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Easy Separation of Δ and Λ Isomers of Highly Luminescent [Ir^{III}]-Cyclometalated Complexes Based on Chiral Phenol-Oxazoline Ancillary Ligands

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Abstract: A new class of neutral cyclometalated iridium(III) complexes with enantiomerically pure C_1-symmetric phenol-oxazolines (**3a,b**) have been synthetized in high yields and fully characterized. Resolution of the corresponding Δ_R and Λ_R or Δ_S and Λ_S isomers was easily achieved by conventional flash chromatography. The corresponding Δ and Λ helicities have been confirmed by CD spectroscopy and X-ray crystallography. Regarding the absorption and luminescence properties with unpolarized light, no significant difference between Δ and Λ isomers has been observed. A strong blue luminescence is observed for deaerated solutions of complexes **5a** and **5b** in CH_3CN.

Keywords: circular dichroism · chiral ligands · iridium · phosphorescence

Introduction

Cyclometalated [Ir^{III}] complexes have attracted increasing interest over the last decade because of their phosphorescent properties:[1] band maximum tunable across the visible region, an emission quantum yield that approaches the theoretical limit of 1 under proper experimental conditions, and a relatively short lifetime of the lowest triplet excited state ($\tau = 1$–$10\ \mu s$).[2] These photophysical properties are ideal in view of application of these complexes as 1) sensors of temperature,[3] oxygen,[4] and metal ions;[5] 2) biological probes;[6] 3) electrochemiluminescent markers;[7] 4) light-emitting electrochemical cells;[8] 5) hydrogen generators[9] and emitters in organic light-emitting diodes (OLEDs and WOLEDs).[10]

Of these applications, the last is the most extensively investigated for neutral complexes, and much effort has been devoted to obtaining sky-blue and stable [Ir^{III}] phosphorescent complexes. The archetype complex is [Ir(ppy)$_3$][11] (ppy = 2-phenyl pyridyl), which displays a green phosphorescence. Modification of the [Ir(ppy)$_3$] complex to move the emission band to lower energies is not difficult and can be achieved by either lowering the energy of the metal-to-ligand charge-transfer (MLCT) state with the introduction of a third ligand that is easy to reduce (lower LUMO), or by using a third ligand with a low-energy ligand-centered (LC) triplet.[12,13] Despite much effort, however, tuning of the emission of complexes of general formula [Ir(F$_2$ppy)$_2$(LL)][14] (LL = an ancillary ligand) towards energies higher than about $\lambda = 450$ nm has been unsuccessful. This is probably due to the fact that the lowest ^{3}LC of the F$_2$ppy ligand lies in this spectral region and cannot be substantially perturbed by the nature of the third ligand, the presence of a larger number of F substituents, or the presence of electron-donating groups on the pyridine moiety of the ppy-type ligand.

Focusing on the developments in the area of functionalized cyclometalated [Ir^{III}] complexes, efforts have recently been made towards the isolation of stereochemically defined cyclometalated iridium complexes as emitters of circularly polarized luminescence.[15] This interest is also founded on the possibility of accomplishing "*…propagation of chiral information…in materials or supramolecular assemblies…*",[16] based on chiral transfer in coordination complexes.

Despite this growing interest, the synthesis and characterization of enantiomerically pure phosphorescent organometallic complexes have not been fully developed. Resolution of stereoisomeric mixtures of [Ir^{III}] complexes into the corresponding Λ and Δ isomers is still an open task and elegant solutions in this direction have been accomplished by 1) co-crystallization of cationic complexes with a proper chiral counterion;[17] 2) liquid chromatography with a chiral stationary phase;[15,18] and 3) synthetic predetermination of the helicity about the metal center, as demonstrated for chiral pinene-phenyl pyridine ligands.[19]

Herein, we report on the synthesis and easy separation of diastereomerically pure Δ and Λ cyclometalated [Ir^{III}] iso-

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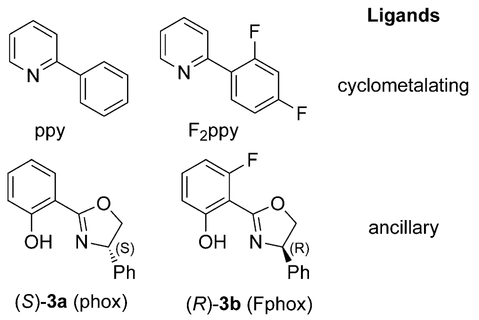
mers by simply introducing enantiomerically pure ancillary ligands. In detail, our approach consists of the condensation of chloro-bridged iridium(III) complexes with chiral phenol–oxazolines (hereafter abbreviated as phox ligands),[20] which results in the formation of diastereoisomeric $\Delta_R\Lambda_R$ or $\Delta_S\Lambda_S$ mixtures depending on the absolute configuration of the phox ligand.[21]

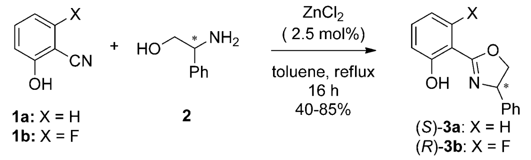
Phenol–oxazolines **3** were chosen as the ancillary ligands based on their ready synthetic availability in enantiomerically pure form, chelating nature, and strong affinity for hard transition metal salts. Last but not least, phox ligands can be subjected to further chemical manipulations with a view to potential applications of these complexes as luminescent sensors to discriminate enantiomers and biological markers.

As a proof of concept, four neutral complexes with the general formula $[Ir(C^{\wedge}N)_2(O^{\wedge}N)]$, in which $C^{\wedge}N$ (cyclometalating ligand) is ppy or F_2ppy and $O^{\wedge}N$ (ancillary ligand) is phox ((*S*)-**3a**) or the corresponding fluoro derivative Fphox ((*R*)-**3b**), have been synthesized. Each complex was separated by conventional flash chromatography into the corresponding Δ and Λ isomers and unambiguously characterized by using single-crystal X ray crystallography and circular dichroism. Moreover, we report here on the photophysical and electrochemical properties of these complexes as compared with the known complex $[Ir(F_2ppy)_2(acac)]$ (acac = acetylacetonate).[22]



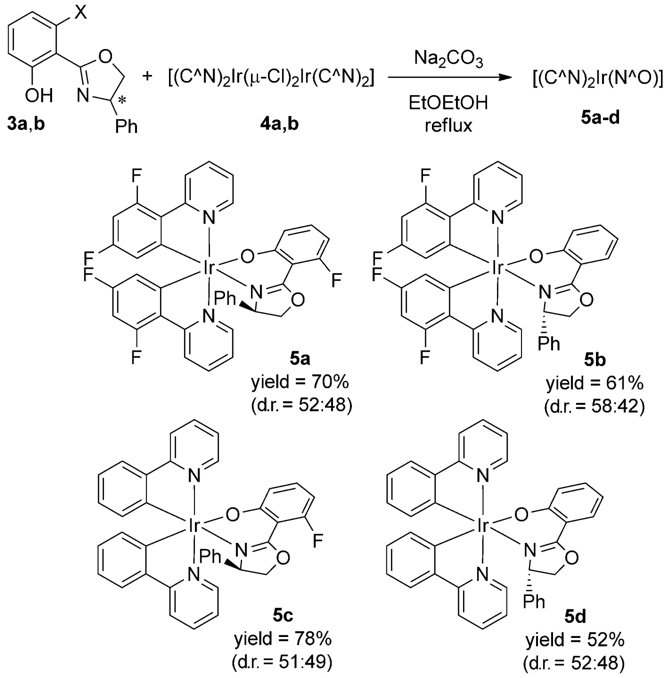
Results and Discussion

Synthesis: Enantiomerically pure phox ligands (*S*)-**3a** and (*R*)-**3b** were readily obtained by following known methodologies.[23] In particular, condensation of commercially available 2-hydroxybenzonitrile (**1a**) or 3-fluoro-2-hydroxybenzonitrile (**1b**) with enantiomerically pure (*S* or *R*)-phenyl glycinol (**2**), in the presence of a catalytic amount of anhydrous $ZnCl_2$ (2.5 mol%), gave the desired phox (**3a**) and Fphox (**3b**) in 68 and 40% yield, respectively (Scheme 1).



