/Å	16.2224(2)	15.7673(2)
c/Å	18.3429(2)	18.1899(2)
α/deg	90.00	90.00
β/deg	116.537(1)	117.832(1)
γ/deg	90.00	90.00
V/Å ³	6917.54(13)	6638.25(12)
$\rho_{\rm calc}/{\rm g}~{\rm cm}^{-3}$	1.836	1.830
μ/cm^{-1}	39.53	42.55
Z	8	8
Space group	<i>C</i> 2/ <i>c</i> (No. 15)	<i>C</i> 2/ <i>c</i> (No. 15)
λ/Å	0.71073	0.71073
T/K	223	223
Reflns collected	23852	22679
Indep reflns	8466	8192
Obs reflns([$I \ge 2\sigma(I)$])	6911	6738
Refined param.	505	561
R	0.026	0.034
$R_{\rm w}^{2}$	0.057	0.084
$[(\sin\theta)/\lambda]/\text{\AA}^{-1}$	0.67	0.67
$\Delta \rho_{\rm max,min}/e {\rm \AA}^{-3}$	1.36 (-1.87)	1.35 (-1.87)

and ³MLCT states (as shown later).^{15,27} The photophysical data are shown in Table 3, together with the calculated radiative $(k_r = \Phi/\tau)$ and nonradiative $(k_{nr} = (1 - \Phi)/\tau)$ rate constants. All the complexes show intense emission at room temperature (Table 3).

Complexes 1–3 exhibit photoluminescence spectra with maxima at 460, 457 and 458 nm respectively, at room temperature in dichloromethane. The spectra of 1–3 show, if compared with the emission spectral shapes of complexes 4 and 5 recently studied²⁷ (see Fig. 2), a less pronounced shoulder at around 523 nm, while the emission looks slightly sharper, with a smaller contribution in the green region of the spectra. To prove this assumption, we have calculated the 1931 *Commission*



Fig. 2 Absorption of complexes 1–3 and emission spectra of complexes 1–5 in dichloromethane solutions at room temperature ($\lambda_{ex} = 350$ nm).

Internationale de L'Eclairage (x,y) coordinates (CIE_{x,y}) for the PL spectra measured in solution, and they are reported in Table 4. It can be seen that for compounds 1–3 the y value is slightly lower then that calculated for 4 and 5, pointing to greater blue character for the former compounds.

The emission quantum yields in degassed solution are relatively high for all the three complexes 1–3, in the range between 27% and 32%, and their extreme oxygen sensitivity is a confirmation of the triplet character of the emission.¹² The excited state lifetimes (τ) measured in dichloromethane solutions are all monoexponential and they fall in a narrow range, with values in the microsecond range typical for similar iridium complexes.^{14,19}

The emission spectra recorded for all compounds at 77 K in butyronitrile glass matrix show a rigidochromic shift of about 10 nm towards higher energies, indicating a dominating ³MLCT character of the emission. At this temperature, complexes 1-3exhibit very similar emission spectra, with maxima at 450 nm. This suggests that for all these compounds the emission arises from the same triplet excited state, as also confirmed by theoretical calculations (see next section).

Theoretical investigations

To provide more insight into the energy levels involved in the electronic transitions, we performed DFT calculations on all the complexes studied. In a similar theoretical investigation recently reported by our group,²⁴ complex 4 was also studied together with other iridium(III) complexes. For this compound, results showed that the lowest triplet excited state was mostly localized on the phenylpyridine ligands. We have included in the present work a few additional data regarding complex 4, in order to have a clearer overview and to better understand its photophysical properties. Using the DFT and TD-DFT methods with the B3LYP hybrid functional together with LANL2DZ and 6-31G* basis sets for iridium and lighter atoms, respectively, the ground state geometries and low-lying excited state energies were calculated. Fig. 3 depicts, for each complex, the molecular orbitals (MOs) mainly involved in the triplet emitting state, while the energy gaps and the detailed molecular orbital description of the excited states are listed in Table 5. The optimized geometrical parameters calculated for complexes 2 and 3 were found to be in good agreement with the X-ray experimental data. For example, the Ir-N(8) calculated/experimental distances for 2 and 3 are 212.4/212.7 and 212.1/211.5 pm, respectively. In addition, the calculated/experimental Ir-C(52) distances are also nicely comparable, which are 202.2/200.9 and 202.3/201.2 pm for 2 and 3, respectively.

The iridium complexes shown in Chart 1 have very similar emission spectra, although they considerably differ in the substitution of the triazole moiety. The time-dependent DFT calculations carried out for these complexes show that their lowest (emitting) triplet state is mostly composed by HOMO \rightarrow LUMO (for 1 and 5) and HOMO \rightarrow LUMO + 1 (for 2, 3 and 4) single excitations (HOMO is highest-occupied molecular orbital, LUMO is lowest-unoccupied molecular orbital). The calculations also show that this emitting state is a mixture between ³MLCT and ³ILCT (inter-ligand charge transfer) states, and also of ³LC (ligand centered) in the case of 5. The calculated transition energies are in good agreement with the

