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# New low-molecular-weight electroluminescent materials for green organic light emitting diodes

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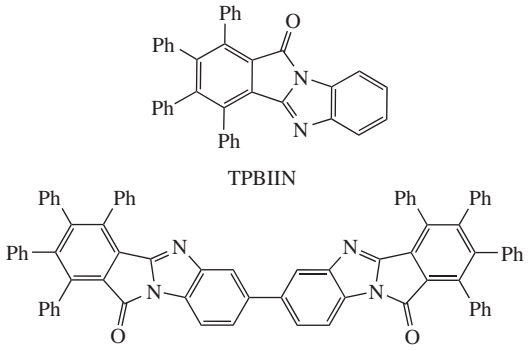
A new family of low-molecular-weight fluorescent emitters comprising a 1,2,3,4-tetraphenylbenzo[4,5]imidazo[2,1-*a*]isoindol-11-one core has been designed and applied to the construction of highly efficient organic light emitting diodes with strong green exciplex emission.

Intensive research on organic light emitting diodes (OLEDs) resulted in the development of a novel generation of flat screens which outperform conventional LCD displays in many aspects.[1] The industrial production of OLED displays (*e.g.*, AMOLED displays) by Korean companies affected significantly the market of all mobile electronic devices.

Another niche for the application of OLEDs is related to energy-saving lighting and signage. Solution-processible conjugated polymers are the most appropriate materials for the design of OLED lighting products.[2–6] Particular attention is also paid to energy-transfer systems comprising the quantum dots of inorganic semiconductors,[7] organic dyes[8,9] and phosphorescent metal complexes[10] as light emitters.

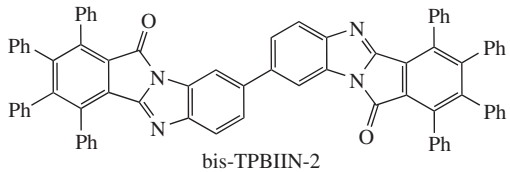
However, solution processible small molecules are also suitable for the design of OLED devices for lighting applications. For example, low-molecular-weight electroluminescent materials comprising tetraarylsilole[11–14] or tetraphenylbenzene[15] units in their molecular frameworks were extensively studied as electroluminescent materials for blue OLEDs. Fluorene-benzothiadiazole hybrid molecules were found very promising fluorescent green emitters.[16] Bright green electroluminescence (up to 15 330 cd $m^{-2}$) with high efficiency (up to 7.9 cd $A^{-1}$) was also achieved using a bisquinoxaline core with appended triphenyl amine units.[17]



