Electrochemiluminescence

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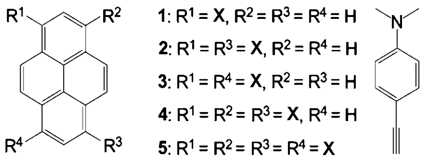
Enhancement of Electrogenerated Chemiluminescence and Radical Stability by Peripheral Multidonors on Alkynylpyrene Derivatives**

Jeong-Wook Oh, Yeon Ok Lee, Tae Hyun Kim, Kyoung Chul Ko, Jin Yong Lee, Hasuck Kim,* and Jong Seung Kim**

Electrogenerated chemiluminescence (ECL) is the emission of light from the electron-transfer reaction between electrochemically generated ion radicals in the vicinity of an electrode.[1] The ECL efficiency of luminophores is one of the most important criteria when evaluating the performance of light-emitting materials.[2–4] Even with strong photoluminescence, however, many molecules do not produce strong ECL, because decomposition of the radical ions causes one of the redox processes to be chemically irreversible.[5] Thus, the increase of radical stability for efficient ECL materials is crucial for the development of new high-performance light-emitting materials. Recently, donor–π-bridge–acceptor (D–π–A) systems have attracted much attention in ECL because the optoelectronic properties of materials can be easily controlled by merely exchanging the donor and/or acceptor moieties.[6,7] However, most studies of the ECL behavior of D–π–A compounds have been developed to change the absorption and emission maxima by altering their photophysical properties through intramolecular charge transfer (ICT)[8,9] or to only characterize the ECL properties of new ECL-active materials.[10,11] Only a few examples of the enhancement of ECL efficiency by systematically improving the radical stability of D–π–A compounds have been reported.[12] In addition, most studies have focused on the conventional linear D–π–A platform for better ICT.[5,12] Herein, we report that the ECL efficiency of organic materials can be enhanced by improving radical stability. Our approach uses a new platform of D–π–A systems that contain a centered acceptor and peripheral multidonors in contrast to the conventional linear type of D–π–A compounds.

We have prepared alkynylpyrene derivatives **1**–**5** that consist of pyrene as an acceptor moiety, *N*,*N*-dimethyl aniline (DMA) as a peripheral donor moiety, and an ethynyl group as a bridge (Scheme 1).[13–16] The five D–π–A compounds were chosen according to the number and substituent position of peripheral donor moieties. Although the pyrene molecule shows poor ECL properties because of the electrochemical instability of its cationic radical,[17] the ECL efficiencies of pyrene derivatives **1**–**5** increase in proportion to the number of the peripheral donors, which suggests that this approach has some promise for the development of highly efficient ECL materials.



Scheme 1. Chemical structures of **1**–**5**.

Compounds **1**–**5** show a strong fluorescence emission in various solvents (Figure 1 a). The emission spectra of solutions in toluene (a nonpolar solvent; blue line) exhibit significant bathochromic shifts as the number of substitutents in this series increases, which is caused by the effective extension of the π conjugation with the addition of DMA–ethynyl moieties. When the compounds are dissolved in solvents of different polarities, the emission spectra of each compound become red-shifted as the polarity of the solvent increases, which indicates a solvatochromic shift through ICT.[15] However, the degree of solvatochromism decreases on moving from **1** to **5**, which can be explained by the suppression of ICT by more effective conjugation that results from the introduction of more DMA–ethynyl units in the series **1**–**5**. The ICT suppression is also confirmed by the decrease of the Stokes shift (Table 1) and the reduction of the full width at half maximum value (Figure 2 b).[9,18] Interestingly, in CH_3CN (a highly polar solvent), the emission maxima values (λ_{max}^{em}) of **1**–**5** are nearly the same. This indicates the bathochromic shift from the extension of conjugation was counteracted by the solvatochromic effect.

The absorption spectra of **1**–**5** show a similar pattern to the emission spectra of solutions in CH_2Cl_2 (Figure 2) but only a subtle solvent dependence is observed in the absorption maxima (λ_{max}^{abs}) values (data not shown). It is noted that,

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[*] K. C. Ko, Prof. J. Y. Lee
Department of Chemistry, Sungkyunkwan University
Suwon 440-746 (Republic of Korea)
E-mail: jinylee@skku.edu

J.-W. Oh,[+] Dr. T. H. Kim,[+] Prof. H. Kim
School of Chemistry, Seoul National University
Seoul 151-747 (Republic of Korea)
Fax: (+82) 2-889-1568
E-mail: hasuckim@snu.ac.kr

Y. O. Lee,[+] Prof. J. S. Kim
Department of Chemistry, Korea University
Seoul 136-701 (Republic of Korea)
E-mail: jongskim@korea.ac.kr

[+] These authors contributed equally to this work.

