

## Bimetallic Iridium(III) Complexes Consisting of Ir(ppy)<sub>2</sub> Units (ppy = 2-Phenylpyridine) and Two Laterally Connected N<sup>N</sup> Chelates as Bridge: Synthesis, Separation, and Photophysical Properties

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Reaction of the precursor complex Ir<sub>2</sub>(ppy)<sub>4</sub>Cl<sub>2</sub> (ppy = 2-phenylpyridine) with the bridging ligand 3,8-dipyridyl-4,7-phenanthroline (L) affords, in 94% yield, the cyclometalated iridium dinuclear complex [(ppy)<sub>2</sub>Ir(μ-L)Ir(ppy)<sub>2</sub>]<sup>2+</sup> (1<sup>2+</sup>) as a mixture of three stereoisomers. This mixture consists of a meso form Δ,Λ and a racemic form (enantiomeric pair Δ,Δ and Λ,Λ) in the ratio 1:1.5. Single-crystal X-ray characterization of the perchlorate salt of the meso form reveals (i) the distortion of the bridging ligand from the planarity and (ii) the location of the two iridium subunits above and below the medium plane of the bridging ligand. Ion-pair chromatography with Δ-TRISPHAT anion (TRISPHAT = tris(tetrachlorobenzenediolato)phosphate(V)) as resolving anion permits the separation of the three stereoisomers. The <sup>1</sup>H NMR spectroscopic analysis of each fraction indicates high diastereomeric purity. Electronic circular dichroism properties and comparison with literature data establish their absolute configuration. The absorption and emission properties of the three stereoisomers show only very small variations. The anisotropic properties can be interpreted as distinct interactions of the isomers with the chiral resolving Δ-TRISPHAT anion.

### Introduction

Covalently linked bimetallic complexes of second and third row d<sup>6</sup> transition metals are of great interest for the study of light-induced electron and energy transfer as well as mixed-valent complexes.<sup>1,2</sup> They are also promising precursors for molecular materials and devices in relation to electronics and light energy conversion.<sup>3,4</sup> Bis-tpy ligands (tpy = 2,2':

6',2''-terpyridine) containing two tpy units attached back-to-back (via their 4' positions) have been extensively studied, in particular with Ru(II) and Os(II), either as homometallic or heterometallic systems.<sup>5</sup> Much less common is the use of laterally connected aromatic polyimines as bridging ligands. In such a way, the coordination axes of the two chelating subunits belong to two well defined planes which are parallel to one another. Such bridging ligands and their corresponding bimetallic complexes have been described in the literature, in particular with Ru(II) and Os(II) as metal centers.<sup>6–10</sup>

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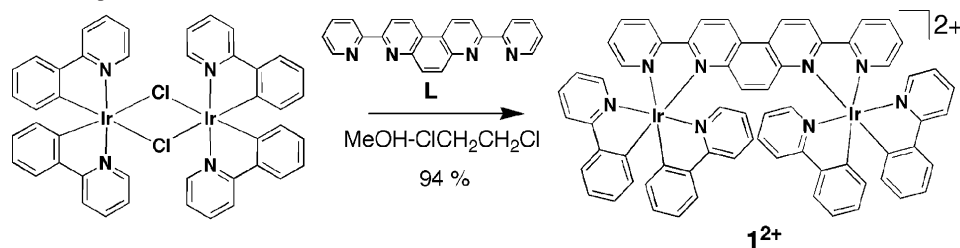
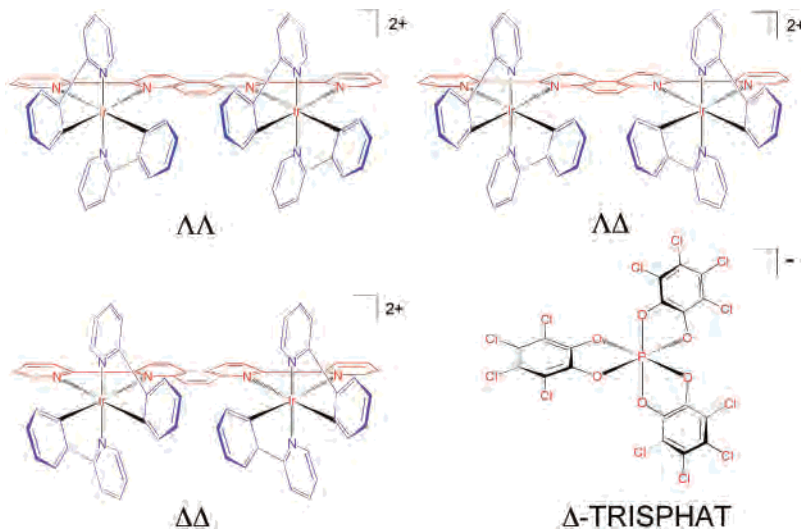
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**Scheme 1.** Synthesis of Complex  $1^{2+}$ **Scheme 2.** ( $\Delta,\Delta$ ), ( $\Delta,\Lambda$ ), and ( $\Lambda,\Lambda$ ) Stereoisomers of Complex  $1^{2+}$  and TRISPHAT Anion ( $\Delta$  Enantiomer)

Ir(III) complexes containing cyclometalating ligands of the 2-phenylpyridine type (ppy) have attracted much interest in the course of the past decade due to their outstanding luminescence properties.<sup>11–16</sup> Neutral iridium(III) complexes are promising candidates as components of molecular light-emitting diodes,<sup>17–19</sup> and they are also interesting chromophores in relation to the construction of multicomponent systems aiming at modeling natural photosynthesis and generating long-lived charge separated states under light irradiation.<sup>20</sup> Up to now, binuclear complexes with bridged Ir(ppy)<sub>2</sub> units have not been much investigated,<sup>21–27</sup> probably

due to the synthetic difficulties related to the preparation of iridium(III) complexes. This is particularly true for bimetallic complexes containing a bridging ligand consisting of two laterally connected N–N bidentate chelates.<sup>21,25</sup>

In the present report, we describe the synthesis of bimetallic  $1^{2+}$  complexes (the bridging ligand is 3,8-dipyridyl-4,7-phenanthroline) as a mixture of three stereoisomers ( $\Lambda,\Lambda$ ;  $\Lambda,\Delta$ ;  $\Delta,\Delta$ ). In addition, we report their separation using enantiopure  $\Delta$ -TRISPHAT as a resolving agent, by forming diastereomeric salts and separating them by chromatography. The X-ray structure of the meso ( $\Lambda,\Delta$ ) form of the  $1^{2+}$  complex as its ClO<sub>4</sub><sup>−</sup> salt could be solved and is discussed. Finally, the electronic absorption and the luminescence properties of the three compounds have been investigated. The complexes are luminescent, both at 77 K in a MeOH/EtOH (1:4) frozen glass and at room temperature in CH<sub>3</sub>CN. Excitation anisotropy measurements have been performed which demonstrate distinct properties for the diastereoisomers associated with two TRISPHAT anions with, in particular, a more pronounced anisotropy for the  $\Delta,\Delta$  isomer than for the  $\Lambda,\Lambda$  configuration.

