Ring Fusion Effects on the Solid-State Properties of α-Oligothiophenes

Xinnan Zhang, James P. Johnson, Jeff W. Kampf, and Adam J. Matzger*

Department of Chemistry and the Macromolecular Science and Engineering Program, University of Michigan, 930 North University, Ann Arbor, Michigan 48109-1055

Received April 22, 2006. Revised Manuscript Received May 19, 2006

The solid-state properties of a series of fused-ring oligothiophenes were studied by UV−visible absorption spectroscopy and single crystal X-ray diffraction. Although the degree of ring fusion has little effect on the solution absorption spectra, the solid-state spectra are dramatically different. Three thieno[3,2-*b*]thiophene-containing oligomers display spectral blue shifts when comparing the solid state to solution because they adopt a herringbone packing motif that leads to H aggregation. The solid-state structure of a dithieno[3,2-*b*:2′,3′-*d*]thiophene-based oligomer contains both herringbone and slipped $\pi-\pi$ interactions, and the overlap of transitions from these different interaction modes results in a broad absorption spectrum in the solid state. The fully fused pentathienoacene adopts a π-stacked packing motif and displays a small blue shift in the solid-state spectrum compared to solution. Time-dependent density functional theory calculations of the electronic transitions of isolated molecules and interacting dimers provide support that the different behavior in the solid-state spectra is due to the unique intermolecular interactions arising in each packing motif.

Introduction

Fused-ring oligo- and polythiophenes are a fascinating class of conjugated materials that combine the rigid planarity of acenes, such as pentacene, with the chemical stability of oligothiophenes.[1−10] Recently, we have demonstrated that, in solution, oligothiophenes with the same number of double bonds but varying extents of sulfur-bridging ring fusion display similar positions of their absorbance maxima but differ dramatically in fluorescence behavior.[4] Such molecular properties can be perturbed significantly in the solid state and the structural similarity of the planarized oligothiophenes examined here offers the flexibility to systematically explore the role of solid-state packing in altering electronic properties: a critical issue in determining the device performance of organic light-emitting diodes (OLEDs) and organic thin-film transistors (OTFTs).[11−16] Furthermore, there is evidence from crystal structures of the dimer of dithieno[3,2-*b*:2′,3′-*d*]thiophene[3] and pentathienoacene (**5**)[8] that fused thiophene rings may promote π stacking. This mode of crystal packing is predicted to facilitate charge transport leading to potentially higher field-effect mobility in OTFT devices when compared to herringbone motifs.[17,18] This possibility motivated us to explore in some detail the solid-state properties of a series of planarized oligothiophenes (Figure 1) that contain fused thiophene rings and the effect of ring fusion on the optical properties and crystal packing of these oligomers. In addition, computational chemistry was employed to understand the correlation between the solid-state optical behavior and packing arrangement.

Optical Properties

We previously reported the synthesis of a series of α-oligothiophenes, in which fused thiophene rings replace

---

* Corresponding author. E-mail: matzger@umich.edu.

(1) Mazaki, Y.; Kobayashi, K. *Tetrahedron Lett.* **1989**, *30*, 3315−3318.
(2) Laquindanum, J. G.; Katz, H. E.; Lovinger, A. J. *J. Am. Chem. Soc.* **1998**, *120*, 664−672.
(3) Li, X. C.; Sirringhaus, H.; Garnier, F.; Holmes, A. B.; Moratti, S. C.; Feeder, N.; Clegg, W.; Teat, S. J.; Friend, R. H. *J. Am. Chem. Soc.* **1998**, *120*, 2206−2207.
(4) Zhang, X.; Matzger, A. J. *J. Org. Chem.* **2003**, *68*, 9813−9815.
(5) Rajca, A.; Miyasaka, M.; Pink, M.; Wang, H.; Rajca, S. *J. Am. Chem. Soc.* **2004**, *126*, 15211−15222.
(6) Zhang, X.; Köhler, M.; Matzger, A. J. *Macromolecules* **2004**, *37*, 6306−6315.
(7) Xiao, K.; Liu, Y. Q.; Qi, T.; Zhang, W.; Wang, F.; Gao, J. H.; Qiu, W. F.; Ma, Y. Q.; Cui, G. L.; Chen, S. Y.; Zhan, X. W.; Yu, G.; Qin, J. G.; Hu, W. P.; Zhu, D. B. *J. Am. Chem. Soc.* **2005**, *127*, 13281−13286.
(8) Zhang, X.; Côté, A. P.; Matzger, A. J. *J. Am. Chem. Soc.* **2005**, *127*, 10502−10503.
(9) Radke, K. R.; Ogawa, K.; Rasmussen, S. C. *Org. Lett.* **2006**, *7*, 5253−5256.
(10) McCulloch, I.; Heeney, M.; Bailey, C.; Genevicius, K.; Macdonald, I.; Shkunov, M.; Sparrowe, D.; Tierney, S.; Wagner, R.; Zhang, W.; Chabinyc, M. L.; Kline, R. J.; Mcgehee, M. D.; Toney, M. F. *Nat. Mater.* **2006**, *5*, 328−333.
(11) Fichou, D. *J. Mater. Chem.* **2000**, *10*, 571−588.
(12) Anthony, J. E.; Brooks, J. S.; Eaton, D. L.; Parkin, S. R. *J. Am. Chem. Soc.* **2001**, *123*, 9482−9483.
(13) Koren, A. B.; Curtis, M. D.; Francis, A. H.; Kampf, J. W. *J. Am. Chem. Soc.* **2003**, *125*, 5040−5050.
(14) Curtis, M. D.; Cao, J.; Kampf, J. W. *J. Am. Chem. Soc.* **2004**, *126*, 4318−4328.
(15) Moon, H.; Zeis, R.; Borkent, E. J.; Besnard, C.; Lovinger, A. J.; Siegrist, T.; Kloc, C.; Bao, Z. N. *J. Am. Chem. Soc.* **2004**, *126*, 15322−15323.
(16) An alternative approach is to examine the same compounds adopting different packing motifs as is achieved in polymorphic materials. For an approach to generating polymorphic crystals, see: Price, C. P.; Grzesiak, A. L.; Matzger, A. J. *J. Am. Chem. Soc.* **2005**, *127*, 5512−5517.
(17) Cornil, J.; Calbert, J. P.; Beljonne, D.; Silbey, R.; Brédas, J. L. *Synth. Met.* **2001**, *119*, 1−6.
(18) Brédas, J. L.; Calbert, J. P.; da Silva, D. A.; Cornil, J. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 5804−5809.

