

## Tuning emission color of electroluminescence from two organic interfacial exciplexes by modulating the thickness of middle gadolinium complex layer

Mingtao Li, Wenlian Li, Lili Chen, Zhiguo Kong, Bei Chu et al.

Citation: *Appl. Phys. Lett.* **88**, 091108 (2006); doi: 10.1063/1.2181194

View online: <http://dx.doi.org/10.1063/1.2181194>

View Table of Contents: <http://apl.aip.org/resource/1/APPLAB/v88/i9>

Published by the [American Institute of Physics](#).

---

### Additional information on Appl. Phys. Lett.

Journal Homepage: <http://apl.aip.org/>

Journal Information: [http://apl.aip.org/about/about\\_the\\_journal](http://apl.aip.org/about/about_the_journal)

Top downloads: [http://apl.aip.org/features/most\\_downloaded](http://apl.aip.org/features/most_downloaded)

Information for Authors: <http://apl.aip.org/authors>

## ADVERTISEMENT



**HAVE YOU HEARD?**

Employers hiring scientists  
and engineers trust  
**physicstodayJOBS**



<http://careers.physicstoday.org/post.cfm>

# Tuning emission color of electroluminescence from two organic interfacial exciplexes by modulating the thickness of middle gadolinium complex layer

Mingtao Li, Wenlian Li,<sup>a)</sup> Lili Chen, Zhiguo Kong, Bei Chu, and Bin Li

Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, 16-Dong NanHu Road, Changchun 130033, People's Republic of China and Graduate School of the Chinese Academy of Sciences, Beijing 100039, People's Republic of China

Zhizhi Hu and Zhiqiang Zhang

Organic Photoelectronic Materials & Technology Development Center, Anshan University of Science and Technology, Anshan 114000, People's Republic of China

(Received 17 October 2005; accepted 7 February 2006; published online 1 March 2006)

Electroluminescent colors of organic light-emitting diodes (OLEDs) can be tuned by modulating the thickness of gadolinium (Gd) complex layer sandwiched between an electron-transporting layer (ETL) and a hole-transporting layer (HTL). The emission colors, which originate from the two interfacial exciplexes simultaneously, can be tuned from green to orange by increasing the thickness of the Gd-complex layer. The atom force microscope images have proved that there are many gaps in the thinner Gd-complex layers. Therefore, besides the exciplex formation between Gd complex and HTL, the exciplex between ETL and HTL is also formed. The results demonstrate that a simple way of color tuning can be realized by inserting a thin layer of color tuning material between HTL with lower ionization potentials and ETL with higher electron affinities. Moreover, photovoltaic device and white OLED based on the two exciplexes are also discussed. © 2006 American Institute of Physics. [DOI: 10.1063/1.2181194]

In recent decades, organic light-emitting diodes (OLEDs) based on exciplex emission are currently under active research. The interfacial exciplex emission usually occurs at the interface between a donor-type (D) molecule and an acceptor-type (A) one. Exciplex (excited complex) is a transient donor-acceptor or charge-transfer complex between the donor with excited state and the acceptor with ground state, therefore the emission attributes to a charge transfer excited state ( $D^+A^-$ )\*, and the emission wavelength corresponds the energy difference between the highest occupied molecular orbital (HOMO) level of a donor and lowest unoccupied molecular orbital (LUMO) level of an acceptor.<sup>1,2</sup> Earlier research on exciplexes was mainly focused on their formation mechanisms and negative effects on electroluminescence (EL).<sup>3,4</sup> Contrarily, it was interestingly found that using exciplex emission as a component of expecting emission to obtain desired EL color was a valuable subject.<sup>5-10</sup> Moreover, the emission color of exciplex is usually changed with the varying applied bias.<sup>5</sup> Therefore, the emission color can be tuned by varying the applied voltage, however, the change is limited.

In this work, we report a way of tuning EL color based on exciplex formation. A layer of Gd-complex, tris-(dibenzoylmethanato)-mono-(bathophenanthroline) gadolinium [Gd(DBM)<sub>3</sub>bath] is sandwiched between 1,3,5-tris(3-methylphenyl-phenylamino)triphenylamine (*m*-MTDATA) and 1,3,5-tris(N-phenylbenzimidazol-2-yl)benzene (TPBI) layers as a color tuning material (CTM), in which *m*-MTDATA and TPBI are served as hole-transporting layer (HTL) and electron-transporting layer (ETL), respectively. The EL colors shift from green to orange with the increasing

