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## Intramolecular $\pi$ Stacking in Cationic Iridium(III) **Complexes with Phenyl-Functionalized Cyclometalated** Ligands: Synthesis, Structure, Photophysical Properties, and Theoretical Studies

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The syntheses of two new heteroleptic cationic iridium complexes containing 2,6-diphenylpyridine (Hdppy) and 2,4,6triphenylpyridine (Htppy) as the cyclometalated ligands, namely,  $[Ir(dppy)_2phen]PF_6$  (1, phen = 1,10-phenanthroline) and  $[Ir(tppy)_2phen]PF_6$  (2), are described. The X-ray crystal structure of 2 reveals a distorted octahedral geometry around the Ir center and close intramolecular face-to-face  $\pi$ - $\pi$  stacking interactions between the pendant phenyl rings at the 2position of the cyclometalated ligands and the N<sup>N</sup> ancillary ligand. This represents a new  $\pi$ - $\pi$  stacking mode in charged Ir complexes. Complexes 1 and 2 are green photoemitters: their photophysical and electrochemical properties are interpreted with the assistance of density functional theory (DFT)

## Introduction

Cyclometalated Ir<sup>III</sup> complexes have attracted considerable attention during the last decade owing to their synthetic versatility, high thermal stability, relatively short excited-state lifetimes, high photoluminescence efficiency, and good emission wavelength tunability.<sup>[1]</sup> They have been widely exploited as emitters in phosphorescent organic light-emitting diodes (PhOLEDs),<sup>[2,3]</sup> solid-state lighting,<sup>[4]</sup> and light-emitting electrochemical cells (LECs).<sup>[5]</sup> LECs offer advantages over conventional OLEDs owing to their simpler device architecture, the use of spin-coating tech-

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calculations. These calculations also establish that the observed intramolecular interactions cannot effectively prevent the lengthening of the Ir-N bonds of the complexes in their metal-centered (<sup>3</sup>MC) states. Complexes 1 and 2 do not emit light in light-emitting electrochemical cells (LECs) under conditions in which the model compound  $[Ir(ppy)_2phen]PF_6$ (3) emits strongly. This is explained by degradation reactions of the <sup>3</sup>MC state of **1** and **2** under the applied bias during LEC operation facilitated by the enhanced distortions in the geometry of the complexes. These observations have important implications for the future design of complexes for LEC applications.

niques in their fabrication, and the use of air-stable electrodes without the need for rigorous encapsulation, all of which are applicable to large-area emission and cheap processing. In LECs, ionic transition metal complexes (iTMCs) of the generic formula  $[(C^N)_2 Ir(N^N)][PF_6]$  perform all the roles needed to generate light.<sup>[6]</sup> When an electrical bias is applied to the LEC, the iTMCs serve to (1) decrease the injection barriers through the displacement of the counterion, (2) transport the electrons and holes through consecutive reduction and oxidation processes, and (3) generate the photons. The devices can operate at very low voltages and yield high brightness and power efficiency with tunable emission color.

The practical applications of iTMC-based LECs are hampered by the current limitations of their stability.<sup>[7]</sup> Nucleophile-assisted ligand-exchange reactions at the metal center can occur, and the new complex that is formed can quench the luminescence. A strategy initiated by Bolink, Constable et al., which involves shielding the Ir atom of the iTMC by intramolecular  $\pi$ - $\pi$  stacking (to form "an intramolecular cage"),<sup>[6a]</sup> has led to dramatic improvements in stability and enhanced lifetimes of the LECs.<sup>[8]</sup> For this purpose, phenyl groups have been attached at the  $\alpha$  positions to the nitrogen atoms of the N<sup>N</sup> ancillary ligands. For example, pendant phenyl group(s) on 2,2'-bipyridine (bpy), www.eurjic.org



1,1-phenanthroline (phen), and 2-(1*H*-pyrazol-1-yl)pyridine (pzpy) ligands engage in face-to-face intramolecular  $\pi$ - $\pi$  stacking interactions with the cyclometalating C^N ligands.<sup>[8,9]</sup> These interligand interactions effectively close the complexes in the ground states (S<sub>0</sub>), the emitting (T<sub>1</sub>) states, and the metal-centered (<sup>3</sup>MC) triplet excited states and, thereby, protect the complexes from attack by nucleophiles such as water.<sup>[8b]</sup>

