Inorganic Chemistry © Cite This: Inorg. Chem. XXXX, XXX, XXX-XXX

Cationic Iridium Complexes with 5-Phenyl-1H-1,2,4-triazole Type Cyclometalating Ligands: Toward Blue-Shifted Emission

Xiaoxiang Wang,[†] Shirun Wang,[†] Fangfang Pan,[†][©] Lei He,^{*,†}[©] and Lian Duan^{*,‡}[©]

[†]College of Chemistry, Key Laboratory of Pesticide and Chemical Biology of Ministry of Education, Hubei International Scientific and Technological Cooperation Base of Pesticide and Green Synthesis, International Joint Research Center for Intelligent Biosensing Technology and Health, Central China Normal University, Wuhan 430079, People's Republic of China

[‡]Key Lab of Organic Optoelectronics and Molecular Engineering of Ministry of Education, Department of Chemistry, Tsinghua University, Beijing 100084, People's Republic of China

S Supporting Information

ABSTRACT: Four cationic iridium complexes with 5-phenyl-1H-1,2,4-triazole (phtz) type cyclometalating ligands (C^N) and different ancillary ligands (N^N), namely, [Ir- $(dphtz)_2(bpy)$]PF₆ (1), [Ir(dphtz)_2(pzpy)]PF₆ (2), [Ir-(Mephtz)₂(pzpy)]PF₆ (3), and [Ir(Mephtz)₂(dma-pzpy)]PF₆ (4), have been designed, synthesized, and fully characterized (dphtz = 1-(2,6-dimethylphenyl)-3-methyl-5-phenyl-1H-1,2,4triazole, Mephtz = 1,3-dimethyl-5-phenyl-1*H*-1,2,4-triazole; bpy = 2,2'-bipyridine, pzpy = 2-(1H-pyrazol-1-yl)pyridine, dma-pzpy = 4-dimethylamino-2-(1*H*-pyrazol-1-yl) pyridine). In solution, complex 1 emits efficient yellow light ($\lambda_{max} = 547$ nm), which is blue-shifted by nearly 40 nm (or by 1187 cm^{-1}) compared with that from the archetypal complex [Ir-



 $(ppy)_2(bpy)$ PF₆ (Hppy = 2-phenylpyridine), owing to the stabilization of the highest occupied molecular orbital by the phtz-type C^N ligand. In the lightly doped rigid films, complex 1 emits green light with a high luminescent efficiency of 0.89. Although complexes 2-4 with electron-rich N^N ligands are weakly emissive or nearly nonemissive in the solution, they emit relatively strong deep-blue light peaked around 435 and 461 nm in the lightly doped films, which is among the bluest reported for cationic iridium complexes. Theoretical calculations reveal that for complex 1, the emission always comes from the chargetransfer (CT) (Ir/C^N \rightarrow N^N) state; for complexes 2 and 3, the ³CT and C^N-centered ³ $\pi - \pi^*$ states lie close in energy and the emission could originate from either or both of them; for complex 4, the emission comes predominantly from the C^Ncentered $3\pi - \pi^*$ state. For blue-emitting complexes 2-4, metal-centered states play an active role in the nonradiative deactivation of the emitting triplet states. Solid-state light-emitting electrochemical cells (LECs) based on complexes 1-3 show yellow-green, blue, and blue-green electroluminescence, respectively, with the yellow-green LEC affording a peak current efficiency of 21.5 cd A⁻¹.

INTRODUCTION

Phosphorescent iridium complexes have aroused significant research interest in the past years, owing to their wide applications in biological imaging or sensing,¹ photocatalysis, and optoelectronic devices,³ to mention but a few. While neutral iridium complexes have been extensively investigated, cationic ones have drawn increasing attention in recent years, owing to their desirable features such as intrinsic ionic nature, good solubility in polar solvent, and rich redox properties. In particular, cationic iridium complexes have been employed as emitting materials in solid-state light-emitting electrochemical cells (LECs),⁴⁻¹² which, as simple, low-cost and efficient thinfilm devices, represent one promising technology toward nextgeneration solid-state lighting.

The archetypal phosphorescent cationic iridium complex, namely, $[Ir(ppy)_2(bpy)]PF_6$ (complex R in Chart 1), with 2phenylpyridine (Hppy) as the cyclometalating ligand (C^N) and 2,2'-bipyridine (bpy) as the ancillary ligand (N^N), emits orange-red light ($\lambda_{max} = 585$ nm in CH₃CN).^{13–15} Because blue light is indispensable for lighting applications, extensive research has been conducted for blue-shifting the emission of complex **R** through widening its energy gap.¹⁶⁻¹⁸ For example, electron-deficient substituents (such as F) have been placed at the phenyl rings of ppy to stabilize the highest occupied molecular orbital (HOMO),¹⁹⁻²² and electron-rich groups have been attached at bpy to destabilize the lowest unoccupied molecular orbital (LUMO).²³ In addition, using N^N ligands with strong ligand field strength stabilizes the HOMO to a large extent,²⁴⁻²⁶ whereas employing electron-rich or nonconjugated N^N ligands destabilizes the LUMO signifi-

Received: May 16, 2019

Chart 1. Archetypal Examples of Cationic Iridium Complexes (R1-R7) with C^N Ligands That Contain Five-Membered Nitrogen-Rich N-Heterocycles^a



[lr(ppy)₂(bpy)]PF₆ (**R**) PL=585 nm, PLQY=0.14 *J. Am. Chem. Soc.* **1987**, 109, 1589

Adv.Funct.Mater. 2009, 19, 3456

[Ir(ptrz)₂(bpy)]PF₆ (**R4**) PL=545 nm, PLQY=0.55 *Inorg. Chem.* **2014**, 53, 7709

Ň



[lr(ppz)₂(bpy)]PF₆ (**R1**) PL=563 nm, PLQY=0.17 *Inorg. Chem.* **2005**, 44, 8723



[lr(dphoxd)₂(bpy)]PF₆ (**R5**) PL=490,522 nm, PLQY=0.31 Dalton Trans. **2015**, 44,15914



[Ir(phtl)₂(bpy)]PF₆ (**R2**) PL=580 nm, PLQY=0.25 *Inorg. Chem.* **2011**, 50, 11514





[lr(*N*-phtl)₂(^tBubpy)]PF₆ (**R3**) PL=520 nm, PLQY=0.45 *Inorg. Chim. Acta* **2012**, 388, 84



[lr(ptrz)₂(taz)]PF₆ (**R7**) PL=525 nm, PLQY<0.1 *Inorg. Chem.* **2014**, 53, 7709

"Bn is short for benzyl group. The archetypal complex (\mathbf{R}) with conventional ppy C^N ligands is also shown.



cantly.^{16,27–30} All these approaches enlarge the energy gap of the complex, leading to blue-shifted emission.¹⁷

It has recently been shown that replacing the pyridine ring in the ppy-type C^N ligand with a five-membered nitrogen-rich heterocycle, such as pyrazole,³¹ triazole,^{32–34} tetrazole,^{35,36} or oxidazole,^{37,38} can largely blue-shift the emission of the complex by stabilizing the HOMO in most cases^{31,34–38} or by destabilizing the LUMO in some cases.^{32,33} Chart 1 summarizes these complexes (complexes **R1–R7**) together with their emission maximums and luminescent efficiencies in degassed CH₃CN solution. This approach for blue-shifting the emission is advantageous over the commonly used fluorinesubstitution at the phenyl ring of ppy, because fluorinesubstitution degrades the electrochemical and thermal stability of the complex.^{39–41} We note that 5-phenyl-1*H*-1,2,4-triazole (phtz), with a five-membered nitrogen-rich triazole ring, fulfills the requirement for such a molecular design. Moreover, phtztype C^N ligands possess high ${}^3\pi-\pi^*$ triplet energy, which is suitable for constructing blue-emitting complexes. ${}^{42-44}$ However, phtz derivatives have so far not been tested as C^N ligands for constructing blue-emitting cationic iridium complexes.

Herein, we report a series of cationic iridium complexes with phtz-type C^N ligands, i.e., $[Ir(dphtz)_2(bpy)]PF_6$ (1), $[Ir(dphtz)_2(pzpy)]PF_6$ (2), $[Ir(Mephtz)_2(pzpy)]PF_6$ (3), and $[Ir(Mephtz)_2(dma-pzpy)]PF_6$ (4; Chart 2). Here 1-(2,6-dimethylphenyl)-3-methyl-5-phenyl-1*H*-1,2,4-triazole (dphtz) and 1,3-dimethyl-5-phenyl-1*H*-1,2,4-triazole (Mephtz) are employed as the phtz-type C^N ligands, while bpy, 2-(1*H*-pyrazol-1-yl)pyridine (pzpy), and 4-dimethylamino-2-(1*H*-pyrazol-1-yl)pyridine (dma-pzpy) are selected as the N^N ligands. Single-crystal structures have been determined to

verify the chemical structures of the four complexes. Photophysical and electrochemical characteristics of the complexes have been systematically investigated with the aid of theoretical calculations. The use of the complexes as emitting materials in LECs has also been evaluated.

EXPERIMENTAL SECTION

General Information. All solvents and reactants were commercially obtained and used as received. NMR spectra, mass spectrometry, and elemental analysis were measured with a BRUKER 400/500 NMR spectrometer, an LTQ-ORBITRAP-ETD mass spectrometer, and an EA3000 elemental analyzer (Eurovector, Italy), respectively. Absorption spectra, photoluminescence (PL) spectra, and the PL transient lifetimes were measured with a Shimadzu UV-2450 spectrophotometer, a HITACHI F-4600 spectrometer, and a transient spectrofluorimeter (Edinburgh Instruments, FLSP920), respectively. The photoluminescent quantum yields (PLQYs) in solution were measured relative to quinine sulfate $(\Phi_p = 0.545 \text{ in } 1 \text{ M H}_2\text{SO}_4)$. The PLQYs in thin films were measured with a Hamamatsu C11347 PLQY measurement system equipped with an integrating sphere. Cyclic voltammetry was conducted with a RST5200 voltammetric analyzer in dichloromethane (for oxidation of complexes 1-4 and reduction of complexes 1-3) or N_iN_j dimethylformamide (for reduction of complex 4) solutions (10^{-3}) M), and the solutions were degassed with argon before measurements. The cyclic voltammetry was performed at a scan rate of 100 mV s⁻¹ by using a glass-carbon plate, a silver wire, and a platinum wire as the working, pseudoreference, and counter electrodes, respectively. Ferrocene and tetrabutylammonium hexafluorophosphate (0.1 M) were employed as the internal standard and the supporting electrolyte, respectively.

