Tris-cyclometalated Iridium(III) Complexes with Three Different Ligands: a New Example with 2-(2,4-Difluorophenyl)pyridine-Based Complex

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An iridium(III) complex comprising three different cyclometalated phenylpyridine-based ligands was designed and synthesized. Interestingly, mixed-ligand complexes could be obtained by using a simple and straightforward procedure. A tris(heteroleptic) Ir^{III} complex was obtained as a mixture of stereoisomers that could not be separated. Photophysical properties of the tris(heteroleptic) complex was investigated by UV/VIS absorption and luminescence spectroscopy, and compared with those of the parent homoleptic complexes. Modelling by time-dependent density functional theory (TD-DFT) was also performed to elucidate the nature and the location of the excited state, and to support the experimental results.

Introduction. – During the past decade, Ir complexes have triggered a great deal of interest due to their outstanding photophysical properties attractive for applications such as light-emitting devices [1–4], solar-energy conversion [5], chemosensors [6][7], and biological labeling reagents [8], but also for other photochemical and photocatalytical applications [9]. Aside from their high quantum yields of luminescence at room temperature issued for the heavy atom-induced spin–orbit coupling [10], their easy tunable emission color and remarkable thermal stability have stimulated the development of efficient and versatile synthetic methods, and this search is notably supported by the broad diversity of possible structures [11]. Among Ir complexes still actively investigated for the aforementioned applications, bis- and tris-cyclometalated Ir^{III} complexes are the most common species. Up to now, the class of heteroleptic cyclometalated Ir complexes was limited to complexes $[Ir(C\hat{}N)_2(C'\hat{}N')]$ with two different cyclometalated ligands. The optical properties of such complexes dramatically depend of the ligands C^N and C′^N′. The choice of the ligands is crucial. The resulting metal-to-ligand charge transfer (^{3}MLCT) is a combination of ^{3}MLCTs between the Ir-center and both cyclometalated ligands. Based on this consideration, being able to coordinate three different cyclometalated ligands C^N, C′^N′, and C″^N″ to the metal seems to be promising to modulate the emission wavelength of the resulting

heteroleptic complexes [Ir(C^N)(C′^N′)(C″^N″)]. This strategy would give access to a new type of tris-cyclometalated complexes with a new possible dimension of tuning the emission color. Recent years have seen the publication of a few reports mentioning the development of a synthetic procedure to access this new and as yet unknown class of complexes with three different ligands. The first evidence of the feasibility of a triple-heteroleptic complex was gained in 2007 with the synthesis of [Ir(dfppy)(ppy)(4F-piq)] (**C$_1$**) where dfppy, ppy, and 4F-piq represent 2-(2,4-difluorophenyl)pyridine, 2-phenylpyridine, and 1-(4-fluorophenyl)isoquinoline, respectively (see *Fig. 1*) [12]. In particular, **C$_1$** was prepared from the reaction of [Ir(acac)$_3$] with various ligand ratios (dfppy, ppy, and 4F-piq) and resulted in the formation of a complex mixture of several possible combinations of ligands upon complexation with the Ir-center. Separation of these complexes by traditional column chromatography could not be achieved as a result of the similar polarity of the different complexes in the mixtures. By using an HPLC apparatus equipped with a semi-preparative reversed-phase column, complex **C$_2$** that was prepared by the same non-selective synthesis could, however, be separated from the side-products [13]. The first synthetic protocol enabling to access to pure complexes of this previously unattainable group of complexes was reported in 2011 [14]. To establish the viability of the method, three different complexes [Ir(dppy)(ppy)(acac)] (**C$_3$**), [Ir(fppy)(ppy)(acac)] (**C$_4$**), and [Ir(2-(pep)py)(ppy)(acac)] (**C$_5$**) where dppy, fppy, 2-(pep)py, and acac stand for 2,4-diphenylpyridine, 2-(4-formylphenyl)pyridine, 2-[4-(phenylethynyl)phenyl]pyridine, and acetylacetonato ligands, respectively, was designed and synthesized using a combinatorial approach. Bis-cyclometallated Ir^{III} complexes **C$_3$**–**C$_5$** were easily obtained from the corresponding mixed-ligand μ-Cl-bridged dimer complexes. Splitting of the mixed-ligand μ-Cl-bridged dimer and introduction of the bidentate acac ligand provided access to the neutral complexes. Anticipating that the separation of the tris-heteroleptic complexes [Ir(L)(L′)(acac)] from the two bis-heteroleptic complexes [Ir(L$_2$)(acac)] and [Ir(L′$_2$)(acac)] would be challenging by column chromatography, a convenient choice of the cyclometalated ligands involved in the synthesis of the iridium μ-Cl-bridged dimers was carried out. In particular, the two ligands were selected to offer a relatively large difference in the R_f values between the two final products [Ir(L$_2$)(acac)] and [Ir(L′$_2$)](acac)], and the targeted [Ir(L)(L′)(acac)]. The scope of this methodology was further extended by *Baranoff* and co-workers who synthesized the cationic complex [Ir(ppy)(dfppy)(dtb-bpy)] [PF$_6$] (**C$_6$**) (dtb-bpy = 4,4′-di(*tert*-butyl)-2,2′-bipyridine) by adding two reaction steps to the former procedure [15]. In this elegant strategy, treatment of [Ir(ppy)(dfppy)(acac)] with HCl resulted in the cleavage of the acac ancillary ligand, and the pure dimer [{Ir(ppy)$_2$(dfppy)$_2$(μ-Cl)}$_2$] could be obtained. Finally, bridge-splitting and substitution reaction of the dimeric Ir^{III} precursor with dtb-bpy furnished **C$_6$** as a pure compound. The key step of the synthesis was definitely the availability of the pure heteroleptic dimer that could be later splitted with the desired ancillary ligand. Previous to this study, a variation of this strategy was reported by *Grätzel* and co-workers by a shorter procedure that enables the synthesis, in one step, of [Ir(ppy)$_2$(acac)], [Ir(dfppy)$_2$(acac)], and [Ir(ppy)(dfppy)(acac)] by reacting [Ir{(COD)(μ-Cl)}$_2$] (COD = 1,5-cyclooctadiene) with the two cyclometalated ppy and dfppy ligands [16]. Acid-induced degradation reaction of [Ir(ppy)(dfppy)(acac)] (**C$_7$**) with HCl enabled recovery of the pure heteroleptic dimer [{Ir(ppy)$_2$(dfppy)$_2$-

