

Highly Efficient Blue-Green and White Light-Emitting Electrochemical Cells Based on a Cationic Iridium Complex with a Bulky Side Group

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Blue-green-emitting cationic iridium complex with high luminescent efficiencies in both solutions and solid-states are essential for high-performance white light-emitting electrochemical cells (LECs). We report here an efficient blue-green-emitting cationic iridium complex [Ir(dfppz)₂(tp-pyim)]PF₆, using 1-(2,4-difluorophenyl)-1*H*-pyrazole (dfppz) as the cyclometalated ligand and 2-(1-(4-tritylphenyl)-1*H*imidazol-2-yl)pyridine (tp-pyim) as the ancillary ligand. $[Ir(dfppz)_2(tp-pyim)]PF_6$ emits efficient bluegreen light with a luminescent quantum yield of 0.54 in CH₃CN solution. Because of the sterically bulky group 4-tritylphenyl that is attached to the ancillary ligand, the intermolecular interaction and excitedstate self-quenching of $[Ir(dfppz)_2(tp-pyim)]PF_6$ in solid states is significantly suppressed. Theoretical calculations reveal that the emission from [Ir(dfppz)₂(tp-pyim)]PF₆ has both metal-to-ligand chargetransfer and ligand-centered ${}^{3}\pi-\pi^{*}$ character. LECs based on [Ir(dfppz)₂(tp-pyim)]PF₆ show highly efficient blue-green electroluminescence with peak current efficiency, external quantum efficiency, and power efficiency of 18.3 cd A^{-1} , 7.6%, and 18.0 lm W^{-1} , respectively. White LECs based on [Ir(dfppz)₂-(tp-pyim)]PF₆ give warm-white light, with Commission Internationale de L'Eclairage coordinates of (0.37, 0.41), a color-rendering index up to 80, and a peak power efficiency of 11.2 Im W^{-1} .

Introduction

In recent years, light-emitting electrochemical cells (LECs) based on ionic transition metal complexes (iTMCs) have spurred much interest because of their great potential in solid-state lighting applications.¹⁻³ In addition to the notable features of conventional polymer-based LECs (single layer, air-stable cathodes, solution process, etc.),⁴ iTMC-based LECs have high electroluminescent (EL) efficiency because of the phosphorescent nature of iTMCs. For iTMC-based LECs, high brightness and efficiency can be achieved at relatively low operating voltages as a result of efficient carrier injection and balanced carrier recombination in LECs.⁴⁻⁷

Among all iTMCs, ionic iridium complexes are most widely used because of their high luminescent efficiency

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- (1) Slinker, J. D.; Bernards, D.; Houston, P. L.; Abruña, H. D.; Bernhard, S.; Malliaras, G. G. *Chem. Commun.* **2003**, 2392. (2) Slinker, J. D.; Rivnay, J.; Moskowitz, J. S.; Parker, J. B.; Bernhard,
- S.; Abruña, H. D.; Malliaras, G. G. J. Mater. Chem. 2007, 17, 2976. (3) Ulbricht, C.; Beyer, B.; Friebe, C.; Winter, A.; Schubert, U. S. Adv.
- Mater. 2009, 21, 4418. (4) Pei, Q. B.; Yu, G.; Zhang, C.; Yang, Y.; Heeger, A. J. Science. 1995,
- (5) Slinker, J. D.; Defranco, J. A.; Jaqutth, M. J.; Silveir, W. R.;
 (5) Slinker, J. D.; Defranco, J. A.; Jaqutth, M. G.; Abruña
- Zhong, Y. W.; Moran-Mirabal, J. M.; Craighead, H. G.; Abruña, H. D.; Marohn, J. A.; Malliaras, G. G. *Nat. Mater.* **2007**, *6*, 894. (6) Pei, Q. B.; Heeger, A. J. *Nat. Mater.* **2008**, *7*, 167.
- (7) Matyba, P; Maturova, K; Kemerink, M; Robinson, N. D.; Edman,
- L. Nat. Mater. 2009, 8, 672.
- Slinker, J. D.; Gorodetsky, A. A.; Lowry, M. S.; Wang, J.; Parker., S.; Rohl, R.; Bernhard, S.; Malliaras, G. G. J. Am. Chem. Soc. 2004, 126, 2763.

and tunable light emission color.^{2,3,8-22} Using carefully designed cationic iridium complexes, highly efficient green,^{10,12,14,18,21} yellow,^{8,15,21,22} orange,^{13,14,20,21} and red^{10,21} LECs have been achieved, with the external quantum efficiency (EQE) and power efficiency for green LECs approaching 15% and 40 lm W⁻¹, respectively.¹⁸ However, the EOE and power efficiency of blue-green LECs, with

- (9) Lowry, M. S.; Goldsmith, J. I.; Slinker, J. D.; Rohl, R.; Pascal,
- R. A.; Malliaras, G. G.; Bernhard, S. *Chem. Mater.* **2005**, *17*, 5712. Tamayo, A. B.; Garon, S.; Sajoto, T.; Djurovich, P. I.; Tsyba, I. M.; Bau, R.; Thompson, M. E. *Inorg. Chem.* **2005**, *44*, 8723. (10)
- (11) Nazeeruddin, M. K.; Wegh, R. T.; Zhou, Z.; Klein, C.; Wang, Q.; De Angelis, F.; Fantacci, S.; Grätzel, M. Inorg. Chem. 2006, 45, 9245.
- (12) Bolink, H. J.; Cappelli, L.; Coronado, E.; Parham., A.; Stössel., P. Chem. Mater. 2006, 18, 2778.
- (13) Su, H.; Wu., C.; Fang., F.; Wong, K. Appl. Phys. Lett. 2006, 89, 261118.
- (14) Su, H.; Fang, F.; Hwu, T.; Hsieh, H.; Chen, H.; Lee, G.; Peng, S.; Wong, K.; Wu, C. *Adv. Funct. Mater.* 2007, *17*, 1019.
 (15) Bolink, H. J.; Cappelli, L.; Cheylan, S.; Coronado, E.; Costa, R. D.; Lardiés, N.; Nazeeruddin, M. K.; Ortí, E. *J. Mater. Chem.* 2007, 17, 5032.
- (16) Su, H.; Chen, H.; Fang, F.; Liu, C.; Wu, C.; Wong, K.; Liu, Y.; Peng, S. J. Am. Chem. Soc. **2008**, 130, 3414. (17) He, L.; Duan, L.; Qiao, J.; Wang, R.; Wei, P.; Wang, L.; Qiu, Y.
- Adv. Funct. Mater. 2008, 18, 2123.
- (18) Bolink, H. J.; Coronado, E.; Costa, R. D.; Lardiés, N.; Ortí, E. Inorg. Chem. 2008, 47, 9149.
- (19) Colman, E. Z.; Slinker, J. D.; Parker, J. B.; Malliaras, G. G.; Bernhard, S. *Chem. Mater.* 2008, *20*, 388.
 (20) Rothe, C.; Chiang, C.; Jankus, V.; Abdullah, K.; Zeng, X.; Jitchati, R.; Batsanov, A. S.; Bryce, M. R.; Monkman, A. P. *Adv. Funct. Mathematical Conference on Conference o* Mater. 2009, 19, 2038.
- (21) He, L.; Qiao, J.; Duan, L.; Dong, G. F.; Zhang, D. Q.; Wang, L. D.; Qiu, Y. Adv. Funct. Mater. 2009, 19, 2950.
- (22) Costa, R. D.; Ortí, E.; Bolink, H. J.; Graber, S.; Schaffner, S.; Neuburger, M.; Housecroft, C. E.; Constable, E. C. Adv. Funct. Mater. 2009, 19, 3456.

