ORGANIC LETTERS

2008
Vol. 10, No. 15
3307−3310

Highly Fluorinated Benzobisbenzothiophenes

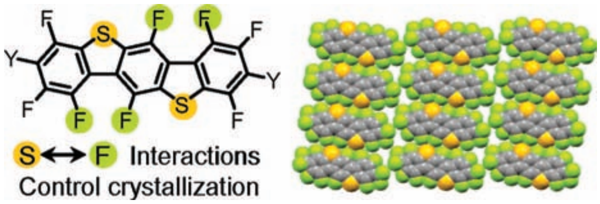
Yongfeng Wang,[†] Sean R. Parkin,[†] Johannes Gierschner,[‡] and Mark D. Watson*,[†]

Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506-0055,
Laboratory for Chemistry of Novel Materials, University of Mons-Hainaut, Mons,
Belgium, and Instituto Madrileño de Estudios Avanzados IMDEA Nanoscience,
Madrid, Spain

mdwatson@uky.edu

Received May 22, 2008

ABSTRACT



Expedient, facile syntheses of highly fluorinated benzobisbenzothiophenes (BBBT) are reported. Defined peripheral arrangements of sulfur and fluorine atoms lead to extensive crystalline networks of edge-to-edge S−F close contacts. The effects of various substitution patterns on self-assembly and electronic properties are described.

One of the many critical factors governing the performance of organic semiconductors is the mode in which they self-assemble to ordered arrays having extensive intermolecular orbital overlap.[1] Some approaches to modify intermolecular orbital overlap are the following: (a) increase the size of the π-system,[2a] (b) decorate the periphery with groups that preclude edge-to-face interactions,[2b] (c) enhance face-to-face interaction via attraction between electron-rich and -poor segments,[2c–e] and (d) construct peripheries from heteroatoms.[2f]

In addition to altering self-assembly, decoration with electron-withdrawing groups such as imide, cyano, or fluorine can convert known p- to n-types.[3] Most organic semiconductors are p-types, such as pentacene,[4] poly-3-hexylthiophene, or oligothiophenes,[5] while n-types are rarer.[6] Lower LUMO

[†] University of Kentucky.

[‡] University of Mons-Hainaut and Instituto Madrileño de Estudios Avanzados IMDEA Nanoscience.

(1) Newman, C. R.; Frisbie, C. D.; da Silva, D. A.; Bredas, J. L.; Ewbank, P. C.; Mann, K. R. *Chem. Mater.* **2004**, *16*, 4436–4451.

(2) (a) Watson, M. D.; Fechtenkoetter, A.; Muellen, K. *Chem. Rev.* **2001**, *101*, 1267–1300. (b) Anthony, J. E.; Eaton, D. L.; Parkin, S. R. *Org. Lett.* **2001**, *4*, 15–18. (c) Facchetti, A.; Yoon, M. H.; Stern, C. L.; Katz, H. E.; Marks, T. J. *Angew. Chem., Int. Ed.* **2003**, *42*, 3900–3903. (d) Patrick, C. R.; Prosser, G. S. *Nature* **1960**, *187*, 1021–1021. (e) Dai, C. ; Nguyen, P.; Marder, T. B.; Scott, A. J.; Clegg, W.; Viney, C. *Chem. Commun.* **1999**, *249*, 3–2494. (f) Yamada, K.; Okamoto, T.; Kudoh, K.; Wakamiya, A.; Yamaguchi, S.; Takeya, Y. *Appl. Phys. Lett.* **2007**, *90*, 072102.

(3) (a) Jones, B. A.; Facchetti, A.; Wasielewski, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **2007**, *129*, 15259–15278. (b) Chesterfield, R. J.; Newman, C. R.; Pappenfus, T. M.; Ewbank, P. C.; Haukaas, M. H.; Mann, K. R.; Miller, L. L.; Frisbie, C. D. *Adv. Mater.* **2003**, *15*, 1278–1282. (c) Facchetti, A.; Deng, Y.; Wang, A.; Koide, Y.; Sirringhaus, H.; Marks, T. J.; Friend, R. H. *Angew. Chem., Int. Ed.* **2000**, *39*, 4547–4551. (d) Facchetti, A.; Mushrush, M.; Yoon, M. H.; Hutchison, G. R.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **2004**, *126*, 13859–13874.

