J|A|C|S
COMMUNICATIONS

Band Gap Control in Conjugated Oligomers via Lewis Acids

Gregory C. Welch, Robert Coffin, Jeff Peet, and Guillermo C. Bazan*

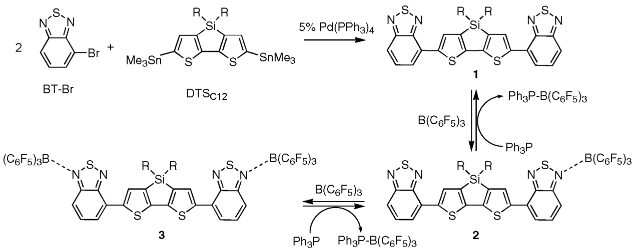
Center for Polymers and Organic Solids, Department of Chemistry & Biochemistry and Department of Materials, University of California, Santa Barbara, California 93106

Received April 7, 2009; E-mail: bazan@chem.ucsb.edu

New approaches to the design of organic chromophores are of interest for a variety of optical and optoelectronic technologies. In the area of solar energy conversion, it is essential that the absorption of the light-harvesting material match the spectral characteristics of the sun.[1] This condition applies equally to dye-sensitized cells[2] and devices based on organic semiconducting materials.[3] Some of the best-performing bulk heterojunction "plastic" solar cells are fabricated with conjugated polymers that have backbones comprising alternating donor/acceptor (D/A) comonomer units. This structural motif leads to excited states with charge-transfer characteristics and to energy transitions on the order of 1.4 eV.[4] Several of these conjugated copolymers contain benzo-2,1,3-thiadiazole (BT) as the electron-acceptor unit and silicon- or carbon-fused bithiophene as the donor fragment.[5−7] Many oligomers containing BT display absorption only within the blue region of the visible spectrum.[8]

While the absorption of conjugated oligomers can be tuned via structural modification, the required synthesis can be rigorous and time-consuming. It occurred to us that it would be possible to modulate the electronic properties of the BT fragment via interactions with Lewis acids that bind nitrogen.[9,10] Herein, we show that this simple approach makes it possible to access a range of chromophores starting with a single, well-defined oligomer. Band gap control is readily achieved by varying the strength of the Lewis acid.

Scheme 1. Synthetic Route to **1** and the Lewis Acid Adducts **2** and **3** (R = $C_{12}H_{25}$)



Our studies focused on **1**, which has an A/D/A structure and was synthesized via the microwave-assisted Stille cross-coupling reaction between BT-Br and DTS$_{C12}$, as outlined in Scheme 1.[11] Precipitation with methanol and purification via chromatography gave the desired product as a red solid in 85% yield. Compound **1** was characterized by multinuclear NMR spectroscopy, high-resolution mass spectrometry, and elemental analysis.[12]

Figure 1 shows that the absorbance spectrum of **1** in *o*-dichlorobenzene (*o*-DCB) exhibits an absorption maximum (λ_{max}) at 503 nm with an onset (λ_{onset}) at 577 nm. A color change from red to green to blue was observed by visual inspection upon addition of 2 equiv of the Lewis acid $B(C_6F_5)_3$.[13] Analysis by UV−vis spectroscopy revealed the disappearance of the primary band of **1** and the appearance of a new transition with λ_{max} = 647 nm. Addition of more than 2 equiv of $B(C_6F_5)_3$ resulted in minimal intensity change at 647 nm and the emergence of a band at λ_{max} = 305 nm due to unbound $B(C_6F_5)_3$. Stepwise addition of 0−2 equiv of $B(C_6F_5)_3$ in increments of 0.1 mol revealed the existence of two separate isosbestic points at ~537 and ~557 nm, indicating the presence of more than two absorbing species in solution.[12] These data are consistent with the stepwise formation of mono- and bis-Lewis acid adducts. On the basis of the propensity of boranes to bind harder nitrogen bases over their softer sulfur counterparts, we propose the structure of the adducts to be **2** and **3**, respectively, as shown in Scheme 1.[14]