thickness of the CTM. The emissions come from two combined exciplexes formed both at the interface between *m*-MTDATA and Gd complex and at the interface between *m*-MTDATA and TPBI. The complexes of other rare earth (RE) with fluorescence, such as europium (Eu) complex and terbium (Tb) complex can be also used as CTM, because exciplexes can be also generated between these complexes and HTL.<sup>4,11</sup> However, characteristic emissions of these RE(III) complexes lead to the discussions to be inconvenient. As the previous report in our group, Gd complex is an electron-transporting material and the exciplex can be generated with N,N'-bis(3-methylphenyl)-N,N'-diphenyl-[1,1'-biphenyl]-4,4'-diamine.<sup>12</sup> When the *m*-MTDATA is used, the exciplex can be more easily formed due to its lower ionization potentials.<sup>13</sup>

The chemical structures of the materials used are shown in Fig. 1. [Gd(DBM)<sub>3</sub>bath] was synthesized in our laboratory and the other chemicals from purchase were directly used without further purification. All devices were grown onto a pre-cleaned indium tin oxide (ITO) coated glass substrate with resistance of 20 Ω/sq. The ITO-coated substrates were routinely cleaned by ultrasonic treatment in solvents and then cleaned by exposure to a UV-ozone ambient. All organic layers were deposited in succession without breaking vacuum ( $3 \times 10^{-4}$  Pa). Thermal deposition rates for organic materials, LiF, and Al were ~1, ~1, and ~10 Å/s, respectively. The surface of thin film of Gd complex was examined using a Nanoscope Dimension™ 3100 atomic force microscope (AFM). The AFM images were obtained over an area of 2 μm × 2 μm polished bare glass and Gd-complex coated glasses with different Gd-complex layer thicknesses of 0.5, 1.0, and 1.5 nm, respectively. EL, photoluminescence (PL) spectra and Commission International de l'Eclairage (CIE) coordinates were measured with a HITACHI MPF-4

<sup>a)</sup> Author to whom correspondence should be addressed; electronic mail: wllioel@yahoo.com.cn

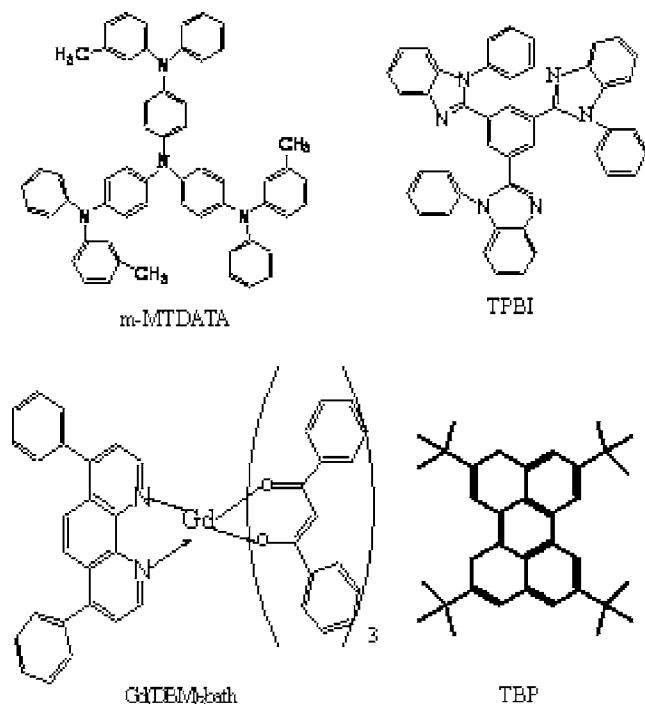
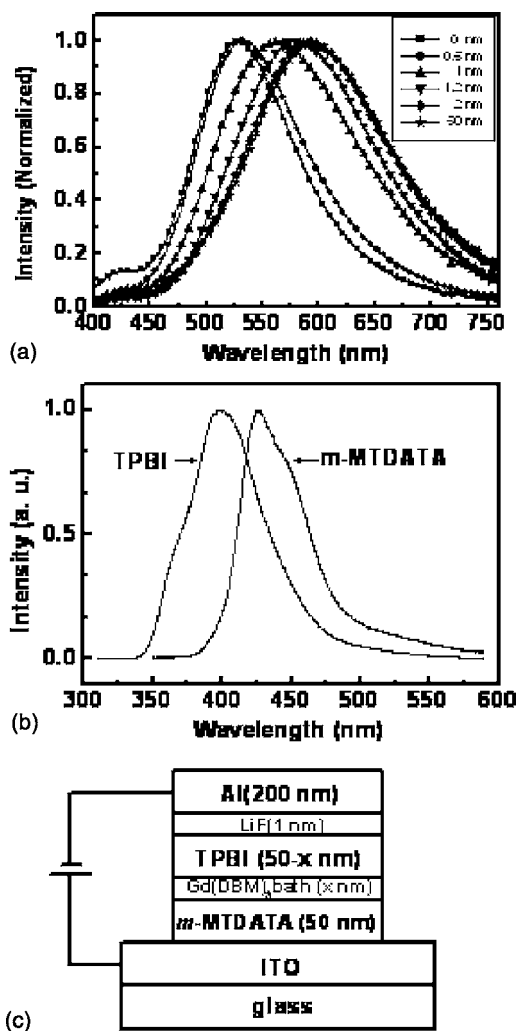