Similarly, our group has reported cationic Ir<sup>III</sup> complexes based on the 2-(5-phenyl-2-phenyl-2*H*-1,2,4-triazol-3-yl)pyridine (Phtz) ancillary ligand, which also show intramolecular  $\pi$ - $\pi$  interactions. Density functional theory (DFT) calculations clearly indicated that these interactions reduce the possibility of ligand-exchange degradation reactions.<sup>[10]</sup> We note that Duan et al. reported that phenyl substitution of the N-heterocyclic carbene ancillary ligand of [Ir(ppy)<sub>2</sub>-(pyphmi)]PF<sub>6</sub> [Hppy = 2-phenylpyridine, pyphmi = 3phenyl-1-(2-pyridyl)imidazolin-2-ylidene-C,C<sup>2'</sup>] leads to weak  $\pi$ - $\pi$  interactions and increased torsion angles, which do not enhance the stability of the LECs.<sup>[5g]</sup>

To the best of our knowledge, the  $\pi$ -stacking strategy has exclusively involved pendant phenyl substitution of the ancillary ligand.<sup>[8–11]</sup> The aim of the present work is to address a fundamental question: what is the effect of attaching pendant phenyl substituents to the cyclometalating (C^N) ligands? We now present the synthesis and characterization of two new complexes  $[Ir(dppy)_2(phen)][PF_6]$  (1) and  $[Ir(tppy)_2(phen)][PF_6]$  (2) (Hdppy = 2,6-diphenylpyridine, Htppy = 2,4,6-triphenylpyridine) (Figure 1). An X-ray crystal structure analysis of **2** shows strong intramolecular  $\pi$ – $\pi$ stacking interactions. The photophysical and electrochemical properties of 1 and 2 are reported, along with DFT/ time-dependent DFT (TD-DFT) calculations. LECs have been fabricated from 1 and 2, and the data are compared with those of the archetypal parent complex [Ir(ppy)2-(phen) [PF<sub>6</sub>] (3), which serves as a reference.



Figure 1. Chemical structures of 1 and 2 and the parent complex 3, which is included for comparison.

## **Results and Discussion**

#### Synthesis

The synthesis of 1 and 2 (Figure 1) followed the standard routes for complexes of the generic formula  $[(C^N)_2Ir-(N^N)][PF_6]$ . The low yield for the formation of 1 and 2 is due to the steric hindrance from the *o*-phenyl substituents, as observed previously with sterically hindered C^N li-

gands.<sup>[12]</sup> The complexes were unambiguously characterized by <sup>1</sup>H NMR spectroscopy, mass spectrometry, and elemental analysis.

#### X-ray Crystal Structure of 2

The solid-state structure of **2** was determined by singlecrystal X-ray diffraction. As depicted in Figure 2, complex **2** adopts a distorted octahedral geometry around the Ir center.



Figure 2. The X-ray molecular structure of the cation in 2; the centroid-to-centroid distances are included.

The structure is characterized by the small C(3)-Ir(1)-N(1) (80.48°), C(3A)-Ir(1)-N(1) (80.48°), and N-Ir(1)-N(OA) (75.57°) bite angles and twisted C(3)-Ir(1)-N (169.59°), C(3A)-Ir(1)-N(OA) (169.59°), and N-Ir(1)-N(OA) (172.19°) bond angles. The Ir-N(phen) (2.209 Å), Ir-C(tppy) (2.005 Å), and Ir-N(tppy) (2.074 Å) distances of 2 closely resemble those previously reported for the parent complex 3: Ir-N(phen) 2.137 and 2.150 Å, Ir-C(ppy) 2.003 and 2.017 Å, Ir-N(ppy) 2.043 and 2.048 Å.[8c] However, there are small differences in some of the bond lengths between structures 2 and 3 as a consequence of the steric interactions of the pendent phenyl groups in 2. Specifically, the Ir–N(tppy) (ca. 2.074 Å) and Ir–N(phen) (ca. 2.209 Å) bonds of 2 are slightly longer than the comparable bonds in 3 [Ir–N(ppy) ca. 2.05 Å, Ir–N(phen) ca. 2.14 Å].<sup>[8c]</sup> Figure 2 illustrates the double face-to-face  $\pi$ -stacking between the pendant phenyl ring of both tppy ligands and the ancillary phen ligand of 2; the interaction is in an optimal offset arrangement at a separation (centroid-to-centroid) of 3.276 Å. This stacking distance is similar to those observed in the [Ir(ppy)<sub>2</sub>(pbpy)]<sup>+</sup> and [Ir(ppy)<sub>2</sub>(dpbpy)]<sup>+</sup> cations (pbpy and dpbpy are 6-phenyl-2,2'-bipyridine and 6,6'-diphenyl-2,2'-bipyridine, respectively).<sup>[8b]</sup> This observation confirms that an intramolecular caged structure is formed by introducing a pendant phenyl group at C(2) of the cyclometalating ppy unit.