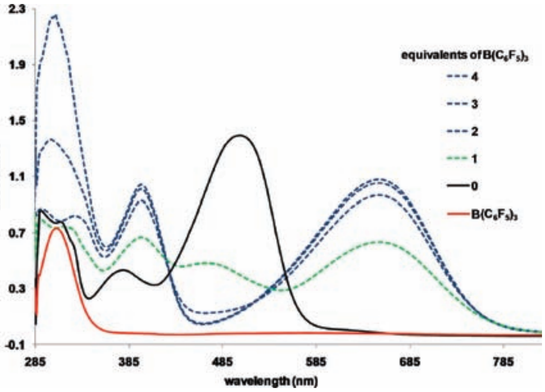


Figure 1. Absorption spectra of **1** plus varying amounts of $B(C_6F_5)_3$ in *o*-DCB at 25 °C ([**1**] = 3.78×10^{-4} M).

Deep-blue **3** was isolated as a solid in greater than 90% yield after addition of 2 equiv of $B(C_6F_5)_3$ to **1** followed by solvent removal.

Its absorption characteristics are identical to those in Figure 1 for the addition of 2 equiv of $B(C_6F_5)_3$. The ^1H NMR spectrum of **3** in CD_2Cl_2 at 25 °C showed four C*H* resonances from 7.4 to 8.4 ppm; the two $B(C_6F_5)_3$ moieties are thus bound at opposite ends of the molecule. The ^{11}B and ^{19}F NMR spectra showed no evidence of free $B(C_6F_5)_3$, and the ^{19}F NMR spectrum exhibited 15 independent signals upon cooling to −30 °C. There is thus restricted rotation about the B−N and B−C_6F_5 bonds.[12,15] Addition of excess PPh_3 to **3** gave rise to an immediate color change from blue to the red characteristic of **1** along with the formation of $Ph_3P-B(C_6F_5)_3$, as determined by ^{31}P NMR spectroscopy.[16] These observations indicate that displacement of the Lewis acid is possible by using a stronger base. Significantly, there is no change in the conjugated framework of **1**.

Complex **2** could not be independently isolated. The ^1H NMR spectrum of a 1:1 ratio of $B(C_6F_5)_3$/**1** in CD_2Cl_2 exhibited broad signals, indicating the exchange of borane between the nitrogen atoms. When the solution was cooled to −30 °C, the exchange was slowed, and a mixture of **1**, **2**, and **3** in a 1:2:1 ratio was observed.[12] Binding of $B(C_6F_5)_3$ to the two BT units is therefore statistical.

While good-quality single crystals of **2** and **3** could not be obtained, it was possible to do so for the adduct containing $B(C_6F_5)_3$ and BT-Br, i.e., species **4**. The solid-state structure of **4** determined by X-ray diffraction studies is summarized in Figure 2.[12] Consistent with our expectations, $B(C_6F_5)_3$ binds to nitrogen instead of sulfur.

10.1021/ja902789w CCC: $40.75

Furthermore, it chooses to do so at the 1-position of the BT unit, opposite the Br atom, presumably because of steric constraints. A similar regiochemistry is expected in **2** and **3** (Scheme 1). Addition of excess borane to **4** or **3** did not result in formation of a second or third B−N bond, respectively, from 25 to −50 °C, as determined by ^{1}H and ^{19}F NMR spectroscopy.[12] This lack of subsequent reactivity is likely due to the combination of steric constraints and the depletion of electronic density within the BT fragment upon binding the first equivalent of $B(C_6F_5)_3$.

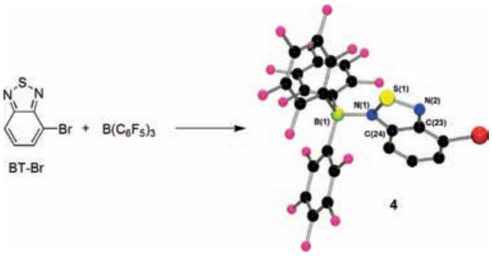


Figure 2. POV-Ray depiction of **4**. Hydrogen atoms have been omitted for clarity.

