Push-Pull Design of Bis(tridentate) Ruthenium(II) Polypyridine Chromophores as Deep Red Light Emitters in Light-Emitting Electrochemical Cells


Dedicated to Professor Rudolf Zentel on the occasion of his 60th birthday

Keywords: Ruthenium / Molecular electronics / Tridentate ligands / Luminescence / N ligands

Light-emitting electrochemical cells (LECs) with a simple device structure were prepared by using heteroleptic bis(tridentate) ruthenium(II) complexes [1](PF$_6$)$_2$-[3](PF$_6$)$_2$ as emitters. The push-pull substitution shifts the emission energy to low energy, into the NIR region. The devices emit deep red light up to a maximum emission wavelength of 755 nm [CIE (International Commission on Illumination) coordinates: x = 0.731, y = 0.269 for [3](PF$_6$)$_2$], which, to the best of our knowledge, is the lowest emission energy for LECs containing bis(tridentate) ruthenium(II) complexes. A device structure of ITO/PEDOT:PSS/ruthenium(II) complex/Ag was used, and the thickness of the emitting layer was measured by AFM [ITO: indium tin oxide, PEDOT: poly(3,4-ethylenedioxythiophene), PSS: poly(styrenesulfonate), AFM: atomic force microscopy]. To enhance the external quantum efficiency (EQE), cells were fabricated with and without poly(methyl methacrylate) (PMMA) as additive in the emitting layer.

Introduction

Light-emitting electrochemical cells (LECs) provide a low-cost alternative to conventional organic light emitting devices (OLEDs) due to their simple device structures and solution processability. LECs feature an ionic emitting layer that enables low turn-on and driving voltages, as well as independence of the work function of electrode materials.[1–6] LECs introduced in 1995 by Pei contained organic polymers as emitters.[7,8] While for all-organic emitters spin statistics predicts a maximum internal quantum efficiency of 25%, transition metal complexes have a theoretical limit of 100%, because in the latter both singlet and triplet excitons can lead to light emission.[9–12] The first LEC with an ionic transition metal complex was reported in 1996 by Lee employing a [Ru(phen)$_3$]$^{2+}$ derivative as emitter (phen: 1,10-phenanthroline).[13] The use of ruthenium(II) complexes as emitters is reasonable because of their outstanding photophysical and electrochemical properties combined with their high thermal and chemical stabilities.[14] So far [Ru(bpy)$_3$]$^{2+}$ (bpy: 2,2’-bipyridine) and its analogues are the most studied ruthenium(II) polypyridine complexes because they have high 3MLCT (MLCT: metal-to-ligand charge transfer) excited state lifetimes ($\tau \approx 1 \mu s$) and luminescence quantum yields ($\Phi = 10\%$) at room temperature in solution.[14–16] [Ru(bpy)$_3$]$^{2+}$ and its derivatives have already been used in LECs showing high external quantum efficiencies (EQEs) of up to 6.4%.[17–20]

However, [Ru(bpy)$_3$]$^{2+}$ is chiral ($\Delta$, $\Lambda$), and unsymmetrical substitution of bpy ligands leads to the formation of stereoisomers, which complicates synthetic procedures.[21,22] The formation of stereoisomers can be avoided by using tridentate, meridional coordinating ligands. For instance achiral [Ru(tpy)$_3$]$^{2+}$ (tpy: 2,2′:6′,2′-terpyridine) gives rise to only a single isomer even in the case of unsymmetrical substitution of the tpy 4′-positions.[23] Additionally, the tridentate coordination provides a higher photostability and
chemical stability relative to the bidentate mode.[24,25] This should prevent thermal and photoinduced ligand exchange, favoring longevity of luminescent and solar cell devices.[26–28] Degradation products due to ligand loss have been identified in LECs with [Ru(bpy)3]2+ complexes, namely bis(aqua)complex [Ru(bpy)2(H2O)2]2+ and oxido-bridged dimer [(Ru(bpy)2(H2O))2O]4+, which have been formed by photoaquation in the presence of water.[16,30–32]

A better stabilization towards (photo) ligand substitution might be achieved by using tridentate ligands.