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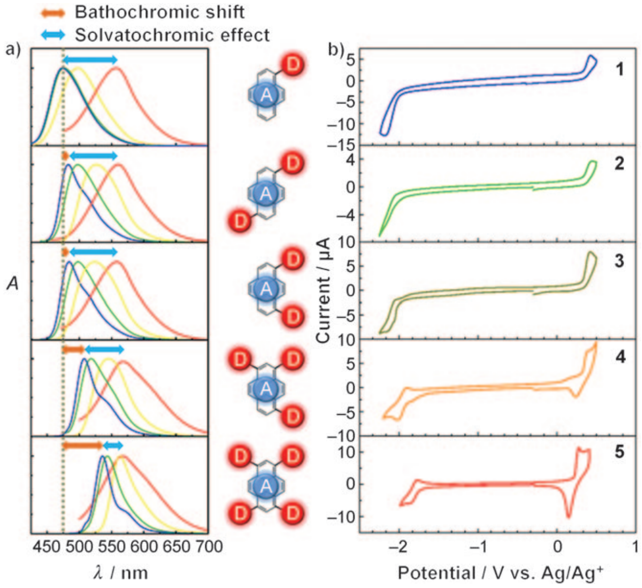

Figure 1. a) Normalized emission spectra of **1**–**5** (3 μM) in various solvents. —— toluene, —— $CHCl_3$, —— CH_2Cl_2, and —— CH_3CN. b) Cyclic voltammograms of **1**–**5** (0.5 mM) on a Pt electrode with Bu_4NPF_6 in CH_2Cl_2 (0.1 M). Scan rate = 100 mV s^{-1}.

Table 1: Photophysical, electrochemical, and theoretical data for **1**–**5**.

Compound	**1**	**2**	**3**	**4**	**5**
λ_{max}^{abs} [nm][a]	406	435	434	483	514
λ_{max}^{em} [nm]	497	526	524	546	556
λ_{max}^{ECL} [nm]	546	580	592	603	624
Stokes shift [nm]	91	91	90	63	42
$\lambda_{max}^{ECL}-\lambda_{max}^{em}$ [nm]	49	54	68	58	68
ε [$\times 10^4$ M^{-1} cm^{-1}]	4.17	8.41	7.05	7.78	7.91
Φ[b]	0.94	1	1	0.75	0.60
E_{pc} [V]	−2.20	−2.17	−2.14	−2.02	−1.85
E_{pa} [V]	0.43	0.44	0.42	0.40	0.28
ΔE_{gap}^{elec} [eV][c]	2.63	2.61	2.56	2.42	2.13
ΔE_{gap}^{opt} [eV][d]	2.53	2.38	2.35	2.28	2.19
ΔE_{gap}^{calc} [eV] (TDDFT)	2.88	2.54	2.53	2.37	2.19

[a] Recorded at the longest wavelengths. [b] Using 9,10-diphenylanthracene (for **1**–**3**) and rhodamine 6G (for **4** and **5**) in CH_2Cl_2. Φ_f = (9,10-diphenylanthracene) 0.95 in EtOH. Φ_f = (rhodamine 6G) 0.95 in EtOH. [c] Electrochemical band gap calculated as the difference between the two peak potentials. [d] HOMO–LUMO gap calculated from the onset of the UV/Vis absorption. The photophysical and electrochemical data were obtained in CH_2Cl_2.

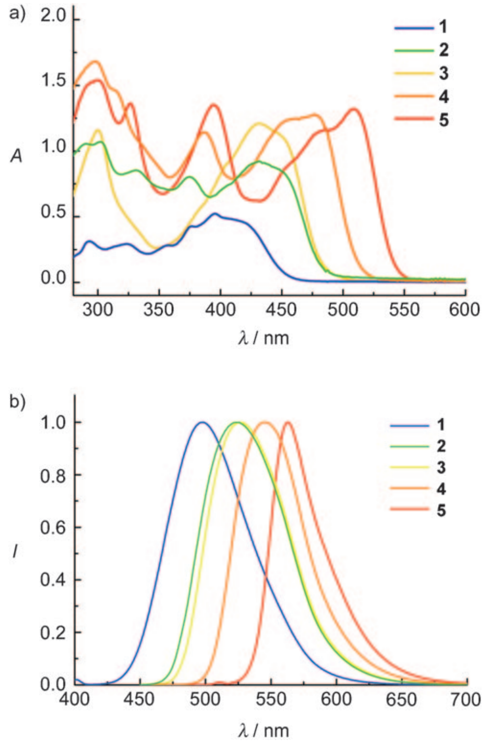

Figure 2. a) UV/Vis spectra of **1**–**5** in CH_2Cl_2. b) Normalized fluorescence spectra of **1**–**5** in CH_2Cl_2.

despite the different molecular symmetry between **2** and **3**, which is similar to the presence of anti and syn isomers, the λ_{max}^{abs} and λ_{max}^{em} values for **2** and **3** are almost equivalent, which suggests that the photophysical properties of our system depend on only the number of substituents and not on the position of substitution. The absorption, emission, electrochemical, and theoretical data of series **1**–**5** are summarized in Table 1.

