



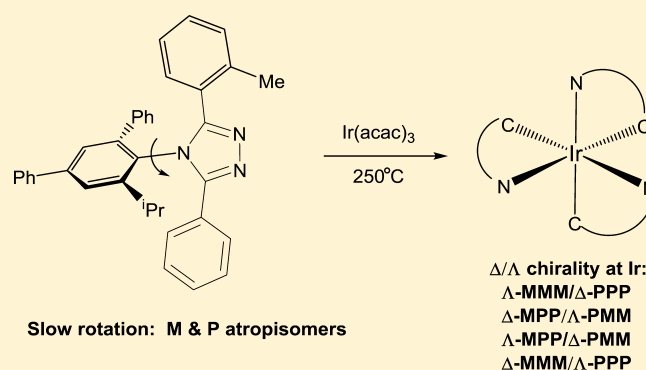
# Highly Quantum Efficient Phosphorescent Sky Blue Emitters Based on Diastereomeric Iridium(III) Complexes of Atropisomeric 5-Aryl-4*H*-1,2,4-triazole Ligands

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## Supporting Information

**ABSTRACT:** Homoleptic  $\text{fac-Ir}^{\text{III}}\text{L}_3$  complexes of 5-aryl-4*H*-1,2,4-triazole ligands are sky blue emitters. When unsymmetrically substituted, the triazole ligands exhibit atropisomerism, and upon cyclometalation to Ir(III) a mixture of diastereomers is formed. We have isolated and structurally characterized all four possible diastereomers of the  $\text{fac-Ir}^{\text{III}}\text{L}_3$  complex formed upon cyclometalation of an atropisomeric 5-aryl-4*H*-1,2,4-triazole ligand onto Ir(III). The phosphorescent blue emitting materials reported herein are among the most efficient to date, with quantum efficiencies above 95%.



The organic light-emitting diode (OLED) is an attractive new technology for commercial and residential lighting applications because of its pleasing diffuse light and flexible form factors.<sup>1</sup> OLED solid-state lighting (SSL) is also environmentally safe because it does not employ mercury vapor found in gas-discharge fluorescent bulbs. However, OLED SSL faces technical challenges to achieve the operational requirements of high power efficiency, high color rendering index, and long device lifetime. To achieve high power efficiency, phosphorescent emitters are used to harvest both triplet and singlet excitons,<sup>2</sup> in principle allowing for 100% internal quantum efficiency versus 25% for fluorescent counterparts.<sup>3</sup> To obtain a high color-rendering index (CRI), the device needs to emit light across the entire visible spectrum. This emission spectrum can be obtained with three primary emitters of red, green, and blue. Of these three types of emitters, phosphorescent red and green emitters are widely available on the market with excellent device lifetimes,<sup>1</sup> while the development of highly efficient, long-lived blue emitters is an ongoing challenge.<sup>1,4</sup>

Among phosphorescent blue emitters, Ir(III) complexes have shown the most promising performance. However, they are limited to a few classes of core structures containing cyclometalated bidentate ligands. These classes include phenyl-imidazoles,<sup>5</sup> phenylpyridines (e.g., FIrpic),<sup>6</sup> phenyl-1*H*-1,2,4-triazoles,<sup>7</sup> phenyl-2*H*-1,2,3-triazoles,<sup>8</sup> and pyrimidine-pyridine.<sup>9</sup> Most of these emitters, with the exception of FIrpic<sup>6a</sup> and substituted FIrpic analogues,<sup>10</sup> have low quantum efficiency ( $\Phi < 0.5$ ).

