JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Article

Thermoluminescence and a New Organic Light-Emitting Diode (OLED) Based on Triplet–Triplet Fluorescence of the Trimethylenemethane (TMM) Biradical

Hayato Namai, Hiroshi Ikeda, Yosuke Hoshi, Nobuyuki Kato, Yoshii Morishita, and Kazuhiko Mizuno

J. Am. Chem. Soc., **2007**, 129 (29), 9032-9036• DOI: 10.1021/ja070946+ • Publication Date (Web): 03 July 2007

Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
ARTICLES

Thermoluminescence and a New Organic Light-Emitting Diode (OLED) Based on Triplet−Triplet Fluorescence of the Trimethylenemethane (TMM) Biradical

Hayato Namai,[†] Hiroshi Ikeda,*[,‡] Yosuke Hoshi,[§] Nobuyuki Kato,[†]
Yoshii Morishita,[§] and Kazuhiko Mizuno[‡]

Contribution from the Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan, Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, Sakai, Osaka 599-8531, Japan, and Advanced Materials R&D Center, Hitachi Chemical Co., Ltd. 48 Wadai, Tsukuba, Ibaraki 300-4247, Japan

Received February 9, 2007; E-mail: ikeda@chem.osakafu-u.ac.jp

Abstract: The results of an investigation of the thermoluminescence (TL) and electroluminescence (EL) of arylated methylenecyclopropanes **1**, systems whose photoinduced electron-transfer (PET) chemistry has been thoroughly studied, are described. In both the TL and EL experiments with **1**, electronically excited triplet trimethylenemethane (TMM) biradicals $^3\mathbf{2}^{\bullet\bullet}$ are generated by back electron transfer (charge recombination) of a TMM radical cation (hole) $\mathbf{2}^{\bullet+}$, formed by isomerization of the substrate radical cation (hole, $\mathbf{1}^{\bullet+}$). The application of this chemistry to the design of new organic light-emitting diodes (OLEDs) is described. The mechanistic features of this reaction system have the potential of overcoming significant problems (e.g., quantum efficiency, difficulty obtaining long wavelength emission, and device durability) normally associated with OLEDs that rely on the use of organic closed-shell hydrocarbons.

Introduction

Organic light-emitting diodes (OLEDs) are artificial luminescent devices that utilize both charge injection (CI), i.e., electron transfer (ET), and charge recombination (CR), i.e., back electron transfer (BET),[1] in a manner that is mechanistically linked to processes involved in bio-, chemi-,[2] and electrochemiluminescence.[3] In recent decades, important developments have been made in the basic science and applications of OLEDs.[4−6] Although some of the significant problems of organic closed-shell hydrocarbon based OLEDs (e.g., low quantum efficiencies, difficulties in obtaining long wavelength emission, and device durability) have been partially solved recently by using Ir complexes, much work remains to be done to develop novel reaction systems that can be applied in this technology.[7]

A combination of ET and BET is involved in photoinduced electron-transfer (PET) reactions of organic substrates. Recently, Roth and we showed that PET reaction can be employed to generate triplet biradicals.[8−10] This is exemplified in the PET promoted degenerate rearrangement of arylated methylenecyclopropanes **1** (Scheme 1).[10] In this process, ET from **1** to an electronically excited sensitizer produces a TMM type radical cation $\mathbf{2}^{\bullet+}$ via ring opening of $\mathbf{1}^{\bullet+}$. BET from the sensitizer radical anion (sens$^{\bullet-}$) to $\mathbf{2}^{\bullet+}$ then leads to formation of a triplet TMM type biradical, $^3\mathbf{2}^{\bullet\bullet}$. The triplet multiplicity of the ground state of $\mathbf{2}^{\bullet\bullet}$ is supported by a linear Curie plot.[10a]

Thermoluminescence (TL) is the term given to light emission triggered by thermal activation.[11] Usually, TL occurs when an electronically excited singlet state of a substrate is formed by BET between a radical cation and a radical anion, formed by simultaneous oxidation and reduction of a substrate promoted by using a number of different generation methods (e.g.,

---

[†] Tohoku University (TU).

[‡] Osaka Prefecture University.

[§] Hitachi Chemical Co. Ltd.

(1) Marcus, R. A. *Ann. Rev. Phys. Chem.* **1964**, *15*, 155−196.

(2) Schuster, G. B. *Acc. Chem. Res.* **1979**, *12*, 366−373.

(3) *Electrogenerated Chemiluminescence*; Bard, A. J., Ed.; Marcel Dekker: New York, 2004.

(4) (a) *Organic Light-emitting Device, A Survey*; Shinar, J., Ed.; Springer-Verlag: New York, 2004. (b) Shinar, J.; Savvateev, V. In *Organic Light-emitting Device, A Survey*; Shinar, J., Ed.; Springer-Verlag: New York, 2004; pp 1−42.