Scheme 1. Synthesis of chiral ancillary phox ligands **3a**,**b**.

The dimeric chloro-bridged iridium(III) complexes $[(C^{\wedge}N)_2Ir(\mu\text{-}Cl)_2Ir(C^{\wedge}N)_2]$ ($C^{\wedge}N$ = ppy (**4a**), $C^{\wedge}N = F_2ppy$ (**4b**)) were synthesized by following the known procedure, through the condensation of $IrCl_3 \cdot 3H_2O$ with the cyclometalating ligands in an ethoxyethanol/water mixture (3:1) at reflux.[24] Dimers **4a** and **4b** were then efficiently coupled with phox ligands **3a,b** in good yields. In particular, when complexes **4a** and **4b** were treated with a slight excess of oxazoline ligands in the presence of Na_2CO_3, complexes **5a**–**d** were isolated as bright-yellow solids in good yields (61–78%, Scheme 2). Interestingly, the isomers proved to be isolable in diastereoisomerically pure form through conventional flash chromatography on silica gel (see the Experimental Section). The stereochemical combinations Δ_R and Λ_S were the more polar isomers within each pair of iridium complexes, and were eluted first from the flash chromatography columns on silica gel (see below for structural determination). This experimental evidence could constitute a valuable preliminary working model to predict the absolute stereochemistry of the Ir center within this class of chiral cyclometalated transition-metal complex.



Scheme 2. Collection of neutral cyclometalated $[Ir^{III}]$ complexes **5a**–**d**. (dr = diastereomeric ratio, determined by HPLC on the crude reaction products). Yields refer to the sum of the diastereoisomers.

X-ray crystallography: The molecular structures of one of the two isomers of **5a**, **5b**, and **5d** are shown in Figure 1, and selected bond lengths and angles are reported in

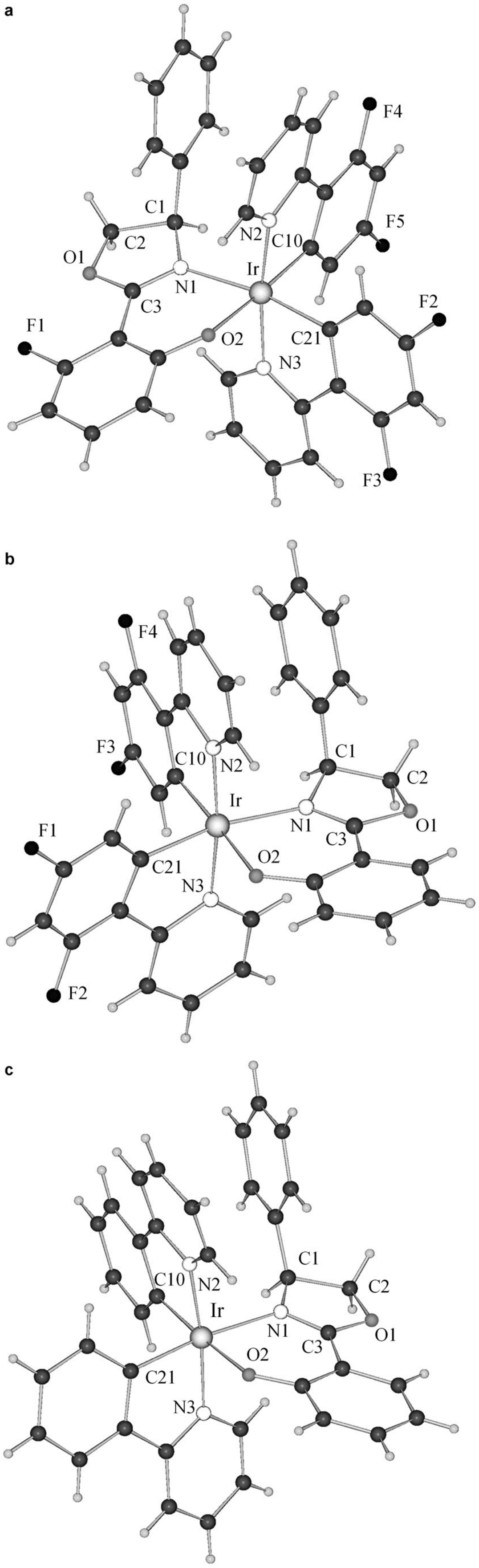


Figure 1. Molecular structure of a) Δ_R-**5a**, b) Λ_S-**5b**, and c) Λ_S-**5d**.

Table S1 in the Supporting Information. Two independent molecules are present in the asymmetric units of **5a** and **5b**. In the three cyclometalated complexes, the [Ir^{III}] center shows a distorted octahedral environment that is coordinated by two identical ppy or F_2ppy ligands and by a third bidentate ligand, which is the enantiomerically pure phenol oxazoline (phox or Fphox).

The absolute configuration at the metal centers has been unambiguously determined by X-ray crystallography as Δ for **5a** and Λ for **5b** and **5d**, respectively. Taking into account the enantiomer of the phenol-oxazoline ligand, the configurations of the complexes are Δ_R, Λ_S, and Λ_S, for the investigated isomers of **5a**, **5b**, and **5d**, respectively. The ppy or F_2ppy ligands are arranged with the pyridine N atoms lying in a *trans* position to each other whereas the σ-bound C atom is *trans* to the N atom of the oxazoline ring. A similar ligand disposition has been found, for example, in [Ir(ppy)$_2$(pic)] (pic = 2-pyridinecarboxylato).[25] In all three complexes, the two Ir−N(pyridine) bonds are very close to each other in length (range 1.99–2.04 Å) and shorter than the Ir−N(oxazoline) bond (range 2.09–2.17 Å). This trend, which has been already observed in the aforementioned [Ir(ppy)$_2$(pic)] complex and related complexes,[25] is ascribed to the *trans* influence of the C atom belonging to the phenyl unit of ppy or F_2ppy.

The oxazoline ring at the asymmetric 5-position features a phenyl group that is aligned almost parallel to one of the ppy or F_2ppy ligands. This orientation of the phenyl ring both alleviates the high steric crowding around the Ir centers and establishes intramolecular π–π interactions. This feature has been observed in trischelate complexes with substituted polypyridyl ligands.[26] In the crystal packing of **5a**, intermolecular π–π interactions involving aromatic rings already engaged in intramolecular π–π interactions generate stacks of molecules running along the *b* axis, together with clathrated molecules of CH_2Cl_2 solvent (Figure S1 in the Supporting Information). Interestingly, these stacks of molecules are formed by only one of the two conformers of **5a**; therefore, half of the columns are formed by one conformer and half are formed by the second conformer (Figure S2 in the Supporting Information). A similar arrangement of molecules in columns held together by intermolecular π–π interactions is also observed in the crystal packing of **5d** (Figures S3 and S4 in the Supporting Information), in which there is one independent molecule and no solvent. In fact, in addition to the aforementioned π–π stacking in **5d**, there are also C−H···π interactions between one methylenic hydrogen of the oxazoline ring and a phenyl unit of the ppy ligand that is not involved in π–π interactions, which strengthens the intermolecular interactions along the columns of **5d**, and C−H···π interactions connecting columns of molecules. The crystal packing of **5b** (Figure S6 in the Supporting Information) does not resemble that of **5a** or **5d** because similar intermolecular π–π stacks are not present. The two independent molecules of **5b** form π–π interactions that involve the pyridine ring of the F_2ppy ligand already engaged in a intramolecular π–π interaction and the F_2ppy ligand

Table 1. Absorption and emission properties in deaerated and air-equilibrated (given in brackets) CH_3CN at 298 K and in $CH_2Cl_2/CHCl_3$ (1:1 v/v) rigid matrix at 77 K for the investigated [Ir^{III}] complexes **5a–d** (mixture of isomers) compared with [$Ir(F_2ppy)(acac)$] under the same experimental conditions. k_q is the quenching constant by dioxygen at 298 K.

