

Constructive Effects of Long Alkyl Chains on the Electroluminescent Properties of Cationic Iridium Complex-Based Light-Emitting Electrochemical Cells

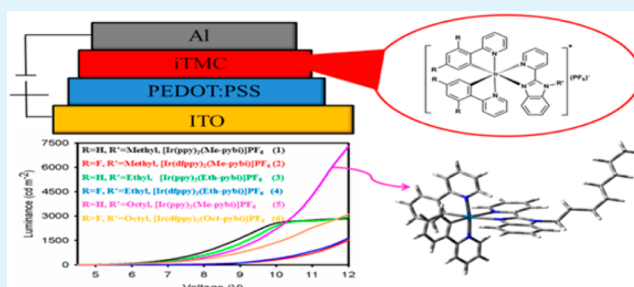
Chozhidakath Damodharan Sunesh,[†] George Mathai,[‡] and Youngson Choe^{*,†}

[†]Department of Polymer Science and Chemical Engineering, Pusan National University, Busan 609-735, South Korea

[‡]Department of Chemistry, Sacred Heart College, Thevara, Kochi 682-013, India

ABSTRACT: A series of cationic iridium complexes (1–6) were synthesized using alkylated imidazole-based ancillary ligands, and the photophysical and electrochemical properties of these complexes were subsequently evaluated. Light-emitting electrochemical cells (LECs) were fabricated from these complexes, and the effects of the alkyl chain length on the electroluminescent properties of the devices were investigated. The LECs based on these complexes resulted in yellow emission (complexes 1, 3, and 5) and green emission (complexes 2, 4, and 6) with Commission Internationale de L'Eclairage (CIE) coordinates of (0.49, 0.50) and (0.33, 0.59), respectively. Our results indicate that the luminance and efficiency of the LECs can consistently be enhanced by increasing the alkyl chain length of the iridium complexes as a result of suppressed intermolecular interaction and self-quenching. Subsequently, a high luminance of 7309 cd m⁻² and current efficiency of 3.85 cd A⁻¹ were achieved for the LECs based on complex 5.

KEYWORDS: light-emitting electrochemical cells, iridium complexes, alkyl chain length, steric hindrance, electroluminescence



1. INTRODUCTION

Light-emitting electrochemical cells (LECs) are the next generation of optoelectronic devices and commonly employ ionic transition metal complexes (iTMCs) or conjugated polymers as the light-emitting material.^{1–5} LECs typically consist of ionic species, which are fabricated in solution and utilize air-stable electrodes, allowing the nonrigorous encapsulation of the devices.⁶ This simple device architecture employs ionic species that migrate toward the respective electrodes under an external bias; subsequent carrier injection and recombination results in the emission of light. These features make LECs a superior candidate for the next generation of display and lighting applications compared to sophisticated multilayered organic light-emitting diodes (OLEDs), which are composed of neutral molecules and require multiple evaporation processes that cause the fabrication of such devices to be quite expensive.

The first solid-state LEC was reported in 1995 and consisted of a polymer blend sandwiched between two electrodes.¹ The polymer blend was composed of a mixture containing an emissive conjugated polymer, an ion conducting polymer, and an inorganic salt. More recently, LECs based on iTMCs have attracted significant attention owing to their various advantages over polymer-based LECs. In general, iTMCs possess desirable thermal and photochemical stabilities. Additionally, iTMCs exhibit high luminance efficiencies owing to the phosphorescent nature of the metal complexes. They are also intrinsically ionic and contribute to both charge transport and emissive

recombination processes and subsequently eliminate the need for the ion-conducting materials used in polymer-based devices. Unlike iTMCs, polymer-based LECs containing multiple components may result in aggregation or phase separation that negatively affects the thin film morphology and limits the device performance. These characteristics make iTMCs the most promising ionic emitter for the fabrication of optoelectronic devices. The first solid state LECs based on iTMCs were reported in 1996 and utilized an ionic ruthenium polypyridyl complex.³ Extensive effort has since been carried out to enhance the device performance of LECs incorporating iTMCs.

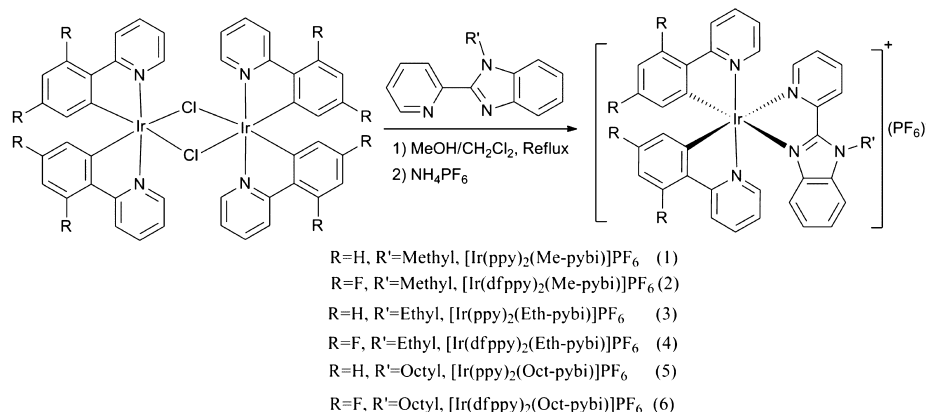
LECs based on various iTMCs such as ionic Ru(II),^{3,4,7–13} Os(II),^{13,14} and Cu(I)^{15–18} complexes have been previously reported. However, these complexes are unable to tune the emission colors to shorter wavelengths because of their limited ligand field splitting energies (LFSEs) and therefore have limited applications in LECs. LECs based on iridium complexes were fabricated for the first time in 2004 with the intention of producing emission wavelengths in the blue region, but they subsequently produced a yellow emission with an efficiency of 5%.¹⁹ The larger LFSEs of Ir(III) makes it a superior material over other iTMCs, and it can produce multicolor devices through the selection of appropriate organic ligands.^{20–44} The structural modification was performed by introducing electron

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Scheme 1. Synthetic Routes and Structures of Cationic Iridium Complexes 1–6



withdrawing groups into the cyclometalated ligand or by attaching electron donating groups to the ancillary ligand. These methods resulted in the enlarged energy gaps through the stabilization of the highest occupied molecular orbital (HOMO) and destabilization of the lowest unoccupied molecular orbital (LUMO).

In addition to tuning the emission colors, it is also necessary to produce a device that exhibits high luminance and efficiency. Steric hindrance is the best strategy because it decreases the intermolecular interaction between the metal complexes.³⁴ The active layer is composed of neat films; therefore, self-quenching will occur and produce an unbalanced carrier injection/recombination that diminishes the performance of the devices. In order to suppress the intermolecular interactions and self-quenching, the complexes should be as far away from each other as possible through the selective design of organic ligands. In 2013, Zhang et al.³⁴ reported yellow light-emitting LECS based on cationic iridium complexes using 1,3,4-oxadiazole (OXD) derivatives as the cyclometalated and ancillary ligands. LECS based on these complexes exhibited a maximum brightness of 22.0 cd m⁻² and a current efficiency of 0.18 cd A⁻¹. Recently, we reported two cationic iridium complexes using the imidazole-based ancillary ligand 2-(4-ethyl-2-pyridyl)-1H-imidazole (EP-Imid), which resulted in blue-green emission for [Ir(ppy)₂(EP-Imid)]PF₆ (**C1**) and green emission for [Ir(dfppy)₂(EP-Imid)]PF₆ (**C2**) (where ppy is 2-phenylpyridine and dfppy is 2-(2,4-difluorophenyl)pyridine).³³ Although color tuning was achieved using these complexes, the complexes only produced a maximum current efficiency of 1.0 cd A⁻¹ and 0.88 cd A⁻¹ for **C1** and **C2**, respectively, owing to the strong intermolecular interactions within the thin solid films. To reduce these interactions, as well as self-quenching, we purposefully designed ancillary ligands with various chain lengths containing methyl, ethyl, and octyl groups.

In this study, we report a series of cationic iridium complexes (1–6) using imidazole-based ancillary ligands, which were prepared by the alkylation of 2-(pyridin-2-yl)-1H-benzo[d]imidazole (Hpybi) with various alkyl halides of varying chain lengths. The effects of the alkyl chain lengths on the electroluminescent properties of LECs were investigated. The device based on complexes **1**, **3**, and **5** produced yellow emissions, while complexes **2**, **4**, and **6** resulted in green emission colors with respect to the selection of cyclometalating ligands such as ppy or dfppy. Although the increase in alkyl chain length did not yield any significant color tuning, it resulted in enhanced luminance from the methyl to the octyl

group. Consequently, a luminance of 7309 cd m⁻² and a current efficiency of 3.85 cd A⁻¹ were achieved for the LECs containing complex **5**. Our results reveal the necessity of reduced intermolecular interactions in cationic iridium complexes for the fabrication of highly efficient LEC devices.

