doi:10.1246/cl.2010.861

Observation of Electrochemiluminescence from Indolo[2,3-*b*]tropone Zinc(II) Complex Using Benzoyl Peroxide as Coreactant

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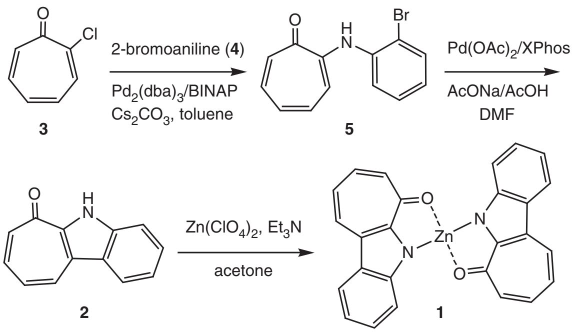
A new luminescent zinc(II) complex with indolo[2,3-*b*]tropone ligand has been synthesized and studied with respect to its electrochemiluminescence (ECL) properties for the first time. We observed a distinct blue-green ECL emission from this compound during electrochemical reduction in dimethyl sulfoxide (DMSO) at room temperature when benzoyl peroxide (BPO) was used as coreactant. As the ECL emission is almost identical to its photoluminescence spectrum, it suggested that the ECL is from the lowest excited state of the complex.

Electrochemiluminescence (ECL) is a process where species generated at electrodes undergo electron-transfer reactions to form excited states that emit light.[1] Organometallic complexes, in particular tris(2,2′-bipyridine)ruthenium(II), $Ru(bpy)_3^{2+}$ and its derivatives, are well-known ECL luminophores due to their excellent properties in photochemistry and electrochemistry which have been extensively studied in both fundamental aspects and analytical applications.[2,3] The interest in transition-metal systems for ECL is not surprising, since many metal complexes display the electrochemical and spectroscopic qualities required of ECL luminophores. Over the past decade, many attempts have been made in designing, synthesis, and investigation of new class of complexes incorporating different metal centers in terms of the improving of ECL efficiency or tuning of emission color in applications for analytical chemistry and organic light emitting diodes (OLED). Although ECL has been established from a few complexes, the field of transition-metal complex based ECL reaction is infancy and certainly to be attractive to further investigation.[4]

Here we report on ECL properties for a novel zinc(II) complex **1** using heterocyclic compound, indolo[2,3-*b*]tropone (**2**) as a ligand, whose structures are shown in Scheme 1. Tropone has been known as a representative nonbenzenoid aromatic compound. By annelation of an indole ring at the 2,3-position of tropone, it leads to the increased polarization of the C=O, and enhances aromaticity of the tropone moiety accordingly. The carbon framework of **2** is thus expected to have an isoelectronic structure similar to carbazole that is a well-known building block for advanced emitter materials in OLEDs applications.[5,6] Moreover, due to the presence of the binding sites in the aminotropone moiety of **2**, it is capable of complexation with metal ion guests, and thus is possible to be used as a luminophore for cation sensing by means of chelation-enhanced emission properties.[7] The tropone-containing coordination compounds, however, have been much less studied until now. To our knowledge, it is the first report regarding photoluminescence (PL) and ECL properties of this compound.



Scheme 1.

In this study, ligand **2**[8–11] was prepared by a newly developed straightforward synthetic method which was accomplished by two-step sequence of palladium-catalyzed amination and the intramolecular Heck reaction starting from 2-chlorotropone (**3**)[12] and 2-bromoaniline (**4**), as shown in Scheme 1. The amination of **3** with **4** was achieved in the presence of $Pd_2(dba)_3$/BINAP/Cs_2CO_3 to give the aminotropone **5** in 80% yield.[13] Then, **5** was transformed into **2** by the palladium-catalyzed intramolecular Heck reaction. For this transformation many reaction conditions with various palladium ligands were examined. The use of Xphos[14] as a ligand and addition of acetic acid combined with sodium acetate were found to be crucial to gain a high yield (90%) of **2**. Finally, reaction of **2** with zinc perchlorate hydrate in the presence of triethylamine gave **1** as yellow crystals. Recrystallization from DMF gave the analytically pure product of a bis(carbonyl-indolato) Zn(II) coordination compound, which is denoted as ZnL_2 (**1**) in this study. Its structure was confirmed by spectroscopic and elemental analyses.[15]

Electrochemistry and ECL experiments were carried out using an experimental setup described recently.[3] A glassy carbon with a diameter of 2 mm was used as the working electrode. A platinum wire and a silver (Ag) wire were employed as a counter electrode (CE) and a quasi-reference electrode (QRE), respectively. All electrode potentials were calibrated with respect to ferrocene (Fc)/ferrocenium (Fc^+) redox couple and converted to V vs. SCE by taking $E°(Fc/Fc^+) = +0.423$ V vs. SCE.[16] Deoxygenation before each experiment was carried out by purging with purified argon gas. ECL spectra were recorded with a fiber optics spectrofluorophotometer (USB2000, Ocean Optics, USA).