As part of our development of highly efficient phosphorescent blue emitters whose color can be tuned through steric effects,<sup>11</sup>

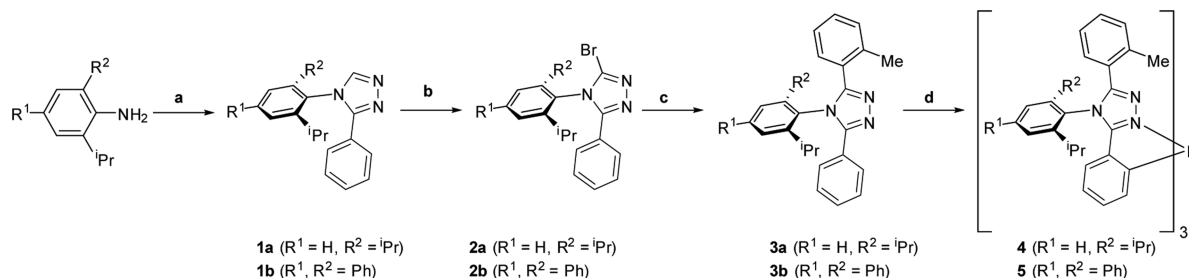
we have synthesized homoleptic iridium(III) complexes containing sterically hindered 5-aryl-4*H*-1,2,4-triazole ligands.<sup>12</sup> We have found that these ligands can display atropisomerism: that is, depending on substitution patterns they may be chiral as the result of hindered internal bond rotation.<sup>13</sup> Upon cyclometalation of the ligand to Ir(III) to afford homoleptic octahedral  $\text{IrL}_3$  compounds, complex mixtures of diastereomers are formed. We have discovered that the individual diastereomers may be separated by liquid chromatography. To the best of our knowledge, this report is the first in which all four atropisomeric diastereomers of a homoleptic octahedral  $\text{ML}_3$  complex have been separated and structurally characterized and their individual photophysical properties have been examined. All of these complexes exhibit high quantum efficiencies ( $\Phi > 0.95$ ).

We prepared two 5-aryl-4*H*-1,2,4-triazole ligands, as shown in Scheme 1. The triazole core was constructed from the condensation reaction of 2,6-diisopropylaniline or 2,4-diphenyl-6-isopropylaniline with 2-phenyl-1,3,4-oxadiazole.<sup>14</sup> Bromination at the C5 position,<sup>15</sup> followed by Suzuki–Miyaura coupling, afforded ligands **3a,b** in 31% and 47% overall yields, respectively. The room-temperature <sup>1</sup>H NMR spectra of **1a–3a** show two doublet resonances for the diastereotopic isopropyl methyl groups (see Figures S1, S3 and S5 in the Supporting Information). Thus, rotation about the N–aryl bond appears to be slow in comparison with the chemical shift difference between the two resonances on the order of 40–150 Hz at 11.75 T (500 MHz) field strength.<sup>16</sup>

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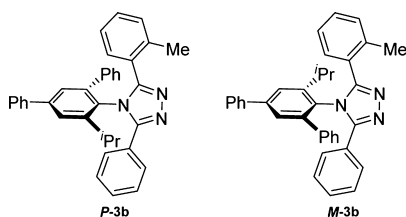


Scheme 1. Synthesis of Ligands 3a,b and Complexes 4 and 5<sup>a</sup>

<sup>a</sup>Legend: (a) 2-phenyl-1,3,4-oxadiazole, trifluoroacetic acid, *o*-dichlorobenzene, reflux; (b) *N*-bromosuccinimide,  $\text{CCl}_4/\text{AcOH}$ , reflux; (c)  $\text{Pd}_2(\text{dba})_3/\text{S-Phos}/\text{K}_3\text{PO}_4$ ,  $\text{H}_2\text{O}$ , *o*-tolylboronic acid, toluene, reflux; (d)  $\text{Ir}(\text{acac})_3$ ,  $250^\circ\text{C}$ ,  $\sim 3$  days.

The cyclometalation of ligand **3a** with iridium(III) acetylacetonate afforded complex **4** in 78% yield after purification.  $^1\text{H}$  NMR spectroscopic and X-ray crystallographic analyses of **4** indicate the sole presence of the *fac* isomer. Four resonances corresponding to the four methyl groups and two resonances for the methine hydrogens on the isopropyl substituents of the ligand indicate that the chiral metal center renders the two methines and the corresponding two sets of methyl groups diastereotopic. The photophysical properties of complex **4** were characterized by UV–vis absorption, luminescence, photoluminescent quantum efficiency (PLQE), and photoluminescence lifetime. Complex **4** is a highly efficient sky blue emitter in toluene solution with photoluminescence peak emission at 475 nm and a PLQE of 97%.