Table 3 Photophysical data for complexes 1-5

	Absorpt	tion ^b	Emission, 298 K ^d						Emission, 77 K ^{cd}		
	λ/nm	ε/M^{-1} cm ⁻¹	λ_{\max}^{e}/nm	Φ^a	\varPhi^b	$ au^a/\mu ext{s}$	$ au^b/\mu { m s}$	$k_{\rm r}/10^5~{ m s}^{-1}$	$k_{\rm nr}/10^5 {\rm ~s^{-1}}$	$\lambda_{\rm max}/{\rm nm}$	$ au/\mu s$
1	259	35500	460 (1)	0.32	0.04	1.2	0.16	2.6	5.6	450	3.7
	307	15770	489 (0.87)								
	370	4100	· · · ·								
	450	170									
2	252	42500	457 (1)	0.31	0.04	1.3	0.18	2.3	5.3	450	3.8
	300	25160	487 (0.81)								
	370	5600	· · · ·								
	450	250									
3	248	43600	458 (1)	0.27	0.03	1.1	0.15	2.5	6.8	450	3.6
	302	24600	487 (0.8)								
	370	6000	× /								
	450	270									
4 ²⁷	257	43800	458 (1)	0.16	0.042	0.53	0.15	3.0	15.8	450	3.6
	280	33700	487 (0.87)								
	350	6700	. ,								
	370	5200									
	451	400									
5 ²⁷	261	51200	459 (1)	0.29	0.042	0.99	0.15	2.9	7.1	451	3.6
	283	46300	488 (0.83)								
	315	19800	· · · ·								
	346	11500									
	370	7200									
	451	2500									

^{*a*} In degassed dichloromethane.^{*b*} In air-equilibrated dichloromethane.^{*c*} In butyronitrile glass.^{*d*} $\lambda_{ex} = 350$ nm; $\Phi =$ emission quantum yield; $\tau =$ excited state lifetime.^{*e*} In parentheses the relative intensities are reported.

Table 4	$CIE_{x,v}$	coordinates	s calculated	from t	he PL s	pectra of	complex	xes
1–5 in di	chloror	nethane solu	ations					

	Complex						
$CIE_{x,y}$ coordinates	1	2	3	4	5		
x y	0.13 0.27	0.15 0.26	0.15 0.27	0.16 0.30	0.15 0.28		

experimental ones, as can be seen in Table 5. The examination of the molecular orbitals mostly contributing to the triplet state of complexes 2-4 (LUMO + 1) shows that this emitting state is strongly localized on the F_2ppy ligand, which nicely explains why substitutions on the triazole moiety mostly do not influence the respective emission spectra. The triplet state of complex 1 shows still a considerable contribution of F_2ppy , although a contribution from the triazole can also be seen. In the case of complex 5, the contribution of the triazole to the triplet excited state is actually larger than that of F_2ppy , although the predicted triplet



Fig. 3 DFT optimized geometries and selected molecular orbitals of complexes 1-5.

Table 5 Energies of the lowest triplet (T) and singlet (S_1) excited states, and character of transitions involving those states and the ground state, calculated for complexes 1–5 using TD-DFT. The experimental triplet energies taken from the 77 K emission spectra are also reported. For each state the transitions between MOs with the highest contributions (in %) are shown

State	Transition wavelengths ^a	Participating MO	Transition character ^b
Complex 1 S ₁	405 nm (calc)	HOMO → LUMO (81%) HOMO → LUMO + 1 (14%)	$ML_bCT + ML_cCT + L_aL_bCT + L_aL_cCT$
Т	443 nm (calc) 450 nm (exp)	HOMO \rightarrow LUMO (45%) HOMO \rightarrow LUMO + 1 (20%) HOMO - 4 \rightarrow LUMO (10%) HOMO - 4 \rightarrow LUMO + 1 (6%)	$ML_bCT + ML_cCT + L_aL_bCT + L_aL_cCT$
Complex 2 S ₁	416 nm (calc)	HOMO → LUMO (96%)	$ML_cCT + L_aL_cCT$
Т	440 nm (calc) 450 nm (exp)	HOMO \rightarrow LUMO + 1 (54%) HOMO - 2 \rightarrow LUMO + 1 (16%) HOMO - 4 \rightarrow LUMO + 1 (13%) HOMO \rightarrow LUMO + 2 (6%)	$ML_bCT + L_aL_bCT$
Complex 3 S ₁	410 nm (calc)	HOMO \rightarrow LUMO (89%) HOMO \rightarrow LUMO + 1 (8%)	$ML_{c}CT + L_{a}L_{c}CT$
Т	442 nm (calc) 450 nm (exp)	HOMO \rightarrow LUMO + 1 (63%) HOMO - 3 \rightarrow LUMO + 1 (15%) HOMO - 4 \rightarrow LUMO + 1 (11%) HOMO - 5 \rightarrow LUMO + 1 (3%)	$ML_bCT + L_aL_bCT$
Complex 4 S ₁	401 nm (calc)	HOMO \rightarrow LUMO (95%)	$ML_cCT + L_aL_cCT$
Т	442 nm (calc) 450 nm (exp)	HOMO \rightarrow LUMO + 1 (46%) HOMO \rightarrow LUMO (15%) HOMO - 2 \rightarrow LUMO + 1 (11%) HOMO - 3 \rightarrow LUMO + 1 (9%)	$ML_bCT + L_aL_bCT$
Complex 5 S ₁	402 nm (calc)	HOMO \rightarrow LUMO (66%) HOMO \rightarrow LUMO + 1 (16%)	$ML_{c}CT + L_{c}L_{b}CT + L_{c}C$
Т	451 nm (calc) 451 nm (exp)	HOMO \rightarrow LUMO (44%) HOMO $-1 \rightarrow$ LUMO (22%) HOMO \rightarrow LUMO $+1$ (14%) HOMO $-1 \rightarrow$ LUMO $+1$ (10%)	$ML_{c}CT + L_{c}L_{b}CT + L_{c}C$