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		PL at room temperature					PL at 77 K <sup>[a]</sup>	Electrochemical data <sup>[a]</sup>	
	$\lambda_{\rm em}^{[a]}$ [nm]	$\Phi_{\rm PL}{}^{\rm [b]}(\tau,\mu {\rm s}){}^{\rm [a]}$	$k_{\rm r}^{\rm [a,c]}  [\times 10^5]$	$k_{\rm nr}^{[\rm a,c]} [\times 10^6]$	$\lambda_{\rm em}^{\rm [d]}$ [nm]	$\Phi_{ m film}{}^{[ m d]}$	$\lambda_{\rm em}$ [nm]	$E_{\rm ox}$ [V]	$E_{\rm red}$ [V]
1	552	0.15 (0.23)	6.6	3.71	595	0.06	515, 552 (sh)	0.80	-1.58
2	546	0.06 (0.31)	2.0	3.06	552	0.10	517, 545 (sh)	0.80	-1.59
3	583	0.39 (0.23)	17.3	2.71	591	0.11	532	0.79	-1.58

Table 1. Photophysical and electrochemical data for 1 and 2.

[a] Data obtained in acetonitrile solution;  $\lambda_{exc} = 355$  nm. [b] Estimated error of  $\pm 10\%$ . [c]  $k_r = \Phi_{PL} \times \tau^{-1}$ . [d] Data obtained from a neat thin film.

#### **Photophysical Properties**

The absorption and emission spectra of 1 and 2 (Figure 3) at room temperature were recorded in degassed acetonitrile solutions. The photophysical characteristics are reported in Table 1. The strong absorption bands in the range 200–350 nm are assigned to spin-allowed  $\pi$ - $\pi$ \* transitions from the ligands. The relatively weak absorption bands that occur in the lower-energy region (350-500 nm) correspond to <sup>1</sup>MLCT (metal-to-ligand charge-transfer), <sup>3</sup>MLCT, <sup>1</sup>LLCT (ligand-to-ligand charge-transfer), <sup>3</sup>LLCT, and ligand-centered (LC)  ${}^{3}\pi - \pi^{*}$  transitions with reference to those reported for other Ir<sup>III</sup> complexes.<sup>[13]</sup> This observation implies that the spin-forbidden <sup>3</sup>MLCT, <sup>3</sup>LLCT, and LC  ${}^{3}\pi-\pi^{*}$  transitions have gained considerable intensity by mixing with the higher-lying spin-allowed <sup>1</sup>MLCT transitions because of the strong spin-orbit coupling endowed by the iridium atom. Generally, for cationic Ir<sup>III</sup> complexes, three excited states, namely, <sup>3</sup>MLCT, <sup>3</sup>LLCT, and LC <sup>3</sup> $\pi$ - $\pi$ \*, contribute to light emission.<sup>[14]</sup> At room temperature, 1 and 2 exhibit intense green emission with peak values at 546 and 552 nm, respectively, in CH<sub>3</sub>CN solutions. The broad and featureless bands indicate that the emissive excited states of these two complexes are predominantly <sup>3</sup>MLCT or <sup>3</sup>LLCT in character, rather than LC  ${}^{3}\pi-\pi^{*}$  transitions, which typically show vibronic structure in the emission spectra.<sup>[15]</sup> The emission spectra of 1 and 2 in CH<sub>3</sub>CN solutions at 77 K remain broad and are blueshifted, which indicates that their excited states retain <sup>3</sup>MLCT and <sup>3</sup>LLCT character at low temperature.<sup>[14]</sup>



Figure 3. Absorption and normalized emission spectra of 1, 2, and 3 in CH<sub>3</sub>CN solutions at room temperature.

