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Improvement of Brightness, Color Purity, and Operational Stability of Electrochemiluminescence Devices with Diphenylanthracene Derivatives

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Abstract

We synthesized a highly soluble ionophilic 9,10-diphenylanthracene (I-DPA) by incorporating imidazolium groups into the DPA core. With the prepared I-DPA as an electrochemiluminescence (ECL) luminophore, the resulting ECL device emitted blue light. In comparison with unmodified DPA, a well-known representative ECL blue emitter, the ECL device including I-DPA emitted brighter and purer blue light with improved operational stability. Due to excellent compatibility of the I-DPA with polyvinylacetate (gelator), we could successfully prepare homogeneous ECL gels, and fabricated flexible blue-emitting ECL devices on a plastic substrate.

KEYWORDS: electrochemiluminescence, electrochemical displays, blue-emitting devices, 9,10-diphenylanthracene derivatives, ECL emitters.

Introduction

Electrochemiluminescence (ECL) is a light emission process through electrochemical redox reactions.^{1,2} For example, an electronically excited state of luminophores is generated by an electron transfer reaction between reduced and oxidized species of the luminophores, which corresponds to the annihilation path.

This ECL phenomenon was conventionally used as one of detection methods for liquid chromatography³⁻⁵ or immunoassays.⁶⁻¹⁰ Recently, the ECL has been applied to emissive displays, because ECL devices require very simple device structure (namely, an ECL layer inserted between two electrodes) and low operational voltage.¹¹⁻¹⁷ However, most devices have employed red (R) or green (G)-colored light emitting luminophores.¹⁸⁻²⁸ Although some ECL blue emitters such as iridium complexes,²⁹⁻³¹ polyaromatic hydrocarbons³²⁻³⁵ and quantum dots³⁶ have been reported, few materials are suitable for display applications due to low color purity and weak ECL intensity. One representative blue ECL luminophore is 9,10-diphenylanthracene (DPA).³⁷⁻⁴⁷ Although the DPA is considered as a highly efficient ECL material,^{37,39,41} its limited solubility restricts applications to solid (or gel)-type flexible ECL devices.

In this work, we tailored the molecular structure of the DPA for flexible blue-emitting ECL devices, by incorporating ionophilic imidazolium groups to C_{19} and C_{24} positions of the DPA with saturated aliphatic chains. Due to non-conjugation between DPA and imidazolium groups, electronic structures of the DPA and emission color were not significantly affected. Instead, the resulting ionophilic DPA derivative (I-DPA) exhibited remarkably improved solubility in organic solvents such as N-methyl-2-pyrrolidone (NMP). Also, the introduced functional groups broke co-planarity of the DPA, which enhanced color purity of emitted blue when ECL devices were fabricated with I-DPA. In comparison with DPA-based devices,

I-DPA-containing ECL devices emitted brighter blue light and showed better operational stability. To demonstrate flexible devices on a plastic substrate, we obtained transparent and homogeneous gel containing I-DPA and polyvinylacetate (PVAc), which is suitable for display. However, another gel containing DPA and PVAc was turbid due to poor compatibility. Accordingly, we successfully demonstrated blue-emitting flexible ECL devices with the I-DPA. These results indicate that the I-DPA could be a promising blue ECL emitter for flexible electronics.

Experimental Section

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Materials. All chemicals were purchased from Sigma-Aldrich and used as received unless otherwise noted. 9,10-diphenylanthracene (DPA) (Tokyo Chemical Industry), ionophilic derivative of DPA (I-DPA), and tetra-n-butylammonium perchlorate (TBAP) were stored in inert atmosphere. The ITO-coated glass (AMG Tech., sheet resistance: 8-12 Ω /sq) and the ITO-coated poly(ethylene terephthalate) (PET) film (AMG Tech., sheet resistance: 18 Ω /sq) were rinsed by acetone (5 min), methanol (5 min), and isopropanol (5 min), and further treated with UV/ozone before use.

Synthesis of Diphenylanthracene Derivatives (I-DPA).

Preparation of 9,10-bis-(4-vinylphenyl)anthracene. (1): 9,10-Dibromoanthracene (2.5 g, 7.44 mmol), bis(tri-*tert*-butylphosphine)palladium (0.01 g, 0.0196 mmol), potassium carbonate (6.17 g, 44.6 mmol) in THF (87.5 mL) and water (37.5 mL) were stirred in a pre-heated oil bath at 100 °C. Then 4-vinylphenylboronic acid (3.305 g, 22.3 mmol) in THF (25 mL) was added dropwise. The resulting mixture was stirred for 30 min. The solution was added to toluene (50 mL), washed with water, and dried by rotary evaporator. The residue was stirred with MgSO₄, acid clay and carbon activated powder, and passed through Celite 545-packed