Unfortunately, excited state features of [Ru(tpy)2]3+ in solution are very unfavorable ($\tau = 0.1–0.2$ ns, $\Phi \approx 0.0005\%$) because of rapid radiationless deactivation of the radiative 3MLCT states via thermally accessible 3MC states (MC: metal-centered; Figure 1).[33,34] Increased excited state lifetimes $\tau$ and quantum yields $\Phi$ have been obtained by structurally modifying [Ru(tpy)2]3+ in order to increase the energy difference between the 3MLCT and 3MC states and hence to avoid radiationless deactivation via the latter states. Push-pull substitution like that in [{(EtOOC-tpy)-Ru(tpy-NH2)2}]2+ (I)(PF6)2, Figure 2) is favorable, as the electron-withdrawing ester group lowers the energy of the 3MLCT state while the electron-donating amino group increases the energy of the 3MC state, thus reducing radiationless deactivation via the latter state and enhancing the excited state lifetime and luminescence quantum yield significantly ($\tau = 34$ ns, $\Phi = 0.18\%$).[35–37] Another strategy employs a strong ligand field to increase the energy difference between the 3MLCT and 3MC states. This can be achieved by N–Ru–N bite angles of 90° as in an ideal octahedron allowing for an optimal overlap of ruthenium and nitrogen orbitals. The N–Ru–N bite angle of tpy is 79° because its five-membered chelate rings result in a suboptimal octahedron orbital overlap.[38] Hammarström et al. designed a complex [{(Ru(dpq)2)]2+: dpq: 2,6-di(quinolin-8-yl)pyridine} with six-membered chelate rings and 90° bite angles featuring high room-temperature lifetime and quantum yield in solution ($\tau = 3.0$ μs, $\Phi = 2\%$).[39,40] The substituted complex [Ru(dpq-COOEt)2]2+ with ester substituents on the 4’-positions reaches even higher values ($\tau = 5.5$ μs, $\Phi = 7\%$).[41] Ruben et al. incorporated carbonyl bridges between the pyridine rings of [Ru(tpy)2]3+ and thus obtained six-membered chelate rings and 90° bite angles leading to high 3MLCT lifetimes and, to the best of our knowledge, to the highest reported quantum yield of bis(tridentate) ruthenium(II) complexes ($\tau = 3.3$ μs, $\Phi = 30\%$).[42] Bis(tridentate) ruthenium(II) complexes have been incorporated in LECs, but until now only complexes with small bite angles (ca. 79°) and hence low solution luminescence quantum yields have been utilized, leading to low EQEs ($\approx 0.1\%$) of the devices.[43–45]

In this paper, we incorporate bis(tridentate) ruthenium(II) complexes [I][PF6]2–[3][PF6]2 as low-energy emitters in LECs (Figure 2). [I][PF6]2–[3][PF6]2 are photostable and chemically stable as a result of their tridentate coordination mode; they feature a sophisticated push-pull substitution with high directionality due to electron-withdrawing ester and electron-donating amino groups.[35–37,46–48] The push-pull substitution lowers the HOMO–LUMO gap (and hence the energy difference between the 3MLCT and 3MC states) and leads to emission in the red spectral region ($\lambda_{em} = 729–744$ nm, Table 1).[35,36,46,47] Red light and NIR emission are particularly favorable for noninvasive bioimaging, telecommunication, night-vision-readable displays, downconversion and triplet–triplet annihilation upconversion.[1,2,49–57] However, according to the energy gap law, low-energy emission is correlated to low luminescence quantum yields and short luminescence lifetimes due to effective radiationless deactivation into the ground state.[58–60] In spite of their low emission energy, complexes [I][PF6]2–[3][PF6]2 possess comparably high luminescence lifetimes and quantum yields at room temperature in solution ($\tau = 34$, 722, and 841 ns; $\Phi = 0.18$, 0.45, and 1.1%, Table 1).

Table 1. Electrochemical and photophysical properties of complexes [1](PF6)2–[3](PF6)2.

<table>
<thead>
<tr>
<th></th>
<th><a href="PF6">1</a>2</th>
<th><a href="PF6">2</a>2</th>
<th><a href="PF6">3</a>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>E1/2red /V[a]</td>
<td>+0.68</td>
<td>+0.81</td>
<td>+0.92</td>
</tr>
<tr>
<td>E1/2ox /V[a]</td>
<td>–1.54</td>
<td>–1.47</td>
<td>–1.25[b]</td>
</tr>
<tr>
<td>λa(295K) /nm[c/d]</td>
<td>502 (19080)</td>
<td>517 (7500)</td>
<td>539 (6360), 475 (5060)</td>
</tr>
<tr>
<td>φ(295K) /%[c]</td>
<td>0.18</td>
<td>0.45</td>
<td>1.1</td>
</tr>
<tr>
<td>τ(295K) /ns</td>
<td>34[c]</td>
<td>722[d]</td>
<td>841[d]</td>
</tr>
</tbody>
</table>

[a] In 0.1 M [nBu4N][PF6] in CH3CN vs. Fe/Fc+. [b] Irreversible, Eo given. [c] In CH3CN. [d] In PrCN.