	Absorption		Emission					Rate constants
	298 K λ [nm]	$\varepsilon \times 10^3$ [$M^{-1}cm^{-1}$]	298 K λ [nm]	τ [μs]	Φ_{em}	77 K λ [nm]	τ [μs]	$k_q \times 10^{10}$ [$M^{-1}s^{-1}$]
5a	232	43.7	497	1.8 (3.1×10^{-2})	0.81 (0.01)	468	2.7	1.6
	332[a]	7.3						
	385[a]	5						
5b	227	42.1	504	2.1 (3.1×10^{-2})	0.80 (0.01)	468	2.7	1.6
	332	6.9						
	377	6						
5c	235[a]	37.7	520	1.9 (2.5×10^{-2})	0.51 (0.008)	494	3.4	2.0
	283[a]	22						
	344	6.5						
5d	257	32.8	524	1.9 (2.6×10^{-2})	0.52 (0.008)	494	3.4	1.9
	347	6.8						
[$Ir(F_2ppy)_2(acac)$]	248	43.5	487	0.86 (3.1×10^{-2})	0.50 (0.016)	469	2.8	1.6
	325[a]	10.8						
	383	4.9						

[a] Shoulder of the absorption band.

of the other conformer (Figure S5 in the Supporting Information). The crystal packing is also reinforced by slipped π–π interactions of a different type and by C−H···π interactions.

Photophysical properties: The absorption and emission spectra (Table 1, Figures 2 and 3) were initially recorded for the diasteroisomeric mixture indicated in Scheme 2. For a discussion of the properties of each diastereoisomer, see below. The absorption spectra of **5a** and **5c** in CH_3CN (Figure 2) show broad bands, quite similar to those of the corresponding homoleptic complexes [$Ir(F_2ppy)_3$] and [$Ir(ppy)_3$]:[11,27] the intense bands below 300 nm can be assigned to spin-allowed LC transitions of the phenyl-pyridyl ligands, which partially overlap with spin-allowed LC transition of the ancillary ligand, whereas the less intense bands above 300 nm are probably due to spin-allowed MLCT transitions. The lowest energy, very weak band is probably due to a transition from the ground state to the lowest ^{3}MLCT state. According to literature reports,[12] in complexes containing phenyl-pyridyl ligands, the highest occupied molecular orbital (HOMO) is mainly located on the metal, with a contribution from the anionic phenyl ring of the ligand. Conversely, the lowest unoccupied molecular orbital (LUMO) is mostly

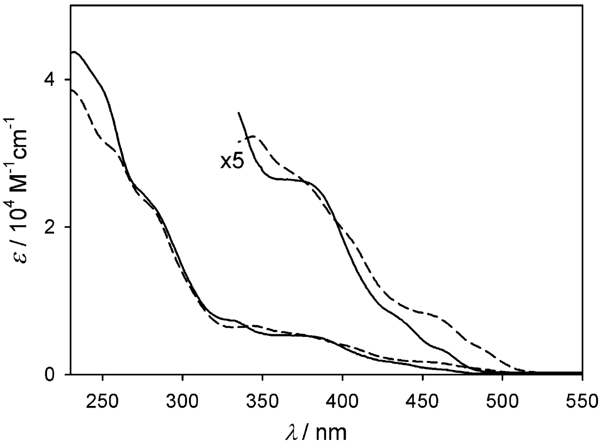


Figure 2. Absorption spectra of **5a** (——) and **5c** (-----) in CH_3CN solution at 298 K.

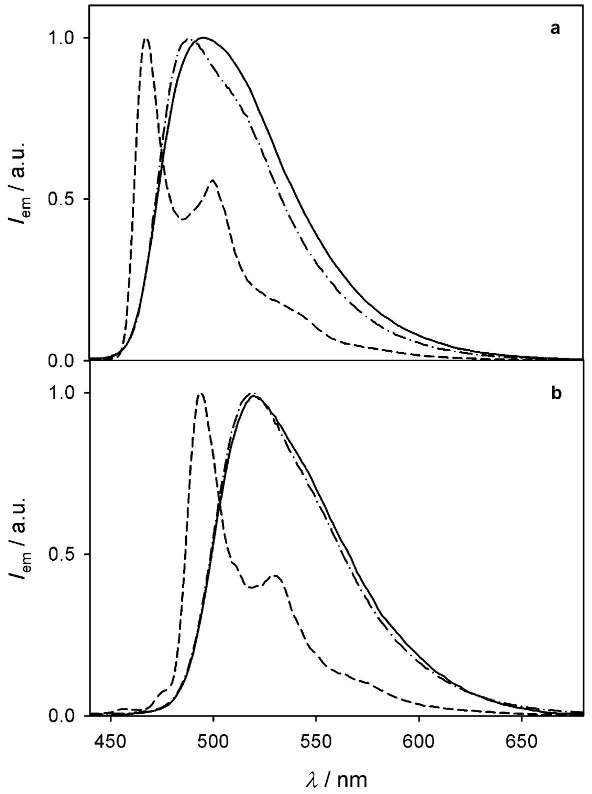


Figure 3. Emission spectra of a) **5a** and b) **5c** in CH_3CN at 298 K (——), and in $CH_2Cl_2/CHCl_3$ (1:1 v/v) at 298 K (–•–•) and 77 K (-----). λ_{ex} = 290 nm (the equimolar mixture of diastereoisomers was analyzed in each case).

located on the pyridyl ring of the ligand. However, it is worth remembering that in [Ir^{III}] cyclometalated complexes both the localized molecular orbital and the spin-labeling descriptions lose part of their meaning because of the substantial covalency of Ir–C bonds and the presence of a heavy metal, which causes a strong spin-orbit coupling.[27c]

The absorption bands displayed by **5c** are slightly redshifted compared with those of **5a**. The other two compounds, **5b** and **5d**, showed absorption spectra that were almost coincident with those of the corresponding compounds containing the Fphox ancillary ligand. Indeed, the ancillary ligand does not strongly influence the lowest electronic transition. The emission spectrum of **5a** in CH_3CN at 298 K shows a broad band centered at 497 nm, which is blueshifted upon decreasing solvent polarity (see spectra in CH_2Cl_2/CH_3Cl in Figure 3a). In the case of **5c**, an emission spectrum with a maximum at 520 nm is observed and is practically unchanged if the polarity changes (Figure 3b). The excited-state lifetime is close to 2 μs for all investigated complexes in deaerated CH_3CN at 298 K, which proves that the corresponding transition is spin forbidden. The emission quantum yield is very high ($\Phi_{em}=0.80$) for **5a** and lower for complexes containing the ppy ligand. The emission is strongly quenched (ca. 70 times) by dioxygen, with a rate constant close to the diffusion limit ($k_q \approx 2\times10^{10}\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$) in agreement with previously reported examples.[28] Moreover, complexes **5b** and **5d** showed photophysical properties (emission spectra, excited state lifetime, and emission quantum yields) similar to those of the analogous complexes that contain the Fphox ligand.

In comparison with other heteroleptic complexes that contain two ppy or F_2ppy ligands and a third ancillary ligand,[29] complexes **5a** and **5c** show one of the "bluest" and brightest luminescence. For example, the known [Ir(F_2ppy)$_2$(acac)] shows a very similar emission band maximum in solution in CH_3CN and in a CH_2Cl_2/CH_3Cl (1:1 v/v) rigid matrix, but a lower emission quantum yield (ca. 50%, see Table 1).

Analogous investigations were carried out on the diastereomerically pure Ir complexes after chromatographic separation. The absorption and emission properties are very similar for the two diastereoisomers of each complex (**5a–d**) upon excitation with unpolarized light. For example, Λ_R- and Δ_R-**5a** complexes exhibit small changes in the absorption band (Figure S7a in the Supporting Information), a small shift in the emission band maximum (Figure S7b in the Supporting Information), and slight differences in the emission quantum yields and lifetime of the emitting excited state (Table S2 in the Supporting Information), both in air-equilibrated CH_3CN and CH_2Cl_2. This result is not surprising; the two diastereoisomers differ only in the helicity on the metal center.