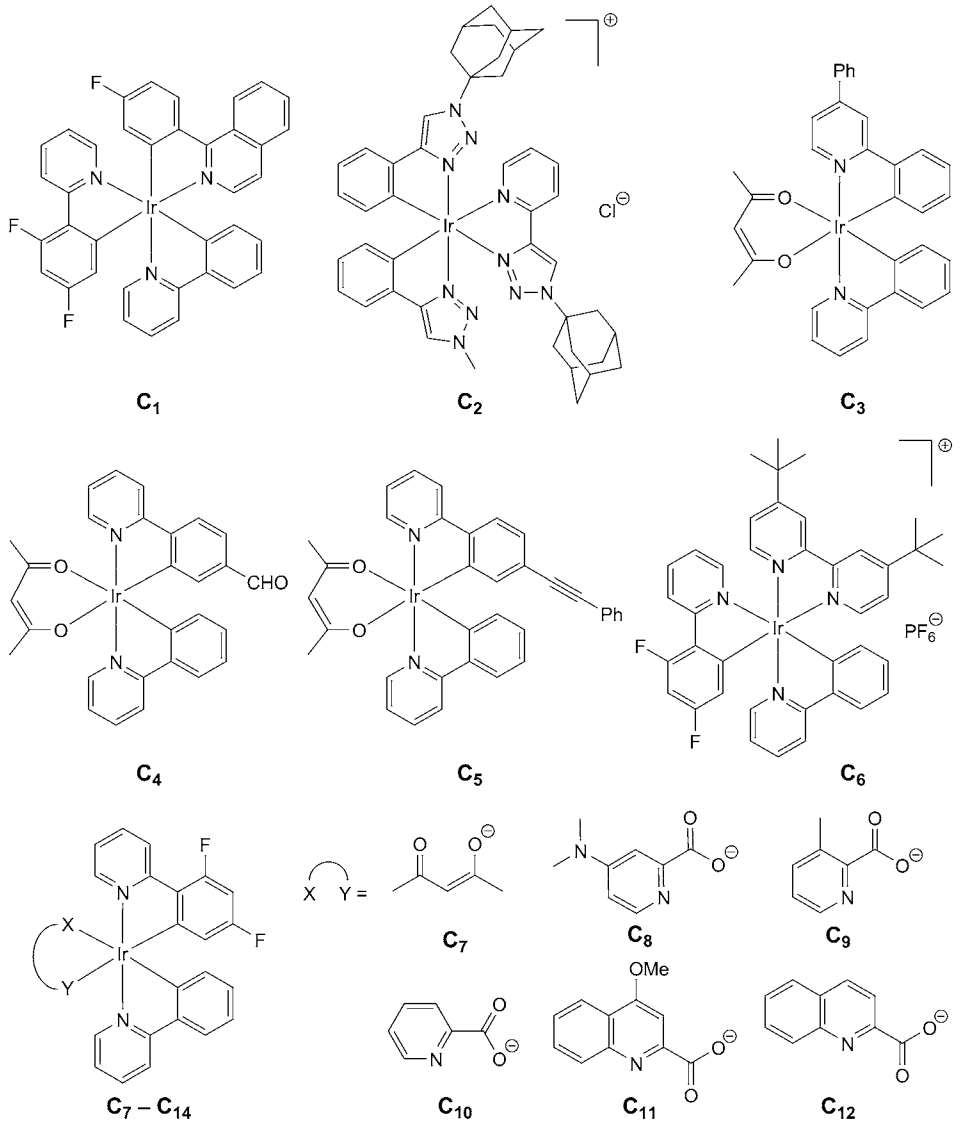


Fig. 1. *Ir^{III} Complexes with three different ligands previously reported in the literature* ([12–16])

$(\mu\text{-Cl})\}_2$] which was subsequently used for the preparation of the various tris-heteroleptic complexes **C$_8$**–**C$_{12}$**.

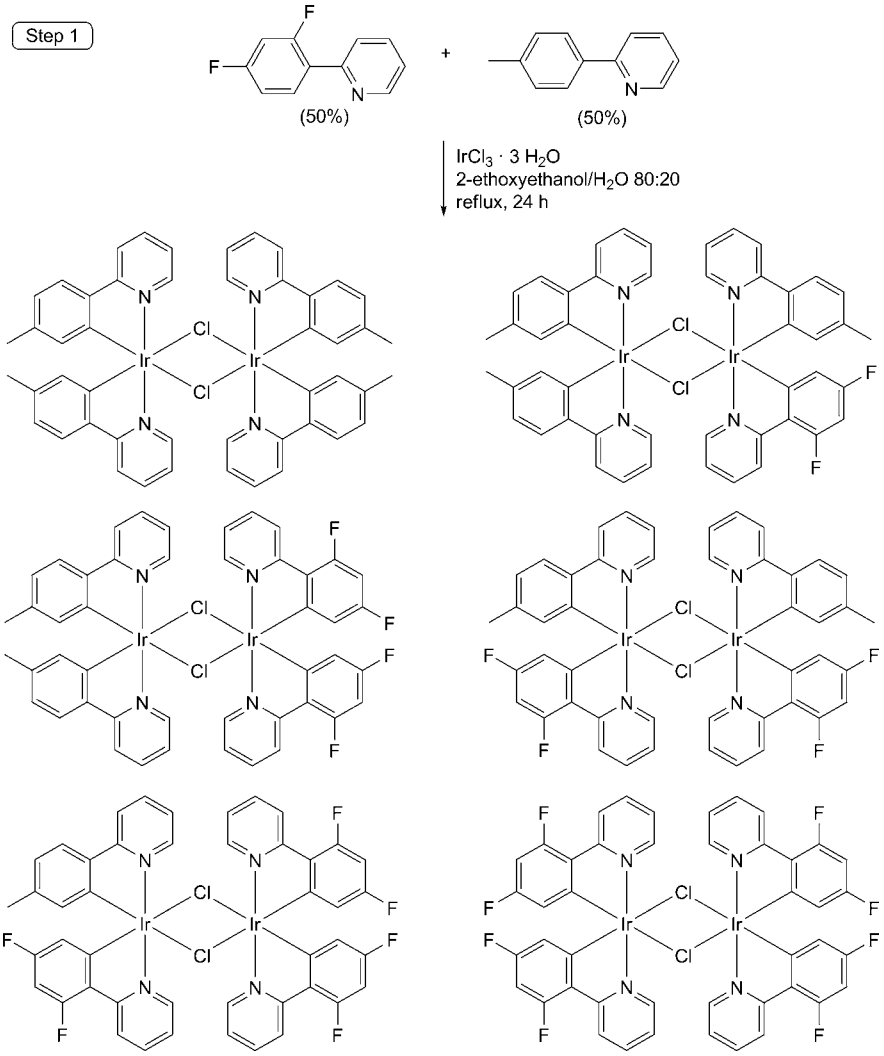
Whereas the higher control of the emission color with these complexes comprising three different ligands has been the main focus of these different reports [15][16], complex stability is a long-standing issue for materials used in the field of organic electronics and especially in Organic Light-Emitting Devices (OLEDs). In this field, tris-cyclometalated Ir complexes have been reported to be the emitters exhibiting the

highest stability [17]. The synthesis of complexes with three different cyclometalated ligands deserves thus to be investigated. Complexes $\mathbf{C_2}-\mathbf{C_{14}}$ clearly do not exhibit sufficient stability for device application. Notably, picolinate-based emitters (such as the well-known Firpic (bis(4,6-difluorophenylpyridinato-N,C^2)picolinato iridium) proved to rapidly degrade upon operation [18]. The reason for the instability of the device has notably been assigned to the dissociation of the picolinate ancillary ligand and the concomitant formation of the $[Ir(dfppy)_2]^+$ fragment. Ionic transition-metal complexes bearing bipyridine-type ligands and commonly used in Light-Emitting Electrochemical Cells (LECs) have also been reported to degrade by ligand-exchange reaction [1][19]. Finally, acetylacetonato-based phosphorescent dopants were also reported as being sensitive to acid-induced degradation in OLEDs as recently exemplified by *Grätzel* and co-workers [16]. Use of emitters bearing acetylacetonato, picolinate, or bipyridine derivatives as ancillary ligands is thus not the best choice.

Herein, we present our results concerning the synthesis of a triple heteroleptic complex [Ir(C^N)(C′^N′)(C″^N″)] comprising three different cyclometalated ligands: 2-phenylpyridine (ppy), 2-(2,4-difluorophenyl)pyridine (dfppy), and 2-(*p*-tolyl)pyridine (tpy). Herein, we describe the stepwise procedure that we have devised to access this complex, which was obtained as a mixture of geometric isomers. The optical and electrochemical properties of the new complex were also investigated. In particular, the emission wavelength of the new complex was determined as corresponding to the average of the emission wavelengths of its respective homoleptic homologues.

