Organic &
Biomolecular
Chemistry

Cite this: *Org. Biomol. Chem.*, 2011, **9**, 5941

www.rsc.org/obc

COMMUNICATION

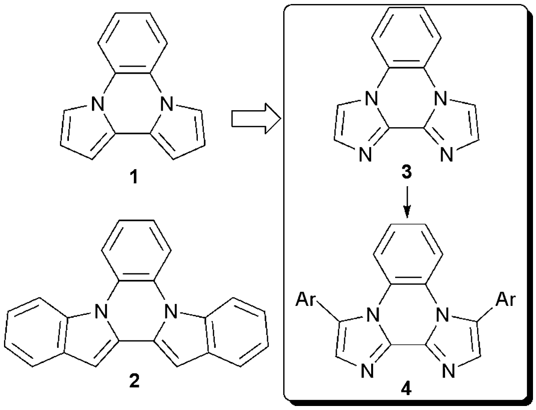
Novel formation of diimidazo[1,2-*a*:2′,1′-*c*]quinoxaline derivatives and their optical properties†

Shoji Matsumoto,*[a] Erdenebolor Batmunkh,[a] Motohiro Akazome,[a] Yoshiyuki Takata[b] and Michiko Tamano[b]

Received 22nd June 2011, Accepted 1st July 2011
DOI: 10.1039/c1ob06002c

Reaction of 1,2-di(imidazolyl)benzene treated with *n*-BuLi proceeded to give diimidazo[1,2-*a*:2′,1′-*c*]quinoxaline in the presence of iodine or Pd(PPh$_3$)$_4$. Blue fluorescence was observed from 3,10-diarylated diimidazoquinoxalines with high quantum yield. They were also applied to organic light-emitting devices as emitters, in which the diphenyl derivative emits a nearly pure blue light.

Heteroaromatics containing nitrogen atoms are extensively utilized in the field of biological and functional materials. In view of the example of optoelectronics, 3-(4-biphenyl)-4-phenyl-5-(4-*tert*-butylphenyl)-1,2,4-triazole (TAZ)[1] and 1,3,5-tris(1-phenylbenz[*b*]imidazol-2-yl)benzene (TPBI) are used as electron-transporting materials in organic electroluminescent devices. Focused on imidazole and benz[*b*]imidazole compounds, their iridium, europium, and boron complexes have been investigated as luminescent materials for organic light-emitting diodes (OLEDs).[2–4] While there have been many studies on the luminescence characteristics of the imidazole derivatives,[5] there have been few reports on the electroluminescent properties of non-chelated imidazole derivatives.[6] We have been investigating the optical properties of 2,2′-bipyrrole derivatives[7] and have found that dipyrrolo- and diindolo[1,2-*a*:2′,1′-*c*]quinoxalines (**1** and **2**, respectively) exhibit fluorescence with a good quantum yield (Φ_F ~ 0.55).[7a] When the pyrrole moieties of **1** are replaced by imidazole moieties, it is expected that the fluorescence properties of the resulting diimidazo[1,2-*a*:2′,1′-*c*]quinoxaline (**3**) change significantly (Scheme 1). To the best of our knowledge, there has been only one report published on the construction of a diimidazo[1,2-*a*:2′,1′-*c*]quinoxaline structure by Ebrahimlo *et al.*[8] They obtained a 20% yield of the diimidazoquinoxaline derivative by the reaction of 2,3-dichloroquinoxaline with a specific isoxazolone derivative. The literature did not deal with its optical properties. Herein, we report the novel formation of **3** and arylated **4**, and their optical and electroluminescent properties. The coupling reaction between the two imidazole rings of 1,2-di(imidazolyl)benzene is achieved to give **3**, which can be utilized for further functionalization. We also reveal the optical properties of **4** that emit blue fluorescence with high quantum yields.



Scheme 1 Structural representations of **1**, **2**, **3**, and **4**.