Scheme 1. Synthesis of the Ligands and [Ir(dfppz)₂(tp-pyim)]PF₆



records of 4.6% and 11 lm W⁻¹, respectively, still lag behind those of other colors.¹⁰ To achieve high-performance white LECs, efficient blue-green-emitting ionic iridium complexes and corresponding blue-green LECs are highly desired.^{16,21} During the operation of iTMC-based LECs, severe excited-state self-quenching always happens because the active layers of LECs comprise neat complexes that are closely packed.^{15,17} To resolve the excited-state-quenching problem and improve the EL efficiency of LECs, we should introduce enhanced steric hindrance or bulky side groups into the complexes.^{14,20} This technique has been proven very effective to obtain highly efficient green and orange LECs^{14,20} but has never been attempted for blue-green LECs.

In this paper, we report highly efficient blue-green and white LECs based on a cationic iridium complex with a bulky side group, namely [Ir(dfppz)₂(tp-pyim)]PF₆ (Scheme 1). 1-(2,4-Difluorophenyl)-1*H*-pyrazole (dfppz), instead of 2-(2,4-difluorophenyl)pyridine (dfppy), was used as the cyclometalated ligand because dfppz can blue-shift the emission of the complex via stabilizing the HOMO (highest occupied molecular orbitals) of the complex.^{10,16} 2-(1-(4-Tritylphenyl)-1*H*-imidazol-2-yl)pyridine (tp-pyim) was used as the ancillary ligand because this pyim-type ligand (pyim is pyridinylimidazole) is more effective than the commonly used bpy-type ligand (bpy is 2,2'-bipyridine) in terms of blue-shifting the emission of the complex.²¹ More importantly, the pyim-type ligand affords an active N atom in the imidazole ring to which functional groups

can be conveniently anchored. The sterically bulky group 4-tritylphenyl (TP) is thus anchored to the imidazole ring and shields the luminescent iridium core in an umbrella shape, suppressing the excited-state self-quenching in solid states significantly and rendering the complex an excellent film-forming property. LECs based on [Ir(dfppz)2-(tp-pyim)]PF₆ showed highly efficient blue-green electroluminescence with Commission Internationale de L'Eclairage (CIE) coordinates of (0.22, 0.41). At 3.2 V, the peak current efficiency, EQE and power efficiency of the bluegreen LEC reached 18.3 cd A^{-1} , 7.6%, and 18.0 lm W^{-1} , respectively. By doping a small amount of red-emitting ionic complex into the blue-green LEC, white LECs were fabricated, with CIE coordinates of (0.37, 0.41), a colorrendering index (CRI) up to 80 and a peak power efficiency of 11.2 Im W^{-1} . The efficiencies of the blue-green and white LECs are the highest among blue-green^{9-11,17,21} and white^{16,21} iTMC-based LECs reported so far.

Experimental Details

General Experiments. All reactants and solvents, unless otherwise stated, were purchased from commercial sources and used as received. Absorption and photoluminescent (PL) spectra were recorded with a UV-vis spectrophotometer (Agilent 8453) and a fluorospectrophotometer (Jobin Yvon, FluoroMax-3), respectively. The PL decay lifetimes were measured on a transient spectrofluorimeter (Edinburgh Instruments, FLSP920) with time-correlated single-photon counting technique. The photolumine-scent quantum yields (PLQYs) (excited at 350 nm) in CH_3CN

solutions were measured with quinine sulfate ($\Phi_p = 0.545$ in 1 M H_2SO_4) as the standard.²³ The solutions were degassed by three freeze-pump-thaw circles before measurements. The PLQYs in thin films were measured with an integrating sphere in a fluorospectrophotometer (Jobin Yvon, FluoroMax-3) according to a reported procedure.²⁴ The surface morphology of thin films was characterized with Atomic Force Microscopy (AFM, SPA-400). Cyclic voltammetry was performed on a Princeton Applied Research potentiostat/galvanostat model 283 voltammetric analyzer in CH₃CN solution $(1 \times 10^{-3} \text{ M})$ at a scan rate of 100 mV/s, with a platinum plate as the working electrode, a silver wire as the reference electrode and a platinum wire as the counter electrode. The supporting electrolyte was tetrabutylammonium hexafluorophosphate (0.1 M) and ferrocene (Fc) was used as the internal standard. The solutions were degassed with argon before measurements.

Material Synthesis. 1-(2,4-Difluorophenyl)-1H-pyrazole (dfppz). Dfppz was synthesized by a slight modification of a reported procedure.²⁵ 1,1,3,3-Tetramethoxy propane (5.5 g, 33 mmol) was dissolved in 95% ethanol (50 mL) and concentrated aqueous HCl solution (5 mL) was then added. Under stirring, (2,4-difluorophenyl) hydrazine hydrochloride (5.4 g, 30 mmol) dissolved in 95% ethanol (100 mL) was slowly added to the solution. The solution was refluxed for 24 h. After neutralization with aqueous Na₂CO₃ solutions, the solution was concentrated under vacuum and the residue was purified by column chromatography on silica gel (200-300 mesh) with petroleum ether/ethyl acetate (20:1) as the eluent, yielding a clear oil liquid (4.3 g, 24 mmol). Yield: 80%. ¹H NMR (chloroform- d_6 , 600 MHz, δ [ppm]): 7.92(t, J = 2.8 Hz, 1H), 7.88-7.82(m, 1H), 7.73(s, 1H), 7.02-6.95(m, 2H), 6.47(t, J = 2.1 Hz, 1H). ESI-MS [m/z]: 181.1 $[M + H]^+$.