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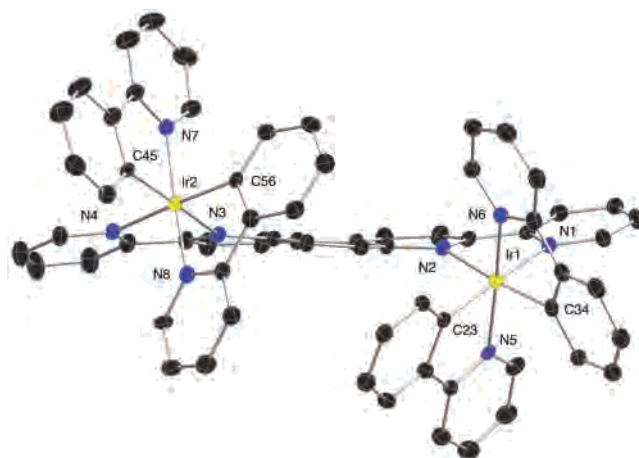
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## Results and Discussion

**Syntheses.** The ligand 3,8-dipyridyl-4,7-phenanthroline<sup>28</sup> (**L**) is represented in Scheme 1. The specificity of this ligand is that it contains two rigidly connected bidentate chelates whose coordination axes have to be roughly parallel to one another. The lack of flexibility for **L** is expected to allow good control over the geometry of its complexes and in particular over the distance between the metal centers occupying its two coordination sites. Compound Ir<sub>2</sub>(ppy)<sub>4</sub>-Cl<sub>2</sub> was obtained as previously reported.<sup>29</sup> The reaction between **L** and the iridium dinuclear precursor Ir<sub>2</sub>(ppy)<sub>4</sub>-Cl<sub>2</sub> in a stoichiometric ratio leads, after silica-gel chromatography and anion exchange, to the [PF<sub>6</sub>]<sup>-</sup> salt of **1**<sup>2+</sup> as a mixture of stereoisomers in 94% yield (Scheme 1).

The high-resolution mass spectrum clearly indicates the expected isotopic patterns and composition for **1**[PF<sub>6</sub>]<sub>2</sub>. Many examples in the literature show that the coordination of a bidentate nitrogen ligand to the Ir(ppy)<sub>2</sub> core maintains a trans configuration of the pyridine groups as in the precursor dimer,<sup>30–32</sup> and this observation has been confirmed both by the <sup>1</sup>H NMR (COSY and ROESY experiments) and the X-ray study. For this reason, the reaction can afford three stereoisomers only: the meso form (Δ,Λ) and the racemic form consisting of an enantiomeric pair (Δ,Δ) and (Λ,Λ) (Scheme 2). At this stage, the <sup>1</sup>H NMR spectrum of **1**[PF<sub>6</sub>]<sub>2</sub> demonstrates the presence of a diastereomeric mixture in the ratio 1:1.5. Various attempts of crystallization of the initial chloro salt permit only enrichment of the meso form. However, crystallization carried out on the perchlorate salt of such an enriched fraction gives single crystals of the meso form.

**Crystal Structure of the Meso Form of **1**[ClO<sub>4</sub>]<sub>2</sub>[CH<sub>3</sub>CN].** To date, only very few crystal structures of dinuclear iridium(III) complexes have been described in the literature.<sup>33</sup> Suitable single crystals of compound **1**[ClO<sub>4</sub>]<sub>2</sub>[CH<sub>3</sub>CN] were obtained by slow diffusion of an acetonitrile solution of the complex into toluene. A perspective view of the dication **1**<sup>2+</sup> with a partial atomic numbering scheme is shown in Figure 1. Selected bond lengths and bond angles are given in Table 1. Clearly, the crystals stemming from the solution mixture of stereoisomers are from the meso diastereomer (Λ,Δ). Each iridium subunit exhibits a pseudo-octahedral geometry around the metal center, and the angles of the trans ligands at the metal center range between 170.41(17)° and 177.83(18)°. The pyridine units of the phenylpyridine ligands are in a trans configuration as observed in the X-ray structure of mononuclear iridium(III) complexes displaying the IrN<sub>4</sub>C<sub>2</sub> coordination set.<sup>30–32</sup> As a conse-



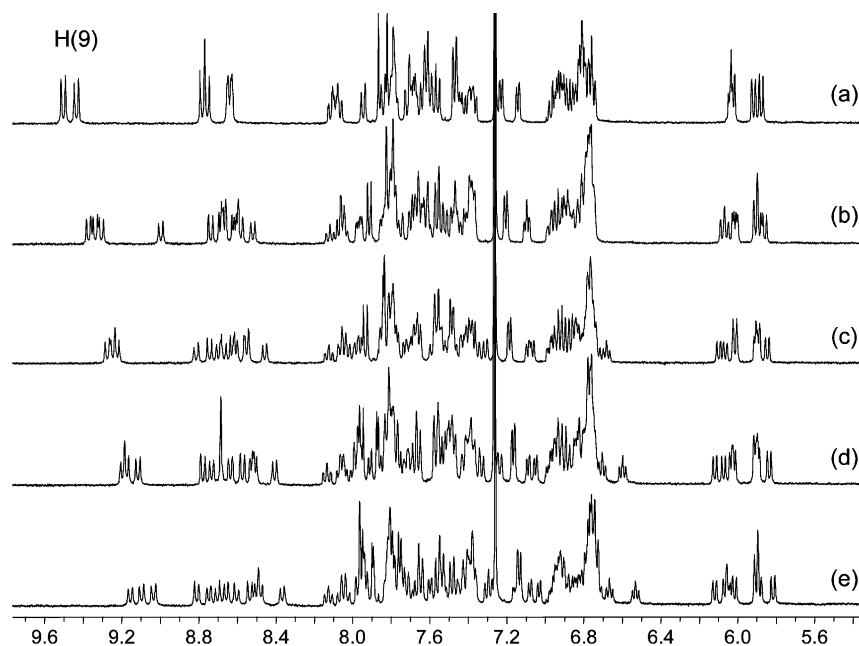
**Figure 1.** Molecular structure of the meso form Δ,Λ (helix *P*) **1**[ClO<sub>4</sub>]<sub>2</sub>[CH<sub>3</sub>CN] with ellipsoid drawn at 50% probability. Proton atoms, anions, and solvent molecules are omitted for clarity.

quence, the two Ir–C bonds of both iridium subunits are in a cis position. The trans influence of the C-donor atoms is reflected in the length of the Ir–N bonds of the bridging ligand which are in the range 2.119(5)–2.205(4) Å as compared to lengths of the Ir–N bonds of the phenylpyridines which are in the range 2.034(4)–2.057(4) Å. A particularly interesting structural feature is the large distortion of the bridging ligand as compared to the flatness and the location of the two iridium subunits above and below the medium plane of the bridging ligand. In spite of this fact, the Ir1–Ir2 distance is 8.171 Å, i.e., significantly shorter than that expected in a nondistorted structure (around 8.5 Å). Such an arrangement may result from the steric constraint between the endo phenylpyridine ligands of the two adjacent iridium subunits. In fact, two different helical forms (*P* and *M*) are observed since no interconversion can occur in the solid state.

**Separation.** For the resolution of chiral entities, preparative chromatographic procedures have overall freed chemists from the constraint of dependency of crystallization. In the case of cationic complexes, many separation protocols are effective ion-pair chromatographic resolutions that involve the addition of nonracemic counterions to the mobile phase.<sup>34–41</sup> However, separations of preformed ionic diastereomer mixtures are also feasible, that of salts of nonra-

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**Figure 2.**  $^1\text{H}$  NMR spectra (400 MHz,  $\text{CDCl}_3/\text{CD}_3\text{CN}$  85/15) of isomeric  $\mathbf{1}[\text{PF}_6]_2$  salts with (a) 0, (b) 0.5, (c) 1.0, (d) 2.0, and (e) 4.0 equiv of  $[\text{n-Bu}_4\text{N}][\Delta\text{-TRISPHAT}]$ .