column. Finally, the solvent was evaporated under vacuum, and the crude product was washed with methanol. A bright yellowish solid was obtained after removing the residual solvent. ¹H-NMR (400 MHz, CDCl₃, δ): 7.74 (dd, 4H, J=4), 7.66 (d, 4H, J=8), 7.43 (d, 4H, J=8), 7.28 (dd, 4H, J=4), 6.88 (dd, 2H, J=11), 5.92 (d, 2H, J=18), 5.42 (d, 2H, J=11). Anal calcd for C₃₀H₂₂ (382.51) C 94.20, H 5.80, N 0, S 0; found C 93.56, H 5.89, N 0, S 0. ¹H-NMR and ¹³C-NMR spectra of **1** are provided in Supporting Information (see Fig. S1 and S2).



Scheme 1. Synthetic route for ionophilic 9,10-diphenylanthracene derivative (I-DPA).

Preparation of 9,10-Bis(4-(2-(3-chloropropylthio)ethyl)phenyl)anthracene (**2**): This compound was prepared, according to the literature.⁴⁸ In brief, 3-chloropropanethiol (2.71 mL, 27.8 mmol) was added to a solution of 9,10-distyrylanthracene (1) (3.5397 g, 9.25 mmol) and AIBN (300 mg, 1.83 mmol) in dry toluene (150 mL). The solution was carefully degassed for 30 min, and the mixture was reacted at 110 °C for 24 h. Then, the solvent was removed in vacuum. After dissolving in a small amount of dichloromethane, the product was

precipitated in methanol and collected. The resulting yellow solid was washed with water. ¹H-NMR (400 MHz, CDCl₃, δ): 7.86–7.32 (m, 16H, Ar-H), 3.70 (t, 4H, J=6.3, CH₂-Cl), 3.10 (t, 4H, J=8.1, CH₂–S), 2.97 (t, 4H, J=8.1, S- CH₂), 2.80 (t, 4H, J=6.9, Ar–CH₂), 2.12 (m, 4H, J=6.3, CH₂–CH₂–CH₂). Anal calcd for C₃₀H₃₆Cl₂S₂ (603.70) C 71.62, H 6.01, N 0, S 10.62; found C 75.36, H 6.12, N 0, S 8.58. ¹H-NMR and ¹³C-NMR spectra of **2** are provided in Fig. S3 and S4.

Preparation of 9,10-Bis[4-(2-(3-(N-1-butylimidazoliumyl)propylthio)ethyl)phenyl]anthracene bischloride (**3**): A solution of **2** (57.5 mg, 0.095 mmol) and 1-butylimidazole (125 μ L, 0.95 mmol) in dry toluene (10 mL) was refluxed under inert atmosphere for 48 h. After removal of the solvent, diethyl ether was added, and the resulting solid was filtered to obtain 9,10-bis(4-(2-(3-(N-1-butylimidazoliumyl)propylthio)ethyl)phenyl)anthracene bischloride (**3**) (brown powder). ¹H-NMR (400 MHz, DMSO-*d*₆, δ): 9.20 (s, 2H, N-CH-N) 7.80 (s+s, 4H, – CH=CH–), 7.60–7.35 (m, 16H, Ar-H), 4.25 (t, 4H J=7.0, CH₂–S), 4.15 (t, 4H, J=7.2, S–CH₂), 2.99 (t, 4H, J=7.7, CH₂-N), 2.92 (t, 4H, J=6.3, N-CH₂), 2.65 (t, 4H, J=6.9, Ar–CH₂), 2.15 (m, 4H, J=7.1, CH₂-CH₂-CH₂), 1.75 (m, 4H, J=7.3, N–CH₂–CH₂), 1.30 (m, 4H, J=7.5, N-CH₂-CH₂–CH₂), 0.89 (t, 6H, J=7.2, CH₂–CH₃). Anal calcd for C₅₀H₆₀Cl₂N₄S₂ (852.08) C 70.48, H 7.10, N 6.58, S 7.53; found C 68.65, H 7.27, N 5.66, S 6.16. ¹H-NMR and ¹³C-NMR spectra of **3** are given in Fig. S4 and S5 of the Supporting Information.

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ECL Device Fabrication and Characterization. ECL devices with the simple structure of ITO/ECL layer/ITO were fabricated in ambient air. TBAP-containing (150 mM) NMP solutions of I-DPA or DPA were prepared. The solutions were placed between a pair of indium tin oxide (ITO) electrodes with polydimethlysiloxane (PDMS) spacers at an interelectrode distance of ~260 μ m. The fabricated ECL cells had an active electrode area of 7 mm × 7 mm. The spectra and luminance of emitted light of ECL devices were recorded on

a spectroradiometer (Konica Minolta, CS-2000). The applied AC voltages were supplied from an arbitrary waveform generator (Duncan Instruments Canada Ltd., Model 645). Transient profiles of the ECL signals were obtained with a photodetector (Hamamatsu, S6775). Transient profiles of the applied voltage and the device current were recorded on an oscilloscope (Tektronix, TDS2014C). All measurements were also performed in ambient air.