(5) *Organic Light-emitting Diodes. Principles, Characteristics, and Processes*; Kalinowski, J., Ed.; Marcel Dekker: New York, 2005.

(6) *Organic Light Emitting-Devices: Synthesis, Properties and Applications*; Mullen, K., Scherf, U., Eds.; Wiley-VCH: Weinheim, 2006.

(7) For a recent report on singlet and triplet emission from OLEDs or polymers, see: (a) Sun, Y.; Giebink, N. C.; Kanno, H.; Ma, B.; Thompson, M. E.; Forrest, S. R. *Nature* **2006**, *440*, 908−912. (b) Mak, C. S. K.; Evans, N. R.; Watkins, S. E.; Williams, C. K.; Holmes, A. B.; Boothby, C. E.; Koehler, A.; Friend, R. H. *Proceedings of SPIE-The International Society for Optical Engineering* **2004**, *5519 (Organic Light-Emitting Materials and Devices VIII)*, 24−34.

(8) (a) Roth, H. D. *J. Phys. Chem. A.* **2003**, *107*, 3432−3437. (b) Roth, H. D. *Pure Appl. Chem.* **2005**, *77*, 1075−1085. (c) Roth, H. D. *J. Photochem. Photobiol. C.* **2001**, *2*, 93−116.

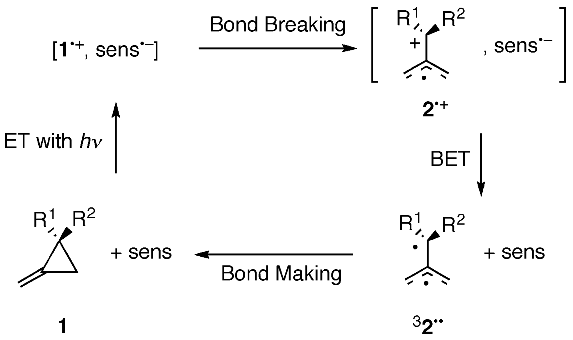
(9) (a) Ikeda, H.; Minegishi, T.; Abe, H.; Konno, A.; Goodman, J. L.; Miyashi, T. *J. Am. Chem. Soc.* **1998**, *120*, 87−95. (b) Ikeda, H.; Minegishi, T.; Miyashi, T. *J. Chem. Soc., Chem. Commun.* **1994**, 297−298. (c) Miyashi, T.; Ikeda, H.; Takahashi, Y. *Acc. Chem. Res.* **1999**, *32*, 815−824.

(10) (a) Ikeda, H.; Akiyama, K.; Takahashi, Y.; Nakamura, T.; Ishizaki, S.; Shiratori, Y.; Ohaku, H.; Goodman, J. L.; Houmam, A.; Wayner, D. D. M.; Tero-Kubota, S.; Miyashi, T. *J. Am. Chem. Soc.* **2003**, *125*, 9147−9157. (b) Ikeda, H.; Nakamura, T.; Miyashi, T.; Goodman, J. L.; Akiyama, K.; Tero-Kubota, S.; Houmam, A.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1998**, *120*, 5832−5833. (c) Miyashi, T.; Takahashi, Y.; Mukai, T.; Roth, H. D.; Schilling, M. L. M. *J. Am. Chem. Soc.* **1985**, *107*, 1079−1080. (d) Miyashi, T.; Ikeda, H.; Takahashi, Y.; Akiyama, K. In *Advances in Electron Transfer Chemistry*; Mariano, P. S., Ed.; JAI: London, 1999; Vol. 6, p 1−39.

(11) Deniau, C.; Déroulède, A.; Kieffer, F.; Rigaut, J. *J. Lumin.* **1971**, *3*, 325−350.

10.1021/ja070946+ CCC: $37.00

Scheme 1. PET Degenerate Rearrangement of Methylenecyclopropane **1** Involving ET and BET Processes[a]



[a] **a**, $R^1 = R^2 =$ Ph; **b**, $R^1 =$ Ph, $R^2 =$ 2-naphthyl; **c**, $R^1 =$ Ph, $R^2 =$ CH_3.

Scheme 2. A Plausible Mechanism for the TL or EL of **1** Involving ET or CI and BET or CR Processes

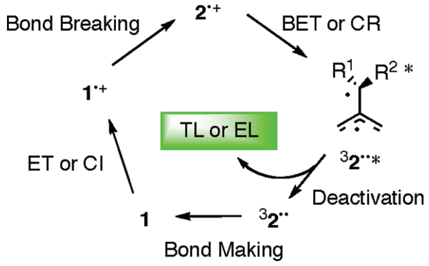
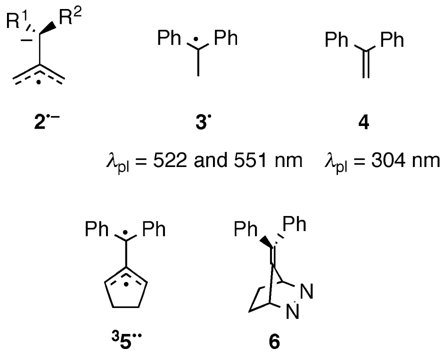