**Table 1.** Selected Bond Lengths ( $\text{\AA}$ ) and Bond Angles (deg) for Meso ( $\Delta,\Delta$ )- $\mathbf{1}[\text{ClO}_4]_2[\text{CH}_3\text{CN}]$

Ir1–C34	2.009(5)	C34–Ir1–C23	83.3(2)	C45–Ir2–C56	84.3(2)
Ir1–C23	2.021(5)	C34–Ir1–N6	80.23(19)	C45–Ir2–N7	80.0(2)
Ir1–N6	2.034(4)	C23–Ir1–N6	93.0(2)	C56–Ir2–N7	92.63(18)
Ir1–N5	2.057(4)	C34–Ir1–N5	96.02(19)	C45–Ir2–N8	94.81(19)
Ir1–N1	2.119(5)	C23–Ir1–N5	80.2(2)	C56–Ir2–N8	80.64(19)
Ir1–N2	2.198(4)	N6–Ir1–N5	172.61(18)	N7–Ir2–N8	171.95(17)
Ir2–C45	2.003(5)	C34–Ir1–N1	99.06(19)	C45–Ir2–N4	97.41(18)
Ir2–C56	2.021(5)	C23–Ir1–N1	174.68(19)	C56–Ir2–N4	177.83(18)
Ir2–N7	2.053(4)	N6–Ir1–N1	92.13(17)	N7–Ir2–N4	89.00(16)
Ir2–N8	2.053(4)	N5–Ir1–N1	94.76 (17)	N8–Ir2–N4	97.84(16)
Ir2–N4	2.147(4)	C34–Ir1–N2	174.16 (19)	C45–Ir2–N3	170.42(17)
Ir2–N3	2.205(4)	C23–Ir1–N2	102.55 (17)	C56–Ir2–N3	103.25(18)

cemic tris(tetrachlorobenzenediolato)phosphate(V) anion (or TRISPHAT, Scheme 2) in particular.<sup>42,43</sup> In fact, it has been recently shown that this anion is a useful diamagnetic NMR chiral solvating agent as well as a powerful resolving reagent for chiral cationic organometallic and metalloorganic complexes.<sup>44,45</sup> The efficiency of the reagent has been explained by the formation of diastereomeric contact ion pairs between the enantiopure anion and chiral cations. The resulting short-range discriminating interactions that occur lead to efficient enantiodifferentiations in NMR spectroscopy and large differences in physical properties (elution, solubility) for the diastereomeric salts, with  $C_2$ - and  $D_3$ -symmetric tris(diimine) octahedral metal complexes in particular.<sup>46,53</sup> It was thus

foreseen that this anion could behave as an NMR chiral solvating reagent for structurally related cation  $\mathbf{1}^{2+}$  and could lead, possibly, to the separation of all stereoisomers.

The mixture of bis-iridium(III) cyclometalated complexes  $\mathbf{1}^{2+}$  was thus studied in combination with an enantiopure TRISPHAT salt. In an NMR tube,  $[\text{n-Bu}_4\text{N}][\Delta\text{-TRISPHAT}]$  was added as a solid to a  $\text{CDCl}_3/\text{CD}_3\text{CN}$  (85/15) solution of  $\mathbf{1}[\text{PF}_6]_2$  salts. A satisfactory separation of the signals of the isomers of  $\mathbf{1}^{2+}$  was observed with only a small amount of nonracemic reagent (0.5–4.0 equiv, Figure 2). Proton H(9) of the cyclometalated ring was most easily monitored, and the stereoisomeric population could be determined by the direct integration of the respective signals. With this quantitative method of determination of the enantio- and diastereomeric purity in our hands, we turned our attention to the development of a resolution procedure.

To separate the three stereoisomers, ion-pair chromatographic conditions that have proven to be effective for the

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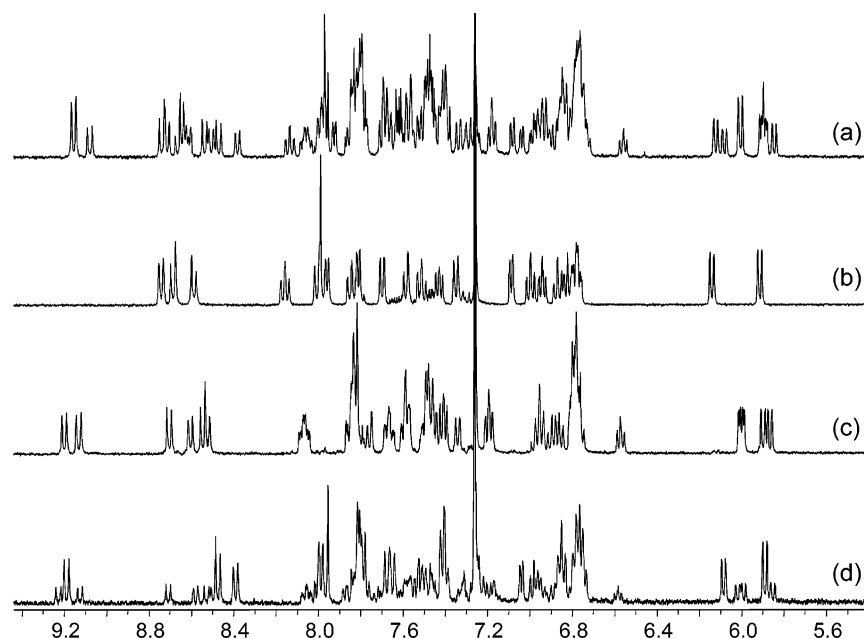
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**Figure 3.**  $^1\text{H}$  NMR spectra (400 MHz,  $\text{CDCl}_3/\text{CD}_3\text{CN}$  85/15) of (a) isomeric mixture of  $[\mathbf{1}][\Delta\text{-TRISPHAT}]_2$  salts, (b) most eluted complex  $[\mathbf{1a}][\Delta\text{-TRISPHAT}]_2$ , (c) second eluted complex  $[\mathbf{1b}][\Delta\text{-TRISPHAT}]_2$ , (d) third eluted complex  $[\mathbf{1c}][\Delta\text{-TRISPHAT}]_2$ .

resolution of “standard” cationic octahedral metal complexes were considered.<sup>47,50,51,54</sup> The potential of TRISPHAT anion to serve as a chromatographic resolving agent for  $\mathbf{1}^{2+}$  was first evaluated by analytical thin layer chromatography (TLC). Solutions of [cinchonidinium][ $\Delta\text{-TRISPHAT}$ ] (2.4 equiv) in acetone and of complex  $\mathbf{1}[\text{PF}_6]_2$  in  $\text{CH}_2\text{Cl}_2$  were mixed and adsorbed on silica gel plates. Development by elution with  $\text{CH}_2\text{Cl}_2$  showed a much-reduced affinity of salts  $\mathbf{1}[\Delta\text{-TRISPHAT}]_2$  for silica gel, as they were retained to a much lower extent ( $R_f = 0.8$ ) than their  $[\text{PF}_6]^-$  precursors ( $R_f = 0$ ).<sup>55</sup> However, only one spot was observed. It seemed to indicate that a concomitant elution of the three TRISPHAT stereoisomeric salts was occurring and thus a lack of chiral discriminations between the TRISPHAT anion and the bis-iridium complexes.