Results and Discussion

Fig. 1a depicts a schematic diagram of the ECL devices, in which the emissive solution is placed between a pair of indium tin oxide (ITO) electrodes similar to conventional ECL devices. To enhance the solubility of DPA moiety in solution and suitability for blue emitting ECL devices, I-DPA including two imidazolium groups was synthesized (Scheme 1). Since the imidazolium side groups were isolated from the DPA core by aliphatic saturated chains, there is no noticeable change in the emission color. Fig. 1b and c show ECL emission spectra at various I-DPA and DPA concentrations, respectively. Indeed, ECL devices based on I-DPA and DPA exhibited similar emission spectra, where the wavelengths (λ_{max}) at maximum intensity were $\lambda_{max, I-DPA} \sim 439$ nm and $\lambda_{max, DPA} \sim 434$ nm. As the luminophore concentration increased, higher brightness was observed, but the spectra and λ_{max} were not changed. The maximum intensity in Fig. 1b and c is plotted as a function of concentration of I-DPA and DPA (Fig. 1d). Overall, emission brightness of the device including I-DPA was much higher than that with DPA. For example, the I-DPA containing device emitted \sim 5.5-times brighter blue light at a concentration of 100 mM. One plausible origin of lower brightness of DPA may be poorer solubility in the NMP-based electrolyte. The 100 mM I-DPA was immediately dissolved at room temperature (RT). Complete dissolution of DPA in the electrolyte could be also achieved at higher temperature (e.g. 80 °C), but a part of DPA in the homogeneous



solution was precipitated again during device fabrication at RT.

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Fig. 1 (a) Schematic of ECL devices with an emissive layer composed of (I-DPA or DPA)/TBAP/NMP between ITO-coated glasses with PDMS spacer. The photographs correspond to the on- and off-states. Emission spectra from ECL devices including (b) I-DPA and (c) DPA under AC peak-to-peak voltage (V_{pp}) of 7.6 V (i.e., -3.8 to +3.8 V) at a frequency of 30 Hz, in which the luminophore concentration range was 20 mM to 100 mM. (d) Plots of the maximum intensity in (b) and (c) as a function of I-DPA and DPA concentration. (e) CIE color coordinates of emitted light from the I-DPA and DPA-containing devices. Insets correspond to ECL devices with 100 mM ECL luminophore.

Another remarkable feature of I-DPA is higher color purity, which is one of desirable factors for practical display applications. Although both devices including I-DPA and DPA emitted blue-colored light (see inset photographs in Fig. 1e), a distinct difference in color purity was observed in addition to the brightness. For example, the Commission Internationale de l'Eclairage (CIE) 1931 color coordinates (x, y) of the device with I-DPA (0.156, 0.076) were closer to the National Television System Committee (NTSC) blue standard (0.14, 0.08), in comparison with that (0.164, 0.058) of DPA-containing device (Fig. 1e). It has been reported that the color purity can be improved by breaking the co-planarity of luminophores.^{49,50} In this context, two bulky imidazolium moieties reduce the co-planarity (Fig. S7 in the Supporting Information), and contribute to the purer blue.



Fig. 2 Dependence of the peak luminance on the applied AC voltage at frequencies from 30 to 500 Hz for ECL devices containing 100mM of (a) I-DPA, and (b) DPA.

To investigate the dependence of luminance on the applied voltage and frequency, we performed voltage sweeps at various frequencies (Fig. 2). We employed AC voltage for ECL by annihilation path.^{51,52} For the I-DPA-based device (Fig. 2a), the emission began at 6.0 V_{PP} (namely, -3.0 to +3.0 V) and 60 Hz, and the luminance was saturated at ~8.0 V. As the applied frequency increased, turn-on voltage was also increased. At higher frequencies under

the same applied voltage, the amount of charge injection (and thus electrochemical redox reactions) per cycle was smaller due to a shorter voltage application period. Therefore, to induce comparable brightness at a higher frequency, a larger voltage input was necessary. A similar frequency dependence of the ECL intensity was reported in the ECL systems of tris(2,2'-bipyridyl)ruthenium(II),¹⁸ thianthrene/2,5-diphenyl-1,3,4-oxadiazole,⁵³ 5-amino-1,2,3,4-tetrahydrophthalazine-1,4-dione (luminol),⁵⁴ and 10-methylphenothiazine.⁵⁵ Although the luminance of DPA-containing devices was much lower, similar behavior was observed (Fig. 2b).