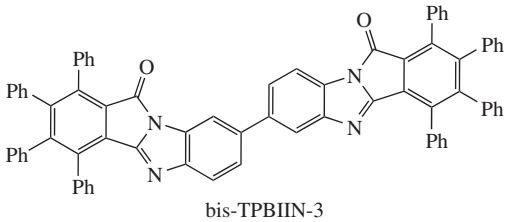
TPBIIN



bis-TPBIIN-1



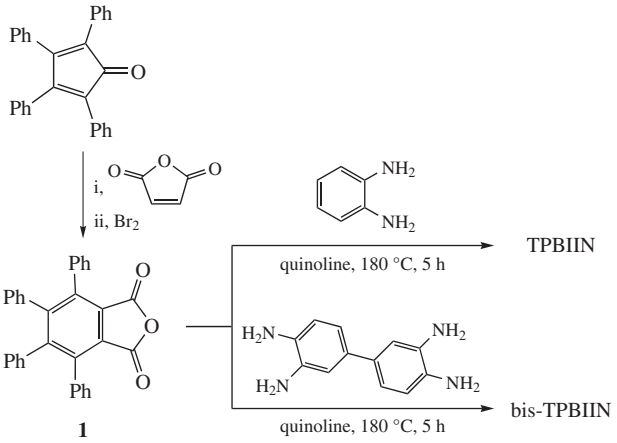
bis-TPBIIN-2



bis-TPBIIN-3

Here we report a new family of small molecular electroluminescent materials for OLEDs based on 1,2,3,4-tetraphenylbenzo[4,5]imidazo[2,1-*a*]isoindol-11-one derivatives such as TPBIIN and bis-TPBIIN. The synthesis of these compounds requires two steps. The first step is the reaction of tetraphenylcyclopentadienone with maleic anhydride, which yields tetraphenylphthalic anhydride **1**, according to a published procedure.[18,19] The condensation of **1** with *o*-phenylenediamine or 3,3′-diaminobenzidine affords TPBIIN and bis-TPBIIN, respectively, in high yields (Scheme 1).† Note that the synthesis of TPBIIN (*via* a different chemical route) and similar compounds was reported previously.[18,20]

The samples of TPBIIN and bis-TPBIIN were characterized using ESI mass spectrometry, FTIR, $^1$H and $^{13}$C NMR spectro-




**Scheme 1**

† Tetraphenylcyclopentadienone (97%), quinoline (98%), chlorobenzene (99%), *o*-phenylenediamine (98%) and maleic anhydride (99%) were purchased from Acros Organics and used as received. Optical spectra (photoluminescence, electroluminescence) were recorded using Avantes AvaSpec-2048 and Varian 3G UV-VIS spectrometers. NMR spectra were obtained using Bruker AMX 400 (400 MHz) and Bruker Avance (600 MHz) instruments.

scopy, H-H COSY and H-C HSQC two-dimensional NMR spectra and chemical analysis. TPBIIN was formed as an individual compound, while bis-TPBIIN was isolated as a mixture of three isomers in a molar ratio of 0.6 : 0.25 : 0.15 (NMR data). The most abundant component of the isomer mixture was unsymmetrical bis-TPBIIN-3; this can be due to its superior thermodynamic stability.

Taking into account strong similarity of the structures of bis-TPBIIN and the steric hindrance of polar carbonyl groups by phenyl rings, it was not surprising that column chromatography did not allow us to achieve even partial separation of the isomeric species. Therefore, the mixture of bis-TPBIIN isomers was utilized as an electroluminescent material in this work.

We studied the photoluminescence (PL) properties of TPBIIN and bis-TPBIIN in solution and in a solid state. The luminescent properties of TPBIIN were published.[21–26] The solution state PL spectrum of TPBIIN is characterized by a sharp maximum at 485 nm with a shoulder at ~540 nm (Figure 1, curves *1*, *2*). The solid state spectrum exhibited two distinct maxima at 500 and 550 nm. The observed change of the PL spectrum going from the solution to the solid state suggests the formation of exciplex states by aggregated TPBIIN molecules. The difference between the solution and solid state PL spectra becomes even more pronounced for bis-TPBIIN (Figure 1, curves *3*, *4*). Indeed, the maximum of the emission band shifted from 495 (in solution) to 560 nm (in a solid state). The observed spectral changes are remarkable for organic materials, especially for small nonplanar molecules such as bis-TPBIIN, and indicate the formation of strongly bound exciplex states in thin films. These observations are very important for OLED applications since exciplex emission might also dominate in the electroluminescence spectra of TPBIIN and bis-TPBIIN. Similar strong exciplex emission bands were revealed previously for zinc complexes with sulfanylamino-substituted ligands.[27]

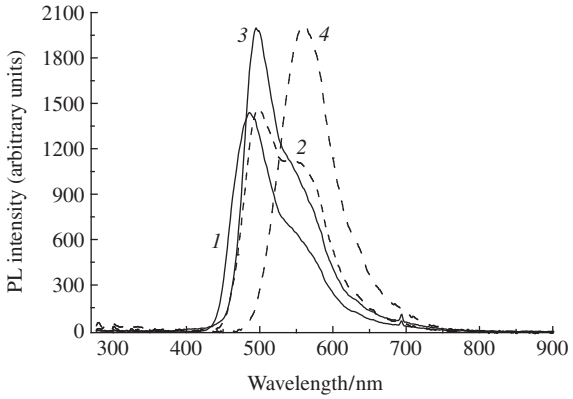



**Figure 1** (*1*, *3*) Solution (in $CHCl_3$) and (*2*, *4*) solid-state PL spectra of (*1*, *2*) TPBIIN and (*3*, *4*) bis-TPBIIN.

