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Intense One- and Two-Photon Excited Fluorescent Bis(BF_2) Core Complex Containing a 1,8-Naphthyridine Derivative

Huifang-Jie Li,[†] Wen-Fu Fu,*[,†,‡] Li Li,[†] Xin Gan,[‡] Wei-Hua Mu,[‡] Wei-Qiang Chen,[†] Xuan-Ming Duan,[†] and Hai-Bin Song[§]

Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Peking 100190, P.R. China, College of Chemistry and Chemical Engineering, Yunnan Normal University, Kunming 650092, P.R. China, and Department of Chemistry, The State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, P.R. China

fuwf@mail.ipc.ac.cn

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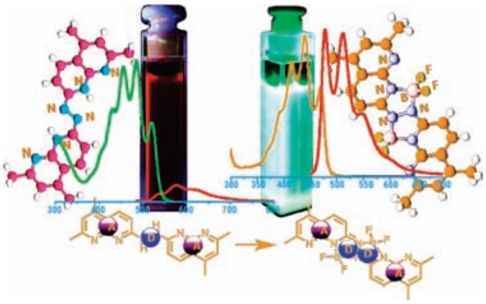
ABSTRACT



The first bis(BF_2) core complex containing a 1,8-naphthyridin derivative (1,2-bis(5,7-dimethyl-1,8-naphthyridin-2-yl)hydrazine) and with yellow-green emission as well as a high quantum yield was synthesized and structurally characterized, and the compound exhibits two-photon absorption and excited fluorescence properties.

Compared to many conventional fluorophores, organic fluorine−boron complexes BODIPY (BODIPY denotes boron dipyrromethene and its derivatives) have attracted plenty of interest in various areas of research because of their high absorption coefficients and fluorescence quantum yields.[1] These properties allow for BODIPY to be applied as fluorescent sensors,[2] laser dyes,[3] light harvesters, and fluorescent switches.[4,5] Despite a large amount of investigation having been done on different aspects of BODIPY, the research on boron complexes is still inadequate.[6] 1,8-Naphthyridine derivatives used as ligands for BF_2 have been the subject of extensive studies for their biocompatibility and their good fluorescence properties,[7] and the N atoms in these compounds can effectively bind with the nitrogenous bases of DNA through hydrogen bonding, thereby allowing for potential applications of the 1,8-naphthyridyl derivatives in medical and biological fields.[8] We introduced BF_2 cores into the conjugated framework of the parent molecule to obtain

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[†] Chinese Academy of Sciences.

[‡] Yunnan Normal University.

[§] Nankai University.

(1) Loudet, A.; Burgess, K. *Chem. Rev.* **2007**, *107*, 4891.

(2) (a) Bricks, J. L.; Kovalchuk, A.; Trieflinger, C.; Nofz, M.; Bschel, M.; Tolmachev, A. I.; Daub, J.; Rurack, K. *J. Am. Chem. Soc.* **2005**, *127*, 13522. (b) Camerel, F.; Bonardi, L.; Schmutz, M.; Ziessel, R. *J. Am. Chem. Soc.* **2006**, *128*, 4548.

(3) (a) Sathyamoorthi, G.; Wolford, L. T.; Haag, A. M.; Boyer, J. H. *Heteroat. Chem.* **1994**, *5*, 245. (b) Chen, T.; Boyer, J. H.; Trudell, M. L. *Heteroat. Chem.* **1997**, *8*, 51.

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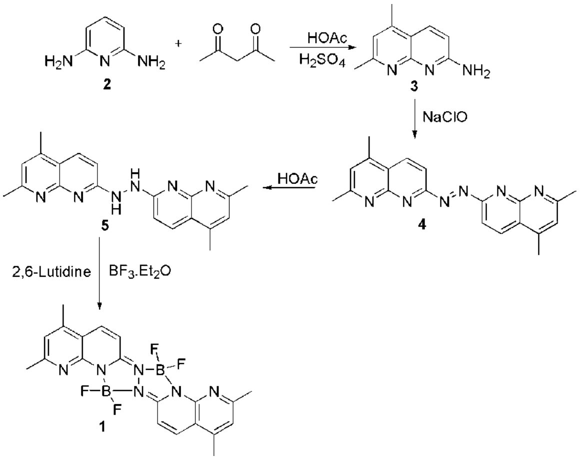
the first intensely fluorescent bis(BF$_2$) core compound containing a 1,8-naphthyridine derivative. Its intriguing structure and high fluorescent quantum yield as well as two-photon absorption (TPA) properties indicate its potential applications in fluorescence microscopy.