Synthesis. pzpy and dma-pzpy were synthesized following reported procedures.^{16,45} The chloro-bridged iridium dimers, [Ir-(dphtz)₂Cl]₂ and [Ir(Mephtz)₂Cl]₂, were prepared by reacting dphtz or Mephtz with IrCl₃·*n*H₂O in refluxed water/2-ethoxylethanol (1:3) under an argon atmosphere according to a reported procedure.⁴⁶

Synthesis of 1-(2,6-Dimethylphenyl)-3-methyl-5-phenyl-1H-1,2,4-triazole (dphtz). Benzoyl chloride (2.67 g, 19 mmol) and ethyl acetimidate hydrochloride (2.35 g, 19 mmol) were dissolved in chloroform (50 mL). To the solution, triethylamine (3.84 g, 38 mmol) was added dropwise under stirring. After being stirred at room temperature for 18 h under an argon atmosphere, the reaction mixture was washed with water and dried over anhydrous sodium sulfate. The solvent was removed under a vacuum, and the residual was dissolved in chloroform (50 mL). To the solution, 2,6-dimethylphenylhydrazine hydrochloride (4.32 g, 25 mmol) and triethylamine (9.60 g, 95 mmol) were added. The mixture was refluxed overnight under an argon atmosphere. The solvent was removed under a vacuum, and the residue was purified by column chromatography on silica gel (200-300 mesh) with ethyl acetate/petroleum ether (1:10) as the eluent, affording a white solid (2.34 g, 8.8 mmol). Yield: 46%. Mp: 96-97 °C. ¹H NMR (CDCl₃, 400 MHz, δ [ppm]): 7.48 (d, J = 7.6 Hz, 2H), 7.39–7.27 (m, 4H), 7.16 (d, J = 7.6 Hz, 2H), 2.55 (s, 3H), 1.98 (s, 6H). ¹³C NMR (CDCl₃, 101 MHz, δ [ppm]): 160.98, 154.45, 136.95, 135.85, 129.99, 129.80, 128.74, 128.69, 127.54, 127.25, 17.62, 14.03. HRMS (ESI, m/z): 264.1504 [M + H]⁺ (calcd. 264.1495). Anal. Found: C, 77.78; H, 6.77; N, 16.08. Anal. Calcd for C17H17N3: C, 77.54; H, 6.51; N, 15.96.

Synthesis of 1,3-Dimethyl-5-phenyl-1H-1,2,4-triazole (Mephtz). The synthesis of Mephtz is similar to that of dphtz, except that methylhydrazine sulfate replaced 2,6-dimethylphenylhydrazine hydrochloride. Yield: 43%. Mp: 72–73 °C. ¹H NMR (CDCl₃, 500 MHz, δ [ppm]): 7.69–7.61 (m, 2H), 7.54–7.46 (m, 3H), 3.93 (s, 3H), 2.43 (s, 3H). ¹³C NMR (CDCl₃, 101 MHz, δ [ppm]): 159.80, 154.95, 129.96, 128.79, 128.55, 127.99, 36.59, 13.81. HRMS (ESI, *m*/z): 174.1036 [M + H]⁺ (calcd. 174.1026). Anal. Found: C, 69.65; H, 6.64; N, 24.31. Anal. Calcd for C₁₀H₁₁N₃: C, 69.34; H, 6.40; N, 24.26.

Synthesis of $[Ir(dphtz)_2(bpy)]PF_6$ (1). $[Ir(dphtz)_2Cl]_2$ (300 mg, 0.20 mmol) and bpy (65 mg, 0.42 mmol) were dissolved in

ClCH₂CH₂CH₂CH₂CH₂OH (10/10 mL). The mixture was refluxed overnight under an argon atmosphere. To the solution, NH_4PF_6 (648 mg, 3.9 mmol) was added. After being stirred at room temperature for 1 h, the reaction mixture was purified by column chromatography on silica gel (200-300 mesh) with acetone/CH2Cl2 (1:20) as the eluent, affording a yellow solid (327 mg, 0.32 mmol). Yield: 80%. Mp > 360 °C (dec.). ¹H NMR (acetone- d^{6} , 400 MHz, δ [ppm]): 8.94 (d, J = 8.0 Hz, 2H), 8.38 (t, J = 7.6 Hz, 2H), 8.27 (d, J = 5.2 Hz, 2H), 7.86–7.76 (m, 2H), 7.54 (t, J = 7.6 Hz, 2H), 7.42 (d, J = 7.6 Hz, 4H), 7.03 (t, J = 7.6 Hz, 2H), 6.83 (t, J = 7.6 Hz, 2H), 6.75 (d, J = 7.2 Hz, 2H), 6.47 (d, J = 7.6 Hz, 2H), 2.13 (s, 6H), 1.93 (s, 6H), 1.71 (s, 6H).¹³C NMR (acetone- d^6 , 101 MHz, δ [ppm]): 165.10, 158.26, 156.96, 151.05, 149.29, 139.80, 136.15, 135.92, 135.16, 133.14, 131.36, 131.28, 131.12, 129.22, 129.13, 128.56, 124.90, 123.81, 122.90, 28.99, 28.80, 28.60, 28.41, 16.68, 16.35, 11.04. HRMS (ESI, m/z): 873.2941 $[M - PF_6]^+$ (calcd. 873.3000). Anal. Found: C, 52.11; H, 4.11; N, 10.94. Anal. Calcd for C444H40F6IrN8P: C, 51.91; H, 3.96; N, 11.01.

Synthesis of $[Ir(dphtz)_2(pzpy)]PF_6$ (2). The synthesis of [Ir-(dphtz)₂(pzpy)]PF₆ followed a procedure similar to that for $[Ir(dphtz)_2(bpy)]PF_6$, except that pzpy replaced bpy, affording an off-white solid. Yield: 72%. Mp > 350 °C (dec.). ¹H NMR (acetone d^{6} , 400 MHz, δ [ppm]): 9.22 (d, J = 2.8 Hz, 1H), 8.58 (d, J = 8.0 Hz, 1H), 8.43 (t, J = 7.2 Hz, 1H), 8.07 (d, J = 5.2 Hz, 1H), 7.66 (t, J = 6.8 Hz, 1H), 7.61-7.51 (m, 3H), 7.47-7.38 (m, 4H), 7.04-6.94 (m, 3H), 6.87-6.71 (m, 4H), 6.46 (t, I = 7.6 Hz, 2H), 2.16-2.10 (m, 6H), 2.00 (s, 3H), 1.94 (s, 3H), 1.83 (s, 3H), 1.79 (s, 3H). ¹³C NMR (acetone-d⁶, 101 MHz, δ [ppm]): 165.07, 164.97, 158.16, 158.15, 150.30, 149.53, 148.00, 144.90, 143.97, 141.86, 136.16, 136.14, 135.90, 135.18, 135.16, 133.38, 133.26, 132.31, 131.52, 131.48, 131.29, 131.10, 130.89, 129.21, 129.13, 125.24, 123.77, 123.44, 122.97, 122.78, 113.63, 111.42, 16.67, 16.41, 16.36, 11.26, 11.04. HRMS (ESI, m/z): 862.2906 [M - PF₆]⁺ (calcd. 862.2952). Anal. Found: C, 50.31; H, 4.14; N, 12.41. Anal. Calcd for C₄₂H₃₉F₆IrN₉P: C, 50.09; H, 3.90; N, 12.52.

Synthesis of $[Ir(Mephtz)_2(pzpy)]PF_6$ (3). The synthesis of [Ir- $(Mephtz)_2(pzpy)]PF_6$ followed a procedure similar to that for $[Ir(dphtz)_2(bpy)]PF_6$, except that $[Ir(dphtz)_2Cl]_2$ and bpy were replaced by [Ir(Mephtz)₂Cl]₂ and pzpy, respectively, yielding an offwhite solid. Yield: 80%. Mp > 350 °C (dec.). ¹H NMR (acetone- d_{61} 500 MHz, δ [ppm]): 9.15 (d, I = 3.0 Hz, 1H), 8.47 (d, I = 8.4 Hz, 1H), 8.33 (td, J = 8.0, 1.5 Hz, 1H), 7.91 (d, J = 5.0 Hz, 1H), 7.82 (d, J = 7.5 Hz, 1H), 7.80 (d, J = 7.5 Hz, 1H), 7.53 (t, J = 6.0 Hz, 1H), 7.37 (d, J = 1.5 Hz, 1H), 7.17-7.04 (m, 2H), 7.03-6.89 (m, 3H), 6.55 (d, J = 7.5 Hz, 1H), 6.52 (d, J = 7.5 Hz, 1H), 4.34 (s, 3H), 4.33 (s, 3H), 1.64 (s, 3H). 1.60 (s, 3H). ¹³C NMR (acetone- d_{61} 101 MHz, δ [ppm]): 164.40, 164.33, 156.08, 150.09, 149.83, 147.33, 144.20, 144.00, 141.51, 133.42, 133.34, 132.08, 132.04, 131.94, 130.40, 130.00, 125.12, 124.99, 124.78, 122.62, 122.46, 113.20, 111.14, 37.47, 10.92, 10.71. HRMS (ESI, m/z): 682.2026 [M - PF₆]⁺ (calcd. 682.2013). Anal. Found: C, 40.85; H, 3.52; N, 15.03. Anal. Calcd for C₂₈H₂₇F₆IrN₉P: C, 40.68; H, 3.29; N, 15.25.

Synthesis of $[Ir(Mephtz)_2(dma-pzpy)]PF_6$ (4). The synthesis of [Ir(Mephtz)₂(dma-pzpy)]PF₆ followed a procedure similar to that of $[Ir(dphtz)_2(bpy)]PF_6$, except that $[Ir(dphtz)_2Cl]_2$ and bpy were replaced by [Ir(Mephtz)₂Cl]₂ and dma-pzpy, respectively, yielding an off-white solid. Yield: 72%. Mp > 350 °C (dec.). ¹H NMR (acetone d_{6} , 500 MHz, δ [ppm]): 9.15 (d, J = 3.0 Hz, 1H), 7.81–7.76 (m, 2H), 7.53 (d, J = 2.5 Hz, 1H), 7.29–7.25 (m, 2H), 7.10–7.00 (m, 2H), 6.99-6.89 (m, 2H), 6.84-6.81 (m, 1H), 6.69 (dd, J = 6.8, 2.6 Hz, 1H), 6.53 (d, J = 7.6 Hz, 2H), 4.34–4.33 (m, 6H), 3.22 (s, 6H), 1.72 (s, 3H), 1.63 (s, 3H). ¹³C NMR (acetone- d_6 , 101 MHz, δ [ppm]): 164.67, 164.40, 156.50, 155.94, 155.91, 150.14, 148.29, 147.71, 145.70, 142.88, 133.71, 133.33, 132.31, 132.06, 130.81, 130.17, 129.82, 124.91, 124.65, 122.17, 122.07, 110.57, 107.69, 93.34, 39.01, 37.42, 37.40, 11.18, 10.63. HRMS (ESI, m/z): 725.2413 [M - PF₆]⁺ (calcd. 725.2435). Anal. Found: C, 41.23; H, 3.84; N, 16.01. Anal. Calcd for C₃₀H₃₂F₆IrN₁₀P: C, 41.42; H, 3.71; N, 16.10.