FIG. 1. The chemical structures of the materials used in this work.

fluorescence spectrophotometer. The photovoltaic properties were measured under illumination from an ultraviolet lamp with  $4 \text{ mW/cm}^2$  output. All measurements were done at room temperature without encapsulation.

The EL spectra of the devices with the different thickness of Gd complex and the device configuration are shown in Figs. 2(a) and 2(c), respectively. Comparing with the PL [see Fig. 2(b)], we can see that the EL emissions do not correspond with the PL spectrum of *m*-MTDATA or TPBI film. When the thicknesses of Gd complex are 0 and 50 nm, the emissions should, respectively, result from the interfaces of *m*-MTDATA/TPBI and *m*-MTDATA/Gd complex, and when the thicknesses are 0.5, 1, 1.2, and 2 nm, considering the nonfluorescent property of Gd complex,<sup>12</sup> the wider emission bands would synchronously result from the two interfaces of *m*-MTDATA/TPBI and *m*-MTDATA/Gd complex. These can be interpreted that exciplex formation may occur more easily at the interface of *m*-MTDATA/TPBI than at the interface of *m*-MTDATA/Gd complex because of the lower HOMO level ( $-5.1 \text{ eV}$ )<sup>13</sup> of *m*-MTDATA and higher LUMO of TPBI ( $-2.7 \text{ eV}$ ).<sup>14</sup>

To understand the formation mechanism of the exciplexes, the device with 10 nm Gd complex is fabricated. The total thicknesses of organic layers in these devices are all fixed at 100 nm to avoid electric field effect on the spectra. However, there is almost no difference in EL comparing with the device with 50 nm Gd complex. It suggests that exciplex is formed at the interface between *m*-MTDATA and Gd complex when Gd-complex layer is thick enough. That is, the exciplex cannot be formed at the interface between Gd complex and TPBI due to their same electron-transporting properties. However, the EL emission peaks shift to shorter wavelength when the thickness of Gd complex is considerably reduced. When the thickness is reduced to 2 nm, the spectrum shifts slimly compared with that of the device with 50 nm Gd complex and while the thickness is gradually reduced to 1.2, 1.0, and 0.5 nm, the spectrum shifts to shorter

FIG. 2. EL spectra of the devices with the different thicknesses of Gd-complex layer at 8 V (a), PL spectra of the films of TPBI and *m*-MTDATA (b), and device configuration (c).

wavelength by 15, 30, and 60 nm, respectively. The findings suggest that the two exciplexes are both at work when such a thin Gd-complex layer is inserted between *m*-MTDATA and TPBI layers. It is likely that the thinner Gd-complex layer should presumably be discontinuous film so that an interaction between TPBI and *m*-MTDATA also occurs to generate exciplex. In order to test the hypothesis, the surface states of various thinner films of Gd complex are examined using an AFM, as shown in Fig. 3. From the AFM images, we can notice that the discontinuous film takes on some *islands* when the Gd-complex layer is ultrathin. When the thickness increases, more *islands* are formed so that an intact film ultimately comes into being. It is clear that there are some gaps among these *islands* when the thickness is thin enough so that its upper layer (TPBI) and nether layer (*m*-MTDATA) can also interact to form exciplex. Therefore, the various EL colors must attribute to the simultaneous emissions of the two exciplexes formed at the two interfaces of *m*-MTDATA/Gd-complex and *m*-MTDATA/TPBI.