Note that both TPBIIN and bis-TPBIIN are readily soluble in low-polarity organic solvents such as chloroform, toluene, chlorobenzene and 1,2-dichlorobenzene, which allow one to prepare thin films of these compounds using solution processing techniques such as spin coating.

Simple OLED devices were fabricated by coating ITO glass with hole injecting layer of PEDOT : PSS, drying it at 200 °C and subsequent deposition of TPBIIN or bis-TPBIIN from solutions in a mixed solvent (chloroform–chlorobenzene, 2 : 1, 10 mg $ml^{-1}$). The devices were finalized by the vacuum deposition of Ca (20 nm)/Ag (100 nm) cathodes [Figure 2(*a*)]. The prepared OLEDs showed weak yellowish green electroluminescence with a maximum brightness of ~200 cd $m^{-2}$ achieved at 13 V for a bis-TPBIIN device.

The observed poor performance of TPBIIN and bis-TPBIIN as electroluminescent materials in single-layer devices suggests the unbalanced injection of holes and electrons. If one type of charge carriers is not injected efficiently, the excitons are generated in the close proximity to one of the electrodes, which leads to massive recombination losses.

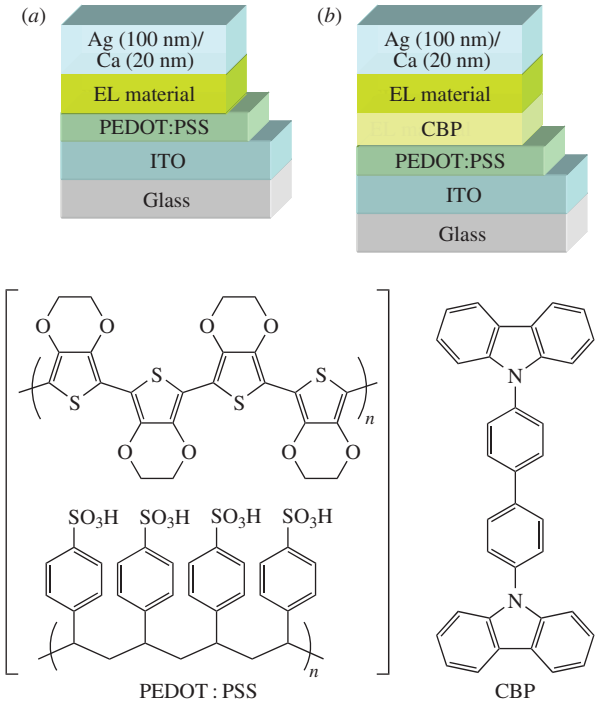



**Figure 2** OLED architectures (*a*) without and (*b*) with hole transport layer CBP (EL material states for TPBIIN or bis-TPBIIN).

*Synthesis of TPBIIN*. Tetraphenylphthalic anhydride (3 g, 6.64 mmol) was mixed with 3 equiv. of *o*-phenylenediamine (2.15 g, 19.91 mmol) and 50 ml of quinoline. The resulting mixture was deaerated and heated in an argon atmosphere at reflux for 7 h. The reaction mixture was cooled and poured into 600 ml of 10% aqueous HCl. The precipitated product was separated by filtration, washed with methanol (3×50 ml) and dried in air. The yield of product was 1.5 g (43%). $^1$H NMR (600 MHz, $CDCl_3$) $\delta$: 6.78 (m, 4H), 6.90 (m, 6H), 7.17 (m, 3H), 7.25 (m, 9H), 7.54 (d, 1H), 7.64 (d, 1H). $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$: 112.35, 121.85, 124.68, 126.19, 126.25, 126.36, 127.01, 127.06, 127.43, 127.5, 127.65, 127.72, 129.65, 129.74, 130.00, 130.32, 130.75, 130.86, 135.42, 135.94, 137.81, 137.97, 138.27, 141.97, 145.64, 148.03, 149.42, 155.84, 160.36.