X-ray Crystallography. The X-ray experiments on single crystals of complexes 1 and 2 were performed with a Bruker Apex Duo CCD diffractometer at 150 K. The X-ray experiments on single crystals of



complexes 3 and 4 were performed with a Rigaku CCD Saturn 724 + diffractometer at 153 K. The diffractometers were equipped with graphite monochromatized Mo K α radiation ($\lambda = 0.71073$ Å). The positions of non-hydrogen atoms were produced by direct phase determination, which were subjected to anisotropic refinement. Hydrogen atoms were theoretically produced, riding on their parent atoms in the refinement. Data analysis was conducted by using the OLEX2 program.⁴⁷

Quantum Chemical Calculations. Calculations on the ground and excited states were conducted with the density functional theory (DFT) at the B3LYP level.^{48,49} "Double- ξ " quality basis sets were used (6-31G** for C, H, N and LANL2DZ for Ir).⁵⁰ The inner core electrons of Ir(III) were replaced by an effective core potential (ECP), and the outer core (5s)²(5p)⁶ electrons and the (5d)⁶ valence electrons of Ir(III) were left.⁵¹ Optimization of the geometries of singlet ground states (S₀) were conducted without any symmetry constraints. Time-dependent DFT (TD-DFT) was used to calculate the first 10 triplets at the optimized S₀ geometries. Optimization of the geometries of selected triplet states was conducted at the spinunrestricted B3LYP level with a spin multiplicity of three. All calculations were done in the presence of CH₃CN solvent. The selfconsistent reaction field (SCRF) theory employing the polarized continuum (PCM) model was used for the solvent effect.⁵² The Gaussian 09 software was used for natural transition orbital (NTO) analysis of triplet transitions.⁵⁴

Fabrication and Characterization of LECs. Indium–tin–oxide (ITO) substrates (15 Ω/\Box) were ultrasonically cleaned in detergent and then in deionized water. Before film depositions, the ITO substrates were subjected to the UV zone for 10 min. The PEDOT:PSS buffer layer was spin-coated onto the ITO substrate and baked at 200 °C on a hot plate for 10 min. The emissive layer was spin coated on top of PEDOT:PSS from the CH₃CN solution in a nitrogen-filled glovebox and then baked at 70 °C on a hot plate for 30 min. The film-coated substrate was transferred into a vacuum chamber, and the Al cathode was thermally evaporated onto the

organic films at 8-10 Å/s. A Keithley 4200 semiconductor characterization system was used to measure the current–time–brightness curves under constant driving voltages. A Photo Research PR705 spectrophotometer was used to measure the electro-luminescent (EL) spectra. All devices were sealed in the glovebox before measurements.

RESULTS AND DISCUSSION

Synthesis and X-ray Crystal Structures. Scheme 1 depicts the synthetic pathway to dphtz and Mephtz and complexes 1–4. dphtz and Mephtz were prepared through a procedure similar to that reported in the literature.⁴² Complexes 1–4 were prepared by cleavages of the chlorobridged iridium dimers, $[Ir(dphtz)_2Cl]_2$ or $[Ir(Mephtz)_2Cl]_2$, with bpy, pzpy, or dma-pzpy N^N ligands, followed by anion-exchange reactions from Cl⁻ to PF₆⁻. The complexes were purified by column chromatography, and their chemical structures were verified by ¹H and ¹³C NMR spectroscopies (Figures S1–S6), high-resolution mass spectrometry, and elemental analysis (see Experimental Section).

Single crystals of complexes 1-4 suitable for X-ray experiments were grown by slow diffusion of hexane into CH_2Cl_2 solution of complexes 1-4. Figure 1 displays the single crystal structures. X-ray crystallographic data and selected crystallographic parameters are presented in Tables S1 and S2 in the Supporting Information. Analogous to reported cationic iridium complexes, $^{15,16,31,33-35}$ complexes 1-4 display distorted octahedral geometries, and the two C^N ligands adopt a *C*,*C*-*cis*,*N*,*N*-*trans* configuration. The Ir–C and Ir–N bond lengths and the ligand bite angles fall within the normal ranges reported for similar cationic iridium complexes. $^{15,16,31,33-35}$ For complexes 1 and 2, the pendant 2,6-



Figure 1. Crystal structures of (a) complex 1, (b) complex 2, (c) complex 3, and (d) complex 4. Thermal ellipsoids were plotted with 40% probability. Solvent molecules, PF_6^- counteranions, and hydrogen atoms were omitted for clarity.

dimethylphenyl rings in dphtz are almost perpendicular to the 1,2,4-triazole planes, as shown by the large dihedral angles (\sim 80°) between them. The coordination bond lengths of complexes 1, R, and R1–R5 were summarized and compared in Table S3. From Table S3, it can be observed that the Ir–C and Ir–N bonds formed between the iridium(III) ion and dphtz C^N ligand in complex 1 exhibit similar lengths to those formed between the iridium(III) ions and ppy, phenyl-pyrazole, phenyl-1,2,3-triazole, phenyl-tetrazole, or phenyl-oxidazole C^N ligands in complexes R and R1–R5.

Photophysical Properties. Figure 2 displays the absorption and PL spectra of complexes 1–4 in CH₃CN solution. Table 1 summarizes detailed photophysical characteristics. Complexes 1–4 all show strong absorption bands in the ultraviolet part (<330 nm) of the spectrum, with large extinction coefficients (>10⁴ M⁻¹ cm⁻¹), which are attributed to spin-allowed ligand-centered ${}^{1}\pi-\pi^{*}$ transitions. Beyond 330 nm, complexes 1–4 show relatively weak absorption bands that extend to the visible part of the spectrum, which can be assigned to ligand-to-ligand charge-transfer (${}^{1}\text{MLCT}$), ${}^{3}\text{MLCT}$, and ligand-centered ${}^{3}\pi-\pi^{*}$ transitions. ${}^{13-15,31}$ The spin-forbidden triplet transitions are partially allowed owing to the strong spin–orbit coupling of the iridium ion.



Figure 2. Absorption and PL spectra of complexes 1-4 in CH₃CN solution. Excitation wavelength for PL is 380 nm for complex 1 and 360 nm for complexes 2 and 3.

In CH₃CN solution, complex 1 emits yellow light centered at 547 nm (Figure 2), which is blue-shifted by nearly 40 nm (or by 1187 cm⁻¹) compared with that of complex R ($\lambda_{max} =$ 585 nm).^{13–15} This blue-shifted emission indicates that, compared to ppy, the phtz-type C^N ligand is capable of blue-shifting the emission of the cationic iridium complex. The blue shift in emission in the dphtz analogue (ca. 40 nm) is

Table 1. Pho	tophysical	and 1	Electrocl	nemical	Data o	of	Comp	lexes	1-4 ii	1 Solution
--------------	------------	-------	-----------	---------	--------	----	------	-------	--------	------------

		PL at room temperature b		PL at 77 K ^c		electrochemical data ^d		
	absorption λ [nm] ($\epsilon \times 10^{-4}$ [M ⁻¹ cm ⁻¹]) ^a	λ [nm]	Φ_{p}	τ [µs]	λ [nm]	τ [μs]	$E_{\rm ox}$ [V]	$E_{\rm red}$ [V]
1	247 (4.05)	547	0.20	1.1	508	8.9	1.05 ^r	-1.88^{r}
	363 (0.82)				543			
	436 (0.09)							
2	256 (3.72)	438	<10 ⁻³	0.015	436	6.0	1.03 ^r	-2.39^{ir}
	365 (0.59)	463			466			
	390 (0.20)				500			
3	247 (3.75)	488	<10 ⁻³	0.006	428	1.0 (13%)	$1.18^{\rm ir}$	-2.45^{ir}
	355 (0.50)				458	8.3 (87%)		
	380 (0.26)				482			
4	257 (5.72)				429	1.0 (12%)	0.88 ^r	-2.60^{ir}
	355 (0.46)				459	5.2 (88%)		
	380 (0.19)				482			

^{*a*}In CH₃CN solution (10⁻⁵ M). ε represents the molar extinction coefficient. ^{*b*}In degassed CH₃CN (10⁻⁵ M) solution. ^{*c*}In CH₃CN glass. ^{*d*}Potentials were reported versus Fc⁺/Fc (Fc is ferrocene); r and ir represent reversible and irreversible processes, respectively; for irreversible processes, peak potentials were reported.

F

comparable to those (20-60 nm) by other C^N ligands with five-membered nitrogen-rich heterocycles such as phenylpyrazole, phenyl-1,2,3-triazole, phenyl-tetrazole, or phenyl-oxidazole ligands (see complexes R1–R5 in Chart 1). $^{31-35}$ It is noted that complex 1 affords yellow emission rather than the blue emission observed in neutral homoleptic iridium complexes with phtz-type C^N ligands.^{42,44} This is because, from the homoleptic iridium complex to complex 1, the energy gap is largely reduced due to the use of the bpy ancillary ligand. In CH₃CN solution, complex 2 emits weak blue light peaked at 463 and 438 nm and complex 3 emits weak blue-green light centered at 488 nm. The emission of complexes 2 and 3 is significantly blue-shifted by 60-80 nm compared to that of complex 1, which should be ascribed to the large LUMO destabilization caused by the electron-rich pzpy N^N ligand.¹⁶ Similar large blue shifts in emission have been observed in complexes with phenyl-1,2,3-triazole or phenyl-tetrazole C^N ligands when electron-rich N^N ligands were used (see complexes R6 and R7 in Chart 1).^{35,55,56} As shown in Figure 2, complexes 1 and 3 afford structureless PL spectra, which indicates that their emission in the solution arises dominantly from ³CT states;^{13,14,31,46} complex **2** affords a structured PL spectrum, which indicates that its emission in the solution comes mainly from a ligand-centered ${}^{3}\pi - \pi^{*}$ state.^{13,31} In degassed CH₃CN solution, complex 1 provides a PLQY of 0.20 and an excited-state lifetime of 1.1 μ s, whereas complexes 2 and 3 afford rather low PLQYs (<0.001) and short excitedstate lifetimes (15 and 6 ns, respectively; Table 1). In degassed CH₃CN solution, complex 4 is nearly nonemissive. The rather weak or even quenched emission of complexes 2-4 indicates that in the fluid solution, there exist effective nonradiative deactivation pathways for the emitting triplet states of these complexes.

