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Asymmetrically 4,7-Disubstituted Benzothiadiazoles as Efficient Non-doped Solution-Processable Green Fluorescent Emitters

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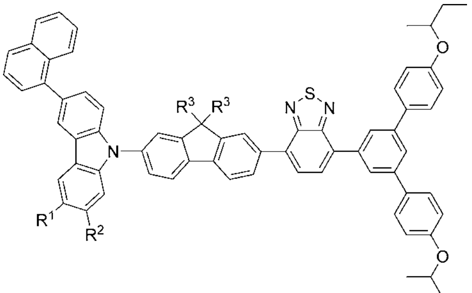
ABSTRACT



1a: R^1 = 1-naphthyl, R^2 = H, R^3 = *n*-octyl
1b: R^1 = H, R^2 = trifluoromethyl, R^3 = ethyl

Asymmetrically 4,7-disubstituted benzothiadiazole derivatives involving a carbazolyl moiety at one end and a solubilizing dendron at the opposite end have been synthesized and characterized. A two-layer electroluminescent device based on one of these solution-processed molecular emitters revealed a maximal luminous efficiency of ∼10.6 cd A^{-1} and green light emission with CIE coordinates (0.34, 0.58).

Solution-processable molecular semiconductors have received increasing attention as active materials in organic optoelectronic devices such as organic light-emitting diodes (OLEDs),[1,2] solid-state lasers,[3] field effect transistors (OFETs),[4] and organic solar cells (OSCs).[5] With respect to their polymer counterparts, small molecular active compounds present the advantages of a monodisperse unequivocal chemical structure and thus of a potentially better reproducibility of synthesis and purification and more

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(1) Lo, S. C.; Burn, P. L. *Chem. Rev.* **2007**, *107*, 1097.

(2) (a) Yang, R. Q.; Xu, Y. H.; Dang, X. D.; Nguyen, T. Q.; Cao, Y.; Bazan, G. C. *J. Am. Chem. Soc.* **2008**, *130*, 3282. (b) Liu, G.; Li, A.-Y.; An, D.; Wu, H.-B.; Zhu, X.-H.; Li, Y.; Miao, X.-Y.; Deng, W.-L.; Yang, W.; Cao, Y.; Roncali, J. *Macromol. Rapid Commun.* **2009**, *30*, 1484.

(3) (a) Samuel, I. D. W.; Turnbull, G. A. *Chem. Rev.* **2007**, *107*, 1272. (b) Lai, W. Y.; Xia, R. D.; He, Q. Y.; Levermore, P. A.; Huang, W.; Bradley, D. D. C. *Adv. Mater.* **2009**, *21*, 355. (c) Xia, R. D.; Lai, W. Y.; Levermore, P. A.; Huang, W.; Bradley, D. D. C. *Adv. Funct. Mater.* **2009**, *19*, 2844. (d) Huang, J.; Liu, Q.; Zou, J. H.; Zhu, X.-H.; Li, A.-Y.; Li, J.-W.; Wu, S.; Peng, J. B.; Cao, Y.; Xia, R.; Bradley, D. D. C.; Roncali, J. *Adv. Funct. Mater.* **2009**, *19*, 2978.