On the other hand, upon excitation with circularly polarized light, each diastereoisomer exhibits a peculiar and distinguishable CD absorption spectrum. Figure 4 shows the CD spectra of the four isomers of **5a** and **5b**. The two isomers of compound **5a**, Δ_R and Λ_R, (Figure 4a and b, ——) show different CD spectra, as do the two isomers of complex **5b** (Figure 4a and b, – – –). The most striking feature is that the spectra of the Δ_R isomer of **5a** and the Λ_S isomer of **5b** are mirrored (Figure 4a) across the entire investigated spectral region, as are the corresponding Λ_R and Δ_S isomers (Figure 4b). This result demonstrates that the stereogenic center on the ancillary ligand greatly influences the overall CD response, although the investigated electronic transitions are not predominantly centered on the ancillary ligand. As evident from the crystal structures, the phenyl ring can give rise to a more favorable π–π interaction with the F_2ppy ligand in one of the two isomers, so that it influences the helicity of the complex. The two isomers with mirror-like behavior are neither enantiomers nor diasteroisomers because they differ at the F substituent on the ancillary ligand. A closer look at the CD spectra of Figure 4 shows that the band with a maximum of about 285 nm is the only one that is identical in position and shape, but not in sign, for the four isomers. For example, the spectrum for (Δ_R)-**5a** in Figure 4a is superimposed on the spectrum of (Δ_S)-**5b** in Figure 4b so that it can be assigned to the F_2ppy ligands, and the sign depends on the helicity of the complex.

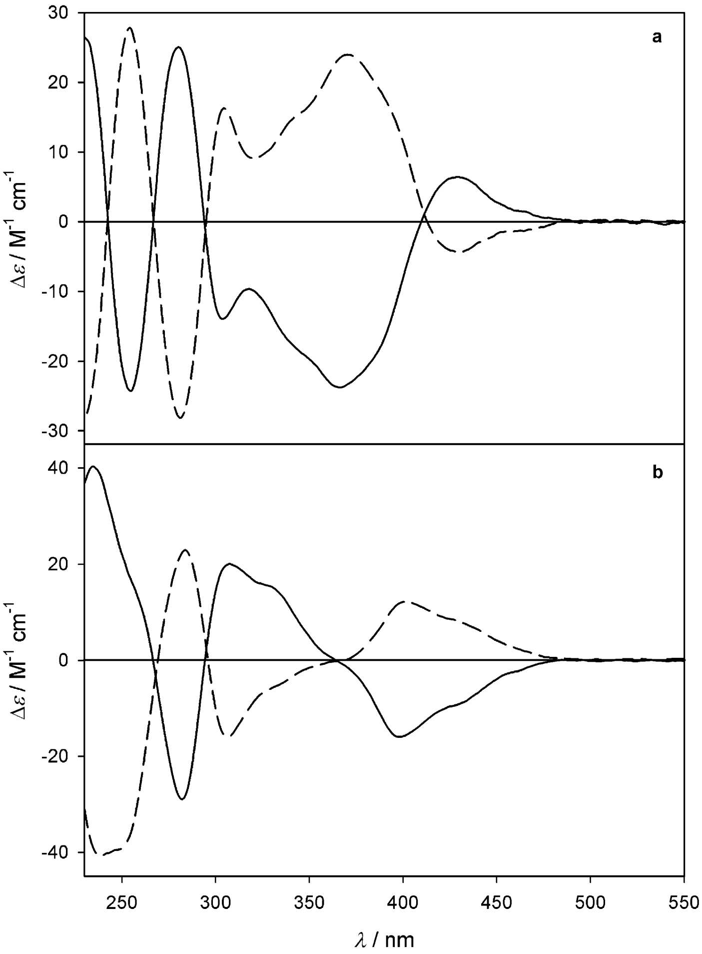


Figure 4. CD spectra of a) Δ_R-**5a** (——) and Λ_S-**5b** (– – –) and b) the corresponding Λ_R-**5a** (——) and Δ_S-**5b** (– – –) isomers in air-equilibrated CH_3CN at 298 K.

However, in the investigated spectral region no electronic transition can be assigned as centered only on the ancillary ligand because it would have appeared the same in the CD spectra of Λ_R- and Δ_R-**5a** or Λ_S- and Δ_S-**5b**. Similar results have been obtained for the other four isomers of **5c** and **5d** (Figure S8 in the Supporting Information). The CD spectrum enables us to clearly distinguish the electronic transitions centered on the F_2ppy ligand or involving the ancillary ligand.

Electrochemical properties: The complexes have been investigated as diastereoisomeric mixtures in CH_3CN that contained tetraethylammonium hexafluorophosphate ($TEAPF_6$) as the supporting electrolyte at 298 K. In the investigated potential region, all the complexes showed a one-electron oxidation and a one-electron reduction process (Table 2).

Table 2. Half-wave potentials ($E_{1/2}$ [V] vs. SCE), unless otherwise noted, of the investigated [Ir^{III}] complexes compared with [$Ir(F_2ppy)(acac)$] in $CH_3CN/TEAPF_6$ solution at 298 K. Working electrode: glassy carbon.

	$E_{1/2}$ [V]	
5a	+1.04[a]	−2.08
5b	+0.96[a]	−2.09
5c	+0.76	−2.21
5d	+0.73	−2.20
[$Ir(F_2ppy)_2(acac)$]	+1.13	−2.06

[a] Anodic peak, E_{pa} at a scan rate of 1 $V s^{-1}$.

Figure 5 shows the cyclic voltammogram of **5d**, which indicates that both the reduction and the oxidation processes are chemically and electrochemically reversible under the investigated experimental conditions. The observed oxidation and reduction processes can be assigned to the metal center and the phenyl pyridyl ligand, respectively, on the basis of close proximity to those reported for [$Ir(ppy)_3$].[27c] The modest positive shift of the oxidation process on going from **5d** to **5c** can be related to the electron-withdrawing substituent on the ancillary ligand, which makes the Ir^{III} oxidation more difficult. On the other hand, the phenyl pyridyl-based reduction is practically unaffected, as expected.

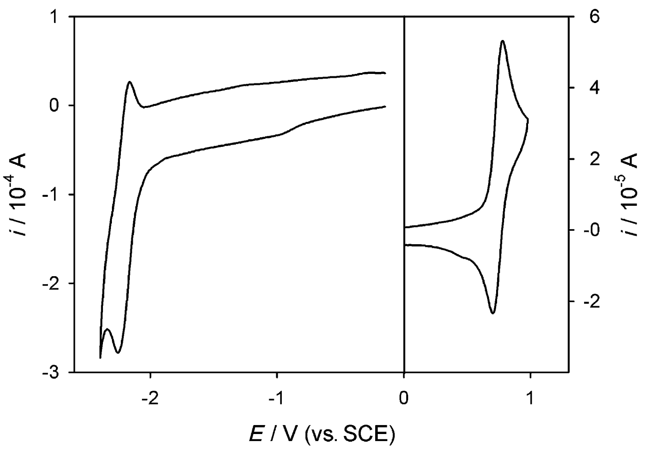


Figure 5. Cyclic voltammogram of a 1 mM solution of **5d** in $CH_3CN/TEAPF_6$ at 298 K. Scan rate: 1 $V s^{-1}$ for the anodic scan and 5 $V s^{-1}$ for the cathodic scan. Working electrode: glassy carbon.

The same trend is registered for the two complexes that contain two F_2ppy ligands, although the reported oxidation process is not chemically reversible at scan rates up to 5 $V s^{-1}$. Compared with the ppy-based complexes, the F_2ppy-based complexes present oxidation and reduction processes that are substantially positively shifted, as expected due to the presence of the fluorine substituents on the cyclometalating ligands. The reduction located on one of the F_2ppy ligands occurs at the same potential as the model [$Ir(F_2ppy)_2(acac)$] complex (Table 2), whereas no comparison can be made for the oxidation process because of the chemical irreversibility associated with the **5a** and **5b** complexes investigated herein.

Thanks to the chemical and electrochemical reversibility of the first oxidation and reduction process observed for **5d**, we have recorded the electrochemiluminescence (ECL) spectrum in $CH_3CN/TEAPF_6$ (Figure S9 in the Supporting Information). This result is important in view of the applications of these complexes in ECL sensors or LEDs.

Conclusion

Novel cyclometalated [Ir^{III}] complexes that contain two ppy or F_2ppy ligands and an ancillary ligand consisting of a phenol-oxazoline (phox and Fphox), have been prepared and characterized from a structural, photophysical, and electrochemical viewpoint.

