Crystal Engineering of Conjugated Oligomers and the Spectral Signature of π Stacking in Conjugated Oligomers and Polymers

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Solid-state morphology of conjugated polymers, in particular the formation of π stacks, is important in the performance characteristics of devices, e.g., LEDs and TFTs. π Stacking, i.e., the close approach ($d = 3.4-3.6$ Å) of the π systems of adjacent molecules, favors the formation of delocalized excitons or excimers that can drastically decrease the photo- and electroluminescence quantum yields.[1] Conversely, π stacking is expected to decrease activation energies for interchain carrier hopping, leading to greater carrier mobility. Thus, crystalline, π-stacked regioregular polymers have higher conductivities than amorphous, regiorandom polymers,[2,3] the conductivity along the π stacks in discotic liquid crystals or columnar composites is larger than that normal to the stacks,[4] and crystalline thiophene oligomers, e.g., T_6, have high field effect mobilities.[5]

The presence of π stacking may often be inferred from X-ray diffraction patterns that show the existence of interplanar spacings that can be attributed to the π-stacking repeat distance (3.4−3.6 Å), but this requires the presence of relatively long-range order which is not always present in a polymeric sample.[6,7] Despite the importance of π stacking to device performance characteristics, there is no commonly recognized spectral "signature" of π stacking that can be used as a convenient diagnostic for its presence.

Many workers have noted that the UV−vis absorption spectra of partially crystalline, conjugated polymers, e.g., regioregular, HT (head-to-tail) poly(3-alkylthio-phenes) (P3ATs), are red-shifted in the solid state as compared to the solution phase, and concomitantly with the bathochromic shift, the absorption peak (featureless in solution) acquires shoulders or "fine structure".[2,3,8] An example of this behavior is shown in Figure S1. Identical behavior has been noted for poly(alkylbisoxazoles) (PABOs),[9] poly(alkylbithiazoles) (PABTz's),[6] poly-(phenylene-ethynylenes) (PPEs),[10] and copolymers containing these chromophores.[7,11] Similar red shifts and appearance of fine structure is seen as a result of aggregation of soluble, conjugated polymers into colloidal particles in fluid suspension.[12] There is general consensus that the large red-shift in λ_{max} is caused by an increase in the effective conjugation length as a result of the chain backbone becoming more planar in aggregates or the solid state.[2,3,8,13,14] However, there is no such consensus on the origin of the fine structure that accompanies the bathochromic shift: some authors ascribe the shoulders to vibronic coupling,[3a,15] others ascribe them to absorptions of molecules with differing, yet discrete, conjugation lengths.[3,8] Recently, solid-state effects (Davydov splitting) and exciton-vibrational coupling have been recognized as a possible source of the fine structure.[10b,16,17]

It is now well-established that short-chain oligomers serve as excellent models for investigating the physical properties of their respective conjugated polymers.[18,19] In this paper, we report the designed use of H-bonding to alter the π stacking of a pair of conjugated oligomers and observe the effects of the altered crystal environment on the UV−vis spectra. The two oligomers **1** and **2**, differ only in the termini of their side chains: **1** has propenyloxymethyl side chains, whereas in **2** the propenyl group has been converted to γ-hydroxypropyl by

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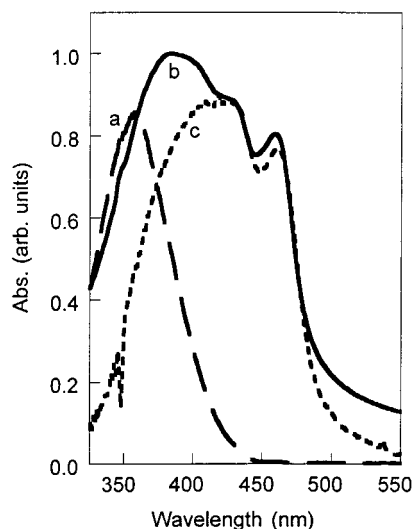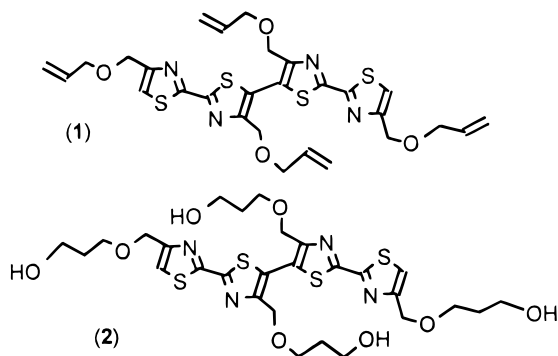(19) Müllen, K.; Wegner, G. *Electronic Materials: the Oligomer Approach*; Wiley-VCH: New York, 1998.