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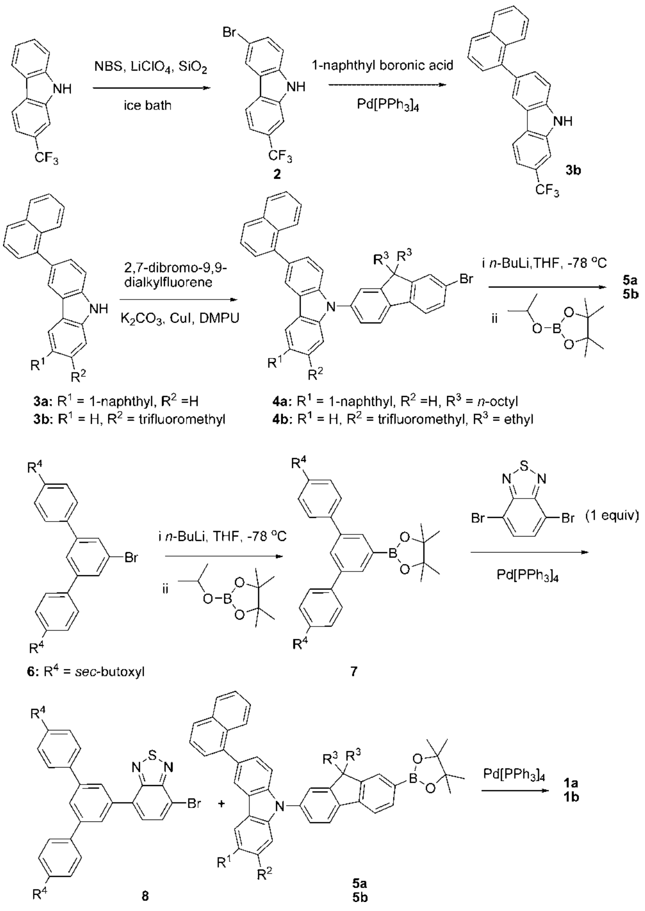
straightforward analysis of structure−properties relationships. Furthermore, when adequately solubilized by design these solution-processable molecular materials afford the possibility of low-cost large area electronics.

The current development of solution-processed small molecular RGB emitters in OLEDs, particularly for display purpose, requires highly efficient light-emitting materials with enhanced electron injection and transport properties.[6,7] Although a number of emitters with predominant hole transporting properties are available, their *wide* applicability as a bulk emitter or dopant in a hole-transporting host might present a potential challenge as it implies the use of hole blockers combining sufficient device durability and convenient synthetic accessibility.[8]

We have recently reported soluble red fluorescent molecular glasses based on dithienylbenzothiadiazole combining high solubility and excellent solution processability with intrinsic morphological stability.[3c,9] Notably, one of these pure red emitters has demonstrated hole injection and electron transporting properties,[9b] unlike many other red-emitting materials that are largely dominated by hole transport.[10,11]

In this context, we present here new efficient non-doped solution-processable green electroluminescent molecular emitters based on asymmetrically 4,7-disubstituted benzothiadiazoles **1a** and **1b** (Scheme 1).

Scheme 1. Synthetic Routes to Compounds **1a**/**1b**



A solubilizing dendron was attached at one side of 2,1,3-benzothiadiazole of compound **1a** to provide the desired solubility. A 3,6-di(1-naphthyl)carbazolyl moiety[12] was introduced at the opposite side of the molecule through a fluorenyl spacer in order to facilitate hole injection and glass formation. Overall the branched structures are expected to afford green emission with a potentially high photoluminescent (PL) efficiency and high color purity in the solid state by suppressing strong intermolecular interactions generally associated with donor−acceptor molecules. For compound **1b** the introduction of a trifluoromethyl group onto the carbazolyl ring is expected to further modulate charge injection/transport properties.

The synthesis of compounds **1a**/**1b** is outlined in Scheme 1. Compound **3a** was prepared as already reported[12] and compound **3b** was synthesized by Suzuki coupling of 6-bromo-2-(trifluoromethyl)carbazole (**2**) with 1-naphtyl boronic acid in 89% yield. Compound **2** was obtained by treating 2-trifluoromethylcarbazole[13] with NBS in the presence of $LiClO_4$ and silica gel in ice-cooled CH_2Cl_2. Some multibromination was observed when the reaction was carried out at room temperature.

Ullmann coupling of compounds **3a/3b** with the respective 2,7-dibromo-9,9-dialkylfluorenes (1.5 equiv) led to bromo compounds **4a**/**4b** in ca. 65% and 53% yields. Successive treatment of **4a**/**4b** with *n*-butyllithium and 2-isoproxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane in anhydrous THF at −78 °C afforded the corresponding Suzuki reagents **5a**/**5b**.