Table I lists the proportions of the formed exciplexes, which are calculated according to the relative emission intensity of each exciplex. It can be seen that the exciplex emissions from *m*-MTDATA/Gd-complex interface ( $E_2^*$ ) are enhanced with the increasing thickness of the Gd-complex layer, but exciplex emissions from *m*-MTDATA/TPBI inter-

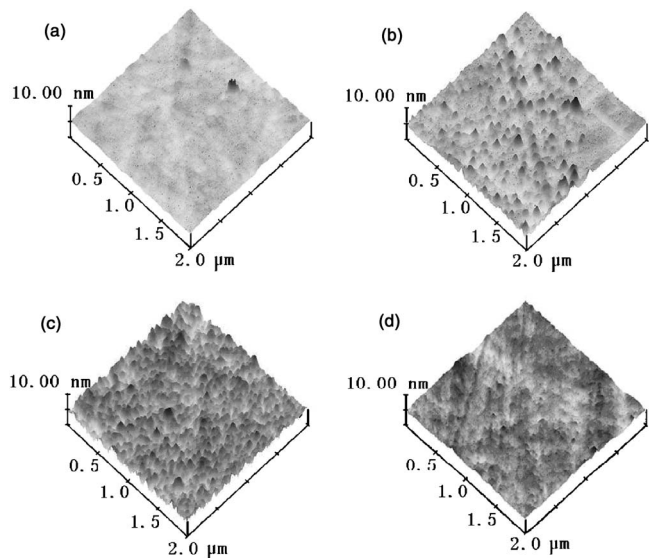


FIG. 3. AFM images obtained over an area of  $2\ \mu\text{m} \times 2\ \mu\text{m}$  for polished glasses coated with different Gd-complex layer thicknesses, bare glass (a), 0.5 nm (b), 1.0 nm (c) and 1.5 nm (d) are shown.

face ( $E_1^*$ ) contrarily decrease, which attribute to different contact degree. As a result, the EL colors shift with the reduced thickness of Gd complex at 8 V.

As the previous reports, the photovoltaic (PV) properties were intensively relative to exciplex formation.<sup>15,16</sup> In this work, we also find that the different formation proportions of the two exciplexes affect their PV effects. The open circuit voltage ( $V_{oc}$ ) gradually increases when the thickness of Gd-complex layer decreases, that is,  $V_{oc}$  of 1.80 V, 2.00 V, 2.05 V and 2.18 V at the thickness of 50 nm, 1 nm, 0.5 nm, 0 nm are determined, respectively. It suggests that the contact between TPBI and *m*-MTDATA can take place through the gaps of the Gd-complex layer and it increases with the decreasing thickness of Gd-complex layer. Therefore, the contact is gradually increased so that the PV effect is much enhanced. We also calculate the  $V_{oc}$  of the devices with 0.5 nm and 1.0 nm Gd complex according to the formation proportion of each exciplex, which are closed to the experimental data. The results demonstrated that the EL color and  $V_{oc}$  are all relative to the proportions of the contacts.

Just as the above discussions, there are some gaps among these *islands* when the Gd-complex layer is reduced. Using the gaps to construct a white OLED is an interesting issue. An ultrathin layer blue dopant, TBP (2,5,8,11-tetra-*t*-butylperylene), is inserted into some gaps to achieved this aim. A white EL with CIE coordinates of  $x=0.319$  and  $y=0.388$  at 10 V is obtained from the device of ITO/*m*-MTDATA(50 nm)/Gd(DBM)<sub>3</sub>bath(1 nm)/TBP(0.5 nm)/TPBI(48.5 nm)/LiF(1 nm)/Al(200 nm). The spectrum of

TABLE I. The proportions of the two exciplexes in the devices with different thicknesses of Gd-complex layer.  $E_1^*$ : exciplex originates from the interface between *m*-MTDATA and TPBI.  $E_2^*$ : exciplex originates from the interface between *m*-MTDATA and Gd(DBM)<sub>3</sub> bath. The proportions of the two exciplexes in the devices with the thicknesses of 0.5, 1.0, 1.2, and 2.0 nm are calculated from EL spectra.

$x$ (nm)	0	0.5	1.0	1.2	2.0	50
$E_1^*$ (%)	100	80	45	30	5	
$E_2^*$ (%)		20	55	70	95	100

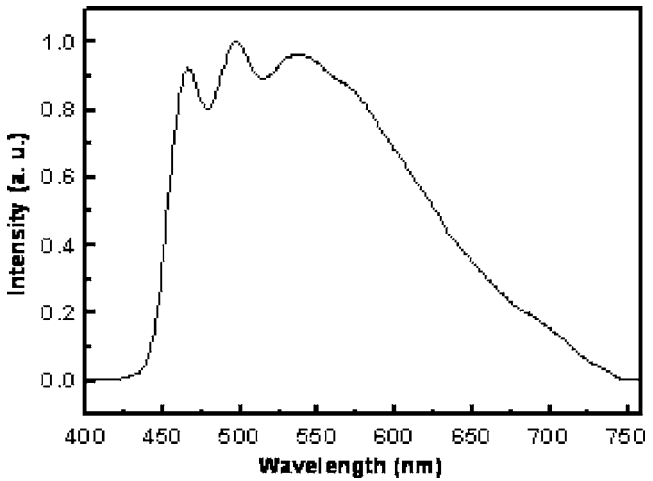


FIG. 4. The EL spectrum of white OLED at 10 V. The CIE coordinates are  $x=0.319$  and  $y=0.388$ . [Device configuration: ITO/*m*-MTDATA(50 nm)/Gd(DBM)<sub>3</sub>bath(1 nm)/TBP(0.5 nm)/TPBI(48.5 nm)/LiF(1 nm)/Al(200 nm)]