Chart 1. A List of Key Compounds and Intermediates



γ-irradiation). As in PET reaction pathways of **1**, TL and EL of OLEDs involve ET (or CI) and BET (or CR) as key mechanistic steps. A major difference between the PET and TL systems is that the energy-deficient nature of BET to $\mathbf{2}^{\bullet+}$ in PET reactions causes production of the ground state biradical $^{3}\mathbf{2}^{\bullet\bullet}$, whereas energy-sufficient BET or CR to $\mathbf{2}^{\bullet+}$ in TL and EL of OLEDs should stimulate formation of the excited-state biradical, $^{3}\mathbf{2}^{\bullet\bullet}$*. Consequently, we expected that $^{3}\mathbf{2}^{\bullet\bullet}$* might be generated in TL and the EL of OLED systems which employ **1** as the substrate, and if so, this open-shell species would serve as an emitter of *triplet–triplet fluorescence* (Scheme 2). Here, we report (i) a TL mechanism for the diphenyl derivative (**1a**), (ii) the potential characteristics of an OLED using **1**, and (iii) a success in fabricating a novel type of OLED that includes a degenerate methylenecyclopropane rearrangement system using the 2-(2-naphthyl)-2-phenyl derivative (**1b**).

Results and Discussion

Thermoluminescence of 1. A degassed methylcyclohexane (MCH) glassy matrix containing **1a** ($R^1 = R^2 =$ Ph, 5 mM) was subjected to γ-irradiation by using a ^{60}Co source at 77 K. MCH is a solvent[12] that has been employed typically in γ-irradiation studies to generate simultaneously radical cations and radical anions. The matrix formed in this process likely contains two types of radical cations ($\mathbf{1a}^{\bullet+}$ and $\mathbf{2a}^{\bullet+}$)[13] and radical anions ($\mathbf{1a}^{\bullet-}$ and $\mathbf{2a}^{\bullet-}$) (see Chart 1).[14] In fact, the maxima at $\lambda_{ab} = 440$ and 500 nm observed at 77 K [Figure 1 (red)] suggest that $\mathbf{2a}^{\bullet+}$ (lit[13] $\lambda_{ab} = 432$ nm, *n*-butyl chloride) and $\mathbf{2a}^{\bullet-}$ (lit[14] $\lambda_{ab} = 496$ nm, 2-methyltetrahydrofuran) are formed in this system.

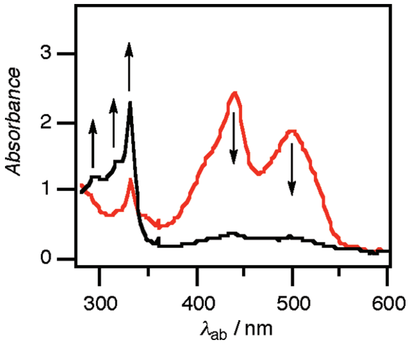


Figure 1. Changes in the UV/vis absorption of a γ-irradiated glassy MCH matrix of **1a** on warming from 77 to ca. 130 K. Arrows indicate major changes in absorptivity.

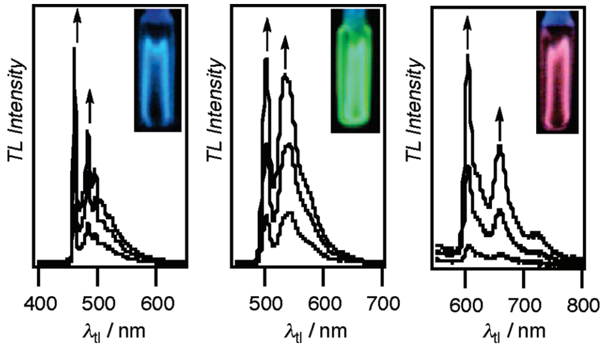


Figure 2. Changes in the TL of γ-irradiated glassy MCH matrices of **1a** (center), **1b** (right), and **1c** (left) observed on warming from 77 to ca. 130 K. Arrows indicate an increase in the intensities of the emission bands.

On warming of the MCH matrix, formed by the γ-irradiation of **1a**, from 77 to *ca.* 130 K, an intense bright green TL ($\lambda_{tl} = 501$ and 533 nm) is observed [Figure 2 (center)]. Growth of the new absorption bands (Figure 1) and emission bands [Figure 2 (center)] occurs simultaneously with the decrease in the absorption bands associated with $\mathbf{2a}^{\bullet+}$ and $\mathbf{2a}^{\bullet-}$ (Figure 1). Similarly, blue [$\lambda_{tl} = 462$ and 484 nm, Figure 2 (left)] and red [$\lambda_{tl} = 603$ and 656 nm, Figure 2 (right)] TL are observed when respective MCH matrices of **1c** ($R^1 =$ Ph, $R^2 = CH_3$) and **1b** ($R^1 =$ Ph, $R^2 =$ 2-naphthyl) are γ-irradiated. The corresponding efficiencies of TL for **1a**, **1b**, and **1c** relative to that of the parent anthracene were *ca.* 1.3, 0.2, and 0.2. Interestingly, TL was not observed when γ-irradiated *n*-butyl chloride and MTHF matrices of these substances were warmed. This is probably due to a lack of the radical anions ($\mathbf{1a}^{\bullet+}$ and $\mathbf{2a}^{\bullet+}$) and radical cations

---

(12) Brocklehurst, B.; Russell, R. D. *Trans. Faraday. Soc.* **1969**, *65*, 2159–2167.