A bis-Suzuki coupling of 1,3,5-tribromobenzene with 2 equiv of 4,4,5,5-tetramethyl-2-*p*-*sec*-butoxyl-phenyl-1,3,2-

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(4) (a) Dimitrakopoulos, C. D.; Malenfant, P. R. L. *Adv. Mater.* **2002**, *14*, 99. (b) Allard, S.; Forster, M.; Souharce, B.; Thiem, H.; Scherf, U. *Angew. Chem., Int. Ed.* **2008**, *47*, 4070. (c) Sirringhaus, H. *Proc. IEEE* **2009**, *97*, 1570.

(5) (a) Llloyd, M. T.; Anthony, J. E.; Malliaras, G. G. *Mater. Today* **2007**, *10*, 36. (b) Roncali, J.; Leriche, P.; Cravino, A. *Adv. Mater.* **2007**, *19*, 2045. (c) Roncali, J. *Acc. Chem. Res.* **2009**; DOI: 10.1021/ar900041b. (d) Jørgensen, M.; Krebs, F. C. *J. Org. Chem.* **2005**, *70*, 6004.

(6) Kulkarni, A. P.; Tonzola, C. J.; Babel, A.; Jenekhe, S. A. *Chem. Mater.* **2004**, *16*, 4556 Special issue on organic electronics.

(7) (a) Chen, A. C. A.; Culligan, S. W.; Geng, Y.-H.; Chen, S.-H.; Klubek, K. P. K.; Vaeth, M.; Tang, C. W. *Adv. Mater.* **2004**, *16*, 783. (b) Lai, W. Y.; Zhu, R.; Fan, Q. L.; Hou, L. T.; Cao, Y.; Huang, W. *Macromolecules* **2006**, *39*, 3707. (c) Wang, L.; Jiang, Y.; Luo, J.; Zhou, Y.; Zhou, J.-H.; Wang, J.; Pei, J.; Cao, Y. *Adv. Mater.* **2009**; DOI: 10.1002/adma.200901039.

(8) Kwong, R. C.; Nugent, M. R.; Michalski, L.; Ngo, T.; Rajan, K.; Tung, Y. J.; Weaver, M. S.; Zhou, T. X.; Hack, M.; Thompson, M. E.; Forrest, S. R.; Brown, J. J. *Appl. Phys. Lett.* **2002**, *81*, 162.

(9) (a) Huang, J.; Li, C.; Xia, Y. J.; Zhu, X. H.; Peng, J. B.; Cao, Y. *J. Org. Chem.* **2007**, *72*, 8580. (b) Huang, J.; Qiao, X. F.; Xia, Y. J.; Zhu, X. H.; Ma, D. G.; Cao, Y.; Roncali, J. *Adv. Mater.* **2008**, *20*, 4172.

(10) Review on red electroluminescent materials: Chen, C. T. *Chem. Mater.* **2004**, *16*, 4389, and references therein.

(11) For instance: (a) Thomas, K. R. J.; Velusamy, M.; Lin, J. T.; Sun, S. S.; Tao, Y.-T.; Chuen, C.-H. *Chem. Commun.* **2004**, 2328. (b) Li, Z. H.; Wong, M. S.; Fukutani, H.; Tao, Y. *Chem. Mater.* **2005**, *17*, 5032. (c) Chen, C.-T.; Wei, Y.; Lin, J.-S.; Moturu, M. V. R. K.; Chao, W.-S.; Tao, Y.-T.; Chien, C.-H. *J. Am. Chem. Soc.* **2006**, *128*, 10992. (d) Lee, Y.-T.; Chiang, C.-L.; Chen, C.-T. *Chem. Commun.* **2008**, 217.

(12) Zhao, L.; Zou, J. H.; Huang, J.; Li, C.; Zhang, Y.; Sun, C.; Zhu, X. H.; Peng, J. B.; Cao, Y.; Roncali, J. *Org. Electron.* **2008**, *9*, 649.

(13) Freeman, A. W.; Urvoy, M.; Criswell, M. E. *J. Org. Chem.* **2005**, *70*, 5014.

