doi:10.1246/cl.2011.576

Mechanochromic and Color-change Properties of 2,6-Di(2-pyridyl)benzo[1,2-*b*:4,5-*b*′]difuran in the Solid and Solution

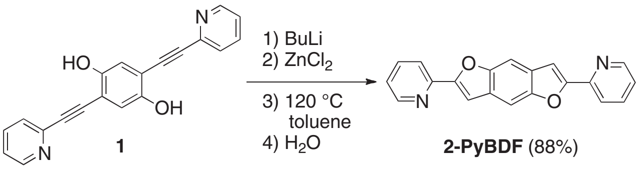
Hayato Tsuji,*[1] Guillaume Marcel Olivier Favier,[1] Chikahiko Mitsui,[1] Sunri Lee,[1] Daisuke Hashizume,[2] and Eiichi Nakamura*[1]
[1]*Department of Chemistry, School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033*
[2]*Advanced Technology Support Division, RIKEN Advanced Science Institute, 2-1 Hirosawa, Wako, Saitama 351-0198*

(Received March 7, 2011; CL-110191; E-mail: tsuji@chem.s.u-tokyo.ac.jp, nakamura@chem.s.u-tokyo.ac.jp)

2,6-Di(2-pyridyl)benzo[1,2-*b*:4,5-*b*′]difuran (**2-PyBDF**) shows a π–π-stacking packing structure in a single crystal and some intriguing properties: mechanochromism in the solid state, and solvent and concentration dependence of absorption and emission spectra.

Benzodifuran (BDF) derivatives belong to a new class of semiconducting materials that exhibit useful properties for organic light-emitting diodes (OLED).[1] During the course of our study on the chemistry and electronic properties of BDF derivatives, we unexpectedly found that 2,6-di(2-pyridyl)benzo-[1,2-*b*:4,5-*b*′]difuran (**2-PyBDF**) displays some unique properties in the solid and solution states. Herein, we report its synthesis, single-crystal structure, mechanochromic behavior both for absorption and for emission, and electrochemical properties.

The synthesis of **2-PyBDF** relied on the zinc-mediated double cyclization reaction that we recently developed (Scheme 1).[1–3] Thus, 2,5-di(2-pyridylethynyl)-*p*-hydroquinone (**1**) was treated with butyllithium followed by zinc chloride to afford **2-PyBDF** in 88% yield. Vacuum sublimation afforded pale green-yellow crystals.



Scheme 1.

This compound was found to be almost planar with a dihedral angle between the pyridyl groups and the BDF core of 2.13(16)° as revealed by single-crystal X-ray crystallography, and the molecules are π–π stacked with an interplane distance of 3.43(6) Å (Figure 1).[4] The packing structure is different from its diphenyl analog, 2,6-diphenyl-BDF, which is also planar but packs in a herringbone manner in the crystalline state.[5] The observed short-distance face-to-face packing of **2-PyBDF** allows the molecules to have a significant overlap of their orbitals, and may favor carrier transportation in the solid state.

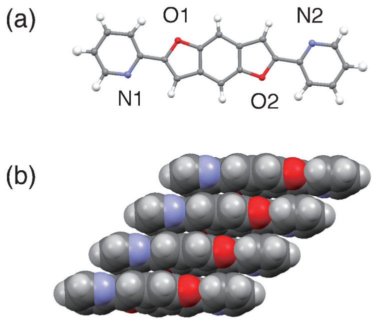


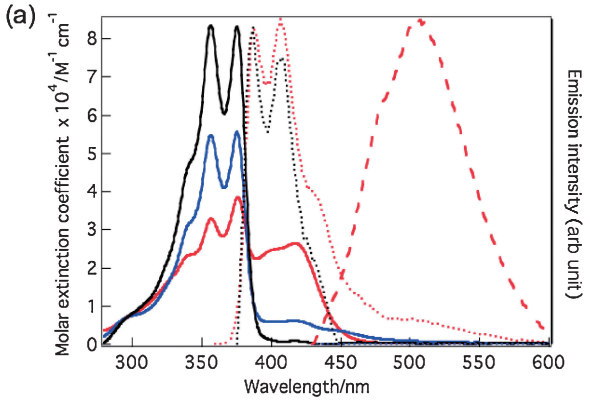
Figure 1. Single-crystal X-ray structure of **2-PyBDF** (black: carbon, white: hydrogen, red: oxygen, blue: nitrogen). (a) ORTEP drawing (30% probability for thermal ellipsoids) and (b) packing structure shown with a space-filling model (viewed along the *c* axis).