Like **1a**–**3a**, NMR spectroscopic analysis of **1b**–**3b** shows diastereotopic methyl groups of the isopropyl substituent.<sup>17</sup> Unlike **1a**–**3a**, however, **1b**–**3b** lack a plane of symmetry and are therefore racemic mixtures of atropisomers.<sup>15</sup> By employing the nomenclature developed for axially chiral biaryl compounds,<sup>13</sup> we can assign the descriptors *M* and *P* to the two atropisomers of ligand **3b** (Figure 1).



**Figure 1.** Two atropisomers of ligand **3b** resulting from hindered rotation about the N–C bond.

Octahedral tris-chelate complexes are also chiral at the metal, and the common descriptors  $\Lambda$  and  $\Delta$  are used to describe the two possible stereogenic configurations around the metal center.<sup>18</sup> In principle, cyclometalation of an atropisomeric ligand such as **3b** to afford a homoleptic octahedral *fac*- $\text{IrL}_3$  complex may result in eight diastereomers. These diastereomers would be obtained as four pairs of enantiomers:  $\Lambda\text{-MMM}/\Delta\text{-PPP}$ ,  $\Delta\text{-MPP}/\Lambda\text{-PMM}$ ,  $\Lambda\text{-MPP}/\Delta\text{-PMM}$ , and  $\Delta\text{-MMM}/\Lambda\text{-PPP}$ . Indeed, the high-temperature cyclometalation reaction between  $\text{Ir}(\text{acac})_3$  and 3.3 equiv of **3b** produced a mixture of products **5** that could be separated by silica gel column chromatography and recrystallization. The four products eluted from the chromatography column in the following order:  $5(\Lambda\text{-MMM}/\Delta\text{-PPP}) > 5(\Delta\text{-MPP}/\Lambda\text{-PMM}) > 5(\Lambda\text{-MPP}/\Delta\text{-PMM}) > 5(\Delta\text{-MMM}/\Lambda\text{-PPP})$ . On the basis of the UV chromatogram areas, the ratio of

these four products was  $\sim 1:3:3:1$ , or what would be expected from a statistical mixture. The combined yield of the four purified products, after silica gel column chromatography and recrystallization from toluene or ethyl acetate/toluene, was 33%. The purity of the separated diastereomers was 95–98% according to UPLC.

The stereochemical identities of **5** were confirmed by X-ray crystallographic analysis. The four pairs of enantiomers crystallize in centrosymmetric space groups. We only observed *fac*- $\text{IrL}_3$  isomers with different relative stereochemistry at the stereogenic aryl–triazole axes and/or Ir centers. The X-ray crystal structures of the four atropisomers of **5** are shown in Chart 1, and metrical parameters are collected in Table 1.

The  $^1\text{H}$  NMR spectra of the four atropisomers of **5** are consistent with the X-ray crystal structures. Thus,  $5(\Lambda\text{-MMM}/\Delta\text{-PPP})$  and  $5(\Delta\text{-MMM}/\Lambda\text{-PPP})$  have different NMR spectra due to different relative stereochemistry between the iridium center and its ligands, but the spectra are simple and in each all three ligands are magnetically equivalent (Figures S13–S15 and S22–S24 in the Supporting Information). By comparison, the  $^1\text{H}$  NMR spectra of  $5(\Delta\text{-MPP}/\Lambda\text{-PMM})$  and  $5(\Lambda\text{-MPP}/\Delta\text{-PMM})$  are relatively complex, with each of the three ligands exhibiting a different set of resonances (Figures S16–S21 in the Supporting Information).

The atropisomers of **5** exhibit unique photophysical properties. While they exhibit photoluminescence quantum efficiencies approaching 100%, their peak emission wavelengths and widths vary slightly from one another, following the trend  $5(\Lambda\text{-MMM}/\Delta\text{-PPP}) < 5(\Delta\text{-MPP}/\Lambda\text{-PMM}) < 5(\Lambda\text{-MPP}/\Delta\text{-PMM}) < 5(\Delta\text{-MMM}/\Lambda\text{-PPP})$  (Table 2 and Figure 2).  $5(\Lambda\text{-MMM}/\Delta\text{-PPP})$  has the highest energy emission (475 nm), which is identical with that of complex **4**. The peak emission width of  $5(\Lambda\text{-MMM}/\Delta\text{-PPP})$ , however, is significantly narrower than that of **4** (fwhm 70 vs 85 nm). In fact, all of the atropisomers of **5** have peak emissions narrower than those of **4**. The X-ray crystal structures of **5** indicate that, in the solid state, the C5–Ar and N4–Ar dihedral angles increase in the same order as peak emission and width (Table 1).<sup>19</sup> As with complex **4**, the four atropisomers of **5** all have faster radiative vs nonradiative rates.