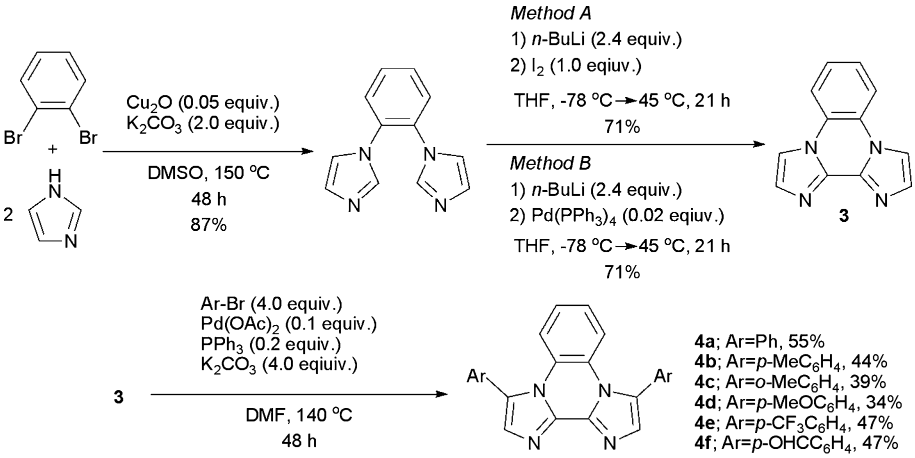
For the efficient preparation of the diimidazo[1,2-*a*:2′,1′-*c*]quinoxaline structure, we tried an intramolecular coupling reaction between the two imidazole rings of 1,2-di(imidazolyl)benzene using iodine, a procedure which was used in the synthesis of **1** and **2**.[7a] 1,2-Di(imidazolyl)benzene was obtained in 87% yield by a Cu$_2$O-catalysed coupling reaction (Scheme 2).[9] When the reaction of 1,2-di(imidazolyl)benzene with iodine was conducted in CH$_3$CN at 80 °C, an unidentified product with low solubility in the solution was obtained. Therefore, we examined the reaction of imidazole anions with iodine, which led to the iodination reaction at one imidazole ring followed by a substitution reaction by attacking the other imidazole ring. When 1,2-di(imidazolyl)benzene was treated with one molar amount of iodine after anion formation using two equivalents of *n*-BuLi, the desired reaction proceeded to give diimidazo[1,2-*a*:2′,1′-*c*]quinoxaline (**3**) in 71% yield at 45 °C (Scheme 2, *Method A*). After further experiments, it was found that in this reaction, iodine could be replaced by a catalytic amount of Pd(PPh$_3$)$_4$, also obtaining **3** in 71% yield (*Method B*). Although the reaction mechanism is not clear, two equivalents of *n*-BuLi were necessary since the reaction with one molar equivalent of *n*-BuLi resulted in recovery of the starting material. From these investigations, we obtained **3** in 62% yield (in two steps)

---

[a] *Department of Applied Chemistry and Biotechnology, Graduate School of Engineering, Chiba University, 1-33 Yayoicho, Inageku, Chiba, 263-8522, Japan. E-mail: smatsumo@faculty.chiba-u.jp; Fax: +81-43-290-3401; Tel: +81-43-290-3369*

[b] *TOYO INK SC HOLDINGS, CO., LTD., 27 Wadai, Tsukuba City, Ibaraki, 300-4247, Japan*

† Electronic supplementary information (ESI) available: Experimental procedures and characterization for all the new compounds, fabrication and characterization methods for OLEDs, energy level diagram of EL device, and the EL spectra of **4e** with nondoped emitting layer for various applied voltages. See DOI: 10.1039/c1ob06002c



Scheme 2 Formation of **3** and **4**.

from commercially available 1,2-dibromobenzene and imidazole. Furthermore, we perceived that owing to the structural simplicity of **3**, the introduction of various substituents was possible. In fact, the introduction of aryl substituents at the 3 and 10 positions of **3** was achieved to give **4** in moderate yield using a Pd-catalysed coupling reaction according to the procedure reported by Miura *et al.*[10]

The absorption and fluorescence spectra of **3** and **4** were measured in THF (Fig. 1 and 2), and their optical properties are summarized in Table 1. The absorption maximum (λ_{max}) of **3** was observed at 309 nm, which is a shorter wavelength than that of **1**. This shift can be rationalized by investigations using density functional theory (DFT) calculations with B3LYP/6-31+G level. The orbital shapes of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of **3** resemble those of **1** (Fig. 3). The energy level of **3** and **1** is significantly affected the HOMO because the orbital of HOMO largely lies on the pyrrole and imidazole groups of **1** and **3**, respectively. Therefore, the difference between the energy level of the HOMO of **3** and that of **1** is larger than the difference between the energy levels of the LUMO, resulting in the observed blue shift of the absorption peak. Blue shift of the emission peak of **3** (λ_{em} = 367 nm), in comparison with that of **1**, was also observed. The fluorescence quantum yield (Φ_F) increased from 0.43 (**1**) to 0.72 (**3**). Furthermore, by changing a solvent from THF to CH_3CN, the emission peak of **3** was not affected, whereas a solvent effect was observed in the case of **1** (R═H). Thus, we found that the various properties of **3** could be changed simply by replacing the pyrrole moieties of **1** with the imidazole moieties.