Results and Discussion

The electrochemical and photophysical properties of complexes [1](PF6)2–[3](PF6)2 have been described previously and are summarized in Table 1. The oxidation potential, E1/2ox, follows the same order as those for the trend in the HOMO and LUMO energies calculated by DFT (B3LYP/LANL2DZ, IEFPCM, CH3CN).

HOMO energies calculated by DFT (B3LYP/LANL2DZ, IEFPCM, CH3CN) are lower (0.2–0.3 eV) and LUMO energies are higher (0.3–0.4 eV) than values obtained from electrochemical data. Nevertheless, the trend of the HOMO and LUMO energies (EHOMO and ELUMO) is correctly reproduced: [1]2+ > [2]2+ > [3]2+.

The injection of electrons and holes from opposite electrodes leads to the formation of radical species. Electron capture and loss both occur on the doubly charged ruthenium complex cation. Reduction is located at the ester-substituted tpy ligands, while oxidation is essentially confined to the ruthenium center. Spin densities calculated by DFT are exemplarily depicted for complex [3]2+ in its reduced and oxidized forms ([3]2+ and [3]3+; Figures 4a and 4b). The plot illustrates the location of reduction and oxidation processes in [3]2+. Electron transfer from [3]2+ to [3]3+ leads to one 1,3MLCT excited state species 1,3[3]2+ and in the ground state.[62] The excited 1MLCT state undergoes efficient ISC to the 2MLCT state (Figure 1).[16] Finally, the 3MLCT state emits light upon returning to the singlet ground state [3]2+ (Figure 1). The spin density of [3]2+ is located on both the ruthenium center and the ester-substituted tpy ligand (Figure 4c), which is in accord with a ruthenium(III) center and a one-electron-reduced tpy ligand.

LEC's incorporating [1](PF6)2–[3](PF6)2 were built with a configuration of ITO/PEDOT:PSS/ruthenium(II) complex/Ag (Figure 5; ITO: indium tin oxide; PEDOT: poly(3,4-ethylendioxythiophene); PSS: poly(styrenesulfonate)). PEDOT:PSS was found to increase reproducibility and shows a HOMO energy level of EHOMO = –5.1 eV.[63] Ag was used as cathode material because it greatly improves lifetimes of LECs compared to other electrode materials like Al.[20] Cells were fabricated with and without 20% (w/w) PMMA in the emitting layer [PMMA: poly(methyl methacrylate)]. PMMA acts as insulator, improves the film life span and decreases charge carrier injection.

Figure 3. HOMO and LUMO levels of complexes [1](PF6)2–[3](PF6)2 as determined by DFT calculations in CH3CN (35–46) and from electrochemical data (B3LYP/LANL2DZ, IEFPCM, CH3CN).

ΔE = 2.17 eV, HOMO and LUMO energies were also obtained by DFT calculations and are summarized in Figure 3.

E / eV vs. vacuum

-3.54
-3.61
-3.83
-3.14
-3.22
-3.51
2.22
2.28
2.17
2.89
2.78
-5.76
-5.89
-6.00
-6.05
-6.11
-6.29
1_exp
2_exp
3_exp
1_dft
2_dft
3_dft

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quality, and increases the distance between ruthenium(II) complexes to avoid self-quenching processes to enhance the EQE and to prolong device lifetimes.[18,20,44,45,64] The PEDOT:PSS and ruthenium(II) complex layers were spin-coated onto an ITO substrate. The Ag cathode was deposited in vacuo by thermal evaporation. The thicknesses of the PEDOT:PSS and the ruthenium complex:PMMA layers were determined by AFM measurements after scratching the layer with a razor (AFM: atomic force microscopy). The thicknesses are 45 ± 5 nm (PEDOT:PSS), 229 ± 19 nm (total thickness of PEDOT:PSS and ruthenium complex without PMMA), and 237 ± 23 nm (total thickness of PEDOT:PSS and ruthenium complex with PMMA). Figure 6 shows a representative AFM image of the scratched LEC with [1](PF₆)₂ and PMMA. AFM images for all scratched LECs are depicted in the Supporting Information (Figure S1).