Color tuning of **4** and **5** is the result of the *o*-tolyl group attached to the C5 carbon of the triazole ring. Previous<sup>11a</sup> and current DFT calculations indicate that the steric effect of this substitution is critical to the blue emission observed in these complexes. In Table 3, the calculated electronic properties of complex **4** are compared to an analogous complex containing an unsubstituted phenyl group attached to the triazole ring (complex **6**). Ortho substitution twists the aryl group in **4** out of conjugation with the triazole ring, resulting in a greater

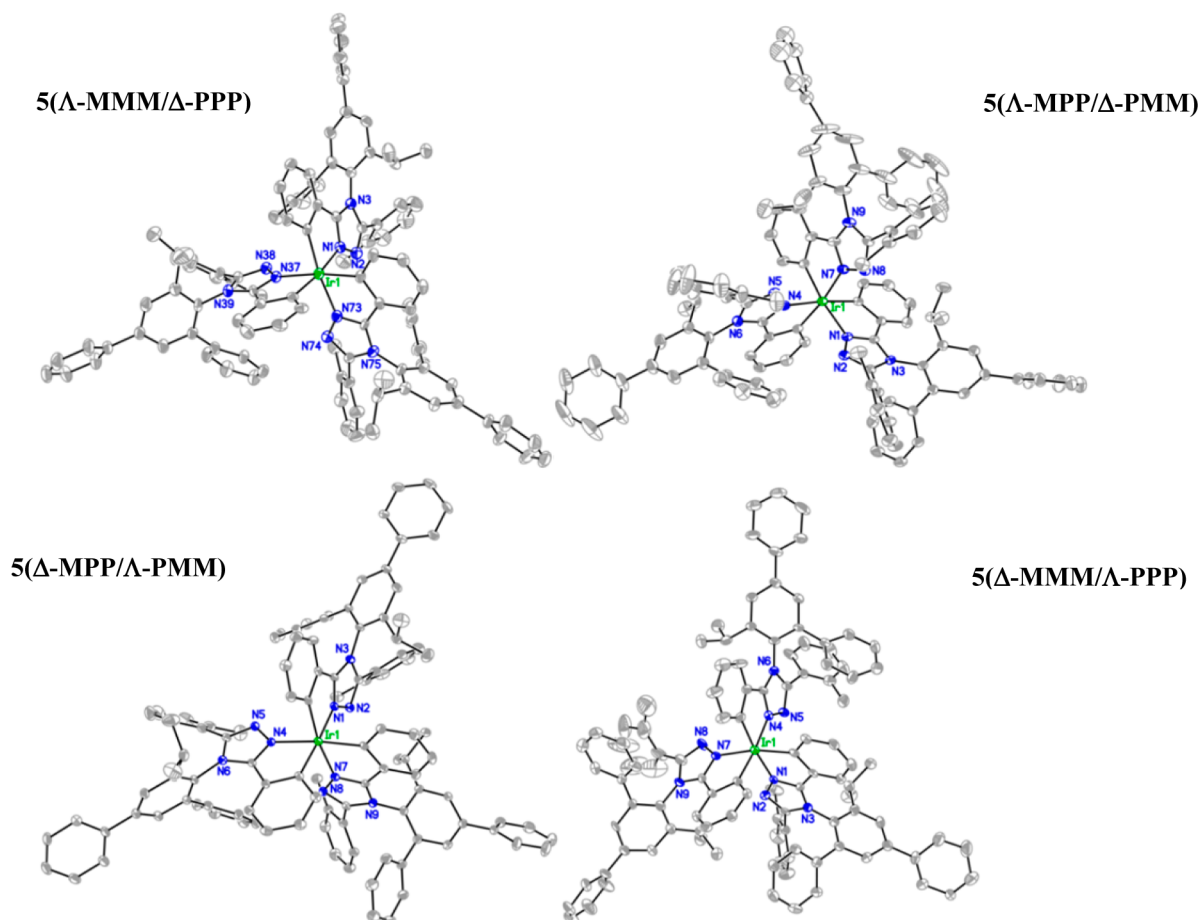
Chart 1. ORTEP Diagrams for 5( $\Delta$ -MMM/ $\Delta$ -PPP), 5( $\Delta$ -MPP/ $\Delta$ -PMM), 5( $\Delta$ -MPP/ $\Delta$ -PMM), and 5( $\Delta$ -MMM/ $\Delta$ -PPP)<sup>a</sup><sup>a</sup>CIF files are included in the Supporting Information.