2. EXPERIMENTAL SECTION

2.1. Materials and Methods. All reactants and solvents were purchased from Sigma-Aldrich, South Korea, except iridium(III) chloride hydrate, 99.9% (IrCl₃·xH₂O) that was purchased from Alfa Aesar and used without further purification. ¹H and ¹³C NMR spectra were recorded on a Varian Unity Inova 500 MHz FT-NMR spectrometer, and the chemical shifts δ (in ppm) were measured relative to the residual CD₂Cl₂ solvent peak with tetramethylsilane as an internal standard. Elemental analyses were performed on Elementar Vario EL CHN elemental analyzer. Solution UV–visible (UV–vis) absorption spectra and photoluminescence (PL) emission spectra of the iridium complexes were acquired in a 1 cm path-length quartz cell using an Agilent 8453 spectrophotometer and an F-7000 FL spectrophotometer, respectively. PL quantum yields (PLQYs) were measured in acetonitrile solutions at an excitation wavelength of 420 nm with quinine sulfate (Φ_p = 0.545 in 1 M H₂SO₄) as the reference substance. Electrochemical measurements of the complexes (10⁻³ M) were performed using cyclic voltammetry and recorded using a potentiostat/galvanostat (Iviumstat) voltametric analyzer with a scan rate of 100 mVs⁻¹. The electrolytic cell contained platinum as the working electrode, platinum wire as the counter electrode, and Ag/AgCl as the reference electrode. The supporting electrolyte was a 0.1 M solution of tetrabutylammonium hexafluorophosphate (TBAPF₆) in acetonitrile. The redox potentials of each measurement were recorded against the ferrocenium/ferrocene (Fc⁺/Fc) couple that was used as an internal standard. The HOMO/LUMO energy levels and the energy gap (E_{gap}) of the complexes were calculated from the oxidation (E_{ox}) and reduction (E_{red}) potentials using the empirical relations:^{45,46}
 $E_{\text{HOMO}} = [-e(E_{\text{ox}}(\text{vs Ag/AgCl}) - E_{1/2}(\text{Fc/Fc} + \text{vs Ag/AgCl}))] - 4.8 \text{ eV}$; $E_{\text{LUMO}} = [-e(E_{\text{red}} - E_{1/2})] - 4.8 \text{ eV}$ and $E_{\text{gap}} = E_{\text{HOMO}} - E_{\text{LUMO}}$; where $E_{1/2}(\text{Fc/Fc} + \text{vs Ag/AgCl})$ is the redox potential of ferrocene, which was found to be 0.43 V. E_{HOMO} and E_{LUMO} are the energy levels of the HOMO and LUMO, respectively.

2.2. Synthesis of Ancillary Ligands. **2.2.1. 1-Methyl-2-(pyridin-2-yl)-1H-benzo[d]imidazole (Me-pybi).** Me-pybi was synthesized from the precursor 2-(pyridin-2-yl)-1H-benzo[d]imidazole (Hpybi) with a yield of 79%. A solution of 35% NaOH was added to a solution of Hpybi (1 g, 5.12 mmol) in 12 mL of DMF. The resulting mixture was stirred at room temperature for 30 min, and then iodomethane (6.14 mmol) was added dropwise with constant stirring for 12 h. The reaction mixture was subsequently extracted with water and ether to remove DMF and excess NaOH. The organic layer was isolated, dried over anhydrous Na₂SO₄, and filtered. The solvent was then removed under reduced pressure. The purification of the crude product was

carried out by column chromatography on silica gel (200–300 mesh) with hexane/ethyl acetate (9:1) as the eluent to yield brown oil that crystallized into a brown solid after a week of standing. ^1H NMR (500 MHz, CD_2Cl_2) δ (ppm): 8.65 (d, $J = 4.64$ Hz, 1H), 8.37 (d, $J = 7.99$ Hz, 1H), 7.88–7.84 (m, 1H), 7.77–7.75 (m, 1H), 7.47–7.45 (m, 1H), 7.37–7.28 (m, 3H), 4.27 (s, 3H).

2.2.2. 1-Ethyl-2-(pyridin-2-yl)-1H-benzo[d]imidazole (Eth-pybi). Eth-pybi was synthesized following the same procedure as Me-pybi, except that iodomethane was replaced with iodoethane. Yield: 74%. ^1H NMR (500 MHz, CD_2Cl_2) δ (ppm): 8.69 (d, $J = 4.62$ Hz, 1H), 8.43 (d, $J = 8.01$ Hz, 1H), 7.86–7.81 (m, 2H), 7.47–7.44 (m, 1H), 7.36–7.29 (m, 3H), 4.87 (q, $J = 7.13$ Hz, 7.13 and 7.12 Hz, 2H), 1.49 (t, $J = 7.13$ and 7.13 Hz, 3H).

2.2.3. 1-Octyl-2-(pyridin-2-yl)-1H-benzo[d]imidazole (Oct-pybi). Oct-pybi was synthesized using 1-bromooctane as the alkylating agent to yield a colorless oil after column chromatography. Yield: 80%. ^1H NMR (500 MHz, CD_2Cl_2) δ (ppm): 8.68 (d, $J = 4.65$ Hz, 1H), 8.38 (d, $J = 8.02$ Hz, 1H), 7.84–7.80 (m, 2H), 7.45–7.42 (m, 1H), 7.34–7.26 (m, 3H), 4.82–4.78 (m, 2H), 1.89–1.82 (m, 4H), 1.40–1.30 (m, 6H), 1.34–1.22 (m, 2H), 0.85 (t, $J = 6.92$ and 6.92 Hz, 3H).

2.3. Synthesis of Cationic Iridium Complexes. The dimeric Ir(III) intermediates, $[\text{Ir}(\text{CN})_2(\mu\text{-Cl})_2]$, were synthesized by refluxing $\text{IrCl}_3 \cdot x\text{H}_2\text{O}$ with 2.5 eq of specific cyclometalated ligands (CN) such as 2-phenylpyridine (ppy) or 2-(2,4-difluorophenyl)pyridine (dfppy) according to previously reported procedures.⁴⁷ All cationic iridium complexes were synthesized in the same manner in which the dimeric Ir(III) intermediates underwent facile reaction with alkylated imidazole-based ancillary ligands followed by ion exchange with ammonium hexafluorophosphate (NH_4PF_6) to afford phosphorescent iridium complexes in high yields.⁴⁸ The resulting complexes were then characterized by various spectroscopic, photophysical, and electrochemical methods. The synthetic routes including the structures of the cationic iridium complexes are shown in Scheme 1. The synthesis of $[\text{Ir}(\text{ppy})_2(\text{Me-pybi})]\text{PF}_6$ (1) is described in detail, and all the other complexes were synthesized by following a similar procedure.

2.3.1. Synthesis of $[\text{Ir}(\text{ppy})_2(\text{Me-pybi})]\text{PF}_6$ (1). The chloro-bridged dimeric iridium complex $[\text{Ir}(\text{ppy})_2\text{Cl}]_2$ (108 mg, 0.1 mmol) and Me-pybi (52 mg, 0.25 mmol) were dissolved in a mixture of CH_2Cl_2 (15 mL) and MeOH (15 mL) that was heated to reflux under nitrogen with constant stirring for 16 h. Upon cooling to room temperature, solid NH_4PF_6 (65 mg, 0.4 mmol) was added into the reaction mixture and stirred for 1 h. The solvent was removed under reduced pressure following the addition of dichloromethane to remove any insoluble inorganic impurities. The addition of hexane to the filtrate yielded the desired product as a yellow solid, which was then filtered and dried in a vacuum oven for 24 h. The crude material was subsequently recrystallized from an acetonitrile/hexane mixture. Yield: 141 mg, 0.17 mmol, 82%. ^1H NMR (500 MHz, CD_2Cl_2) δ (ppm): 8.59 (d, $J = 8.20$ Hz, 1H), 8.21–8.17 (m, 1H), 8.10 (d, 4.56 Hz, 1H), 7.95 (d, $J = 7.87$ Hz, 1H), 7.89 (d, $J = 7.86$ Hz, 2H), 7.78–7.67 (m, 4H), 7.61–7.58 (m, 2H), 7.52–7.42 (m, 2H), 7.13–7.03 (m, 3H), 6.99–6.91 (m, 4H), 6.43–6.33 (m, 3H), 4.43 (s, 3H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ (ppm): 168.3, 152.6, 151.4, 149.9, 149.1, 147.6, 147.4, 144.7, 144.5, 139.9, 138.4, 137.2, 132.7, 131.9, 131.1, 130.4, 128.5, 126.6, 125.7, 125.0, 123.7, 122.8, 120.1, 118.7, 111.7, 33.8. Anal. calcd (%) for $\text{C}_{35}\text{H}_{27}\text{N}_5\text{PF}_6\text{Ir}$: C 49.18, H 3.18, N 8.19; found, C 49.21, H 3.15, N 8.24.