To gain an insight into the ECL properties of **1**–**5**, cyclic voltammetry (CV) has been performed with Bu_4NPF_6 in CH_2Cl_2 (0.1 M) on a Pt electrode (Figure 1 b). The CV data of **1**–**5** show two distinctive patterns. Firstly, the characters of the redox curves become more reversible as the number of donor groups appended to the alkynylpyrene increases. This indicates that the radical stabilities in alkynylpyrene derivatives are strikingly improved by increasing the numbers of donors, thus the electrochemically stable radical can be obtained merely by introducing more donor groups to the pyrene center. The unstable cation radical of pyrene is one of the severe intrinsic drawbacks in ECL.[17] These unstable radicals may induce unwanted chemical processes that form dimerization or polymerization products. For compound **5**, the peak potential differences of the forward and reverse peaks (ΔE_{pp}) on the cathodic and anodic curves are 80 mV and 130 mV, respectively, which is compatible with those of electrochemically reversible ferrocene under the same experimental conditions. The enhanced radical stability of **4** and **5** after reduction or oxidation is due to strong π-electron conjugation[4] in these compounds; the conjugation, which is confirmed by photophysical results, explicitly plays an important role in the ECL process. Secondly, the electrochemical HOMO–LUMO band gap (HOMO = highest occupied molecular orbital, LUMO = lowest unoccupied molecular orbital) gradually decreases as the number of donor groups increases, which is in good agreement with energy-gap trends obtained from the lowest UV/Vis absorption values, the maximum values of emission and ECL spectra, and the ab initio calculations (see Figure S1 in the Supporting Information). This result also suggests that more effective conjugation in series **1**–**5** occurs by increasing the number of donors.

Figure 3a shows that the ECL intensities of the compounds enhance remarkably as the number of donor unit increases from **1** to **5**. Even though **5** has the lowest quantum yield ($\Phi = 0.60$) of the five compounds, it is surprisingly unusual that **5** shows an ECL intensity that is 36 times greater than that of **1**, which is due to the enhanced radical stability by highly conjugated system; this is supported by the analysis of the photophysical and electrochemical data. The red-shift of the ECL emission maxima (λ_{max}^{abs}) on going from **1** to **5** is also explained by the π conjugation, as in the photophysical data.

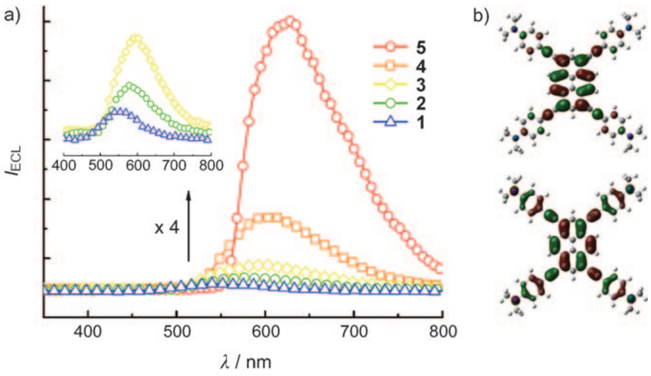

Figure 3. a) ECL spectra of **1**–**5** (0.5 mм) in Bu_4NPF_6 in CH_2Cl_2 (0.1 м) with pulsing (1 Hz) between peak potentials for reduction and oxidation of compounds. b) LUMO (top) and HOMO (bottom) orbital surfaces of **5**.

To gain a better understanding of the experimentally observed properties, we performed DFT calculations with the B3LYP exchange functional by using 6-31G* basis sets in a suite of Gaussian 03 programs.[19] As shown in Figure 3b, the HOMO electrons of **5** are delocalized over the substituents and the pyrene ring (for the orbital surfaces **1**–**4**, see the Supporting Information). Thus, as the compound has more substituents, the electrons can move over a larger space, which results in the absorption peaks becoming red-shifted. To investigate the radical stability, we performed calculations for the cation and anion radicals of **1**–**5**. The calculated non-adiabatic reduction (cation→neutral) potential for the cation radicals of **1**–**5** are −5.71, −5.27, −5.29, −5.02, and −4.81 eV, respectively, which implies that the less substituted compounds (**1**–**3**) are more stabilized upon the addition of one electron than the more substituted compounds (**4** and **5**). Thus, the cation radicals of the more substituted compounds are considered to be more stable than those of less substituted ones. On the other hand, the calculated vertical detachment energy (VDE) of the anion radicals **1**–**5** are 0.59, 0.86, 0.85, 1.00, and 1.12 eV, respectively, which also supports our analysis based on the photophysical and electrochemical measurements.