Table 1 Optical properties of **3** and **4**

Compound	λ_{max}(nm)[a] [ε (M^{-1} cm^{-1})]	λ_{em}(nm)[b] [Φ_F]	CIE (*x*, *y*)
3	309 [10,400]	367 [0.72][c]	---
	307.5[d] [4,800]	367[e] [0.70][c]	---
4a	335 [11,500]	428 [0.82][f]	0.142, 0.133
4b	336 [14,300]	434 [0.76][f]	0.143, 0.155
4c	321 [12,800]	415 [0.47][f]	0.142, 0.144
4d	335 [14,100]	441 [0.67][f]	0.144, 0.220
4e	343 [14,200]	432 [0.93][f]	0.140, 0.106
4f	366 [16,800]	454 [0.68][f]	0.156, 0.342
1	321 [10,600]	416 [0.43][f]	---
	320[d] [10,700]	434[e] [0.17][c]	---

[a] Measured in THF (3.0×10^{-5} M). [b] Measured in THF (3.0×10^{-7} M). Excited at λ_{max}. [c] Determined by *p*-terphenyl (Φ_F = 0 87, excited at 265 nm) as a standard. [d] Measured in CH_3CN (3.0×10^{-5} M). [e] Measured in CH_3CN (3.0×10^{-7} M). Excited at λ_{max}. [f] Determined by quinine sulfate (Φ_F = 0.55, excited at 366 nm) as a standard.

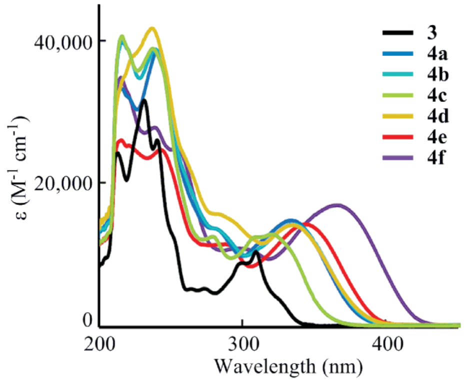


Fig. 1 UV-Vis absorption spectra of **3**, and **4a–4f** in THF (3.0×10^{-5} M).

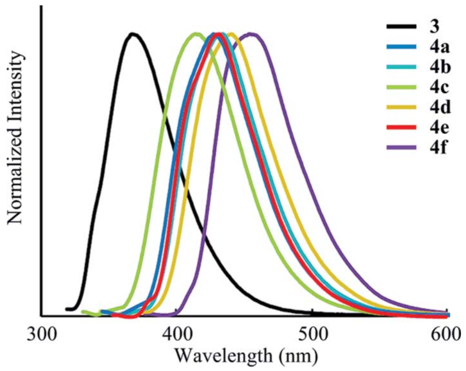


Fig. 2 Fluorescence spectra of **3**, and **4a–4f** in THF (3.0×10^{-7} M). Excited at λ_{max}.

The absorption and emission spectra of **4a** bearing two phenyl rings at the 3 and 10 positions of **3** exhibited a red shift. λ_{em} was reached in a blue region (428 nm), and Φ_F was slightly increased in comparison with that of **3**. When methyl or methoxy groups were introduced at the *para* position in the phenyl rings of **4a**,

Table 2 Performance of EL devices containing compounds **4a** and **4e**[a]

Device[b]	Compound	λ_{EL} (nm)	V_{oc} (V)	L_{max} (cd m^{-2})	PE (lm W^{-1})	CE (cd A^{-1})	EQE (%)	CIE (*x*, *y*)
A	**4a**	420	12	123 [15]	0.12 [12.5]	0.42 [12.5]	0.03[c]	0.161, 0.132
A	**4e**	445	6	320 [11.5]	0.55 [5]	0.91 [5.5]	0.96[c]	0.150, 0.111
B	**4a**	437	5	4,116 [11]	0.55 [5]	0.88 [5]	1.12[c]	0.150, 0.104
B	**4e**	438	5	292 [9]	0.08 [4.5]	0.11 [4.5]	0.06[c]	0.202, 0.226