10.1021/cm0609348 CCC: $33.50

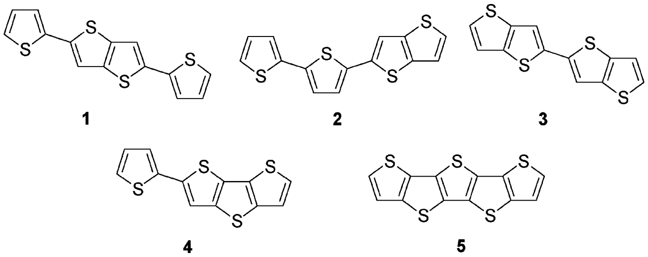


Figure 1. Chemical structures of the fused-ring oligothiophenes investigated.

one or more thiophene units (compounds **1**−**4**).[4] Their electronic properties in solution were investigated in combination with nonfused α-terthiophene and fully fused pentathienoacene (**5**). It is generally recognized that increasing the planarity of conjugated systems leads to a decrease of the highest occupied molecular orbital−lowest unoccupied molecular orbital gap and a corresponding red shift of absorption spectra. However, in contrast to this expectation, introduction of sulfur linkages into α-oligothiophenes has little effect on the absorption spectra in solution. It was found that the compounds containing six double bonds (**3**, **4**, **5**, and α-terthiophene) show very similar longest wavelengths of absorption in CH_2Cl_2. Although introduction of sulfur linkages leads to minor shifts and narrowing of the absorption spectra, a dramatic blue shift in the emission spectra was observed with increasing degree of ring fusion. The smaller Stokes shifts observed in the fused-ring systems are consistent with increased rigidity imparted by sulfur linkages.

To explore the optical properties of these oligomers in the solid state, UV−vis experiments were performed. Solution and solid-state spectra comparisons among these oligomers are shown in Figure 2. Isomers **1** and **2**, which differ only in the position of the thieno[3,2-*b*]thiophene unit, have comparable absorption maxima in solution. In the solid state, the spectra of both isomers are blue shifted to differing degrees. Compounds **3**, **4**, and **5** show similar behavior in solution as well, but dramatic differences are observed in their solid-state absorption spectra. Oligomers **3** and **5** display blue shifted absorption spectra in the solid state compared to solution, while the spectrum of **4** is significantly broadened and has major red shifted transitions (Figure 2). Clearly, there is no simple connection between molecular structure and perturbation of the optical spectra upon moving from solution to the solid state even in this series of close analogues.

Two factors figure prominently in controlling the spectral changes arising upon transition from solution to the solid state: planarity and intermolecular interaction. Typically, the backbone of conjugated oligomers and polymers becomes more planar in the solid state, which leads to an increase in the effective conjugation length and corresponding red shifts of absorption spectra compared to solution. For example, such behavior is observed in oligobithiazoles,[19] poly(3-alkylthiophene),[20,21] and poly(alkylthieno[3,2-*b*]thiophene).[6] In contrast, the solid-state spectra of most thiophene-based oligomers are blue shifted compared to solution (Figure 2) signaling that additional intermolecular interactions play an important role in determining the solid-state optical properties. For example, compounds **1**, **2**, and **3**, all of which contain thieno[3,2-*b*]thiophene units, display large blue shifts (41−48 nm) in the solid state suggesting H aggregation.[22,23] When two interacting molecules have their long axes parallel to each other, as illustrated in Figure 3, the coupling between the transition dipoles leads to Davydov splitting of the excited level into two exciton bands, in which the low-energy transitions are forbidden.[23] The small shoulders observed experimentally in the solid-state optical spectra at relatively long wavelength correspond to these low-energy transitions (409 nm for **1**, 429 nm for **2**, and 384 nm for **3** as indicated in Figure 2). The major absorption bands in the solid state correspond to the allowed high-energy transitions of interacting molecules (Figure 3, H aggregation). This type of aggregation is also found in nonfused oligothiophenes: the absorption maxima of α-quinquethiophene and α-sexithiophene are blue shifted by 25 and 17 nm, respectively.[24,25] In addition, isomers **1** and **2** display different absorption λ_{max}, indicating unequal Davydov splitting, which can be estimated from the difference between the energies of the major band and the low-energy shoulder: 3.75 eV (330 nm) − 3.03 eV (409 nm) = 0.72 eV for **1**; 3.85 eV (322 nm) − 2.89 eV (429 nm) = 0.96 eV for **2**.