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Fig. 3 Dynamic profiles of applied voltage ($V_{PP} = 8.6$ V, square wave) (black), current (red), and ECL intensity (blue) for the (a) I-DPA, and (c) DPA-containing ECL devices at a frequency of 60 Hz. Representative enlarged profiles of the area squared in a and c were given in (b) and (d), respectively.

The transient applied voltage, current, and ECL intensity were recorded to understand device dynamics (Fig. 3). A square-wave voltage oscillating between -4.3 to +4.3 V at a frequency of 60 Hz was applied. Because two additional groups on the DPA core of I-DPA increase molecular weight and size, lower diffusivity in the electrolyte layer and longer delay time are anticipated. However, the response time (0.3~0.4 ms for I-DPA and 0.2~0.3 ms for DPA) that corresponds to time interval between profiles of device current and ECL signal was similar (see Fig. 3b and 3d). This result implies that the effect of imidazolium side groups on device dynamics is not significant.



Fig. 4 Time dependence of luminance for I-DPA (blue dot) and DPA (black dot) containing ECL devices.

Also, we examined operational stability of the device (Fig. 4). While the light emission of the device with DPA became undetectable after \sim 300 s, the device based on I-DPA emitted twice longer (\sim 600 s). This result is likely due to the difference in luminophore solubility. The annihilation process in the ECL is composed of a series of redox reactions. In general, aggregated (or partially dissolved) chemical species retard electrochemical reactions. Thus, I-

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DPA could serve as more advantageous blue emitting luminophores showing brighter and longer emission. One common issue that should be addressed for all reported ECL devices is the relatively poor long-term stability. One method to improve device operating time is incorporating inorganic nanoparticles (NPs) into ECL electrolytes.⁵⁶ For example, the ECL device with $Ru(bpy)_3^{2+}$ produces oxidized $Ru(bpy)_3^{3+}$ and relatively unstable reduced $Ru(bpy)_3^{1+}$ during emission by the annihilation route. As the device operates, more stable oxidized $Ru(bpy)_3^{1+}$ is accumulated near the electrodes, resulting in population imbalance between $Ru(bpy)_3^{1+}$ and $Ru(bpy)_3^{3+}$, and degradation of device performance. This imbalance was improved by adding TiO₂ NPs into the ECL electrolyte based on the interacting electron transfer between Ru-complexes and TiO₂ NPs. As a result, the device long-term performance could be improved. In a similar way, if inorganic NPs having energy levels of conduction and valence band well matched with I-DPA are developed, further improvement of operational stability of the device in this work is expected. This would be a future work.

To demonstrate flexible ECL devices, a solid-state ECL layer should be required. Thus, we prepared homogeneous ECL gels containing DPA or I-DPA by adding 13 wt% polyvinylacetate (PVAc, weight average molecular weight (M_w) = 500k). A homogeneous DPA-containing gel was obtained at 80 °C. However, when the gel was placed on the ITO-coated PET substrate at 25 °C for device fabrication, it became opaque because of incompatibility of DPA and PVAc in the gel (Fig. S8). On the other hand, ECL gels with I-DPA maintained homogeneous state at 25 °C, irrespective of time (Fig. S8). This indicates that I-DPA is more suitable for gel-type ECL devices. ECL gel containing I-DPA was inserted between two ITO-coated PET films for a flexible device (Fig. 5a). The resulting ECL devices successfully worked even under bending strain (Fig. 5b).



Fig. 5 (a) Schematic of the fabrication process for bendable ECL devices with ECL gels on a plastic substrate. (b) Photographs of the ON states for fabricated ECL devices composed of I-DPA before bending (left image) and after bending (right image), where the applied voltage and frequency were $V_{PP} = 8.6 \text{ V} (-4.3 \text{ to } +4.3 \text{ V})$ and 60Hz, respectively.

Conclusion

We have successfully developed a new blue ECL emitter, I-DPA, by incorporating ionophilic imidazolium moiety into the DPA. The resulting I-DPA exhibited much improved solubility in organic solvents. Also, the introduced imidazolium groups broke the co-planarity of molecular structure, inducing further purer blue light emission when we fabricated ECL

devices with I-DPA. In comparison with DPA-containing devices, ECL devices including I-DPA emitted brighter blue light, and showed much better operational stability. Moreover, only I-DPA allowed one to obtain a gel-type ECL layer due to incompatibility of compounds in the DPA-containing gel. With the I-DPA gel, we successfully demonstrated flexible blueemitting ECL devices on a plastic substrate. We anticipate that the I-DPA could serve as an attractive blue ECL emitter to flexible, multicolor ECL devices.

Supporting Information ¹H-NMR and ¹³C-NMR spectra (400 MHz) of compounds **1**, **2**, and **3**, calculation of dihedral angles of DPA and I-DPA, and photographs of ECL gels containing either I-DPA or DPA.

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