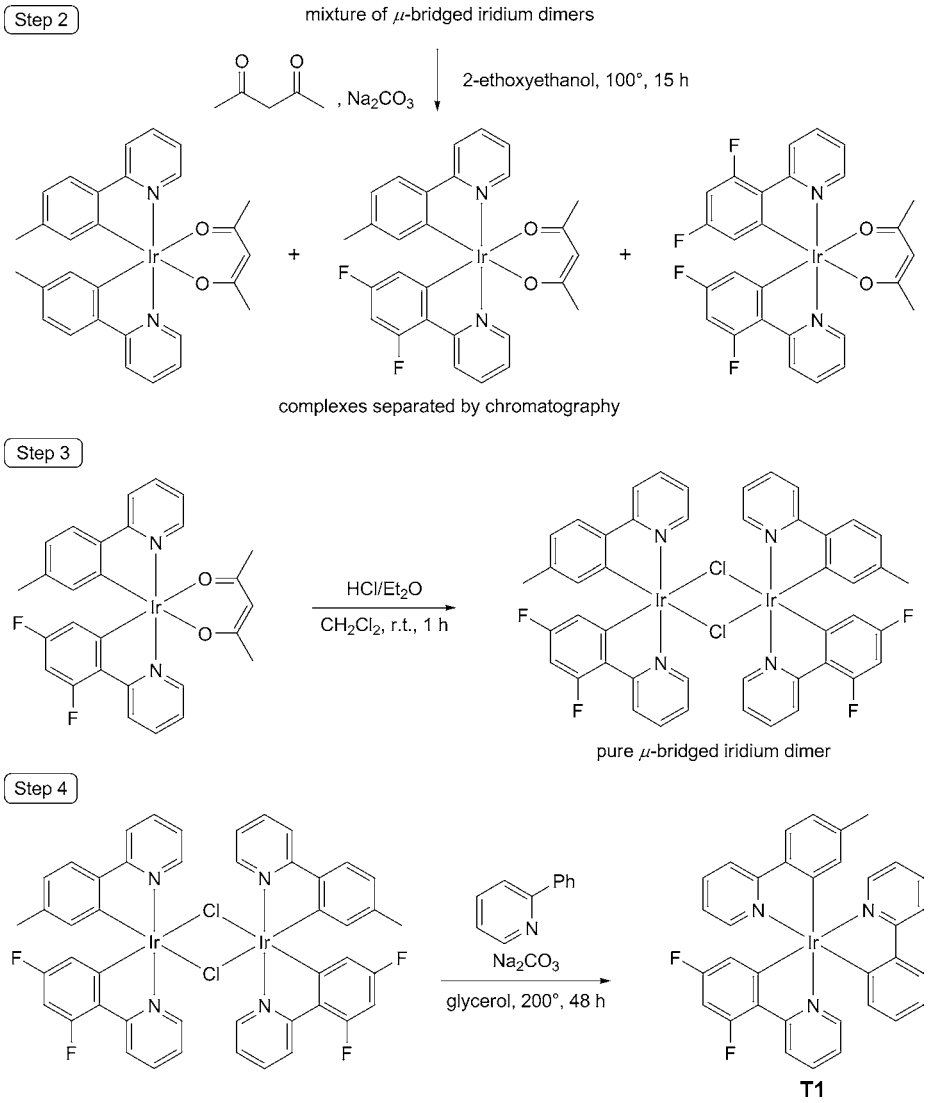
Results and Discussions. – Synthesis of the tris-cyclometalated Ir^{III} complex [Ir(tpy)(dfppy)(ppy)] consisted in an adaptation of the synthetic procedure previously reported by *Beeby* and co-workers [14]. The global strategy is depicted in the *Schemes 1* and *2*. Briefly, the first step consisted in the preparation of the di-μ-Cl-bridged Ir dimers by mixing the two ligands C^N and C′^N′ with $IrCl_3 \cdot 3\,H_2O$. A statistical mixture of the six possible dimers was obtained. Subsequent to this synthesis, the inseparable mixture of dimers was engaged in a reaction with acetylacetone (acac) furnishing the three possible complexes: $[Ir(C^N)_2(acac)]$, $[Ir(C'^N')_2(acac)]$, and [Ir(C^N)(C′^N′)(acac)] (*Step 2*). The key step of the synthetic strategy is definitely the convenient choice of the two ligands used to generate the dimers. Indeed, the complex **T1** is composed of three different cyclometalated ligands, but only two of them are used to generate the dimers. To be separable by traditional chromatography on silica gel, the two complexes $[Ir(C^N)_2(acac)]$ and $[Ir(C'^N')_2(acac)]$ must have a sufficient difference of polarity from the targeted [Ir(C^N)(C′^N′)(acac)] [14–16]. All possible combinations were thus examined by TLC before performing the reaction in large scale. From this viewpoint, introducing the two ligands tpy and dfppy was the best choice because of the easiest separation between $[Ir(dfppy)_2(acac)]$ and $[Ir(tpy)_2(acac)]$ rather than with $[Ir(ppy)_2(acac)]$. The targeted [Ir(dfppy)(tpy)(acac)] was isolated from the mixture in a reasonable yield (35%), considering that this statistical approach gave in the same synthesis $[Ir(dfppy)_2(acac)]$ and $[Ir(tpy)_2(acac)]$ in 17 and 11% yields, repectively (see *Scheme 3*). The reaction yields obtained in this step were significantly higher than those previously reported by *Beeby* and co-workers with other cyclometalated ligands. Indeed, in their case, the different acac derivatives were only obtained with reaction yields ranging from 7 to 11% yield [14].

Scheme 1. *Statistical Mixture of* μ*-Dichloro-Bridged Ir Dimers Obtained during the First Step*



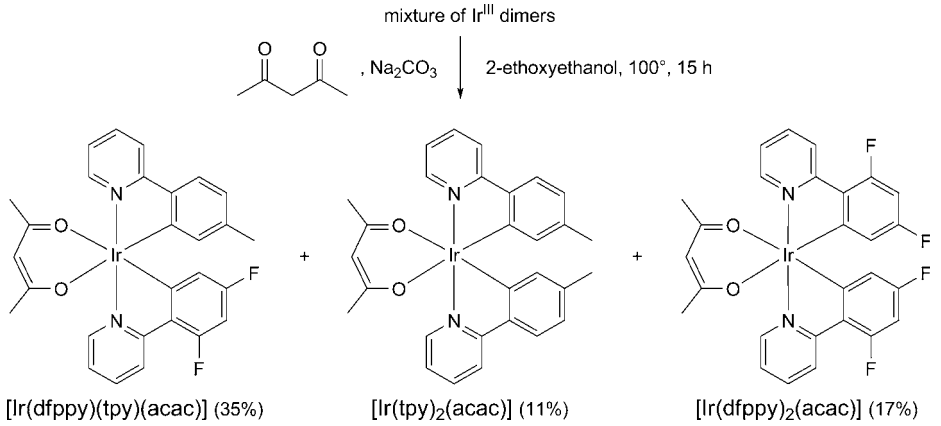
The second key point is the regeneration of the pure $[Ir(C\hat{}N)(C'\hat{}N')(\mu\text{-}Cl)]_2$ dimer under acidic conditions (*Step 3*). Treatment of the heteroleptic [Ir(tpy)(dfppy)-(acac)] with HCl gave the pure dimer $[Ir(tpy)(dfppy)(\mu\text{-}Cl)]_2$ in good yield (72%). Finally, bridge splitting and substitution reaction with the cyclometalated ancillary ligand ppy furnished the tris-heteroleptic [Ir(dfppy)(ppy)(tpy)] complex **T1** in 27% yield (*Step 4*; see also *Scheme 4*). The reaction yield of this last step was quite low (27% yield) but higher than the very low reaction yields previously reported by *De Cola* and co-workers [13] (11% yield), and *Beeby* and co-workers [14] (7–11% yield). To the best of our knowledge, it even constitutes the best reaction yield ever reported for this class of heteroleptic complexes. As a drawback, complex **T1** was not obtained a unique

Scheme 2. *Synthesis of [Ir(C^N)(C′^N′)(C″^N″)] and Structure of [Ir(dfppy)(ppy)(tpy)]* **T1**

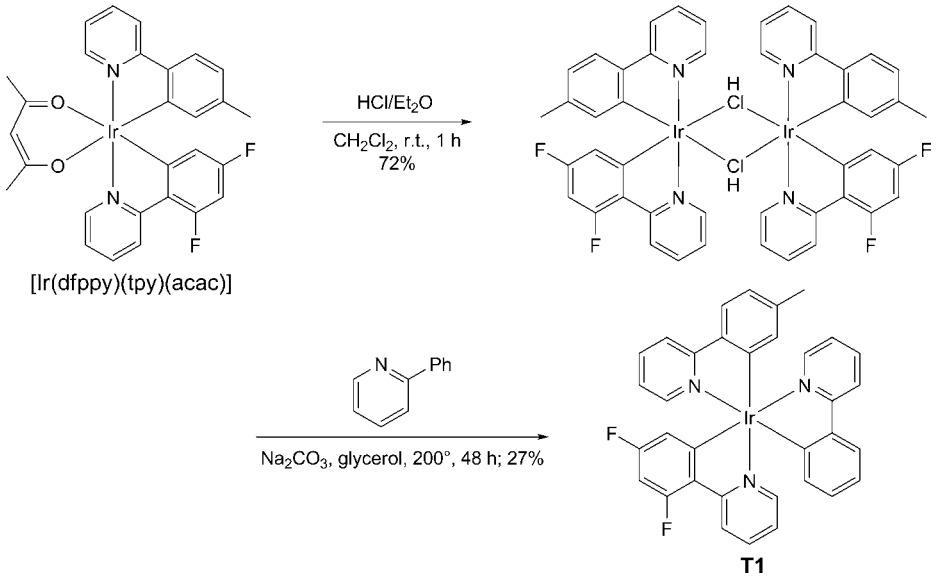


isomer but as a mixture of geometric isomers. To get evidence of the structures, heteroleptic di-μ-Cl-bridged dimer as well as the different Ir complexes were characterized by NMR spectroscopy. First, the formation of the mixed-ligand dinuclear species [Ir(dfppy)(tpy)(μ-Cl)]$_2$ as a racemic mixture of the possible diastereoisomers was evidenced. This formation was evidenced in the ^{1}H-NMR spectrum by the presence of two sets of signals attributed to each [Ir(dfppy)(tpy)] moiety of the dimer, in which the two tpy and the two dfppy from each [Ir(C^N)(C′^N′)] moiety are magnetically nonequivalent (see *Fig. 2*). Similarly, the ^{1}H-NMR spectrum of **T1** unambiguously