This compound exhibits unique photophysical properties that show concentration dependence. In a dilute solution in CH_2Cl_2 (2.1×10^{-6} M, Figure 2a, black solid line), a sharp absorption band with vibrational fine structure was observed in the near UV region with maxima of 356 and 375 nm. Photoirradiation of this solution at 350 nm caused deep blue emission (Figure 2a, black dotted line; Figure 2c), corresponding to a structured band at 375–450 nm, which is essentially a mirror image of the absorption spectrum with a small Stokes shift.

Interestingly, a 10-fold concentrated solution (2.1×10^{-5} M) exhibited a yellow color (Figure 2b) because of the new absorption band in the visible region (400–450 nm, Figure 2a, red solid line). Upon excitation of this solution at 350 nm, some shoulders were observed at 450–600 nm in addition to the structured emission band at 375–450 nm (red dotted line). Excitation at 420 nm afforded only the broad structureless band (red dashed line). A solution of the intermediate concentration (8.4×10^{-5} M) also showed an additional absorption band at longer wavelength (blue solid line) with much weaker relative intensity than that of the concentrated solution. We tentatively attribute the origin of these new absorption and emission bands found in the concentrated solution to the formation of a molecular complex, details of which are unclear at the present time.

The photophysical properties of **2-PyBDF** in the solid state are also intriguing. The sublimed sample (sample S) showed near UV-light absorption and emission of blue light, similar to the diluted solution. Photoexcitation at 340 nm of this crystalline sample showed an emission band with a maximum wavelength λ_{PL} of 467 nm (Figure 3b, blue).

Interestingly, recrystallization of the sublimed **2-PyBDF** crystal from 1,1,2,2-tetrachloroethane (TCE) afforded a yellow solid (Figure 3a, sample R). Photoexcitation (at 340 nm) of sample R furnished yellow emission, exhibiting a red-shifted broad band with a maximum $\lambda_{PL} = 565$ nm (Figure 3b, red). Even more interestingly, mechanical grinding of sample R caused a color change into pale yellow under ambient light, as illustrated in Figure 3a (sample G). The emission color under UV irradiation also changed from yellow to bluish.[6,7] Because the ^{1}H NMR spectrum of the ground sample (dissolved in TCE) was identical with that of the unground sample, the mechanical



(b) Ambient light (c) UV light (365 nm)

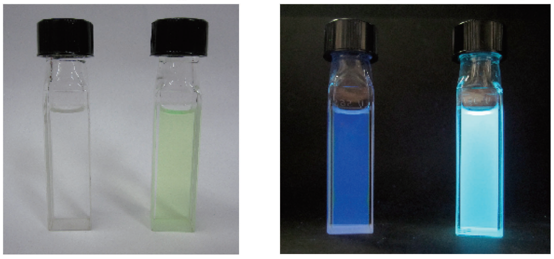


Figure 2. Concentration dependence of photophysical properties of **2-PyBDF** in $\mathrm{CH_2Cl_2}$. (a) UV absorption spectra (solid line. Black: 2.1×10^{-6} M, blue: 8.4×10^{-6} M, red: 2.1×10^{-5} M) and emission spectra (black dotted line 2.1×10^{-6} M excited at 350 nm, red dotted line: 2.1×10^{-5} M excited at 350 nm, and red dashed line: 2.1×10^{-5} M excited at 420 nm). (b) Photos of the solutions under ambient light (left: 1.9×10^{-6} M, right: 2.0×10^{-5} M) and (c) photos of the solutions under UV light (365 nm) irradiation (left: 1.9×10^{-6} M, right: 2.0×10^{-5} M).

grinding did not change the molecular structure, however it altered the alignment of the molecule in the solid state.

Electrochemical-property measurements showed that the compound has an unexpectedly low LUMO level. The differential pulse voltammetry (DPV) trace of ca. 0.5 mM THF solution of **2-PyBDF** showed a reduction peak at −1.58 V (vs. Fc/Fc$^+$). The estimated LUMO energy level was −3.22 eV,[8] which is much lower than those of other BDFs, which are generally ca. −2.4 eV,[1] and rivals those of n-type semiconducting materials,[9] such as bathocuproine (BCP),[10] siloles,[11] and phospholes.[12] DPV in THF gave an oxidation peak at 0.89 V, from which the HOMO energy level was estimated to be −5.69 eV. This value is close to those of other BDFs. These data demonstrate that there are some specific interactions that significantly affect the LUMO energy level of **2-PyBDF**, resulting in a color change in both solid and solution states under certain conditions.