This assumption was confirmed by performing a preparative TLC experiment ( $\text{SiO}_2$ , 0.25 mm, 20 cm  $\times$  20 cm) using a mixture of [cinchonidinium][ $\Delta\text{-TRISPHAT}$ ] (37  $\mu\text{mol}$ ) and complex  $\mathbf{1}[\text{PF}_6]_2$  (16  $\mu\text{mol}$ ) adsorbed on the plate. Development using  $\text{CH}_2\text{Cl}_2$  as an eluent, abrasion from the glass surface of the resulting thin orange band, and extraction of the TRISPHAT salts from the silica confirmed the analysis as the signals of the three distinct complexes were observed in  $^1\text{H}$  NMR spectroscopy (2:1:1 ratio).

However, it was also noticed that this mixture of TRISPHAT stereoisomeric salts exhibited a good solubility in low polarity solvents and in mixtures of toluene and  $\text{CH}_2\text{Cl}_2$  in particular. Considering that the migration of the salts with low polar toluene as an eluent could optimize the electrostatic attraction between the ions, and therefore maximize the diastereoselective ion pairing interactions, the

chromatographic separation was attempted with mixtures of toluene and  $\text{CH}_2\text{Cl}_2$  as eluents. The well-defined orange band observed previously, when using  $\text{CH}_2\text{Cl}_2$  as an eluent only, was now stretched over several centimeters. This enlarged band was then arbitrarily divided into three parallel sub-bands that were abraded from the glass surface and stirred separately in  $\text{CH}_2\text{Cl}_2$ . The resulting suspensions were filtered and concentrated in vacuo. NMR measurements of each re-collected fraction indicated that the isolation of three distinct bis-iridium(III) complexes had been achieved with, however, a poor stereoisomeric purity for each. Two further purifications of each isolated fractions by preparative TLC with four sequential elutions with  $\text{CH}_2\text{Cl}_2$ /toluene (70/30) were necessary to obtain a decent isomeric purity. Separated fractions  $[\mathbf{1a}][\Delta\text{-TRISPHAT}]_2$ ,  $[\mathbf{1b}][\Delta\text{-TRISPHAT}]_2$ , and  $[\mathbf{1c}][\Delta\text{-TRISPHAT}]_2$  were obtained in extremely modest chemical yield ( $\leq 10\%$ ). Nevertheless,  $^1\text{H}$  NMR spectroscopic analysis (see Figure 3) revealed that the two first eluted fractions contained compounds with very high diastereomeric purity (dr  $> 48:1:1$ ,  $\mathbf{1a}:\mathbf{1b}:\mathbf{1c}$ ) and (dr = 1:47:2,  $\mathbf{1a}:\mathbf{1b}:\mathbf{1c}$ ) for the first and the second eluted fractions, respectively, the last eluted fraction being isolated only with a poor stereoisomeric ratio (dr = 1:22:27,  $\mathbf{1a}:\mathbf{1b}:\mathbf{1c}$ ).<sup>56</sup>

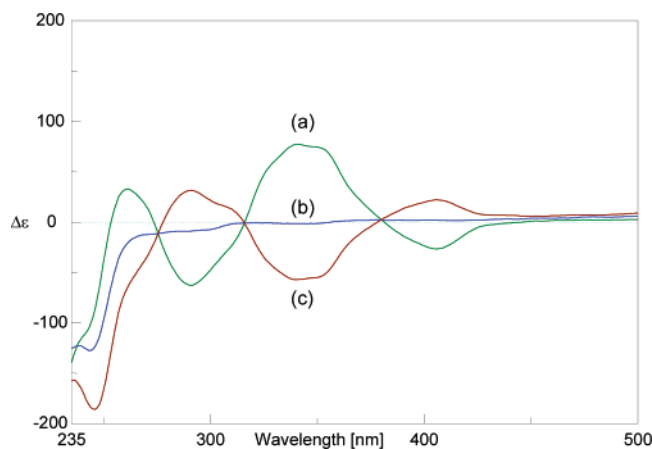
Chiroptical properties of these three isolated fractions were studied by electronic circular dichroism (ECD) as shown in Figure 4. For regions at low energy ( $\lambda > 300$  nm), in which  $\Delta\text{-TRISPHAT}$  is CD-inactive,<sup>57</sup> the ECD spectra of  $[\mathbf{1a}][\Delta\text{-TRISPHAT}]_2$  and  $[\mathbf{1c}][\Delta\text{-TRISPHAT}]_2$  displayed almost symmetrical curves ( $\Delta\epsilon_{406} = -26.6$  and  $+22.1$   $\text{M}^{-1}\cdot\text{cm}^{-1}$ ,  $\Delta\epsilon_{340} = +77.2$  and  $-57.1$   $\text{M}^{-1}\cdot\text{cm}^{-1}$ , in  $\text{CH}_2\text{Cl}_2$

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(55) Lacour, J.; Barchechath, S.; Jodry, J. J.; Ginglinger, C. *Tetrahedron Lett.* **1998**, 39, 567–570.

(56) The stereomeric purity was determined by integration of appropriate  $^1\text{H}$  NMR signals.

(57) Bas, D.; Burgi, T.; Lacour, J.; Vachon, J.; Weber, J. *Chirality* **2005**, 17, S143–S148.

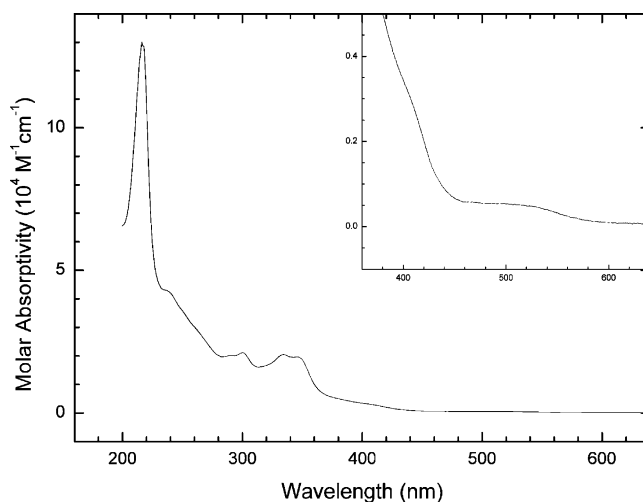


**Figure 4.** Circular dichroism spectra of (a)  $[\Delta,\Delta\text{-1a}][\Delta\text{-TRISPHAT}]_2$ , (b)  $[\Delta,\Lambda\text{-1b}][\Delta\text{-TRISPHAT}]_2$ , and (c)  $[\Lambda,\Lambda\text{-1c}][\Delta\text{-TRISPHAT}]_2$  in  $\text{CH}_2\text{-Cl}_2$  (298 K,  $c = 3.2 \times 10^{-6}$  M, respectively).

with  $c = 3.2 \times 10^{-6}$  M, respectively).<sup>58</sup> For the second eluted complex **1b**  $[\Delta\text{-TRISPHAT}]_2$ , the ECD spectrum showed, on the contrary, no Cotton effects at wavelengths superior to 300 nm. It was then quite clear that the two cationic complexes **1a** and **1c** corresponded to the chiral stereoisomers while compound **1b** was the meso  $\Delta,\Lambda$  derivative.