The PL spectra of complexes 1-4 at 77 K were measured and presented in Figure S7 and the emission peaks and excitedstate lifetimes were summarized in Table 1. At 77 K, complex 1 emits green light peaked at 508 and 543 nm. In contrast to the weakly emissive or nonemissive feature in the solution at room temperature, at 77 K, complexes 2-4 afford bright blue emission peaked around 430 and 460 nm. At 77 K, complexes 1-3 all show significantly enhanced excited-state lifetimes (>5 μ s) compared to those measured at room temperature in the solution (Table 1), largely because of the significantly suppressed nonradiative deactivations in the frozen matrix at low temperatures. $^{\rm 57}$

Figure 3 depicts the PL spectra of complexes 1–4 in the 2 wt % doped poly(methyl methacrylate) (PMMA) films. The



Figure 3. PL spectra of complexes **1**–**4** in 2 wt % doped PMMA films. The excitation wavelength is 360 nm.

PL spectra in the neat films are displayed in Figure S8 in the Supporting Information. Detailed photophysical characteristics of the films were listed in Table 2. In the doped PMMA film, complex 1 emits green light centered at 512 nm, while in the neat film, it emits yellow-green light centered at 544 nm, which is red-shifted by 32 nm compared to that in the doped film (Figure S8a). In both doped and neat films, complex 1 affords featureless emission spectra, which indicates that the emission

Table 2. Photophysical Data of Complexes 1–4 in Thin Films

	PL of 2 wt	% doped	PMMA films	PL of neat films					
	λ [nm]	PLQY	τ [µs]	λ [nm]	PLQY	τ [µs]			
1	512	0.89	1.34	544	0.63	0.88			
2	436, 463	0.22	0.7 (16%)	468	0.03	0.11 (65%)			
			3.2 (84%)			0.57 (35%)			
3	436, 461	0.21	0.9 (33%)	485	0.02	0.10 (40%)			
			3.2 (67%)			0.54 (60%)			
4	434, 461	0.20	0.9 (27%)	444, 468	< 0.01	0.07 (91%)			
			3.4 (73%)			0.47 (9%)			

always arises from the ³CT state. In the doped PMMA films, complexes 2-4 emit blue light peaked around 435 and 460 nm, which is among the bluest reported for cationic iridium complexes; $^{16,17,24,30,37,45,58-61}$ complexes 2–4 all show structured PL spectra (Figure 3), which indicates that their emission in the doped films mainly arises from ligand-centered ${}^{3}\pi-\pi^{*}$ states. In the neat films, complexes 2 and 4 exhibit moderately red-shifted (by 10-20 nm) emission (Figure S8b and d), and complex 3 exhibits largely red-shifted (by 30-40 nm) emission (Figure S8c), as compared to their emission in the doped PMMA films. In the neat films, complex 2 shows a slightly structured but relatively broad PL spectrum (Figure S8b), which indicates that the emission could arise from both ligand-centered ${}^{3}\pi - \pi^{*}$ and ${}^{3}CT$ states; complex 3 shows a featureless PL spectrum (Figure S8c), which indicates the origination of emission from a ³CT state. Complex 4 shows a structured PL spectrum (Figure S8d), which indicates that the emission comes mainly from a ligand-centered ${}^{3}\pi - \pi^{*}$ state. Apparently, for complexes 2 and 3, when passing from the doped film to the neat film, the emitting triplet state is varied from the ligand-centered ${}^{3}\pi - \pi^{*}$ to the ${}^{3}CT$ states, which indicates that these two states are close-lying in energy and the emission could occur from either or both of them.^{37,38,62,63} For complex 3, it is further noted that the emitting triplet state is varied from the ³CT state to the ligand-centered ³ π - π * state when passing from the solution to the doped PMMA film, as evidenced by the change of the emission spectrum from a featureless one to a structured one (Figures 2 and 3), which further indicates the closeness of these two states in energy.

As shown in Table 2, in the 2 wt % doped PMMA film, complex 1 provides a rather high PLQY of 0.89, and complexes 2-4 provide PLQYs of 0.22, 0.21, and 0.20, respectively, which are significantly increased compared to those measured in the solution, because of the reduced nonradiative deactivation in the rigid films. In the neat films, complexes 1-4 all display reduced PLQYs and excited-state lifetimes as compared to those measured in the doped PMMA films (Table 2), because of the phosphorescence concentration quenching in the neat films. It is noteworthy that complex 1 in the neat film still shows a high PLQY of 0.63, which indicates its great potential for use in LECs.

Theoretical Calculations. To understand the photophysical characteristics of complexes 1-4, theoretical calculations were performed with the DFT approach (see Experimental Section). Figure 4 displays the optimized S_0 geometries along with the energy levels and surface distributions of HOMO and LUMO orbitals. Illustrations on more molecular orbitals are presented in Table S4. The optimized geometrical parameters, as shown in Table S5 in the Supporting Information, agree with those found in the single crystal structures (Table S2). For all the complexes, the occupied orbitals, including HOMO, HOMO-1, HOMO-2, and HOMO-3, distribute predominantly over the C^N ligands and the iridium ions, except that the HOMO-1 of complex 4 distributes mainly on the iridium ion and the dmapzpy N^N ligand. The LUMO orbitals are localized predominantly over the N^N ligands, whereas the LUMO+1, LUMO+2, and LUMO+3 orbitals are localized over either the C^N ligands or the N^N ligands (Table S4).

As shown in Figure 4, compared to the archetypal complex **R**, complex **1** shows a stabilized (by 0.12 eV) HOMO level and a similar LUMO level. This reveals that, compared to ppy, the phtz-type C^N ligand stabilizes the HOMO of the complex,



Figure 4. Optimized S_0 geometries and energy levels, surface distributions of HOMO (lower images) and LUMO (upper images) orbitals computed for complexes 1–4. Energy levels of complex R are also shown.

which leads to the blue-shifted emission, as experimentally observed. From complex 1 to complex 2, the LUMO level is destabilized owing to the use of the electron-rich pzpy N^N ligand in complex 2.¹⁶ From complex 2 to complex 3, the energy levels remain almost unchanged, because they use similar C^N ligands and the same pzpy N^N ligand. From complex 3 to complex 4, the LUMO level is further destabilized owing to the use of highly electron-rich dmapzpy N^N ligand in complex 4.⁴⁵ These LUMO destabilizations lead to further blue-shifted emission for complexes 2-4, as experimentally observed.

TDDFT calculations were conducted at the optimized S_0 geometries to explore the triplet-state characteristics. By analyzing the dominant transitions and the surface distributions of the molecular orbitals in the transitions, the character of the triplet states was obtained. Table 3 summarizes the characteristics of triplet states. For complex 1, the T₁ state exhibits mixed ³MLCT (Ir \rightarrow N^N)/³LLCT (C^N \rightarrow N^N) character, that is, pure CT character. The T₂ state shows mixed ³MLCT (Ir \rightarrow N^N)/³ π - π * (N^N-centered) character. The T₃ state exhibits mixed ³MLCT (Ir \rightarrow C^N)/³ π - π * (C^N-centered) character as well as some ³MLCT (Ir \rightarrow N^N)/³LLCT (C^N \rightarrow N^N) character. As shown by photophysical characterizations, the emission of complex 1 always comes from the ³CT state. Therefore, for complex 1, the T₁ state always represents the lowest emitting triplet state.

For complexes 2 and 3, the situation becomes more complicated. As shown in Table 3, for complex 2, the T_1 and T₃ states show mixed ³MLCT (Ir \rightarrow C^N)/³ π - π * (C^Ncentered) character as well as some ${}^{3}MLCT$ (Ir \rightarrow $N^N)/{^3}LLCT$ (C^N \rightarrow N^N) character, whereas the T₂ state exhibits predominantly mixed ³MLCT (Ir \rightarrow $N^N)/{^3}LLCT$ (C^N \rightarrow N^N) character, that is, pure CT character. For complex 3, the T_1 state shows mixed ³MLCT (Ir \rightarrow N^N)/³LLCT (C^N \rightarrow N^N) character, that is, pure CT character, while the T_2 and T_3 states show mixed ³MLCT (Ir \rightarrow C^N)/³ π - π^* (C^N-centered) character. As shown in Table 3, for both complexes 2 and 3, the T_1 , T_2 , and T_3 states are close-lying in energy (within 0.1 eV), and thereby, the emission could come from any of them. $^{37,38,62-64}$ Photophysical characterizations have revealed that the PL of complexes 2 and 3 can arise from either ³CT or ligandcentered ${}^{3}\pi - \pi^{*}$ or both of them depending on the local

Table 3.	Characteristics	of Sele	ected Tripl	et States	Calculated	from	the	TDDFT	Approach
----------	-----------------	---------	-------------	-----------	------------	------	-----	-------	----------

	state	$E (eV)^a$	dominant transitions ^b	dominant character
1	T_1	2.62	$H \rightarrow L (96\%)$	$d\pi(Ir)$ - $\pi(C^N) \rightarrow \pi^*(N^N)$
	T_2	2.98	$H - 2 \rightarrow L (40\%), H - 10 \rightarrow L (36\%)$	$d\pi(Ir)$ - $\pi(N^N) \rightarrow \pi^*(N^N)$
	T ₃	3.04	$H \rightarrow L + 1$ (34%), $H \rightarrow L + 2$ (26%)	$d\pi(Ir)$ - $\pi(C^N) \rightarrow \pi^*(C^N)$
			$H - 1 \rightarrow L + 3 (11\%)$	$d\pi(Ir)$ - $\pi(C^N) \rightarrow \pi^*(N^N)$
2	T_1	3.04	$H \rightarrow L + 1$ (23%), $H \rightarrow L + 2$ (23%)	$d\pi(Ir)$ - $\pi(C^N) \rightarrow \pi^*(C^N)$
			$\mathrm{H} \rightarrow \mathrm{L} \ (22\%), \ \mathrm{H} - 1 \rightarrow \mathrm{L} + 3 \ (10\%)$	$d\pi(Ir)$ - $\pi(C^N) \rightarrow \pi^*(N^N)$
	T_2	3.05	$H \rightarrow L (74\%)$	$d\pi(Ir)$ - $\pi(C^N) \rightarrow \pi^*(N^N)$
	T ₃	3.09	$H \rightarrow L + 3$ (38%), $H - 1 \rightarrow L + 2$ (16%)	$d\pi(Ir)$ - $\pi(C^N) \rightarrow \pi^*(C^N)$
				$d\pi(Ir)$ - $\pi(C^N) \rightarrow \pi^*(N^N)$
3	T_1	3.03	$H \rightarrow L (90\%)$	$d\pi(Ir)$ - $\pi(C^N) \rightarrow \pi^*(N^N)$
	T_2	3.06	$H \rightarrow L + 2$ (39%), $H - 1 \rightarrow L + 3$ (15%)	$d\pi(Ir)$ - $\pi(C^N) \rightarrow \pi^*(C^N)$
			$H \rightarrow L + 1 (14\%)$	
	T ₃	3.10	H \rightarrow L + 3 (39%), H – 1 \rightarrow L + 2 (21%)	$d\pi(Ir)$ - $\pi(C^N) \rightarrow \pi^*(C^N)$
4	T_1	3.04	$H \rightarrow L + 1 (60\%)$	$d\pi(Ir)$ - $\pi(C^N) \rightarrow \pi^*(C^N)$
	T_2	3.10	$H \rightarrow L + 2$ (44%), $H - 2 \rightarrow L + 1$ (14%)	$d\pi(Ir)$ - $\pi(C^N) \rightarrow \pi^*(C^N)$
			$H - 3 \rightarrow L + 1 (13\%)$	
	T ₃	3.22	$H - 1 \rightarrow L (58\%), H \rightarrow L (20\%)$	$d\pi(Ir)$ - $\pi(N^N) \rightarrow \pi^*(N^N)$
				$d\pi(Ir)$ - $\pi(C^N) \rightarrow \pi^*(N^N)$
	T_4	3.35	$\mathrm{H} \rightarrow \mathrm{L}$ (64%), $\mathrm{H} - 1 \rightarrow \mathrm{L}$ (16%)	$d\pi(Ir)$ - $\pi(C^N) \rightarrow \pi^*(N^N)$
_	1.			