In summary, we synthesized a new molecule **2-PyBDF** that shows unique properties such as mechanochromism and solvent and concentration dependence of the photophysical properties. Studies on the origin of these intriguing properties and organic electronic applications will be the subject of future studies.

This work was supported by a Grant-in-Aid for Scientific Research on Innovative Areas (for H.T., No. 21108509, “pi-Space”) from MEXT, Japan. We also thank MEXT (KAKENHI for E.N., No. 22000008, H.T., No. 20685005) and the Global COE Program for Chemistry Innovation. This work was partly supported by the Strategic Promotion of Innovative R&D, JST. C.M. thanks JSPS for the Research Fellowship for Young Scientists (No. 21•9262).

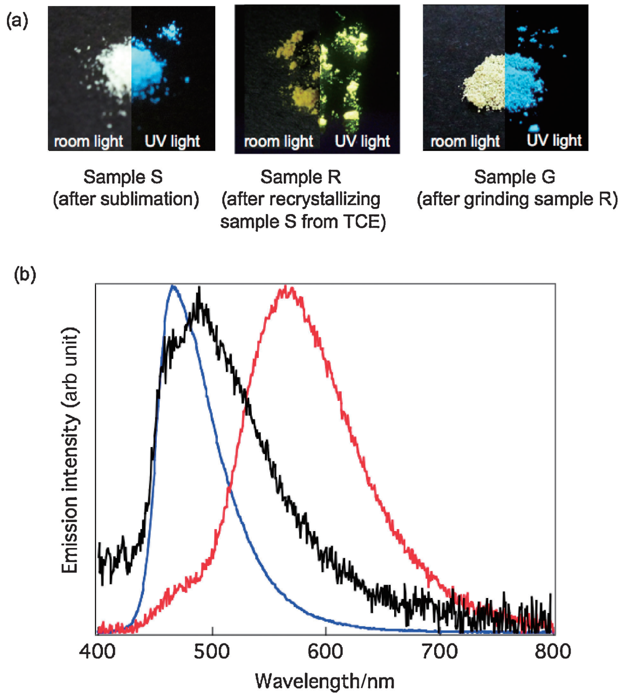


Figure 3. Photophysical properties of **2-PyBDF** in the solid state. (a) Pictures of the solid sample under UV light (365 nm) irradiation. Sample S: after sublimation; sample R: after recrystallization of sample S from TCE; sample G: after grinding of sample R. (b) Photoluminescence spectra of these solids excited at 340 nm (blue: sample S; red: sample R; black: sample G).

References and Notes

1 a) H. Tsuji, C. Mitsui, L. Ilies, Y. Sato, E. Nakamura, *J. Am. Chem. Soc.* **2007**, *129*, 11902. b) H. Tsuji, C. Mitsui, Y. Sato, E. Nakamura, *Adv. Mater.* **2009**, *21*, 3776.

2 a) M. Nakamura, L. Ilies, S. Otsubo, E. Nakamura, *Angew. Chem.* **2006**, *118*, 958; M. Nakamura, L. Ilies, S. Otsubo, E. Nakamura, *Angew. Chem., Int. Ed.* **2006**, *45*, 944. b) M. Nakamura, L. Ilies, S. Otsubo, E. Nakamura, *Org. Lett.* **2006**, *8*, 2803.

3 H. Tsuji, Y. Yokoi, C. Mitsui, L. Ilies, Y. Sato, E. Nakamura, *Chem.—Asian J.* **2009**, *4*, 655.

4 Crystal data: Monoclinic, $P2_1/c$, $a = 14.3141(3)$ Å, $b = 4.77162(9)$ Å, $c = 11.0320(2)$ Å, $\beta = 105.5820(10)°$, $V = 725.80(2)$ Å^3, $Z = 2$, $R = 0.0443$ (for $I > 2\sigma(I)$), $wR = 0.1148$ (for all data), GOF = 1.166, $T = 140$ K.