With this result in hand, the question of the absolute configuration of complexes **1a** and **1c** in salts  $[\mathbf{1a}][\Delta\text{-TRISPHAT}]_2$  and  $[\mathbf{1c}][\Delta\text{-TRISPHAT}]_2$  was tackled. By comparison with von Zelewsky's work on facial tris-cyclometalated Ir(III) complexes,<sup>59,60</sup> CD spectra a and c can be assigned to  $\Delta,\Delta$  and  $\Lambda,\Lambda$  configurations for the cationic complexes **1a** and **1c**. The anionic and cationic three-bladed propellers within salts  $[\mathbf{1a}][\Delta\text{-TRISPHAT}]_2$  and  $[\mathbf{1c}][\Delta\text{-TRISPHAT}]_2$  are of homochiral and heterochiral relationship, respectively.<sup>61</sup>

**Photophysical Studies.** The ground state absorption spectra of the three isomers ( $\Delta,\Delta$ ;  $\Delta,\Lambda$  and  $\Lambda,\Lambda$ ) in acetonitrile solutions at room temperature are identical. The common absorption profile is presented in Figure 5, and the main photophysical features are compiled in Table 2. The absorption spectra of the three isomers show a sharp and intense band that peaked at 216 nm ( $\epsilon \sim 1.3 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ ) assigned to permitted  ${}^1\pi,\pi^*$  transitions of the ppy ligands.<sup>13</sup> Weaker bands are observed around 350 nm. The assignment of these bands is more difficult, because their low intensity ( $\epsilon \sim 2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ) is not compatible with spin allowed  $\pi,\pi^*$  transitions, and although  ${}^1\text{MLCT}$



**Figure 5.** Ground state absorption spectra of the three  $1^{2+}$  isomers ( $\Delta,\Delta$ ;  $\Delta,\Lambda$ ; and  $\Lambda,\Lambda$ ) in acetonitrile solutions at room temperature. The inset shows an enlargement of the low-energy region of the spectrum.

transitions are possible in this energy region, they are uncommon. In other cyclometalated complexes, these MLCT bands failed at slightly lower energies and were assigned to singlet and triplet transitions; for the latter, strong spin-orbit coupling by the Ir center ( $\zeta_{\text{Ir}} = 3909 \text{ cm}^{-1}$ )<sup>62</sup> gives to the formally spin-forbidden  ${}^3\text{MLCT}$  transitions an intensity comparable to the allowed  ${}^1\text{MLCT}$  ones. In our case, it seems reasonable to attribute a mixed (LC-CT) character to these bands, by further considering the possibility of intraligand CT transitions involving the phenanthroline-type ligand. As far as the long tail ( $\epsilon \sim 3 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ) further extending toward lower energy ( $\lambda > 350 \text{ nm}$ ) is concerned, spin-orbit effect due to the metal center could be involved, as mentioned above.

**Luminescence.** The emission spectra of the three isomers in solution (room temperature) and frozen glass (77 K) are compared in Figure 6. At room temperature, the position of the emission maxima and the shape of the spectra are not affected by the chirality of the isomers. On switching from room temperature to 77 K, a blue shift of the emission (ca.  $1050 \text{ cm}^{-1}$ ) is observed, while the shape of the spectra remains broad and structureless. These results rule out an LC nature of the emission (expected to show a structured profile), and are consistent with a CT nature of the excited states (on going from room temperature to 77 K, a hypsochromic shift of the emission is expected, since in the frozen state the reorganization of the solvent is prevented).

In air-equilibrated acetonitrile solutions, the three isomers under study show unusually low quantum yields ( $\phi$  ca.  $6 \times 10^{-3}$ , rt) compared to similar  $[(\text{ppy})_2\text{Ir}(\mu\text{-L})\text{Ir}(\text{ppy})_2]$  homobimetallic bridged complexes.<sup>25</sup> Slightly different values of quantum yields and luminescence lifetimes for the  $\Delta,\Delta$ ;  $\Delta,\Lambda$ ; and  $\Lambda,\Lambda$  isomers are observed (variations on the order 8–14%) so that the radiative rate constant  $k_r$ , defined as the  $\phi/\tau$  ratio, keeps constant ( $k_r = 1.3 \times 10^5 \text{ s}^{-1}$ , see Table 1).

(58) The first eluted complex possesses a more intense Cotton effect compared to that obtained for the third eluted complex due, of course, to its higher isomeric purity.

(59) Schaffner-Hamann, C.; von Zelewsky, A.; Barbieri, A.; Barigelletti, F.; Müller, G.; Riehl, J. P.; Neels, A. *J. Am. Chem. Soc.* **2004**, *126*, 9339–9348.

(60) Yang, L. R.; von Zelewsky, A.; Stoeckli-Evans, H. *Chem. Commun.* **2005**, 4155–4157.

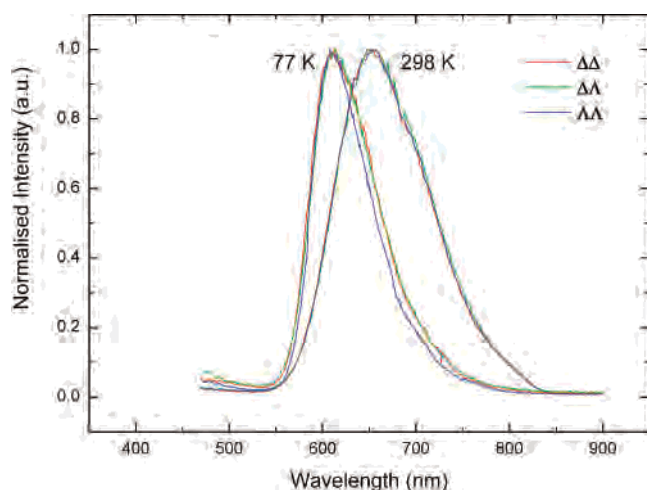
(61) This result fits also nicely with the known behavior of configurationally stable tris(diimine) complexes of type  $[\text{ML}_3]^{n+}$  for which a preferred elution over silica gel is generally observed for the homochiral  $[\Delta\text{-ML}_3][\Delta\text{-TRISPHAT}]_n$  pair over the heterochiral  $[\Lambda\text{-ML}_3][\Delta\text{-TRISPHAT}]_n$ . In this case, and as could be expected, complexes  $(\Delta,\Delta)\text{-1a}$ ,  $(\Delta,\Lambda)\text{-1b}$ , and then  $(\Lambda,\Lambda)\text{-1c}$  are eluted sequentially in presence of  $\Delta\text{-TRISPHAT}$ . See refs 39, 42, 43, and 45.

(62) Montalti, M.; Credi, A.; Prodi, L.; Gandolfi, M. T. *Handbook of Photochemistry*; Taylor and Francis: Boca Raton, FL, 2006.