Scheme 3. *Synthesis of [Ir(dfppy)(tpy)(acac)], [Ir(dfppy)$_2$(acac)], and Ir(tpy)$_2$(acac)], and Corresponding Yields*



Scheme 4. *Regeneration of the Dimer and Synthesis of the Complex* **T1**



indicated the presence of *fac*- and *mer*-isomers. The broad signal in the 2.12 – 2.18-ppm region established the formation of at least five stereoisomers (see *Fig. 3*). Broadness of the NMR signals were directly related to the presence of different geometrical isomers in the final product resulting from the presence of the dfppy ligand in the final complex **T1**. Indeed, the difficult thermally-induced *mer*-to-*fac* isomerization of tris-cyclometalated complexes comprising dfppy ligands has already been reported in the literature, and defluorination reactions were observed during isomerization [14][20]. Complexity of the mixture obtained during the synthesis of **T1** was confirmed by ^{19}F-

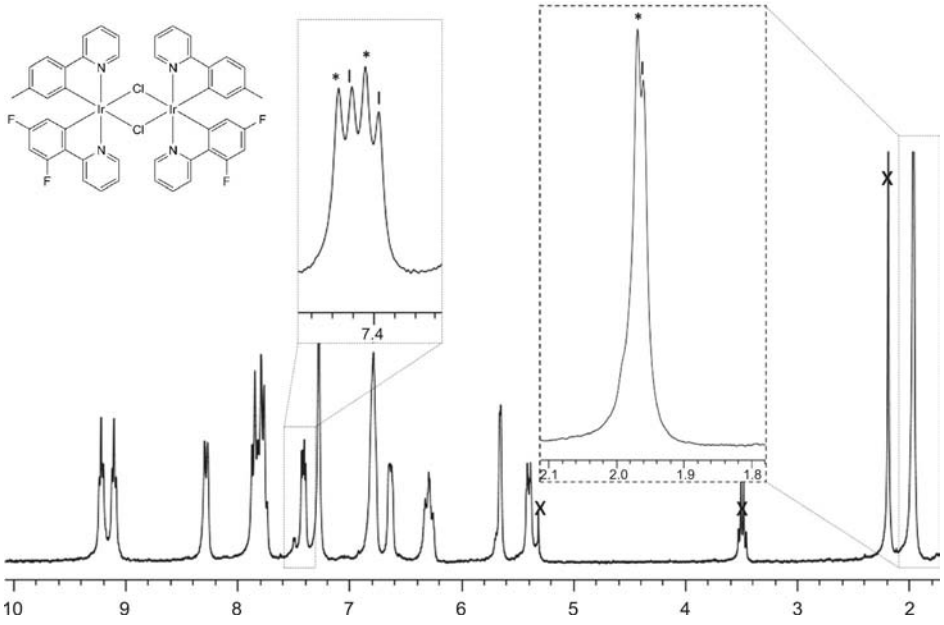


Fig. 2. *300-MHz ^{1}H-NMR Spectrum of [Ir(dfppy)(tpy)(μ-Cl)]$_2$ in $CDCl_3$*

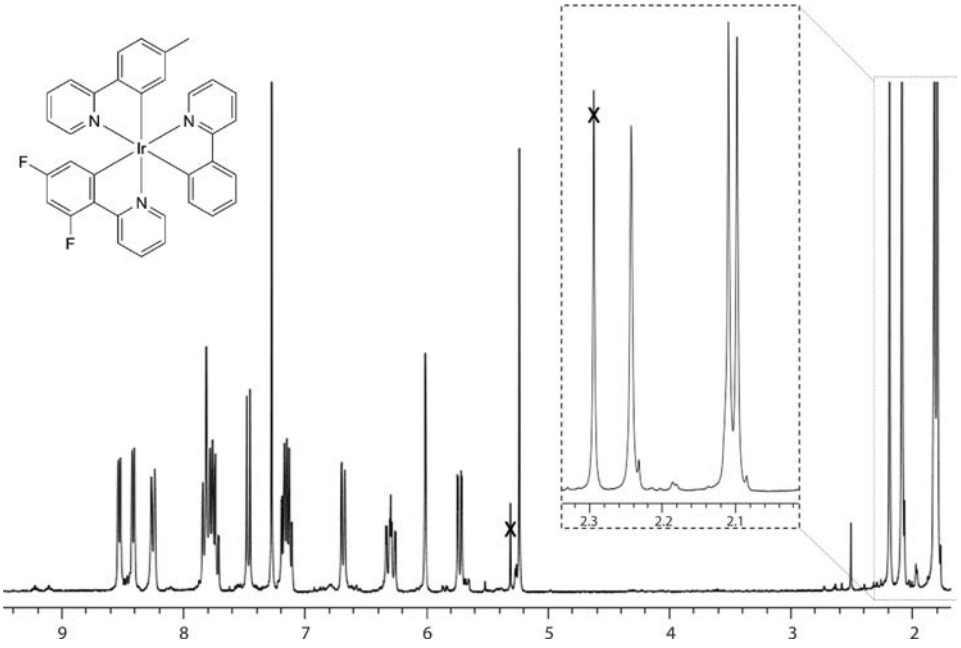


Fig. 3. *300-MHz ^{1}H-NMR Spectrum of* **T1** *[Ir(dfppy)(tpy)(ppy)] in $CDCl_3$*