(4) (a) Lin, Y. Y.; Gundlach, D. J.; Nelson, S. F.; Jackson, T. N. *IEEE Electron Device Lett.* **1997**, *18*, 606–608. (b) Kelly, T. W.; Boardman, L. D.; Dunbar, T. D.; Muyres, D. V.; Pellerite, M. J.; Smith, T. P. *J. Phys. Chem. B* **2003**, *107*, 5877–5881.

(5) (a) Chabinyc, M. L.; Toney, M. F.; Kline, R. J.; McCulloch, I.; Heeney, M. *J. Am. Chem. Soc.* **2007**, *129*, 3226–3237. (b) Dimitrakopoulos, C. D.; Purushothaman, S.; Kymissis, J.; Callegari, A.; Shaw, J. M. *Science* **1999**, *283*, 822–824. (c) Sirringhaus, H.; Brown, P. J.; Friend, R. H.; Nielsen, M. M.; Bechgaard, K.; Langeveld-Voss, B. M. W.; Spiering, A. J. H.; Janssen, R. A. J.; Meijer, E. W.; Herwig, P.; de Leeuw, D. M. *Nature* **1999**, *401*, 685–688.

(6) (a) Haddon, R. C.; Perel, A. S.; Morris, R. C.; Palstra, T. T. M.; Hebard, A. F.; Fleming, R. M. *Appl. Phys. Lett.* **1995**, *67*, 121–123. (b) Bao, Z.; Lovinger, A. J.; Brown, J. *J. Am. Chem. Soc.* **1998**, *120*, 207–208. (c) Pappenfus, T. M.; Chesterfield, R. J.; Frisbie, C. D.; Mann, K. R.; Casado, J.; Raff, J. D.; Miller, L. L. *J. Am. Chem. Soc.* **2002**, *124*, 4184–4185.

10.1021/ol8003468 CCC: $40.75

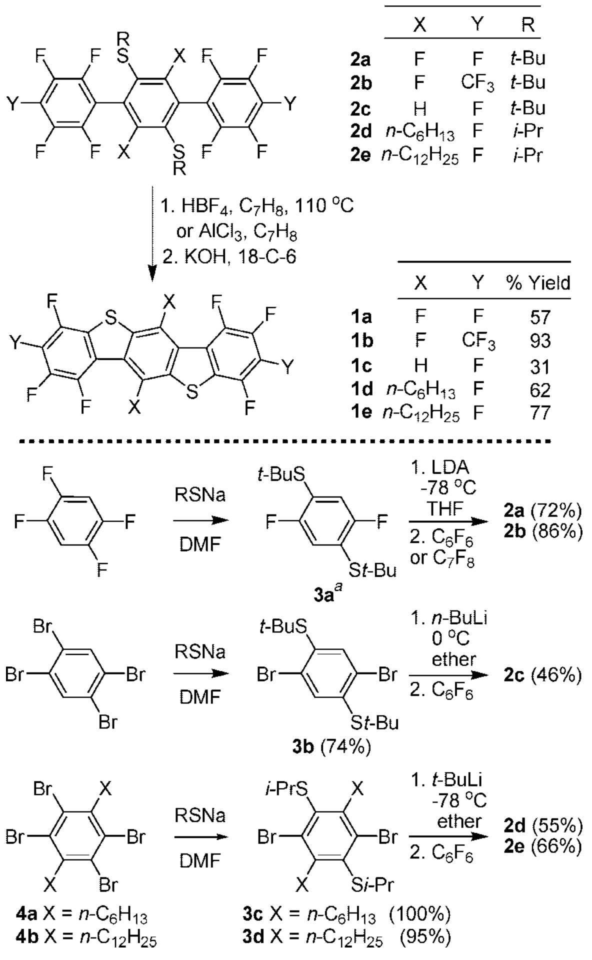
energy levels can facilitate electron injection and transport, leading to n-type characteristics.[1]

A recent search of the Cambridge Structural Database reveals 99 structures with close contacts (less than the sum of van der Waals radii) between organofluorine and thienyl sulfur atoms. This interaction may be electrostatic as in the interaction of thienyl sulfur atoms with oxygen atoms[7] or it may resemble that which imparts a rich supramolecular chemistry to chalcogenodiazoles, where nitrogen lone pairs donate into nitrogen−chalcogen σ^* orbitals.[8] Regardless of the nature of the S−F interaction, it stands to reason that lath-shaped molecules with triangular arrangements of thienyl sulfur atoms and two fluorine atoms could crystallize into infinite sheets resembling urea self-assembly. Indeed, the crystal structure of perfluorodibenzothiophene reveals close contacts between every sulfur atom and two fluorine atoms.[9]