The synthetic route toward complex **1** is shown in Scheme 1. Compounds **3** and **4** were synthesized according to a literature procedure in good yields.[9] Compound **5** was previously obtained by reacting **4** with acetic acid under a nitrogen atmosphere at ambient temperature and has been reported by our group.[10] The desired fluorine−boron complex **1** was prepared in a satisfactory yield (56%) using diethyl ether as a solvent by the reaction of 1,2-bis(5,7-dimethyl-1,8-naphthyridin-2-yl)hydrazine and BF_3•Et_2O in the presence of 2,6-lutidine, and its structure was determined by NMR, ESI MS, elemental analysis, and X-ray crystallography. The crystal data and details on data collection as well as the structure refinement of **1** are summarized in the Supporting Information (SI).

Scheme 1. Synthesis of Complex **1**



The X-ray crystal analysis of compounds **1** and **5** revealed that the two naphthyridyl rings are nearly coplanar and that the special structure of **5** results from the formation of two five-membered rings by the interaction of N(3) or N(3A) and H atoms with a short distance of 2.044 Å (Figure 1a).[11]

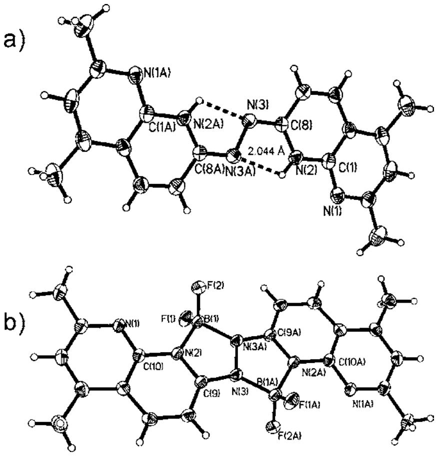


Figure 1. Perspective view of **5** (a) and complex **1** (b) representing the thermal ellipsoids with 50% probabilities.

A perspective view of **1** is shown in Figure 1b along with an atom numbering scheme. The asymmetric unit of **1** consists of half the molecule, while the whole molecule is generated by inversion. The two BF$_2$ cores were complexed with N−N and two 1,8-naphthyridine moieties, respectively, and they exhibit the familiar "S-frame" pattern. In addition, two central five-membered CNBN$_2$ rings with average B−N(3), B−N(2), N(2)−C(9), C(9)−N(3), and N(3)−N(3A) bond lengths of 1.571(2), 1.579(2), 1.356(2), 1.329(2), and 1.407(2) Å, respectively, were found for the complex.

The absorption and emission spectra that were recorded for complex **1** in CH_2Cl_2 are shown in Figure 2, and the UV−vis absorption spectra of **1** and **5** were found to be dependent on the type of solvent (Figures S1 and S2, SI). The absorption spectrum of **1** has well-resolved vibronic peaks at 392, 415, 440, and 470 nm with an ε_{max} of 30 083 dm^3 mol^{-1} cm^{-1}, and the vibration progressions ranging from 1370 to 1450 cm^{-1} are close to C═C and C═N stretching frequencies of complex **1**. In general, the formation of BODIPY compounds should result in a red shift of the absorption and emission spectra; however, complex **1** has a remarkable blue-shifted absorbance relative to the absorbance of **5** in CH_2Cl_2 solution (432, 456, 486, and 521 nm, the vibration progressions ranging from 1220 to 1380

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(4) (a) Li, F.; Yang, S. I.; Ciringh, Y.; Seth, J.; Martin, C. H.; Singh, D. L.; Kim, D.; Birge, R. R.; Bocian, D. F.; Holten, D.; Lindsey, J. S. *J. Am. Chem. Soc.* **1998**, *120*, 10001. (b) Lammi, R. K.; Ambroise, A.; Balasubramanian, T.; Wagner, R. W.; Bocian, D. F.; Holten, D.; Lindsey, J. S. *J. Am. Chem. Soc.* **2000**, *122*, 7579. (c) Rousseau, T.; Cravino, A.; Bura, T.; Ulrich, G.; Ziessel, R.; Roncali, J. *Chem. Commun.* **2009**, 1673.

(5) Golovkova, T. A.; Kozlov, D. V.; Neckers, D. C. *J. Org. Chem.* **2005**, *70*, 5545.