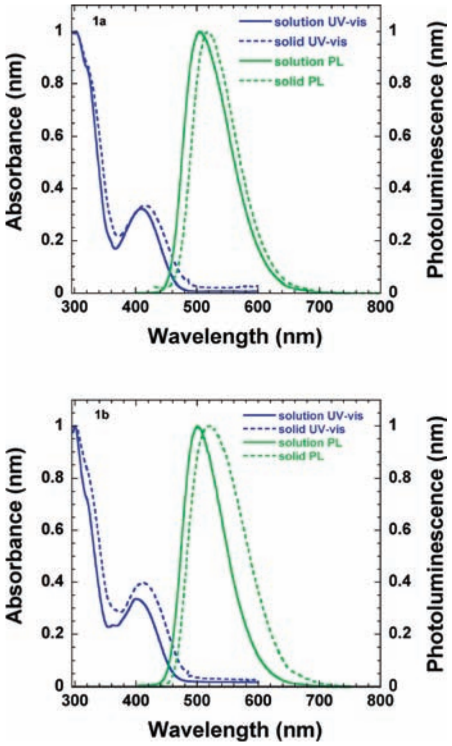

Figure 1. UV−vis absorption and PL spectra of **1a**/**1b** in *p*-xylene solution and as-cast films on quartz (PL excitation = 380 nm).

dioxaborolane resulted in compound **6** in 86% yield, which underwent further lithiation and boronation reactions to yield Sukuki reagent **7**. Precursor compound **8** was thus prepared in 78% yield by a mono-Suzuki coupling of **7** and 4,7-bromo-2,1,3-benzothiadiazole.

Finally, the target compounds **1a** and **1b** were obtained in ca. 93% yields by coupling a slight excess of precursor **8** with Suzuki reagents **5a** and **5b**, respectively. This high coupling efficiency greatly facilitated purification by routine column chromatography. Furthermore, the high solubility of compound **8** in ethanol and petroleum ether allows easy removal of the excess of reagent. The identity and purity of compounds **1a/1b** was confirmed by ^{1}H NMR, MALDI-TOF mass spectrometry, and microanalysis (see Supporting Information). These new compounds show a high solubility in common organic solvents such as CH_2Cl_2, THF, toluene, and *p*-xylene. For instance, 25 mg of **1a**/**1b** is rapidly dissolved in 1 mL of *p*-xylene at room temperature without saturation.

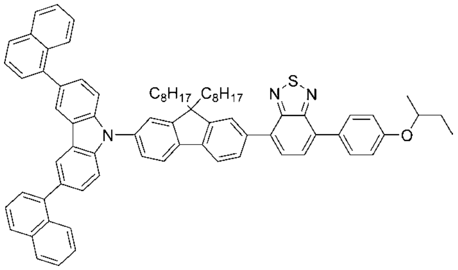

Figure 2. Molecular structure of compound **1c**.

The UV−vis and PL spectra of **1a**/**1b** in dilute solution and as thin solid films are shown in Figure 1, and the relevant data are summarized in Table 1. Thin films of **1a** and **1b** spun-cast from *p*-xylene solutions show emission maxima at 518 and 521 nm, respectively. These highly green emissive solids show absolute solid-state PL efficiencies of ca. 0.72 for **1a** and 0.51 for **1b**, measured in an integrating sphere under 325 nm He-Cd laser excitation. Furthermore, comparison of the solid state PL spectra of **1a**/**1b** to those of compound **1c** (λ_{em} = 568 nm, see Supporting Information) and 4,7-bis(9,9-diarylfluoren-2-yl)-2,1,3-benzothiadiazole (λ_{em} = 544 nm)[14] shows that the new compounds present a significantly improved green color purity, thus confirming the effectiveness of the 3,5-di(*p*-*sec*-butoxylphenyl)phenyl end-capping group to reduce intermolecular interactions.