For the case of dithieno[3,2-*b*:2′,3′-*d*]thiophene-based compound **4**, although this oligomer shows a similar absorption maximum in solution (352 nm) when compared to **3** and α-terthiophene, its solid-state absorption spectrum is drastically broadened and has significant red shifted features (Figure 2). The broadness of the solid-state spectrum can be explained by positing the overlap of transitions due to different types of intermolecular interactions. The blue shifted absorption band (330 nm) of compound **4** indicates H aggregation of interacting molecules in the solid state. In addition, compound **4** displays prominent transitions at 372 and 400 nm, which are shifted to longer wavelength compared to solution. Adoption of a more planar conformation in the solid state is one possible factor contributing to the red shift of the spectra. However, density functional theory (DFT) calculations do not indicate an increased tendency toward deplanarization in this molecule when compared to other oligomers (see Supporting Information). This suggests that the large bathochromic shift is mainly caused by J aggregation of adjacent molecules in the solid state wherein molecules present head-to-tail alignment (staggered) as shown in Figure 3.[22,23] The low-energy transition is allowed for this type of aggregate, which leads to a red shift of the absorption spectrum. Thus, compound **4** exhibits both H and J aggregation in the solid state as revealed by its absorption spectrum.

---

(19) Koren, A. B.; Curtis, M. D.; Kampf, J. W. *Chem. Mater.* **2000**, *12*, 1519−1522.

(20) McCullough, R. D.; Lowe, R. D.; Jayaraman, M.; Anderson, D. L. *J. Org. Chem.* **1993**, *58*, 904−912.

(21) Chen, T. A.; Wu, X. M.; Rieke, R. D. *J. Am. Chem. Soc.* **1995**, *117*, 233−244.

(22) Cornil, J.; Beljonne, D.; Calbert, J. P.; Brédas, J. L. *Adv. Mater.* **2001**, *13*, 1053−1067.

(23) Moliton, A.; Hiorns, R. C. *Polym. Int.* **2004**, *53*, 1397−1412.

(24) Garnier, F.; Horowitz, G.; Fichou, D. *Synth. Met.* **1989**, *28*, C705−C714.

(25) Yassar, A.; Horowitz, G.; Valat, P.; Wintgens, V.; Hmyene, M.; Deloffre, F.; Srivastava, P.; Lang, P.; Garnier, F. *J. Phys. Chem.* **1995**, *99*, 9155−9159.