(6) (a) Zhang, G.; Chen, J.; Payne, S. J.; Kooi, S. E.; Demas, J. N.; Fraser, C. L. *J. Am. Chem. Soc.* **2007**, *129*, 8942. (b) Cogné-Laage, E.; Allemand, J. F.; Ruel, O.; Baudin, J. B.; Croquette, V.; Blanchard-Desce, M.; Jullien, L. *Chem.—Eur. J.* **2004**, *10*, 1445. (c) Porrès, L.; Mongin, O.; Blanchard-Desce, M. *Tetrahedron Lett* **2006**, *47*, 1913. (d) Zheng, Q.; Xu, G.; Prasad, P. N. *Chem.—Eur. J.* **2008**, *14*, 5812. (e) Halik, M.; Wenseleers, W.; Grasso, C.; Stellacci, F.; Zojer, E.; Barlow, S.; Brédas, J. -L.; Perry, J. W.; Marder, S. R. *Chem. Commun.* **2003**, 1490.

(7) (a) Nakatani, K.; Horie, S.; Saito, I. *J. Am. Chem. Soc.* **2003**, *125*, 8972. (b) Hikishima, S.; Minakawa, N. *Angew. Chem., Int. Ed.* **2005**, *44*, 596. (c) Katz, J. L.; Geller, B. J.; Foster, P. D. *Chem. Commun.* **2007**, 1026.

(8) (a) He, C.; Lippard, S. J. *J. Am. Chem. Soc.* **2000**, *122*, 184. (b) Dohno, C.; Uno, S. N.; Sakai, S.; Oku, M.; Nakatani, K. *Bioorg. Med. Chem.* **2009**, *17*, 2536. (c) Minakawa, N.; Ogata, S.; Takahashi, M.; Matsuda, A. *J. Am. Chem. Soc.* **2009**, *131*, 1644.

(9) (a) Brown, E. V.; Granneman, G. R. *J. Am. Chem. Soc.* **1975**, *97*, 621. (b) Henry, R. A.; Hammond, P. R. *J. Heterocycl. Chem.* **1977**, *14*, 1109. (c) Launay, J. P.; Tourrel-Pagis, M.; Lipskier, J. F.; Marvaud, V.; Joachim, C. *Inorg. Chem.* **1991**, *30*, 1033.

(10) Fu, W. -F.; Li, H. F. -J.; Wang, D. -H.; Zhou, L. -J.; Li, L.; Gan, X.; Xu, Q. -Q.; Song, H. -B. *Chem. Commun.* **2009**, 5524.

(11) Crystallographic data for **1**: $C_{20}H_{18}B_2F_4N_6$, $M = 440.02$, $T = 113(2)$ K. Orthorhombic, space group *Pbca*, $a = 8.538(2)$, $b = 14.696(3)$, $c = 15.467(3)$ Å, $\alpha = 90$, $\beta = 90$, $\gamma = 90°$, $V = 1940.6(7)$ Å^3, $Z = 4$, $Dc = 1.506$ Mg m^{-3}; reflections collected, 14 645, $R_{int} = 0.0578$. Final R indices [$I > 2\sigma I$]: $R_1 = 0.0453$, $wR_2 = 0.1153$. R indices (all data): $R_1 = 0.0613$, $wR_2 = 0.1273$.

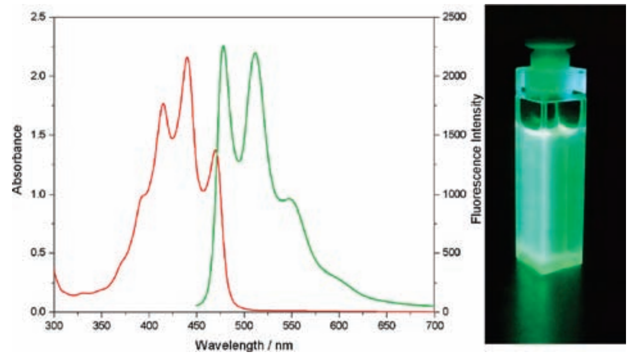

Figure 2. Linear absorption (—, 7.3 × 10^{-5} M) and emission (- - -, 1.1 × 10^{-6} M, excitation at 440 nm) spectra of **1** in dichloromethane, and photograph of dichloromethane solution of **1** under irradiation of 365 nm light.