Figure 1. UV−vis spectra of (a) oligomer **1** in CH_2Cl_2 solution, and thin films of (b) oligomer **1** and (c) H-bonded oligomer **2**.

hydroboration and subsequent, basic peroxide oxidation.[20] The different side chains of **1** and **2** are not

expected to perturb in any significant way the $\pi-\pi^*$ transition in the oligomer backbone because the changes occurring on the side chain are insulated from the backbone by four intervening, saturated atoms. Indeed, in dilute solution, both oligomers show a featureless $\pi-\pi^*$ absorption ($^1A_g \rightarrow {}^1B_u$) near $\lambda_{max} = 360$ nm (Figure 1). In the solid state, the spectra of the two oligomers are quite different, however. Oligomer **1** shows a broad peak with three clearly defined shoulders at 392, 422, and 459 nm. The shift to longer wavelengths and the appearance of the fine structure thus mimic precisely the behavior of the polymer systems described above (cf. Figure S1). Surprisingly, the spectrum of **2** shows only the two longer wavelength peaks at 422 and 459 nm, even though the $\pi-\pi^*$ chromophores would appear to be identical in the two oligomers. The difference in the solid-state spectra of **1** and **2** can be explained by reference to their respective solid-state structures.

Figure 2 shows a view down the *a* axis of **1** and shows columns (π stacks) of molecules that are stacked with the long axis of the molecule (i.e., the conjugated backbone) tilted with respect to the *a* axis. Figure 3 shows a side view of two adjacent columns with the side
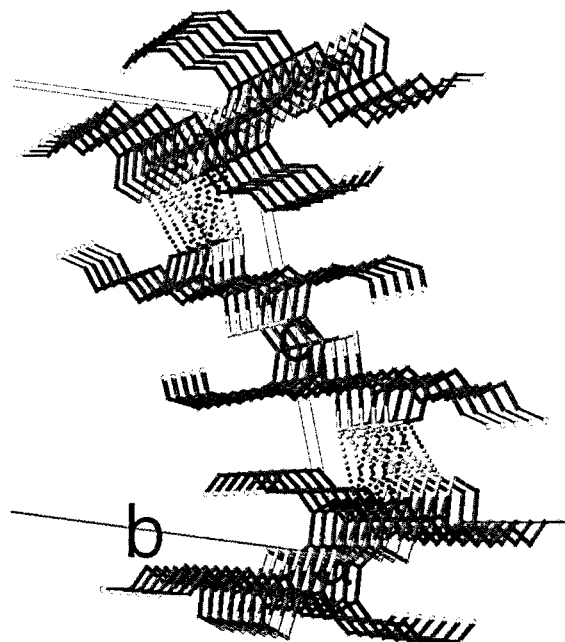
(20) Syntheses and systematic nomenclature for **1** and **2** are given in the Supporting Information.

Figure 2. View down the *a* axis of **1**. Within the columns, the molecules are canted obliquely to the direction of view, and intercolumnar interactions are indicated by the dashed lines.

chains removed for clarity. Short S···S and S···N interactions (~3.6 and 3.4 Å, respectively) between adjacent π stacks are present as shown by the dashed lines in Figures 2 and 3. Alternate π stacks in the crystals of **1** are tilted in opposite directions as illustrated in Figure 3, and they are translationally inequivalent, i.e., there are two molecules per unit cell. The planes of the molecules within a given stack are 3.45 Å apart, and as a result of the tilting with respect to the stacking axis, the molecules adopt a "slipped" or "staircase" arrangement that actually *minimizes* the intermolecular π overlap (see Figure S2 in the Supporting Information for a view of the packing perpendicular to the plane of the thiazole rings). In oligomer **2**, the π stacks are assembled into two-dimensional sheets by H bonds between the OH groups at the ends of the side chains (Figure 4). In this arrangement, the π stacks all tilt in the same direction (so there is now only one molecule per unit cell), and the π stacks are now fully separated by the side chains. In other words, the interactions *between* the π stacks (as seen in **1**) are "turned off" in **2**, leaving only the intermolecular interactions *within* a given column of molecules.

In view of the differences in the spectra and solid-state structures of **1** and **2**, we believe that solid-state splitting of the energy levels of the excitons is the best explanation for the fine structure observed in the absorption spectra of these oligomers and, by extension, to the classes of conjugated, heteroaromatic polymers and oligomers enumerated above. According to molecular exciton theory,[21−23] the translationally inequivalent