^{*a*} The calculated (calc) transition wavelengths are represented by linear combinations of the electronic transitions shown in column 3. The experimental (exp) transition wavelengths obtained from the corresponding emission spectra are also shown for comparison purposes.^{*b*} The interligand charge transfer (ILCT) and the metal-to-ligand charge transfer (MLCT) states are represented by $L_x L_y CT$ and $ML_x CT$, respectively, where $L_x L_y$ denotes charge transfer from the ligand *x* to the ligand *y* and ML_x denotes charge transfer from the metal to the ligand *x*. The subscripts used for the ligands were a, b and c, which correspond to the ligands F₂ppy-1, F₂ppy-2 and triazole, respectively. LC denotes ligand centered.

energy is still very similar to that predicted for the other complexes. The representation of excited states by a linear combination of single excitations between molecular orbitals may sometimes lead to counterintuitive results,^{23,38} as for example for compounds 2-4, where the triplet states are mainly HOMO \rightarrow LUMO + 1 in character. However, if we take into account that the energy difference between LUMO and LUMO + 1 is small (0.17 eV for 2, 0.11 eV for 3, and 0.09 eV for 4), and that the calculated energy of the excited states are in very good agreement with the experimental ones, it turns out that TD-DFT gives in fact good results for iridium complexes.

The calculations suggest that, for this type of $Ir(F_2ppy)$ heteroleptic complexes bearing pyridyl-triazole ancillary ligands, substitution onto the phenylpyridine moiety should be carried out if one is interested in achieving a better tuning of the emission wavelengths.

Electrochemistry

Cyclic voltammetry experiments for complexes 1–3 were run in the presence of ferrocene (FeCp₂) as internal reference, in dry, degassed acetonitrile and results are reported in Table 6. For compounds 1–3, the first reduction process is reversible while the second is quasi-reversible. For compound 1, the i_a/i_c ratio for the reduction waves increases with increasing the scan rate. The first reduction has a peak-to-peak separation smaller than 80 mV whereas the second reduction has a peak-to-peak separation of 120 mV. The oxidation was irreversible at all scan rates and potential ranges tried. The reduction processes of complex 2 exhibit interesting behaviour: if the scan is stopped after the first reduction peak, the peak does not show a reversible return wave, while if scanned up to -2.5 V, it becomes quasi-reversible (scan rate = 500 mV s⁻¹) (see Fig. S3, ESI†). Moreover, the oxidation wave shows a reversibility which is scan rate dependent: at

Table 6Electrochemical redox potentials of the iridium complexes $1-3^a$

Compound	$E_{\rm red}/V$	$\Delta E_{\mathrm{pp}}{}^{b}/\mathrm{mV}$	$E_{\rm red}/V$	$\Delta E_{\mathrm{pp}}{}^{b}/\mathrm{mV}$	$E_{\rm ox}/{\rm V}$	$\Delta E_{\rm pp}^{\ b}/{\rm mV}$
1	-2.66	120	-2.39	78	0.98 ^c	_
2 3	-2.61 -2.58	136 140	-2.36 -2.34	90 90	1.02 0.99	90 85
^{<i>a</i>} In acetonit	rile vs F	c/Fc ⁺ . ^b Peak	to-peak	separation.	^c Irreve	rsible.

100 mV s⁻¹ no return wave is detected, while at 1000 mV s⁻¹ the process becomes reversible.

For complex 3 the oxidation process observed at 0.99 V is reversible. The cyclic voltammogram of the free triazole ligands (not shown) does not show any reversible reduction and oxidation processes within the solvent electrochemical window.

Electrophosphorescent polymer LEDs

For complexes 1–5 the energies of the HOMO level were experimentally determined in air using a photoelectron spectrometer. The results are in good agreement with the energies predicted with DFT calculations and are displayed in Table 7. The lower experimental value obtained for complex 2 can be attributed to a larger experimental error.

Polymer light-emitting diodes (PLEDs) with 1 and 3 were fabricated under inert conditions, using the studied compounds as dopants in a poly(9-vinylcarbazole) (PVK) matrix. Devices were made with different doping concentrations of iridium complex, and for some of them a layer of PEDOT:PSS acting as

Table 7Experimental and calculated HOMO energies for complexes1-5

Compound	HOMO _{exp} /eV	HOMO _{calc} /eV		
1	5.77	5.70		
2	5.68	5.86		
3	5.80	5.82		
4	5.85	5.87		
5	5.82	5.82		

a hole-transporting material was added. The device structure can be represented as follows: glass/ITO/PEDOT:PSS (100 nm)/ PVK:Bu-PBD (20%) + Ir emitter (x%) (80 nm)/TPBI (20 nm)/Ba (5 nm)/Al (80 nm) (full details about these acronyms are given in the Experimental section). The doping concentration for the iridium emitters was 8% or 10% in weight.