Figure 5. General device structure of the LECs and photograph of the LEC with [1](PF₆)₂ without PMMA.

A voltage of 3 V was applied to each cell for at least 10 min. The LEC incorporating complex [2](PF₆)₂ (without PMMA) shows red light emission. The other cells did not emit under these conditions. For these cells, a higher voltage on a new pixel was applied in steps of 0.5–1 V until emission was observed. LEC characteristics are summarized in Table 2. The reported voltage is the minimum voltage for which emission is observed, and all other data refer to this voltage. Cells with [1](PF₆)₂ without PMMA do not emit up to a voltage of 6 V. When PMMA is present, the LEC with [1](PF₆)₂ emits with a turn on voltage of 4 V. The driving voltages are generally a few volts higher for cells with PMMA, which is consistent with the insulating character of PMMA.[20] Emission wavelengths of the devices are fully comparable to the emissions in solution and differ only by ΔE = ± 0.02 eV (Tables 1 and 2, Figures S2 and S3). [3](PF₆)₂ features a slightly redshifted electroluminescence in LECs in the absence of PMMA (Figure S4, Tables 1 and 2). Figure 7a exemplarily depicts the emission spectra of [2](PF₆)₂ in CH₃CN and in LECs with and without PMMA.

The longest emission wavelength maximum (λem,max = 755 nm) was obtained for the LEC with [3](PF₆)₂ without PMMA at an applied voltage of 4 V. To the best of our knowledge, this is the longest emission wavelength of a LEC with a mononuclear bis(tridentate) ruthenium(II) complex. The CIE (International Commission on Illumination) coordinates[65] of the emitted light are given in Table 2 and in all cases correspond to deep red light at the edge of the CIE chromaticity diagram. Light intensity, current density, and EQE curves are plotted against time (Supporting Information, Figures S4–S7). Exemplarily, Figure 7b shows the EQE-intensity-current density vs. time plots for the LEC with [2](PF₆)₂ without PMMA at an applied voltage of 3 V. All values increase at initial stages until they reach a maximum after a few minutes. Then they slowly decrease as typically observed for this kind of LECs.[44,45] Maximum light emission occurs after t_em,max = 2–14 min. Devices with PMMA should have a higher t_em,max than devices without PMMA, because PMMA hinders ion migration and forma-
Table 2. LEC device characteristics for complexes \([1]\)(PF\(_6\)\)_2–\([3]\)(PF\(_6\)\)_2.

<table>
<thead>
<tr>
<th></th>
<th>([1])(PF(_6))_2 without PMMA</th>
<th>([1])(PF(_6))_2 with PMMA(^{[a]})</th>
<th>([2])(PF(_6))_2 without PMMA</th>
<th>([2])(PF(_6))_2 with PMMA(^{[a]})</th>
<th>([3])(PF(_6))_2 without PMMA</th>
<th>([3])(PF(_6))_2 with PMMA(^{[a]})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Height of emitting layer /nm</td>
<td>182 ± 16</td>
<td>190 ± 12</td>
<td>168 ± 33</td>
<td>191 ± 31</td>
<td>193 ± 27</td>
<td>194 ± 12</td>
</tr>
<tr>
<td>(U) V</td>
<td>–</td>
<td>4</td>
<td>3</td>
<td>6</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>(\lambda_{\text{em,max,LEC}}) /nm</td>
<td>–</td>
<td>733(^{[55]})</td>
<td>731</td>
<td>722</td>
<td>755</td>
<td>745</td>
</tr>
<tr>
<td>(\lambda_{\text{em,max,acetonitrile}}) /nm</td>
<td>–</td>
<td>734</td>
<td>729</td>
<td>729</td>
<td>744</td>
<td>744</td>
</tr>
<tr>
<td>(t_{\text{em,max}}) /min</td>
<td>–</td>
<td>ca. 11–14</td>
<td>13</td>
<td>2</td>
<td>9</td>
<td>4</td>
</tr>
<tr>
<td>(L_{\text{em,max}}) /cd m(^{-2})</td>
<td>–</td>
<td>0.32</td>
<td>1.8</td>
<td>3.36</td>
<td>0.75</td>
<td>0.64</td>
</tr>
<tr>
<td>(t_{\text{current,max}}) /min</td>
<td>–</td>
<td>13</td>
<td>31</td>
<td>3</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>(I_{\text{d,max}}) /mA cm(^{-2})</td>
<td>–</td>
<td>313</td>
<td>103</td>
<td>518</td>
<td>213</td>
<td>231</td>
</tr>
<tr>
<td>(\text{EQE}_{\text{max}}) /%</td>
<td>–</td>
<td>0.001</td>
<td>0.016</td>
<td>0.028</td>
<td>0.007</td>
<td>0.013</td>
</tr>
<tr>
<td>(t_{\text{EQE,max}}) /min</td>
<td>–</td>
<td>14–15</td>
<td>10</td>
<td>1</td>
<td>9</td>
<td>1</td>
</tr>
<tr>
<td>CIE coordinates ((x, y))</td>
<td>–</td>
<td>0.709, 0.291</td>
<td>0.725, 0.275</td>
<td>0.717, 0.283</td>
<td>0.731, 0.269</td>
<td>0.729; 0.271</td>
</tr>
</tbody>
</table>