As shown in Figure 3, the 2-phenyl substituents cause a significant blueshift in the emission wavelengths of 1 and 2 (31 and 37 nm, respectively) compared to that of 3. The larger blueshift for 2 is ascribed to the additional electron-

donating phenyl group at C(4) of the pyridyl ring.<sup>[16]</sup> The emission for 3 ( $\lambda_{max} = 583$  nm in MeCN; Figure 3) is consistent with previously reported data for this complex (579 nm in MeCN;<sup>[17]</sup> 575 nm in CH<sub>2</sub>Cl<sub>2</sub>).<sup>[18]</sup> The emission spectra for 1–3 have the same trend in a non-coordinating solvent such as CH<sub>2</sub>Cl<sub>2</sub> (see Figure S5 in the Supporting Information).

For 1 and 2 in CH<sub>3</sub>CN, the photoluminescence quantum yields (PLQYs) are 0.15 and 0.06, respectively. Complex 1 shows a significantly higher radiative rate constant than that of 2; this may be the reason that 1 has a higher PLQY in solution, as the nonradiative rate constants for both 1 and 2 are quite similar. Conversely, in thin films, the PLQY of 2 ( $\Phi = 0.10$ ) is higher than that for 1 ( $\Phi = 0.06$ ), as the steric bulk of the extra phenyl substituent now has the beneficial effect of reducing self-quenching. The excitedstate lifetimes of 1 and 2 in solution are 0.23 and 0.31 µs, respectively, which are typical for phosphorescent emission in [(C^N)<sub>2</sub>Ir(N^N)][PF<sub>6</sub>] complexes.<sup>[8]</sup> The radiative decay rates ( $k_r$ ) of 1–3 in CH<sub>3</sub>CN solution were calculated as  $6.6 \times 10^5$  for 1,  $2.0 \times 10^5$  for 2, and  $17.3 \times 10^5$  for 3.

#### **Electrochemical Properties**

The electrochemical behavior of 1 and 2 in CH<sub>3</sub>CN solution was investigated by cyclic voltammetry, and the data are reported versus ferrocene/ferrocenium in Table 1. Complexes 1 and 2 exhibit quasireversible oxidation and reduction peaks at  $E_{\rm ox} = 0.80$  V and  $E_{\rm red} = -1.58/-1.59$  V, respectively, which are very similar to the data obtained under the same conditions for 3 [0.79 and -1.58 V this work (cf. 0.85 and -1.54 V in CH<sub>2</sub>Cl<sub>2</sub>)].<sup>[19]</sup> These data are consistent with oxidation primarily at the Ir center and the phenyl ring of the cyclometalated ligand, whereas the reduction is localized on the ancillary ligand.

#### **Quantum Chemical Calculations**

The geometries and electronic structures of 1 and 2 were calculated by DFT/TD-DFT methods at the B3LYP/(6-31G\*+LANL2DZ) level to provide additional insights into the structures and nature of the emissive excited states. Figure 4 displays the atomic orbital compositions of the lowest unoccupied and highest occupied molecular orbitals (LUMO and HOMO, respectively) of the cations of 1 and 2. The LUMO of both complexes is almost the same and resides on the phenanthroline group. The HOMO is composed of a mixture of  $\pi$  orbitals of the phenyl group at C(2)