Fig. 4 shows the electroluminescent (EL) spectra of complexes 1 and 3 for the studied devices. No emission coming from the host polymer matrix was observed, meaning that efficient energy transfer from the host to the guest iridium complex takes place. The electroluminescent spectra of both complexes are almost identical, with a maximum at 495 nm and a shoulder at 466 nm. Also, the spectra are red-shifted by about 6-8 nm in comparison to those recorded in solution. In addition, a noticeable difference arises from the relative intensity of these two emission maxima: in the film, the band at lower energy (~495 nm), becomes more intense than the higher energy one (\sim 466 nm). This feature affects the color chromaticity of the device, resulting in $CIE_{x,y}$ coordinates which are far more close to a blue-green than to a pure blue color. During the preparation of this report, Cheng and coworkers³⁹ published a paper on LEDs doped with complex 1. The devices, which were prepared by vacuum deposition, exhibited similar EL behaviour, leading to a blue/green-emitting device. This effect was not clearly understood, but it was suggested to be related to a couple of factors, such as (i) the cathode materials (LiF/Al) used in the device or (ii) the triplet energy of the host material, which can influence the charge recombination zone leading to an excited state with lower energy.

The plot of luminance vs. voltage for the devices with 8% doping of iridium emitter is shown in Fig. 4. The turn-on voltage (V_{t-on}) , *i.e.* the voltage needed to reach 1 cd m⁻², is about 18 V for the devices without a PEDOT:PSS layer while, when such a layer is present, the devices made with complex **1** and **3** turn on at 17 and 13 V respectively. The presence of a hole-injection layer (PEDOT) makes the charge injection easier, thus lowering turn-on voltages.

In Fig. 5 the external quantum efficiency (EQE) plots obtained for devices made with complexes 1 and 3 are shown. The devices performances were relatively poor when compared to some of the best iridium-doped PLEDs,^{20,40} but nonetheless they are in



Fig. 4 Left: EL spectra of PLEDs doped with Ir complexes 1 and 3. In parentheses the $CIE_{x,y}$ coordinates are reported. Right: Luminance vs. voltage for the devices with 8% doping.



Fig. 5 External quantum efficiencies (EQE) as a function of current density of devices doped with complex 1 (left) and complex 3 (right).

the same range of other promising devices reported in the literature. $^{\rm 41-44}$

As reported by Neher *et al.*,⁴⁵ the low efficiencies of these devices may be related to a significant quenching effect exerted by the electron-transporting material (Bu-PBD) blended in the emissive layer which can act as an energy trap. This material has a non-emissive triplet state which lies at lower energy if compared to our complexes and might therefore induce efficient triplet harvesting.

From Fig. 5 it clearly emerges that complex 3 has better performances than complex 1. For complex 1, the highest external quantum efficiencies were obtained when the PEDOT:PSS layer was present: EQE around 0.4% was reached with 8% doping, while with 10% doping the efficiency was around 0.3%. With complex 3, maximum EQEs of 0.48% and 0.6% were reached with and without PEDOT, respectively. In general for this series, with the only exception for the device made with complex 3 (10%), we can say that the devices containing a PEDOT:PSS layer are better performing than the devices without this layer. A maximum current efficiency of 0.88 cd A^{-1} was achieved when using complex 1 (8%) together with a PEDOT:PSS layer, while a value of 1.25 cd A⁻¹ was achieved using complex 3 (8%). These first results likely indicate that a self-quenching process is occurring at higher dopant percentages, as the device performances seem to decrease upon increasing the concentration of iridium(III) emitter, an effect often ascribed to triplet-triplet annihilation. It has to be noted that the devices rapidly reached the maximum efficiency peak, followed by a roll-off (see Fig. 5) which is often observed in similar systems and it could be attributed to a lack of stability and to a relatively high operating voltage.18,20,44

Conclusions

We reported the synthesis and the full characterization of new heteroleptic iridium complexes, each one bearing two F_2ppy and one 1,2,3-triazole-based ligand. The emission spectra in solution are slightly blue shifted with respect to their analogous complexes with 1,2,4-triazoles moieties, and due to their narrower shape they display color coordinates closer to that of pure blue. The DFT calculations showed that the triplet emitting state of the complexes can be described by a mixture between

³MLCT and ³ILCT states, those states being more localized on the F_2ppy ligands for complexes 1–4. Electrochemistry recorded in acetonitrile solutions shows reversible or quasi-reversible redox processes. In preliminary device tests 1 and 3 were used as dopants in PVK-based OLEDs. A change in the EL spectral shape was observed, resulting in a green shift in the color point for these devices when compared to the color point of the PL spectra from solution measurements. External quantum efficiencies of about 0.4% and 0.6% were obtained for the prepared devices. We have therefore shown that the newly presented emitting materials can be used as phosphorescent dopants in the fabrication of PLEDs.

Experimental

Photophysics

Absorption spectra were measured on a Varian Cary 5000 double-beam UV-Vis-NIR spectrometer and baseline corrected. Steady-state emission spectra were recorded on 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 dispersion⁻¹; 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 using the time-correlated single-photon counting (TCSPC) option on the Fluorolog 3. NanoLEDs (295, 402 and 431 nm; FWHM < 750 ps) with repetition rates between 10 kHz and 1 MHz were used to excite the sample. The excitation sources were mounted directly on 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 (TAC) to the excitation pulse. Signals were collected using an IBH DataStation Hub photon counting module and data analysis was performed 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. Emission quantum yields were measured by the method of Crosby and Demas⁴⁶ using quinine bisulfate in 1.0 N sulfuric acid as reference ($\Phi = 0.546$). All solvents were spectrometric grade and all solutions were filtered through a 0.2 µm syringe filter before measurement. Deaerated samples were prepared by the freeze-pump-thaw technique.