[a] V_{oc} = turn-on voltage, L_{max} = maximum luminance, PE = powere efficiency, CE = current efficiency. EQE = external quantum efficiency. Values in brackets show the applied voltage (V). [b] Device A: ITO (150 nm)/PEDOT : PSS (40 nm)/**4** : PVK : PBD (3 : 65 : 32) (70 nm)/TPBI (30 nm)/LiF (1 nm)/Al (150 nm). The hole-transporting and emitting layers were prepared by the spin-coating method. Device B: ITO (150 nm)/α-NPD (40 nm)/**4** (30 nm)/TPBI (30 nm)/LiF (1 nm)/Al (200 nm). Each layers were fabricated by the vacuum deposition method. [c] Estimated at 0.4 mA.

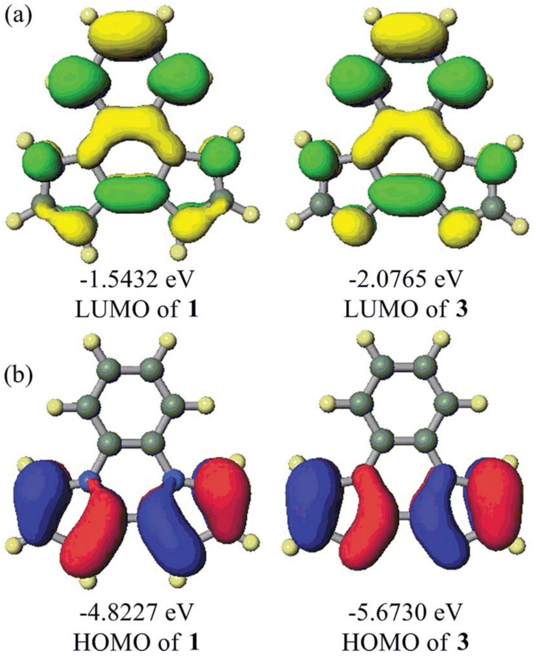


Fig. 3 Orbitals and energies of (a) LUMO and (b) HOMO of **1** and **3** calculated by DFT/B3LYP/6-31+G.

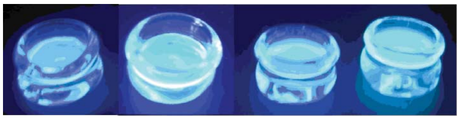


Fig. 4 Photographs of the emitted light from **4a**, **4b**, **4e**, and **4f**.

producing **4b** and **4d**, respectively, their emission peaks shifted to a longer wavelength than that of **4a**. Electron-withdrawing substituents such as trifluoromethyl (**4e**) and formyl groups (**4f**) also gave red shift of absorption and emission peaks. **4c** bearing a methyl group at the *ortho* position of the phenyl rings will have little π-conjugation between the parent diimidazoquinoxaline and the aryl substituents owing to steric hindrance. The absorption and emission peaks of **4c** were observed to have a blue shift and to decrease Φ_F (0.47) lower than that of **3** and other **4**. Thus, conjugation with the substituted aryl groups is to some extent important in maintaining a high fluorescence quantum yield.

The fluorescence emissions of **4a**–**4f** are exhibited in the light-blue to blue region (Fig. 4). In OLEDs, blue fluorescent materials can serve either as blue light sources[11] or as host materials for lower energy fluorescent or phosphorescent dyes.[12] Because the fluorescence of **4a** and **4e** is almost in the pure blue region according to their Commission International de l'Éclairage (CIE) chromaticity coordinates (Table 1), we carried out preliminary investigations of the possibility of using them as emitters in OLEDs. Both of **4a** and **4e** showed the fluorescence even in solid state with moderate Φ_F (**4a**: λ_{em} = 441 nm, Φ_F = 0.33; **4e**: λ_{em} = 430 nm, Φ_F = 0.30) (Fig. 5). Thus, they can give the light-emission in the aggregated state. The performance characteristics of devices using **4a** and **4e** are summarized in Table 2. First, we examined Device A fabricated by a spin-coating method to produce an emitting layer with the following configuration: ITO (150 nm)/PEDOT : PSS (40 nm)/**4** : PVK : PBD (3 : 65 : 32)[13] (70 nm)/TPBI (30 nm)/LiF (1 nm)/Al (150 nm) (ITO: indium tin oxide; PEDOT : PSS: poly(ethylenedioxythiophene) : poly(stylenesulfonate); PVK: poly(*N*-vinylcarbazole); PBD: 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole). While the electroluminescent peak (λ_{EL}) of **4a** was at 420 nm (Fig. 5), a heterogeneity in the light-emitting layer was observed. However, the device containing **4e** gave fine luminance at 437 nm in the blue region (CIE coordinates: x = 0.150 and y = 0.111) without any surface irregularity. The maximum luminance of the electroluminescent (EL) device containing **4e** was 320 cd m^{-2} at 11.5 V.