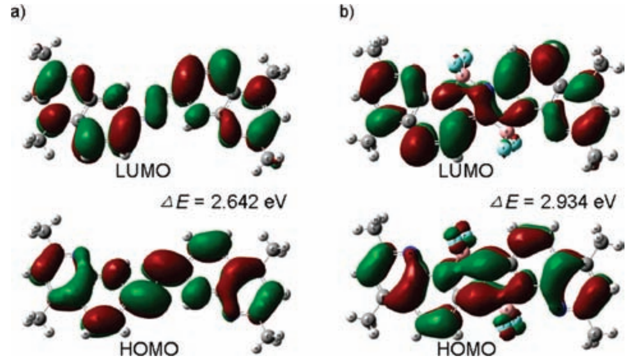

Figure 3. Contour plots and orbital energies of the HOMO and LUMO for **5** (a) and **1** (b).

cm^{-1}) (Figure S3, SI).[12] This implies that the intramolecular charge transfer (ICT) in **1** was suppressed by the introduction of the BF_2 cores into **5**. The hypothesis is further supported by time-dependent density functional theory (TD-DFT) calculations.[13] Calculation results showed that the HOMO and LUMO energy gaps for compounds **1** and **5** should be at 2.93 (423 nm) and 2.64 (470 nm) eV, and this is essentially consistent with the experimental results (Figure 3). These results suggest a change in the distributing electron density on going from compound **5** with a symmetrical Acceptor−Donor−Acceptor (A−D−A) type to compound **1** with an A−D−D−A pattern.

Compound **1** has an intense solid-state emission with a λ_{max} at 542 nm, while **5** exhibits a relative weak red emission at 630 nm in the solid state at room temperature (Figures S4 and S5, SI). The fluorescence spectrum of complex **1** has two emission maximum peaks at 478 ($\tau = 121$ ns) and 512 ($\tau = 124$ ns) nm which are of an almost mirror-image symmetry to the corresponding absorption spectrum in CH_2Cl_2 (Figure 2). The emission quantum yields of **1** were measured using fluorescein in 0.1 N NaOH as a reference and were found to be 0.965 and 0.767 in CH_2Cl_2 and DMSO, respectively, and only 0.009 for **5** in CH_2Cl_2 solution (Figure S6, SI).[14] The enhanced emission of **1** compared to that of the precursor **5** can be explained by their crystal structures as shown in Figure 1. The crystal structure of **1** clearly shows that the π-conjugated framework of the complex exhibiting B−N interactions results in a rigid molecular structure and hinders the free rotation of the 1,8-naphthyridine rings around the N−N single bond. A loss of energy from the excited states via the nonirradiative pathway was thus prevented.

Symmetric charge transfer and the molecular interactions such as in the A−D−A or A−D−D−A patterns and in the systems exhibiting hydrogen bonds are an efficient way to enlarge the TPA cross-section.[15,16] Figure 4 shows that the spectral profile and the peak position during two-photon excited fluorescence (TPEF) for **1** upon excitation at 780 nm are the same as that from single-photon excited fluores-

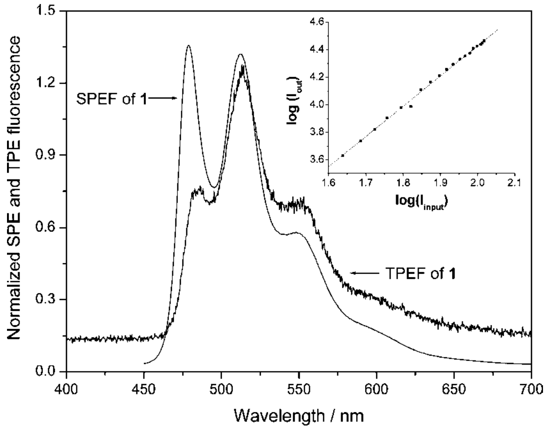

Figure 4. SPEF of **1** (CH_2Cl_2, 1.1 × 10^{-6} M) and TPEF of **1** (acetonitrile, 1.2 × 10^{-5} M). Inset: Fluorescence peak intensities versus laser intensity upon excitation at 780 nm.

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(12) (a) Wakamiya, A.; Taniguchi, T.; Yamaguchi, S. *Angew. Chem., Int. Ed.* **2006**, *45*, 3170. (b) Yoshino, J.; Kano, N.; Kawashima, T. *Chem. Commun.* **2007**, 559.

(13) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Vreven, T., Jr.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; aboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision C.02; Gaussian, Inc.: Wallingford CT, 2004.

(14) Demas, J. N.; Crosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991.

(15) Albota, M.; Beljonne, D.; Brédas, J. -L.; Ehrlich, J. E.; Fu, J. -Y.; Heikal, A. A.; Hess, S. E.; Kogej, T.; Levin, M. D.; Marder, S. R.; McCord-Maughon, D.; Perry, J. W.; Röckel, H.; Rumi, M.; Subramaniam, G.; Webb, W. W.; Wu, X. -L.; Xu, C. *Science* **1998**, *281*, 1653.