2.3.2. Synthesis of $[\text{Ir}(\text{dfppy})_2(\text{Me-pybi})]\text{PF}_6$ (2). Complex 2 was synthesized from $[\text{Ir}(\text{dfppy})_2\text{Cl}]_2$ (122 mg, 0.1 mmol) and Me-pybi (52 mg, 0.25 mmol) in a mixture of $\text{CH}_2\text{Cl}_2/\text{MeOH}$ under nitrogen followed by ion exchange from Cl^- to PF_6^- . Yield: 166 mg, 0.18 mmol, 90%. ^1H NMR (500 MHz, CD_2Cl_2) δ (ppm): 8.64 (d, $J = 8.19$ Hz, 1H), 8.32 (d, $J = 8.35$ Hz, 1H), 8.28–8.24 (m, 3H), 8.07 (d, $J = 1.74$ Hz, 1H), 7.83–7.75 (m, 2H), 7.60 (d, $J = 8.46$ Hz, 1H), 7.53–7.48 (m, 2H), 7.18–7.15 (m, 2H), 7.05–6.97 (m, 3H), 6.83–6.89 (m, 3H), 6.38 (d, $J = 8.28$ Hz, 1H), 4.45 (s, 3H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ (ppm): 164.7, 163.2, 161.1, 155.1, 152.4, 151.1, 150.1, 149.3, 147.4, 140.7, 139.5, 139.4, 139.3, 137.1, 128.8, 126.9, 126.2, 124.2, 124.0, 123.8, 118.1, 114.9, 114.2, 112.1, 99.5, 33.9. Anal. calcd (%) for

$\text{C}_{35}\text{H}_{23}\text{N}_5\text{PF}_{10}\text{Ir}$, C 45.36, H 2.50, N 7.56; found, C 45.41, H 2.55, N 7.65.

2.3.3. Synthesis of $[\text{Ir}(\text{ppy})_2(\text{Eth-pybi})]\text{PF}_6$ (3). The synthesis of 3 was similar to that of 1, except that Me-pybi was replaced by Eth-pybi. Yield: 148 mg, 0.17 mmol, 85%. ^1H NMR (500 MHz, CD_2Cl_2) δ (ppm): 8.43 (d, $J = 7.1$ Hz, 1H), 8.25–8.22 (m, 1H), 8.12 (d, 4.3 Hz, 1H), 7.96 (d, $J = 8.0$ Hz, 1H), 7.90 (d, $J = 7.95$ Hz, 2H), 7.78–7.70 (m, 4H), 7.65–7.60 (m, 2H), 7.50–7.44 (m, 2H), 7.14–7.04 (m, 3H), 6.99–6.90 (m, 4H), 6.42–6.30 (m, 3H), 4.98 (q, $J = 7.18$ Hz, 7.17 and 7.17 Hz, 2H), 1.71 (t, $J = 7.32$ and 7.32 Hz, 3H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ (ppm): 168.4, 152.6, 151.7, 149.9, 149.0, 147.4, 147.3, 144.6, 144.5, 140.0, 138.4, 137.2, 132.7, 131.9, 131.1, 130.4, 128.5, 126.6, 125.7, 125.1, 123.7, 122.8, 120.1, 118.7, 111.9, 39.8, 24.7. Anal. calcd (%) for $\text{C}_{36}\text{H}_{29}\text{N}_5\text{PF}_6\text{Ir}$, C 49.77, H 3.36, N 8.06; found, C 49.79, H 3.39, N 8.01.

2.3.4. Synthesis of $[\text{Ir}(\text{dfppy})_2(\text{Eth-pybi})]\text{PF}_6$ (4). Complex 4 was synthesized by reacting $[\text{Ir}(\text{dfppy})_2\text{Cl}]_2$ and Eth-pybi. Yield: 174 mg, 0.19 mmol, 92%. ^1H NMR (500 MHz, CD_2Cl_2) δ (ppm): 8.63 (d, $J = 4.76$ Hz, 1H), 8.48 (d, $J = 8.3$ Hz, 1H), 8.34–8.26 (m, 3H), 8.16 (d, $J = 1.74$ Hz, 1H), 8.10–8.07 (m, 2H), 7.84–7.64 (m, 4H), 7.56–7.47 (m, 2H), 7.06–6.97 (m, 2H), 6.69–6.60 (m, 3H), 6.51 (d, 8.35 Hz, 1H), 4.98 (q, $J = 7.22$ Hz, 7.22 and 7.21 Hz, 2H), 1.71 (t, $J = 7.32$ and 7.32 Hz, 3H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ (ppm): 164.7, 163.2, 161.0, 155.1, 152.4, 151.1, 150.1, 149.3, 147.4, 140.7, 139.5, 139.4, 139.2, 137.1, 128.9, 126.9, 126.2, 124.2, 124.0, 123.8, 118.1, 114.9, 114.2, 112.1, 99.5, 39.8, 24.7. Anal. calcd (%) for $\text{C}_{36}\text{H}_{25}\text{N}_5\text{PF}_{10}\text{Ir}$, C 45.96, H 2.68, N 7.44; found, C 45.93, H 2.73, N 7.49.

2.3.5. Synthesis of $[\text{Ir}(\text{ppy})_2(\text{Oct-pybi})]\text{PF}_6$ (5). Complex 5 was synthesized by reacting $[\text{Ir}(\text{ppy})_2\text{Cl}]_2$ and Oct-pybi. Yield: 162 mg, 0.17 mmol, 85%. ^1H NMR (500 MHz, CD_2Cl_2) δ (ppm): 8.37 (d, $J = 8.23$ Hz, 1H), 8.24–8.20 (m, 1H), 8.1 (d, 5.43 Hz, 1H), 7.96 (d, $J = 7.92$ Hz, 1H), 7.89 (d, $J = 7.88$ Hz, 2H), 7.78–7.69 (m, 4H), 7.64–7.62 (m, 1H), 7.59 (d, $J = 8.44$ Hz, 1H), 7.49–7.43 (m, 2H), 7.14–7.04 (m, 3H), 6.99–6.90 (m, 4H), 6.42–6.32 (m, 3H), 4.84–4.74 (m, 2H), 2.12–1.98 (m, 4H), 1.54–1.43 (m, 6H), 1.39–1.19 (m, 2H), 0.86 (t, $J = 6.88$ and 6.88 Hz, 3H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ (ppm): 168.3, 152.7, 151.8, 151.5, 149.7, 148.9, 147.5, 144.6, 144.4, 140.1, 138.4, 136.9, 132.6, 131.9, 131.1, 130.5, 128.5, 126.7, 125.8, 125.2, 123.7, 122.9, 120.1, 118.8, 111.9, 46.6, 32.1, 30.2, 29.5, 27.1, 22.9, 14.2. Anal. calcd (%) for $\text{C}_{42}\text{H}_{41}\text{N}_5\text{PF}_6\text{Ir}$, C 52.93, H 4.34, N 7.35; found, C 52.97, H 4.36, N 7.42.

2.3.6. Synthesis of $[\text{Ir}(\text{dfppy})_2(\text{Oct-pybi})]\text{PF}_6$ (6). Complex 6 was synthesized by reacting $[\text{Ir}(\text{dfppy})_2\text{Cl}]_2$ and Oct-pybi. Yield (186 mg, 0.18 mmol, 91%). ^1H NMR (500 MHz, CD_2Cl_2) δ (ppm): 8.44 (d, $J = 8.22$ Hz, 1H), 8.24–8.20 (m, 3H), 8.11 (d, $J = 5.36$ Hz, 1H), 7.85–7.77 (m, 3H), 7.66–7.62 (m, 2H), 7.56–7.47 (m, 3H), 7.19 (t, $J = 7.79$ and 7.79 Hz, 1H), 7.05–6.96 (m, 2H), 6.68–6.60 (m, 3H), 6.51 (d, 8.38 Hz, 1H), 4.87–4.76 (m, 2H), 2.09–1.98 (m, 4H), 1.49–1.43 (m, 6H), 1.40–1.19 (m, 2H), 0.90 (t, $J = 6.99$ and 6.99 Hz, 3H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ (ppm): 164.8, 162.8, 161.0, 155.2, 152.6, 151.7, 151.3, 149.8, 149.1, 147.1, 140.9, 139.5, 139.4, 139.2, 136.9, 128.9, 127.0, 125.8, 124.3, 124.1, 123.9, 118.3, 114.9, 114.2, 112.2, 99.5, 46.7, 32.1, 30.2, 29.5, 27.1, 22.9, 14.2. Anal. calcd (%) for $\text{C}_{42}\text{H}_{37}\text{N}_5\text{PF}_{10}\text{Ir}$, C 49.22, H 3.64, N 6.83; found, C 49.25, H 3.68, N 6.78.