The absorption spectra of **1** and **3** in the solid state were compared to those in solution. The spectrum of solid **1** showed minimal change in λ_{max} relative to that for **1** in solution, although the appearance of a shoulder at 544 nm is indicative of multichromophore interactions.[12] No such differences were observed for **3**, consistent with the fact that the bound $B(C_6F_5)_3$ increases the distance between optically active fragments to the point where significant through-space interactions do not take place.[17]

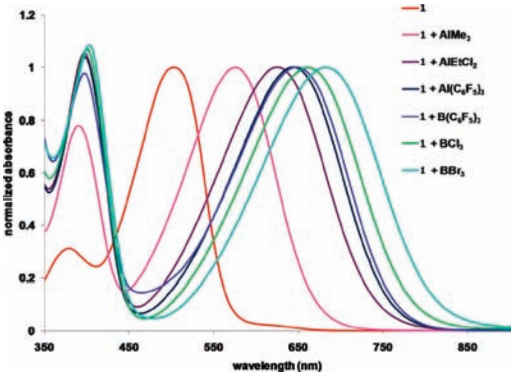


Figure 3. Normalized absorption spectra of **1** in *o*-DCB in the presence of 2 equiv of various Lewis acids.

To explore the generality of the band gap modification, a range of Lewis acids [$AlMe_3$, $AlEtCl_2$, $Al(C_6F_5)_3$, BCl_3, and BBr_3] were added to **1** in *o*-DCB and the UV−vis spectra of the resulting mixtures recorded. As can be seen in Figure 3, a series of red-shifted complexes that cover most of the visible region were obtained. Addition of the relatively weak acid $AlMe_3$ resulted in the formation of a violet solution, a 70 nm red shift in λ_{max}, and a 109 nm red shift in λ_{onset}. The effect of the strongest Lewis acid, BBr_3, was more pronounced, yielding a blue-green-colored complex. In this case, λ_{max} and λ_{onset} were remarkably red-shifted by 178 and 257 nm, respectively, relative to **1**.[12] Indeed, the optical absorption of the BBr_3 analogue of **3** approaches that of known polymers containing DTS and BT repeat units.[5] The general trend shows that the larger red shifts are obtained with stronger Lewis acids.

The nature of the bathochromic shifts was investigated computationally.[12] Comparison of the DFT-optimized structures of **1** and **3**[18] shows that the HOMO and LUMO become less delocalized across the π-conjugated backbone upon Lewis acid attachment. In other words, the Lewis acid withdraws electron density away from the BT unit, altering the electron density of the chromophore. Additionally, it is noteworthy that there is a synergistic lowering of the absolute energies of the two frontier molecular orbitals. The LUMO, however, is lowered by an additional 0.43 eV relative to the HOMO, thereby giving rise to the narrower band gap.

In conclusion, the synthesis, structural characterization, and optical properties of **1**, **2**, and **3** demonstrate a simple strategy for tuning the optical properties of an A/D/A chromophore with charge-transfer excited-state characteristics. The basic strategy involves Lewis acid complexation to a basic site within the π-delocalized framework. Our current thinking is that this complexation increases the electron affinity of the BT acceptor group, thereby stabilizing the charge-transfer characteristics of the excited state. While the red-shifting of nitrogen-containing conjugated organic materials can be achieved by protonation[19] or metal-ion complexation,[20] the present method offers the ability to progressively shift to lower-energy transitions by increasing the strength of the Lewis acid. We anticipate that the approach will be general for small molecules, oligomers, and even D/A-conjugated copolymers in which the acceptor fragments provide sterically unencumbered lone pairs of electrons.

Acknowledgment. Financial support from the National Science Foundation (DMR 0606414), the Institute for Collaborative Biotechnologies, and the Office of Naval Research is gratefully acknowledged. G.C.W. is the recipient of a Canadian NSERC PDF Scholarship.

Note Added after ASAP Publication. The Supporting Information PDF file published ASAP July 8, 2009, was an incomplete early version. The final version Supporting Information PDF file was published July 16, 2009.