white EL is shown in Fig. 4, which is composed of the blue emission of TBP, green and orange emissions of the above-mentioned exciplexes.

In conclusion, this work presented the OLEDs with tunable emission color based on varying emission proportions of two exciplexes resulting from two interfaces, which was realized by changing the thickness of Gd complex as the color-modulating layer. When the Gd complex layer was thin enough, the discontinuous film was formed and offered contacts between its upside (TPBI) and underside (*m*-MTDATA), which was demonstrated to be important to the changing EL colors and the varying PV characteristics. Using the discontinuous properties of Gd-complex film, a white device could be constructed. It provided roadmaps for developing OLED materials, organic PV devices and designing other new electronic devices.

- <sup>1</sup>S. A. Jenekhe and J. A. Osaheni, Science **265**, 765 (1994).
- <sup>2</sup>S. A. Jenekhe, Adv. Mater. (Weinheim, Ger.) **7**, 309 (1995).
- <sup>3</sup>C. Adachi, T. Tsutsui, and S. Saito, Appl. Phys. Lett. **56**, 799 (1990).
- <sup>4</sup>Z. Hong, C. Liang, R. Li, W. Li, D. Zhao, D. Fan, D. Wang, B. Chu, F. Zang, L. S. Hong, and S. T. Lee, Adv. Mater. (Weinheim, Ger.) **13**, 1241 (2001).
- <sup>5</sup>K. Itano, H. Ogawa, and Y. Shirota, Appl. Phys. Lett. **72**, 636 (1998).
- <sup>6</sup>J. F. Wang, Y. Kawabe, S. E. Shaheen, M. M. Morrell, G. E. Jabbour, P. A. Lee, J. Anderson, N. R. Armstrong, B. Kippelen, E. A. Mash, and N. Peyghambarian, Adv. Mater. (Weinheim, Ger.) **10**, 230 (1998).
- <sup>7</sup>M. Cocchi, D. Virgili, G. Giro, V. Fattori, P. Di Marco, J. Kalinowski, and Y. Shirota, Appl. Phys. Lett. **80**, 2401 (2002).
- <sup>8</sup>L. C. Palilis, A. J. Makinen, M. Uchiada, and Z. H. Kafafi, Appl. Phys. Lett. **82**, 2209 (2003).
- <sup>9</sup>M. Mazzeo, D. Pisignano, F. D. Sala, J. Thompson, R. I. R. Blyth, G. Gigli, R. Cingolani, G. Sotgiu, and G. Barbarella, Appl. Phys. Lett. **82**, 334 (2003).
- <sup>10</sup>S. P. Singh, Y. N. Mohapatra, M. Qureshi, and S. Sundar Manoharan, Appl. Phys. Lett. **86**, 113505 (2005).
- <sup>11</sup>W. L. Li, J. Q. Yu, G. Sun, Z. R. Hong, Y. Yu, Y. Zhao, J. B. Beng, and T. Tsutsui, Synth. Met. **91**, 263 (1997).
- <sup>12</sup>C. J. Liang, D. Zhao, Z. R. Hong, R. G. Li, W. L. Li, and J. Q. Yu, Thin Solid Films **371**, 207 (2000).
- <sup>13</sup>Y. Shirota, Y. Kuwabara, H. Lnada, T. Wakimoto, H. Nakada, Y. Yonemoto, S. Kawami, and K. Imai, Appl. Phys. Lett. **65**, 807 (1994).
- <sup>14</sup>Y. T. Tao, C. W. Ko, and E. Balasubramaniam, Thin Solid Films **417**, 61 (2002).
- <sup>15</sup>Z. R. Hong, C. S. Lee, S. T. Lee, W. L. Li, and Y. Shirota, Appl. Phys. Lett. **81**, 2878 (2002).
- <sup>16</sup>B. Chu, D. Fan, W. L. Li, Z. R. Hong, and R. G. Li, Appl. Phys. Lett. **81**, 10 (2002).