**Table 2.** Photophysical Properties of ( $\Delta,\Delta$ ), ( $\Delta,\Lambda$ ), and ( $\Lambda,\Lambda$ ) Stereoisomers of  $\mathbf{1}^{2+}$ 

complex	absorption <sup>a</sup>		excitation			emission <sup>c</sup>					
	$\lambda_{\max}$ (nm)	$\epsilon$ ( $M^{-1} \text{ cm}^{-1}$ )	$\lambda_{\max}$ (nm)	$r_0^d$	$\beta^e$ (deg)	295 K <sup>a</sup>				77 K <sup>b</sup>	
						$\lambda_{\max}$ (nm)	$\phi$	$k_r$ ( $s^{-1}$ )	$\tau$ (ns)	$\lambda_{\max}$ (nm)	$\tau$ ( $\mu s$ )
$\Delta\Delta$	510	500	504	0.33	20.0	654	$6.4 \times 10^{-3}$	$1.3 \times 10^5$	48.8	612	3.2
	405 sh	3100	402 sh	0.14	41.2						
	346	19 700	347								
	334	20 500									
	290	20 100									
$\Delta\Lambda$	510	500	504	0.15	40.2	654	$5.5 \times 10^{-3}$	$1.3 \times 10^5$	43.6	612	2.9
	405 sh	3100	402 sh	0.05	49.8						
	346	19 700	347								
	334	20 500									
	290	20 100									
$\Lambda\Lambda$	510	500	504	0.09	46.0	654	$5.9 \times 10^{-3}$	$1.3 \times 10^5$	47.1	612	3.1
	405 sh	3100	402 sh	0.02	52.7						
	346	19 700	347								
	334	20 500									
	290	20 100									

<sup>a</sup> Acetonitrile solvent. <sup>b</sup> MeOH/EtOH (1:4) mixture. <sup>c</sup> Excitation at  $\lambda = 335$  and 400 nm for the emission spectra, and at  $\lambda = 331$  and 373 nm for the emission lifetimes. <sup>d</sup> Limiting excitation anisotropy. <sup>e</sup> Displacement angle between absorption and emission dipoles, see text.



**Figure 6.** Normalized emission spectra of the three  $\mathbf{1}^{2+}$  isomers ( $\Delta,\Delta$ ;  $\Delta,\Lambda$ ; and  $\Lambda,\Lambda$ ) in acetonitrile solutions at 298 K (right), and in frozen MeOH/EtOH (1:4) mixture at 77 K (left).

This implies that in all cases the same emitting state is observed, and that, according to equation

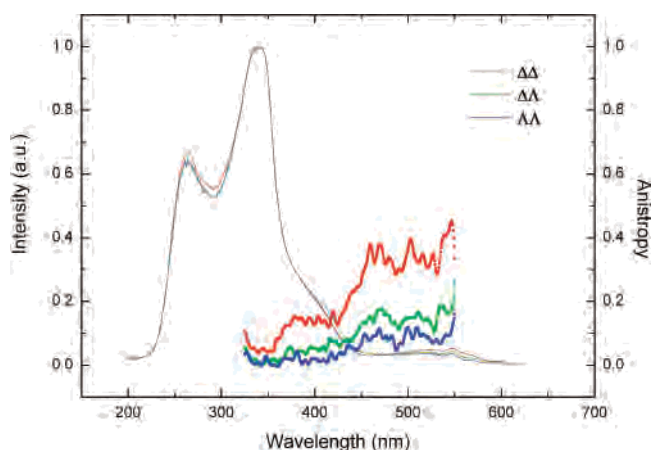
$$\phi = \frac{k_r}{k_r + k'_{nr}}$$

where the nonradiative rate constant  $k'_{nr}$  includes all non-radiative processes, comprising oxygen quenching, the luminescence behavior is regulated by nonradiative processes.

In vitrified frozen solutions at 77 K, all complexes are strongly luminescent, and their lifetimes increase to ca. 3  $\mu s$ , consistent with previously reported data for similar cyclometalated Ir(C^N)<sub>2</sub>L complexes.<sup>25</sup>

The positions of the maxima in the excitation spectra (reported in Figure 7) in the spectral range 300–600 nm for the isomers under study are very close to those in their absorption spectra; that is, pumping either LC or MLCT transitions, the same luminescent excited state is populated.

**Anisotropy.** Because the photophysical properties of the three different isomers showed only small variations in the parameters determined by standard steady-state luminescence



**Figure 7.** Isotropic (lines) and anisotropic (dots) steady-state luminescence excitation spectra of the three  $\mathbf{1}^{2+}$  isomers ( $\Delta,\Delta$ ;  $\Delta,\Lambda$ ; and  $\Lambda,\Lambda$ ) in frozen MeOH/EtOH (1:4) mixture at 77 K.

techniques, we decided to look at their emission anisotropy behavior. The measurements of excitation anisotropy spectra provide information on the relative orientation between absorption and emission transition dipoles of the lumino-phore. In a dilute glassy solution, the measured anisotropy is unaffected by depolarizing processes such as rotational diffusion or energy transfer, thus corresponding to the fundamental or limiting anisotropy  $r_0$ .<sup>63</sup> This is a product of the loss of anisotropy due to photoselection (resulting in a reduction of the anisotropy by a factor of  $2/3$ ) and that due to the angular displacement of the dipoles, according to the equation

$$r_0 = \frac{2}{5} \left( \frac{3 \cos^2 \beta - 1}{2} \right)$$

where  $\beta$  is the displacement angle between the absorption and emission dipoles. Two limiting cases can be distinguished: (i) for  $\beta = 0^\circ$ , i.e., for parallel transition dipole

(63) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*; Plenum: New York, 1999.

moments, one observes  $r_0 = +0.40$ ; (ii) for  $\beta = 90^\circ$ , i.e., for orthogonal transition dipole moments,  $r_0 = -0.20$ . Notably, the anisotropy value is zero when  $\beta = 54.7^\circ$ .<sup>63</sup>

The excitation anisotropy spectra for the three isomers ( $\Delta,\Delta$ ;  $\Delta,\Lambda$ ; and  $\Lambda,\Lambda$ ) recorded in dilute frozen solutions at 77 K are reported in Figure 7, together with luminescence excitation spectra. The two lowest absorption bands (at  $370 < \lambda < 430$  nm, and at  $\lambda > 450$  nm) show constant (on average) and distinct polarization values, indicating that only one electronic transition is contributing in each case. The mean values for the limiting anisotropy  $r_0$  and the derived displacement angle  $\beta$  for the two low-energy transitions are reported in Table 2.

From the anisotropy spectra, one sees that, in the energy region 370–430 nm, absorption and emission transition dipole moments are never collinear ( $r_0 \ll +0.40$ ), as expected for an emission taking place from an excited state ( $T_1$ ) different from the absorbing state ( $S_1$ ). For the lowest energy absorption band (500–530 nm region) of the three isomers, higher, yet different, values for  $r_0$  are found. In this wavelength region, formally forbidden GS-to-triplet transitions take place which mirror the triplet-to-GS transitions of the emission; on this basis high values for  $r_0$  could be expected. Actually, for the  $\Delta,\Delta$  isomer,  $r_0 = +0.33$  is found, a value not far from +0.40, corresponding to parallel transition dipoles for absorption and emission. By contrast, the anisotropy value of the lowest energy transition for the  $\Lambda,\Delta$  isomer is lower,  $r_0 = 0.15$  (roughly one-half of the limiting anisotropy found in the  $\Delta,\Delta$  case), and nearly double with respect to the anisotropy value for the  $\Lambda,\Lambda$  isomer,  $r_0 = 0.09$ . We interpret this trend as due to the distinct interaction of the isomers with the chiral resolving anion  $\Delta$ -TRISPHAT.