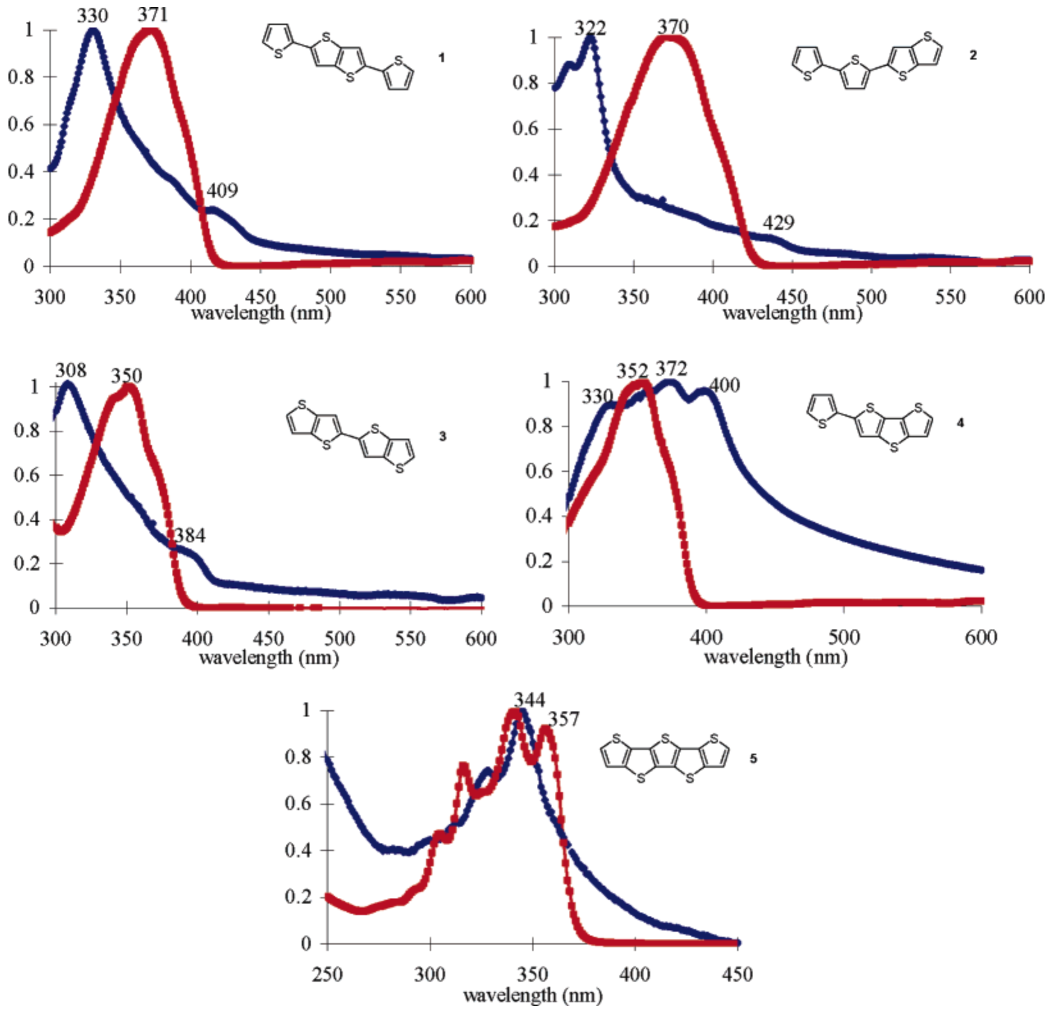


Figure 2. Normalized solid-state (blue) and solution (red) absorption spectra overlays for compounds **1**−**5**.

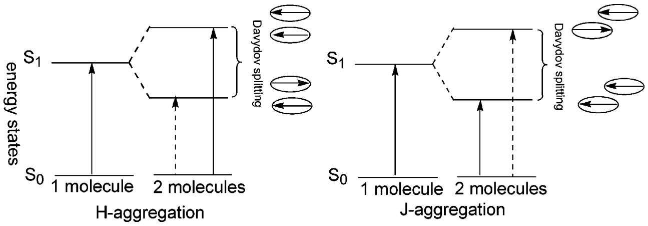


Figure 3. Electronic transitions in different dimeric aggregates: H aggregation (low-energy transition is forbidden) and J aggregation (low-energy transition is allowed).[22,23]

Introduction of another sulfur linkage leads to production of fully fused pentathienoacene (**5**).[8] The shift between the solid-state and solution spectra of this rigid molecule is less dramatic compared to other oligomers. A considerably smaller blue shift ($\Delta\lambda_{max} = 13$ nm) is observed, consistent with H aggregation and a smaller splitting of the excited level than in thieno[3,2-*b*]thiophene-based oligomers (**1**, **2**, and **3**).[7]

Solid-State Structures of Oligomers

To understand the correlation between optical properties and intermolecular interactions in the solid state, the crystal structures of compounds **1**−**5** were determined. In close analogy to pentacene,[26] compound **1** crystallizes in the triclinic space group $P\bar{1}$ with two symmetry-independent half molecules per unit cell residing on inversion centers. The structure of symmetrical compound **1** is planar as shown in Figure 4. The orientationally disordered structure of the fused thieno[3,2-*b*]thiophene unit,[27] due to the similar sizes of S and C−H, has previously been observed.[28] This compound

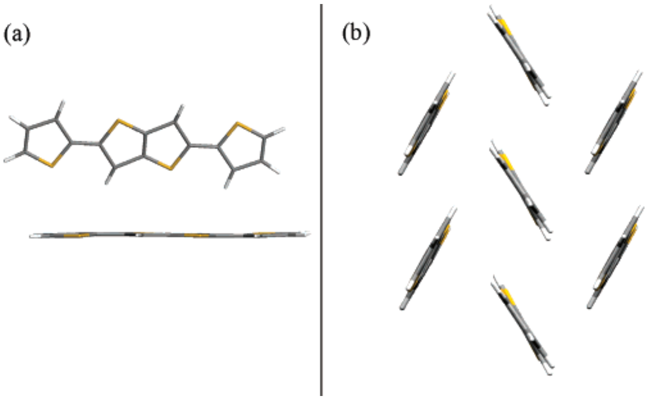


Figure 4. (a) Herringbone packed dimer and (b) packing motif of compound **1**.

---

(26) Holmes, D.; Kumaraswamy, S.; Matzger, A. J.; Vollhardt, K. P. C. *Chem.*—*Eur. J.* **1999**, *5*, 3399−3412.

(27) Noh, Y. Y.; Azumi, R.; Goto, M.; Jung, B. J.; Lim, E. H.; Shim, H. K.; Yoshida, Y.; Yase, K.; Kim, D. Y. *Chem. Mater.* **2005**, *17*, 3861−3870.

(28) Flippen-Anderson, J. L.; Deschamps, J. R.; Gilardi, R. D.; George, C. *Cryst. Eng.* **2001**, *4*, 131−139.