Supporting Information Available: General experimental and characterization procedures and a CIF file for **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Roncali, J. *Macromol. Rapid Commun.* **2007**, *28*, 1761.
(2) Gratzel, M. *J. Photochem. Photobiol., C* **2003**, *4*, 145.
(3) Scharber, M. C.; Wuhlbacher, D.; Koppe, M.; Denk, P.; Waldauf, C.; Heeger, A. J.; Brabec, C. L. *Adv. Mater.* **2006**, *18*, 789.
(4) Dennler, G.; Scharber, M. C.; Brabec, C. J. *Adv. Mater.* **2009**, *21*, 1323.
(5) Hou, J.; Chen, H. Y.; Zhang, S.; Li, G.; Yang, Y. *J. Am. Chem. Soc.* **2008**, *130*, 16144.
(6) Peet, J.; Kim, Y.; Coates, N. E.; Ma, W. L.; Moses, D.; Heeger, A. J.; Bazan, G. C. *Nat. Mater.* **2007**, *6*, 497.
(7) Kim, J. Y.; Lee, K.; Coates, N. E.; Moses, D.; Nguyen, T. Q.; Dante, M.; Heeger, A. J. *Science* **2007**, *317*, 222.
(8) Anant, P.; Lucas, N. T.; Jacob, J. *Org. Lett.* **2008**, *10*, 5533. (b) Kato, S.; Matsumoto, T.; Shigeiwa, M.; Gorohmaru, H.; Maeda, S.; Ishi-i, T.; Mataka, S. *Chem.—Eur. J.* **2006**, *12*, 2303. (c) van Mullekon, H. A. M.; Vekemans, J. A. J. M.; Meijer, E. W. *Chem.—Eur. J.* **1998**, *4*, 1235.
(9) Focante, F.; Mercandelli, P.; Sironi, A.; Resconi, L. *Coord. Chem. Rev.* **2006**, *250*, 170.
(10) (a) Fraleoni-Morgera, A.; Giorgini, L.; Zanirato, P. *Dyes Pigments* **2008**, *76*, 394. (b) Cazenobe, I.; Ledoux, I.; Zyss, J.; Thornton, A.; Bruce, D. W.; Kakkar, A. K.; Lesley, G. M. J.; Woodward, A.; Taylor, N. J.; Marder, T. B. *Chem. Mater.* **1998**, *10*, 1355. (c) Lopez-Garriga, J. J.; Babcock, G. T.; Harrison, J. F. *J. Am. Chem. Soc.* **1986**, *108*, 7131. (d) Apblett, A.; Chivers, T.; Richardson, J. F. *Can. J. Chem.* **1986**, *64*, 849.
(11) Son, H. J.; Han, W. S.; Chun, J. Y.; Kwon, S. N.; Ko, J.; Kang, S. O. *Organometallics* **2008**, *27*, 2464.
(12) See the Supporting Information.
(13) Piers, W. E. *Adv. Organomet. Chem.* **2005**, *52*, 1.
(14) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533.
(15) Focante, F.; Camurati, I.; Resconi, L.; Guidotti, S.; Beringhelli, T.; D'Alfonso, G.; Donghi, D.; Maggioni, D.; Mercandelli, P.; Sironi, A. *Inorg. Chem.* **2006**, *45*, 1683.
(16) Jacobsen, H.; Berke, H.; Döring, S.; Kehr, G.; Erker, G.; Fröhlich, R.; Meyer, O. *Organometallics* **1999**, *18*, 1724.
(17) Bazan, G. C. *J. Org. Chem.* **2007**, *72*, 8651.
(18) Methyl and chlorine substituents were used in place of the dodecyl side chains and C_6F_5 aryl rings, respectively.
(19) (a) Hancock, J. M.; Jenekhe, S. A. *Macromolecules* **2008**, *41*, 6864. (b) Fukumoto, H.; Yamamoto, T. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 2975. (c) Monkman, A. P.; Pålsson, L. O.; Higgins, R. W. T.; Wang, C.; Bryce, M. R.; Batsanov, A. S.; Howard, J. A. K. *J. Am. Chem. Soc.* **2002**, *124*, 6049.
(20) Tolosa, J.; Zucchero, A. J.; Bunz, U. H. F. *J. Am. Chem. Soc.* **2008**, *130*, 6498.

JA902789W