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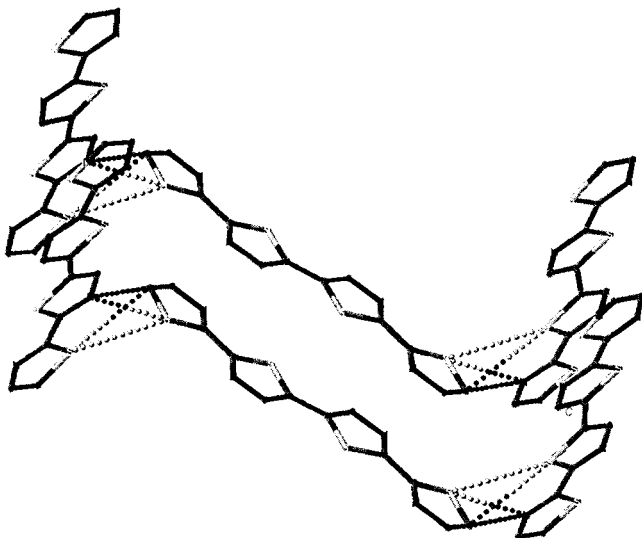
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Figure 3. View of the molecular packing of **1** perpendicular to the stacking axis (*a* axis), showing the alternating tilt of adjacent stacks. The *a* axis is approximately vertical in this view, and the side chains have been removed for clarity.
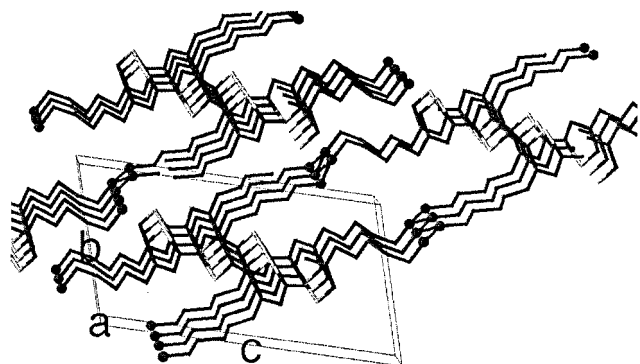

Figure 4. View down the *a* axis of **2** showing the segregation of the π stacks in the matrix of the H-bonded, hydroxy-terminated side chains.

sites occupied by the two molecules in the unit cell of **1** give rise to two exciton branches (factor group or Davydov splitting). If the unit cell contains only one molecule, then only one transition is allowed. Interactions between the translationally equivalent molecules then spreads the energy of the exciton branches into bands. Each branch has an allowed, $k = 0$ transition,

and that transition may be either to the top of the energy band or to the bottom, depending on the sign of the intermolecular coupling. With a positive coupling constant, the allowed transition is to the top of the band, and vice versa (these interactions are identical to the "H aggregates" and "J aggregates" long recognized in the spectra of dye molecules).[22] The slipped or staircase stacking pattern as seen in the structures of **1** and **2** can give either a positive or negative coupling constant depending on the degree of slippage, i.e., the ratio of offset to the transition dipole length.[22]

The above analysis suggests that the absorption spectrum of **2** should consist of a single peak, whereas that of **1** would consist of two peaks, rather than the observed two and three peaks, respectively. Thermal population of higher phonon k states leads to spectra in which the intensity of the absorption band is proportional to the density of states (DOS) in the exciton band.[21b,24] Alternately, simultaneous production of vibrational and electronic excitons can relax the $k = 0$ selection rule and lead to a continuum of states centered about the vibronic energies.[25] In either mechanism, the spectrum shows features related to the DOS, and the width of the absorption peak is related to the width of the exciton band. We therefore believe the features seen in the spectra of **1** and **2** at 422 and 459 nm are related to the DOS of the exciton band associated with the columnar stacking,[16,21b,26] and the band at 392 nm in **2** is associated with the second exciton branch. If one assumes the width of the 422–459 nm peak represents 4 J,[21b,c] the intracolumnar coupling constant, then the value, $J = 2330$ cm^{-1} (0.29 eV) is obtained. The Davydov splitting can be estimated from the separation of the peaks from the two exciton branches (392 and 422 nm): $W_D = 25510 - 23700 = 1810$ cm^{-1} (0.22 eV) (see Figure 8S for an illustration of the energy level scheme). These values are larger than normally found for organic crystals, e.g., anthracene, and can be ascribed to the face-to-face, staircase packing motif that leads to larger intermolecular interactions.

The staircase packing observed here for **1** and **2** has also been found in several other bithiazole-conting oligomers.[6,27] Perhaps more importantly, the structures of many polymers, including PNBTz,[28] other PABTz's, PPP, PEDOT, and P3ATs,[29] have two repeat units per unit cell and feature the same type of slipped π stacking as found in **1** and **2**. Hence, it is expected that the type of exciton splitting displayed by the oligomers will be repeated for these polymers and accounts for the fine structure on their π–π* absorption peaks. The fine structure, in conjunction with the bathochromic shift between solution and solid-state spectra, can be used as a diagnostic or spectral signature of π stacking. The structures presented here also show that it is possible to use H-bonding to control the morphology of π stacking in conjugated materials, and our current research is directed toward the use of H-bonding to control the orientation of molecules on substrates and in devices, e.g. thin film transisitors to enhance device performance.

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Supporting Information Available: Descriptions of experimental procedures, preparation of **1**, **2** and their precursors; UV−vis spectra of regioregular and irregular P3ATs; views of the molecular packing in **2**; energy level diagram for Davydov splitting and exciton band structure; ORTEP drawings of the molecular structures of **1** and **2** with atomic numbering schemes; and tables of crystallographic data for **1** and **2** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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