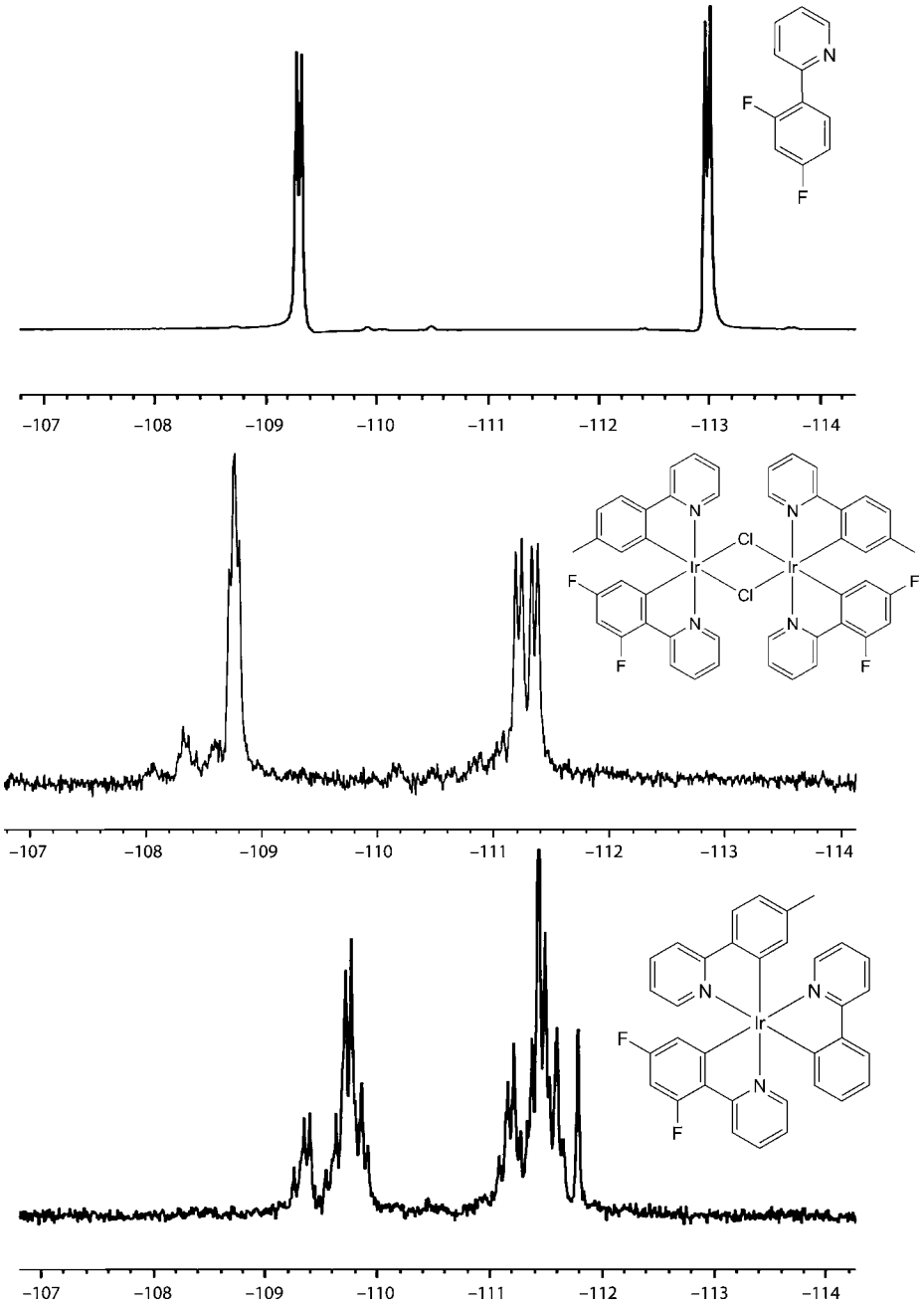


Fig. 4. *[19]F-NMR Spectra of the ligand dfppy, the mixed iridium dimer, and* **T1**

NMR by using the fluorinated ligand dfppy as an NMR probe (see *Fig. 4*). The two *doublet*s of the fluorinated ligand in the mixed-ligand dinuclear species [Ir(dfppy)-(tpy)(μ-Cl)]$_2$ appeared clearly shifted, relative to their chemical shifts of the free dfppy ligand. Notably, an overlap of two sets of *doublet*s could be clearly observed for the dimers, evidencing the presence of diastereoisomers. Upon formation of the neutral complex **T1**, a higher degree of complexity was achieved, and presence of *mer*- and *fac*-isomers was indicated by the presence of two sets of *multiplet*s. Due to the overlap of the signals, the relative yield of each isomer could not be determined by NMR.

Finally, the formation of the heteroleptic complex **T1** was unambiguously confirmed by elemental analyses and high-resolution ESI-mass spectrometry, which displayed a molecular-ion peak at *m*/*z* 705.1592 (M^+) corresponding to the molecular formula $C_{34}H_{24}F_2IrN_3$. No traces of contamination of **T1** by side-products from ligand-exchange reactions or defluorination processes were detected by mass spectrometry, confirming the sample to be only constituted of geometrical isomers. The isolated **T1** complex, after chromatography, is only composed of a mixture of isomers, *i.e.*, two possible diastereoisomers of *fac*-**T1**, and four possible diastereoisomers of *mer*-**T1** (see *Fig. 5*). This is evidenced by the presence of at least five *singlet*s attributable to the Me group of the tpy ligand (see *Fig. 3*). The UV/VIS absorption spectrum of the heteroleptic complex [Ir(dfppy)(tpy)(ppy)] was investigated at room temperature in CH_2Cl_2 and MeCN, and compared with the spectra of homoleptic complexes [Ir(dfppy)$_3$], [Ir(tpy)$_3$], and [Ir(ppy)$_3$] in order to determine the influence of the substitution pattern on the photophysical properties. Photophysical data are compiled in *Table 1*. As shown in *Fig. 6*, similar UV/VIS absorption spectra were obtained for the four complexes. The spectra were dominated by an intense absorption band located at 250–330 nm assigned to spin-allowed $\pi-\pi^*$ transitions on the cyclometalating ligands. Weaker absorption bands were also detected at lower energies with a long tail extending to 550 nm, which correspond to spin-allowed and spin-forbidden metal-ligand charge-transfer transition (^{1}MLCT and ^{3}MLCT), and ligand-centered ^{3}LC transitions, respectively (see *Fig. 6*,*a*). All Ir complexes exhibited high photoluminescence (PL) quantum yields (φ_p 0.40–0.52), indicating the efficient mixing of singlet and triplet *excited states via* spin–orbit coupling. While examining their luminescence lifetimes, complex **T1** exhibited a phosphorescence lifetime similar to that obtained with the corresponding tris-cyclometalated Ir^{III} complexes (see *Table 1*) [21]. All complexes displayed very similar and featureless emission spectra. Interestingly, fine tuning of the emission wavelength could be obtained by combining the three different ligands within the same metal complex (*Fig. 6*,*b*). Photophysical studies of the new complex [Ir(dfppy)(tpy)(ppy)] (**T1**) revealed its emission wavelength to correspond to the average of the emission wavelengths of the three homoleptic complexes (see *Fig. 6*). Compared to the emission of [Ir(ppy)$_3$] (λ_{em} 512 nm), [Ir(tpy)$_3$] (λ_{em} 517 nm),

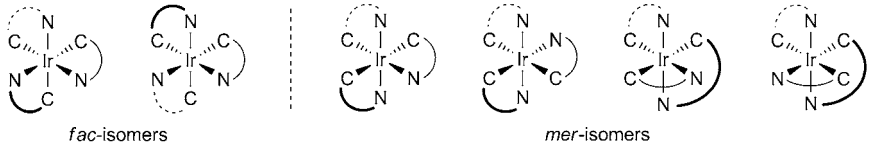


Fig. 5. *The six possible isomers of* **T1**

Table 1. *Physical Data of the Compounds*

Compound	λ_{abs} [a]) [nm] (log ε)	λ_{em} [b]) [nm]	λ_{abs} [c]) [nm] (log ε)	λ_{em} [d]) [nm]	τ [e]) [ns]	τ [f]) [μs]	φ_p [g])	$k_q(O_2)$ [$M^{-1}s^{-1}$]	E_{ox} [h]) [V]
fac-[Ir(ppy)$_3$]	335 (3.9), 372 (3.7), 405 (3.0), 448 (2.9), 486 (2.8)	518	258 (4.0), 340 (3.9, sh), 378 (3.8 sh), 400 (3.0), 456 (3.0), 488 (2.9, sh)	512	26	2.1	0.40	$2.0 \cdot 10^{10}$	0.76
fac-[Ir(dfppy)$_3$]	351 (3.9), 379 (3.7), 425 (3.1), 456 (2.8)	497	261 (4.0), 345 (3.9, sh), 380 (3.8), 455 (3.0, sh)	472, 492	30	1.6	0.43	$1.7 \cdot 10^{10}$	1.14
fac-[Ir(tpy)$_3$]	369 (4.0), 411 (3.8), 449 (3.4), 482 (3.0)	517	286 (4.5), 367 (4.1), 407 (3.8, sh), 447 (3.6, sh), 486 (3.4)	517	22	2.1	0.50	$2.3 \cdot 10^{10}$	0.76
[Ir(dfppy)(tpy)(ppy)]	327 (3.9), 356 (4.0), 397 (3.6), 422 (3.3), 454 (2.8)	506	279 (4.4), 330 (4.0, sh), 350 (3.8, sh), 393 (3.8, sh), 442 (3.4, sh), 497 (2.9)	501	29	2.3	0.52	$1.7 \cdot 10^{10}$	0.91

[a]) Recorded in aerated MeCN at 298 K. ε is the absorption coefficient. [b]) Recorded in MeCN solns. at 298 K. Excitation wavelength was 455 nm for all Ir complexes. [c]) Recorded in CH_2Cl_2 at 298 K. ε is the absorption coefficient; sh stands for shoulder. [d]) Recorded in CH_2Cl_2 solns. at 298 K. Excitation wavelength was 380 nm for all Ir compounds. [e]) Luminescence lifetime measured in aerated ACN solns. at 298 K. [f]) Luminescence lifetime measured in N_2-saturated ACN solns. at 298 K. [g]) Quantum yield was measured in ACN (acetonitrile) relative to *fac*-[Ir(ppy)$_3$] ($\varphi_p = 0.40$) [21]. [h]) Oxidation potential reported is adjusted to the potential of ferrocene which was used as an internal reference. Conditions of cyclic-voltammetric measurements (*Voltalab 6* radiometer): ACN, platinum working electrode; sat. calomel electrode was used as reference electrode. Scan rate, 500 mV/s. Supporting electrolyte, tetrabutylammonium hexafluorophosphate. Potentials were determined from half-peak potentials.

and [Ir(dfppy)$_3$] (λ_{em} 472 nm), emission of [Ir(dfppy)(tpy)(ppy)] with a unique tpy ligand was blue-shifted (λ_{em} 501 nm, $\Delta\lambda_{em}$ 16 nm) compared to that of [Ir(tpy)$_3$], clearly demonstrating that the emission properties of **T1** were not only dominated by the lowest-energy ligand tpy (see *Fig. 7*) [22].