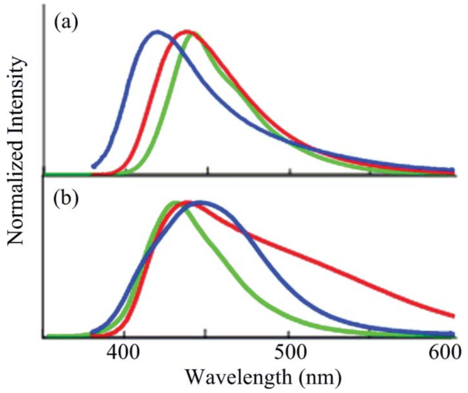


Fig. 5 Fluorescence spectra in solid state (green line) and EL spectra (blue line from device A (spin-coating method), and red line from device B (vacuum deposition method)) of (a) **4a** and (b) **4e**.

Recently, OLED devices with an nondoped emitting layer have also attracted considerable attention for device fabrication because the doping method requires complicated evaporation techniques with precise process control.[14] Therefore, we also examined the performance of Device B, which was nondoped and prepared by the vacuum deposition method, with the following configuration: ITO (150 nm)/α-NPD (40 nm)/**4** (30 nm)/TPBI (30 nm)/LiF (1 nm)/Al (200 nm) (α-NPD: 4,4′-bis((1-naphthyl)phenylamino)-1,1′-diphenyl). **4a** exhibited a nearly pure blue EL spectrum with CIE coordinates of $x = 0.150$ and $y = 0.104$, which are close to the standard blue values of the National Television Standards Committee (NTSC) ($x = 0.14$, $y = 0.08$). The device using **4a** demonstrated good performance, with a maximum luminance of 4,116 cd m^{-2} and a current efficiency of 0.88 cd A^{-1}. Its external quantum efficiency was 1.12% at 0.4 mA. However, the EL spectrum of **4e** exhibited an unintentional color change when the applied voltage was increased (Fig. S2†).

In summary, diimidazo[1,2-*a*:2′,1′-*c*]quinoxaline derivatives were synthesized, and their optical properties were investigated. The new methods to construct a diimidazo[1,2-*a*:2′,1′-*c*]quinoxaline skeleton were achieved by the reaction of anionic 1,2-di(imidazolyl)benzene with iodine or a Pd-catalyst with good yields. Enhancement of the fluorescent quantum yield was achieved by changing the pyrrole moieties of **1** to imidazole moieties. Blue fluorescence with a high quantum yield was obtained from**4** bearing aryl groups at the 3 and 10 positions of **3**. We also showed that **4** have the potential to be used as efficient emitting materials in OLEDs. Our investigations to further improve the EL properties and on the use of diimidazoquinoxalines as fluorescence sources are under way.

Notes and references

1 (*a*) M. Strukelj, F. Papadimitrakopoulos, T. M. Miller and L. J. Rothberg, *Science*, 1995, **267**, 1969–1972; (*b*) J. Kido, C. Ohtaki, K. Hongawa, K. Okuyama and K. Nagai, *Jpn. J. Appl. Phys.*, 1993, **32**, L917–L920.

2 (*a*) L. He, J. Qiao, L. Duan, G. Dong, D. Zhang, L. Wang and Y. Qiu, *Adv. Funct. Mater.*, 2009, **19**, 2950–2960; (*b*) L. Chen, C. Yang, J. Qin, J. Gao and D. Ma, *Inorg. Chim. Acta*, 2006, **359**, 4207–4214; (*c*) L. Zhao, S. B. Li, G. A. Wen, B. Peng and W. Huang, *Mater. Chem. Phys.*, 2006, **100**, 460–463.