2.4. Fabrication and Characterization of LEC Devices. LEC devices were fabricated using poly(3,4-ethylenedioxythiophene):poly styrenesulfonate (PEDOT:PSS) as the buffer layer and iridium complexes as light emitting layer materials. PEDOT:PSS (Clevios AI 4083) solutions were also used as hole conducting materials to smooth the anodic indium tin oxide (ITO) surfaces.⁴² Prior to the fabrication process, ITO glass plates were cleaned in an ultrasonic bath containing mixed solvents such as ethanol, acetone, and isopropyl alcohol for 30 min followed by UV–ozone treatment for 20 min. The PEDOT:PSS solutions were then spin coated onto the ITO surfaces at 2000 rpm for 20 s and baked at 120 °C for 10 min. The active layer solutions were prepared separately in acetonitrile using 20 mg of the complexes (1–6) with a concentration of 0.022 M. The solutions were kept inside the shaking incubator for 24 h and then filtered using a 0.1 μm PTFE filter. These solutions were then spin coated onto the top of the ITO/PEDOT:PSS layer and subjected to an annealing process at 70 °C for

1 h in a vacuum oven. The samples were then transferred to a thermal evaporator where aluminum (100 nm) deposition was conducted using a shadow mask under high vacuum. The resulting devices exhibited the structure of ITO/PEDOT:PSS/iTMCs/Al. The electroluminescent properties of these devices were evaluated using Keithley characterization systems. The current density and luminance versus voltage sweeps were measured using a Keithley 2400 source meter and calibrated with a silicon photodiode. An Avantes luminance spectrometer was used to measure the EL spectrum and Commission Internationale de L'Eclairage (CIE) coordinates.

3. RESULTS AND DISCUSSION

3.1. Photophysical Properties. The room-temperature UV–vis absorption spectra of complexes 1–6 in acetonitrile are shown in Figure 1. The absorption spectra of complexes 1, 3,

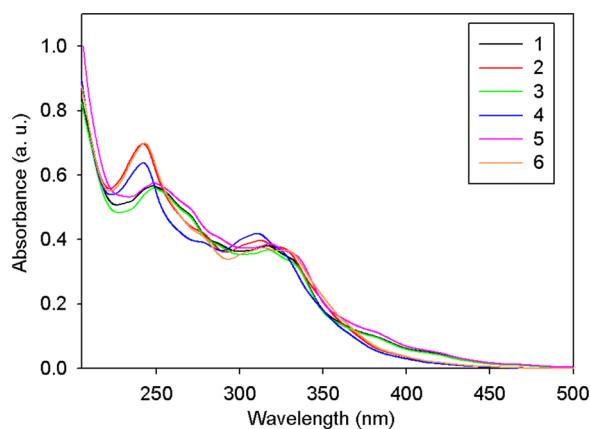


Figure 1. UV–vis absorption spectra of cationic iridium complexes 1–6 in acetonitrile at room temperature.

and 5 show similar absorption bands that vary from those of complexes 2, 4, and 6 and differ from one another according to the length of the alkyl chain on the ancillary ligand. However, complexes 1–6 all displayed broad and intense absorption bands in the UV region of the spectrum (200–350 nm). These bands were attributed to the spin-allowed ligand-centered (LC) $^1\pi-\pi^*$ transitions of both the cyclometalated and ancillary ligands. Weak absorption bands were observed starting at 360 nm and extending into the visible region, and they corresponded to the spin-allowed metal-to-ligand charge transfer ($^1\text{MLCT}$), spin-forbidden metal-to-ligand charge transfer ($^3\text{MLCT}$), ligand-to-ligand charge-transfer ($^3\text{LLCT}$ and $^1\text{LLCT}$), and ligand-centered (LC) $^3\pi-\pi^*$ transitions of the complexes.⁴⁹ The absorption spectra of complexes 2, 4, and 6 were significantly blue-shifted by approximately 20 nm compared to those of phenylpyridine complexes such as 1, 3, and 5, because of the presence of electron withdrawing fluorine atoms on the cyclometalated ligands. Although different alkyl groups were present on the ancillary ligand, the ligand did not display any significant differences in the absorption properties of the complexes, indicating that the absorption spectra were independent of the alkyl chain length.

Figure 2 displays the PL emission spectra of complexes 1–6 in acetonitrile (10^{-5} M) at room temperature. The emission spectra of the complexes exhibited broad and featureless emission peaks for complexes 1–6, which indicated that the emissive excited states have $^3\text{MLCT}$ or $^3\text{LLCT}$ characteristics instead of LC $^3\pi-\pi^*$ characteristics.^{50,51} The photophysical characteristics of complexes 1–6 are summarized in Table 1. The emission spectra of complexes 1 (572 nm), 3 (579 nm),

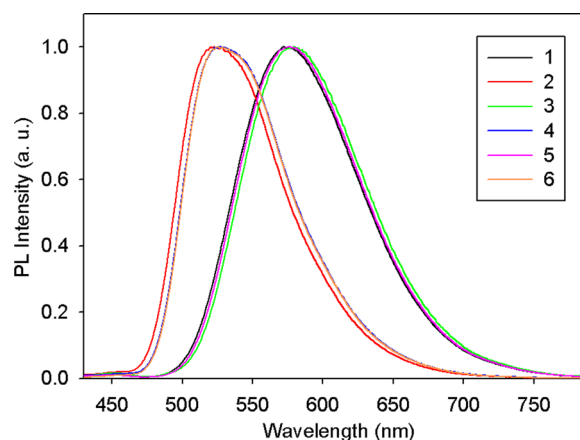


Figure 2. Photoluminescence (PL) emission spectra of cationic iridium complexes 1–6 in acetonitrile at room temperature.

and 5 (576 nm) exhibited similar emission characteristics with yellow emission, despite three different sizes of alkyl groups being attached to the imidazole-based ancillary ligand. These results confirm that the addition of the alkyl groups with varying chain lengths do not affect the emission maxima of these complexes. Similar trends were also observed for complexes 2, 4, and 6 with emission maxima at 522, 527, and 526 nm, respectively, which correspond to green emission. The emission spectra of complexes 2, 4, and 6 were blue-shifted approximately 50 nm compared to those of complexes 1, 3, and 5, because of the presence of electron withdrawing fluorine atoms on the cyclometalated ligands, which significantly affected the energy levels of these complexes. In addition, PL quantum yields (PLQYs) of complexes 1–6 were measured and show high quantum yields of 0.40–0.54 in acetonitrile solutions. Among the complexes, 5 exhibits higher PLQYs of 0.54, indicating that the rigidity of octyl group in the imidazole based ancillary ligand, which is beneficial for reducing nonradiative deactivation processes.

3.2. Electrochemical Properties. The electrochemical properties of complexes 1–6 were evaluated by cyclic voltammetry and the redox potentials were measured versus ferrocenium/ferrocene (Fc^+/Fc) using 0.1 M TBAPF₆ in acetonitrile. The measured redox potentials are listed in Table 1. As shown in Figure 3, complexes 1–6 exhibited reversible oxidation and reduction processes in acetonitrile, attributed to the transportation of both holes and electrons, which are beneficial for the incorporation of these complexes into LECs.²² Complexes 1, 3, and 5 show almost the same oxidation peaks with corresponding peak potentials of 1.18, 1.16, and 1.18 V, respectively, which can be attributed to the oxidation of Ir(III) to Ir(IV) with minor contributions from the cyclometalated ligand. Alternatively, the oxidation potentials of complexes 2, 4, and 6 are anodically shifted to 1.49, 1.49, and 1.51 V, respectively. The higher oxidation potentials of these complexes are attributed to the presence of electron withdrawing fluorine atoms that reduce the electron density around the iridium center and therefore inhibit the oxidation of complexes.^{52,53} Similarly, the complexes exhibited reversible reduction peaks at -1.63 V (1), -1.53 V (2), -1.61 V (3), -1.56 V (4), -1.64 V (5), and -1.49 V (6) because of the reduction of the ancillary ligands. Additionally, each complex exhibited a peak at approximately -1.10 V that can be attributed to the reduction of the cyclometalated ligand. The

Table 1. Photophysical and Electrochemical Properties of Cationic Iridium Complexes 1–6

complex	absorbance, λ (nm)	PL emission, λ_{max} (nm)	PL quantum yield (Φ_p)	electrochemical data		
				E_{ox} (V)	E_{red} (V)	E_{gap}
1	248, 317, 385, 420	572	0.45	1.18	-1.63 -1.12	2.81
2	242, 275, 312, 400	522	0.40	1.49	-1.53 -1.05	3.02
3	249, 319, 383, 421	579	0.43	1.16	-1.61 -1.10	2.77
4	242, 276, 310, 397	527	0.41	1.49	-1.56 -1.10	3.05
5	249, 319, 381, 420	576	0.54	1.18	-1.64 -1.11	2.82
6	242, 276, 312, 403	526	0.50	1.51	-1.49 -1.02	3.0