2-(1-(4-Tritylphenyl)-1H-imidazol-2-yl)pyridine (tp-pyim). 2-(1H-imidazol-2-yl)pyridine and 4-trityl-iodobenzene were prepared by reported procedures.^{26,27} 2-(1H-Imidazol-2-yl)pyridine (0.29 g, 2 mmol) and 4-trityl-iodobenzene (1.11 g, 2.5 mmol), 1,10-phenanthroline (0.24 g, 1.2 mmol), copper(I) iodide (0.11 g, 0.6 mmol), and cesium carbonate (1.63 g, 5 mmol) were dissolved in dimethylformamide (40 mL). The mixture was refluxed in the dark for 20 h under an argon atmosphere and then cooled to room temperature. The solvent was removed under vacuum. The residue was extracted with dichloromethane (150 mL) and purified by column chromatography on silica gel (200-300 mesh) with dichloromethane/methanol (50:1) as the eluent, yielding a white solid (0.35 g, 0.76 mmol). Yield: 38%. ¹H NMR (acetone d_6 , 600 MHz, δ [ppm]): 8.25(d, J = 4.08 Hz, 1H), 8.05(d, J =7.56 Hz, 1H), 7.81(td, J = 7.56 and 2.04 Hz, 1H), 7.38–7.31(m, 7H), 7.27–7.17(m, 15H). ESI-MS [*m*/*z*]: 464.5 [M+H]⁺.

[Ir(dfppz)₂(tp-pyim)]PF₆. The dichloro-bridged diiridium complex [Ir(dfppz)₂Cl]₂ (0.40 g, 0.34 mmol) and tp-pyim (0.33 g, 0.7 mmol) were dissolved in 1,2-ethanediol (30 mL). The mixture was refluxed at 150 °C for 15 h under an argon atmosphere and then cooled to room temperature. To the reaction mixture was added 50 mL methanol. NH₄PF₆ (1.8 g, 11 mmol) in deionized water (50 mL) was then slowly added into the solution under stirring, resulting in a light-yellow suspension. The suspension was filtrated and the resultant precipitate was washed with deionized water and dried under vacuum at 70 °C for 12 h. The crude product was purified

by column chromatography on silica gel (200-300 mesh) with CH₂Cl₂/acetone (30:1) as the eluent. The product was then recrystallized from dichloromethane/hexane, yielding a light-yellow powder (0.54 g, 0.46 mmol). Yield: 68%. ¹H NMR (dimethylsulfoxide $d_{6},600 \text{ MHz}, \delta[\text{ppm}]$): 8.63(d, J = 2.7 Hz, 2H), 8.03–7.92(m, 3H), 7.68(s, 2H), 7.54-7.47(m, 4H), 7.41-7.35(m, 7H), 7.31-7.23(m, 9H), 7.14-7.06(m, 2H), 6.91(d, J = 1.38 Hz, 1H), 6.83-6.79(m, 2H), 6.75(d, J = 8.22 Hz, 1H), 5.67(td, J = 8.25 and 2.04 Hz, 2H). ESI-MS [m/z]: 1014.3 $[M - PF_6]^+$. Anal. Found: C, 52.68; H, 3.38; N, 8.35. Anal. Calcd. for C₅₁H₃₅F₁₀N₇PIr: C, 52.85; H, 3.04; N, 8.46.

Quantum Chemical Calculations. Density functional theory (DFT) and time-dependent DFT (TD-DFT) at the B3LYP level were adopted for calculations on the ground and excited electronic states of the complex.^{28,29} "Double- ξ " quality basis sets were employed for the C, H, N and F (6-31G*) and the Ir (LANL2DZ). An effective core potential replaces the inner core electrons of Ir leaving the outer core $(5s)^2(5p)^6$ electrons and the $(5d)^6$ valence electrons of Ir(III). The geometry of the singlet ground state (S_0) was fully optimized with a C1 symmetry constraint. All calculations were carried on with Gaussian 03 software package using a spin-restricted formalism.³⁰

Fabrication of LECs. Indium-tin-oxide (ITO) substrates with sheet resistance of 15 Ω/\Box were sufficiently cleaned and treated with UV-zone before use. The poly(3,4-ethylenedioxythiophene: poly(styrene sulfonate) (PEDOT: PSS) layer was spin-coated onto the ITO substrate in air and baked at 200 °C for 10 min. The light-emitting layer was spin coated onto the PEDOT-coated substrate in a nitrogen-filled glovebox from CH₃CN solutions and baked at 70 °C for 30 min. The substrate was then transferred into a metal-evaporating chamber, where the aluminum cathode was evaporated at 8-10 Å/s. The resultant device was transferred back to the glovebox and carefully encapsulated. The device was characterized with a Keithley 4200 semiconductor characterization system in ambient conditions. The EL spectrum was collected with a Photo Research PR705 spectrophotometer.

Results and Discussion

Synthesis and Characterization. Scheme 1 depicts the synthetic route of the ligands and $[Ir(dfppz)_2(tp-pyim)]PF_6$. Dfppz was synthesized by the condensation of (2,4-difluorophenyl)hydrazine and 1,1,3,3-tetramethoxypropane. Tp-pyim was synthesized by copper(I)-catalyzed C-N coupling reactions between 2-(1*H*-imidazol-2-yl)pyridine (Hpyim) and 4-trityl-iodobenzene. Because of the active N-H bond in the imidazole, the bulky TP group can be easily attached to the imidazole ring. $[Ir(dfppz)_2(tp-pyim)]PF_6$ was synthesized, with a good yield of ca. 70%, by reacting dimeric iridium(III) intermediates [Ir(dfppz)₂Cl]₂ with tp-pyim, followed by a counterion exchange reaction from Cl^{-} to PF_{6}^{-} . All the ligands and the complex were fully characterized by ESI (electron spray ionization) mass spectroscopy, ¹H NMR, and elemental analysis (see Experimental Section).