X-Ray crystallography

Data sets were collected with a Nonius KappaCCD diffractometer, equipped with a rotating anode generator. Programs used: data collection COLLECT,47 data reduction Denzo-SMN,48 absorption correction SORTAV49,50 and Denzo,51 SHELXS-97,⁵² structure refinement structure solution SHELXL-97,53 graphics SCHAKAL.54 CCDC 678024 and 678025.†

Density functional theory calculations

The ground state geometries of the iridium complexes were calculated by using density functional theory (DFT). The B3LYP functional,^{55,56} together with the 6-31G basis set for the lighter atoms (C, H, N and F) and the relativistic effective core potential LANL2DZ for iridium⁵⁷ were used in the DFT calculations. The excited states were calculated using those optimized geometries with the time-dependent DFT (TD-DFT), where 10 triplets and 10 singlets were generated The program used was Gaussian03.58

OLEDs preparation and characterization

Poly(9-vinylcarbazole) (PVK, $M_w = 1100000$) and Bu-PBD (2-(4-biphenylyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole) were obtained from Aldrich. Poly(3,4-ethylenedioxythiophene) : poly(styrenesulfonate) (PEDOT:PSS, 1:6 dispersion in water, electronic grade AI4083) and 1,3,5-tris[N-(phenyl)benzimidazole] benzene (TPBI) were purchased from HC Starck and from Sensient Imaging Technologies, respectively.

The device structure consists of a 120 nm transparent ITO layer as the bottom electrode, supported on a glass substrate. A 100 nm PEDOT:PSS layer and the emissive layer were spun in sequence on top of ITO, using a spincoater P6700 from Specialty Coating Systems. Then, a TPBI layer (20 nm), the barium electrode (5 nm) and the aluminium top metal contact (80 nm) were evaporated in sequence using a MBraun evaporation chamber. The ITO was treated for 10 min with UV/O₃ (UVO Cleaner 144AX, Jelight Company) prior to any further processing. The PEDOT:PSS layer was spin-coated from a water solution of the polymer. To achieve a 100 nm thick layer the following spin cycle was used: 200 rpm with 200 ms acceleration time (5 s) then 1000 rpm with 200 ms acceleration (10 s). The device was then annealed at 180 °C for 2 min. Then, the emissive layer was spun from a THF solution containing 15 mg ml⁻¹ of PVK, 20 wt% of Bu-PBD with respect to PVK mass and varying mass ratios of the iridium complex. The polymer-THF solution was stirred at room temperature for 1 h before the Bu-PBD and iridium complex additions. The PVK-THF-Bu-PBD-iridium complex solution was stirred for a further hour at room temperature, and filtered through a 5 mm PTFE filter (Millex, Millipore) prior to spinning. To get a polymer layer with a thickness of 75–90 nm the

solution was spin-coated (Delta6 RC spincoater from Suss Microtec) at 3800 rpm (10 s), followed by 900 rpm (25 s). The barium electrode (5 nm) was evaporated on top of the film in a vacuum chamber at a pressure of $2.0-5.0 \times 10^{-6}$ mbar at a rate of 2 Å s^{-1} . The aluminium top electrode (80 nm) was then immediately evaporated on top of the barium without reducing the vacuum.

All measurements were run in an inert atmosphere directly after device fabrication. Voltage scans were then performed from zero to a preset positive voltage and then back to zero. The LEDs were characterized by attaching a computer-controlled low-noise single-channel direct-current (DC) power source that can act as both voltage source and current source, and a voltage meter or current meter (Keithley 2600, Keithley Instruments). Light from the diode was coupled to a photodiode and read out by an electrometer/high-resistance meter (Keithley 6517, Keithley Instruments). The output of the data was handled by a Labview (National Instruments)-based program. Calibration of the photodiode was done at a fixed current with a luminance meter (LS-100 Minolta). For every diode with a different spectral distribution of light, the photocurrent as measured by the photodiode was correlated to the light output in candelas per square meter by this calibration.

When recording an EL spectrum, a fiber-optic coupled spectrometer (USB2000, Ocean Optics) was used. The emission was corrected for the wavelength dependence of the spectrometer.

Cyclic voltammetry

Cyclic voltammetry (CV) was performed using a Voltalab 40 system from Radiometer Analytical which consists of a PGZ301 potentiostat and Voltamaster 4 software. The working and the counter electrodes were a Pt disc and a Pt wire respectively, whereas Ag wire was used as a pseudoreference electrode. All glassware was dried prior to use. The dry electrolyte tetrabutylammonium hexafluorophosphate (>99.0% purity), the analyte and ferrocene (FeCp₂) used as the reference were dried and degassed at high temperature and at reduced pressure in a Schlenk flask in order to eliminate any moisture and oxygen. The flask was then evacuated and filled three times with N₂ flow. Acetonitrile freshly distilled from P2O5 was added via syringe directly into the sealed Schlenk flask, the solution 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 done under nitrogen atmosphere.