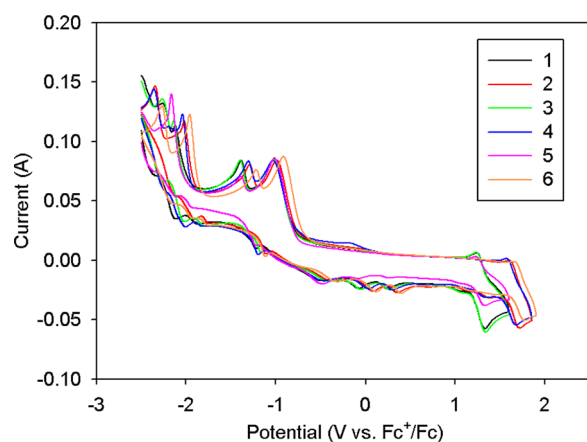


Figure 3. Cyclic voltammograms of cationic iridium complexes 1–6 in acetonitrile (10^{-3} M). The potentials were recorded versus Fc^+/Fc (Fc is ferrocene).

HOMO and LUMO energies and the electrochemical energy gaps (E_{gap}) of the complexes were calculated from their corresponding oxidation and reduction potentials. The calculated HOMO–LUMO energy gaps of the complexes

were 2.81 V (1), 3.02 V (2), 2.77 V (3), 3.05 V (4), 2.82 V (5), and 3.0 V (6). The E_{gap} of complexes 1, 3, and 5 were similar, which indicates the alkyl chain lengths do not significantly affect the electrochemical properties of the complexes, as seen in complexes 2, 4, and 6. However, a large difference in energy gaps was observed between these two classes of complexes, arising from the electron withdrawing fluorine atoms, which caused significant HOMO stabilization compared to that in complexes 1, 3, and 5.

3.3. Density Functional Theory (DFT) Calculations. To gain insight into the photophysical and electrochemical properties of the iridium complexes, we performed DFT calculations using the Gaussian 09 suite of programs. The geometries of the complexes were optimized by using the B3LYP functional, and the Ir atom was treated by the LANL2DZ basis set, while all other atoms were treated by the 6-31G(d,p) basis set. The energy and electron density contours calculated for the HOMO and the LUMO of complexes 1–5 in the ground state are displayed in Figure 4. As shown in Figure 4, the HOMOs of all complexes were located on the t_{2g} orbitals of iridium ion and phenyl π orbitals of cyclometalated ligands, which were consistent with other previously reported complexes.^{35,47} However, complexes 2 and

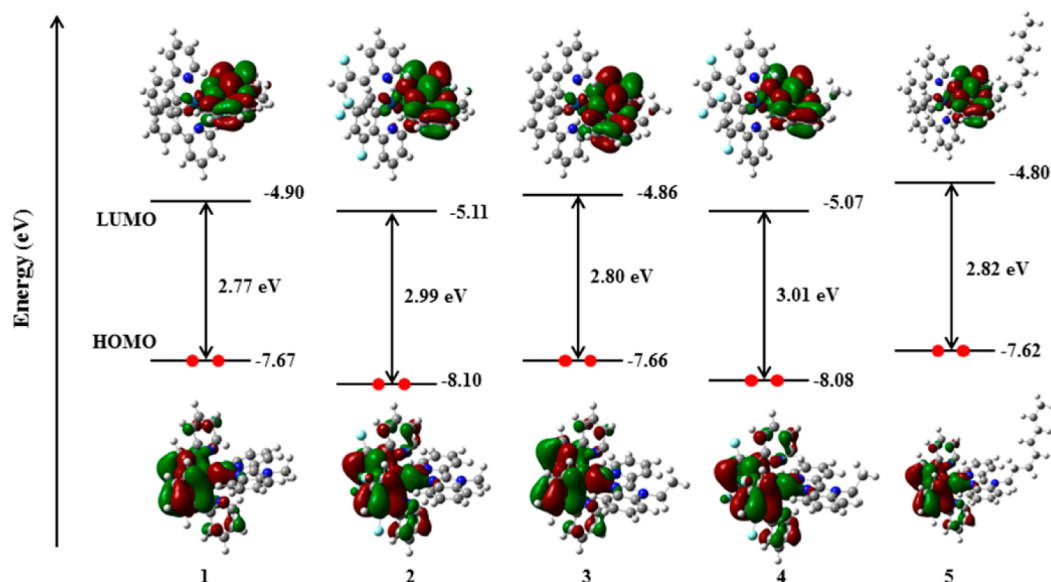


Figure 4. Energy and electron density contours calculated for the HOMOs and the LUMOs of complexes 1–5 in the ground state.

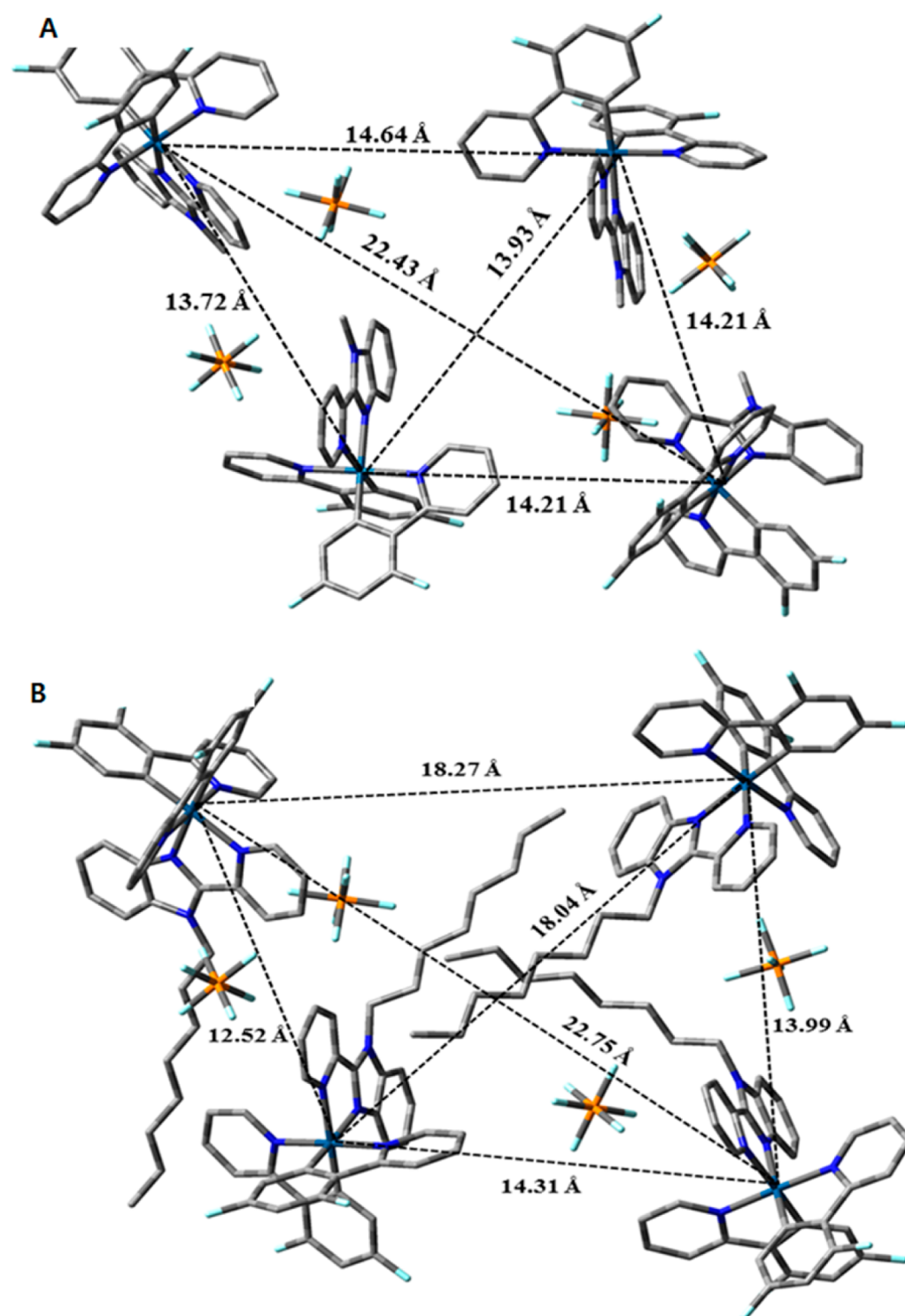


Figure 5. Arrangement and intermolecular distance of optimized packing structure of four molecules of complexes (A) 2 and (B) 6 in tetragonal form.