In particular, in the case of the  $\Lambda,\Lambda$  and  $\Lambda,\Delta$  stereoisomers, for which a weaker interaction with the counteranion is expected with respect to the  $\Delta,\Delta$  analogue, a similar angle between the absorption and emission transition dipoles is found ( $\beta$  ca.  $40$ – $45^\circ$ ), while in the more perturbed case of the  $\Delta,\Delta$  enantiomer a closer to collinear situation is observed.

## Conclusions

In conclusion, we could prepare a rare example of dinuclear Ir(III) complex whose bridging ligand consists of two bidentate N–N chelates whose coordination axes are parallel to one another. The synthetic procedure is based on the reaction between  $\text{Ir}_2(\text{ppy})_4\text{Cl}_2$  and the bridging ligand **L**, 3,8-dipyridyl-4,7-phenanthroline, which affords the desired complex in high yield as a mixture of diastereoisomers. The meso form of the complex could be crystallized as its  $\text{ClO}_4^-$  salt, and its X-ray structure was solved. Unexpectedly, the central ligand is significantly distorted from planarity, leading to a helical shape for the dinuclear complex. Using optically pure  $\Delta$ -TRISPHAT, the three stereoisomers (the meso form and the two enantiomers of the racemic mixture) could be separated by column chromatography, the identity of each diastereoisomer being determined in comparison to literature data on the basis of  $^1\text{H}$  NMR and circular dichroism data.

## Experimental Section

**Synthesis.**  $^1\text{H}$  NMR spectra were acquired on a Bruker AVANCE 300 (300 MHz) or AVANCE 500 (500 MHz) spectrometer using the deuterated solvent as the lock and residual solvent as the internal reference. Mass spectra were obtained by using a Bruker MicroTOF spectrometer (ES-MS). UV–vis spectra were recorded with a Kontron Instruments UVIKON 860 spectrometer at room temperature.

The starting compounds 3,8-dipyridyl-4,7-phenanthroline **L**<sup>28</sup> and  $\text{Ir}_2(\text{2-phenylpyridine})_4\text{Cl}_2$ <sup>29</sup> were synthesized as previously described.

**[PF<sub>6</sub>]<sub>2</sub>[H<sub>2</sub>O].** A solution of [tetrakis(2-phenylpyridine-*C*<sup>2</sup>,*N*<sup>1</sup>)-(μ-dichloro)diiridium] (0.0247 g, 0.023 mmol) in MeOH (4 mL) was added to a solution of 3,8-bis-(2-pyridyl)-4,7-phenanthroline **L**<sup>28</sup> (0.008 g, 0.023 mmol) in 1,2-dichloroethane (2 mL). The yellow solution turned quickly orange and then red when heated to reflux for 2 h. After cooling to room temperature, a saturated aqueous solution of KPF<sub>6</sub> (2 mL) was added. A red solid is obtained after filtration and washed with water. This solid can be purified over silica gel chromatography, eluting with a mixture of  $\text{CH}_3\text{CN}/\text{H}_2\text{O}/\text{KNO}_3(\text{sat})$  (100/3/0.3 to 100/10/1) to deliver **1**<sup>2+</sup> as a red solid (35 mg, 94%), as a mixture of diastereoisomers in 1:1.5 ratio (NMR determination).  $R_f = 0.22$  ( $\text{CH}_3\text{CN}/\text{H}_2\text{O}/\text{KNO}_3(\text{sat})$ : 100/10/1).  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_3\text{OD}$ ) major diastereoisomer: 9.78 (2H, d,  $J = 9$  Hz,  $\text{H}_{1,10}$ ); 9.08 (2H, d,  $J = 9$  Hz,  $\text{H}_{2,9}$ ); 8.95 (2H, d,  $J = 8$  Hz,  $\text{Py}_3$ ); 8.25 (2H, ddd,  $J = 8, 7.5$  and  $1.5$  Hz,  $\text{Py}_4$ ); 8.11 (2H, br d,  $J = 8$  Hz,  $\text{Ppy}_3$ ); 7.99 (2H, d,  $J = 8$  Hz,  $\text{Ppy}_3$ ); 7.98 (2H, dd,  $J = 5.5$  and  $1.5$  Hz,  $\text{Py}_6$ ); 7.92 (2H, s,  $\text{H}_{5,6}$ ); 7.84 (2H, dd,  $J = 8$  and  $1.5$  Hz,  $\text{Ppy}_4$ ); 7.79 (2H, dd,  $J = 7.5$  and  $1.5$  Hz,  $\text{P}_3$ ); 7.78 (2H, dd,  $J = 7.5$  and  $1.5$  Hz,  $\text{Ppy}_4$ ); 7.71 (2H, dd,  $J = 7.5$  and  $1.5$  Hz,  $\text{P}_3$ ); 7.58 (2H, dd,  $J = 6$  and  $1.5$  Hz,  $\text{Ppy}_6$ ); 7.57 (2H, ddd,  $J = 5.5, 7.5$  and  $1.5$  Hz,  $\text{Py}_5$ ); 7.54 (2H, dd,  $J = 6$  and  $1.5$  Hz,  $\text{Ppy}_6$ ); 7.06 (2H, td,  $J = 7.5$  and  $1$  Hz,  $\text{P}_4$ ); 7.01 (2H, td,  $J = 7.5$  and  $1$  Hz,  $\text{P}_4$ ); 6.95 (2H, ddd,  $J = 7.5, 6$  and  $1.5$  Hz,  $\text{Ppy}_5$ ); 6.94 (2H, ddd,  $J = 8, 6$  and  $1$  Hz,  $\text{Ppy}_5$ ); 6.88 (2H, td,  $J = 7.5$  and  $1.5$  Hz,  $\text{P}_5$ ); 6.84 (2H, td,  $J = 7.5$  and  $1.5$  Hz,  $\text{P}_5$ ); 6.09 (2H, dd,  $J = 6$  and  $1.5$  Hz,  $\text{P}_6$ ); 6.03 (2H, dd,  $J = 6$  and  $1.5$  Hz,  $\text{P}_6$ ). Representative signals of the minor diastereoisomer: 9.68 (2H, d,  $J = 9$  Hz,  $\text{H}_{1,10}$ ); 9.02 (2H, d,  $J = 9$  Hz,  $\text{H}_{2,9}$ ); 8.94 (2H, d,  $J = 8.5$  Hz,  $\text{Py}_3$ ); 7.92 (2H, s,  $\text{H}_{5,6}$ ); 6.09 (2H,  $J = 6$  and  $1.5$  Hz,  $\text{P}_6$ ); 6.03 (2H,  $J = 6$  and  $1.5$  Hz,  $\text{P}_6$ ). HR-ES-MS: 1481.273 ( $[\text{M} - \text{PF}_6]^+$ ;  $\text{C}_{66}\text{H}_{46}\text{F}_6\text{Ir}_2\text{N}_8\text{P}_2^{2+}$ ; calcd 1481.275). **[ClO<sub>4</sub>]<sub>2</sub>** meso isomer  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{CN}$ ): 9.57 (2H, d,  $J = 9$  Hz,  $\text{H}_{1,10}$ ); 8.89 (2H, d,  $J = 9$  Hz,  $\text{H}_{2,9}$ ); 8.75 (2H, d,  $J = 8$  Hz,  $\text{Py}_3$ ); 8.19 (2H, ddd,  $J = 8, 7.7$  and  $1.5$  Hz,  $\text{Py}_4$ ); 8.05 (2H, d,  $J = 8$  Hz,  $\text{Ppy}_3$ ); 7.93 (2H, d,  $J = 8$  Hz,  $\text{Ppy}_3$ ); 7.91 (2H, dd,  $J = 5.5$  and  $1.5$  Hz,  $\text{Py}_6$ ); 7.84 (2H, s,  $\text{H}_{5,6}$ ); 7.84 (2H, dd,  $J = 8$  and  $1.5$  Hz,  $\text{Ppy}_4$ ); 7.77 (2H, dd,  $J = 8$  and  $1.5$  Hz,  $\text{Ppy}_4$ ); 7.75 (2H, dd,  $J = 8$  and  $1.3$  Hz,  $\text{P}_3$ ); 7.68 (2H, dd,  $J = 8$  and  $1.3$  Hz,  $\text{P}_3$ ); 7.53 (2H, dd,  $J = 6, 1.5$  Hz,  $\text{Ppy}_6$ ); 7.52 (2H, ddd,  $J = 5.5, 7.7$  and  $1.5$  Hz,  $\text{Py}_5$ ); 7.50 (2H, dd,  $J = 6$  and  $1.5$  Hz,  $\text{Ppy}_6$ ); 7.07 (2H, td,  $J = 8$  and  $1.3$  Hz,  $\text{P}_4$ ); 7.04 (2H, td,  $J = 7.5$  and  $1.3$  Hz,  $\text{P}_4$ ); 6.93 (2H, ddd,  $J = 8, 6$  and  $1.4$  Hz,  $\text{Ppy}_5$ ); 6.91 (2H, ddd,  $J = 8, 6$  and  $1.4$  Hz,  $\text{Ppy}_5$ ); 6.90 (2H, td,  $J = 8$  and  $1.4$  Hz,  $\text{P}_5$ ); 6.84 (2H, td,  $J = 8$  and  $1.4$  Hz,  $\text{P}_5$ ); 6.09 (2H, dd,  $J = 7.6$  and  $1.4$  Hz,  $\text{P}_6$ ); 6.03 (2H, dd,  $J = 7.6$  and  $1.4$  Hz,  $\text{P}_6$ ). Anal. Calcd for  $\text{C}_{66}\text{H}_{48}\text{N}_8\text{O}_4\text{F}_{12}\text{P}_2\text{Ir}_2$ : C, 48.23; H, 2.94; N, 6.82. Found: C, 49.02; H, 3.39; N, 6.39.