Since ZnL_2 (**1**) is not dissolved in water or acetonitrile, DMSO was chosen as a solvent for electrochemistry and photochemistry studies. We could not observe ECL response from ZnL_2 (**1**) via ion annihilation like $Ru(bpy)_3^{2+}$ usually involving homogeneous electron transfer between electrogenerated redox species, upon sweeping sequentially between negative and positive potentials over a short-time interval.[17] However, when a small amount of benzoyl peroxide (BPO) was added into the solution, a significant enhanced ECL emission was observed from the electrode surface during cathodic electrochemical reduction.

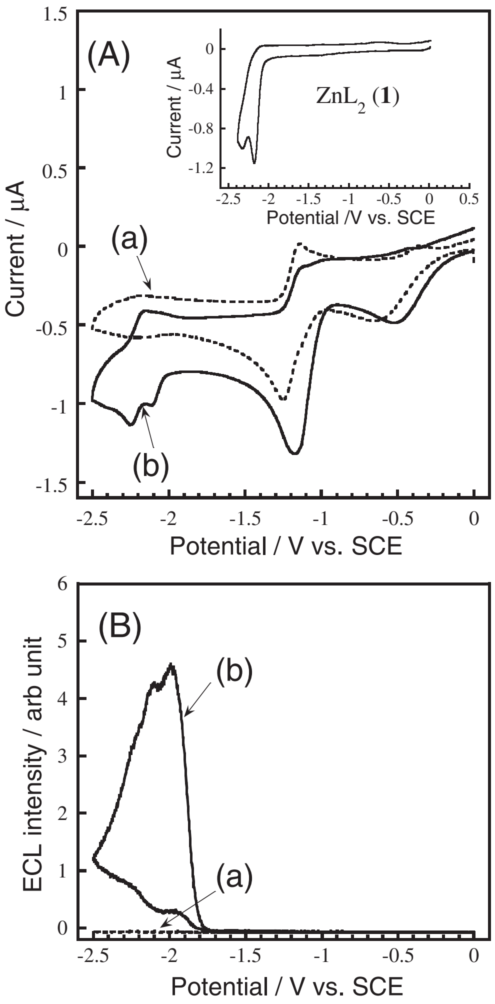


Figure 1. Cyclic voltammograms (A) and the corresponding ECL responses (B) of 1 mM BPO (a) and 1 mM BPO + 1 mM ZnL$_2$ (**1**) (b) in 0.1 M TBAPF$_6$/DMSO at 0.05 V s^{-1}. The inset of (A) represents the cyclic voltammogram of 1 mM ZnL$_2$ in DMSO containing 0.1 M TBAPF$_6$.

Figure 1 shows the simultaneous cyclic voltammograms and the corresponding ECL responses of 0.5 mM ZnL$_2$ (**1**) and 1.0 mM BPO in DMSO solution with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF$_6$) as supporting electrolyte. The dotted curves (a) were the background responses of 1 mM BPO. The cyclic voltammogram shows that BPO was reduced at −1.25 V vs. SCE prior to the reduction of ZnL$_2$ (**1**) and no ECL was found at this potential, indicating that no luminescence was generated by only BPO reduction. The inset of Figure 1A shows the cyclic voltammogram of ZnL$_2$ (**1**) which gives two reduction waves at half-wave potentials of $E_{1/2} = -2.0$ and −2.2 V vs. SCE, respectively. When the electrode potential approached the reduction potential of ZnL$_2$ (**1**), a distinct ECL signal was detected from the electrode, as is seen in Figure 1B. It was supposed that one-electron reduction was involved in the first reduction wave that produced an anion radical species (ZnL$_2^{\bullet -}$) at the electrode surface, although the detailed electrochemical mechanisms along with the reaction products identification need to be further investigated.