We report here that the benzobisbenzothiophene (BBBT) scaffold, if fully fluorinated, provides two such antiparallel triangular F−S−F units, thus leading to extensive edge-to-edge interactions. This report does not delineate the nature of these interactions, but rather demonstrates their use as a supramolecular synthon. We also report a facile rapid synthesis of BBBT molecules, based largely on nucleophilic aromatic substitution chemistry ($\mathrm{SN_{Ar}}$). These highly fluorinated BBBT molecules may also be further functionalized via $\mathrm{SN_{Ar}}$ chemistry. Crystal packing, solubility, and the positions of frontier orbitals are modified by altering the nature of substituents.

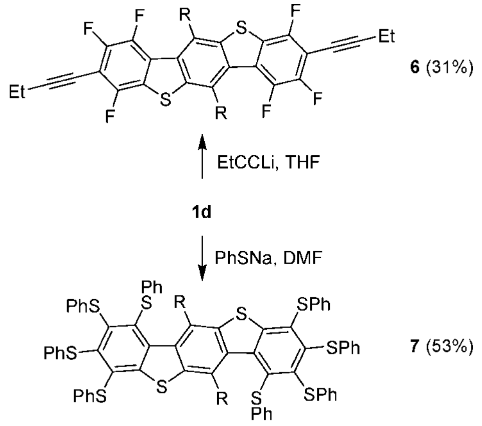
All BBBTs reported here were prepared via relatively short synthetic sequences (Scheme 1). Heavily halogenated building blocks allowed all new bonds forming the polycyclic framework to be constructed by nucleophilic aromatic substitution ($\mathrm{SN_{Ar}}$) over 3 steps. For comparison, the recently reported[10] parent BBBT required 6−7 steps. Compounds **3** were prepared via substitution of bromine or fluorine by alkyl thiolate. The yield of **3a** was not determined as it was obtained as a minor coproduct during the synthesis of 1,2,4,5-tetrakis(*tert*-butylthio)benzene for other purposes. Compounds **3** were converted to para-bis-metalates via ortho-lithiation or halogen−lithium exchange and reacted with excess perfluoroarene to produce terphenylenes **2**. The final step in each sequence is one-pot dealkylation[11] of compounds **2** and ring closure via the intramolecular $\mathrm{SN_{Ar}}$ reaction.

Scheme 1. Synthesis of BBBT's **1**



[a] Yield not determined. See text.

Scheme 2. Functionalization of BBBT **1d**. R = $n\text{-}C_6H_{13}$



R = $n\text{-}C_6H_{13}$.

Highly fluorinated BBBTs **1** can also serve as building blocks via substitution of selected or all fluorine atoms. The preliminary examples shown in Scheme 2 are each the result of a single unoptimized trial. The regioselectivity of partial subsitution reactions should be a function of the nucleophile and the relative directing abilities of the sulfur- and carbon-centered substituents. Compound **6**, which is a potential substrate for alkyne metathesis, was isolated from the reaction of **1d** with butynyllithium. As expected based on reports[12] of other perthiolated π-sys-

---

(7) Pomerantz, M. *Tetrahedron Lett.* **2003**, *44*, 1563–65.

(8) Cozzolino, A. F.; Vargas-Baca, I.; Mansour, S.; Mahmoudkhani, A. H. *J. Am. Chem. Soc.* **2005**, *127*, 3184–3190.

(9) Jones, J. B.; Brown, D. S.; Massey, A. G. *Phosphorus, Sulfur, Silicon* **1988**, *35*, 67–70.

(10) Ebata, H.; Miyazaki, E.; Yamamoto, T.; Takimiya, K. *Org. Lett.* **2007**, *9*, 4499–4502.

(11) (a) U.S. Patent 6376,716, B1. (b) Reddy, T. J.; Iwama, T.; Halpern, H. J.; Rawal, V. H. *J. Org. Chem.* **2002**, *67*, 4635–4639.

tems, the reduction wave onset of **7** is approximately 200 mV more positive than its precursor **1d** (Table 1).