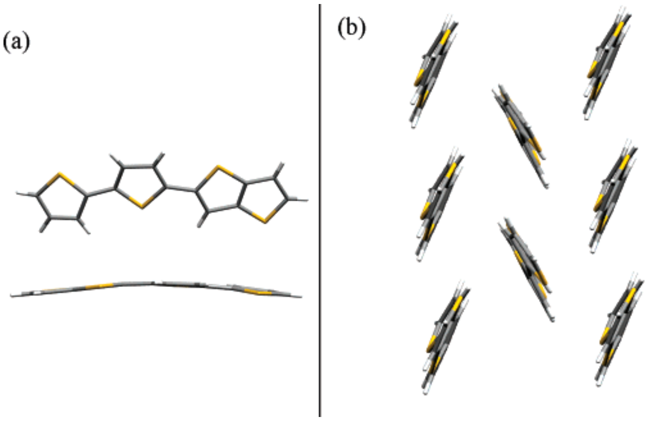


Figure 5. (a) Herringbone packed dimer and (b) packing motif of compound **2**.

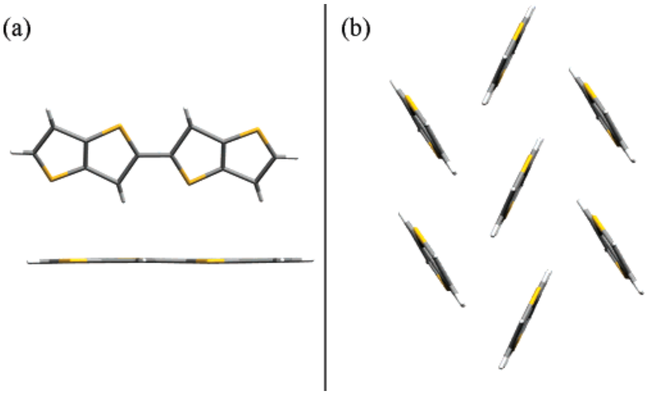


Figure 6. (a) Herringbone packed dimer and (b) packing motif of compound **3**.

adopts an edge-to-face (herringbone) packing motif (Figure 4). The C−H···*π* interactions between the C−H of thieno[3,2-*b*]thiophene units and the quaternary carbon of the thiophene ring connect inequivalent molecules together with an interplanar angle of 59°. Isomer **2**, in which a thieno[3,2-*b*]thiophene ring is joined to a bithiophene unit, crystallizes in the $P2_1$ space group and has two inequivalent molecules per unit cell. The structure of this unsymmetrical compound is slightly curved in contrast to that of **1** (Figure 5), and this conformation could contribute to a blue shift of the major band in its solid-state spectrum. However, DFT calculations do not indicate significant changes in the electronic transitions of **2** when comparing the curved and planar conformations (see Supporting Information). This suggests that the difference in solid-state absorption spectra is due to intermolecular interactions. Compound **2** adopts a herringbone-packing motif with a more acute interplanar angle (52°) between two interacting molecules than in compound **1** (Figure 5). The two edge-to-face packed molecules have the thieno[3,2-*b*]thiophene units pointing to different directions; thus, no close S···S contacts between fused rings of herringbone-packed pairs are observed. C−H···*π* interactions exist between a C−H of the outer thiophene ring and two carbons of the thieno[3,2-*b*]thiophene portion of two closely packed molecules. In this packing motif, the two long axes of interacting molecules are perfectly aligned with each other, whereas the herringbone-packed dimers are slightly slipped in compound **1** (Figures 4 and 5). The aligned molecules allow strong dipolar interactions, which lead to a larger Davydov splitting and a blue shift of the major absorption band in compound **2** relative to **1**. Introduction of another thieno[3,2-*b*]thiophene unit leads to little change of structural arrangement. Bithieno[3,2-*b*]thiophene (**3**) packs with a very similar structure as **1**. It crystallizes in the $P\bar{1}$ space group with two symmetry independent molecules per unit cell, and the two thieno[3,2-*b*]thiophene units are strictly coplanar with respect to each other. It also adopts a herringbone-packing motif as shown in Figure 6. C−H···*π* interactions exist between the thieno[3,2-*b*]thiophene units of interacting molecules. Therefore, these thieno[3,2-*b*]thiophene-containing oligomers (**1**, **2**, and **3**) all adopt herringbone packing motifs. In such arrangements, molecules tend to pack with their long axes parallel to each other, consistent with the arrangement of H aggregated molecules (Figure 3). This leads to the blue shifts in solid-state absorption spectra, a phenomenon that has been reported in nonfused α-oligothiophenes adopting herringbone packing.[11,29]

Dithieno[3,2-*b*:2′,3′-*d*]thiophene-based compound **4** packs in a strikingly different manner than the thieno[3,2-*b*]thiophene-based oligomers. It crystallizes in the $Pca2_1$ space group and has two inequivalent molecules per unit cell, which have slightly different interplanar angles (3 and 4°) between the thiophene and the dithieno[3,2-*b*:2′,3′-*d*]thiophene ring. One short S···S contact of 3.49 Å exists only between the fused dithieno[3,2-*b*:2′,3′-*d*]thiophene units of translationally related molecules. The packing arrangement of oligomer **4** contains edge-to-face packed dimers with an interplanar angle of 46°. Close interactions exist from one C−H of the nonfused thiophene ring to a carbon and sulfur of a dithieno[3,2-*b*:2′,3′-*d*]thiophene unit in an inequivalent molecule. The edge-to-face packed dimers have their long axes parallel to each other, which induces the formation of H aggregates and causes blue shifting of the major band of the solid-state spectra compared to solution. The structure of **4** also contains *π*−*π* interactions between pairs of herringbone-packed dimers. These two interacting molecules are slipped and angled (16°) with dithieno[3,2-*b*:2′,3′-*d*]thiophene units pointing in the same direction. The *π*−*π* interaction exists between the outer ring of the dithieno[3,2-*b*:2′,3′-*d*]thiophene of one molecule and the inner ring of another molecule with a close C···C distance of 3.25 Å. This slipped *π*-stacked arrangement resembles J aggregation (Figure 3), which leads to low-energy (red shifted) transitions in the solid-state absorption spectrum. In this case, introduction of one dithieno[3,2-*b*:2′,3′-*d*]thiophene unit leads to a solid-state packing pattern having both herringbone and *π*-stacked properties. Overlap of transitions from interacting molecules with different types of packing results in a broad solid-state absorption spectrum.