4 exhibited a significant stabilization of the HOMO by lowering its energy due to their electron withdrawing fluorine atoms. In contrast to HOMO, the electron density contribution of the LUMOs of all complexes lies on the π^* orbital of the ancillary ligand. The LUMO+1 were calculated for all complexes, which are slightly above the LUMO orbitals and exhibited similar electron density distributions as the LUMO orbitals. However, the LUMO+2 orbitals of all complexes differed from the LUMO orbitals, which were located on the t_{2g} orbitals of

iridium ion and phenyl π orbitals of cyclometalated ligands. The HOMO–LUMO energy gaps were calculated for the series of complexes and exhibited the same trend that was observed in the electrochemical energy gaps: 1 (2.77 eV), 2 (2.99 eV), 3 (2.80 eV), 4 (3.01 eV), and 5 (2.82 eV). These results confirm that the alkyl chain length does not significantly increase the energy gaps of the complexes; however, a blue-shift in energy levels was observed only by replacing the cyclometalated ligands from ppy to dfppy.

To study the intermolecular interactions between iridium complexes having varying chain lengths, we performed theoretical calculations using semiempirical method (PM6 method). The interaction energies were measured for the optimized structures and were found to decrease from methyl to octyl group with energies of 56.68 kJ/mol for the complex having methyl side chain, 55.84 kJ/mol for ethyl side chain, and 37.6 kJ/mol for octyl side chain. This indicates the decreased intermolecular interaction for the complexes containing octyl side chain. The intermolecular distances for the optimized geometry were also calculated. The intermolecular distance of optimized packing structure of the tetramer for both methyl and octyl substituted complexes are shown in Figure 5. In the structures, the Ir atoms are at the corners of a rhombus for methyl substituted compound (complex 2) and at the corners of a trapezium for the octyl substituted compound (complex 6). In the case of complex 6, the Ir–Ir distances between diagonal molecules are 18.04 and 22.75 Å, which has greatly increased compared to that of complex 2 (13.93 and 22.43 Å, respectively) indicating the reduced steric interactions of the complex containing octyl side chains.

3.4. Electroluminescent Properties of LECs. LECs were fabricated for studying the effects of the alkyl chain length on the electroluminescent properties of complexes 1–6. The resulting devices had a structure of ITO/PEDOT:PSS(40 nm)/iTMC(75 nm)/Al. Figure 6 displays the EL spectra of the

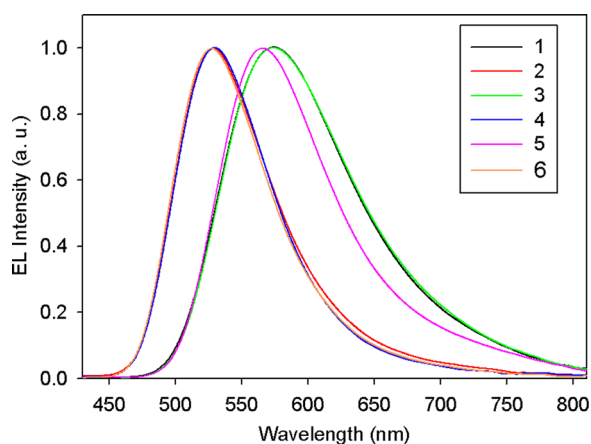


Figure 6. Electroluminescence (EL) spectra of the ITO/PEDOT:PSS/cationic iridium complexes 1–6/Al.

LECs incorporating the cationic iridium complexes 1–6, which produced broad and unstructured emission peaks that resembled the PL spectra in acetonitrile. The detailed electrical characteristics of the complexes are shown in Table 2. LECs

Table 2. Electrical Characteristics of the LECs Containing Cationic Iridium Complexes 1–6.

complex	maximum luminance (cd m ⁻²)	maximum current density (mA cm ⁻²)	maximum current efficiency (cd A ⁻¹)	EL λ_{\max} (nm)	CIE coordinates
1	2842	263.94	1.48	575	(0.49, 0.50)
2	1520	135.48	1.12	527	(0.33, 0.60)
3	2933	253.98	1.23	574	(0.49, 0.50)
4	1642	196.71	0.83	529	(0.33, 0.59)
5	7309	243.13	3.85	566	(0.47, 0.52)
6	3112	248.99	2.16	527	(0.32, 0.61)

incorporating complexes 1 and 3 exhibited similar emission properties with the maximum emission at 575 nm; however, a blue shift in the emission spectra was observed for complex 5 (which contained an octyl side group) due to the reduced intermolecular interaction compared to complexes 1 and 3.³⁵ The CIE coordinates of complexes 1, 3, and 5 were (0.49, 0.50), (0.49, 0.50), and (0.47, 0.52), respectively, and corresponded to yellow emission. However, the complexes containing dfppy cyclometalated ligands significantly shifted the emission spectra to the shorter wavelength region. LECs based on these complexes emit green light (527 nm) with CIE coordinates of (0.33, 0.60), (0.33, 0.59), and (0.32, 0.61) for complex 2, 4, and 6, respectively. The blue shift in the emission spectra of these complexes resulted from the electron withdrawing fluorine atoms that more effectively stabilized the HOMO and therefore shifted the emission color to a shorter wavelength region.

To determine any additional effects of alkyl chain length, we evaluated the electrical properties of the LECs. Figure 7

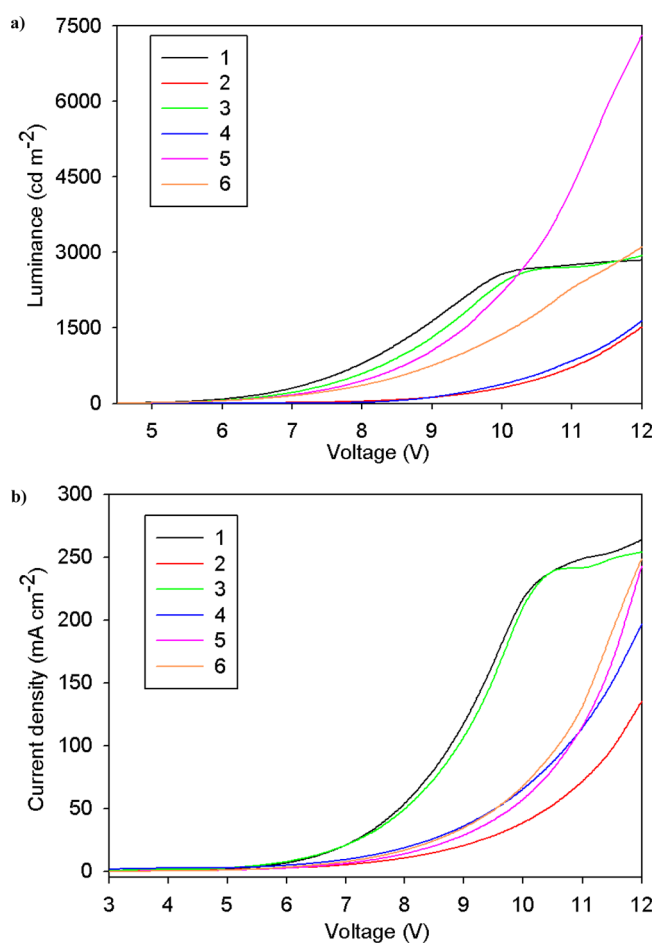


Figure 7. (a) Luminance and (b) current density versus voltage curves of ITO/PEDOT:PSS/cationic iridium complexes 1–6/Al.

displays the luminance and current density versus the voltage curves of the LEC devices with a sweep rate of 0.5 V/sec. As shown in Figure 7, the luminance and current density of the devices containing cationic iridium complexes slowly increased as the voltage increased, which is a typical characteristic of LECs.^{1,19} The stagnant nature of the LECs results from the slow mobility of counterions toward the electrode surface,

delayed carrier injection, and recombination. However, a gradual increase in luminance and current density was observed after a specific voltage was obtained, and the system subsequently reached a maximum intensity. It is important to note that the luminance of all devices increased as the chain length increased, which is due to the decreased intermolecular interactions between the molecules. When we increased the chain length from the methyl group to the octyl group, a prominent increase in luminance intensity was observed for complexes containing octyl groups as a result of the decreased intermolecular interaction between the two complex molecules. Consequently, an increased carrier injection and recombination occurred as the voltage increased. Additionally, the 2-phenylpyridine-based complex (**5**) exhibited better performances than the corresponding difluorophenylpyridine complexes because of the lower charge injection barrier of complex **5**, which promoted a more balanced charge recombination compared to that of complex **6**.