Materials and characterization

All reagents were of analytical grade and used as received. Solvents were purified according to the standard procedures. All reactions were performed under an inert atmosphere (e.g. Schlenk-line techniques), except where noted. The dichlorobridged iridium complex $[(F_2ppy)_2Ir(\mu-Cl)]_2$ was prepared following literature procedures.26,59

Molecular characterization of the triazole ligands and intermediates was performed by ¹H NMR, ¹⁹F NMR and ¹³C NMR spectroscopy using a Varian Mercury Vx 400 MHz, a Varian Gemini 300 MHz or a Varian Mercury Plus 200 MHz

spectrometer and applying a temperature of 298 K, by mass spectrometry using a Perceptive Biosystems Voyager DE-PRO MALDI-TOF-MS spectrometer or a Finnigan LCQ Decca XP Max ESI-MS spectrometer (using an Alltima HP C18 50 mm, 3 μ m column with an acetonitrile–water eluent gradient, and 0.1% formic acid in the eluent for ionization), by GC-MS using a Shimadzu GCMS-QP5000 spectrometer (applying a Zebron ZB-5 15m, 0.1 μ m or a Zebron ZB-35 30m, 0.25 μ m capillary column in a Shimadzu GC-17A chromatograph) and by FT-IR using a Perkin Elmer Spectrum One ATR FT-IR.

Molecular characterization of the iridium complexes was performed by ¹H and ¹⁹F NMR spectra recorded on an ARX 300 and ARX 400 spectrometer from Bruker Analytische Messtechnik (Karlsruhe, Germany). The ¹H NMR chemical shifts (δ) of the signals are given in ppm and referenced to residual protons in the deuterated solvents: chloroform-d₁ (7.26 ppm), dimethyl sulfoxide- d_6 (2.50 ppm), acetone- d_6 (2.09 ppm), or dichloromethane (5.31 ppm). The signal splittings were abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. All coupling constants (J) are given in Hertz (Hz). Column chromatography (CC) was performed with silica gel 60 (particle size 63–200 µm, 230–400 mesh, Merck) using common flash procedures.⁶⁰ Electrospray ionization (ESI) mass spectra were recorded on a Bruker Daltonics (Bremen, Germany) MicroTof with loop injection. Elemental analysis was provided by Mikroanalytisches Labor Beller (Göttingen, Germany). Thermogravimetric analysis (TGA) was performed by a TGA Q500 V6.7 thermal analyzer under N₂ stream with a scanning rate of 10 °C min-1. The HOMO energies were measured in air with a Riken Keiki AC2 photoelectron spectrometer (standard deviation of 0.02 eV), with a deuterium lamp as the source of UV light and a grating type monochromator. The UV spot area (area of sample that is irradiated) was 4 mm square. The light power used was 50 nW. Spectra were corrected for relative light intensity at each wavelength (steps of 0.10 eV, total range from 3.4 eV to 6.2 eV).

Synthesis details

2-(1H-1,2,3-Triazol-5-yl)pyridine (L1) has only been generally described in a report that describes the synthesis of the azidomethyl pivalate building block.³³ More specifically, azidomethyl pivalate (7.55 g) and 2-pyridyl acetylene (5.0 g) are dissolved in a 1 : 1 mixture of water and tert-butanol (150 mL). Copper sulfate (342 mg) and sodium ascorbate (287 mg) are added. The reaction mixture is stirred for 24 h at room temperature, during which time a suspension is formed. The mixture is poured into a 5% aqueous ammonia solution, and this solution is thereafter extracted with ethyl acetate. The organic ethyl acetate layer is dried with MgSO₄, and concentrated. Finally, the residue is purified by silica column chromatography (1% MeOH in CHCl₃). Yield of the protected intermediate: 7.65 g (61%). ¹H NMR (200 MHz, CDCl₃) δ: 8.62 (m, 1H); 8.39 (s, 1H); 8.20 (d, 1H, J = 4.2 Hz); 7.80 (m, 1H); 7.28 (m, 1H); 6.31 (s, 2H); 1.20(s, 9H). ¹³C NMR (50 MHz, CDCl₃) δ: 177.5; 149.8; 149.5; 148.3; 136.9; 123.3; 123.1; 120.4; 69.8; 38.8; 26.8. FT-IR: 1727 cm⁻¹.

The methyl pivalate protected triazole (7.65 g) and NaOH (2.58 g) are dissolved in 60 mL MeOH–H₂O (1 : 1). The mixture is heated for 24 h at 85 °C. Then, the reaction mixture is extracted

with chloroform, and the organic extracts are dried with MgSO₄. Filtration and evaporation of the volatiles gives a residue that contains the product and some trimethylacetic acid. The latter can be removed by stirring the solid in a small amount of water (avoid using too much water, as the product dissolves in water too). Drying the residue after washing gives a yield of 2.32 g (53%) of an off-white powder. ¹H NMR (CDCl₃ with some CD₃OD) δ : 8.75 (d, 1H, J = 4.2 Hz); 8.4 (s, 1H); 8.0 (d, 1H, J = 7.8 Hz); 7.8 (m, 1H); 7.3 (m, 1H). ¹³C NMR (CDCl₃ with some CD₃OD) δ : 150.0; 149.1; 146.0; 137.4; 128 (broad); 123.2; 120.9. LC-MS gives an ion mass of [M + H⁺] = 147 g mol⁻¹.