Cyclic voltammetry (CV) was performed in methylene chloride/acetonitrile in the presence of Bu_4NPF_6 as supporting electrolyte. Compounds **1a**/**1b** are reversibly reduced at ca. −1.40 V vs Ag/AgCl (Figure 3). With respect to **1a**, the introduction of CF_3 substituent on the carbazole ring in **1b** results in a substantial increase of the oxidation potential but leaves the reduction potential pratically unaffected. The LUMO energy levels estimated from the CV data of −2.93 eV for **1a** and −2.94 eV for **1b** seem appropriate for efficient electron injection (Table 1). The anodic peak potentials lead to estimated HOMO levels of ca. −5.61 and −5.84 eV for **1a** and **1b**, respectively, in good proximity to the values of −5.85 and −6.12 eV obtained by UPS measurements.[15]

Thermal gravimetry analysis shows that compounds **1a**/**1b** are stable well above 350 °C. Differential scanning calorimetry (DSC) measurements on as-prepared samples reveal a distinct glass transition with T_g of ~95 °C for **1a**

Table 1. Summary of Optical and Electrochemical Data

	UV−vis (λ^{abs}_{max}, nm)[a]		PL (λ^{em}_{max}, nm, (quantum yield))					
	solution	solid	solution[b]	solid[c]	reduction[d] (V)	oxidation[e] (V)	LUMO[f] (eV)	HOMO (eV)
1a	302, 408	285, 413	504 (0.67)	518 (0.72)	−1.42	1.26	−2.93	−5.61[g] (−5.85)[h]
1b	300, 400	301, 413	500 (0.58)	521 (0.51)	−1.41	1.49	−2.94	−5.84[g] (−6.12)[h]

[a] In *p*-xylene. [b] ~10^{-6} mol L^{-1} in *p*-xylene using quinine bisulfate in 0.1 mol L^{-1} H_2SO_4 as the reference (ϕ_r = 0.54). [c] Measured in an integrating sphere under 325 nm laser excitation. [d] Derived from E_0 values. [e] Derived from anodic peak potentials vs Ag/AgCl reference electrode. [f] Derived from E_0 values. [g] Derived from anodic peak potentials with reference to the energy level of ferrocene of −4.8 eV vs vacuum level. [h] Measured by UPS.

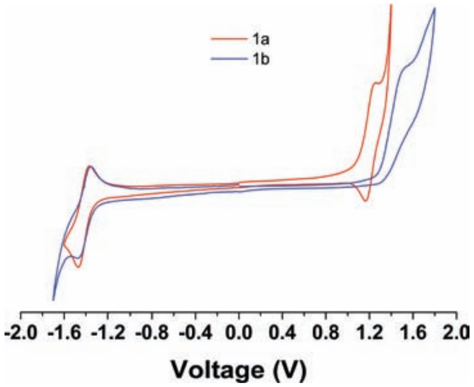

Figure 3. Cyclic voltammograms of **1a**/**1b** in 5:1 CH_2Cl_2/CH_3CN, supporting electrolyte 0.10 M n-Bu_4NPF_6, scan rate 50 mV s^{-1}.

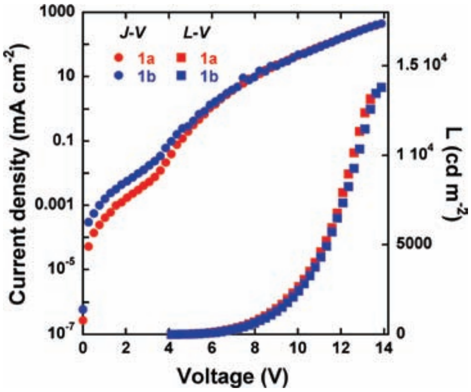

Figure 4. *L-V-J* characteristics of devices ITO/PEDOT:PSS/PVK/**1a**(**1b**)/Ba/Al.

and ~130 °C for **1b** in the first heating run. Neither crystallization nor melting was observed upon heating up to 300 °C.

The new compounds exhibit excellent film-forming properties. Atomic force microscopy images of spin-cast films of **1a** and **1b** from *p*-xylene solution show smooth, continuous, and featureless morphology with a surface root-mean-square roughness value of 0.35 and 0.42 nm, respectively (see Supporting Information). This stable homogeneous amorphous morphology appears favorable for light-emitting diodes with reduced leak currents and improved thermal stability during device operation.