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of the cyclometalated ligands and iridium d orbitals: the phenyl groups at C(4) or C(6) make no contribution to the HOMOs. These data are consistent with studies on analogous complexes.<sup>[8]</sup> To further understand the emission processes of 1 and 2, TD-DFT methods were used to calculate the low-lying triplet states  $(T_1)$  at the optimized geometry of the ground state  $(S_0)$ . The orbital diagrams show that the T<sub>1</sub> state for 1 mainly originates from HOMO $\rightarrow$ LUMO (74%), and the T<sub>1</sub> state for **2** mainly originates from HOMO $\rightarrow$ LUMO+1 (56%) and HOMO $\rightarrow$ LUMO+3 (20%) transitions (Figure S6). These data suggest that the lowest excited states are induced by <sup>3</sup>MLCT (iridium→ancillary ligand) with some <sup>3</sup>LLCT character (cyclometalated ligands $\rightarrow$  phen). In addition, the unpaired-electron spin density distribution calculated for 1 and 2 perfectly matches the topology of the HOMO-JUMO excitation in which the  $T_1$  state originates and confirms the mixed <sup>3</sup>MLCT/ <sup>3</sup>LLCT character of the lowest triplet state (Figure S7).<sup>[8d]</sup> The photophysical properties and the calculated results illustrate that the emission of 1 and 2 mainly originates from the T<sub>1</sub> states and agree with the experimentally observed



broad unstructured emission spectra of both complexes

Figure 4. HOMO and LUMO distributions of 1 and 2.

The metal-centered (3MC) states result from the excitation of an electron from the occupied  $t_{2g}$  (d $\pi$ ) HOMO to the unoccupied  $e_{2g}$  (d $\sigma^*$ ) level, which is regarded as the origin of the degradation process for RuII- and IrIII-based LECs.<sup>[7]</sup> In the <sup>3</sup>MC states, the rupture of metal-ligand bonds can induce opening of the structure and, thereby, enhance the reactivity of complex; thus, photodegradation is facilitated, and the device becomes unstable. The robust intramolecular  $\pi$ -stacking observed in the complexes reported by Bolink et al. minimizes the expansion of the metal-ligand bonds in the excited state, and this prevents the unwanted ligand-exchange reactions.<sup>[8]</sup> To evaluate the stability of 1 and 2, the molecular structures of the  ${}^{3}MC$ states were fully optimized from the minimum-energy structure of S<sub>0</sub> with Ir-N<sub>ppy</sub> bond lengths lengthened to 2.70 Å.[8h] The metal-centered character of the triplet states for 1 and 2 was confirmed by the spin densities, which were calculated for the optimized <sup>3</sup>MC state geometries. The spin densities are mainly concentrated on the iridium atom with

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1.47 eV unpaired electrons for both 1 and 2 in their <sup>3</sup>MC states. The key bond lengths that affect the stabilities of 1 and 2 in the <sup>3</sup>MC states are presented in Figure 5. The Ir–N<sub>phen</sub> bond lengths of 2.23 Å for 1 and 2 in the <sup>3</sup>MC state are similar to the Ir–N<sub>phen</sub> bond lengths (2.26 Å) in T<sub>1</sub>. The structures show that the face-to-face  $\pi$  stacking, as observed in the X-ray crystal structure of 2 (Figure 2), is retained in the <sup>3</sup>MC states with centroid-to-centroid distances of 4.006 and 4.022 Å for 1 and 2, respectively.



Figure 5. Minimum–energy structures calculated for the  ${}^{3}MC$  states of 1 and 2. Distances R1 and R2 are the optimized Ir–N<sub>cyclometalated ligand</sub> bond lengths [Å].

However, a crucial point is that the intramolecular  $\pi$ - $\pi$  interactions in 1 and 2 do not prevent opening of the structure in the <sup>3</sup>MC state, unlike iridium complexes with a pendant phenyl group on the ancillary ligand such as [Ir(ppy)<sub>2</sub>-(pbpy)]<sup>+</sup>.<sup>[8b]</sup> For example, as shown in Figure 5, the calculated Ir–N bond lengths (R1 and R2) of 1 increased from 2.13 Å in the ground state (S<sub>0</sub>) to 2.61 Å in the <sup>3</sup>MC state, and the changes are the same in **2**. Complex **3** exhibits similar changes to the corresponding bond lengths (Figure S8).