5 Unpublished data.

6 For recent examples of mechanochromic material: a) T. Mutai, H. Satou, K. Araki, *Nat. Mater.* **2005**, *4*, 685. b) A. R. Sheth, J. W. Lubach, E. J. Munson, F. X. Muller, D. J. W. Grant, *J. Am. Chem. Soc.* **2005**, *127*, 6641. c) S. Mizukami, H. Houjou, K. Sugaya, E. Koyama, H. Tokuhisa, T. Sasaki, M. Kanesato, *Chem. Mater.* **2005**, *17*, 50. d) Y. Sagara, T.

Mutai, I. Yoshikawa, K. Araki, *J. Am. Chem. Soc.* **2007**, *129*, 1520. e) H. Ito, T. Saito, N. Oshima, N. Kitamura, S. Ishizaka, Y. Hinatsu, M. Wakeshima, M. Kato, K. Tsuge, M. Sawamura, *J. Am. Chem. Soc.* **2008**, *130*, 10044. f) J. Kunzelman, M. Kinami, B. R. Crenshaw, J. D. Protasiewicz, C. Weder, *Adv. Mater.* **2008**, *20*, 119. g) Y. Sagara, T. Kato, *Angew. Chem., Int. Ed.* **2008**, *47*, 5175. h) Y. Sagara, T. Kato, *Nat. Chem.* **2009**, *1*, 605. i) T. Abe, T. Itakura, N. Ikeda, K. Shinozaki, *Dalton Trans.* **2009**, 711. j) G. Zhang, J. Lu, M. Sabat, C. L. Fraser, *J. Am. Chem. Soc.* **2010**, *132*, 2160.

7 A. L. Balch, *Angew. Chem., Int. Ed.* **2009**, *48*, 2641.

8 Deduced from the following equation: E_{HOMO} or $E_{\mathrm{LUMO}} = -(4.80 + E_{\mathrm{DPV}})$.

9 For reviews: a) Y. Shirota, H. Kageyama, *Chem. Rev.* **2007**, *107*, 953. b) Y. Shirota, in *Organic Light-Emitting Devices: Synthesis, Properties, and Applications*, ed. by K. Müllen, U. Scherf, Wiley-VCH, Weinheim, **2006**, pp. 245–263. c) C. Adachi, T. Tsutsui, in *Organic Light-Emitting Devices: A Survey*, ed. by J. Shinar, Springer, New York, **2004**, pp. 43–69.

10 C. Adachi, M. A. Baldo, S. R. Forrest, M. E. Thompson, *Appl. Phys. Lett.* **2000**, *77*, 904.

11 a) K. Tamao, M. Uchida, T. Izumizawa, K. Furukawa, S. Yamaguchi, *J. Am. Chem. Soc.* **1996**, *118*, 11974. b) H. Murata, G. G. Malliaras, M. Uchida, Y. Shen, Z. H. Kafafi, *Chem. Phys. Lett.* **2001**, *339*, 161. c) L. C. Palilis, H. Murata, M. Uchida, Z. H. Kafafi, *Org. Electron.* **2003**, *4*, 113.

12 a) H. Tsuji, K. Sato, L. Ilies, Y. Itoh, Y. Sato, E. Nakamura, *Org. Lett.* **2008**, *10*, 2263. b) Y. Matano, T. Miyajima, T. Fukushima, H. Kaji, Y. Kimura, H. Imahori, *Chem.—Eur. J.* **2008**, *14*, 8102. c) Y. Dienes, M. Eggenstein, T. Kárpáti, T. C. Sutherland, L. Nyulászi, T. Baumgartner, *Chem.—Eur. J.* **2008**, *14*, 9878. d) T. Sanji, K. Shiraishi, T. Kashiwabara, M. Tanaka, *Org. Lett.* **2008**, *10*, 2689. e) Y. Matano, M. Nakashima, H. Imahori, *Angew. Chem., Int. Ed.* **2009**, *48*, 4002. f) K. Geramita, J. McBee, T. D. Tilley, *J. Org. Chem.* **2009**, *74*, 820. g) A. Fukazawa, Y. Ichihashi, Y. Kosaka, S. Yamaguchi, *Chem.—Asian J.* **2009**, *4*, 1729. h) H. Tsuji, K. Sato, Y. Sato, E. Nakamura, *J. Mater. Chem.* **2009**, *19*, 3364. i) A. Saito, T. Miyajima, M. Nakashima, T. Fukushima, H. Kaji, Y. Matano, H. Imahori, *Chem.—Eur. J.* **2009**, *15*, 10000. j) H. Tsuji, K. Sato, Y. Sato, E. Nakamura, *Chem.—Asian J.* **2010**, *5*, 1294.

13 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.