The fully fused oligomer **5** displays a different solid-state structure compared to other oligomers (Figure 8). It crystallizes in the *Pnma* space group with one molecule in the asymmetric unit.[8] The backbone of this fully fused oligomer is rigidly planar. The molecules are held together by an extensive network of S···S contacts. In a given molecule,

---

(29) Fichou, D. *Handbook of Oligo- and Polythiophene*; Wiley-VCH: Weinheim, 1999.

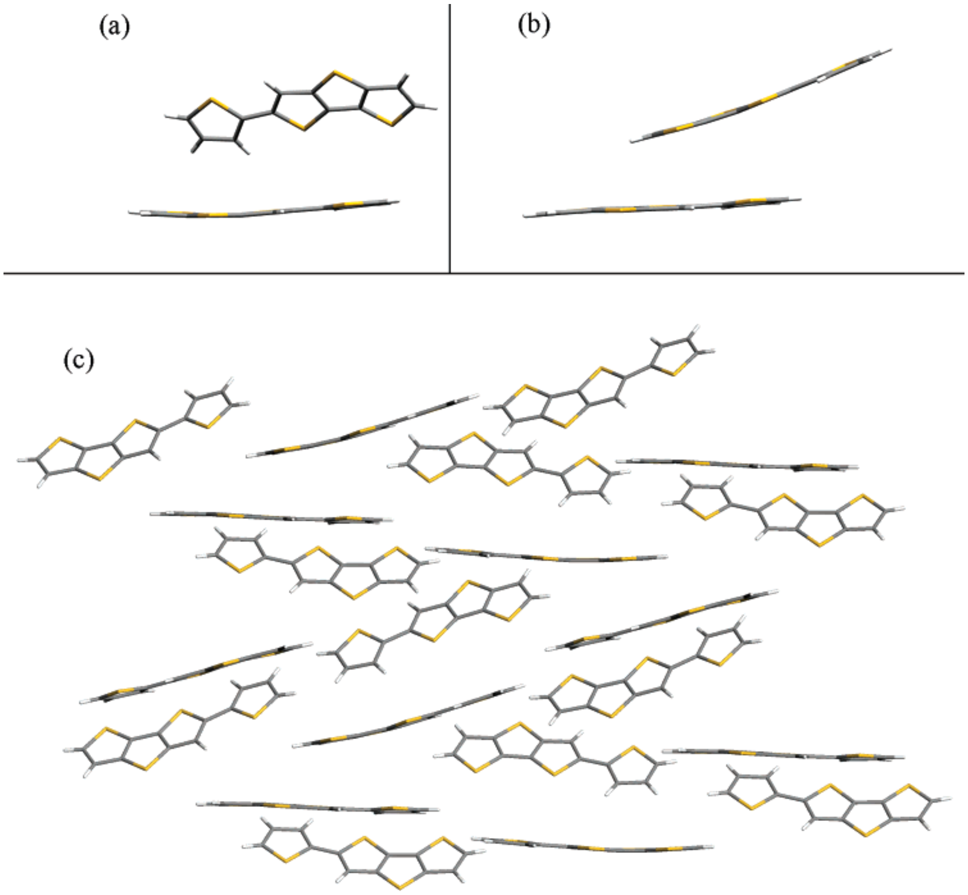


Figure 7. (a) Herringbone packed dimer, (b) slipped π-stacked dimer, and (c) packing motif of compound **4**.

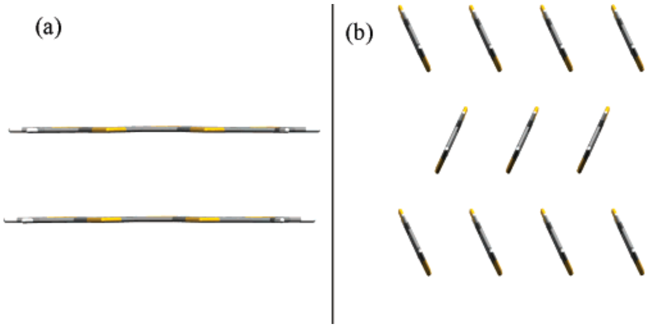


Figure 8. (a) π-Stacked dimer and (b) packing motif of compound **5**.

the central sulfur is bis-chelated by S···S interactions with two pentathienoacene molecules through the second and fourth thiophene rings. In addition, the second and fourth rings also contact the first and the fifth thiophene rings. No close C−H···π interactions are observed. It adopts a face-to-face (π-stacked) packing motif along the *c* axis with π-stacked molecules slightly slipped at a close $\pi-\pi$ distance of 3.52 Å. In this face-to-face arrangement, the two interacting molecules have their long axes parallel to each other, which leads to H aggregation and a blue shift of the absorption spectrum in the solid state. This general packing motif is also observed in the compound with four fused thiophene rings.[30]

From crystal structures of compounds **1**−**5** as well as those of nonfused oligothiophenes, it appears that introduction of sulfur linkages into oligothiophenes favors a transition from a herringbone to a π-stacked packing mode. This change in packing leads to the different behavior in the solid-state absorption spectra compared to solution.