"Vertical excitation energies. "Dominant excitations with contributions (in parentheses) larger than 10%; H and L represent HOMO and LUMO, respectively.

environment of the complex. Therefore, for complexes 2 and 3, the emission could arise from either T_1 or T_2 or T_3 states.

For complex 4, the situation becomes simple again. As shown in Table 3, the T_1 and T_2 states of complex 4 are nearly degenerate in energy and both show mixed ³MLCT (Ir \rightarrow C^N)/³ π - π^* (C^N-centered) character. The T_4 state, as the pure ³CT state (Ir/C^N \rightarrow N^N), lies above T_1 by 0.31 eV. For complex 4, the ³CT state is remarkably destabilized away from the C^N-centered ³ π - π^* states, due to the use of the highly electron-rich dma-pzpy N^N ligand, and is thus unlikely to contribute to the emission.⁴⁵ The photophysical characterizations reveal that the emission of complex 4 always shows dominant ligand-centered ³ π - π^* character. Therefore, for complex 4, the emission always comes from the T₁ or T₂ states.

To further confirm the character assigned to the triplet states shown in Table 3, natural transition orbital (NTO) analysis, which is a simpler and better method for analyzing character of electronic transitions (especially for those with multiconfigurational characteristics),⁶⁵ was performed on the triplet transitions of complexes 1-4 (Figure S9 and analysis therein). The character of the triplet states obtained by the NTO analysis is consistent with that obtained by the direct TDDFT method shown in Table 3.

The low-lying triplet states of complexes 1–4 were fully optimized at the UB3LYP level to further investigate their characteristics (see Experimental Section). The geometrical parameters, computed triplet energies, and Cartesian coordinates of optimized geometries are summarized in Tables S5, S6, and S7, respectively, in the Supporting Information. For complexes 1, 3, and 4, optimization starting from the S₀ geometry led to the T₁ state, while for complex 2, it leads to the T₂ state. For the T₁ state of complex 2 and the T₂ state of complex 3 that possess C^N-centered ${}^{3}\pi - \pi^{*}$ character (Table 3), optimizations were started from the geometry with an adjusted structure of one C^N ligand (e.g., reduction of the C–C inter-ring bond). Figure 5 displays the geometries, distributions of spin density, and energy level diagrams of the optimized triplet states. As shown in Figure 5a, for complex 1,

the spin density of the T_1 state is localized over the iridium ions, cyclometalated phenyl rings of dphtz C^N ligands, and the bpy N^N ligand, which accords with the dominant ³MLCT (Ir \rightarrow N^N)/³LLCT (C^N \rightarrow N^N) character for the T_1 state (Table 3).

As shown in Figure 5b, for complex 2, the spin density of the T_1 state is localized over the iridium ion and one dphtz C^N ligand, which is consistent with the dominant ³MLCT (Ir \rightarrow C^N)/³ π - π * (C^N-centered) character for the T_1 state; the spin density of the T_2 state is localized over the iridium ions, the cyclometalated phenyl rings of dphtz C^N ligands, and the pzpy N^N ligand, in accordance with the dominant ³MLCT (Ir \rightarrow N^N)/³LLCT (C^N \rightarrow N^N) character for the T_2 state (Table 3).

As shown in Figure 5c, for complex 3, the spin-density distributions of the T_1 and T_2 states resemble those observed for complex 2, except that the character for the T_1 and T_2 states is reversed, that is, the T_1 state is the ³MLCT (Ir \rightarrow N^N)/³LLCT (C^N \rightarrow N^N) state, whereas the T_2 state is the ³MLCT (Ir \rightarrow C^N)/³ π - π * (C^N-centered) state. It is noted that for complexes 2 and 3, the fully relaxed T_1 and T_2 states are still close-lying in energy, within 0.07 eV for complex 2, and 0.05 eV for complex 3. For complex 3, the fully relaxed T_2 state lies even below the T_1 state (Figure 5c).

As shown in Figure 5d, for complex 4, the spin density of the T_1 state is localized over one Mephtz C^N ligand and the iridium ion, which accords with the dominant ³MLCT (Ir \rightarrow C^N)/³ π - π * (C^N-centered) character for the T_1 state (Table 3).

For iridium complexes, metal-centered states (${}^{3}MC$) (d–d transitions) induce large nonradiative deactivation of the emitting triplet states, especially for blue-emitting ones.^{26,35,43,57,66} The ${}^{3}MC$ states of complexes 1–4 were thereby optimized by starting from the geometries with elongated Ir–N bonds. Two types of ${}^{3}MC$ states have been obtained. The elongation of Ir–N_{CAN} bonds led to the ${}^{3}MC_{1}$ state, whereas the elongation of Ir–N_{NAN} bonds, combined with the rotation of the pyridine ring along the inter-ring bond,



Figure 5. Schematic energy diagrams and unpaired-electron spin-density contours $(0.002 \text{ e bohr}^{-3})$ computed for the optimized triplet states of (a) complex 1, (b) complex 2, (c) complex 3, and (d) complex 4.

led to the ${}^{3}MC_{2}$ state. As shown in Figure 5a-d, the spin densities of the ³MC states are localized mainly over the iridium ions, which agrees with the metal-centered character of ${}^{3}MC$ state. On the ${}^{3}MC_{1}$ states, complexes 1–4 still display distorted octahedral geometries, but the two Ir– $N_{C \land N}$ bonds (ca. 2.5 Å) are remarkably lengthened compared with those (ca. 2.1 Å) on the S₀ states (Table S5). On the ${}^{3}MC_{2}$ states, complex 1 also exhibits a distorted octahedral geometry, but the two Ir-N_{bpy} bonds (ca. 2.5 Å) are remarkably elongated, and the bpy ligand is twisted with a large dihedral angle of 19° between the two pyridine rings (Table S5). For complexes 2-4 on the ${}^{3}MC_{2}$ states, the pyridine rings of the ancillary ligands are rotated around the inter-ring bonds by $38-49^{\circ}$ and stay away from the central iridium ions (Ir-N_{pyridine} \approx 3.5 Å), which indicates the full decoordination of the pyridine rings. As a result, complexes 2-4 on the ${}^{3}MC_{2}$ states display distorted trigonal bipyramid molecular geometries, which are similar to those found on the ³MC states of other complexes with asymmetric ancillary ligands.^{26,35,66}

As shown in Figure 5a, for yellow-emitting complex 1, the ${}^{3}MC_{1}$ and ${}^{3}MC_{2}$ states lie much higher (by 0.33 and 0.47 eV, respectively) in energy than the T₁ state, which are thus unlikely to cause a large nonradiative deactivation for the T₁ state. As shown in Figure 5b–d, for blue-emitting complexes 2–4, both the ${}^{3}MC_{1}$ and ${}^{3}MC_{2}$ states lie below the lowest

emitting triplet states; therefore, easy population to the ${}^{3}MC_{1}$ and ³MC₂ states is expected. On the other hand, the ³MC₂ states of complexes 2-4 lie close in energy (ca. 0.5 eV) to the S_0 states at their fully relaxed geometries (Figure 5b-d), which indicates that they should play a role in the deactivation of the emission process.^{26,66} In general, to fully evaluate the possibility of nonradiative deactivations caused by ³MC states, the transition state between the emitting and ³MC states and the minimum energy crossing point between the ${}^{3}MC$ and S_{0} states should be comprehensively considered.⁶⁷ Nevertheless, for complexes 2-4, the rather weak emission in the solution strongly indicates that the low-lying ${}^{3}MC$ states play an active role in the nonradiative deactivation. 43,57,67 It is noted that other blue or blue-green emitting cationic iridium complexes (complexes R6 and R7 in Chart 1) with phenyl-1,2,3-triazole or phenyl-tetrazole C^N ligands also show low luminescent efficiencies in the solution, which has been attributed to the severe nonradiative deactivations caused by the ³MC states. 35,38,55,56

Electrochemical Properties. Cyclic voltammetry in solution was performed to investigate the electrochemical properties of complexes 1–4. Figure 6 displays the cyclic voltammograms, and the redox potentials are listed in Table 1. As shown in Figure 6, complex 1 shows reversible oxidation and reduction processes, with the oxidation and reduction



Figure 6. Cyclic voltammograms of complexes 1-4 in solution. The small peaks around -1.5 V arise from some unknown impurities which also appear in the blank test. For complexes 1-3, the solvent is CH₂Cl₂. For complex 4, the solvent is CH₂Cl₂ for oxidation and DMF for reduction. The scan rate is 100 mV s⁻¹.

potentials at 1.05 and -1.88 V, respectively. Compared to complex R with an oxidation potential of 0.87 V,⁶⁸ complex 1 shows an anodically shifted (by 0.18 V) oxidation potential, which indicates a stabilized HOMO for complex 1. This HOMO stabilization agrees with the theoretical calculations (vide supra). The redox potentials of complexes 1, R, and R1-R5 are summarized and compared in Table S3. From Table S3, it can be observed that, as compared to ppy in complex R, phtz and 2-phenyl-2H-1,2,3-triazole type C^N ligands in complexes 1 and R3 can stabilize the HOMO of the complex, whereas the 4-phenyl-1H-1,2,3-triazole type C^N ligand in complex R2 destabilizes the LUMO of the complex without largely altering the HOMO level. It is thus experimentally shown that the positions of nitrogen atoms in the triazole rings of C^N ligands play a key role in the energy levels of the complexes. Nevertheless, replacing the pyridine ring in ppy with a fivemembered nitrogen-rich N-heterocycle always leads to an enlarged energy gap and blue-shifted emission for the complex (Table S3). It is noteworthy that most cationic iridium complexes with phenyl-1,2,3-triazole, phenyl-tetrazole, or phenyl-oxidazole C^N ligands exhibit irreversible oxidation processes.^{33,34,37,38} The reversible oxidation and reduction processes of complex 1 indicate that it is a suitable emitting material for LECs.