Table 1. Electrochemical and UV−Vis Data for **1**, **5**, and **7**

	$E_{red}{}^{a}$ cath./onset (V)	$\lambda_{max}{}^{b}$ peak/edge (nm)	LUMO^{c} (eV)	$E_g{}^{d}$ (eV)	HOMO^{e} (eV)
1a	−2.13/−1.99	372/383	−2.81	3.24	−6.05
1b	−1.72/−1.60	400/416	−3.20	2.98	−6.18
1c	−2.33/−2.18	366/379	−2.62	3.27	−5.89
1d	−2.42/−2.22	383/397	−2.58	3.12	−5.70
5^{f}		369/380	−2.50	3.26	−5.76
7	−2.04/−2.03	467/490	−2.77	2.53	−5.30

[a] Versus Fc/Fc$^+$ ($E_{1/2}$ = 0.60V in this system). [b] Solution absorption spectra. [c] Estimated from reduction wave onset (LUMO = $-E_{red}$ − 4.8). [d] Estimated from the absorption edge. [e] Estimated from HOMO = LUMO − E_g. [f] Reference 10.

Energy gaps E_g of the lowest allowed optical transitions (Table 1) are 3.24 and 3.27 eV for **1a** and **1c**, determined from the absorption edges of UV−vis spectra (Figure 1). They are very similar to the unsubstituted compound **5** (3.26 eV),[10] while that for **1b** is significantly lower (2.98 eV). Substitution effects can be well understood[13] by quantum-chemical calculations, carried out at the DFT (density functional theory) level of theory, employing the B3LYP functional and the 6-311+G* basis set within the GAUSSIAN03 package.[14] According to calculations, the transition responsible for E_g is described mainly by the HOMO−LUMO transition. Fluorination at the teminal positions ("Y", Scheme 1) induces a hypsochromic shift that is essentially negated by a bathochromic shift due to fluorination in the lateral positions, leading to little difference in E_g for **1a**,**c** relative to **5**. Due to terminal CF_3 substiuents, the $S_0 \rightarrow S_1$ band of compound **1b** is significantly red-shifted compared to that of the perfluorinated compound **1a**. The calculated overall shift is 0.32 eV, in reasonable agreement with the experimental value (0.26 eV). Simulated spectra relating the pure vertical transitions ($S_0 \rightarrow S_{1,2,3}$) are included in the Supporting Information for comparison.

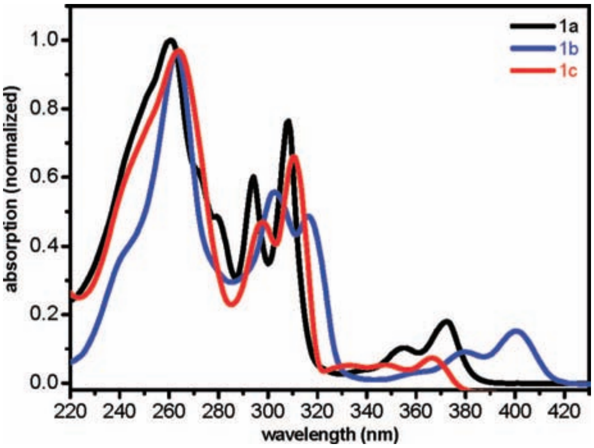


Figure 1. Solution absorption spectra for **1a**−**c** (10^{-6} M THF).

Solution electrochemical measurements of **1a**, **1b**, and **1c** revealed reduction peaks at −1.99, −1.60, and −2.18 V (vs Fc/Fc$^+$). From reduction wave onsets (Table 1), LUMO levels are estimated to be −2.81, −3.20, and −2.62 eV, respectively. These values cannot be strictly compared with that reported from another laboratory for the parent **5** (LUMO = −2.50 eV),[10] but the effect of fluorination is clear. Greater fluorine substitution lowers the LUMO (**1a** vs **1c**) and more electron-withdrawing CF_3 groups provide the largest effect.

Single-crystal X-ray analyses revealed that all BBBTs **1a**−**e** form slip stacks with face-to-face orientation. With the exception of **1d**, all assemble with S−F close contacts. Partial packing diagrams are included in Figure 2 along with that of the nonfluorinated parent **5** for comparison. BBBT **5** packs in a typical herringbone-like arrangement with edge-to-face interactions along its long edges.