Detailed device performances are shown in Table 2. LECs incorporating complex **1** resulted in a luminance of 2842 cd m⁻², a current density of 263.94 mA cm⁻², and a peak current efficiency of 1.48 cd A⁻¹. However, the device containing **2** exhibited a luminance, current density, and current efficiency of 1520 cd m⁻², 135.48 mA cm⁻², and 1.12 cd A⁻¹, respectively. Similarly, the performance of the device containing **3** or **4** exhibited enhanced performances with a luminance of 2933 and 1642 cd m⁻², respectively. However, the current efficiencies of the LECs based on these complexes were lower than that of **1** and **2** because of the higher current density generated for these complexes. When moving from the methyl group to the octyl group, the luminance increased 2-fold with current efficiencies of 3.85 and 2.16 cd A⁻¹ for **5** and **6**, respectively. Our results suggest that the alkyl chain lengths have a significant impact on the electroluminescent properties of LECs, which reduce the intermolecular interactions between the molecules, therefore greatly enhancing the device performance of systems containing compounds with longer chains compared to that of systems containing compounds with shorter alkyl chains.

4. CONCLUSIONS

Six cationic iridium complexes with imidazole-based ancillary ligands containing various alkyl chain lengths were synthesized and incorporated into LEC devices, and the effects of chain length on the electroluminescent properties of the devices were evaluated. LECs based on these complexes resulted in yellow electroluminescence when utilizing complexes containing the ppy cyclometalated ligand (complexes **1**, **3**, and **5**). However, green emission was produced from the complexes containing dfppy cyclometalated ligands (complexes **2**, **4**, and **6**). Although the chain length did not influence the color of the complexes, it did play a pivotal role in the device performance by reducing the intermolecular interactions between iridium molecules. Consequently, a very high luminance of 7309 cd m⁻², current density of 243.13 mA cm⁻², and current efficiency of 3.85 cd A⁻¹ were observed for LECs containing complex **5**.

AUTHOR INFORMATION

Corresponding Author

*Tel.: +8251 510 2396. Fax: +8251 512 8634. E-mail: choe@pusan.ac.kr.

Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Pei, Q.; Yu, G.; Zhang, C.; Yang, Y.; Heeger, A. J. Polymer Light-Emitting Electrochemical Cells. *Science* **1995**, *269*, 1086–1088.
- (2) Sun, Q. J.; Li, Y. F.; Pei, Q. B. Polymer Light-Emitting Electrochemical Cells for High-Efficiency Low-Voltage Electroluminescent Devices. *J. Disp. Technol.* **2007**, *3*, 211–224.
- (3) Lee, J. K.; Yoo, D. S.; Handy, E. S.; Rubner, M. F. Thin Film Light Emitting Devices from an Electroluminescent Ruthenium Complex. *Appl. Phys. Lett.* **1996**, *69*, 1686–1688.
- (4) Slinker, J.; Bernards, D.; Houston, P. L.; Abruna, H. D.; Bernhard, S.; Malliaras, G. G. Solid-State Electroluminescent Devices Based on Transition Metal Complexes. *Chem. Commun.* **2003**, *19*, 2392–2399.
- (5) Slinker, J. D.; Rivnay, J.; Moskowitz, J. S.; Parker, J. B.; Bernhard, S.; Abruna, H. D.; Malliaras, G. G. Electroluminescent Devices from Ionic Transition Metal Complexes. *J. Mater. Chem.* **2007**, *17*, 2976–2988.
- (6) deMello, J. C.; Tessler, N.; Graham, S. C.; Friend, R. H. Ionic Space-Charge Effects in Polymer Light-Emitting Diodes. *Phys. Rev. B* **1998**, *57*, 12951–12963.
- (7) Rudmann, H.; Rubner, M. F. Single Layer Light-Emitting Devices with High Efficiency and Long Lifetime Based on Tris(2,2'-bipyridyl)ruthenium(II) Hexafluorophosphate. *J. Appl. Phys.* **2001**, *90*, 4338–4345.
- (8) Gao, F. G.; Bard, A. J. Solid-State Organic Light-Emitting Diodes Based on Tris(2,2'-bipyridine)ruthenium(II) Complexes. *J. Am. Chem. Soc.* **2000**, *122*, 7426–7427.
- (9) Bolink, H. J.; Cappelli, L.; Coronado, E.; Gavina, P. Observation of Electroluminescence at Room Temperature from a Ruthenium(II) Bis-Terpyridine Complex and Its Use for Preparing Light-Emitting Electrochemical Cells. *Inorg. Chem.* **2005**, *44*, 5966–5968.
- (10) Kalyuzhny, G.; Buda, M.; McNeill, J.; Barbara, P.; Bard, A. J. Stability of Thin-Film Solid-State Electroluminescent Devices Based on Tris(2,2'-bipyridine)ruthenium(II) Complexes. *J. Am. Chem. Soc.* **2003**, *125*, 6272–6283.
- (11) Soltzberg, L. J.; Slinker, J. D.; Flores-Torres, S.; Bernards, D. A.; Malliaras, G. G.; Abruna, H. D.; Kim, J. S.; Friend, R. H.; Kaplan, M. D.; Goldberg, V. Identification of a Quenching Species in Ruthenium Tris-Bipyridine Electroluminescent Devices. *J. Am. Chem. Soc.* **2006**, *128*, 7761–7764.
- (12) Lyons, C. H.; Abbas, E. D.; Lee, J. K.; Rubner, M. F. Solid-State Light-Emitting Devices Based on the Trischelated Ruthenium(II) Complex. 1. Thin Film Blends with Poly(ethylene oxide). *J. Am. Chem. Soc.* **1998**, *120*, 12100–12107.
- (13) Gao, F. G.; Bard, A. J. High-Brightness and Low-Voltage Light-Emitting Devices Based on Trischelated Ruthenium(II) and Tris(2,2'-bipyridine)osmium(II) Emitter Layers and Low Melting Point Alloy Cathode Contacts. *Chem. Mater.* **2002**, *14*, 3465–3470.
- (14) Hosseini, A. R.; Koh, C. Y.; Slinker, J. D.; Torres, S. F.; Abruna, H. D.; Malliaras, G. G. Addition of a Phosphorescent Dopant in Electroluminescent Devices from Ionic Transition Metal Complexes. *Chem. Mater.* **2005**, *17*, 6114–6116.
- (15) Armaroli, N.; Accorsi, G.; Holler, M.; Moudam, O.; Nierengarten, J. F.; Zhou, Z.; Wegh, R. T.; Welter, R. Highly Luminescent Cu^I Complexes for Light-Emitting Electrochemical Cells. *Adv. Mater.* **2006**, *18*, 1313–1316.
- (16) Kalsani, V.; Schmittel, M.; Listorti, A.; Accorsi, G.; Armaroli, N. Novel Phenanthroline Ligands and Their Kinetically Locked Copper(I) Complexes with Unexpected Photophysical Properties. *Inorg. Chem.* **2006**, *45*, 2061–2067.