(16) Liu, Z.; Shao, P.; Huang, Z.; Liu, B.; Chen, T.; Qin, J. *Chem. Commun.* **2008**, 2260.

cence (SPEF) upon excitation at 440 nm. This implies that the fluorescence emissions originate from the same excited state.[17] Furthermore, the left part of the multiple peaks obtained from TPEF is weaker than those obtained from SPEF, which is probably due to the relatively high sample concentrations being used which causes the reabsorption of **1**.[18] To confirm the character of the TPA, the dependence of the two-photon excited output fluorescence of **1** in CH_3CN on the input laser power was conducted. Typical plots of $\log(I_{out})$ versus $\log(I_{in})$ demonstrate that the intensity of the up-converted fluorescence was measured as a function of input laser intensity as shown in Figure 4 (slope = 2.19). Therefore, the curve of I_{out} versus I_{in} fits a quadratic parabolas well, which possesses the character of the TPEF process in nature.[19]

The TPA spectrum of **1** that was obtained by using the two-photon-induced fluorescence technique has two TPA peaks with λ_{max} at 730 and 850 nm (Figure 5).[20] The former corresponds to the shoulder peak at 375 nm in the single-photon absorption (SPA) spectrum, while the latter is related to the absorption maximum at 440 nm in the SPA spectrum in CH_3CN solution (Figure S1, SI). Compared to TPA properties of the reported compounds containing A−π−A and A−D−A chromophores, a two-photon absorption cross-section (δ) of **1** is moderate, but it has a relatively large two-photon action cross-section ($\eta\delta$), where η is the fluorescence quantum yield.[21]

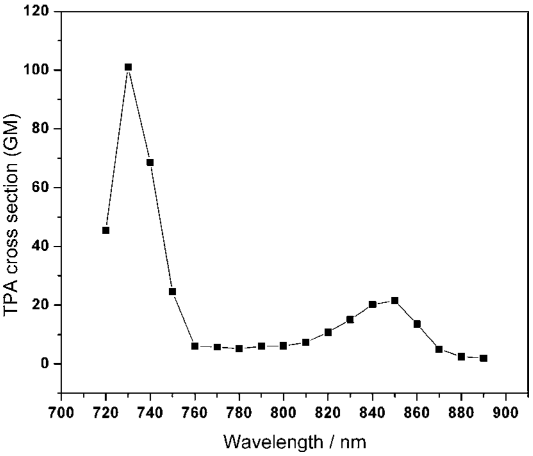

Figure 5. Two-photon absorption spectrum of complex **1** in CH_3CN with the concentration of 1.4×10^{-5} M, GM = 10^{-50} cm^4 s photon^{-1}

In summary, we synthesized the first bis(BF_2) core compound containing a 1,8-naphthyridine derivative. Its excellent photophysical properties were well investigated and explained by molecular structure analysis and quantum chemical calculations. The results indicate that a new family of fluorescent probes has key properties that enable it to be used for TPEF, and it may be a candidate for use in fluorescence microscopy because of a relatively large two-photon action cross-section. The work on functionalizing such new two-photon chromophores with potential practical applications is currently in progress.

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Supporting Information Available: X-ray crystallographic file in CIF format for **1** is provided. Details of experiments, theoretical calculations, and ^1H NMR, TOF MS (EI), UV−vis absorption, and emission spectra for the new compound. This material is available free of charge via the Internet at http://pubs.acs.org.

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[17] Liu, Z. -Q.; Fang, Q.; Wang, D.; Cao, D. -X.; Xue, G.; Yu, W. -T.; Lei, H. *Chem.—Eur. J.* **2003**, *9*, 5074.

[18] Liu, Z. -Q.; Fang, Q.; Cao, D. -X.; Wang, D.; Xu, G. -B. *Org. Lett.* **2004**, *6*, 2933.

[19] Bhawalkar, J. D.; He, G. S.; Prasad, P. N. *Rep. Prog. Phys.* **1996**, *59*, 1041.

[20] (a) Xu, C.; Webb, W. W. *J. Opt. Soc. Am. B* **1996**, *13*, 481. (b) Pond, S. J. K.; Rumi, M.; Levin, M. D.; Parker, T. C.; Beljonne, D.; Day, M. W.; Bredas, J. L.; Marder, S. R.; Perry, J. W. *J. Phys. Chem. A* **2002**, *106*, 11470.

[21] (a) Woo, H. Y.; Korystov, D.; Mikhailovsky, A.; Nguyen, T. -Q.; Bazan, G. C. *J. Am. Chem. Soc.* **2005**, *127*, 13794. (b) Pond, S. J. K.; Tsutsumi, O.; Rumi, M.; Kwon, O.; Zojer, E.; Brédas, J. -L.; Marder, S. R.; Perry, J. W. *J. Am. Chem. Soc.* **2004**, *126*, 9291.