As shown in Figure 6, complex 2 shows a reversible oxidation process and an irreversible reduction process. The oxidation potential of complex 2 (1.03 V) is almost identical to that of complex 1. However, the reduction potential (-2.39 V)of complex 2 is significantly cathodically shifted (by ca. 0.5 V) compared to that (-1.88 V) of complex 1, which indicates a significantly destabilized LUMO for complex 2. As shown in Figure 6, for complex 3, its oxidation and reduction processes are both irreversible. In particular, the broad irreversible oxidation wave of complex 3 indicates some irreversible electrochemical reactions occur during the oxidation process, which makes it difficult to compare the oxidation potential of complex 3 with those of other complexes. Similar to complex 2, complex 3 with a pzpy N^N ligand shows a significantly cathodically shifted (by ca. 0.5 V) reduction potential compared to complex 1. As shown in Figure 6, complex 4 shows a similar oxidation potential to complex 3 but a further cathodically shifted (by 0.15 V) reduction potential, which indicates a further stabilized LUMO level for complex 4. These LUMO destabilizations agree with the theoretical calculations (*vide supra*).

LECs. Complexes 1–4 were employed as emitting materials for LECs (see Experimental Section). The device structure is ITO/PEDOT:PSS (40 nm)/complex:BMIMPF₆ (1:0.8) (100 nm)/Al. The ionic liquid BMIMPF₆ (1-butyl-3-methylimidazolium hexafluorophosphate) was added into the emitting layer to shorten the device response time.⁶⁹ Figure 7 displays the EL



Figure 7. EL spectra of LECs using complexes 1-3.

spectra. The LECs based on complexes 1, 2, and 3 show yellow-green, blue, and blue-green EL, centered at 542, 469, and 496 nm, with Commission Internationale de L'Eclairage (CIE) coordinates of (0.38, 0.58), (0.18, 0.30), and (0.28, 0.41), respectively. All the EL spectra are similar to the PL spectra of the light emitting layers (Figure S10). It is noted that complex 2 affords a broad EL spectrum, which could be attributed to (i) origination of emission from both ³CT and ligand-centered ${}^{3}\pi - \pi^{*}$ states, as observed in the PL of neat film and (ii) polarization of molecular orbitals of the ionic complex under an electrical field.¹⁶ The LEC based on complex 4 was nearly nonemissive under electrical operation, largely because of the extremely low PLQY of complex 4 in the concentrated film (Table 2) and the high electron-injection barrier (ca. 2.0 eV) at the cathode side, resulting from the high LUMO level of complex 4.

Figure 8 shows the current-density and brightness versus time curves of LECs. Table 4 summarizes the device data. Under a constant driving voltage of 3.0 V, the LEC using complex 1 provides a peak brightness and a peak current efficiency of 80.0 cd m⁻² and 21.5 cd A⁻¹, respectively. The LECs using complexes 2 and 3 require higher operating voltages to turn on, which should be ascribed to the increase of electron-injection barriers at the cathode side, caused by the enhanced LUMO levels of complexes 2 and 3 as compared to complex 1.^{18,70} Under a constant driving voltage of 4.0 V, the LEC using complex 2 affords a peak brightness and a peak current efficiency of 10.1 cd m⁻² and 0.72 cd A⁻¹, respectively, and the values for the LEC using complex 3 are 3.3 cd m^{-2} and 0.65 cd A⁻¹, respectively. The relatively low device performances for the LECs using complexes 2 and 3 should be related to (i) difficult electron injection at the cathode side and thereby unbalanced carrier recombination in the light emitting layer^{18,71} and (ii) low luminescent efficiencies of complexes 2 and 3 in concentrated films. Nevertheless, the high efficiency of the yellow-green LEC using complex 1 and largely blue-shifted electroluminescence from the LECs using complexes 2 and 3 indicate that phtz-type C^N ligands are promising for the

Table 4. Device Data o	f LECs Usin	ng Comple	exes 1–3
------------------------	-------------	-----------	----------

	bias (V)	$t_{\rm on} \ ({\rm min})^a$	$t_{\max} (\min)^{b}$	$B_{\rm max}~({\rm cd}~{\rm m}^{-2})^c$	$\eta_{\max} \; (\mathrm{cd} \; \mathrm{A}^{-1})^d$	EQE (%) ^e	$t_{1/2} (\min)^f$	EL λ (nm)	CIE (x,y)
1	3.0	0.65	9.2	80.0	21.5	7.5	51	542	(0.38, 0.58)
2	4.0	0.76	2.1	10.1	0.72	0.40	2.1	469	(0.18, 0.30)
3	4.0	0.86	2.0	3.3	0.65	0.29	3.2	496	(0.28, 0.41)
-			a 1.			_		1	

^{*a*}The time needed to reach 1 cd m⁻². ^{*b*}The time needed to reach the maximum brightness. ^{*c*}The maximum brightness. ^{*d*}The maximum current efficiency. ^{*f*}The half-lifetime of the device.



Figure 8. Current-density (J) and brightness (B) versus time curves for (a) the LEC using complex 1 at 3.0 V and (b) the LECs using complex 2 or 3 at 4.0 V.

development of complexes with blue-shifted emission for LEC applications. Further optimization of the emission color, efficiency, and the energy levels of the complexes through ligand control would lead to LECs with further enhanced performances.

CONCLUSION

The phtz-type C^N ligands are for the first time examined in cationic iridium complexes for blue-shifted emission. In solution, $[Ir(dphtz)_2(bpy)]PF_6$ (1) afforded yellow emission, which was blue-shifted by nearly 40 nm (or by 1187 cm⁻¹) compared with that of $[Ir(ppy)_2(bpy)]PF_6$, due to the HOMO stabilization caused by the phtz-type C^N ligand. Although $[Ir(dphtz)_2(pzpy)]PF_6$ (2), $[Ir(Mephtz)_2(pzpy)]PF_6$ (3), and $[Ir(Mephtz)_2(dma-pzpy)]PF_6$ (4) showed only weak or even no emission in solution, they afforded relatively strong deepblue emission in the doped films. Theoretical calculations showed that in complexes 2 and 3, the CT states ($Ir/C^N \rightarrow$ pzpy) and C^N-centered ${}^{3}\pi - \pi^{*}$ states are close-lying in energy and the emission could come from either or both of them; in complex 4, the blue emission came predominantly from the C^N-centered ${}^{3}\pi - \pi^{*}$ state. LECs based on complexes 1-3 afforded yellow-green, blue, and blue-green

electroluminescence, respectively, with the yellow-green LEC affording a high peak current efficiency of 21.5 cd A^{-1} . The work reveals that fluorine-free cationic iridium complexes with blue-shifted emission can be successfully constructed with phtz-type C^N ligands, which are promising emitting materials for advanced optoelectronic applications. To improve the luminescent efficiencies of the complexes, the nonradiative deactivations should be suppressed by destabilizing the dark ³MC states, and the radiative deactivation should be strengthened by means such as increasing the ³MLCT contribution in the emitting triplet states.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.9b01433.

X-ray crystallographic data (Table S1), selected crystallographic parameters (Table S2), comparisons between different complexes (Table S3), surface distributions of other molecular orbitals (Table S4), geometrical parameters of optimized geometries (Table S5), computed triplet energies (Table S6), Cartesian coordinates of optimized geometries (Table S7), ¹H and ¹³C NMR spectra (Figures S1–S6), PL spectra at 77 K and in the neat films (Figures S7–S8), NTO analysis of triplet transitions (Figure S9), and PL spectra of the emissive layers of LECs (Figure S10) (PDF)

Accession Codes

CCDC 1886078–1886081 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: helei@mail.ccnu.edu.cn.

*E-mail: duanl@mail.tsinghua.edu.cn.

ORCID 🔍

Fangfang Pan: 0000-0002-3091-6795

Lei He: 0000-0003-2106-740X

Lian Duan: 0000-0001-7095-2902

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We are thankful for the financial support from the National Natural Science Foundation of China (Grant No. 51773074), the Self-Determined Research Funds of CCNU from the Colleges' Basic Research and Operation of MOE, and the Program of Introducing Talents of Discipline to Universities of China (111 program, B17019).

REFERENCES

(1) Lo, K. K.-W. Luminescent Rhenium(I) and Iridium(Iii) Polypyridine Complexes as Biological Probes, Imaging Reagents, and Photocytotoxic Agents. *Acc. Chem. Res.* **2015**, *48*, 2985–2995.

(2) Zhou, Q.-Q.; Zou, Y.-Q.; Lu, L.-Q.; Xiao, W.-J. Visible-Light-Induced Organic Photochemical Reactions Via Energy Transfer Pathways. *Angew. Chem., Int. Ed.* **2019**, *58*, 1586.

(3) Choy, W. C. H.; Chan, W. K.; Yuan, Y. P. Recent Advances in Transition Metal Complexes and Light-Management Engineering in Organic Optoelectronic Devices. *Adv. Mater.* **2014**, *26*, 5368–5399.

(4) Slinker, J. D.; Gorodetsky, A. A.; Lowry, M. S.; Wang, J. J.; Parker, S.; Rohl, R.; Bernhard, S.; Malliaras, G. G. Efficient Yellow Electroluminescence from a Single Layer of a Cyclometalated Iridium Complex. J. Am. Chem. Soc. 2004, 126, 2763–2767.

(5) Costa, R. D.; Orti, E.; Bolink, H. J.; Monti, F.; Accorsi, G.; Armaroli, N. Luminescent Ionic Transition-Metal Complexes for Light-Emitting Electrochemical Cells. *Angew. Chem., Int. Ed.* **2012**, *51*, 8178–8211.

(6) Meier, S. B.; Tordera, D.; Pertegas, A.; Roldan-Carmona, C.; Orti, E.; Bolink, H. J. Light-Emitting Electrochemical Cells: Recent Progress and Future Prospects. *Mater. Today* **2014**, *17*, 217–223.