Derivatives **1a**,**b** crystallize with predicted full edge-to-edge arrangements with eight S−F close contacts per molecule. BBBT **1b** assembles to sheets with all unsaturated atoms lying in parallel planes while the molecular planes of **1a** tilt slightly against similar planes containing the molecular centroids. Both fully fluorinated BBBTs form slip π-stacks along two dimensions, a feature that has been shown to improve FET performance.[15] For **1a**, one π-stacking axis is defined by 10 close contacts per molecule (6 C−C, 4 C−S), and the other by two S−S close contacts. The average face-to-face (atom-to-plane) distance is 3.34 Å. For **1b**, π-overlap is minimal and defined along each of two dimensions by 4 C−S distances (3.51 Å) which approximate the sum of the vdW radii of carbon and sulfur. The interplanar distance is exceptionally small (3.2 Å), similar to that reported[16] for perfluoropentacene and likewise attributed to electrostatic attraction. The large slip along the short molecular axis may also contribute. Whether recrystallized via vapor sublimation[17] or from solution, **1b** forms foil-like, "large" flexible plates.

While BBBTs **1d**,**e** lack central fluorine atoms to complete the F−S−F edge-to-edge interactions, side chains preclude edge-to-face interactions along their long edges. The side chains of **1d**, **1e**, and **6** expand the π-stacking distance (3.40−3.45 Å) relative to the other BBBTs.

BBBT **1c** (X = H) serves as a control, lacking fluorine atoms on the central benzene ring to complete the F−S−F groups. It is the only derivative reported here that exhibits a herringbone-like packing with edge-to-face interactions (at molecular termini). Its crystal plates were exceedingly thin, twinned, and somewhat disordered, and therefore the precision of the reported structure is relatively low for a small molecule. However, the molecular structure and packing motif are unambiguous. Edge-to-edge close contacts (S−F, H−F) bridge adjacent oblique, rather than (nearly) parallel, molecular planes. BBBT **1c** is highly soluble in common