Indeed, if the phosphorescent emission peak of homoleptic [IrL$_3$] complexes is assumed to be essentially dominated by the excited triplet energy of ligand-centered ^{3}MLCT and ^{3}LC, emission of the complex **T1** results from a subtle interplay of the contribution of the different ligands [23]. To complicate the assignment, emission of **T1** that was experimentally determined corresponds to the contribution of the different possible stereoisomers of this complex, which has potentially six stereoisomers, four meridional and two facial. Their respective ratio in the final product could not be determined, and it is well-established that stereoisomers of a same complex can exhibit extremely different photophysical properties, with *fac*-isomers often exhibiting higher

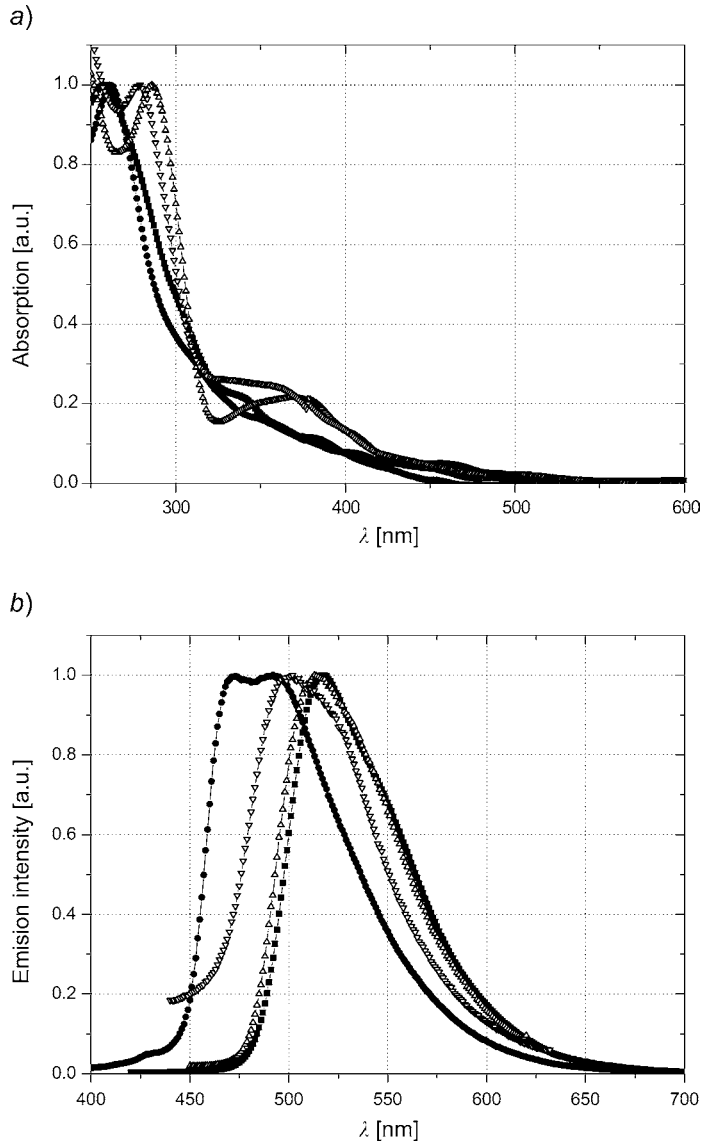


Fig. 6. a) *UV/VIS Absorption and* b) *photoluminescence*. Spectra recorded at $5 \cdot 10^{-3}$ M of [Ir(ppy)$_3$] (▽), [Ir(dfppy)$_3$] (●), [Ir(tpy)$_3$] (■), and [Ir(dfppy)(tpy)(ppy)] (△), recorded in CH_2Cl_2 at room temperature (λ_{exc} 380 nm)

emissive properties than the *mer*-isomers [24][25]. To shed light on the emission of **T1**, theoretical calculations were carried out.

Ground-state geometries of the four complexes were fully optimized without symmetry restrictions using the Gaussian software suite at the B3LYP/LANL2DZ level. Energy gaps of ligands and Ir complexes, as well as their respective contour plots

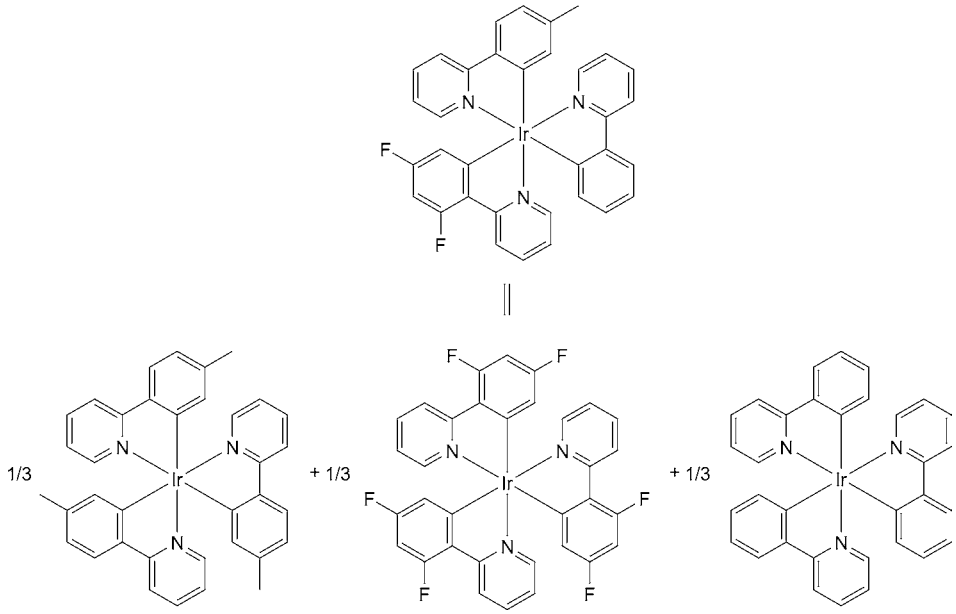


Fig. 7. *Schematic view of the optical properties of* **T1**

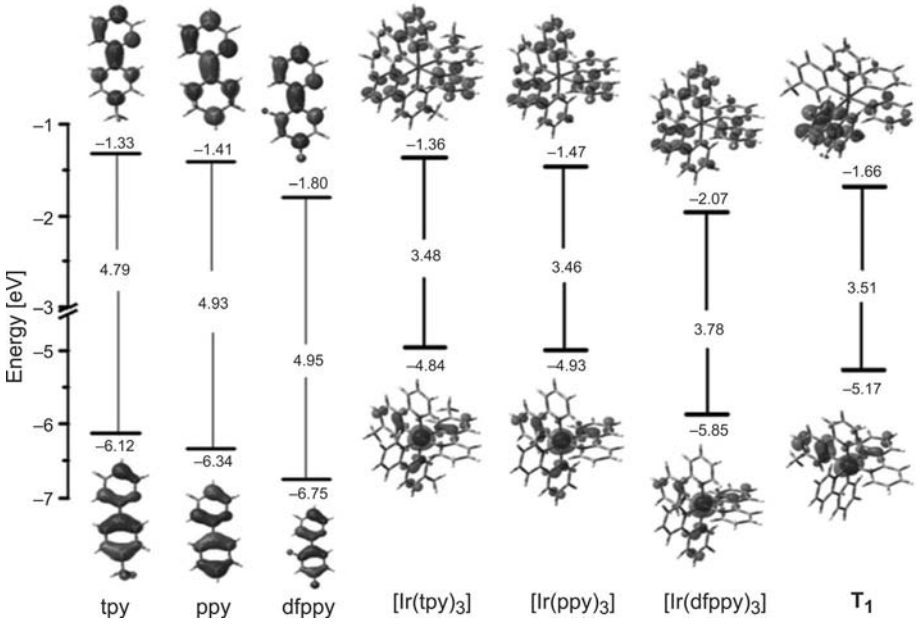


Fig. 8. *Calculated energy gaps of ligands and* fac*-isomers of the investigated Ir complexes in ground states* (for clarity, only HOMO and LUMO levels are depicted).