Photophysical Properties. Figure 1 shows the absorption and PL spectra of [Ir(dfppz)₂(tp-pyim)]PF₆ in CH₃CN

⁽²⁷⁾ Li, Q.; Rukavishnikov, A. V.; Petukhov, P. A.; Zaikova, T. O.; Keana, J. W. org. Lett. 2002, 4, 3631.

⁽²⁸⁾ Becke, A. D. J. Chem. Phys. 1993, 98, 5648.

 ⁽²⁹⁾ Lee, C.; Yang, W. T.; Parr, R. G. *Phys. Rev. B.* **1988**, *37*, 785.
 (30) Frisch, M. J.; et al. *Gaussian 03*, Revision B.05; Gaussian, Inc.: Wallingford, CT, 2004.



Figure 1. Absorption and PL spectra of [Ir(dfppz)₂(tp-pyim)]PF₆ in CH₃-CN solution (1×10^{-5} M) and neat film.

solution and as neat film. Those in the CH₂Cl₂ solution are shown in the Supporting Information (Figure S1). Detailed photophysical characteristics of [Ir(dfppz)₂-(tp-pyim)]PF₆ in CH₃CN solution are summarized in Table 1. The intense absorption in the ultraviolet region below 350 nm belongs to ${}^{1}\pi - \pi^{*}$ transitions of the ligands while the relatively weak absorption bands extending to the visible region correspond to ${}^{1}MLCT$ (metal-toligand charge-transfer), ${}^{1}LLCT$ (ligand-to-ligand chargetransfer), ${}^{3}MLCT$, ${}^{3}LLCT$, and ligand-centered (LC) ${}^{3}\pi - \pi^{*}$ transitions. The spin-forbidden ${}^{3}MLCT$, ${}^{3}LLCT$, and LC ${}^{3}\pi - \pi^{*}$ transitions gain much intensity by mixing with the higher-lying spin-allowed ${}^{1}MLCT$ transitions because of the strong spin–orbit coupling induced by the heavy iridium atom. 31

In CH₃CN solution, [Ir(dfppz)₂(tp-pyim)]PF₆ emits efficient blue-green light with a peak emission and a shoulder emission at 494 and 472 nm, respectively. The vibronic structure in the emission spectra indicates that the emissive excited states contain considerable LC ${}^{3}\pi - \pi^{*}$ character. ${}^{32-34}$ Upon cooling the solution to 77 K, the emission spectrum becomes much more structured and exhibits a considerable blue-shift of 15 nm, which indicates that the emissive excited states contain considerable ³LLCT or ³MLCT character as well as the LC ${}^{3}\pi - \pi^{*}$ character.^{10,34} The photophysical properties of [Ir(dfppz)₂-(tp-pyim)]PF₆ contrast with those of the blue-green-emitting complex [Ir(dfppy)₂(ph-pyim)]PF₆ (complex 2 in reference 21), which uses dfppy as the cyclometalated ligands and 2-(1-phenyl-1H-imidazol-2-yl)pyridine (ph-pyim) as the ancillary ligand and contains no bulky side groups.²¹ In CH₃CN solution, [Ir(dfppy)₂(ph-pyim)]PF₆ exhibits a featureless emission spectrum with a sole peak at 489 nm and the emission has been assigned to ³MLCT or ³LLCT states, with little LC ${}^{3}\pi - \pi^{*}$ contribution.²¹

In diluted CH₃CN solution, $[Ir(dfppz)_2(tp-pyim)]PF_6$ has a high PLQY of 0.54 and a PL decay lifetime of 3.99 μ s. The relatively long PL decay lifetime further confirms that

the emissive excited states contain much LC ${}^{3}\pi-\pi^{*}$ character. The calculated nonradiative decay rate (K_{nr}) (1.16 × 10⁵ s⁻¹) of [Ir(dfppz)₂(tp-pyim)]PF₆ in CH₃CN solution is much lower than those of other blue-greenemitting cationic iridium complexes (in the range of 5–7× 10⁵ s⁻¹).^{17,21} This is presumably due to the shielding effect of the nonpolar bulky TP group, which protects the luminescent core from being interacted with polar solvent molecules, thus suppressing the nonradiative deactivation of the excited states in solutions.^{14,20}

Table 2 summarizes the PL characteristics of [Ir(dfppz)2-(tp-pyim)]PF₆ in thin films and, as comparisons, those of [Ir(dfppy)₂(ph-pyim)]PF₆ are also shown. [Ir(dfppz)₂(tppyim)]PF₆ exhibits vibronic emission spectra in both the 5% (by weight) doped poly(methyl methacrylate) (PMMA) film and neat film (see Figure S2 in the Supporting Information), which indicates that the emissive excited states of [Ir(dfppz)₂(tp-pyim)]PF₆, with much LC ${}^{3}\pi - \pi^{*}$ character, remain the same in the 5% doped PMMA film and neat film. In contrast, [Ir(dfppy)₂(ph-pyim)]PF₆ exhibits a vibronic emission spectrum in the 5% doped PMMA film but a featureless and largely red-shifted emission spectrum in neat film (see Figure S3 in the Supporting Information), which indicates that the emissive excited states of [Ir(dfppy)₂(ph-pyim)]PF₆ change from LC ${}^{3}\pi-\pi^{*}$ to ${}^{3}MLCT$ on going from the 5% doped PMMA film to neat film. The change of the emissive excited states should be due to the change of the local environment of the complex, as previously observed for a similar cationic iridium complex.¹⁵ For Ir(dfppz)₂(tp-pyim)]PF₆, the emissive excited states are unaltered and the emission spectra are less red-shifted on going from the 5% doped PMMA film to neat film (see Figure S2 in the Supporting Information), which indicates that the bulky TP group helps to separate the molecules from each other and maintain the color purity of the blue-green emission in concentrated films.