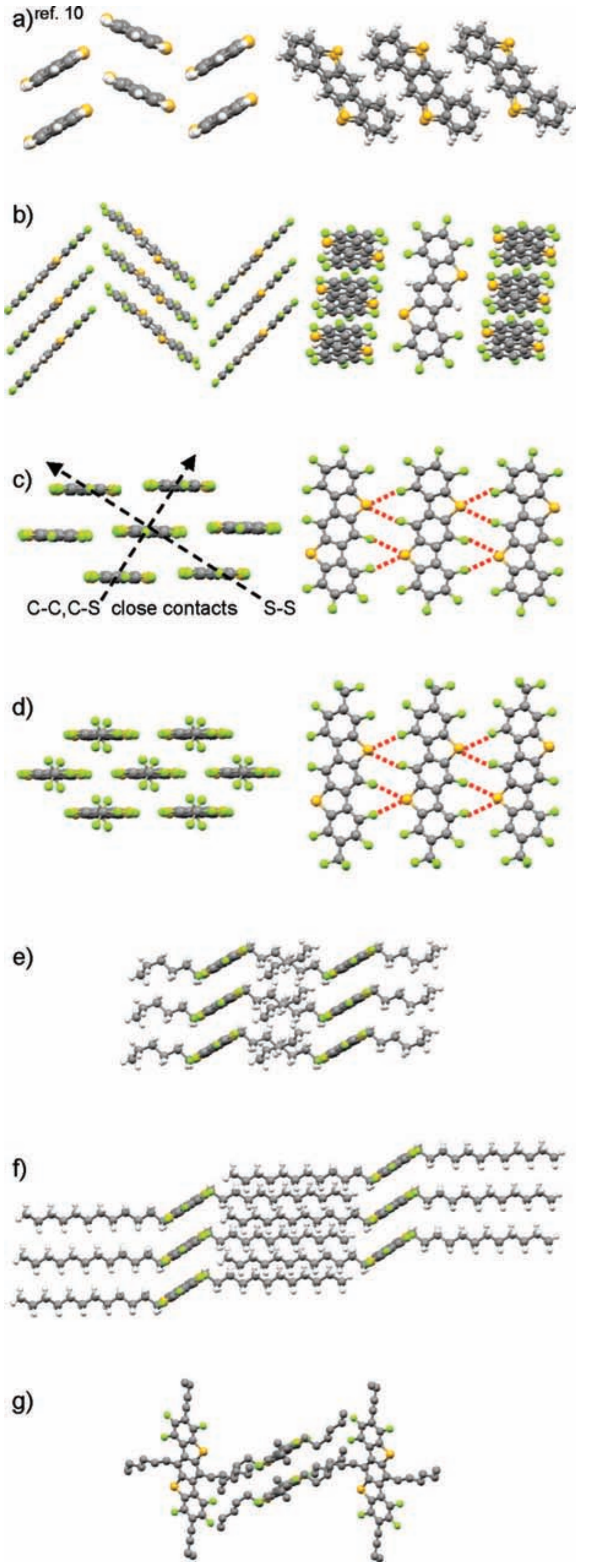


Figure 2. Crystal packing diagrams for (a) **5**,[10] (b) **1c**, (c) **1a**, (d) **1b**, (e) **1d**, (f) **1e**, and (g) **6**. Red dashed lines: S−F close contacts.

organic solvents at room temperature while alkylated **1c**,**d** require mild heating and analogues with full F−S−F groups (**1a**,**b**) are soluble only at elevated temperature (e.g., boiling toluene).

In summary, we have established an efficient route to prepare fluorinated polycyclics **1**. Experimental and computational estimates of the effects of substituents on the energy gap and frontier orbital energy levels are in accord: CF_3 substituents (**1b**) induce a bathochromic shift of the (optical) energy gap and decrease the LUMO level relative to the fluorine substituents of **1a**. Fluorine atoms attached to the central benzene ring lower the LUMO in comparison to protons at the same positions (**1a** vs **1c**). Although the nature and strength of the fluorine−sulfur interaction is unknown in this case, the crystal packing of **1a**,**b** indicates its utility in engineering self-assembly. Interactions between antiparallel, triangular F−S−F units along each side of the lath-shaped molecules, combined with face-to-face electrostatic attraction, preclude edge-to-face interactions. Two S−F units (**1c**) are insufficient to preclude edge-to-face arrangements, except when bulky alkyl chains are included.

Acknowledgment. We thank the National Science Foundation (CHE 0616759) and the Donors of the American Chemical Society (ACS-PRF) for financial support. J.G. is a Ramón y Cajal research fellow (Spanish Ministry for Science and Education). Y.W. is a Kentucky Opportunity Graduate fellow.

Supporting Information Available: Synthesis and characterization details, crystallographic information file (CIF), simulated absorption spectra, CV data, and complete ref 14. This material is available free of charge via the Internet at http://pubs.acs.org.

OL8003468

---

(12) (a) Tucker, J. H. R.; Gingras, M.; Brand, H.; Lehn, J. M. *J. Chem. Soc., Perkin Trans. 2.* **1997**, *7*, 1303–1307. (b) Mayor, M.; Buschel, M.; Fromm, K. M.; Lehn, J. M.; Daub, J. *Ann. N.Y. Acad. Sci.* **2002**, *960*, 16–28.

(13) (a) Milián Medina, B.; Beljonne, D.; Egelhaaf, H.-J.; Gierschner, J. *J. Chem. Phys.* **2007**, *126*, 111101. (b) Anthony, J. E.; Gierschner, J.; Landis, C. A.; Parkin, S. R.; Sherman, J. B.; Bakus, R. C., II *Chem. Commun.* **2007**, 4746–4748.

(14) Frisch, M. J., et al., *Gaussian 03*, revision C.02; Gaussian, Inc.: Wallingford, CT, 2004. The full reference is given in the Supporting Information.

(15) (a) Takimiya, K.; Kunugi, Y.; Konda, Y.; Ebata, H.; Toyoshima, Y.; Otsubo, T. *J. Am. Chem. Soc.* **2006**, *128*, 3044–3050. (b) Yoon, M. H.; Facchetti, A.; Stern, C. E.; Marks, T. J. *J. Am. Chem. Soc.* **2006**, *128*, 5792–5801. (c) Payne, M. M.; Parkin, S. R.; Anthony, J. E.; Kuo, C. C.; Jackson, T. N. *J. Am. Chem. Soc.* **2005**, *127*, 4986–4987.

(16) Sakamoto, Y.; Suzuki, T.; Kobayashi, M.; Gao, Y.; Fukai, Y.; Inoue, Y.; Sato, F.; Tokito, S. *J. Am. Chem. Soc.* **2004**, *126*, 8138–8140.

(17) Laudice, R. A.; Kloc, C.; Simpkins, P. G.; Siegrist, T. *J. Cryst. Growth* **1998**, *187*, 449–54.