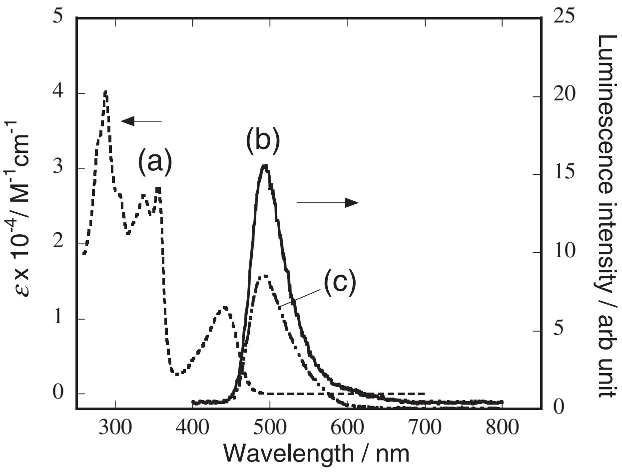


Figure 2. UV–vis absorption (a), PL (b), and ECL (c) spectra for ZnL$_2$ (**1**). The vertical axis in the left represents the molar absorption coefficient (ε). PL spectrum was measured in DMSO containing 50 μM ZnL$_2$ (**1**) with excitation at 430 nm. ECL spectrum was recorded in a TBAPF$_6$/DMSO solution in the presence of 0.5 mM ZnL$_2$ (**1**) by pulsing the electrode potential between 0 and −2.6 V vs. Ag QRE at 0.2 Hz for 5 min integration and 1 mM BPO was added as coreactant.

The UV–vis absorption and emission spectra of ZnL$_2$ (**1**) in DMSO are shown in Figure 2. In Figure 2a, the strong absorption bands at 280 and 350 nm (with molar absorption coefficients of $\varepsilon \approx 40000\,\mathrm{M^{-1}\,cm^{-1}}$ and $\varepsilon \approx 28000\,\mathrm{M^{-1}\,cm^{-1}}$) and a moderately strong absorption at 430 nm ($\varepsilon \approx 10500\,\mathrm{M^{-1}\,cm^{-1}}$) were similar to that of the free ligand **2**. These absorption bands are mainly due to intraligand-**2**-π–π^* transitions and shifted toward longer wavelengths upon complexation with Zn(II) by 38 nm.

Figure 2b shows a PL spectrum with a maximum emission wavelength of 500 nm when excited at 430 nm at room temperature. It is worth noting that free ligand **2** exhibited PL emission at wavelength of 460 nm but the intensity was 10 times lower than that of ZnL$_2$ (**1**). The fluorescence quantum yields for ligand **2** and ZnL$_2$ (**1**) were measured as 5.3×10^{-4} and 1.2×10^{-2}, respectively. The reduction of PL intensity for ligand **2** can be explained in terms of the photoinduced electron transfer,[7] because ligand **2** contains a heterocyclic nitrogen with nonbinding electron pair. This electron donation effect, however, can be hindered by complex formation with Zn(II), and as consequence leading to a much stronger PL intensity. Besides, the complexation with Zn(II) may also result in the promotion of the intermolecular or intramolecular excimer (framework of **1** possesses 2 units of **2**) formations, which lead to the enlargement of the π-conjugated system in the complex. A red shift of PL spectrum of ZnL$_2$ (**1**) in Figure 2b was thus observed. The change of excitation wavelength from 250 to 450 nm could not influence the location of characteristic emission band in Figure 2b, suggesting that the origin of the emission was from the lowest excited state of ZnL$_2$ (**1**).

The ECL spectrum was measured with a fluorophotometer by continuously pulsing the electrode potential between 0 and −2.6 V vs. Ag QRE in 0.1 M TBAPF$_6$/DMSO solution in the presence of 0.5 mM ZnL$_2$ (**1**) and 1.0 mM BPO. Since the ECL

$$\mathrm{BPO} + e^- \rightarrow \mathrm{BPO}^{\bullet-} \qquad (1)$$
$$\mathrm{BPO}^{\bullet-} \rightarrow C_6H_5CO_2^- + C_6H_5CO_2^\bullet \qquad (2)$$
$$C_6H_5CO_2^\bullet + e^- \rightarrow C_6H_5CO_2^- \qquad (3)$$
$$ZnL_2\,(\mathbf{1}) + e^- \rightarrow ZnL_2^{\bullet-} \qquad (4)$$
$$C_6H_5CO_2^\bullet + ZnL_2^{\bullet-} \rightarrow {}^*ZnL_2 + C_6H_5CO_2^- \qquad (5)$$
$${}^*ZnL_2 \rightarrow ZnL_2\,(\mathbf{1}) + h\nu\ (500\ \mathrm{nm}) \qquad (6)$$

Scheme 2.

emission (Figure 2c) closely matches the PL spectrum in DMSO solution ($\lambda_{max} \approx 500$ nm), it can be attributed to the same excited state as was observed in PL. The ECL mechanism is thus proposed in Scheme 2.