*Synthesis of bis-TPBIIN*. Tetraphenylphthalic anhydride (4 g, 8.85 mmol) was mixed with 3 equiv. of 3,3′-diaminobenzidine (0.74 g, 2.95 mmol) and 75 ml of quinoline. The resulting mixture was deaerated and heated in an argon atmosphere at reflux for 7 h. The reaction mixture was then cooled down, poured into 600 ml of 10% aqueous HCl. The precipitated product was separated by filtration, washed with methanol (3×50 ml) and dried in air. The crude product was dissolved in toluene and poured on the top of a silica gel column (silica 40–60 μm, 60 Å). Elution with a mixture of toluene with methanol (99.6 : 0.4, v/v) produced bright yellow fluorescent solution of bis-TPBIIN. The yield of the product was 700 mg (23%). $^1$H NMR (600 MHz, $CDCl_3$) $\delta$: 6.83 (m, 8H), 6.95 (m, 12H), 7.21 (m, 6H), 7.28 (m, 14H), 7.44–7.55 (m, 2H), 7.60 (m, 1.2H), 7.70 (m, 0.8H), 7.78 (s, 0.3H), 7.82 (s, 0.5H), 7.93 (s, 0.6H), 7.96 (s, 0.6H). $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$: 110.85, 110.95, 112.38, 112.41, 120.38, 120.44, 121.89, 121.93, 124.03, 124.06, 125.32, 125.59, 125.67, 125.80, 126.26, 126.39, 126.44, 126.75, 126.86, 126.90, 127.02, 127.07, 127.16, 127.22, 127.35, 127.42, 127.44, 127.48, 127.51, 127.59, 127.67, 127.73, 127.86, 128.25, 128.69, 128.91, 129.06, 129.11, 129.76, 129.79, 129.89, 129.96, 130.02, 130.30, 130.34, 130.56, 130.77, 130.88, 130.90, 130.96, 131.87, 132.59, 132.65, 135.32, 135.35, 135.39, 135.40, 135.48, 135.51, 135.54, 135.83, 135.87, 135.95, 137.61, 137.62, 137.68, 137.79, 137.84, 137.90, 137.94, 137.98, 138.00, 138.04, 138.08, 138.27, 138.30, 139.10, 139.41, 139.68, 139.92, 142.01, 142.08, 142.10, 145.60, 145.73, 147.71, 148.04, 148.06, 148.16, 148.78, 148.98, 150.12, 150.17, 156.10, 156.22, 156.46, 156.51, 160.22, 160.26.

Considering the molecular structures of TPBIIN and bis-TPBIIN, one could assume that they would form anions more readily than cations. This hypothesis was proved by cyclic voltammetry measurements which revealed that both compounds undergo reversible one-electron reduction with the half-wave potentials $E_{1/2}$ = –1.13 (TPBIIN) and –1.20 V (bis-TPBIIN) *vs.* SCE. At the same time, no reversible oxidation processes were observed in the DMF solutions of test materials. This means that injection of holes in TPBIIN and bis-TPBIIN thin films might be hindered compared to the injection of electrons.

To improve hole injection in OLEDs, we applied an additional hole-transport layer. To fabricate such devices, the coating of PEDOT:PSS films on cleaned ITO slides and their drying at 190 °C for 15 min was followed by the vacuum deposition of CBP (30 nm) and bis-TPBIIN (80 nm) layers. Finally, a metal cathode was deposited on the top of organic layers by thermal evaporation. The architecture of the produced device is shown in Figure 2(*b*).