Complexes **5a** and **5b** show blue luminescence with a very high quantum yield in deaerated CH_3CN. A metal-centered oxidation process and a reduction process located on the ppy ligand have been reported for all the investigated complexes. The reported photophysical and electrochemical data suggest that, as expected, the presence of a fluorine substituent on the phenol ring of the ancillary ligand does not influence the properties of the resulting complexes. Therefore, this position can be exploited to insert other functional groups, that is, a metal-coordinating unit, such as terpyridine, to construct a supramolecular device.

Most importantly, the presence of an enantiomerically pure chiral ancillary ligand enables the facile separation of Λ and Δ isomers by conventional flash chromatography, which gives the corresponding Λ_R and Δ_R or Λ_S and Δ_S diastereoisomers in excellent yield and high stereochemical purity. The two diastereoisomers of each Ir^{III} complex exhibit very similar photophysical properties upon excitation with unpolarized light, whereas they are clearly distinguishable by CD spectroscopy according to their helicity. This result is very promising in view of using these complexes as luminescent sensors of chiral molecules after proper functionalization of the ancillary ligand.

Experimental Section

General: ^{1}H NMR spectra were recorded by using Varian 200 (200 MHz) and Varian 400 (400 MHz) spectrometers. Chemical shifts are reported in ppm referenced to TMS, with the solvent resonance as the internal standard ($CDCl_3$, $\delta = 7.27$ ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, pd = pseudo-doublet, t = triplet, pt = pseudo-triplet, q = quartet, pq = pseudo-quartet, m = multiplet, coupling constants (Hz). ^{13}C NMR spectra were recorded by using Varian 200 (50 MHz) and Varian 400 (100 MHz) spectrometers with complete proton decoupling. Chemical shifts are reported in ppm referenced to TMS with the solvent as the internal standard ($CDCl_3$, $\delta = 77.0$ ppm). ^{19}F NMR spectra were recorded by using a Varian 400 (376.99 MHz) spectrometer with $BF_3{\cdot}Et_2O$ in $CDCl_3$ as the external standard ($\delta = -131.3$ ppm). GC-MS spectra were recorded by EI ionization at 70 eV by using a Hewlett–Packard 5971 with GC injection. Spectra are reported as *m/z* (rel. intensity). LC-ESI mass spectra were obtained by using an Agilent Technologies MSD1100 single-quadrupole mass spectrometer. Chromatographic purification was performed by using 240–400 mesh silica gel. Elemental analyses were carried out by using an EACE 1110 CHNOS analyzer. Optical rotations were determined in a 1 mL cell with a path length of 10 mm (Na D line). Melting points were determined by using a Bibby Stuart Scientific Melting Point Apparatus SMP 3 and are not corrected (decomp.: decomposition). All anhydrous solvents were supplied by Fluka in Sureseal bottles and used as received. 2-Ethoxyethanol was distilled from $MgSO_4$. $IrCl_3{\cdot}3H_2O$ was supplied by Strem. ppy and F_2ppy ligands were procured from commercial sources and used without further purification.

Typical procedure for the synthesis of phox ligands (3 a,b): Dry toluene (8 mL), dried $ZnCl_2$ (2.5 mol %), phenol (3.1 mmol, 1 equiv), and (*S* or *R*)-**2** (1.2 equiv) were placed in a flamed two-necked flask equipped with a condenser. The mixture was heated at reflux overnight, then the volatile components were removed under reduced pressure and EtOAc (10 mL) was added. After stirring for 10 min, the insoluble materials were removed by filtration and the filtrate concentrated under reduced pressure. phox ligands **3** were obtained by purification by using flash chromatography (eluent: *c*Hex/AcOEt/TEA 90:10:1→70:30:1).

*Data for (S)-**3 a***: White wax (yield = 68 %). $[\alpha]_D = +34$ ($c = 0.85$, CH_2Cl_2); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 4.27$ (t, $J = 8.0$ Hz, 1 H), 4.83 (t, $J = 9.2$ Hz, 1 H), 5.50 (t, $J = 9.6$ Hz, 1 H), 9.93 (t, $J = 7.4$ Hz, 1 H), 7.06 (d, $J = 8.4$ Hz, 1 H), 7.28–7.43 (m, 6 H), 7.74 (d, $J = 7.2$ Hz), 12.2 ppm (s, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 68.9$, 74.2, 110.6, 117.0, 118.9, 126.6 (2C), 128.0, 128.4, 129.0 (2C), 133.8, 141.7, 160.2, 166.5 ppm; ESI-MS: *m/z*: 240 $[M+1]$; elemental analysis calcd (%) for $C_{15}H_{13}NO_2$ (239.09): C 75.30, H 5.48, N 5.85; found: C 75.23, H 5.40, N 5.88.

*Data for (R)-**3 b***: White solid (yield = 40 %). M.p. 57–60 °C; $[\alpha]_D = -20.7$ ($c = 0.6$, CH_2Cl_2); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 4.34$ (t, $J = 8.4$ Hz, 1 H), 4.89 (dd, $J = 1.4$, 10.2 Hz, 1 H), 5.45 (dd, $J = 1.4$, 8.4 Hz, 1 H), 6.63 (dd, $J = 1.0$, 8.0 Hz, 1 H), 6.90 (dd, $J = 1.2$, 8.4 Hz, 1 H), 7.29–7.47 ppm (m, 6 H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 67.2$, 74.4, 100.1 (d, $J = 12.9$ Hz, 1C), 106.0 (d, $J = 22.0$ Hz, 1C), 112.8 (d, $J = 3.1$ Hz, 1C), 126.4 (2C), 127.9, 128.8 (2C), 133.4 (d, $J = 11.8$ Hz, 1C), 114.1, 161.1 (d, $J = 256.0$ Hz, 1C), 161.8 (d, $J = 4.6$ Hz, 1C), 165.3 ppm (d, $J = 2.5$ Hz, 1C); ESI-MS: *m/z*: 258 $[M+1]$; elemental analysis calcd for $C_{15}H_{12}FNO_2$ (257.09): C 70.03, H 4.70, N 5.44; found: C 69.97, H 4.72, N 5.41.

Synthesis of the dimeric cyclometalated iridium(III) complexes 4:[24] $IrCl_3{\cdot}3H_2O$ (100 mg, 0.28 mmol) and the desired cyclometalating ligand (ppy or F_2ppy; 0.70 mmol, 2.5 equiv) were added to degassed ethoxyethanol/water (3:1, 4 mL). The mixture was heated at reflux overnight (≈16 h), then cooled. Water was added (15 mL) and the insoluble bright yellow solid was collected by filtration.

Synthesis of the phox cyclometalated iridium(III) complexes 5: The desired dimeric cyclometalated iridium(III) complex (**4 a** or **4 b**; 0.08 mmol) was added to a mixture of phox ((*S*)-**3 a** or (*R*)-**3 b**; 0.22 mmol) and Na_2CO_3 (0.8 mmol) in ethoxyethanol (3 mL). The mixture was heated at reflux overnight (≈16 h), then cooled to RT and the solvent removed by low pressure distillation. The crude was purified by flash chromatography to give diastereomerically pure $\Delta_{R(S)}$-**5** and $\Lambda_{R(S)}$-**5** in nearly 1:1 ratio.

Data for ($\Delta_R + \Lambda_R$)-5 a: Yellow solid. Yield = 70 % (d.r. = 59:41). Flash chromatography (*c*Hex/EtOAc = 90:10).