Calculations

The influence of intermolecular interactions on the solid-state spectra was investigated through computation. Time-dependent density functional theory (TDDFT) is a reliable method to predict electronic transitions of conjugated oligomers.[31,32] Calculations using this method at the B3LYP/6-31G* level on isolated oligomers **3**, **4**, and **5** predict electronic transitions at 351.3, 352.7, and 342.0 nm, respectively (Table 1), which are in excellent agreement with the experimental data acquired in solution (350 nm for **3**, 352 nm for **4**, and 357 nm for **5**). In addition, the electronic transitions of nearest neighbor dimers were computed to determine if these intermolecular interactions could account for the alteration of the absorption spectra upon moving from solution to the solid state. The calculated perturbations on the electronic transitions after introducing a second molecule are different for each packing arrangement (Table 1). For the thieno[3,2-*b*]thiophene based oligomer **3**, the herringbone-packed dimer displays an 18.8 nm blue shift of the major transition band compared to the isolated molecule. This

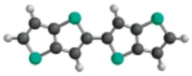
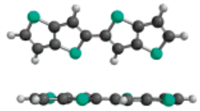
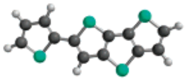
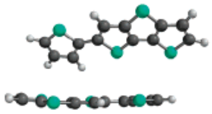
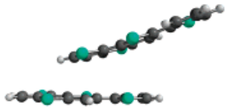
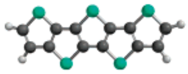
---

(30) Mazaki, Y.; Kobayashi, K. *J. Chem. Soc., Perkin Trans. 2* **1992**, 761−764.

(31) Bauernschmitt, R.; Ahlrichs, R. *Chem. Phys. Lett.* **1996**, *256*, 454−464.

(32) Casida, M. E.; Jamorski, C.; Casida, K. C.; Salahub, D. R. *J. Chem. Phys.* **1998**, *108*, 4439−4449.

Table 1. Calculated Electronic Transitions of Oligomers 3, 4, and 5

		λ_{max} in nanometers (intensity)		λ_{max} in nanometers (intensity)
3		351.3 (0.89)		332.7 (1.31)[a]
4		352.7 (0.78)		346.4 (1.29)
				373.3 (0.20) 360.5 (0.14) 350.4 (1.08)
5		342.0 (0.76)		330.1 (1.12)

[a] The closer interacting dimer was calculated for compound **3**.

indicates that the herringbone-packing motif corresponds to the formation of H aggregates and leads to a blue shift of the absorption spectrum. In the case of dithieno[3,2-*b*:2′,3′-*d*]thiophene-based oligomer **4**, the herringbone-packed dimer and the slipped π-stacked dimer were each individually examined and compared to the isolated molecule. For the herringbone-packed dimer, the calculated major electronic transition (346.4 nm) is blue shifted compared to that of the isolated molecule (352.7 nm) whereas the slipped π-stacked dimer has a calculated major electronic transition band at 350.4 nm. In addition, there are two prominent new transitions (360.5 and 373.3 nm), which are red shifted compared to the isolated molecule. Thus, this slipped π-stacking interaction causes a red shift of the solid-state absorption spectrum. Because compound **4** has both aggregation modes in the solid state (Figure 7), a relatively complicated and broadened solid-state absorption spectrum is observed. Introduction of another sulfur linkage leads to the fully fused oligomer **5**. The calculated λ_{max} of a cofacial dimer is 11.9 nm blue shifted compared to the isolated molecule, which is very close to the experimentally observed shift of 13 nm. Therefore, the computational results, based only on consideration of the closest dimers,[33] support the hypothesis that the intermolecular interactions caused by different packing motifs result in the different behavior in the solid-state absorption spectra.

Conclusion

The solid-state properties of a series of fused-ring oligothiophenes, differing in the number and position of sulfur linkages, were investigated. It was found that although ring fusion has little effect on the absorption spectra in solution, dramatic changes occur in the solid-state spectra as a result of intermolecular interactions. To understand these phenomena, the solid-state structures of compounds **1**−**5** were studied by X-ray diffraction, and the electronic transitions of isolated and closely interacting molecules were calculated by TDDFT methods. The herringbone packing of thieno[3,2-*b*]thiophene-based oligomers (**1**, **2**, and **3**) causes formation of H aggregates and leads to a corresponding blue shift in the solid-state absorption spectra. For oligomer **4**, the solid-state spectrum is broadened and contains red shifted features because the interacting molecules form both H and J aggregates in the solid state caused by herringbone and slipped $\pi-\pi$ interactions, respectively. The fully fused oligomer **5** displays a relatively small blue shift in its solid-state spectrum and adopts a π-stacked packing motif. Overall, a series of structurally related thiophene-based oligomers with similar inherent electronic properties exhibit dramatically different solid-state behavior. This is a result of the varying intermolecular interactions, and these differences will affect charge transport in the solid: a critical issue for organic semiconducting materials.