3 H. Wang, P. He, S. Liu, J. Shi and M. Gong, *Inorg. Chem. Commun.*, 2010, **13**, 145–148.

4 T.-R. Chen, R.-H. Chien, M.-S. Jan, A. Yeh and J.-D. Chen, *J. Organomet. Chem.*, 2006, **691**, 799–804.

5 (*a*) H.-J. Zhu, J.-S. Wang, J. L. Donocan, C. L. Devane, B. B. Gibson and J. S. Markowitz, *J. Chromatogr., B: Anal. Technol. Biomed. Life Sci.*, 2007, **846**, 351–354; (*b*) J. You, X. Zhao, Y. Suo, H. Wang, Y. Li and J. Sun, *Anal. Chim. Acta*, 2006, **565**, 168–177; (*c*) S. Park, O.-H. Kwon, S. Kim, S. Park, M.-G. Choi, M. Cha, S. Y. Park and D.-J. Jang, *J. Am. Chem. Soc.*, 2005, **127**, 10070–10074; (*d*) K. Feng, F.-L. Hsu, D. Van DerVeer, K. Bota and X. R. Bu, *J. Photochem. Photobiol., A*, 2004, **165**, 223–228; (*e*) S. K. Das, *Chem. Phys. Lett.*, 2002, **361**, 21–28; (*f*) G. Krishnamoorthy and S. K. Dogra, *J. Colloid Interface Sci.*, 2000, **228**, 335–343; (*g*) G. Krishnamoorthy and S. K. Dogra, *Chem. Phys. Lett.*, 2000, **323**, 234–242; (*h*) G. Krishnamoorthy and S. K. Dogra, *Spectrochim. Acta, Part A*, 1999, **55**, 2647–2658.

6 (*a*) J.-F. Lee, Y.-C. Chen, J.-T. Lin, C.-C. Wu, C.-Y. Chen, C.-A. Dai, C.-Y. Chao, H.-L. Chen and W.-B. Liau, *Tetrahedron*, 2011, **67**, 1696–1702; (*b*) L. He, J. Qiao, L. Duan, G. Dong, D. Zhang, L. Wang and Y. Qiu, *Adv. Funct. Mater.*, 2009, **19**, 2950–2960; (*c*) Z. Fang, S. Wang, L. Zhao, Z. Xu, J. Ren, X. Wang and Q. Yang, *Mater. Lett.*, 2007, **61**, 4803–4806; (*d*) L. Zhao, S. B. Li, G. A. Wen, B. Peng and W. Huang, *Mater. Chem. Phys.*, 2006, **100**, 460–463.

7 (*a*) S. Matsumoto, S. Qu, T. Kobayashi, M. Kanehiro, M. Akazome and K. Ogura, *Heterocycles*, 2010, **80**, 645–656; (*b*) S. Matsumoto, T. Kobayashi and K. Ogura, *Heterocycles*, 2006, **68**, 283–294; (*c*) S. Matsumoto, T. Kobayashi and K. Ogura, *Heterocycles*, 2005, **66**, 319–332.