\(^{[a]}\) 20\% (w/w).

Figure 7. (a) Normalized emission spectra of \([2]\)(PF\(_6\)\)_2 (black squares: CH\(_3\)CN solution; red hollow circles: LEC with PMMA, 6 V; blue stars: LEC without PMMA, 3 V). (b) Current density (black squares), emission intensity (red hollow circles), and EQE (blue stars) as a function of time in the LEC with \([2]\)(PF\(_6\)\)_2 without PMMA at an applied voltage of 3 V.

The device was a Lambertian source and a calibrated Si photodiode was placed at an angle normal to the device surface.\(^{[66,67]}\)

\[
L = K_m \cdot I \cdot \frac{R}{A_{\text{LEC}}} \cdot \frac{A_{\text{photodiode}}}{A_{\text{LEC}}} \cdot \frac{\int \mathcal{V}(\lambda) S_{\text{emission}}(\lambda) \, d\lambda}{\int \mathcal{V}(\lambda) S_{\text{response}}(\lambda) \, d\lambda}
\]

where \(K_m = 683 \text{ lm W}^{-1}\) at 555 nm, \(I\): current, \(R\): distance between LEC and photodiode, \(A_{\text{LEC}}\): area of the limiting aperture, \(A_{\text{photodiode}}\): area of the photodiode, \(\mathcal{V}(\lambda)\): photopic response curve, \(S_{\text{emission}}(\lambda)\): emission spectrum, \(S_{\text{response}}(\lambda)\): responsivity of the Si photodiode, \(\lambda\): wavelength.

The highest luminance is \(L = 3.4 \text{ cd m}^{-2}\) for the LEC with \([2]\)(PF\(_6\)\)_2 with PMMA at an applied voltage of 6 V. The smaller luminance of LECs with \([1]\)(PF\(_6\)\)_2 (\(L = 0.3 \text{ cd m}^{-2}\)) is likely due to the lower luminescence quantum yield of \([1]\)(PF\(_6\)\)_2 in solution (Table 2). The lower luminance of \([3]\)(PF\(_6\)\)_2 (\(L \approx 0.7 \text{ cd m}^{-2}\)) might be due to the small overlap of its NIR emission (\(\lambda_{\text{em}} \approx 750 \text{ nm}\)) with the human eye response curve (Figure S8). The current density reaches its maximum after \(t_{\text{current,max}} = 3–31\) min. For LECs with complex \([3]\)(PF\(_6\)\)_2 there is no clear dependency of \(t_{\text{current,max}}\) on the voltage or the presence of PMMA. In contrast, \(t_{\text{current,max}}\) values in LECs with \([2]\)(PF\(_6\)\)_2 are smaller at high voltages (6 V, 3 min) and larger at lower voltages (3 V, 31 min), which confirms that ion migration is faster at higher voltages.\(^{[6]}\) Current densities are in the range \(I_d = 103–518 \text{ mA cm}^{-2}\), which is consistent with previously reported LECs with a bis(terpyridine)ruthenium(II) complex (ca. 200–300 mA cm\(^{-2}\)).\(^{[44]}\) As expected, current densities are high for high applied voltages (Table 2). EQE values are 0.001–0.028\%. The highest EQE value (0.028\%) is obtained for the LEC with \([2]\)(PF\(_6\)\)_2 with PMMA. LECs containing \([1]\)(PF\(_6\)\)_2 only lead to a small EQE (0.001\%), which is probably caused by the smaller solution quantum yield of \([1]\)(PF\(_6\)\)_2 relative to those of \([2]\)(PF\(_6\)\)_2 and \([3]\)(PF\(_6\)\)_2 (Table 1). The maximum EQE of the LEC with \([3]\)(PF\(_6\)\)_2 (0.013\%) is less than the EQE for the LEC with \([2]\)(PF\(_6\)\)_2 (0.028\%), which is in contrast to the relative emission quanti-
PMMA has a positive effect on the EQE. In LECs with [2](PF₆)₃ and [3](PF₆)₂, the EQE is increased by a factor of two by using PMMA.[20,83] The maximum values of the EQE are obtained after 1–15 min. In LECs with PMMA of [2](PF₆)₃ and [3](PF₆)₂, the maximum EQE is reached after only one minute, which is attributed to the fast ion migration and rapid device degradation due to the high applied voltages of 5–6 V.[60]