Compounds **1a**/**1b** were first investigated as non-doped solution-processed emitters in single-layer diode structures ITO/PEDOT:PSS/**1a**(**1b**)/Ba/Al. The devices showed nearly pure green emission ($\lambda_{em} \approx 520$ nm) with CIE coordinates (0.305−0.318, 0.60), very close to the European Broadcast Union color gamut green point CIE ($x = 0.29$, $y = 0.60$). Onset voltages of ~2.8 and 3.3 V (at a luminance of 1 cd m^{-2}) were determined for **1a** and **1b**, respectively. These low values suggest efficient charge injection into the emitting layer. Furthermore, this result also suggests that transport of at least one of the two types of charge carriers could be efficient. However the low device efficiencies (LE_{max}, ~1 cd A^{-1}) suggest unbalanced charge injection or poor charge confinement in the active layer.

Consequently, double-layer devices consisting of an electron blocking PVK layer ITO/PEDOT:PSS/PVK/**1a** (**1b**)/Ba/Al were fabricated. The device performance was greatly improved with a maximal luminous efficiency of 10.6 cd A^{-1} (corresponding to η^{ext}_{max} of ~3.7%[16]) for **1a** and 7.5 cd A^{-1} (η^{ext} ~2.6%) for **1b**, respectively. At a current density of ca. 20 mA cm^{-2}, $V = 8.7$ V, $L = 1228$ cd m^{-2}, $LE = 6.70$ cd A^{-1}, $\lambda_{max} = 528$ nm with CIE coordinates (0.344, 0.580) for **1a** and $V = 9.0$ V, $L = 1308$ cd m^{-2}, $LE = 6.18$ cd A^{-1}, $\lambda_{max} = 528$ nm with CIE coordinates (0.336, 0.577) for **1b**. It is important to note that the device characteristics achieved here, especially without a hole-blocker, rank among the best reported so far for non-doped solution-processed green fluorescent molecular emitters (see Supporting Information).[17] These preliminary characterization of the single- and two-layer light-emitting devices also suggest that electron transport is facilitated in these new emitting materials.

In summary, soluble green fluorescent molecular glasses based on 2,1,3-benzothiadiazole derivatives have been synthesized and characterized. These truly solution-processable molecular green emitters have been used as active materials in highly efficient green light-emitting devices. We have shown that the 3,5-di(*p-sec*-butoxylphenyl)phenyl moiety is an efficient end-cap block to alleviate intermolecular interactions, leading to green emission with improved color purity and PL efficiency. An in-depth analysis of the device operation, in particular, charge transport, is underway which should warrant further optimization of the device architecture and molecular structure.

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Supporting Information Available: Experimental and characterization detail of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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[14] Ku, S. Y.; Chi, L.-C.; Hung, W.-Y.; Yang, S.-W.; Tsai, T.-C.; Wong, K.-T.; Chen, Y.-H.; Wu, C.-I. *J. Mater. Chem.* **2009**, *19*, 773.

[15] D'Andrade, B. W.; Datta, S.; Forrest, S. R.; Djurovich, P.; Polikarpov, E.; Thompson, M. E. *Organ. Electron.* **2005**, *6*, 11.

[16] η^{ext} was verified by measurement in an integrating sphere.

[17] (a) Zhou, Y.; He, Q.-Q.; Yang, Y.; Zhong, H. Z.; He, C.; Sang, G.-Y.; Liu, W.; Yang, C.-H.; Bai, F.-L.; Li, Y.-F. *Adv. Funct. Mater.* **2008**, *18*, 3299. (b) Liu, F.; Tang, C.; Chen, Q.-Q.; Li, S.-Z.; Wu, H.-B.; Xie, L.-H.; Peng, B.; Wei, W.; Cao, Y.; Huang, W. *Org. Electron.* **2009**, *10*, 256. (c) Lo, M. Y.; Zhen, C. G.; Lauters, M.; Jabbour, G. E.; Sellinger, A. *J. Am. Chem. Soc.* **2007**, *129*, 5808.