(13) Ikeda, H.; Namai, H.; Kato, N.; Ikeda, T. *Tetrahedron Lett.* **2006**, *47*, 1857–1860.

(14) Ikeda, H.; Namai, H.; Kato, N.; Ikeda, T. *Tetrahedron Lett.* **2006**, *47*, 1501–1504.

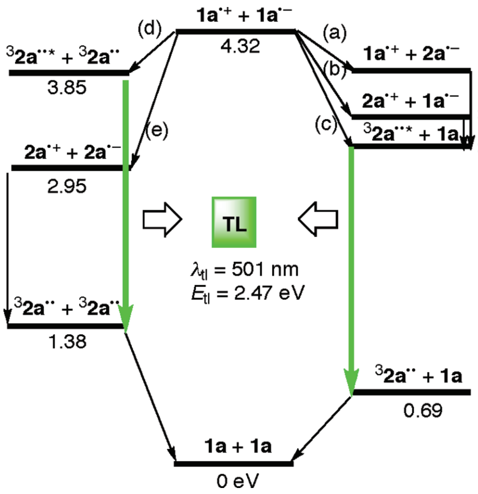


Figure 3. Energy diagram of TL for **1a**. Relative energies (eV) are based on the total energy of two molecules of **1a**.

($\mathbf{1a}^{\bullet-}$ and $\mathbf{2a}^{\bullet-}$) in the *n*-butyl chloride and MTHF matrices, respectively (see the mechanism shown below).

The TL and absorption bands, observed by γ-irradiation of **1a**, closely resemble the photoluminescence bands (λ_{pl} = 491 and 519 nm, λ_{ex} = 328 nm in MCH matrices) and absorption bands (λ_{ab} = 298, 316, and 328 nm in MCH matrices) of the structurally related diphenyl-substituted five-membered cyclic TMM biradical $^3\mathbf{5}^{\bullet\bullet}$ (Chart 1),[15,16] generated independently by the photodeazetization of diazene **6** in an MCH matrix. These findings show that the TL bands at 501 and 533 nm and the absorption bands at 296−330 nm are associated with the excited triplet state of TMM biradical $^3\mathbf{2a}^{\bullet\bullet}$* and its ground state $^3\mathbf{2a}^{\bullet\bullet}$, respectively. To our knowledge, this is the first observation of TL from an electronically excited biradical species.

A plausible mechanism that accounts for TL from **1a** consists of five steps (Scheme 2) and involves (i) γ-irradiation induced ET to give $\mathbf{1a}^{\bullet+}$ and $\mathbf{1a}^{\bullet-}$,[13,14] (ii) ring opening of $\mathbf{1a}^{\bullet+}$ or $\mathbf{1a}^{\bullet-}$ to give $\mathbf{2a}^{\bullet+}$ or $\mathbf{2a}^{\bullet-}$,[13,14] (iii) BET to give $^3\mathbf{2a}^{\bullet\bullet}$*, (iv) light emission from $^3\mathbf{2a}^{\bullet\bullet}$*, and (v) regeneration of **1a** from $^3\mathbf{2a}^{\bullet\bullet}$.[10] An energy diagram for this sequence, constructed by using the TL energy (λ_{tl} = 501 nm, E_{tl} = 2.47 eV), redox potentials of **1a** and related compounds, and the estimated energy of the biradical, $\Delta E(^3\mathbf{2a}^{\bullet\bullet})$ = 0.69 eV, is given in Figure 3.[17] The energy of the $\mathbf{1a}^{\bullet+}/\mathbf{1a}^{\bullet-}$ pair is estimated to be +4.32 eV relative to the total energy of two molecules of **1a**. The four possible pathways (a−d in Figure 3) for production of $^3\mathbf{2a}^{\bullet\bullet}$* include stepwise routes via $\mathbf{2}^{\bullet+}$ or $\mathbf{2}^{\bullet-}$ (a and b) and bond-dissociative BET routes[18] (c and d). The most likely precursor of $^3\mathbf{2a}^{\bullet\bullet}$* is the pair $\mathbf{2a}^{\bullet+}$ and $\mathbf{1a}^{\bullet-}$ since ring opening of $\mathbf{1a}^{\bullet+}$ is more exergonic than that of $\mathbf{1a}^{\bullet-}$.[13,14] The resulting triplet biradical $^3\mathbf{2a}^{\bullet\bullet}$* then decays to $^3\mathbf{2a}^{\bullet\bullet}$ with light emission. Therefore, TL in the **1a** system corresponds to *triplet−triplet fluorescence*[19] from $^3\mathbf{2a}^{\bullet\bullet}$*. Finally, $^3\mathbf{2a}^{\bullet\bullet}$ formed in this manner quantitatively reverts to **1a**. Note that reaction of $\mathbf{2a}^{\bullet+}$ and $\mathbf{2a}^{\bullet-}$ to produce two molecules of $^3\mathbf{2a}^{\bullet\bullet}$ (path e) does not participate in TL because the energy gap (1.57 eV) in the radical ion pair $\mathbf{2a}^{\bullet+}/\mathbf{2a}^{\bullet-}$ and biradical pair $^3\mathbf{2a}^{\bullet\bullet}/{}^3\mathbf{2a}^{\bullet\bullet}$ is smaller than E_{tl} = 2.47 eV and the hypothetical BET between $\mathbf{2a}^{\bullet+}/\mathbf{2a}^{\bullet-}$ giving the pair $^3\mathbf{2a}^{\bullet\bullet}*/{}^3\mathbf{2a}^{\bullet\bullet}$ is energetically unfavorable. Because TL associated with decay of $^3\mathbf{2a}^{\bullet\bullet}$* resembles PL of the 1,1-diphenylethyl radical ($\mathbf{3}^{\bullet}$, Chart 1), the emission from $^3\mathbf{2a}^{\bullet\bullet}$* occurs from the diphenylmethyl radical fluorophore mainly.[16,19,20] The remaining allyl subunit is not involved in fluorescence, but it plays an important role in the bond forming process leading back to **1a**.