The PL decays of [Ir(dfppz)₂(tp-pyim)]PF₆ in doped or neat films all exhibit monoexponential characteristics. In the 5% doped PMMA film, the PL decay lifetime of $[Ir(dfppz)_2(tp-pyim)]PF_6$ is 4.42 μ s, whereas in the neat film, the PL decay lifetime is $3.04 \,\mu s$, which does not decrease significantly as compared to that in the 5% doped PMMA film. In the 5% doped PMMA film, the PLQY of $[Ir(dfppz)_2(tp-pyim)]PF_6$ is 0.79, whereas in the neat film, the PLQY remains as high as 0.54. In contrast, the PL decay of [Ir(dfppy)₂(ph-pyim)]PF₆ in neat film exhibits a biexponential characteristic $[1.06 \,\mu s \,(49\%), 0.40 \,\mu s \,(51\%)]$ due to the strong intermolecular interactions. Moreover, the PLQY of [Ir(dfppy)₂(ph-pyim)]PF₆ in neat film remains only 0.14, decreasing sharply as compared to that (0.72) in the 5% doped PMMA film. The largely retained PL decay lifetime and PLQY of [Ir(dfppz)₂(tp-pyim)]PF₆ in neat film indicates that the sterically bulky TP group works effectively in suppressing the intermolecular interactions and excited-state self-quenching of the complex in solid states.^{14,20} In the film of [Ir(dfppz)₂(tp-pyim)]PF₆ mixed with an ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate (BMIMPF₆), the PL decay lifetime

⁽³¹⁾ Sprouse, S.; King, K. A.; Spellane, P. J.; Watts, R. J. J. Am. Chem. Soc. 1984, 106, 6647.

 ⁽³²⁾ Colombo, M. G.; Güdel, H. U. *Inorg. Chem.* 1993, *32*, 3081.
 (33) Colombo, M. G.; Hauser, A.; Güdel, H. U. *Inorg. Chem.* 1993, *32*,

<sup>3088.
(34)</sup> Lowry, M. S.; Hudson, W. R.; Pascal, R. A., Jr.; Bernhard, S. J. Am. Chem. Soc. 2004, 126, 14129.

absorption ^{<i>a</i>} λ (nm) (ε (× 10 ⁴ M ⁻¹ cm ⁻¹))		room-ter	mperature emission	amission at	electrochemical data ^c		
	λ (nm)	$\Phi_{\rm p}\left(\tau\left(\mu {\rm s}\right)\right)^{b}$	$K_{\rm r} (imes 10^5 { m s}^{-1})$	$K_{\rm nr} (imes 10^5 { m s}^{-1})$	$77 \text{ K} \lambda \text{ (nm)}$	$E_{\rm ox}^{1/2}$ (V)	$E_{\rm red}^{1/2}$ (V)
243 (4.18), 304 (1.98) 325 (1.11)	472 494	0.54 (3.99)	1.35	1.16	459, 491 522	1.21	-1.94

Table 1. Photophysical and Electrochemical Characteristics of [Ir(dfppz)₂(tp-pyim)]PF₆ in CH₃CN Solutions

^{*a*} In CH₃CN solutions (1 × 10⁻⁵ M). ε denotes the molar extinction coefficients. ^{*b*} In degassed CH₃CN (1 × 10⁻⁵ M) solutions. The Φ_p was measured versus quinine sulfate ($\Phi_p = 0.545$ in 1 M H₂SO₄). ^{*c*} Collected in CH₃CN solutions (10⁻³ M). The data were versus Fc⁺/Fc.

Table 2. PL Characteristics of [Ir(dfppz) ₂ (tp-pyim)]PF ₆ an	nd [Ir(dfppy) ₂ (ph-pyim)]PF ₆ in Thin Films. ^{<i>a</i>}
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	[Ir(dfppz) ₂ (tp-pyim)]PF ₆			[Ir(dfppy) ₂ (ph-pyim)]PF ₆			
	PL λ (nm)	τ (μ s)	PLQY	PL λ (nm)	τ (μ s)	PLQY	
neat film	476, 499	3.04	0.54	501	1.06 (49%) 0.40 (51%)	0.14	
film with BMIMPF ₆ ^b 5 wt % doped PMMA film	473, 494 466, 490	3.77 4.42	0.67 0.79	469, 488	2.94	0.72	

^{*a*} Thin films (ca. 100 nm thick) were deposited on quartz substrates and excited at 350 nm. ^{*b*} The molar ratio between $[Ir(dfppz)_2(tp-pyim)]PF_6$ and BMIMPF₆ is 1:1.



Figure 2. Cyclic voltammogram of $[Ir(dfppz)_2(tp-pyim)]PF_6$ in CH₃CN solution $(1 \times 10^{-3} \text{ M})$ (the small wave around -1.38 V arises from some unknown impurities in the conducting electrolyte). Potentials were recorded versus Fc⁺/Fc.

is 3.77 μ s and the PLQY remains 0.67, both of which are higher than those of the neat film because of the diluting effect of the ionic liquid.^{14,16,18,22}

Electrochemical Properties. Figure 2 shows the cyclic voltammogram of [Ir(dfppz)₂(tp-pyim)]PF₆ in CH₃CN solution and the redox potentials are listed in Table 1. As shown in Figure 2, both the oxidation and reduction processes are reversible, which are beneficial for the application of [Ir(dfppz)₂(tp-pyim)]PF₆ in electroluminescent devices. The oxidation potential (1.21 V) of [Ir(dfppz)₂-(tp-pyim)]PF₆ is shifted anodically (by 70 mV) with respect to that (1.14 eV) of [Ir(dfppy)₂(ph-pyim)]PF₆,²¹ which is consistent with the previous report that the dfppz ligand stabilizes the HOMO of the complex as compared to the dfppy ligand.^{10,16} The reduction potential (-1.94 V)of $[Ir(dfppz)_2(tp-pyim)]PF_6$ is the same as that (-1.94 V) of $[Ir(dfppy)_2(ph-pyim)]PF_6$.²¹ Because the reduction of the complexes occurs on the ancillary ligands where the lowest unoccupied molecular orbitals (LUMOs) of the complexes are localized,²¹ the same reduction potentials of [Ir(dfppz)₂(tp-pyim)]PF₆ and [Ir(dfppy)₂(ph-pyim)]PF₆ suggest that the bulky TP group exerts little influence on the LUMO level of the complex.