Table 1. X-ray Structural Data for the Four Diastereomers of 5

	5( $\Delta$ -MMM/ $\Delta$ -PPP)	5( $\Delta$ -MPP/ $\Delta$ -PMM)	5( $\Delta$ -MPP/ $\Delta$ -PMM)	5( $\Delta$ -MMM/ $\Delta$ -PPP)
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
av Ir–N bond (Å)	2.09	2.08	2.07	2.09
av Ir–C bond (Å)	2.02	2.02	2.02	2.01
C5–Ar dihedral (deg)	46.57 (47.98, 48.17, 43.57)	46.62 (46.75, 46.64, 46.47)	48.57 (49.11, 35.66, 60.65)	55.47 (52.98, 54.83, 58.60)
N4–Ar dihedral (deg)	73.50 (71.56, 75.15, 73.79)	75.83 (83.37, 68.02, 76.09)	80.36 (82.63, 70.75, 87.71)	84.33 (89.90, 78.23, 84.86)

HOMO–LUMO gap and higher triplet energy in comparison to that in complex **6**. Indeed, a report in the patent literature indicates that iridium(III) complexes of 5-phenyl-4H-1,2,4-triazole ligands are green emitters ( $\lambda_{\text{em}} \sim 500$  nm),<sup>20</sup> whereas the emitters of the present study exhibit blue emission. This type of color tuning, which is not dependent on electron-withdrawing functionalities,<sup>21</sup> has also been reported for iridium(III) complexes of 5-aryl-1H-1,2,4-triazole ligands.<sup>11</sup>

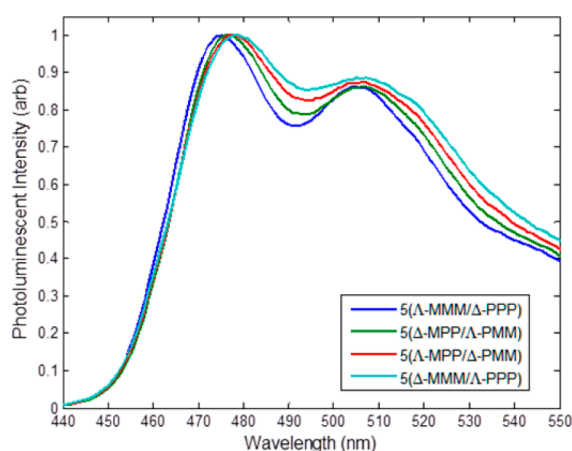
In conclusion, we have identified a new class of phosphorescent blue emitters based on homoleptic iridium(III) complexes of 5-aryl-4H-1,2,4-triazole ligands. Complexes **4** and **5** exhibit high quantum efficiencies. Their emission peaks are in the sky blue range (470–480 nm), suitable for solid-state lighting. In these respects they compare well to blue emitters based on 5-aryl-1H-1,2,4-triazoles previously reported by Burn and Samuel; however, their blue emission is not as deep.<sup>7b</sup> When unsymmetrically substituted, 5-aryl-4H-1,2,4-triazole ligands are chiral due to hindered bond rotation, and this results in a mixture of atropisomers upon cyclometalation. In the case of ligand **3b**,