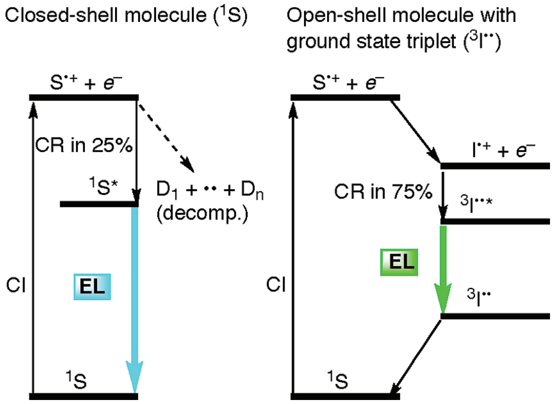


Figure 4. A conceptual diagram showing that larger η_{int} values are expected for EL from an open-shell molecule with a ground state triplet as compared to a closed-shell molecule.

Characteristics of Potential OLEDs Based on 1. A strategy for the design of novel OLEDs, which use highly reactive open-shell molecules like $^3\mathbf{2}^{\bullet\bullet}$ as light-emitting species, seems at first to be impractical owing to the need for high durability of these devices. However, OLEDs of this type have several potentially advantageous characteristics, including ease of production of long wavelength EL with readily prepared small molecules, increase in the internal EL quantum efficiency (η_{int}), and efficient regeneration of the starting material (Figure 4).

The ability to produce long wavelength EL by using systems in which $^3\mathbf{2}^{\bullet\bullet}$ is the light-emitting species arises from the HOMO−SOMO or SOMO−LUMO energy gaps found in open-shell molecules. These energy gaps are generally much smaller than the HOMO−LUMO gaps present in structurally related closed-shell molecules. For example, $\mathbf{3}^{\bullet}$ has absorption maxima (λ_{pl}) at 522 and 551 nm (λ_{ex} = 336 nm) in MCH,[16] while structurally related 1,1-diphenylethylene (**4**) has a λ_{pl} at 304 nm. In fact, this expectation was confirmed by the observation of green TL from $^3\mathbf{2a}^{\bullet\bullet}$*.

The expectation that systems based on $^3\mathbf{2}^{\bullet\bullet}$ would have large internal EL quantum efficiencies (η_{int}) is related to spin multiplicity rules. In general, fluorescence from ^{1}S of closed-shell systems can have a maximum η_{int} of 25% because ^{1}S* is formed by the CR of a hole $S^{\bullet+}$ in statistically predicted 25% yield and fluorescence takes place by a singlet−singlet transition (Figure 4). The triplet excited state (^{3}S*) is generated simultaneously in 75% yield and undergoes nonradiative decays mainly along with inefficient, spin-forbidden, energy wasting deactivation. In contrast, the triplet excited states ($^3I^{\bullet\bullet}$*) of open-shell molecules (intermediates), like $^3\mathbf{2}^{\bullet\bullet}$, that are generated in 75% yield can undergo *triplet−triplet transitions* to produce simul-

---

(15) Turro, N. J.; Mirbach, M. J.; Harrit, N.; Berson, J. A.; Platz, M. S. *J. Am. Chem. Soc.* **1978**, *100*, 7653−7658.