*(Δ_R)-**5 a** (first eluted isomer)*: M.p. decomp; $[\alpha]_D = -408$ ($c = 1.0$, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 4.19$ (dd, $J = 4.2$, 8.8 Hz, 1 H), 4.72 (t, $J = 8.8$ Hz, 1 H), 4.90 (dd, $J = 4.2$, 8.8 Hz, 1 H), 5.25 (dd, $J = 2.4$, 9.2 Hz, 1 H), 5.80 (dd, $J = 2.4$, 9.2 Hz, 1 H), 6.12 (dd, $J = 8.0$, 13.2 Hz, 1 H), 6.28–6.35 (m, 4 H), 6.46 (d, $J = 8.4$ Hz, 1 H), 6.82 (t, $J = 7.2$ Hz, 2 H), 6.98 (t, $J = 7.2$ Hz, 1 H), 7.05–7.15 (m, 2 H), 7.17 (t, $J = 7.2$ Hz, 1 H), 7.45 (t, $J = 9.2$ Hz, 1 H), 7.54 (d, $J = 8.4$ Hz, 1 H), 7.75 (t, $J = 8.0$ Hz, 1 H), 8.25 (d, $J = 8.4$ Hz, 1 H), 8.50 (d, $J = 5.6$ Hz, 1 H), 8.81 ppm (d, $J = 6.0$ Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 69.7$, 75.6, 96.6 (pt, ^2J(C,F) = 26.3 Hz, 1C), 97.6 (pt, ^2J(C,F) = 26.3 Hz, 1C), 100.3 (d, ^2J(C,F) = 24.0 Hz, 2C), 113.3 (d, ^2J(C,F) = 17.0 Hz, 1C), 114.0 (d, ^2J(C,F) = 17.0 Hz, 1C), 120.9, 121.4, 121.8, 122.6 (d, ^2J(C,F) = 20.1 Hz, 1C), 123.1 (d, ^2J(C,F) = 20.1 Hz, 1C), 125.3 (2C), 127.5 (2C), 128.1 (4C), 133.1, 133.3, 137.1, 137.7, 139.9, 147.6, 147.8, 152.1, 152.2, 161.5, 162.6 (d, ^1J(C,F) = 180.0 Hz, 1C), 165.1 (d, ^1J(C,F) = 194.7 Hz, 4C), 171.7 ppm; ^{19}F NMR (376.99 MHz): $\delta = -88.99$ (t, $J = 12.4$ Hz, 1F), -88.75 (t, $J = 10.9$ Hz, 1F), -87.15 (q, $J = 9.8$ Hz, 1F), -86.5 (q, $J = 9.4$ Hz, 1F), -83.22 ppm (dd, $J = 6.8$, 12.4 Hz, 1F); ESI-MS: *m/z*: 830 $[M+1]$, 1683 $[2M+Na]$; elemental analysis calcd (%) for $C_{37}H_{23}F_5IrN_3O_2$ (829.13): C 53.62, H 2.80, N 5.07; found: C 53.58, H 2.82, N 5.02.

*(Λ_R)-**5 a** (second eluted isomer)*: M.p. decomp; $[\alpha]_D = -180$ ($c = 1.0$, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 4.04$ (dd, $J = 5.4$, 9.2 Hz, 1 H), 4.35 (t, $J = 9.2$ Hz, 1 H), 4.43 (dd, $J = 5.4$, 9.2 Hz, 1 H), 5.07 (dd, $J = 2.4$, 9.0 Hz, 1 H), 5.49 (dd, $J = 2.4$, 9.0 Hz, 1 H), 6.17 (dd, $J = 7.4$, 11.2 Hz, 1 H), 6.24 (d, $J = 8.0$ Hz, 2 H), 6.26–6.34 (m, 1 H), 6.70 (d, $J = 8.0$ Hz, 2 H), 6.85 (t, $J = 7.4$ Hz, 1 H), 6.96 (q, $J = 8.0$ Hz, 1 H), 6.99–7.17 (m, 3 H), 7.30 (t, $J = 5.8$ Hz, 1 H), 7.60 (t, $J = 8.0$ Hz, 1 H), 7.91 (t, $J = 8.0$ Hz, 1 H), 8.10 (d, $J = 8.8$ Hz, 1 H), 8.37 (d, $J = 8.8$ Hz, 1 H), 8.43 (d, $J = 4.8$ Hz, 1 H), 9.10 ppm (d, $J = 6.0$ Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 68.4$, 75.9, 96.5 (pt, ^2J(C,F) = 27.8 Hz, 1C), 97.7 (pt, ^2J(C,F) = 27.8 Hz, 1C), 100.4 (d, ^2J(C,F) = 22.4 Hz, 2C), 113.9 (d, ^2J(C,F) = 19.3 Hz, 1C), 115.8 (d, ^2J(C,F) = 19.3 Hz, 1C), 119.6, 120.4, 120.9, 121.8, 122.2 (d, ^2J(C,F) = 8.9 Hz, 1C), 122.4 (d, ^2J(C,F) = 8.9 Hz, 1C), 126.5 (2C), 128.1, 128.4 (3C), 133.0, 133.1, 134.1, 137.4, 138.1, 140.1, 148.8, 149.9, 153.1, 155.0, 159.4, 162.6 (d, ^1J(C,F) = 185.1 Hz, 1C), 165.1 (d, ^1J(C,F) = 197.5 Hz, 4C), 172.3 ppm; ^{19}F NMR (376.99 MHz): $\delta = -89.42$ (t, $J = 12.1$ Hz, 1F), -89.35 (t, $J = 9.4$ Hz, 1F), -87.47 (q, $J = 9.4$ Hz, 1F), -86.54 (q, $J = 9.4$ Hz, 1F), -86.30 ppm (dd, $J = 8.3$, 12.4 Hz, 1F); ESI-MS: *m/z*: 830 $[M+1]$, 1683 $[2M+Na]$; elemental analysis calcd for $C_{37}H_{23}F_5IrN_3O_2$ (829.13): C 53.62, H 2.80, N 5.07; found: C 53.60, H 2.77, N 5.05.

Data for ($\Delta_S + \Lambda_S$)-5 b: Yellow solid. Yield = 61 % (d.r. = 51:49). Flash chromatography (*c*Hex/EtOAc = 85:15).

*(Λ_S)-**5 b** (first eluted isomer)*: M.p. decomp; $[\alpha]_D = +465$ ($c = 1.1$, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 4.16$ (dd, $J = 3.6$, 9.2 Hz, 1 H), 4.67 (t, $J = 9.2$ Hz, 1 H), 4.97 (dd, $J = 3.6$, 9.2 Hz, 1 H), 5.32 (d, $J = 6.4$ Hz, 1 H), 5.81 (d, $J = 9.2$ Hz, 1 H), 6.25 (d, $J = 6.8$ Hz, 1 H), 6.29–6.34 (m, 3 H), 6.44 (t, $J = 7.2$ Hz, 1 H), 6.73 (d, $J = 8.0$ Hz, 1 H), 6.80 (t, $J = 7.6$ Hz, 2 H), 6.98 (t, $J = 7.2$ Hz, 1 H), 7.07 (t, $J = 7.2$ Hz, 1 H), 7.12 (t, $J = 7.6$ Hz, 1 H), 7.21 (t, $J = 6.8$ Hz, 1 H), 7.44 (t, $J = 8.8$ Hz, 1 H), 7.52 (d, $J = 8.4$ Hz, 1 H), 7.73 (t, $J = 7.6$ Hz, 1 H), 7.79 (d, $J = 8.0$ Hz, 1 H), 8.25 (d, $J = 8.4$ Hz, 1 H), 8.47 (d, $J = 6.0$ Hz, 1 H), 8.84 ppm (d, $J = 5.6$ Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 70.8$, 75.1, 96.5 (pt, ^2J(C,F) = 27.1 Hz, 1C), 97.5 (pt, ^2J(C,F) = 27.1 Hz, 1C), 109.2, 113.2, 113.4 (d, ^2J(C,F) = 13.1 Hz, 1C), 114.0 (d, ^2J(C,F) = 13.1 Hz, 1C), 121.3, 121.8, 122.5 (d, ^2J(C,F) = 20.1 Hz, 1C), 123.1 (d, ^2J(C,F) = 20.1 Hz, 1C), 125.1, 125.2 (4C), 127.4, 128.0 (4C), 133.9, 137.0, 137.5, 140.1, 147.6, 147.7, 152.5, 152.6, 157.3, 157.4, 162.8, 165.2 (d, ^1J(C,F) = 149.1 Hz, 4C), 169.5 ppm; ^{19}F NMR (376.99 MHz): $\delta = -89.02$ (t, $J = 12.4$ Hz, 1F), -89.74 (t, $J = 10.9$ Hz, 1F), -87.30 (q, $J = 9.8$ Hz, 1 H), -86.42 ppm (q, $J = 9.4$ Hz, 1F); ESI-MS: *m/z*: 812 $[M+1]$, 1645 $[2M+Na]$; elemental analysis calcd (%) for $C_{37}H_{24}F_4IrN_3O_2$ (811.14): C 54.81, H 2.98, N 5.18; found: C 54.77, H 2.94, N 5.21.