(7) Henwood, A. F.; Zysman-Colman, E. Luminescent Iridium Complexes Used in Light-Emitting Electrochemical Cells (Leecs). *Top. Curr. Chem.* **2016**, 374, 36.

(8) Housecroft, C. E.; Constable, E. C. Over the Lec Rainbow: Colour and Stability Tuning of Cyclometallated Iridium(Iii) Complexes in Light-Emitting Electrochemical Cells. *Coord. Chem. Rev.* 2017, 350, 155–177.

(9) Martinez-Alonso, M.; Cerda, J.; Momblona, C.; Pertegas, A.; Junquera-Hernandez, J. M.; Heras, A.; Rodriguez, A. M.; Espino, G.; Bolink, H.; Orti, E. Highly Stable and Efficient Light-Emitting Electrochemical Cells Based on Cationic Iridium Complexes Bearing Arylazole Ancillary Ligands. *Inorg. Chem.* **2017**, *56*, 10298–10310.

(10) Ertl, C. D.; Momblona, C.; Pertegas, A.; Junquera-Hernandez, J. M.; La-Placa, M.-G.; Prescimone, A.; Orti, E.; Housecroft, C. E.; Constable, E. C.; Bolink, H. J. Highly Stable Red-Light-Emitting Electrochemical Cells. J. Am. Chem. Soc. **2017**, *139*, 3237–3248.

(11) Costa, R. D. Light-Emitting Electrochemical Cells; Springer: Cham, Switzerland, 2017.

(12) Ma, D.; Tsuboi, T.; Qiu, Y.; Duan, L. Recent Progress in Ionic Iridium(Iii) Complexes for Organic Electronic Devices. *Adv. Mater.* **2017**, *29*, 1603253.

(13) Colombo, M. G.; Hauser, A.; Gudel, H. U. Evidence for Strong Mixing between the Lc and Mlct Excited-States in Bis(2-Phenyl-pyridinato- C^2 ,N') (2,2'-Bipyridine)Iridium(Iii). *Inorg. Chem.* **1993**, 32, 3088–3092.

(14) King, K. A.; Watts, R. J. Dual Emission from an Ortho-Metalated Ir(Iii) Complex. J. Am. Chem. Soc. **1987**, 109, 1589–1590. (15) Costa, R. D.; Orti, E.; Bolink, H. J.; Graber, S.; Schaffner, S.; Neuburger, M.; Housecroft, C. E.; Constable, E. C. Archetype Cationic Iridium Complexes and Their Use in Solid-State Light-Emitting Electrochemical Cells. Adv. Funct. Mater. **2009**, 19, 3456– 3463.

(16) He, L.; Duan, L.; Qiao, J.; Wang, R. J.; Wei, P.; Wang, L. D.; Qiu, Y. Blue-Emitting Cationic Iridium Complexes with 2-(1h-Pyrazol-1-Yl)Pyridine as the Ancillary Ligand for Efficient Light-Emitting Electrochemical Cells. *Adv. Funct. Mater.* **2008**, *18*, 2123– 2131.

(17) He, L. In *Light-Emitting Electrochemical Cells*; Costa, R. D., Eds.; Springer: Cham, Switzerland, 2017; Chapter 8, pp 203–235.

(18) He, L.; Wang, X.; Duan, L. Enhancing the Overall Performances of Blue Light-Emitting Electrochemical Cells by Using an Electron-Injecting/Transporting Ionic Additive. ACS Appl. Mater. Interfaces 2018, 10, 11801–11809.

(19) Lowry, M. S.; Goldsmith, J. I.; Slinker, J. D.; Rohl, R.; Pascal, R. A.; Malliaras, G. G.; Bernhard, S. Single-Layer Electroluminescent

Devices and Photoinduced Hydrogen Production from an Ionic Iridium(Iii) Complex. Chem. Mater. 2005, 17, 5712–5719.

(20) Shavaleev, N. M.; Scopelliti, R.; Graetzel, M.; Nazeeruddin, M. K.; Pertegas, A.; Roldan-Carmona, C.; Tordera, D.; Bolink, H. J. Pulsed-Current Versus Constant-Voltage Light-Emitting Electrochemical Cells with Trifluoromethyl-Substituted Cationic Iridium(Iii) Complexes. J. Mater. Chem. C 2013, 1, 2241–2248.

(21) Tordera, D.; Buenzli, A. M.; Pertegas, A.; Junquera-Hernandez, J. M.; Constable, E. C.; Zampese, J. A.; Housecroft, C. E.; Orti, E.; Bolink, H. J. Efficient Green-Light-Emitting Electrochemical Cells Based on Ionic Iridium Complexes with Sulfone-Containing Cyclometalating Ligands. *Chem. - Eur. J.* **2013**, *19*, 8597–8609.

(22) Shavaleev, N. M.; Xie, G.; Varghese, S.; Cordes, D. B.; Slawin, A. M. Z.; Momblona, C.; Orti, E.; Bolink, H. J.; Samuel, I. D. W.; Zysman-Colman, E. Green Phosphorescence and Electroluminescence of Sulfur Pentafluoride-Functionalized Cationic Iridium(Iii) Complexes. *Inorg. Chem.* **2015**, *54*, 5907–5914.

(23) Nazeeruddin, M. K.; Wegh, R. T.; Zhou, Z.; Klein, C.; Wang, Q.; De Angelis, F.; Fantacci, S.; Gratzel, M. Efficient Green-Blue-Light-Emitting Cationic Iridium Complex for Light-Emitting Electrochemical Cells. *Inorg. Chem.* **2006**, *45*, 9245–9250.

(24) Li, J.; Djurovich, P. I.; Alleyne, B. D.; Yousufuddin, M.; Ho, N. N.; Thomas, J. C.; Peters, J. C.; Bau, R.; Thompson, M. E. Synthetic Control of Excited-State Properties in Cyclometalated Ir(Iii) Complexes Using Ancillary Ligands. *Inorg. Chem.* **2005**, *44*, 1713–1727.

(25) Shavaleev, N. M.; Monti, F.; Costa, R. D.; Scopelliti, R.; Bolink, H. J.; Orti, E.; Accorsi, G.; Armaroli, N.; Baranoff, E.; Gratzel, M.; Nazeeruddin, M. K. Bright Blue Phosphorescence from Cationic Bis-Cyclometalated Iridium(Iii) Isocyanide Complexes. *Inorg. Chem.* **2012**, *51*, 2263–2271.

(26) Monti, F.; Kessler, F.; Delgado, M.; Frey, J.; Bazzanini, F.; Accorsi, G.; Armaroli, N.; Bolink, H. J.; Orti, E.; Scopelliti, R.; Nazeeruddin, M. K.; Baranoff, E. Charged Bis-Cyclometalated Iridium(Iii) Complexes with Carbene-Based Ancillary Ligands. *Inorg. Chem.* **2013**, *52*, 10292–10305.

(27) Mydlak, M.; Bizzarri, C.; Hartmann, D.; Sarfert, W.; Schmid, G.; De Cola, L. Positively Charged Iridium(Iii) Triazole Derivatives as Blue Emitters for Light-Emitting Electrochemical Cells. *Adv. Funct. Mater.* **2010**, *20*, 1812–1820.

(28) Yang, C. H.; Beltran, J.; Lemaur, V.; Cornil, J.; Hartmann, D.; Sarfert, W.; Frohlich, R.; Bizzarri, C.; De Cola, L. Iridium Metal Complexes Containing N-Heterocyclic Carbene Ligands for Blue-Light-Emitting Electrochemical Cells. *Inorg. Chem.* **2010**, *49*, 9891– 9901.

(29) Zhang, F.; Ma, D.; Duan, L.; Qiao, J.; Dong, G.; Wang, L.; Qiu, Y. Synthesis, Characterization, and Photophysical and Electroluminescent Properties of Blue-Emitting Cationic Iridium(Iii) Complexes Bearing Nonconjugated Ligands. *Inorg. Chem.* **2014**, *53*, 6596–6606.

(30) Hasan, K.; Pal, A. K.; Auvray, T.; Zysman-Colman, E.; Hanan, G. S. Blue-Green Emissive Cationic Iridium(Iii) Complexes Using Partially Saturated Strongly-Donating Guanidyl-Pyridine/-Pyrazine Ancillary Ligands. *Chem. Commun.* **2015**, *51*, 14060–14063.

(31) Tamayo, A. B.; Garon, S.; Sajoto, T.; Djurovich, P. I.; Tsyba, I. M.; Bau, R.; Thompson, M. E. Cationic Bis-Cyclometalated Iridium(Iii) Diimine Complexes and Their Use in Efficient Blue, Green, and Red Electroluminescent Devices. *Inorg. Chem.* **2005**, *44*, 8723–8732.

(32) Beyer, B.; Ulbricht, C.; Escudero, D.; Friebe, C.; Winter, A.; Gonzalez, L.; Schubert, U. S. Phenyl-1h-[1,2,3]Triazoles as New Cyclometallating Ligands for Iridium(Iii) Complexes. *Organometallics* **2009**, *28*, 5478–5488.

(33) Ladouceur, S.; Fortin, D.; Zysman-Colman, E. Enhanced Luminescent Iridium(Iii) Complexes Bearing Aryltriazole Cyclometallated Ligands. *Inorg. Chem.* **2011**, *50*, 11514–11526.

(34) Shavaleev, N. M.; Scopelliti, R.; Graetzel, M.; Nazeeruddin, M. K. Phosphorescent Cationic Iridium(Iii) Complexes with Cyclo-

metalating 1h-Indazole and 2h-[1,2,3]-Triazole Ligands. *Inorg. Chim.* Acta 2012, 388, 84–87.

(35) Monti, F.; Baschieri, A.; Gualandi, I.; Serrano-Perez, J. J.; Junquera-Hernandez, J. M.; Tonelli, D.; Mazzanti, A.; Muzzioli, S.; Stagni, S.; Roldan-Carmona, C.; Pertegas, A.; Bolink, H. J.; Orti, E.; Sambri, L.; Armaroli, N. Iridium(Iii) Complexes with Phenyl-Tetrazoles as Cyclometalating Ligands. *Inorg. Chem.* **2014**, *53*, 7709–7721.

(36) Pla, P.; Junquera-Hernandez, J. M.; Bolink, H. J.; Orti, E. Emission Energy of Azole-Based Ionic Iridium(Iii) Complexes: A Theoretical Study. *Dalton Trans* **2015**, *44*, 8497–8505.

(37) Wang, Z.; He, L.; Duan, L.; Yan, J.; Tang, R.; Pan, C.; Song, X. Blue-Green Emitting Cationic Iridium Complexes with 1,3,4-Oxadiazole Cyclometallating Ligands: Synthesis, Photophysical and Electrochemical Properties, Theoretical Investigation and Electroluminescent Devices. *Dalton Trans* **2015**, *44*, 15914–15923.