(16) Ikeda, H.; Namai, H.; Taki, H.; Miyashi, T. *J. Org. Chem.* **2005**, *70*, 3806−3813.

(17) The value of $\Delta E(^3\mathbf{2a}^{\bullet\bullet})$ = 0.69 eV was estimated on the assumption that no significant substituent effects occur on $\Delta E(^3\mathbf{2a}^{\bullet\bullet})$ between $^3\mathbf{2a}^{\bullet\bullet}$ and the corresponding bis(4-methoxyphenyl) derivative. See ref 10a.

(18) Karki, S. B.; Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R.; Zona, T. A. *J. Am. Chem. Soc.* **1997**, *119*, 431−432.

(19) Turro, Berson, Platz *et al.* reported that the emission observed for $^3\mathbf{5}^{\bullet\bullet}$ is *fluorescence* based on its lifetime. See ref 15.

(20) (a) Bromberg, A.; Meisel, D. *J. Phys. Chem.* **1985**, *89*, 2507−2513. (b) Bromberg, A.; Schmidt, K. H.; Meisel, D. *J. Am. Chem. Soc.* **1985**, *107*, 83−91.

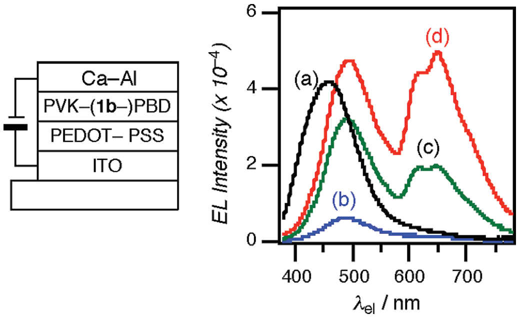


Figure 5. (left) Structure of the bilayer OLED with or without dopant **1b**. (right) EL spectra of the OLED with [(b) 10 V, (c) 15 V, (d) 20 V] or without [(a) 15 V] **1b**.

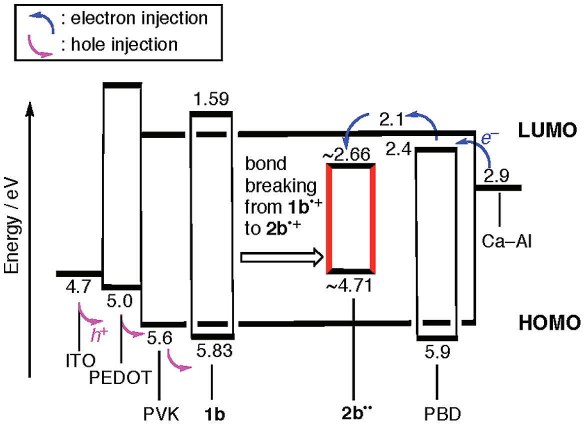


Figure 6. Schematic energy-level diagram for the [ITO/PEDOT−PSS/PVK−**1b**−PBD/Ca−Al] OLED. See ref 22.

taneously triplet ground states ($^{3}\mathrm{I}^{\bullet\bullet}$) and efficient *fluorescence* emission. As a result, OLEDs based on this chemistry/photophysics can have theoretically maximum η_{int} values of 75%.

A new way of overcoming the low durability of OLED devices, typically caused by undesirable chemical reactions of substrate holes (radical cations), might be found in the use of open-shell molecules whose chemistry leads to efficient regeneration of the starting substrate. For example, in the system described above, light emission from the key intermediate $^{3}\mathbf{2}^{\bullet\bullet}$ is associated with its quantitative conversion to the original substrate (Figure 4).[10]

An OLED Based on 1b. To provide a proof-of-concept example, we have developed a unique long wavelength emitting OLED system based on a methylenecyclopropane substrate **1**. A bilayer OLED was fabricated by using indium tin oxide (ITO) as the anode, poly(3,4-ethylenedioxy-2,4-thiophene)−polystyrene sulfonate (PEDOT−PSS) as the hole-injection/transport material, poly(*N*-vinyl)carbazole (PVK) and 2-(4-biphenylyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) as host materials, and Ca−Al as the cathode {[ITO/PEDOT−PSS/PVK−PBD (67:13)/Ca−Al]} [Figure 5 (left)]. Application of a voltage of 15 V to this OLED produces an EL band with a maximum (λ_{el}) at 458 nm corresponding to emission from PVK* [Figure 5 (right, a)]. The PVK−PBD layer was then doped with 2-(2-naphthyl)-2-phenyl-1-methylenecyclopropane **1b** (20 wt %). The EL spectra of the resulting OLED [ITO/PEDOT−PSS/PVK−**1b**−PBD (67:20:13)/Ca−Al] are strongly dependent on the applied voltage. At 10 V, weak EL occurs with a λ_{el} at ca. 490 nm [Figure 5 (right, b)].[21−25] When the applied voltage is increased to 20 V, EL with a λ_{el} at 617 and 650 nm appears together with the emission band at ca. 493 nm [Figure 5 (right, d)]. We suggest that the 617 and 650 nm emission bands correspond to those observed at 603 (2.06 eV) and 656 nm in the TL of **1b** [Figure 2 (right)] and therefore that $^{3}\mathbf{2}^{\bullet\bullet *}$ which is formed serves as the light-emitting species in the OLED process.