2-[(Pentafluorophenyl)ethynyl]-pyridine has been described elsewhere.³⁴

[4-(Pentafluorophenyl)-5-(pyridin-2-yl)-1H-1,2,3-triazol-1-yl] methyl pivalate. 2-[(Pentafluorophenyl)ethynyl]pyridine (1.0 g), azidomethyl pivalate (0.64 g, 1.1 eq.) and the Ru catalyst^{35,36} Cp*Ru(PPh₃)₂Cl (1 mol%, 30 mg) are stirred in dioxane (25 mL; predried on molecular sieves) at 100 °C, while the mixture is kept under an argon atmosphere. The reaction can be monitored by ¹⁹F NMR and ¹H NMR. Extra azide is added, if not present any more. After 5 days of stirring, the mixture is evaporated to dryness and the residue is purified by silica column chromatography (1% MeOH in CHCl₃), and by a further column chromatography step (hexane-ethyl acetate 4 : 1). The product still contains some small impurities, but is used without further purification in the next step. ¹H NMR (200 MHz, CDCl₃) δ: 8.70 (m, 1H); 7.73 (m, 1H); 7.39 (m, 1H); 7.21 (d, 1H, J = 8.0 Hz); 6.67 (s, 2H); 1.05 (s, 9H). ¹⁹F NMR (376 MHz, CDCl₃) δ: -138.3 (m, 2F); -151.7 (m, 1F); -160.9 (m, 2F). MALDI-TOF-MS (CHCl₃): m/z 427.2 ([M + H⁺]), 449.3 ([M + Na⁺]).

2-[4-(Pentafluorophenyl)-1*H***-1,2,3-triazol-5-yl]pyridine (L2).** The methyl pivalate protected triazole derivative described above (1.0 g) is dissolved in a mixture of 1 M NaOH (aq., 5.2 mL) and MeOH (5.2 mL), and this solution is stirred for 10 min, after which the pH is lowered to 7. The aqueous mixture is extracted with chloroform, the collected organic layers are dried with Na₂SO₄, filtered, and the filtrate is evaporated to dryness. The conversion is about 60–70%, as derived from ¹⁹F NMR. Purification with silica column chromatography (hexane–ethyl acetate 4 : 1) yields a powder product (24%). ¹H NMR (200 MHz, CDCl₃) δ : 8.60 (d, 1H, *J* = 4.8 Hz); 7.75 (m, 2H); 7.30 (m, 1H). ¹⁹F NMR (188 MHz, CDCl₃) δ : –138.4 (m, 2F); –153.0 (m, 1F); –162.0 (m, 2F). LC-MS (MeCN–H₂O): *m/z* 313 ([M + H⁺]).

2-[(3,5-Difluorophenyl)ethynyl]pyridine. 2-Pyridyl acetylene (2.0 g, 1.1 eq.), 3,5-difluorobromobenzene (3.40 g) and copper iodide (168 mg, 5 mol%) are stirred in triethylamine (50 mL). This mixture is deoxygenated by several pump-freeze-thaw cycles using vacuum and argon. The palladium catalyst $PdCl_2(PPh_3)_2$ (619 mg; 5 mol%) is added, and again the reaction mixture is degassed several times. The solution is stirred at 80 °C overnight, after which it is poured into a saturated aqueous solution of NH₄Cl. Extraction with dichloromethane, drying of the collected organic layers with Na₂SO₄, filtration and evaporation of the filtrate to a residue is followed by silica column chromatography (hexane-ethyl acetate 4:1) giving a 78% yield of the solid product. ¹H NMR (200 MHz, CDCl₃) δ: 8.60 (m, 1H); 7.68 (m, 1H); 7.55 (m, 1H); 7.30 (m, 1H); 7.10 (m, 2H); 6.82 (m, 1H). ¹⁹F NMR (188 MHz, CDCl₃) δ: -109.3 (s, 2F). GC-MS (CHCl₃): m/z 215.

2-[4-(3,5-Difluorophenyl)-1*H*-1,2,3-triazol-5-yl]pyridine (L3). 2-[(3,5-Difluorophenyl)ethynyl]pyridine (1.3 g) and trimethylsilylazide (0.77 mL) are dissolved in DMF (25 mL; dried over molecular sieves). The mixture is heated and stirred at 90 °C, and is kept under an argon atmosphere (no argon overflow is applied to keep the trimethylsilylazide in the mixture). The reaction can be followed ¹⁹F NMR, and when necessary more trimethylsilylazide is added. When the reaction is complete, typically after several days, the mixture is poured into water and the product is extracted from the water layer with ether. The collected organic layers are dried with Na₂SO₄ and evaporated to dryness. The residue is stirred in a mixture of chloroform and pentane, giving a precipitate that is collected, washed with pentane and dried. Yield: 0.47 g (30%) of an off-white powder. ¹H NMR (200 MHz, CDCl₃ with some CD₃OD) δ: 8.70 (m, 1H); 7.74 (m, 2H); 7.30 (m, 3H); 6.83 (m, 1H). ¹⁹F NMR (188 MHz, CDCl₃ with some CD₃OD) δ : -109.9 (s, 2F). LC-MS (MeCN-H₂O): m/z 259 ([M + H⁺]). MALDI-TOF-MS (CHCl₃-MeOH): m/z 259.0 ([M + H⁺]).