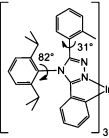
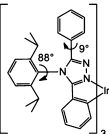
we have isolated and structurally characterized the four possible atropisomeric octahedral *fac*-Ir<sup>III</sup>L<sub>3</sub> complexes. Two atropisomers of an octahedral Ir(III) complex containing a pyrene-functionalized pyridine–imine ligand were reported recently; these complexes were the first examples of metal-containing atropisomers in which the rotationally restricted bond was “not between two chelating atoms”.<sup>22</sup> The atropisomers of **5** would appear to be the second such example, and we believe this is the only system in which the four atropisomers of a homoleptic octahedral ML<sub>3</sub> complex (in which L exhibits axial chirality) have been structurally characterized.<sup>23</sup> Moreover, we believe this is the first report wherein the photophysical properties of phosphorescent atropisomers have been studied.<sup>24</sup> We will aim to understand substituent effects on emission wavelength and efficiency in homoleptic iridium(III) complexes containing 1,2,4-triazole ligands and will report our findings in due course.

**Table 2. Photoluminescence Data for Complex 4 and the Atropisomers of Complex 5**

complex	$k_r$ ( $10^5 \text{ s}^{-1}$ ) <sup>a</sup>	$k_{nr}$ ( $10^4 \text{ s}^{-1}$ ) <sup>b</sup>	$\lambda_{em}$ (nm)	PLQE (%) <sup>c</sup>	fwhm (nm)	$\tau$ ( $10^{-6} \text{ s}$ ) <sup>d</sup>
4	$5.9 \pm 0.32$	$1.7 \pm 3.4$	475	97	85	1.7
5( $\Lambda$ -MMM/ $\Delta$ -PPP)	$6.5 \pm 0.35$	$3.1 \pm 3.7$	475	95	70	1.5
5( $\Delta$ -MPP/ $\Lambda$ -PMM)	$6.9 \pm 0.37$	$0.66 \pm 4.0$	477	99	73	1.4
5( $\Lambda$ -MPP/ $\Delta$ -PMM)	$7.1 \pm 0.38$	$1.2 \pm 4.1$	478	98	76	1.4
5( $\Delta$ -MMM/ $\Lambda$ -PPP)	$6.5 \pm 0.35$	$2.5 \pm 3.7$	478	96	79	1.5

<sup>a</sup>The error analysis is described in the Supporting Information. <sup>b</sup>The large experimental error in the nonradiative rate measurement is a consequence of high quantum efficiency; see the Supporting Information. <sup>c</sup>The luminescence spectra were measured at 298 K with excitations at 300, 320, 340, and 360 nm in toluene. Emission spectra were independent of exciting wavelength. <sup>d</sup>The lifetime of the triplet state was measured with excitation set at 343 nm in toluene solutions.

**Figure 2.** Photoluminescence spectra of the four atropisomers of 5 in toluene.**Table 3. Computed Molecular Electronic Properties (in eV) and Dihedral Angles for 4 and 6<sup>a</sup>**

Complex	HOMO	LUMO	H–L <sub>gap</sub>	T <sub>1</sub> [nm]
<b>4</b> 	-4.84	-1.35	3.49	2.64 [470]
<b>6</b> 	-4.83	-1.47	3.37	2.54 [487]

<sup>a</sup>For computational details, see the Supporting Information and ref 11a.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Text, tables, figures, and CIF and MOL files giving synthetic procedures, analytical data, and <sup>1</sup>H NMR spectra for 2-phenyl-1,3,4-oxadiazole, 2,4-diphenyl-6-isopropylaniline, compounds 1a,b, 2a,b, 3a,b, 4 and the four diastereomers of 5, procedures

for measuring the photophysical properties of 4 and the diastereomers of 5, computational details for 4 and 6, X-ray structure analyses, including tables of anisotropic thermal parameters, hydrogen atom parameters, bond angles, torsion angles, and interatomic distances for complexes 4 and 5( $\Lambda$ -MMM/ $\Delta$ -PPP), 5( $\Delta$ -MPP/ $\Lambda$ -PMM), 5( $\Lambda$ -MPP/ $\Delta$ -PMM), and 5( $\Delta$ -MMM/ $\Lambda$ -PPP). The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00198.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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