(38) Lan, Y.; Li, G.; Wang, Z.; He, Y.; Liu, Y.; He, L. Fluorine-Free Blue-Emitting Cationic Iridium Complexes with Oxadiazole-Type Cyclometalating Ligands and Their Use in Light-Emitting Electrochemical Cells. *Dyes Pigm.* **2017**, *144*, 158–167.

(39) Sivasubramaniam, V.; Brodkorb, F.; Hanning, S.; Loebl, H. P.; van Elsbergen, V.; Boerner, H.; Scherf, U.; Kreyenschmidt, M. Fluorine Cleavage of the Light Blue Heteroleptic Triplet Emitter Firpic. J. Fluorine Chem. **2009**, 130, 640–649.

(40) Zheng, Y. H.; Batsanov, A. S.; Edkins, R. M.; Beeby, A.; Bryce, M. R. Thermally Induced Defluorination During a Mer to Fac Transformation of a Blue-Green Phosphorescent Cyclometalated Iridium(Iii) Complex. *Inorg. Chem.* **2012**, *51*, 290–297.

(41) Tordera, D.; Serrano-Perez, J. J.; Pertegas, A.; Orti, E.; Bolink, H. J.; Baranoff, E.; Nazeeruddin, M. K.; Frey, J. Correlating the Lifetime and Fluorine Content of Iridium(Iii) Emitters in Green Light-Emitting Electrochemical Cells. *Chem. Mater.* **2013**, *25*, 3391–3397.

(42) Lo, S.-C.; Shipley, C. P.; Bera, R. N.; Harding, R. E.; Cowley, A. R.; Burn, P. L.; Samuel, I. D. W. Blue Phosphorescence from Iridium(Iii) Complexes at Room Temperature. *Chem. Mater.* **2006**, *18*, 5119–5129.

(43) Zhou, X.; Burn, P. L.; Powell, B. J. Bond Fission and Non-Radiative Decay in Iridium(Iii) Complexes. *Inorg. Chem.* **2016**, *55*, 5266–5273.

(44) Li, X.; Zhang, J.; Zhao, Z.; Wang, L.; Yang, H.; Chang, Q.; Jiang, N.; Liu, Z.; Bian, Z.; Liu, W.; Lu, Z.; Huang, C. Deep Blue Phosphorescent Organic Light-Emitting Diodes with Ciey Value of 0.11 and External Quantum Efficiency up to 22.5%. *Adv. Mater.* **2018**, *30*, 1705005.

(45) He, L.; Lan, Y.; Ma, D.; Song, X.; Duan, L. Fluorine-Free, Highly Efficient, Blue-Green and Sky-Blue-Emitting Cationic Iridium Complexes and Their Use for Efficient Organic Light-Emitting Diodes. J. Mater. Chem. C 2018, 6, 1509–1520.

(46) Lamansky, S.; Djurovich, P.; Murphy, D.; Abdel-Razzaq, F.; Lee, H.-E.; Adachi, C.; Burrows, P. E.; Forrest, S. R.; Thompson, M. E. Highly Phosphorescent Bis-Cyclometalated Iridium Complexes: Synthesis, Photophysical Characterization, and Use in Organic Light Emitting Diodes. J. Am. Chem. Soc. **2001**, *123*, 4304–4312.

(47) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. Olex2: A Complete Structure Solution, Refinement and Analysis Program. J. Appl. Crystallogr. 2009, 42, 339–341.
(48) Becke, A. D. Density-Functional Thermochemistry. Iii. The Role of Exact Exchange. J. Chem. Phys. 1993, 98, 5648.

(49) Lee, C. T.; Yang, W. T.; Parr, R. G. Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron-Density. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1988**, 37, 785–789.

(50) Hay, P. J. Theoretical Studies of the Ground and Excited Electronic States in Cyclometalated Phenylpyridine Ir(Iii) Complexes Using Density Functional Theory. *J. Phys. Chem. A* **2002**, *106*, 1634–1641.

(51) Hay, P. J.; Wadt, W. R. Ab Initio Effective Core Potentials for Molecular Calculations. Potentials for K to Au Including the Outermost Core Orbitals. *J. Chem. Phys.* **1985**, *82*, 299–310.

(52) Tomasi, J.; Mennucci, B.; Cammi, R. Quantum Mechanical Continuum Solvation Models. *Chem. Rev.* 2005, 105, 2999–3093.

(53) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobavashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09; Gaussian, Inc.: Wallingford, CT, 2009.

(54) Lu, T.; Chen, F. Multiwfn: A Multifunctional Wavefunction Analyzer. J. Comput. Chem. 2012, 33, 580-592.

(55) Fernandez-Hernandez, J. M.; Ladouceur, S.; Shen, Y.; Iordache, A.; Wang, X.; Donato, L.; Gallagher-Duval, S.; de Anda Villa, M.; Slinker, J. D.; De Cola, L.; Zysman-Colman, E. Blue Light Emitting Electrochemical Cells Incorporating Triazole-Based Luminophores. J. Mater. Chem. C 2013, 1, 7440–7452.

(56) Donato, L.; Abel, P.; Zysman-Colman, E. Cationic Iridium(Iii) Complexes Bearing a Bis(Triazole) Ancillary Ligand. *Dalton Trans* **2013**, 42, 8402–8412.

(57) Sajoto, T.; Djurovich, P. I.; Tamayo, A.; Yousufuddin, M.; Bau, R.; Thompson, M. E.; Holmes, R. J.; Forrest, S. R. Blue and near-Uv Phosphorescence from Iridium Complexes with Cyclometalated Pyrazolyl or N-Heterocyclic Carbene Ligands. *Inorg. Chem.* **2005**, 44, 7992–8003.

(58) Darmawan, N.; Yang, C. H.; Mauro, M.; Raynal, M.; Heun, S.; Pan, J. Y.; Buchholz, H.; Braunstein, P.; De Cola, L. Efficient near-Uv Emitters Based on Cationic Bis-Pincer Iridium(Iii) Carbene Complexes. *Inorg. Chem.* **2013**, *52*, 10756–10765.

(59) Evariste, S.; Sandroni, M.; Rees, T. W.; Roldan-Carmona, C.; Gil-Escrig, L.; Bolink, H. J.; Baranoff, E.; Zysman-Colman, E. Fluorine-Free Blue-Green Emitters for Light-Emitting Electrochemical Cells. J. Mater. Chem. C 2014, 2, 5793–5804.

(60) Coe, B. J.; Helliwell, M.; Sanchez, S.; Peers, M. K.; Scrutton, N. S. Water-Soluble Ir(Iii) Complexes of Deprotonated N-Methylbipyridinium Ligands: Fluorine-Free Blue Emitters. *Dalton Trans* **2015**, *44*, 15420–15423.

(61) Henwood, A. F.; Pal, A. K.; Cordes, D. B.; Slawin, A. M. Z.; Rees, T. W.; Momblona, C.; Babaei, A.; Pertegas, A.; Orti, E.; Bolink, H. J.; Baranoff, E.; Zysman-Colman, E. Blue-Emitting Cationic Iridium(Iii) Complexes Featuring Pyridylpyrimidine Ligands and Their Use in Sky-Blue Electroluminescent Devices. *J. Mater. Chem. C* **2017**, *5*, 9638–9650.

(62) Bolink, H. J.; Cappelli, L.; Cheylan, S.; Coronado, E.; Costa, R. D.; Lardies, N.; Nazeeruddin, M. K.; Orti, E. Origin of the Large Spectral Shift in Electroluminescence in a Blue Light Emitting Cationic Iridium(Iii) Complex. J. Mater. Chem. 2007, 17, 5032-5041.
(63) He, L.; Wang, Z.; Duan, L.; Yang, C. P.; Tang, R. R.; Song, X. Z.; Pan, C. Y. Toward Fluorine-Free Blue-Emitting Cationic Iridium Complexes: To Generate Emission from the Cyclometalating Ligands with Enhanced Triplet Energy. Dalton Trans 2016, 45, 5604-5613.
(64) Zanoni, K. P. S.; Kariyazaki, B. K.; Ito, A.; Brennaman, M. K.;

(64) Zanoni, K. P. S.; Kariyazaki, B. K.; Ito, A.; Brennaman, M. K.; Meyer, T. J.; Murakami Iha, N. Y. Blue-Green Iridium(Iii) Emitter and Comprehensive Photophysical Elucidation of Heteroleptic Cyclometalated Iridium(Iii) Complexes. *Inorg. Chem.* **2014**, *53*, 4089–4099.

(65) Martin, R. L. Natural Transition Orbitals. J. Chem. Phys. 2003, 118, 4775–4777.

(66) Matteucci, E.; Monti, F.; Mazzoni, R.; Baschieri, A.; Bizzarri, C.; Sambri, L. Click-Derived Triazolylidenes as Chelating Ligands: Achievement of a Neutral and Luminescent Iridium(Iii)-Triazolide Complex. *Inorg. Chem.* **2018**, *57*, 11673–11686.

(67) Chen, M.; Wang, S.; Song, X.; He, L. Elucidating the Non-Radiative Deactivation Pathways in a Cationic Iridium Complex with 2,4-Di(1-H-Pyrazol-1-Yl)Pyridine as the Ancillary Ligand. *J. Phys. Chem. C* **2018**, *122*, 28256–28264.

(68) Costa, R. D.; Orti, E.; Tordera, D.; Pertegas, A.; Bolink, H. J.; Graber, S.; Housecroft, C. E.; Sachno, L.; Neuburger, M.; Constable, E. C. Stable and Efficient Solid-State Light-Emitting Electrochemical Cells Based on a Series of Hydrophobic Iridium Complexes. *Adv. Energy Mater.* **2011**, *1*, 282–290.

(69) Parker, S. T.; Slinker, J. D.; Lowry, M. S.; Cox, M. P.; Bernhard, S.; Malliaras, G. G. Improved Turn-on Times of Iridium Electroluminescent Devices by Use of Ionic Liquids. *Chem. Mater.* **2005**, *17*, 3187–3190.

(70) He, L.; Wang, Z.; Yang, C.; Duan, L.; Tang, R.; Song, X.; Pan, C. Phosphorescent Cationic Iridium Complexes with Phenyl-Imidazole Type Cyclometalating Ligands: A Combined Experimental and Theoretical Study on Photophysical, Electrochemical and Electroluminescent Properties. *Dyes Pigm.* **2016**, *131*, 76–83.

(71) Su, H.-C.; Hsu, J.-H. Improving the Carrier Balance of Light-Emitting Electrochemical Cells Based on Ionic Transition Metal Complexes. *Dalton Trans* **2015**, *44*, 8330–8345.