Synthesis of the iridium complexes. This synthetic strategy was adapted from already published procedures.^{26,27} To 0.2 mmol (1 eq.) of $[(F_2ppy)_2Ir(\mu-Cl)]_2$ and 0.44 mmol (2.2 eq.) of the pyridine-1,2,3-triazole ligand L1, L2 or L3 were stirred in 15 mL of CH₂Cl₂ and 5 mL of EtOH and the reaction was kept under reflux for 16 h under nitrogen atmosphere. Upon completion of the reaction (TLC), all solvents were removed under reduced pressure and the resulting yellow solid was chromatographed on silica gel (CC), with a dichloromethane–acetonitrile mixture (9 : 1) as eluent. The yellow solid obtained after drying the product under vacuum is washed with a minimum amount of ethyl acetate, and dried affording the pure product.

(F₂ppy)₂Ir(pta) (1): Yield: 50%. ¹H NMR (300 MHz, CD₂Cl₂) δ : 8.17 (t, 2H, J = 9.7 Hz); 8.06 (s, 1H); 7.69 (m, 1H), 7.47 (m, 2H); 6.97 (ddd, 1H, J = 6.4, 5.6, 2.5 Hz); 6.86 (dddd, 2H, J = 11.9, 7.3, 5.8, 1.4 Hz); 6.43 (m, 2H); 5.78 (dd, 1H, J = 8.5, 2.3 Hz); 5.68 (dd, 1H, J = 8.8, 2.2 Hz). ¹⁹F{¹H} NMR (282 MHz, CD₂Cl₂) δ : -108.03 (dd, J = 10.40 Hz, 1F), -108.62 (d, J = 10.20 Hz, 1F), -109.98 (dd, J = 10.50 Hz, 1F), -110.62 (d, J = 10.20 Hz, 1F). MS (ESI+, MeOH): m/z 719.11 ([M + H⁺]), 741.09 ([M + Na⁺]). HRMS calcd for C₂₉H₁₇F₄IrN₆ 719.1154 ([M + H]⁺); found 719.1145. Anal. Calcd for C₂₉H₁₇F₄IrN₆·1/ 3CH₂Cl₂: C, 47.23; H, 2.39; N, 11.27. Found: C, 47.42; H, 2.65; N, 11.28%.

(**F**₂**pp**)₂**Ir**(**pta**)**F**₅**Ph** (2): Yield: 44%. ¹H NMR (300 MHz, CD₂Cl₂) δ: 8.29 (dd, 2H, J = 15.4, 8.4 Hz); 7.78 (m, 4H); 7.59 (ddd, 2H, J = 18.3, 5.8, 0.9 Hz); 7.33 (d, 1H, J = 8.0 Hz); 7.12 (ddd, 1H, J = 7.5, 5.6, 1.3 Hz); 7.0 (dddd, 2H, J = 17.5, 7.3, 5.9, 1.4 Hz); 6.54 (dddd, 2H, J = 12.5, 11.7, 9.3, 2.4 Hz); 5.87 (dd, 1H, J = 8.4, 2.4 Hz); 5.79 (dd, 1H, J = 8.8, 2.4 Hz). ¹⁹F{¹H} NMR (282 MHz, CD₂Cl₂) δ: -139.22 (td, J = 13.45, 7.30 Hz, 2F), -154.61 (t, J = 20.88 Hz, 1F), -162.21 to -162.54 (m, 2F), -107.73 (d, J = 10.51 Hz, 1F), -108.38 (d, J = 10.22 Hz, 1F), -109.74 (d, J = 10.52 Hz, 1F), -110.46 (d, J = 10.23 Hz, 1F). MS (ESI+, MeOH): m/z 885.4 ([M + H⁺]), 907.5 ([M + Na⁺]). HRMS calcd for C₃₅H₁₆F₉IrN₆ 907.0816 ([M + Na]⁺); found 907.0792. Anal. Calcd for C₃₅H₁₆F₉IrN₆: C, 47.57; H, 1.82; N, 9.51. Found: C, 47.65; H, 1.93; N, 9.44%.

(F₂ppy)₂Ir(pta)3,5FPh (3): Yield: 65%. ¹H NMR (400 MHz, CD₂Cl₂) δ : 8.29 (dd, 2H, J = 18.60 Hz); 7.91–7.84 (m, 1H); 7.84–7.67 (m, 5H); 7.57 (ddd, 1H, J = 5.83, 0.70 Hz); 7.28–7.17 (m,

2H); 7.05 (dddd, 2H, J = 18.19, 5.72 Hz); 6.97 (ddd, 1H, J = 7.35, 1.37 Hz); 6.89 (tt, 1H, J = 9.07, 2.36 Hz); 6.53 (dddd, 2H, J = 15.13, 9.26 Hz); 5.87 (dd, 1H, J = 8.44 Hz); 5.78 (dd, 1H, J = 8.78 Hz). ¹⁹F{¹H} NMR (282 MHz, CD₂Cl₂) δ : -107.89 (d, J = 10.47 Hz, 1F), -108.48 (d, J = 10.23 Hz, 1F), -109.85 (d, J = 10.48 Hz, 1F), -110.21 (s, 2F), -110.50 (d, J = 10.24 Hz, 1F). MS (ESI+, MeOH): m/z 831.3 ([M + H⁺]), 853.2 ([M + Na⁺]). HRMS calcd for C₃₅H₁₉F₆IrN₆ 853.1099 ([M + Na]⁺); found 853.1104. Anal. Calcd for C₃₅H₁₉F₆IrN₆: C, 50.66; H, 2.31; N, 10.13. Found: C, 50.30; H, 2.22; N, 9.99%.

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