#### Light-Emitting Cells (LECs)

To investigate the electroluminescent properties of the complexes, LECs were prepared with a structure of ITO/ PEDOT:PSS (50 nm)/iridium complex-IL (molar ratio 4:1 w/w; 75 nm)/A1 (120 nm). ITO is indium tin oxide, PEDOT:PSS is poly(3,4-ethylenedioxythiophene)/poly(styrene sulfonate), and IL is the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate (BMIMPF<sub>6</sub>), which reduces drastically the turn-on time of LECs and enhances the ionic conductivity of the thin film.<sup>[20]</sup> This is the standard LEC architecture that our groups have used previously.<sup>[21]</sup> As a benchmark, model complex 3 was studied in the present work. As expected, upon applying a bias of 3 V to the device with complex 3, light emission was observed within a few minutes, as reported previously by us<sup>[19]</sup> and by Bolink et al.<sup>[8c]</sup> for this complex. However, for 1 and 2, under identical conditions no light emission was observed even after the application of a bias of 3 V for as long as 24 h. Moreover, no light emission was observed at a higher bias (8 V) for 24 h. These studies demonstrate that although 1 and 2 show efficient photoluminescence they are not suitable for LECs. This can be explained by the disDate: 02-04-14 16:12:26

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torted molecular structure induced by the double  $\pi$  stacking (as revealed by X-ray analysis) and by the theoretical calculations that show that the intramolecular  $\pi$ - $\pi$  interactions in **1** and **2** do not effectively prevent the transition to a more open structure with an expanded Ir–N coordination sphere in the excited states. Consequently, we conclude that the double  $\pi$  stacking in **1** and **2** is detrimental to stability and it is likely that the complexes degrade in the excited state through reactions with adventitious nucleophiles and so luminescence is quenched.

## Conclusions

This combined experimental and theoretical study has provided new insights into the established strategy of using intramolecular  $\pi$ - $\pi$  stacking in cationic Ir<sup>III</sup> complexes to enhance LEC performance. Complexes 1 and 2 possess the new feature of pendant phenyl rings at the  $\alpha$  position to the nitrogen atom of the cyclometalating units. X-ray analysis of 2 shows that it has a distorted octahedral geometry with strong intramolecular face-to-face  $\pi$ - $\pi$  stacking interactions between the pendant phenyl units and the ancillary ligands. DFT calculations establish that the intramolecular interactions are retained in the excited triplet states and that this mode of  $\pi$ - $\pi$  stacking does not prevent the opening of the Ir-N coordination sphere in the excited states. Consequently, although the complexes are photoluminescent, they do not emit light in LECs under conditions in which the model compound [Ir(ppy)<sub>2</sub>phen]PF<sub>6</sub>, emits strongly. This is presumably because of degradation reactions of the <sup>3</sup>MC state of 1 and 2 under the applied bias during LEC operation. This combined experimental and theoretical study provides new insights into structure-property relationships in ionic Ir complexes and demonstrates convincingly that intramolecular  $\pi$ - $\pi$  stacking can be detrimental to LEC performance in specific cases owing to enhanced distortions in the geometry of the complex. This is valuable information for the future design of complexes for LEC applications.

## **Experimental Section**

Materials, Synthesis, and Characterization: All reagents and solvents employed were commercially available and used as received without further purification. The solvents for syntheses were freshly distilled from appropriate drying reagents. All experiments were performed under a nitrogen atmosphere by using standard Schlenk techniques. <sup>1</sup>H NMR spectra were measured with a Bruker Avance 500 MHz spectrometer with tetramethylsilane as the internal standard. Mass spectra were recorded by using matrix-assisted laser desorption-ionization time-of-flight (MALDI-TOF) mass spectrometry. Elemental analyses (C, H, and N) were obtained by using a Perkin-Elmer 240C elemental analyzer. UV/Vis absorption spectra were recorded with a Hitachi U3030 spectrometer. The emission spectra were recorded with a Hitachi F-7000 fluorescence spectrophotometer. The excited-state lifetimes were measured with a transient spectrofluorimeter (Edinburgh FLS920) with a time-correlated single-photon-counting technique. The photoluminescence

quantum yields (PLQYs) in solution and in neat films were measured with an integrating sphere in a fluorospectrophotometer. Cyclic voltammetry was performed with a BAS 100 W instrument at a scan rate of 100 mV s<sup>-1</sup> in CH<sub>3</sub>CN with a three-electrode configuration: a glassy-carbon electrode as the working electrode, an aqueous saturated calomel electrode as the pseudo-reference electrode, and a platinum wire as the counter electrode. A 0.1 M solution of tetra-*n*-butylammonium perchlorate (TBAP) in CH<sub>3</sub>CN was used as the supporting electrolyte, and ferrocene was selected as the internal standard.