A plausible emission mechanism for the OLED containing **1b** resembles, in part, that for the TL shown in Scheme 2. As depicted in the energy correlation in Figure 6, a hole from the ITO anode is injected into **1b** via PEDOT−PSS and PVK. The resulting new hole $\mathbf{1b}^{\bullet+}$ undergoes bond breaking to give another hole $\mathbf{2b}^{\bullet+}$. Simultaneously, an electron is transported from the Ca−Al cathode to PVK via PBD and finally injected into the $\mathbf{2b}^{\bullet+}$. The resulting $^{3}\mathbf{2b}^{\bullet\bullet *}$ emits light at 617 and 650 nm in a process leading back to **1b**.

In its current form, the new OLED system based on **1b** is limited by the need for high voltages and its low luminescence intensity (30.0 cd m^{-1}) and current efficiency (0.158 cd A^{-1}).[26,27] In spite of these shortcomings, the strategy for the design of OLEDs, based on chemical reactions of and light emission from short-lived open-shell molecules, may yet prove viable in the construction of highly efficient devices.[28]

Conclusion

The results of this investigation, probing the TL and EL of methylenecyclopropanes **1**, have elucidated possible chemical mechanisms involving the light emission from the open-shell, triplet TMM biradical $^{3}\mathbf{2}^{\bullet\bullet *}$. In addition, we have observed TL in this system that involves the three primary colors, blue, green, and red, suggesting that it might be possible to tune the emission color. Finally, this effort has provided a proof-of-concept example of a unique, long wavelength emitting OLED system based on a methylenecyclopropane substrate. The findings suggest that the design strategy for fabrication of OLEDs based on small, reactive open-shell molecules as emitters is viable. In this regard it is interesting to note that an OLED based on 5,12-diphenylnaphthacene ($C_{30}H_{20}$), a large complex molecule, generates a green emission[29] similar to the one using **1a** ($C_{16}H_{14}$). In addition, the mechanistic features of this reaction system have the potential of overcoming other significant problems (e.g., quantum efficiency and device durability) normally associated with OLEDs that rely on the use of organic closed-shell hydrocarbons. Especially, device durability is the most significant problem. Therefore, the use of a reactive species

---

[21] This EL band may be assigned to an exciplex of PVK and **1b**. Further studies on this band are now in progress and will be published elsewhere.

[22] The energy of the HOMO of $\mathbf{2b}^{\bullet\bullet}$ (ca. 4.7 eV) was estimated analyzing the calibration of ionization potentials (IPs) determined from the DFT calculation and the oxidation potentials (E^{ox}) reported by Wayner for structurally related organic radicals. See refs 23−25 and the Supporting Information.

[23] Wayner, D. D. M.; McPhee, D. J.; Griller, D. *J. Am. Chem. Soc.* **1988**, *110*, 132−137.

[24] Sim, B. A.; Milne, P. H.; Griller, D.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1990**, *112*, 6635−6638.

[25] Workentin, M. S.; Wayner, D. D. M. *Res. Chem. Intermed.* **1993**, *19*, 777−785.

[26] This may be due to possible undesired reactions of TMM radical cations $\mathbf{2}^{\bullet+}$ or biradical $\mathbf{2}^{\bullet\bullet}$ toward molecular oxygen or some reactant. For reactions of TMM biradicals, see ref 27.

[27] (a) Little, R. D. *Chem. Rev.* **1996**, *96*, 93−114. (b) Allan, A. K.; Carroll, G. L.; Little, R. D. *Eur. J. Org. Chem.* **1998**, 1−12.

[28] Although an OLED with the dimethoxy derivative of **1a** showed a similar performance, their luminescence intensity and current efficiency were slightly lower than those of **1b**. A similar attempt using **1a** gave unfruitful results. Nothing was attempted for **1c**. Further studies are now in progress and will be published elsewhere.

[29] Cosimbescu, L.; Hatwar, T. K. U.S. Pat. Appl. Publ. (2005), 25 pp.

like ^{3}**2**$^{\bullet\bullet}$* is an absurd and paradoxical approach from the aspect of the durability of the device. While it is not clear at the present time whether the new concept can be put to practical use, the paradoxical approach falls into a new category of luminescence that is driven by BET or CR.

Experimental Section

General Method. See the Supporting Information for details.