Theoretical Calculations. Figure 3 shows the optimized geometry of [Ir(dfppz)₂(tp-pyim)]PF₆, together with the selected molecular surfaces. More molecular surfaces can be found in the Supporting Information (Table S1). As shown in Figure 3, the bulky TP group shields the luminescent iridium core in an umbrella shape. In contrast to other cationic iridium complexes whose HOMOs reside on the iridium ion and the phenyl groups of the cyclometalated ligands,²¹ the HOMO of [Ir(dfppz)₂(tppyim)]PF₆ resides on the TP group of tp-pyim ligand. The HOMO-1 resides on the iridium ion and the phenyl groups of dfppz ligands. The HOMO and HOMO-1, with the calculated energy levels of -8.03 eV and -8.06 eV, respectively, are almost equivalent in energy. The HOMO-3, HOMO-4, HOMO-6, HOMO-8 and HOMO-9 all reside on the TP group of tp-pyim ligand (see Table S1 in the Supporting Information). As revealed by the following TDDFT calculations, these occupied orbitals residing on the TP group are not involved in the low-lying emissive excited-states. The HOMO-2, HOMO-5, HOMO-10, and HOMO-11 all reside on the iridium ion and the dfppz ligands. The HOMO-7 resides mainly on the iridium ion and dfppz ligands, with a small distribution on the pyim of tp-pyim ligand. The HOMO-12 resides on the pyim of tp-pyim ligand (see Table S1 in the Supporting Information). The LUMO and LUMO+1 of [Ir(dfppz)₂(tppyim)]PF₆ reside on the pyim of tp-pyim ligand, with nearly no distribution on the TP group (Figure 3c and 3d).

To gain deep insight into the emission nature of [Ir(dfppz)₂-(tp-pyim)]PF₆, we calculated the first three triplet states of [Ir(dfppz)₂(tp-pyim)]PF₆ through the TD-DFT approach. Table 3 summarizes the vertical excitation energies and molecular orbitals involved in the excitations. The T₁ state originates from the excitation of HOMO-1 \rightarrow LUMO, with character of mixed ³MLCT (Ir \rightarrow pyim of tppyim) and ³LLCT (dfppz \rightarrow pyim of tp-pyim). The T₂ state originates mainly from the excitations of HOMO-7 \rightarrow LUMO and HOMO-12 \rightarrow LUMO, with character of mixed ³MLCT (Ir \rightarrow pyim of tp-pyim), ³LLCT (dfppz \rightarrow pyim of tp-pyim), and LC ³ π - π * (pyim-based). The T₃ state



Figure 3. Molecular surfaces of $[Ir(dfppz)_2(tp-pyim)]PF_6$. (a) HOMO; (b) HOMO-1; (c) LUMO; (d) LUMO+1. All the MO surfaces correspond to an isocontour value of $|\Psi| = 0.025$.

Table 3	Calculated Tri	nlet States of	[Ir(dfnnz).	(tn-nvim)]PF	through TDDFT	Annroach
I able 5.	Calculated III	piet States of	III(UIPPZ)2	(up-pynn) I I (6 unougn IDDFI	Approach

states	$E [eV]^a$	excitations ^b	nature
T_1	2.73	$H-1 \rightarrow L (100\%)$	$d\pi(Ir)$ - $\pi(dfppz) \rightarrow \pi^*(pvim of tp-pvim)$
T_2	2.90	$H-7 \rightarrow L (44\%)$	$d\pi(Ir)$ - $\pi(dfppz) \rightarrow \pi^*(pyim of tp-pyim)$ $\pi(vim of tr pyim) \rightarrow \pi^*(vim of tr pyim)$
		H-12 → L (51%) H-12 → L+1 (5%)	π (pyini of tp-pyini) $\rightarrow \pi^*$ (pyini of tp-pyini) π (pyini of tp-pyini) $\rightarrow \pi^*$ (pyini of tp-pyini) π (pyini of tp-pyini) $\rightarrow \pi^*$ (pyini of tp-pyini)
T ₃	3.03	$H \rightarrow L (100\%)$	π (tp of tp-pyim) $\rightarrow \pi^*$ (pyim of tp-pyim)

^a Calculated excitation energies for the triplet states. ^b H and L denote the HOMO and LUMO, respectively; data in parentheses are the contributions of the excitations.

originates mainly from the excitation of HOMO \rightarrow LUMO, with intraligand-charge-transfer character (TP of tppyim \rightarrow pyim of tp-pyim). According to the photophysical characterizations and the fact that T₁ and T₂ states are close-lying in energy (within 0.17 eV), it is believed that the emission of [Ir(dfppz)₂(tp-pyim)]PF₆ originates mainly from the T₁ and T₂ states, that is, the observed light emission originates not only from the ³MLCT (Ir \rightarrow pyim of tp-pyim) and ³LLCT (dfppz \rightarrow pyim of tp-pyim) states but also from the ³ π - π * states (pyim-based).

Previously, we performed TDDFT calculations on [Ir-(dfppy)₂(ph-pyim)]PF₆, of which the T₁ state has ³MLCT, ³LLCT character, and the T₂ and T₃ states have ³MLCT, LC ³ π - π * character.²¹ In CH₃CN solution or neat film, the emission of [Ir(dfppy)₂(ph-pyim)]PF₆ with featureless spectra has been assigned to ³MLCT or ³LLCT states (the T₁ state).²¹ However, in the 5% doped PMMA film, the emission with structured spectra can be assigned to LC ³ π - π * states (T₂ or T₃ states). On going from the 5% doped PMMA film to neat film, the emissive excited states of [Ir(dfppy)₂(ph-pyim)]PF₆ change from the T₂ or T₃ states to the T₁ state, because of the change of the local environment of the complex.¹⁵ This change in the emissive excited states does not happen for [Ir(dfppz)₂(tp-pyim)]PF₆ because of the bulky TP group attached to the complex.