**Crystal Structure.** Single-crystal X-ray diffraction experiments were carried out using Kappa CCD and graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). For all computations, the MolEN



**Table 3.** Crystallographic Data for **1**[ClO<sub>4</sub>]<sub>2</sub>[CH<sub>3</sub>CN]

	<b>1</b> [ClO <sub>4</sub> ] <sub>2</sub> [CH <sub>3</sub> CN]
formula	C <sub>68</sub> H <sub>49</sub> Cl <sub>2</sub> Ir <sub>2</sub> N <sub>9</sub> O <sub>8</sub>
<i>M<sub>w</sub></i>	1575.46
cryst syst	monoclinic
space group	C2/c
<i>a</i> (Å)	51.3660(6)
<i>b</i> (Å)	15.0240(2)
<i>c</i> (Å)	16.3830(2)
α (deg)	90
β (deg)	107.8870(6)
γ (deg)	90
<i>V</i> (Å <sup>3</sup> )	12032.0(3)
<i>Z</i>	8
color	orange
<i>D</i> <sub>calcd</sub> (g cm <sup>-3</sup> )	1.739
μ (mm <sup>-1</sup> )	4.575
<i>T</i> /K	173
<i>R</i> <sup>a</sup>	0.0593
<i>R<sub>w</sub></i> <sup>b</sup>	0.0843

$${}^a R = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad {}^b R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w(|F_o|)^2]^{1/2}.$$

package was used,<sup>64</sup> and structures were drawn using CrystalMaker. Crystal data and details of data collection for complexes **1**[PF<sub>6</sub>]<sub>2</sub> are provided in Table 3.

**Photochemistry and Photophysics.** UV–vis spectra for acetonitrile solutions of the complexes were measured on a Perkin-Elmer Lambda 9 spectrophotometer. The steady-state luminescence spectra for air equilibrated dilute (abs < 0.15 at the excitation wavelength) acetonitrile solutions of the investigated complexes were measured at room temperature and at 77 K in frozen CH<sub>3</sub>-OH/CH<sub>3</sub>CH<sub>2</sub>OH (1:4) mixture using a Spex Fluorolog spectrometer, equipped with a Hamamatsu R928 tube. Excitation wavelengths of 335 and 400 nm were used, obtaining the same quantum yields. While uncorrected luminescence band maxima are used throughout the text, corrected spectra were employed for the determination of the luminescence quantum yields. The correction procedure is based on a calibration curve obtained with the use of a standard lamp, which takes care of the wavelength-dependent phototube response. From the wavelength integrated area *I* of the corrected luminescence spectra, luminescence quantum yields were obtained for the samples with reference to [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> (*φ<sub>r</sub>* = 0.028 in air-equilibrated water)<sup>65</sup> and by using the following equation<sup>66</sup>

$$\frac{\phi}{\phi_r} = \left( \frac{I \cdot n^2}{A} \right) \left( \frac{A_r}{I_r n_r^2} \right)$$

where *A* and *n* are absorbance values at the employed excitation wavelength and refractive index of the solvent, respectively. Measurements at 77 K were conducted by employing capillary tubes immersed in liquid nitrogen and hosted within homemade quartz Dewar. Band maxima and relative luminescence intensities were obtained with uncertainty of 2 nm and 20%, respectively. Excitation spectra in the range 200–600 nm were recorded following the variation of emission intensity at 654 nm.

The luminescence lifetimes were obtained with an IBH 5000F single-photon equipment by using Nanoled excitation sources at 331 and 373 nm. Analysis of the luminescence decay profiles against time was accomplished by using software provided by the manufacturer. The lifetime values are obtained with an estimated uncertainty of 10%.

Anisotropy measurements of MeOH/EtOH (1:4) dilute frozen solutions were performed at 77 K on a Perkin-Elmer LS-50B spectrofluorometer in L-format (single channel) configuration, dipping a glass capillary tube containing the solution of the analyte under investigation in a cold finger Dewar filled with liquid nitrogen. The luminescence intensities *I* were measured with two Melles-Griot polarizing filters set either vertically (V) or horizontally (H) in the excitation and emission beams. The anisotropy values *r* have been calculated with the formula<sup>63</sup>

$$r = \frac{I_{VV} - GI_{VH}}{I_{VV} + 2GI_{VH}}$$

where the first index refers to the excitation polarizer and the second to the emission polarizer position, and where *G* = *I<sub>HV</sub>*/*I<sub>HH</sub>* is the ratio of the sensitivities of the detection system for vertically and horizontally polarized light.

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**Supporting Information Available:** <sup>1</sup>H NMR spectra of a mixture of the stereoisomers (Λ,Λ; Λ,Δ; Δ,Δ; 500 MHz) and of the meso form **1**[ClO<sub>4</sub>]<sub>2</sub> (Λ,Δ; 300 MHz). X-ray crystallographic file in CIF format for the structure determination of compound Δ,Λ (helice *P*) **1**[ClO<sub>4</sub>]<sub>2</sub>[CH<sub>3</sub>CN]. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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