*(Δ_S)-**5 b** (second eluted isomer)*: M.p. decomp; $[\alpha]_D = +159$ ($c = 1.0$, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 4.21$ (dd, $J = 3.6$, 9.2 Hz, 1 H), 4.26 (t, $J = 9.2$ Hz, 1 H), 4.36 (dd, $J = 3.6$, 9.2 Hz, 1 H), 5.11 (d, $J = 6.6$ Hz,

1 H), 5.52 (d, $J=6.6$ Hz, 1 H), 6.28–6.35 (m, 2 H), 6.45 (t, $J=7.2$ Hz, 1 H), 6.61 (d, $J=8.4$ Hz, 1 H), 6.71–6.75 (m, 3 H), 7.13–7.24 (m, 5 H), 7.59 (t, $J=8.4$ Hz, 1 H), 7.72 (d, $J=9.6$ Hz, 1 H), 7.85 (t, $J=8.4$ Hz, 1 H), 8.12 (d, $J=8.4$ Hz, 1 H), 8.27 (d, $J=6.0$ Hz, 1 H), 8.33 (d, $J=8.4$ Hz, 1 H), 8.89 ppm (d, $J=6.0$ Hz, 1 H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta=69.7$, 75.0, 96.5 (pt, ^{2}J(C,F)=27.0 Hz, 1C), 97.5 (pt, ^{2}J(C,F)=27.0 Hz, 1C), 110.4, 113.2, 113.9 (d, ^{2}J(C,F)=16.2 Hz, 1C), 116.5 (d, ^{2}J(C,F)=16.2 Hz, 1C), 120.8, 122.2 (pt, ^{2}J(C,F)=20.1 Hz, 2C), 124.9, 127.1 (4C), 128.2, 128.4 (4C), 129.4, 133.7, 137.2, 137.8, 140.6, 149.2, 150.3, 154.1, 155.6, 161.4, 163.0, 165.1 (d, ^{1}J(C,F)=150.1 Hz, 4C), 169.5 ppm; ^{19}F NMR (376.99 MHz): $\delta=-89.40$, −89.29 (m, 2F), −87.43 (q, $J=9.4$ Hz, 1F), −86.84 ppm (q, $J=9.4$ Hz, 1F); ESI-MS: m/z: 812 [M+1]; elemental analysis calcd (%) for $C_{37}H_{24}F_4IrN_3O_2$ (811.14): C 54.81, H 2.98, N 5.18; found: C 54.78, H 2.99, N 5.15.

Data for ($\Delta_R+\Lambda_R$)-5c: Yellow solid. Yield=78% (d.r.=51:49). Flash chromatography (*c*Hex/EtOAc=80:20).

*(Δ_R)-**5c** (first eluted isomer)*: M.p. decomp; $[\alpha]_D=-313$ ($c=1.0$, CHCl$_3$); ^{1}H NMR (400 MHz, CDCl$_3$): $\delta=4.13$ (dd, $J=3.6$, 9.2 Hz, 1 H), 4.66 (t, $J=9.2$ Hz, 1 H), 4.86 (dd, $J=3.6$, 9.2 Hz, 1 H), 5.91 (d, $J=6.8$ Hz, 1 H), 6.10 (dd, $J=8.0$, 11.6 Hz, 1 H), 6.24 (d, $J=6.8$ Hz, 2 H), 6.38 (d, $J=7.6$ Hz, 1 H), 6.44 (d, $J=8.4$ Hz, 1 H), 6.65–6.81 (m, 6 H), 6.92 (t, $J=7.2$ Hz, 1 H), 6.99–7.14 (m, 4 H), 7.34–7.39 (m, 2 H), 7.50 (d, $J=7.6$ Hz, 1 H), 7.68 (t, $J=7.6$ Hz, 1 H), 7.82 (d, $J=8.0$ Hz, 1 H), 8.56 (d, $J=6.0$ Hz, 1 H), 8.86 ppm (d, $J=6.0$ Hz, 1 H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta=75.4$, 77.4, 99.7 (pt, ^{2}J(C,F)=14.7 Hz, 2C), 118.1, 118.9, 120.1, 121.0, 121.1, 121.5, 123.7, 124.2, 125.6, 126.5, 127.0, 127.8, 128.0, 128.9, 129.0, 129.2, 131.3, 132.1, 132.6, 132.8, 136.1, 136.6, 140.2, 144.3, 145.4, 147.7, 147.9, 153.3, 161.7, 162.9 (d, ^{1}J(C,F)=255.7 Hz, 1C), 164.1, 167.9, 169.3 ppm; ^{19}F NMR (376.99 MHz): $\delta=-83.61$ ppm (dd, $J=6.8$, 13.6 Hz, 1F); ESI-MS: m/z: 758 [M+1], 1537 [2M+Na]; elemental analysis calcd (%) for $C_{37}H_{27}FIrN_3O_2$ (757.17): C 58.72, H 3.60, N 5.55; found: C 58.70, H 3.57, N 5.53.

*(Λ_R)-**5c** (second eluted isomer)*: M.p. decomp; $[\alpha]_D=-328$ ($c=1.0$, CHCl$_3$); ^{1}H NMR (400 MHz, CDCl$_3$): $\delta=4.06$ (dd, $J=3.6$, 9.2 Hz, 1 H), 4.21 (t, $J=9.2$ Hz, 1 H), 4.42 (dd, $J=3.6$, 9.2 Hz, 1 H), 5.71 (d, $J=7.6$ Hz, 1 H), 6.10 (d, $J=7.2$ Hz, 1 H), 6.12 (d, $J=7.2$ Hz, 1 H), 6.28 (pq, $J=8.8$ Hz, 2 H), 6.61 (d, $J=8.0$ Hz, 2 H), 6.70 (pqt, $J=7.6$ Hz, 2 H), 6.79 (t, $J=8.0$ Hz, 2 H), 6.94 (q, $J=7.6$ Hz, 1 H), 7.06–7.12 (m, 3 H), 7.23 (t, $J=7.6$ Hz, 1 H), 7.47 (d, $J=7.6$ Hz, 1 H), 7.52 (t, $J=7.6$ Hz, 1 H), 7.64 (d, $J=8.0$ Hz, 1 H), 7.69 (d, $J=8.0$ Hz, 1 H), 7.83 (t, $J=8.0$ Hz, 1 H), 7.97 (d, $J=8.4$ Hz, 1 H), 8.29 (d, $J=6.0$ Hz, 1 H), 9.07 ppm (d, $J=5.6$ Hz, 1 H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta=69.8$, 75.7, 99.6 (d, ^{2}J(C,F)=22.4 Hz, 1C), 101.8 (d, ^{2}J(C,F)=70.0 Hz, 1C), 102.1, 117.9, 118.2, 119.9, 120.0, 120.1, 120.7, 121.1, 121.6, 123.5, 124.0, 126.8, 127.7, 128.3, 129.1, 129.3, 131.9, 132.3, 132.4, 134.4, 136.2, 136.9, 140.7, 143.4, 144.5, 148.8, 149.2, 150.0, 151.5, 161.5, 162.2 (d, ^{1}J(C,F)=253.4 Hz, 1C), 168.3, 168.5 ppm; ^{19}F NMR (376.99 MHz): $\delta=-86.29$ ppm (dd, $J=6.8$, 12.4 Hz, 1F); ESI-MS: m/z: 758 [M+1], 1537 [2M+Na] elemental analysis calcd (%) for $C_{37}H_{27}FIrN_3O_2$ (757.17): C 58.72, H 3.60, N 5.55; found: C 58.59, H 3.62, N 5.47.

Data for ($\Delta_S+\Lambda_S$)-5d: Yellow solid. Yield=59% (d.r.=52:48). Flash chromatography (*c*Hex/EtOAc=70:30).