Film-Forming Properties. Because of the film-forming properties of organic electronic materials are crucial for the performances of the resultant devices, the surface morphologies of thin films of $[Ir(dfppz)_2(tp-pyim)]PF_6$ were examined. As shown in Figure 4, smooth and amorphous



Figure 4. AFM topographic images of thin films (ca. 100 nm thick) on top of PEDOT:PSS: (a) neat $[Ir(dfppz)_2(tp-pyim)]PF_6$, (b) $[Ir(dfppz)_2(tp-pyim)]PF_6$ mixed with BMIMPF₆ (molar ratio 1:1).

thin films can be formed by spin-coating $[Ir(dfppz)_2(tp-pyim)]PF_6$ from CH₃CN solutions. The root-mean-square (rms) roughness of neat $[Ir(dfppz)_2(tp-pyim)]PF_6$ film is as small as 0.34 nm, indicating that $[Ir(dfppz)_2(tp-pyim)]PF_6$ has an excellent film-forming property. For the thin film of $[Ir(dfppz)_2(tp-pyim)]PF_6$ mixed with BMIMPF₆ (molar ratio 1:1), the rms value increases slightly to 0.38 nm. Even at this high doping concentration of the ionic liquid in $[Ir(dfppz)_2(tp-pyim)]PF_6$ (molar ratio 1:1), no particular aggregation or phase separation between the two species were observed, indicating the good compatibility of $[Ir(dfppz)_2(tp-pyim)]PF_6$ with BMIMPF₆.¹⁴

LECs. LECs were fabricated with a structure of ITO/ PEDOT:PSS (40 nm)/ $[Ir(dfppz)_2(tp-pyim)]PF_6$:BMIMPF_6 (molar ratio 1:1) (100 nm) /Al (120 nm), where the PEDOT: PSS layer was used to smooth the ITO surface and BMIMPF_6

LECs	1: x : y^a	$t_{\rm on}$ (min) ^b	t_{\max} (min) ^c	$B_{\rm max} ({\rm cd} \; {\rm m}^{-2})$	$\eta_{\rm c,\ max} ({\rm cd} {\rm A}^{-1})^{ d}$	EL λ (nm)	CRI	$\operatorname{CIE}\left(x,y\right)$
blue-green	1:1:0	4.5	29.0	14.5	18.3 (7.6%)	474, 494	80	(0.22, 0.41)
white	1:1: 0.008	3.5	22.5	7.9	11.4 (5.6%)	495, 600		(0.37, 0.41)

^{*a*} The device structure is ITO/PEDOT: PSS (40 nm)/[Ir(dfppz)₂(tp-pyim)]PF₆:BMIMPF₆:[Ir(ppy)₂(qlbi)]PF₆ (1:*x*:*y*, molar ratio) (100 nm)/Al (100 nm), where 1:*x*:*y* denotes the molar ratio between [Ir(dfppz)₂(tp-pyim)]PF₆, BMIMPF₆, and [Ir(ppy)₂(qlbi)]PF₆. ^{*b*} The time required to reach 1 cd m⁻². ^{*c*} The time required to reach the maximum brightness. ^{*a*} The number in the parentheses denotes the corresponding EQE values.



Figure 5. EL spectrum of the blue-green LEC (biased at 3.2 V) and PL spectrum of the light-emitting layer.

was added to shorten the response time of LECs.³⁵ With this device structure, LECs can be routinely fabricated with good reproducibility in electroluminescent performances. Detailed electrical characteristics of LECs are summarized in Table 4. Figure 5 shows the EL spectrum of the blue-green LEC, with a peak emission and a shoulder emission at 494 and 474 nm, respectively. The CIE coordinates of the blue-green electroluminescence are (0.22, 0.41), which are better than those [(0.25, 0.46)] of the LEC based on [Ir(dfppy)₂(ph-pyim)]PF₆,²¹ because of the maintained color purity of the blue-green emission of [Ir(dfppz)₂-(tp-pyim)]PF₆ in concentrated films. The EL spectrum resembles the PL spectrum of the light-emitting layer, except that a long tail develops in the long-wavelength region of the EL spectrum (Figure 5).

Figure 6 shows the time-dependent current density and brightness curves of LECs. The biasing voltage is chosen at 3.2 V, which is close to the band gap (3.15 eV) of [Ir(dfppz)₂(tp-pyim)]PF₆. As shown in Figure 6, both the current density and brightness increase gradually with time, which is a typical characteristic of LECs.^{4,8} The peak current efficiency, EQE, and power efficiency reached 18.3 cd A^{-1} , 7.6%, and 18.0 lm W^{-1} , respectively. At 3.2 V, it took 29 min for the device to reach a maximum brightness of 14.5 cd m^{-2} . When biased at a higher voltage of 4.0 V, the device showed a faster response and it took 3 min for the device to reach a maximum brightness of 94 cd m⁻². At 4.0 V, the peak current efficiency remained 16.6 cd A^{-1} . The high EL efficiency is attributed to the high luminescent efficiency of [Ir-(dfppz)₂(tp-pyim)]PF₆, the suppressed excited-state selfquenching in solid states and the efficient carrier injection and recombination in LECs.





Figure 6. Time-dependent current-density and brightness curves of the blue-green and white LECs biased at 3.2 V.

At the same biasing voltage of 4.0 V, the current density of the LEC based on [Ir(dfppz)₂(tp-pyim)]PF₆ is lower than that of the LEC based on [Ir(dfppy)₂(ph-pyim)]-PF₆,²¹ because the bulky TP group increases the intersite distance and thereby hinders charge-hopping between molecules in the active layer.^{20,36} However, at 4.0 V, the maximum brightness and efficiency (94 cd m⁻², 18.3 cd A⁻¹, respectively) of the LEC based on [Ir(dfppz)₂(tppyim)]PF₆ are higher than those (39 cd m⁻², 8.4 cd A⁻¹, respectively) of the LEC based on [Ir(dfppz)₂(tppyim)]PF₆, because of the enhanced PLQY of [Ir(dfppz)₂(tppyim)]PF₆ in concentrated films. As previously reported, bulky side groups attached to the complex would hinder charge-hopping between molecules and so decrease the brightness of LECs.^{20,36} This negative effect, as shown here, can be largely counteracted by the simultaneously enhanced PLQY of the complex in concentrated films.

On the basis of the efficient blue-green LEC, white LECs were fabricated. The device structure is ITO/PEDOT: PSS (40 nm)/[Ir(dfppz)₂(tp-pyim)]PF₆:BMIMPF₆:[Ir(ppy)₂-(qlbi)]PF₆ (molar ratio 1:1:0.008) (100 nm)/Al (120 nm), where [Ir(ppy)₂(qlbi)]PF₆ is bis(2-phenylpyridinato-N, C^{2'})iridium(III)[3-(1-phenyl-1H-benzo[d]imidazol-2-yl)isoquinoline] hexafluorophosphate, a red-emitting cationic iridium complex developed in our lab.²¹ The biasing voltage is still chosen at 3.2 V. Figure 7 shows the EL spectrum of the white LEC, along with the PL spectrum of the light-emitting layer. The relative intensity of the red component to the blue one in the EL spectrum is much larger than that in the PL spectrum, which indicates that, as well as the energy transfer from [Ir(dfppz)₂(tp-pyim)]PF₆ to [Ir(ppy)₂(qlbi)]PF₆, charge-trapping on [Ir(ppy)₂(qlbi)]-PF₆ plays an important role for the operation of the white

⁽³⁶⁾ Rudmann, H.; Shimada, S.; Rubner, M. F. J. Am. Chem. Soc. 2002, 124, 4918.