In summary, a series of pyrene derivatives that bear peripheral DMA–ethynyl units have been prepared to show unique patterns in photophysical and electrochemical properties. Compound **5**, which has four peripheral DMA–ethynyl moieties, exhibits a marked enhancement in ECL intensity compared to the other compounds **1**–**4**; this is attributable to its highly conjugated network that gives an extraordinary stability of cation and anion radicals in oxidation and reduction process, respectively. This result is a promising step in the development of highly efficient light-emitting materials for applications such as organic light-emitting diodes.

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[1] I. S. Shin, J. I. Kim, T. H. Kwon, J. I. Hong, J. K. Lee, H. Kim, *J. Phys. Chem. C* **2007**, *111*, 2280–2286.
[2] J. I. Kim, I. S. Shin, H. Kim, J. K. Lee, *J. Am. Chem. Soc.* **2005**, *127*, 1614–1615.
[3] X. Liu, L. Shi, W. Niu, H. Li, G. Xu, *Angew. Chem.* **2007**, *119*, 425–428; *Angew. Chem. Int. Ed.* **2007**, *46*, 421–424.
[4] C. Booker, X. Wang, S. Haroun, J. Zhou, M. Jennings, B. L. Pagenkopf, Z. Ding, *Angew. Chem.* **2008**, *120*, 7845–7849; *Angew. Chem. Int. Ed.* **2008**, *47*, 7731–7735.
[5] S. Rashidnadimi, T. H. Hung, K. T. Wong, A. J. Bard, *J. Am. Chem. Soc.* **2008**, *130*, 634–639.
[6] J. A. Marsden, J. J. Miller, L. D. Shirtcliff, M. M. Haley, *J. Am. Chem. Soc.* **2005**, *127*, 2464–2476.
[7] A. Elangovan, K. M. Kao, S. W. Yang, Y. L. Chen, T. I. Ho, Y. O. Su, *J. Org. Chem.* **2005**, *70*, 4460–4469.
[8] A. Elangovan, S.-W. Yang, J.-H. Lin, K.-M. Kao, T.-I. Ho, *Org. Biomol. Chem.* **2004**, *2*, 1597–1602.
[9] T. I. Ho, A. Elangovan, H. Y. Hsu, S. W. Yang, *J. Phys. Chem. B* **2005**, *109*, 8626–8633.
[10] R. Y. Lai, X. Kong, S. A. Jenekhe, A. J. Bard, *J. Am. Chem. Soc.* **2003**, *125*, 12631–12639.
[11] F. Fungo, K. T. Wong, S. Y. Ku, Y. Y. Hung, A. J. Bard, *J. Phys. Chem. B* **2005**, *109*, 3984–3989.
[12] X. Jiang, X. Yang, C. Zhao, K. Jin, L. Sun, *J. Phys. Chem. C* **2007**, *111*, 9595–9602.
[13] M. Levitus, K. Schmieder, H. Ricks, K. D. Shimizu, U. H. F. Bunz, M. A. Garcia-Garibay, *J. Am. Chem. Soc.* **2001**, *123*, 4259–4265.
[14] H. Maeda, T. Maeda, K. Mizuno, K. Fujimoto, H. Shimizu, M. Inouye, *Chem. Eur. J.* **2006**, *12*, 824–831.
[15] Y. O. Lee, H. S. Jung, J. H. Lee, K. No, J. S. Kim, *Bull. Korean Chem. Soc.* **2007**, *28*, 2107–2110.
[16] H. M. Kim, Y. O. Lee, C. S. Lim, J. S. Kim, B. R. Cho, *J. Org. Chem.* **2008**, *73*, 5127–5130.
[17] R. Y. Lai, J. J. Fleming, B. L. Merner, R. J. Vermeij, G. J. Bodwell, A. J. Bard, *J. Phys. Chem. A* **2004**, *108*, 376–383.
[18] W. J. Yang, C. H. Kim, M. Y. Jeong, S. K. Lee, M. J. Piao, S. J. Jeon, B. R. Cho, *Chem. Mater.* **2004**, *16*, 2783–2789.
[19] Gaussian 03, M J. Frisch et al., Gaussian, Inc, Wallingford, CT, **2004**.