Syntheses. 2-(2-Naphthyl)-2-phenyl-1-methylenecyclopropane (**1b**) and 2-methyl-2-phenyl-1-methylenecyclopropane (**1c**) were prepared from 2-(α-styryl)naphthalene and α-methylstyrene, respectively, by using the procedures previously reported for the synthesis of 2,2-diphenyl-1-methylenecyclopropane (**1a**).[10]

1b: Colorless solids (*n*-hexane); mp 32−34 °C. Anal. Calcd for $C_{20}H_{16}$: C = 93.71%, H = 6.29%. Found: C = 93.43%, H = 6.37%; IR (KBr, cm^{-1}) 3055, 3022, 1599, 1493, 1447, 1020, 893, 820, 741, 698; ^{1}H NMR (200 MHz, $CDCl_3$, δ_{ppm}) 1.99 (s, 2 H), 5.65 (s, 1 H), 5.86 (s, 1 H), 7.21−7.80 (m, 12 H); ^{13}C NMR (50 MHz, $CDCl_3$, δ_{ppm}) 21.31, 33.04, 104.43, 125.65, 126.10, 126.39 (2 C), 126.74, 127.62, 127.79, 128.08 (3 C), 128.34 (2 C), 132.20, 133.39, 139.27, 141.08, 143.67; LRMS (70 eV, *m/z*, %) 256 (M$^+$, 100), 241 (43), 215 (19), 178 (18), 165 (18), 128 (19).

1c: Colorless oil; IR (neat, cm^{-1}) 2968, 1603, 1495, 1447, 1030, 887, 770, 698, 534; ^{1}H NMR (200 MHz, $CDCl_3$, δ_{ppm}) 1.38 (s, 2 H), 1.53 (s, 3 H), 5.47 (s, 1 H), 5.59 (s, 1 H), 7.16−7.30 (m, 5 H); ^{13}C NMR (50 MHz, $CDCl_3$, δ_{ppm}) 20.39, 23.48, 23.73, 102.92, 125.86, 126.42 (2 C), 128.27 (2 C), 141.79, 145.13; HRMS (EI) Calcd for $C_{11}H_{12}$, 144.0934; found, 144.0935; LRMS (70 eV, *m/z*, %) 144 (M$^+$, 14), 143 (20), 130 (11), 129 (100), 128 (49), 127 (14), 115 (12).

Measuring the UV/vis Absorption Spectra of γ-Irradiated Glassy Matrices. A solution of MCH, *n*-butyl chloride, or 2-methyltetrahydrofuran (1 mL) containing the substrate (5 mM) in a flat vessel [synthetic quartz, 2 × 10 × 40 mm^3 (thickness × width × height)] was degassed by five freeze (77 K)−pump (10^{-2} Torr)−thaw (ambient temperature) cycles and then sealed at 10^{-2} Torr. A glassy matrix was obtained by steeping the vessel in liquid nitrogen. This vessel was irradiated with γ-rays from a 4.0 TBq ^{60}Co source in liquid N_2 at 77 K for 40 h. The changes in the absorption spectra between before and after irradiation were observed at 77 K with an absorption spectrophotometer.

Measuring the TL Spectrum. A TL spectrum of the sample matrix on annealing from 77 to ca. 130 K was collected in the dark using a photonic multichannel spectral analyzer linked to a personal computer.

Fabrication of OLEDs. Patterned ITO coated glass was cleaned by using the usual method and then treated in an UV/O_3 chamber. PEDOT−PSS was spin-coated on the ITO plate to give a hole-transporting layer thickness of ca. 40 nm. After calcination, PVK−PBD with or without **1b** was spin-coated to give an emitting layer thickness of ca. 100 nm. The Ca (20 nm)−Al (150 nm) cathode was thermally deposited onto the emitting layer under vacuum ($<10^{-3}$ Pa) and sealed under N_2.

Measuring the EL Spectrum. An EL spectrum of OLED was collected with a spectroradiometer linked to a DC voltage current source monitor and a personal computer.

Acknowledgment. H.I. and K.M. gratefully acknowledge financial support from a Grant-in-Aid for Scientific Research on Priority Areas (Nos. 14050008 and 17029058 in the Area No. 417) and others (Nos. 16655018, 18037063, and 19350025) from the Ministry of Education, Culture, Sports, Science, and Technology of Japan. H.I. thanks the Shorai Foundation, the Mazda Foundation, and the Iketani Science and Technology Foundation for financial support. We also thank Professor Emeritus K. Tokumaru (University of Tsukuba) and Professor T. Majima (Osaka University) for their valuable discussions and Professor M. Ueda (Tohoku University) for his generous assistance.

Supporting Information Available: General methods of the experiments, preparation of **1**, a correlation between calculated IP and E^{ox} (V vs SCE in CH_3CN) of the benzyl and structurally related radicals, and a movie of TL of a γ-irradiated glassy MCH matrix of **1a**, and a photo of the white emission from the bilayer OLED with dopant **1b**. This material is available free of charge via the Internet at http://pubs.acs.org.

JA070946+