- (17) Zhang, Q. S.; Zhou, Q. G.; Cheng, Y. X.; Wang, L. X.; Ma, D. G.; Jing, X. B.; Wang, F. S. Highly Efficient Electroluminescence from Green-Light-Emitting Electrochemical Cells Based on Cu^I Complexes. *Adv. Funct. Mater.* **2006**, *16*, 1203–1208.
- (18) Felici, M.; Contreras-Carballada, P.; Smits, J. M. M.; Nolte, R. J. M.; Williams, R. M.; De Cola, L.; Feiters, M. C. Cationic Heteroleptic Cyclometalated Iridium^{III} Complexes Containing Phenyl-Triazole and Triazole-Pyridine Clicked Ligands. *Molecules* **2010**, *15*, 2039–2059.
- (19) 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.
- (20) Costa, R. D.; Ortí, E.; Tordera, D.; Pertegás, 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.
- (21) He, L.; Duan, L.; Qiao, J.; Zhang, D.; Wang, L.; Qiu, Y. Enhanced Stability of Blue-Green Light-Emitting Electrochemical Cells Based on a Cationic Iridium Complex with 2-(1-Phenyl-1H-pyrazol-3-yl)pyridine as the Ancillary Ligand. *Chem. Commun.* **2011**, *47*, 6467–6469.
- (22) Chen, B.; Li, Y.; Yang, W.; Luo, W.; Wu, H. Efficient Sky-Blue and Blue-Green Light-Emitting Electrochemical Cells Based on Cationic Iridium Complexes Using 1,2,4-Triazole-pyridine as the Ancillary Ligand with Cyanogen Group in Alkyl Chain. *Org. Electron.* **2011**, *12*, 766–773.
- (23) Sun, L.; Galan, A.; Ladouceur, S.; Slinker, J. D.; Colman, E. Z. High Stability Light-Emitting Electrochemical Cells from Cationic Iridium Complexes with Bulky 5,5′ Substituents. *J. Mater. Chem.* **2011**, *21*, 18083–18088.
- (24) Zhang, J.; Zhou, L.; Al-Attar, H. A.; Shao, K.; Wang, L.; Zhu, D.; Su, Z.; Bryce, M. R.; Monkman, A. P. Efficient Light-Emitting Electrochemical Cells (LECs) Based on Ionic Iridium(III) Complexes with 1,3,4-Oxadiazole Ligands. *Adv. Funct. Mater.* **2013**, *23*, 4667–4677.
- (25) Kessler, F.; Costa, R. D.; Censo, D. D.; Scopelliti, R.; Ortí, E.; Bolink, H. J.; Meier, S.; Sarfert, W.; Grätzel, M.; Nazeeruddin, M. K.; Baranoff, E. Near-UV to Red-Emitting Charged Bis-Cyclometalated Iridium(III) Complexes for Light-Emitting Electrochemical Cells. *Dalton Trans.* **2012**, *41*, 180–191.
- (26) Sunesh, C. D.; Sunseong, O.; Chandran, M.; Moon, D.; Choe, Y. Effect of Ionic Liquids on the Electroluminescence of Yellowish-Green Light-Emitting Electrochemical Cells Using Bis(2-(2,4-difluorophenyl)pyridine)4,7-diphenyl-1,10-phenanthroline-iridium(III) Hexafluorophosphate. *Mater. Chem. Phys.* **2012**, *136*, 173–178.
- (27) Tordera, D.; Pertegas, A.; Shavaleev, N. M.; Scopelliti, R.; Ortí, E.; Bolink, H. J.; Baranoff, E.; Grätzel, M.; Nazeeruddin, M. K. Efficient Orange Light-Emitting Electrochemical Cells. *J. Mater. Chem.* **2012**, *22*, 19264–19268.
- (28) Sunesh, C. D.; Mathai, G.; Cho, Y. R.; Choe, Y. Optoelectronic Properties of Green and Yellow Light-Emitting Electrochemical Cells Based on Cationic Iridium Complexes. *Polyhedron* **2013**, *57*, 77–82.
- (29) Costa, R. D.; Ortí, E.; Bolink, H. J.; Graber, S.; Housecroft, C. E.; Constable, E. C. Light-Emitting Electrochemical Cells Based on a Supramolecularly-Caged Phenanthroline-Based Iridium Complex. *Chem. Commun.* **2011**, *47*, 3207–3209.
- (30) Sunesh, C. D.; Chandran, M.; Mathai, G.; Choe, Y. Highly Luminescent Yellow and Yellowish-Green Light-Emitting Electrochemical Cells Based on Cationic Iridium Complexes with Phenanthroline Based Ancillary Ligands. *Opt. Mater.* **2013**, *35*, 407–413.
- (31) Meier, S. B.; Sarfert, W.; Junquera-Hernández, J. M.; Delgado, M.; Tordera, D.; Ortí, E.; Bolink, H. J.; Kessler, F.; Scopelliti, R.; Grätzel, M.; Nazeeruddin, M. K.; Baranoff, E. A Deep-Blue Emitting Charged Bis-Cyclometalated Iridium(III) Complex for Light-Emitting Electrochemical Cells. *J. Mater. Chem. C* **2013**, *1*, 58–68.
- (32) Chen, B.; Li, Y.; Chu, Y.; Zheng, A.; Feng, J.; Liu, Z.; Wu, H.; Yang, W. Highly Efficient Single-Layer Organic Light-Emitting Devices Using Cationic Iridium Complex as Host. *Org. Electron.* **2013**, *14*, 744–753.
- (33) Sunesh, C. D.; Mathai, G.; Choe, Y. Green and Blue-Green Light-Emitting Electrochemical Cells Based on Cationic Iridium Complexes with 2-(4-Ethyl-2-pyridyl)-1H-Imidazole Ancillary Ligand. *Org. Electron.* **2014**, *15*, 667–674.
- (34) Su, H.; Fang, F. C.; Hwu, T. Y.; Hsieh, H. H.; Chen, H. F.; Lee, G. H.; Peng, S. M.; Wong, K. T.; Wu, C. C. Highly Efficient Orange and Green Solid-State Light-Emitting Electrochemical Cells Based on Cationic Ir^{III} Complexes with Enhanced Steric Hindrance. *Adv. Funct. Mater.* **2007**, *17*, 1019–1027.
- (35) He, L.; Qiao, J.; Duan, L.; Dong, G. F.; Zhang, D. Q.; Wang, L. D.; Qiu, Y. Toward Highly Efficient Solid-State White Light-Emitting Electrochemical Cells: Blue-Green to Red Emitting Cationic Iridium Complexes with Imidazole-Type Ancillary Ligands. *Adv. Funct. Mater.* **2009**, *19*, 2950–2960.
- (36) Costa, R. D.; Ortí, 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.
- (37) Liao, C. T.; Chen, H. F.; Su, H. C.; Wong, K. T. Improving the Balance of Carrier Mobilities of Host–Guest Solid-State Light-Emitting Electrochemical Cells. *Phys. Chem. Chem. Phys.* **2012**, *14*, 1262–1269.
- (38) Costa, R. D.; Cespedes-Guirao, F. J.; Ortí, E.; Bolink, H. J.; Gierschner, J.; Fernandez-Lazaro, F.; Sastre-Santos, A. Efficient Deep-Red Light-Emitting Electrochemical Cells Based on a Perylenediimide–Iridium-Complex Dyad. *Chem. Commun.* **2009**, 3886–3888.
- (39) Costa, R. D.; Fernandez, G.; Sanchez, L.; Martin, N.; Ortí, E.; Bolink, H. J. Dumbbell-Shaped Dinuclear Iridium Complexes and Their Application to Light-Emitting Electrochemical Cells. *Chem.—Eur. J.* **2010**, *16*, 9855–9863.
- (40) Liao, C. T.; Chen, H. F.; Su, H. C.; Wong, K. T. Tailoring Carrier Injection Efficiency to Improve the Carrier Balance of Solid-State Light-Emitting Electrochemical Cells. *Phys. Chem. Chem. Phys.* **2012**, *14*, 9774–9784.
- (41) Su, H. C.; Lin, Y. H.; Chang, C. H.; Lin, H. W.; Wu, C. C.; Fang, F. C.; Chen, H. F.; Wong, K. T. Solid-State Light-Emitting Electrochemical Cells Employing Phosphor-Sensitized Fluorescence. *J. Mater. Chem.* **2010**, *20*, 5521–5526.
- (42) 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.
- (43) Costa, R. D.; Ortí, 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.
- (44) Hu, T.; He, L.; Duan, L.; Qiu, Y. Solid-State Light-Emitting Electrochemical Cells Based on Ionic Iridium(III) Complexes. *J. Mater. Chem.* **2012**, *22*, 4206–4215.
- (45) Liu, Y.; Liu, M. S.; Jen, A. K.-Y. Synthesis and Characterization of a Novel and Highly Efficient Light-Emitting Polymer. *Acta Polym.* **1999**, *50*, 105–108.
- (46) Hwang, S. W.; Chen, Y. Synthesis and Electrochemical and Optical Properties of Novel Poly(aryl ether)s with Isolated Carbazole and *p*-Quaterphenyl Chromophores. *Macromolecules* **2001**, *34*, 2981–2986.
- (47) Nonoyama, M. Benzo[*h*]quinolin-10-yl-*N*-iridium(III) Complexes. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 767–768.
- (48) Sprouse, S.; King, K. A.; Spellane, P. J.; Watts, R. J. Photophysical Effects of Metal-Carbon σ bonds in Ortho-Metalated Complexes of Ir(III) and Rh(III). *J. Am. Chem. Soc.* **1984**, *106*, 6647–6653.
- (49) He, L.; Duan, L.; Qiao, J.; Wang, R.; Wei, P.; Wang, L.; 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.

(50) Colombo, M. G.; Gudel, H. U. Synthesis and High-Resolution Optical Spectroscopy of Bis[2-(2-thienyl)pyridinato-C3,N'](2,2'-bipyridine)iridium(III). *Inorg. Chem.* **1993**, *32*, 3081–3087.

(51) Lowry, M. S.; Hudson, W. R.; Pascal, R. A.; Bernhard, S. Accelerated Luminophore Discovery Through Combinatorial Synthesis. *J. Am. Chem. Soc.* **2004**, *126*, 14129–14135.

(52) Adachi, C.; Kwong, R. C.; Djurovich, P.; Adamovich, V.; Baldo, M. A.; Thompson, M. E.; Forrest, S. R. Endothermic Energy Transfer: A Mechanism for Generating Very Efficient High-Energy Phosphorescent Emission in Organic Materials. *Appl. Phys. Lett.* **2001**, *79*, 2082–2084.

(53) 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.