Experimental Section

Solid-State UV−Visible Absorption Measurement. UV−visible absorption spectroscopy was performed on a CARY 300 Bio UV−visible spectrophotometer. The films of compounds **1**−**3** and **5** were prepared by drop casting CH_2Cl_2 solutions onto quartz slides at room temperature. After taking the solid-state spectra, the films were dissolved in CH_2Cl_2, and their UV−visible spectra were compared to the freshly prepared solution; identical spectra were observed indicating no decomposition took place. Polymorphism observed in films of **4** necessitated an alternative method of collecting the solid-state UV−visible spectrum corresponding to the crystal structure. Measurements were performed by dispersing 1.3 wt % of crystals in a KBr matrix formed into an optically clear

---

(33) Interactions beyond the nearest neighbor and inclusion of more than one neighboring molecule are undoubtedly important in explaining the quantitative changes in the spectra. Preliminary calculations using a close-packed trimer of **5** extracted from the crystal leads to an additional blue shift of 4.3 nm. Examination of the end-to-end dimer finds a red shift (4.9 nm) whereas a side-to-side dimer yields a blue shift (4.8 nm).

pellet at high pressure. The data were collected in absorption mode using a KBr blank for baseline subtraction. For all other compounds, powder X-ray diffraction data of the drop-cast films showed several peaks corresponding to the pattern simulated from their crystal structures.

Single-Crystal X-ray Diffraction.[34] Crystals of compounds **1**, **3**, and **4** for X-ray analysis were grown by slow evaporation from benzene for **1** and **3** and 2-propanol for **4**. Crystals of compound **2** were grown upon cooling of a saturated DMSO solution. For compounds **1**, **2**, and **4**, data collection was performed on a Siemens/Bruker SMART 1K system ($\lambda = 0.710\,73$ Å). For compound **3**, data was collected at the Small-Crystal Crystallography Beamline 11.3.1 at the Advanced Light Source (ALS; $\lambda = 0.775\,00$ Å). For all samples, a series of frames sufficient to cover the entire diffraction sphere with additional frames for good multiplicity of observations (redundancy) was performed by scans in ω and φ. The frames were integrated using Saint Plus, processed with SADABS, and corrected for absorption. All structure solution and refinement was performed using the SHELXTL program package. With the exception of **3** the structures are highly disordered exhibiting a superposition of sulfur and carbon positions. This type of disorder is common in oligiothiophene-type structures.[28] Because the primary interest in this study was the packing interactions which are largely unaffected by the disorder, the structures are reported here. However, many of the carbon−sulfur and carbon−carbon geometries are a statistical average of the mixed occupancies. A summary of the crystallographic parameters is given in the Supporting Information. Additional details are provided in the Supporting Information as CIF files.

Calculations. The electronic transitions of isolated molecules and dimers were computed using the TDDFT method at the B3LYP/6-31G* level as implemented in Gaussian 03.[35] The computed structures of compounds **4** and **5** were exported from their crystal structures. The bonds to H atoms were optimized by the AM1 method. Because the structure of bithieno[3,2-*b*]thiophene (**3**) contains one orientationally disordered thieno[3,2-*b*]thiophene unit, the disordered atoms (S and C−H) were assigned to give the lowest energy conformation with respect to the nondisordered thieno[3,2-*b*]thiophene ring. The bonds to the disordered S and C atoms and H atoms were optimized by the AM1 method.

Acknowledgment. This work was supported by the National Science Foundation (CHE-0316250). Samples for crystallographic analysis at the synchrotron were submitted through the SCrALS (Service Crystallography at Advanced Light Source) program. Crystallographic data of compound **3** were collected at the Small-Crystal Crystallography Beamline 11.3.1 at the ALS that was developed by the Experimental Systems Group of the ALS. The ALS is supported by the U.S. Department of Energy, Office of Energy Sciences Materials Sciences Division, under Contract No. DE-AC03-76SF00098 at Lawrence Berkeley National Laboratory.

Supporting Information Available: CIF files as well as crystallographic information and structure refinement for compounds **1**−**4**, powder X-ray diffraction data, energy profile calculations of compounds **3** and **4**, and electronic transition calculations (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

CM0609348

---

(34) Sheldrick, G. M. *SHELXTL*, version 6.12; Bruker Analytical X-ray: Madison, WI, 2001. Sheldrick, G. M. *SADABS*, version 2.10, Program for Empirical Absorption Correction of Area Detector Data; University of Gottingen: Gottingen, Germany, 2003; *Saint Plus*, version 7.01, Bruker Analytical X-ray: Madison, WI, 2003.

(35) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; 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.; Bakken, V.; 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.; Baboul, 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 B.02; Gaussian, Inc.: Pittsburgh, PA, 2003.