**Synthesis:** Ligands Hdppy<sup>[12]</sup> and Htppy<sup>[12]</sup> and complex  $3^{[17]}$  were synthesized as described in the literature. The  $\mu$ -dichloro-bridged diiridium C^N ligand complexes, which are precursors to complexes 1 and 2, were synthesized from Hdppy and Htppy, respectively, by following standard literature procedures for analogs.<sup>[22]</sup>

[Ir(dppy)<sub>2</sub>(phen)][PF<sub>6</sub>] (1): A mixture of 2,6-diphenylpyridine (508 mg, 2.2 mmol), IrCl<sub>3</sub>·3H<sub>2</sub>O (352 mg, 1.0 mmol), 2-ethoxyethanol (12 mL), and water (4 mL) was heated at 120 °C. After 12 h, the mixture was cooled to 20 °C, and the precipitate was collected by filtration, washed with water, and then dissolved in  $CH_2Cl_2$ . The organic solution was separated, dried with MgSO<sub>4</sub>, filtered, and evaporated to give a pale green solid, presumed to be the bis-µ-chloro-bridged complex, which was used directly in the next step. A mixture of this complex (138 mg, 0.1 mmol) and phenanthroline (36 mg, 0.2 mmol) in dichloromethane (30 mL) and methanol (15 mL) was heated under reflux for 24 h in the dark. After cooling to room temperature, the mixture was filtered; an excess of solid KPF<sub>6</sub> was then added, and the mixture was stirred for 1 h at room temperature. The solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography with a mixture of dichloromethane/ethyl acetate (4:1 v/v) as eluent to yield 1 (8 mg) as a yellow solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.20 (d, J = 7.5 Hz, 2 H), 8.02 (d, J = 7.5 Hz, 2 H), 7.98 (s, 2 H), 7.88 (d, J = 7.5 Hz, 2 H), 7.63–7.67 (m, 4 H), 7.20–7.24 (m, 6 H), 7.02 (t, J = 7.5 Hz, 2 H), 6.81 (d, J =8 Hz, 2 H), 6.62 (t, J = 3.5 Hz, 4 H), 6.48 (d, J = 8 Hz, 2 H), 6.11 (s, 2 H), 5.01 (d, J = 7 Hz, 2 H) ppm.  $C_{48}H_{36}F_6IrN_4P$  (1006.02): calcd. C 57.31, H 3.61, N 5.57; found C 57.36, H 3.65, N 5.61. ESI-MS:  $m/z = 833.2 [M - PF_6]^+$ .

[Ir(tppy)<sub>2</sub>(phen)][PF<sub>6</sub>] (2): By following the same procedure as that for 1, 2,4,6-triphenylpyridine (676 mg, 2.2 mmol) gave a pale green solid, presumed to be the bis-µ-chloro-bridged complex, which was used directly in the next step. A mixture of this complex (168 mg, 0.1 mmol) and phenanthroline (36 mg, 0.2 mmol) in dichloromethane (30 mL) and methanol (15 mL) was heated under reflux for 24 h in the dark. Workup and purification as described for 1 yielded 2 (15 mg). <sup>1</sup>H NMR (500 MHz, [D<sub>6</sub>]dimethyl sulfoxide:  $\delta$ = 8.69 (d, J = 1.5 Hz, 2 H), 8.37–8.42 (m, 4 H), 8.07 (s, 2 H), 7.98– 8.00 (m, 4 H), 7.67 (d, J = 4 Hz, 2 H), 7.48–7.50 (m, 8 H), 7.17– 7.22 (m, 4 H), 7.03–7.06 (m, 2 H), 6.96 (d, J = 2 Hz, 2 H), 6.84 (d, J = 7.5 Hz, 2 H), 6.64 (t, J = 7.5 Hz, 2 H), 6.56 (t, J = 7.5 Hz, 2 H), 6.06 (t, J = 7.5 Hz, 2 H), 5.11 (d, J = 7.5 Hz, 2 H) ppm. C<sub>60</sub>H<sub>44</sub>F<sub>6</sub>IrN<sub>4</sub>P (1158.22): calcd. C 62.22, H 3.83, N 4.84; found C 62.27, H 3.91, N 4.88. ESI-MS:  $m/z = 983.2 [M - PF_6]^+$ . Single crystals of 2 were obtained by slow evaporation of a dilute CH<sub>2</sub>Cl<sub>2</sub> solution of the complex.