of HOMO and LUMO are depicted in the *Fig. 8*. Features of the frontier orbitals of *fac*-**T1** in the ground-state are shown in *Fig. 9*. As can be seen in *Fig. 8*, electron densities of the ground-state for HOMO, HOMO-1, and HOMO-2 are mainly based on the tpy and ppy moities and the Ir-atom. The HOMO level is mostly composed by d_{xy}, d_{yz}, and d_{zx} orbitals and can be thus considered as the t_{2g} orbital, based on the ligand-field theory [26]. On the contrary, the LUMO level is centered on the dfppy ligand with no interactions with the metal-centered orbitals. With the electron densities arising only from the π-contribution of the dfppy ligand, this orbital is typically a ligand-π^* orbital. Emission energy of the different complexes was also theoretically investigated. The calculated emission energies for $[Ir(ppy)_3]$ (2.48 eV, 500 nm), $[Ir(tpy)_3]$ (2.48 eV, 500 nm), **T1** (2.51 eV, 492 nm), and $[Ir(dfppy)_3]$ (2.68 eV, 462 nm) were slightly higher as compared to the corresponding experimental values (512, 517, 501, and 472 nm for $[Ir(ppy)_3]$, $[Ir(tpy)_3]$, **T1**, and $[Ir(dfppy)_3]$, resp.), but the trend was the same (*Table 2*). As experimentally determined, the emission energy of **T1** was intermediate between those of $[Ir(ppy)_3]$ and $[Ir(tpy)_3]$, and $Ir(dfppy)_3$. In particular, theoretical emission wavelength of **T1** (492 nm) corresponded to the average of the three homoleptic ones (488 nm). Finally, electrochemical properties of **T1** and the homoleptic complexes were investigated by cyclic voltammetry. The electrochemical data are collected in *Table 1* (see Figs. in *Supplementary Information,* available upon request from the authors). All complexes showed a *quasi*-reversible couple at *ca.*

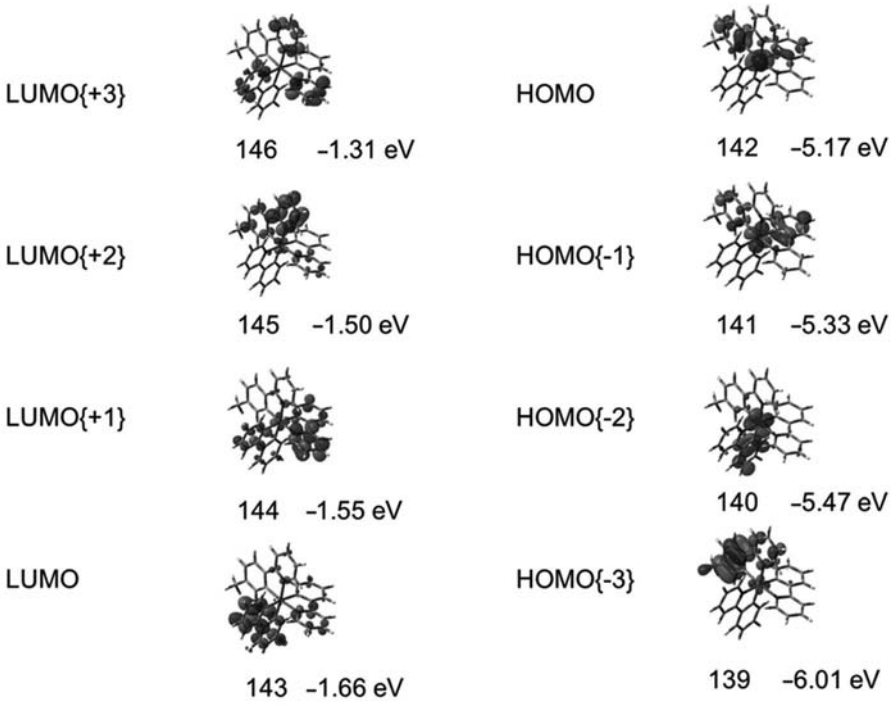


Fig. 9. *Contour plots of selected frontier orbitals of* fac-$\mathbf{T_1}$ *in ground state*

Table 2. *Calculated and Experimental* (CH_2Cl_2) *Emission Wavelength and Their Differences,* Δ, *for the Studied* Ir^{III} *Complexes*

Compound	$\lambda_{calc.}$ [nm][a])	$\lambda_{exp.}$ [nm]	Δ [nm]
fac-[Ir(ppy)$_3$]	500	512	12
fac-[Ir(dfppy)$_3$]	462	472	10
fac-[Ir(tpy)$_3$]	500	517	17
[Ir(dfppy)(tpy)(ppy)]	492	501	9

[a]) At UB2LYP/LANL2DZ level.

+0.76 to +1.14 V *vs.* saturated calomel electrode (SCE), attributed to a metal-centered $Ir^{III/IV}$ oxidation process. These potentials follow the order [Ir(ppy)$_3$] = [Ir(tpy)$_3$] < [Ir(dfppy)(tpy)(ppy)] < [Ir(dfppy)$_3$], in agreement with the decreasing electron-donating ability of the cyclometalating ligands. Indeed, the oxidation potential is strongly dependent on the electronic environment of the Ir^{III} cation, and a better electron-donor ligand shifts the oxidation potential to a less positive value [27]. Compared to the homoleptic systems, the oxidation potential of complex **T1** was consistent with the electron-donating effects of the different cyclometalating ligands. Notably, the two ppy and tpy substituents rendered the complex easier to oxidize than the homoleptic [Ir(dfppy)$_3$]. On the contrary, the dfppy ligand with its electron-withdrawing F-atoms distinctly increased the oxidation potential of **T1** from 0.76 V for [Ir(tpy)$_3$] and [Ir(ppy)$_3$] to 0.91 V. The electrochemical behavior of **T1** was thus markedly different from those of [Ir(tpy)$_3$] and [Ir(ppy)$_3$], indicating the contribution of both ligands, ppy and tpy, to its HOMO level, as theoretically demonstrated.

Conclusions. – In conclusion, we reported on the preparation and the photophysical properties of a tris-cyclometalated Ir^{III} complex possessing three different cyclometalated ligands. To the best of our knowledge, the complex **T1** studied in this work is the first example of a new and as yet unknown class of 2-phenylpyridine-based complexes. The synthesis of this new class of compounds is a real synthetic challenge that deserves to be explored. The simple and straightforward procedure reported herein can be easily extrapolated to a wide range of cyclometalated ligands. In particular, the complex was obtained with the best reaction yield ever reported for this class of complex. As the main drawback of our strategy, the use of 2-(2,4-difluorophenyl)pyridine (dfppy) as a ligand strongly influenced the synthesis of **T1** in that only a mixture of geometrical isomers could be obtained, this ligand impeding all *mer*-to-*fac* isomerizations. This point has to be considered for future syntheses of complexes when a pure geometrical isomer is desired. Interestingly, we also confirmed the full potential of this approach as a color-tuning methodology. This new approach opens the way towards a higher control of the emission wavelength by the convenient choice of the three ligands.