8 A. R. M. Ebrahimlo, J. Khalafy and R. H. Prager, *Aust. J. Chem.*, 2009, **62**, 126–132.

9 Y.-H. So, *Macromolecules*, 1992, **25**, 516–520.

10 S. Pivsa-Art, T. Satoh, Y. Kawamura, M. Miura and M. Nomura, *Bull. Chem. Soc. Jpn.*, 1998, **71**, 467–473.

11 Recent reports: (*a*) A. L. Fisher, K. E. Linton, K. T. Kamtekar, C. Pearson, M. R. Bryce and M. C. Petty, *Chem. Mater.*, 2011, **23**, 1640–1642; (*b*) T. Qin, W. Wiedemair, S. Nau, R. Trattnig, S. Sax, S. Winkler, A. Vollmer, N. Koch, M. Baumgarten, W. J. W. List and K. Müllen, *J. Am. Chem. Soc.*, 2011, **133**, 1301–1303; (*c*) J. Wang, W. Wan, H. Jiang, Y. Gao, X. Jiang, H. Lin, W. Zhao and J. Hao, *Org. Lett.*, 2010, **12**, 3874–3877; (*d*) Y. Yang, P. Cohn, A. L. Dyer, S.-H. Eom, J. R. Reynolds, R. K. Castellano and J. Xue, *Chem. Mater.*, 2010, **22**, 3580–3482; (*e*) H. Wettach, S. S. Jester, A. Colsmann, U. Lemmer, N. Rehmann, K. Meerholz and S. Höger, *Synth. Met.*, 2010, **160**, 691–700; (*f*) S. Tao, Y. Zhou, C.-S. Lee, X. Zhang and S.-T. Lee, *Chem. Mater.*, 2010, **22**, 2138–2141; (*g*) N. Cocherel, C. Poriel, L. Vignau, J. Bergamini and J. Rault-Berthelot, *Org. Lett.*, 2010, **12**, 452–455; (*h*) Y. Wu, X. Hao, J. Wu, J. Jin and X. Ba, *Macromolecules*, 2010, **43**, 731–738; (*i*) S.-H. Liao, J.-R. Shiu, S.-W. Liu, S.-J. Yeh, Y.-H. Chen, C.-T. Chen, T. J. Chow and C.-I. Wu, *J. Am. Chem. Soc.*, 2009, **131**, 763–777; (*j*) K.-S. Kim, Y.-M. Jeon, J.-W. Kim, C.-W. Lee and M.-S. Gong, *Org. Electron.*, 2008, **9**, 797–804; (*k*) J. N. Moorthy, P. Natarajan, P. Wenkatakrishnan, D.-F. Huang and T. J. Chow, *Org. Lett.*, 2007, **9**, 5215–5218.

12 (*a*) T. Zhang, M. Liu, T. Li, J. Ma, D. Liu, W. Xie, C.-L. Wu, S.-W. Liu, S.-C. Yeh and C.-T. Chen, *J. Phys. Chem. C*, 2011, **115**, 2428–2432; (*b*) P.-I. Lee, S. L.-C. Hsu and P. Lin, *Macromolecules*, 2010, **43**, 8051–8057; (*c*) K. Zhang, Y. Tao, C. Yang, H. You, Y. Zou, J. Qin and D. Ma, *Chem. Mater.*, 2008, **20**, 7324–7331; (*d*) C. Zhang, X. Liu, L. Qin, W. Zhu and L. Wang, *J. Lumin.*, 2007, **122-123**, 590–592; (*e*) W.-C. Shen, Y. K. Su and L.-W. Ji, *Mater. Sci. Eng., A*, 2007, **445–446**, 509–512; (*f*) P. Coppo, M. Duati, V. N. Kozhevnikov, J. W. Hofstraat and L. D. Cola, *Angew. Chem., Int. Ed.*, 2005, **44**, 1806–1810; (*g*) T.-W. Lee, O. O. Park, H. N. Cho, J.-H. Hong, C. Y. Kim and Y. C. Kim, *Synth. Met.*, 2001, **122**, 437–441; (*h*) M. D. McGehee, T. Bergstedt, C. Zhang, A. P. Saab, M. B. O'Regan, G. C. Bazan, V. I. Srdanov and A. J. Heeger, *Adv. Mater.*, 1999, **11**, 1349–1354; (*i*) J. Kido, K. Hongawa, K. Okuyama and K. Nagai, *Appl. Phys. Lett.*, 1994, **64**, 815–817.

13 The ratio of compounds for the light-emitting layer was determined to increase the electron-transporting properties. See: C. Jiang, W. Yang, J. Peng, S. Xiao and Y. Cao, *Adv. Mater.*, 2004, **16**, 537–541.

14 (*a*) J.-F. Gu, G.-H. Xie, L. Zhang, S.-F. Chen, Z.-Q. Lin, Z.-S. Zhang, J.-F. Zhao, L.-H. Xie, C. Tang, Y. Zhao, S.-Y. Liu and W. Huang, *J. Phys. Chem. Lett.*, 2010, **1**, 2849–2853; (*b*) C.-H. Wu, C.-H. Chien, F.-M. Hsu, P.-I. Shih and C.-F. Shu, *J. Mater. Chem.*, 2009, **19**, 1464–1470; (*c*) Y. Wei and C.-T. Chen, *J. Am. Chem. Soc.*, 2007, **129**, 7478–7479; (*d*) S.-L. Lin, L.-H. Chan, R.-H. Lee, M.-Y. Yen, W.-J. Kuo, C.-T. Chen and R.-J. Jeng, *Adv. Mater.*, 2008, **20**, 3947–3952; (*e*) C. J. Tonzola, A. P. Kulkarni, A. P. Gifford, W. Kaminsky and S. A. Jenekhe, *Adv. Funct. Mater.*, 2007, **17**, 863–874.