Figure 7. EL spectrum of the white LEC (biased at 3.2 V) and PL spectrum of the light-emitting layer. The inset on the top right depicts the energy level diagram of the white LEC (the dashed lines represent the energy levels of $[Ir(ppy)_2(qlbi))]PF_6$).

LEC.^{16,21} The inset in Figure 7 illustrates the energy level diagram of the white LEC, from which it can be concluded that both holes and electrons can be trapped by small-gap [Ir(ppy)₂(qlbi)]PF₆. The CIE coordinates of the white electroluminescence are (0.37, 0.41) and the CRI value is up to 80, which corresponds to a warm-white light that is appropriate for solid-state lighting applications.

The time-dependent current density and brightness curves of the white LEC were depicted in Figure 6. Detailed electrical characteristics were summarized in Table 4. The peak current efficiency, EQE, and power efficiency of the white LEC reached 11.4 cd A^{-1} , 5.6%, and 11.2 lm W^{-1} , respectively, higher than those of the white LEC based on [Ir(dfppy)₂(ph-pyim)]PF₆, BMIMPF₆, and [Ir(ppy)₂(qlbi)]-PF₆ (molar ratio 1:0.35:0.002).²¹

For the white LEC based on $[Ir(dfppz)_2(tp-pyim)]PF_6$, the current density, brightness and efficiency are lower than those of the blue-green LEC (Figure 6). This is quite different from the situation in the white LEC based on $[Ir(dfppy)_2(ph-pyim)]PF_6$, which showed higher current density, brightness, and efficiency than the blue-green LEC, attributed to the lowered carrier-injection barrier upon doping the small-gap [Ir(ppy)₂(qlbi)]PF₆.²¹ In LECs based on [Ir(dfppz)₂(tp-pyim)]PF₆ and BMIMPF₆ (molar ratio 1:1), the doping concentration of BMIMPF₆ is large enough so that adequate ions can accumulate at the electrode interfaces, eliminating the carrier-injection barriers. This can be confirmed by the evidence that the bluegreen LEC based on [Ir(dfppz)₂(tp-pyim)]PF₆ turned on quickly at a low biasing voltage that is almost equal to the band gap of the emitting complex. Therefore, in LECs based on [Ir(dfppz)₂(tp-pyim)]PF₆ and BMIMPF₆ (molar ratio 1:1), lowering the carrier-injection barrier upon doping the small-gap $[Ir(ppy)_2(qlbi)]PF_6$ is not likely to change the device performance much as carrier-injection barrier is no longer the key problem. On the contrary, charge-trapping on [Ir(ppy)₂(qlbi)]PF₆ plays a key role on the device performance. Because of the trap of electrons and holes on [Ir(ppy)₂(qlbi)]PF₆, the white LEC showed lower current density than the blue-green LEC; moreover, the recombination zone in the white LEC moves closer to the electrode interfaces, increasing the possibility of exciton-quenching and thereby decreasing the brightness and efficiency. Besides, the low luminescence efficiency of $[Ir(ppy)_2(qlbi)]PF_6$ (PLQY = 0.03 in CH₃CN solution) should also be responsible for the lowered brightness and efficiency of the white LEC.²¹ It is believed that much higher performance will be achieved for the white LECs by using red-emitting ionic complexes with high luminescent efficiency and appropriate energy levels.

It is also noted that all LECs reported here showed limited device stability, which has remained a big challenge for LECs. Currently, detailed mechanisms for the degradation of iTMCs-based LECs are unclear. The addition of large amounts of ionic liquid in LECs, though shortening the response time, generally accelerates the degradation of LECs.^{22,35} Several approaches have been proposed to enhance the stability of LECs, such as freezing the p-i-n junction once the junction is established,³⁷ introducing supramolecular interactions within the molecules³⁸ or driving LECs under voltage pulses.³⁹ For practical applications, further study to improve the stability of LECs is greatly needed.

Conclusions

A highly efficient blue-green-emitting cationic iridium complex [Ir(dfppz)₂(tp-pyim)]PF₆, which contains a bulky side group in the ancillary ligand, has been synthesized and fully characterized. LECs based on [Ir(dfppz)₂(tp-pyim)]PF₆ showed highly efficient blue-green electroluminescence, with peak current efficiency, EQE and power efficiency of 18.3 cd A^{-1} , 7.6% and 18.0 lm W^{-1} , respectively. White LECs based on [Ir(dfppz)₂(tp-pyim)]PF₆ showed warm white light, with CIE coordinates of (0.37, 0.41), a CRI value up to 80 and a power efficiency of 11.2 lm W^{-1} . Further work will be focused on improving the performance of white LECs, with the aim to enhance the power efficiency over those (~15 lm W^{-1}) of electrical bulbs, and prolonging the operating lifetime of LECs to the practical application level.

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Supporting Information Available: Absorption and PL spectra of $[Ir(dfppz)_2(tp-pyim)]PF_6$ in degassed CH₂Cl₂ solutions (Figure S1); PL spectra of $[Ir(dfppz)_2(tp-pyim)]PF_6$ in the 5% doped PMMA film and neat film (Figure S2); PL spectra of $[Ir(dfppy)_2(ph-pyim)]PF_6$ in the 5% doped PMMA film and neat film (Figure S3); the calculated molecular surfaces and energy levels of $[Ir(dfppz)_2(tp-pyim)]PF_6$ (Table S1); the complete author list of ref 30 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

(39) Rudmann, H.; Rubner, M. F. J. Appl. Phys. 2001, 90, 4338.

⁽³⁷⁾ Shao, Y.; Bazan, G. C.; Heeger, A. J. Adv. Mater. 2007, 19, 365.

⁽³⁸⁾ Graber, S.; Doyle, K.; Neuburger, M.; Housecroft, C. E.; Constable, E. C.; Costa, R. D.; Ortí, E.; Repetto, D; Bolink, H. J. J. Am. Chem. Soc. 2008, 130, 14944.