Conclusions

Heteroleptic bis(tridentate) ruthenium(II) complexes [1](PF₆)₃–[3](PF₆)₂ (Figure 1) were used as emitters in LECs with a ITO/PEDOT:PS/ruthenium(II) complex/Ag device structure. Red to NIR light emission was observed in the solid-state devices (λ_em = 722–755 nm; CIE: x = 0.709–0.731, y = 0.291–0.269). To the best of our knowledge, these are the lowest emission energies for LECs containing bis(tridentate) ruthenium(II) complexes. The low-energy emission is favored by the pronounced push-pull character of the complexes, which results in a small HOMO–LUMO gap. PMMA as additive (20% w/w) in the ruthenium complex layer requires higher driving voltages but yields higher external quantum efficiencies. Future perspectives include the steric protection of the ruthenium core by bulkier ligands to prevent a change in the coordination sphere by ligand substitution and self-quenching as well as the usage of other counterions to investigate their effect on the LEC performance.

Experimental Section

General Procedures: Complexes [1](PF₆)₃–[3](PF₆)₂ were prepared as described previously.[45,36,46,47] Before spin-coating, the complexes were further purified by reversed phase HPLC with a JASCO semi-preparative HPLC system with a Reprosil C₁₈ column (5 μm) by using CH₃CN/water (96:4, v/v) as an eluent (10 mL min⁻¹) and UV/Vis detection at 502–539 nm. Patterned ITO glass substrates, which were cleaned in an ultrasonic bath, sequentially with acetone, isopropl alcohol, and deionized water, were treated with UV/O₃ for 10 min before spin-coating. PEDOT:PSS (1:6 weight%, Al 4083; suspension in water; 1.3–1.7% solid content) was filtered (HP, 0.45 μm) and spin-coated (4000 rpm, 30 s, 4 s acceleration) onto the ITO substrate. After drying (1 h, 120 °C under reduced pressure), the substrate was transferred into an argon atmosphere. Ruthenium complexes (10 mg mL⁻¹) and PMMA (0 or 2 mg mL⁻¹, M_w 120000) were dissolved in acetonitrile on an argon atmosphere and spin-coated onto the PEDOT:PSS layer (1000 rpm, 20 s, no acceleration). Silver electrodes were vapor-deposited on the substrates under a pressure of 3 × 10⁻⁶ Torr. The current–voltage characteristics were measured by using a source measurement unit (Keithley 236). The luminance and efficiencies were calculated from photocurrent measurement data obtained with a calibrated Si photodiode (Hamamatsu S5227–101BQ). Electroluminescence spectra of the devices were obtained by an ICCD camera through an ARC 275 monochromator. AFM measurements were conducted in intermittent contact mode with two different instruments: A Veeco Dimension AFM was used for the measurement of the total height of the PEDOT:PSS and the
emitting layers and a XE-100 AFM was used to measure the thickness of the PEDOT:PSS layer. The spin-coated PEDOT:PSS and PEDOT:PSS-ruthenium complex layers were scratched with a razor, and the thickness of the layers was determined by the measured height differences.

**DFT Studies:** The DFT calculations were carried out with the Gaussian 09(DFT)[84] series of programs. The LANL2DZ basis set[84] was used in the B3LYP formulation of DFT. No symmetry constraints were imposed on the molecules. The presence of energy minima was checked by analytical frequency calculations. The integral-equation-formalism polarizable continuum model (IEFPCM, CH3CN) was employed for solvent modeling in all calculations. All calculations were performed without explicit counterions and solvent molecules.

**Supporting Information** (see footnote on the first page of this article): AFM images of scratched PEDOT:PSS/ruthenium complex layers; emission spectra of [(PF6)2]− in solution and in LECs; current density vs. EQE intensity curves of the LECs; human eye response curve and emission spectra of [(PF6)2]− in LECs.

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