It was found that BPO could serve as a good coreactant in this system. According to an early study by Choi and Bard,[18] BPO was first reduced to $BPO^{\bullet-}$ at the electrode by accepting one electron, and then this newly formed species immediately decomposed to benzoate anion and benzoate radical ($C_6H_5CO_2^\bullet$) following eqs 1–3. Because the generated $C_6H_5CO_2^\bullet$ was a sufficiently strong oxidizing agent, whose $E^\circ(C_6H_5CO_2^\bullet/C_6H_5CO_2^-)$ value larger than +1.5 V vs. SCE,[19] once ZnL_2 (**1**) was electrochemically reduced to $ZnL_2^{\bullet-}$ (eq 4), $C_6H_5CO_2^\bullet$ could oxidize $ZnL_2^{\bullet-}$ to its excited state $^*ZnL_2$ according to eq 5.

In considering the energetics of the ECL system, the energy available between $C_6H_5CO_2^\bullet$ and $ZnL_2^{\bullet-}$ in eq 5 was calculated using $E_{1/2}(ZnL_2/ZnL_2^{\bullet-})$ and $E^\circ(C_6H_5CO_2^\bullet/C_6H_5CO_2^-)$, and compared with the lowest excited state energy (E_s) of ZnL_2 (**1**), which was determined from the λ_{max} at PL spectrum in Figure 2b. The standard enthalpy ($-\Delta H^\circ$) of such a process at constant temperature can be calculated according to the following equation.[20]

$$-\Delta H^\circ = E^\circ(C_6H_5CO_2^\bullet/C_6H_5CO_2^-) - E_{1/2}(ZnL_2/ZnL_2^{\bullet-}) - 0.1\ (\mathrm{eV}) \qquad (1)$$

where 0.1 eV is an estimate of the temperature–entropy approximation term ($T\Delta S$) at 25 °C. If $E^\circ(C_6H_5CO_2^\bullet/C_6H_5CO_2^-)$ was assumed to be + 1.5 V vs. SCE, $-\Delta H^\circ$ was calculated to be 3.5 eV, which is larger than E_s (2.5 eV) of ZnL_2 (**1**). Therefore, the lowest excited state of ZnL_2 (**1**) can be directly generated. Further quantitative investigations on ECL efficiency and life time of the excited state are now in progress.

In conclusion, we have established an efficient synthesis of a new luminescent znic(II) complex, ZnL_2 (**1**), with indolo[2,3-*b*]tropone ligand. This is the first observation of the ECL of this compound in DMSO during a cathodic electrochemical process when BPO was used as coreactant. Since the ECL emission is almost identical to the PL spectrum of ZnL_2 (**1**), ECL emission is suggested to be from the lowest excited state of ZnL_2 (**1**). BPO served as a good coreactant in this system. The electrochemical reduction of BPO can generate a strong oxidizing agent, $C_6H_5CO_2^\bullet$, which oxidizes the electrochemically reduced anion radical species $ZnL_2^{\bullet-}$ to its excited state. Because ECL of ZnL_2 (**1**) is accompanied with a blue shift in the emission ($\lambda_{max} \approx$ 500 nm), in comparison with the other metallic complex compounds, indolo[2,3-*b*]tropone moiety can be used as a promising ligand for construction of organometallic luminescence in future practical applications.

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15 Selected physical properties of **1** are as follows; Mp >300 °C. IR (KBr) ν_{max} = 3465w, 3446w, 3427w, 1603m, 1510s, 1435s, 1223s, 721m cm^{-1}; ^1H NMR (DMSO-d_6): δ 7.26 (t, J = 9.9 Hz, 2H), 7.33 (t, J = 7.6 Hz, 2H), 7.58 (t, J = 7.6 Hz, 2H), 7.65 (d, J = 9.9 Hz, 2H), 7.89 (t, J = 9.9 Hz, 2H), 8.36 (d, J = 7.6 Hz, 2H), 8.38 (d, J = 7.6 Hz, 2H), 8.70 (d, J = 9.9 Hz, 2H); ^{13}C NMR (DMSO-d_6): δ 117.9, 120.7, 121.1, 121.3, 125.5, 127.1, 127.3, 128.6, 132.1, 138.6, 147.0, 151.2, 177.7. Anal. Calcd for $C_{26}H_{16}N_2O_2Zn \cdot 0.5DMF$: C, 67.36; H, 4.01; N, 7.14%. Found: C, 67.10; H, 4.00; N, 7.19%.

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