**X-ray Crystallography:** The data collection for **2** was performed with a Bruker Smart Apex II CCD diffractometer with graphite-monochromated Mo- $K_a$  radiation ( $\lambda = 0.71069$  Å) at 293 K. Absorption corrections were performed by using the multiscan technique. The crystal structure was solved by direct methods with SHELXTL-97<sup>[23]</sup> and refined by full-matrix least-squares tech-

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niques by using SHELXTL-97 within WINGX.<sup>[24]</sup> The hydrogen atoms of the aromatic rings were included in the structure factor calculation at idealized positions by using a riding model. Anisotropic thermal parameters were used to refine all non-hydrogen atoms except for some of the nitrogen and carbon atoms. Structural data in CIF format is available as Supporting Information. CCDC-956631 contains 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.

**Theoretical Calculations:** The ground and excited electronic states of the complexes were investigated by performing DFT and TD-DFT calculations at the B3LYP level.<sup>[25]</sup> The 6-31G\* basis sets were employed to optimize the C, H, N atoms, and the LANL2DZ basis sets were employed for the Ir atom. An effective core potential (ECP) replaces the inner core electrons of iridium to leave the outer core (5s)<sup>2</sup>(5p)<sup>6</sup> electrons and the (5d)<sup>6</sup> valence electrons of the Ir<sup>III</sup> ion. The geometry of the metal-centered triplet (<sup>3</sup>MC) was fully optimized and calculated at the spin-unrestricted UB3LYP level with a spin multiplicity of three. All calculations reported here were performed with the Gaussian 09 software package.<sup>[26]</sup>

Device Preparation and Characterization: PEDOT:PSS is poly(3,4ethylenedioxythiophene):poly(styrene sulfonate) (CLEVIOS<sup>TM</sup> P VP Al 4083 aqueous dispersion, 1.3–1.7% solid content Heraeus); solvents were obtained from Aldrich. ITO-coated glass substrates  $(20 \Omega/sq)$  were cleaned and treated with oxygen plasma before use. The PEDOT:PSS layer was spin-coated onto the ITO substrate and baked at 100 °C for 30 min to yield a film with a thickness of ca. 100 nm. After cooling to room temperature, the solutions of 1-3 and the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate (BMIMPF<sub>6</sub>) in CH<sub>2</sub>Cl<sub>2</sub> were spin-coated onto the substrate, and then the layer with a thickness of ca 90 nm was baked at 80 °C for 2 h. The film was transferred into a metal evaporating chamber in which an aluminum cathode (120 nm) was evaporated under low pressure ( $<5 \times 10^{-4}$  mbar). The electroluminescence (EL) spectra were obtained with a Photo Research PR650 spectrophotometer under ambient conditions by applying a constant voltage with a Keithley 2400 source meter.

Supporting Information (see footnote on the first page of this article): <sup>1</sup>H NMR spectra of 1 and 2; cyclic voltammograms of 1-3; theoretical calculations of 1-3; emission spectra of 1-3 in solution.

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## **Iridium Complexes**

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/KAP1

Intramolecular  $\pi$  Stacking in Cationic Iridium(III) Complexes with Phenyl-Functionalized Cyclometalated Ligands: Synthesis, Structure, Photophysical Properties, and Theoretical Studies

**Keywords:** Iridium / Luminescence / Photophysics / Density functional calculations / Light-emitting cells



A combined experimental and theoretical study of the cationic iridium complexes  $[Ir(dppy)_2phen]PF_6$  (1) and  $[Ir(tppy)_2phen]-PF_6$  (2) is described. The complexes are green photoemitters. Strong intramolecular

 $\pi$ - $\pi$  stacking leads to enhanced distortions in the geometry of the complexes, which is detrimental to their use in light-emitting electrochemical cells (LECs).

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