The fabricated OLED devices showed a turn-on voltage of 3–4 V, a maximal brightness of 14000 cd $m^{-2}$ at 14 V and an efficiency of 5–6 cd $A^{-1}$. The reference OLEDs comprising conventional electroluminescent material Alq3 [tris(8-hydroxyquinolinato)aluminum] instead of bis-TPBIIN in the same device configuration exhibited inferior characteristics: a turn-on voltage of 6.0–6.5 V, a maximal brightness of 7500 cd $m^{-2}$ at 14 V and an efficiency of 1.5–2.2 cd $A^{-1}$. The EL spectrum of the OLED based on bis-TPBIIN and a photograph of the operating device are shown in Figure 3. It is notable that EL spectrum fits quite well to the solid state PL spectrum of bis-TPBIIN represented by exciplex emission band. Therefore, the emission coming from the light-emitting device should also be attributed to the exciplex states. It is intriguing that the exciplex emission is so strong in the case of bis-TPBIIN that it allows for the fabrication of highly efficient OLED devices.

In conclusion, we have designed a new family of solution processible electroluminescent materials comprising a 1,2,3,4-tetraphenylbenzo[4,5]imidazo[2,1-*a*]isoindol-11-one core, which can be easily synthesized in bulk quantities starting from readily available precursors. The bis-TPBIIN material exhibits unusually strong exciplex emission, which is untypical of nonplanar small molecules. Efficient self-assembling of bis-TPBIIN in a solid state might be responsible for the observed strong exciplex emission. A combination of bis-TPBIIN with an appropriate hole-transporting material allowed us to fabricate highly efficient green OLEDs outperforming reference devices comprising Alq3 as an electroluminescent material. Thus, the results demonstrate that TPBIIN, bis-TPBIIN and related compounds form a promising family of fluorescent emitters.

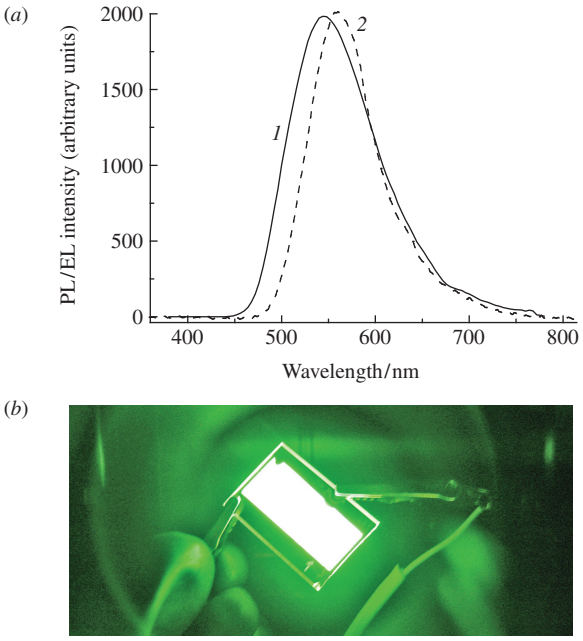



**Figure 3** (*a*) (*1*) EL spectrum of OLED comprising bis-TPBIIN as electroluminescent material compared to (*2*) PL spectrum of bis-TPBIIN in solid state and (*b*) a photograph of the operating device.