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Experimental Part

General. All starting materials and solvents were purchased from *Aldrich* or *Alfa Aesar*, and used as supplied commercially. Electrochemical data were obtained using a *Voltalab 6* radiometer. The redox potentials were measured in MeCN with $Bu_4N(PF_6)$ (0.1M) as a supporting electrolyte. The working electrode was a Pt disk, and as reference a sat. calomel electrode (SCE) at a scan rate of 0.5 V/s was used. Ferrocene was used as a standard, and the potentials were determined from half-peak potentials. Photoluminescene (PL) lifetimes were determined from ns laser flash photolysis (LFP) experiments (*Qswitched* ns Nd/YAG laser (λ_{exc} 355 nm, 9-ns pulses); *Luzchem LFP 212*). ^{1}H- and ^{13}C-NMR spectra: at r.t. in 5-mm o.d. tubes on a *Bruker Avance 300* spectrometer equipped with a QNP probe head at 300 (^{1}H) and 75 MHz (^{13}C); δ in ppm rel. to $CDCl_3$ (δ(H) 7.26 and δ(C) 77.0) as internal standard, J in Hz. MS: at Spectropole of Aix-Marseille University; in m/z. ESI-MS: *3200 QTRAP* (*Applied Biosystems SCIEX*) mass spectrometer; in m/z. HR-MS: *QStar Elite* (*Applied Biosystems SCIEX*) mass spectrometer; in m/z. Elemental analyses: *Thermo Finnigan EA 1112* elemental-analysis apparatus, with the Eager 300 software.

Molecular-orbitals calculations were carried out using the Gaussian 03 suite of programs. The electronic absorption spectra for the different compounds were calculated with the time-dependent density functional theory at B3LYP/LANL2DZ level on the relaxed geometries calculated at B3LYP/LANL2DZ level. The geometries were frequency checked (no imaginary frequencies) [28].

Preparation of the Mixture of Dimers. To a soln. of 2-(2,4-difluorophenyl)pyridine (0.5 g, 2.6 mmol) and 2-(*p*-tolyl)pyridine (0.44 g, 2.6 mmol) in a 30 ml of 2-ethoxyethanol/H_2O 80:20 was added $IrCl_3 \cdot 3\,H_2O$ (0.6 g, 1.8 mmol). The mixture was refluxed for 24 h. After cooling to r.t., H_2O was added (50 ml), and the product was filtered off and dried under vacuum. The mixture of the six possible dimers was isolated as a yellow powder (0.85 g, 80–86%).

Preparation of [Ir(dfppy)(tpy)(acac)]. To a suspension of the mixture of dimers (0.5 g) in 2-ethoxyethanol (30 ml) were added acetylacetone (0.13 g, 1.3 mmol) and Na_2CO_3 (0.47 g, 4.4 mmol). The mixture was refluxed for 15 h. After cooling to r.t., the solvent was evaporated. The product was extracted with CH_2Cl_2 (50 ml), and the org. phase was washed with H_2O (50 ml) and brine (50 ml). The org. phase was dried ($MgSO_4$) and was filtered. The solvent was evaporated. The different products were separated by CC (SiO_2; a gradient of CH_2Cl_2 in petroleum ether). The following products were isolated in the order of increasing polarity: [Ir(dfppy)$_2$(acac)] (0.17 g, 29%), [Ir(dfppy)(tpy)(acac)] (0.2 g, 35%), and [Ir(tpy)$_2$(acac)] (0.065 g, 11%).

[Ir(dfppy)(tpy)(acac)] (= *[3,5-Difluoro-2-(pyridin-2-yl-κN)phenyl-κC^l][5-methyl-2-(pyridin-2-yl-κN)phenyl-κC^l][4-(oxo-κO)pent-2-en-2-olate-κO]iridium*). ^{1}H-NMR (300 MHz, $CDCl_3$): 8.53 (*dd*, J = 5.7, 0.9, 1 H); 8.42 (*dd*, J = 5.7, 0.9, 1 H); 8.25 (*d*, J = 8.1, 1 H); 7.77 (*m*, 3 H); 7.47 (*d*, J = 7.5, 1 H); 7.15 (*m*, 2 H); 6.69 (*dd*, J = 7.8, 1.2, 1 H); 6.30 (*m*, 1 H); 6.01 (*s*, 1 H); 5.73 (*dd*, J = 9.0, 2.4, 1 H); 5.24 (*s*, 1 H); 2.09 (*s*, 3 H); 1.82 (*s*, 3 H); 1.80 (*s*, 3 H). HR-ESI-MS: 650.1348 (M^+, $C_{28}H_{23}F_2IrN_2O_2^+$; calc. 650.1358). Anal. calc. for $C_{28}H_{23}F_2IrN_2O_2$: C 51.76, H 3.57, O 4.93; found: C 51.85, H 3.64, O 4.96.

Preparation of [Ir(dfppy)(tpy)Cl$_2$Ir(dfppy)(tpy)] (= *Di-μ-chloro{bis[3,5-difluoro-2-(pyridin-2-yl-κN)phenyl-κC^l]}bis[5-methyl-2-(pyridin-2-yl-κN)phenyl-κC^l]diiridium*). Conc. HCl (1 ml) was added to Et_2O (10 ml) at 0°. The mixture was stirred for 20 min, and $MgSO_4$ (2.5 g, 21 mmol) was added. The soln. was filtered and added to a soln. of [Ir(dfppy)(tpy)(acac)] (0.23 g, 0.35 mmol) in CH_2Cl_2 (20 ml). The mixture was stirred at r.t. for 1 h. Then, MeOH (20 ml) was added, and the solvent was reduced to the half, until precipitation. The product was then filtered. The pure dimer was isolated as a yellow powder. Yield: 0.15 g (72 %). ^{1}H-NMR (300 MHz, $CDCl_3$): 9.22 (*m*, 2 H); 9.11 (*m*, 2 H); 8.28 (*d*, J = 8.4, 2 H); 7.81 (*m*, 6 H); 7.42 (*d*, J = 7.8, 1 H); 7.40 (*d*, J = 7.8, 1 H); 6.80 (*m*, 4 H); 6.64 (*m*, 2 H); 6.29 (*m*, 2 H); 5.66 (*d*, J = 3.3, 2 H); 5.40 (*dt*, J = 9.3, 3.0, 2 H); 1.969 (*s*, 3 H); 1.959 (*s*, 3 H). HR-ESI-MS: 1172.1180 (M^+, $C_{46}H_{32}Cl_2F_4Ir_2N_4^+$; calc. 1172.1180). Anal. calc. for $C_{46}H_{32}Cl_2F_4Ir_2N_4$: C 47.14, H 2.75, N 4.78; found: C 47.17; H 2.81; N 4.79.

Preparation of [Ir(dfppy)(tpy)(ppy)] (= *[3,5-Difluoro-2-(pyridin-2-yl-κN)phenyl-κC^l][5-methyl-2-(pyridin-2-yl-κN)phenyl-κC^l][2-(pyridin-2-yl-κN)phenyl-κC^l]iridium*). To a suspension of [Ir(dfppy)-(tpy)Cl$_2$Ir(dfppy)(tpy)] (0.28 g, 0.239 mmol) in glycerol (10 ml) were added 2-phenylpyridine (0.11 g, 0.717 mmol) and Na_2CO_3 (0.25 g, 0.239 mmol). The mixture was then refluxed for 48 h. After cooling to

r.t., H_2O (50 ml) was added to the mixture, and the product was filtered and extracted with CH_2Cl_2 (50 ml). The org. phase was washed with H_2O (50 ml) and brine (50 ml), and dried ($MgSO_4$), filtered, and the solvent was evaporated. The product was then purified by CC (SiO_2; gradient of CH_2Cl_2 and petroleum ether). The compound was isolated as a yellow powder. Yield: 90 mg (27%). ^{1}H-NMR (300 MHz, $CDCl_3$): 8.28 (*m*, 1 H); 7.86 (*m*, 2 H); 7.55 (*m*, 8 H); 6.87 (*m*, 6 H); 6.74 (*m*, 1 H); 6.63 (*m*, 1 H); 6.37 (*m*, 2 H); 2.15 (*m*, 3 H). HR-ESI-MS: 705.1592 (M^+, $C_{34}H_{24}F_2IrN_3^+$; calc. 705.1569). Anal. calc. for $C_{34}H_{24}F_2IrN_3$: C 57.94, H 3.43, N 5.96; found: C 51.95, H 3.51, N 5.99.

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