*(Λ_S)-**5d** (first eluted isomer)*: M.p. decomp; $[\alpha]_D=+290$ ($c=1.0$, CHCl$_3$); ^{1}H NMR (400 MHz, CDCl$_3$): $\delta=4.11$ (dd, $J=3.6$, 8.8 Hz 1 H), 4.61 (t, $J=8.8$ Hz, 1 H), 4.95 (dd, $J=3.6$, 8.8 Hz 1 H), 5.98 (d, $J=6.8$ Hz, 1 H), 6.17 (d, $J=7.2$ Hz, 2 H), 6.36–6.41 (m, 2 H), 6.66–6.81 (m, 7 H), 6.91 (t, $J=7.6$ Hz, 1 H), 6.99–7.11 (m, 4 H), 7.18 (t, $J=7.2$ Hz, 1 H), 7.36 (t, $J=6.4$ Hz, 1 H), 7.51 (d, $J=6.8$ Hz, 1 H), 7.66 (t, $J=7.6$ Hz, 1 H), 7.78–7.83 (m, 2 H), 8.52 (d, $J=5.6$ Hz, 1 H), 8.88 ppm (d, $J=4.8$ Hz, 1 H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta=70.7$, 74.9, 109.5, 112.5, 118.0, 118.9, 119.9, 120.9, 121.1, 121.6, 123.7, 124.1, 125.4, 125.5, 126.9, 127.7 (3C), 128.9, 129.3, 129.9, 131.3, 132.1, 133.4, 135.9, 136.4, 140.5, 144.3, 145.5, 147.7, 148.1 (2C), 153.8, 162.5, 167.9, 169.4, 169.9 ppm; ESI-MS: m/z: 740 [M+1], 1501 [2M+Na]; elemental analysis calcd (%) for $C_{37}H_{28}IrN_3O_2$ (739.18): C 60.15, H 3.82, N 5.69; found: C 60.09, H 3.84, N 5.61.

*(Δ_S)-**5d** (second eluted isomer)*: M.p. decomp; $[\alpha]_D=+212$ ($c=1.0$, CHCl$_3$); ^{1}H NMR (400 MHz, CDCl$_3$): $\delta=4.12$ (t, $J=9.2$ Hz, 1 H), 4.22 (dd, $J=3.6$, 9.2 Hz, 1 H), 4.35 (dd, $J=3.6$, 9.2 Hz, 1 H), 5.85 (d, $J=7.6$ Hz, 1 H), 6.16 (d, $J=7.6$ Hz, 1 H), 6.41 (t, $J=6.8$ Hz, 1 H), 6.47 (t, $J=6.8$ Hz, 1 H), 6.55 (t, $J=6.0$ Hz, 1 H), 6.64–6.71 (m, 4 H), 6.79 (t, $J=6.8$ Hz, 1 H), 6.85 (t, $J=6.8$ Hz, 1 H), 7.12–7.20 (m, 5 H), 7.50 (t, $J=7.0$ Hz, 2 H), 7.64 (d, $J=8.0$ Hz, 1 H), 7.70 (d, $J=8.4$ Hz, 1 H), 7.73–7.78 (m, 2 H), 7.91 (d, $J=8.0$ Hz, 1 H), 8.06 (d, $J=6.0$ Hz, 1 H), 8.86 ppm (d, $J=5.6$ Hz, 1 H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta=69.2$, 74.8, 110.4, 112.5, 117.8, 118.1, 120.2, 120.7, 120.9, 121.8, 123.6, 123.9, 125.2, 126.5, 127.6, 128.0, 128.3, 128.8, 129.0, 129.2, 129.4, 132.1, 133.2, 135.0, 136.1, 136.7, 141.2, 143.9, 144.7, 149.3, 149.9, 150.5, 151.9, 162.5, 168.3, 168.4, 169.5 ppm; ESI-MS: m/z: 740 [M+1], 1501 [2M+Na]; elemental analysis calcd (%) for $C_{37}H_{28}IrN_3O_2$ (739.18): C 60.15, H 3.82, N 5.69; found: C 60.12, H 3.80, N 5.64.

X-ray crystallography: The diffraction experiments for **5a**, **5b**, and **5d** were carried out at RT by using a Bruker SMART Apex II CCD-based diffractometer with graphite-monochromated Mo$_{K\alpha}$ radiation ($\lambda=0.71073$ Å). Intensity data were measured over the full diffraction sphere by using ω scans with a width of 0.3°. The software SMART[30] was used for collecting frames of data, indexing reflections, and determining the lattice parameters. The collected frames were then processed for integration by using the software SAINT,[30] and an empirical absorption correction was applied by using SADABS.[31] The structures were solved by direct methods (SIR97)[32] and subsequent Fourier syntheses, and were refined by full-matrix least-squares calculations on F^2 (SHELXTL),[33] which attributed anisotropic thermal parameters to all non-hydrogen atoms. The hydrogen atoms that were located in the Fourier difference map were placed in calculated positions and refined with idealized geometry by using $U_{iso}(H)=1.2U_{eq}(C)$. Both **5a** and **5b** show two independent molecules in the asymmetric unit. Complex **5a** crystallizes with two CH_2Cl_2 solvent molecules in the asymmetric unit, whereas in **5b** the disordered lattice solvent molecules (CH_2Cl_2) could not be modeled reasonably, so the SQUEEZE routine in PLATON[34] was used to generate reflection data that do not include a contribution from the diffuse solvent. The structure of **5b** also showed some degree of twinning. Crystal data and experimental details are reported in Table S1 in the Supporting Information. CCDC-845832, CCDC-845833, and CCDC-845834 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Photophysics: The experiments were carried out in CH_3CN at RT. UV/Vis absorption spectra were recorded by using a Perkin–Elmer λ650 spectrophotometer. Fluorescence spectra were obtained for air-equilibrated solutions by using a Varian Cary Eclipse spectrofluorimeter equipped with a Hamamatsu R928 phototube. Fluorescence quantum yields were measured by following the method of Demas and Crosby[35] (standard used: [Ir(F_2ppy)(acac)], acac=acetylacetonate, $\Phi_{em}=0.64$ in deaerated CH_2Cl_2).[28] Degassing was performed by four cycles of freeze-pump-thaw, reaching a pressure of 1×10^{-5} mbar. Fluorescence lifetime measurements were performed by using an Edinburgh FLS920 spectrofluorometer equipped with a TCC900 card for data acquisition in time-correlated single-photon counting experiments (0.5 ns time resolution) with a D_2 lamp and a LDH-P-C-405 pulsed-diode laser. The estimated experimental errors are 2 nm on the band maximum, 5% on the molar absorption coefficient and fluorescence lifetime, and 15% on the fluorescence quantum yield.

Electrochemistry: The electrochemical experiments were carried out in argon-purged CH_3CN solution at 298 K. For the cyclic voltammetry, the working electrode was a glassy carbon electrode (0.08 cm^2), the counter electrode was a Pt spiral, and a silver wire was used as a quasi-reference electrode (AgQRE). The potentials reported are referenced to SCE by measuring the AgQRE potential with respect to ferrocene ($E_{1/2}=0.395$ V vs. SCE for Fc$^+$/Fc). The concentration of the compounds examined was of the order of 1×10^{-3} M; 0.1 M tetraethylammonium hexafluorophosphate (TEAPF$_6$) was added as the supporting electrolytes. Cyclic voltammograms were obtained with scan rates in the range 0.05–5 V s^{-1}. The estimated experimental error on the $E_{1/2}$ value is ±10 mV.

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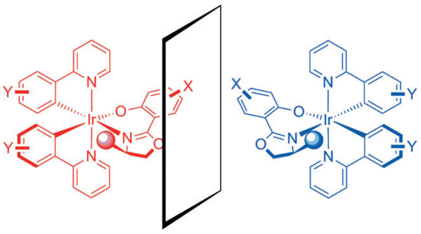
Iridium Phosphor

E. Marchi, R. Sinisi, G. Bergamini, M. Tragni, M. Monari, M. Bandini,* P. Ceroni** .... ▮▮▮▮–▮▮▮▮

Easy Separation of Δ and Λ Isomers of Highly Luminescent [Ir^{III}]-Cyclometalated Complexes Based on Chiral Phenol-Oxazoline Ancillary Ligands



Phox and hounds: Δ and Λ isomers of Ir^{III} complexes based on 2-phenyl-pyridyl (ppy) cyclometalating ligands and chiral phenol-oxazoline ancillary ligands (see figure) are readily available through simple separation on an achiral stationary phase. Blue luminescence, combined with an excellent emission quantum yield ($\Phi_{em}=0.80$), is recorded for complexes with F$_2$ppy ligands.