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## References

1 T. Yamada and Y. Tsubata, *J. Synth. Org. Chem. Jpn*., 2012, **70**, 473.
2 N. T. Kalyani and S. J. Dhoble, *Renewable Sustainable Energy Rev.*, 2012, **16**, 2696.
3 E. I. Mal'tsev, M. A. Brusentseva, D. A. Lypenko, V. I. Berendyaev, V. A. Kolesnikov, B. V. Kotov and A. V. Vannikov, *Polym. Adv. Technol*., 2000, **11**, 325.
4 S. M. King, I. I. Perepichka, I. F. Perepichka, F. B. Dias, M. R. Bryce and A. P. Monkman, *Adv. Funct. Mater*., 2009, **19**, 586.
5 I. F. Perepichka, D. F. Perepichka, H. Meng and F. Wudl, *Adv. Mater*., 2005, **17**, 2281.
6 V. A. Kostyanovsky, D. K. Susarova, G. Adam, R. N. Lyubovskaya and P. A. Troshin, *Mendeleev Commun.*, 2013, **23**, 26.
7 A. A. Vashchenko, V. S. Lebedev, A. G. Vitukhnovskii, R. B. Vasiliev and I. G. Samatov, *JETP Lett.*, 2012, **96**, 113.
8 E. I. Maltsev, V. V. Prokhorov, O. M. Perelygina, D. A. Lypenko and A. V. Vannikov, *Inorg. Mater.: Appl. Res*., 2011, **2**, 325.
9 J. Yu. Mayorova, P. A. Troshin, A. S. Peregudov, S. M. Peregudova, M. G. Kaplunov and R. N. Lyubovskaya, *Mendeleev Commun*., 2007, **17**, 156.
10 M. Ya. Goikhman, I. V. Podeshvo, N. L. Loretsyan, I. V. Gofman, R. Yu. Smyslov, T. N. Nekrasova, V. E. Smirnova, A. A. Polevoi and A. V. Yakimanskii, *Russ. Chem. Bull., Int. Ed*., 2012, **61**, 966 (*Izv. Akad. Nauk, Ser. Khim*., 2012, 961).
11 H. Murata, Z. H. Kafafi and M. Uchida, *Appl. Phys. Lett*., 2002, **80**, 189.
12 L. C. Palilis, A. J. Mäkinen, M. Uchida and Z. H. Kafafi, *Appl. Phys. Lett*., 2003, **82**, 2209.
13 B. Z. Tang, X. Zhan, G. Yu, P. P. S. Lee, Y. Liub and D. Zhu, *J. Mater. Chem.*, 2001, **11**, 2974.
14 B. Mi, Y. Dong, Z. Li, J. W. Y. Lam, M. Häußler, H. H. Y. Sung, H. S. Kwok, Y. Dong, I. D. Williams, Y. Liu, Y. Luo, Z. Shuai, D. Zhu and B. Z. Tang, *Chem. Commun*., 2005, 3583.
15 C. Huang, C.-G. Zhen, S. P. Su, K. P. Loh and Z.-K. Chen, *Org. Lett.*, 2005, **7**, 391.
16 K. M. Omer, S.-Y. Ku, K.-T. Wong and A. J. Bard, *J. Am. Chem. Soc.*, 2009, **131**, 10733.
17 J. M. Hancock, A. P. Gifford, Y. Zhu, Y. Lou and S. A. Jenekhe, *Chem. Mater*., 2006, **18**, 4924.
18 W. Dilthey, I. ter Horst and A. Schaefer, *J. Prakt. Chem. (Leipzig)*, 1937, **148**, 53.
19 *Organic Syntheses. An Annual Publication of Satisfactory Methods for the Preparation of Organic Chemicals*, J. Wiley & Sons, New York, 1943, vol. 23, p. 93.
20 E. Mueller and G. Zountsas, *Chem. Ber*., 1972, **105**, 2529.
21 T. Deno, B. G. Delvin, S. H. Eldin, A. Igbal, K. Kunimoto and J. Otani, *US Patent, 6080516 A*, C07D, C09B, H05B, 1998.
22 B. G. Delvin, S. H. Eldin, A. Igbal, K. Kunimoto and J. Otani, *WO Patent, 9833866*, C09B, C09K, C07D, 1998.
23 B. G. Delvin, J. Otani and K. Kunimoto, *WO Patent, 9833865*, C09K, C07D, C09B, H01L, 1998.
24 B. G. Delvin, J. Otani, K. Kunimoto, T. Deno, A. Igbal and S. H. Eldin, *WO Patent, 9833864*, C07D, H05B, C09B, C09K, 1998.
25 T. Deno, K. Komada, A. Igbal and B. G. Delvin, *WO Patent, 9833863*, C07D, H05B, C09K, C09B, 1998.
26 T. Deno, B. G. Delvin, K. Komada, K. Kunimoto and J. Otani, *WO Patent, 9833862*, C09B, C07D, C09K, 1998.
27 M. G. Kaplunov, S. S. Krasnikova, S. L. Nikitenko, N. L. Sermakasheva and I. K. Yakushchenko, *Nanoscale Res. Lett.*, 2012, **7**, 1.

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