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Poly(benzo[1,2-*b*:4,5-*b*′]dithiophene-4,8-diylvinylene). Synthesis, Properties, and Electronic Structure of a New Dithiophene-Fused *p*-Phenylenevinylene Conducting Polymer

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ABSTRACT: A new conducting polymer poly(benzo[1,2-*b*:4,5-*b*′]dithiophene-4,8-diylvinylene) (**1**), has been synthesized by the pyrolysis of the soluble precursor polymer **2**, which was itself prepared by a multistep synthesis. The polymer is burgundy, and a film has λ_{max} = 503 nm (2.47 eV) and a band-gap (band edge) of 1.89 eV. Upon doping ($FeCl_3$) the polymer film becomes light blue–green and has a conductivity of 60 S cm^{-1}. The original absorption peak at 503 nm decreases, while two new near-IR absorptions at 860 and 1860 nm appear during doping, which is reversible. Quantum mechanical calculations show a rather low rotational barrier in the monomer, and additional calculations on various oligomers and the polymer suggest that the stable form of the polymer is aromatic and planar.

Introduction

As part of our long-standing program to study new highly conjugated, electrically conducting polymers,[3-8] we are currently attempting to design, prepare, and characterize materials which might show enhanced conductivity. This may be achieved in several ways, including synthesizing materials which are more ordered on a molecular level, stretch-orienting polymer chains, and increasing the dimensionality of the polymer array. To this end we are designing and preparing systems which, in addition to the one-dimensionality of the polymer backbone, also have controlled degrees of increased dimensionality transverse to the chain axis direction. This should increase interchain electronic interactions and provide the needed two-dimensional conduction network. Our approach combines the known attributes of charge-transfer complexes which contribute to their electrical conductivity, and even superconductivity, where conduction occurs along stacks of these ring systems, with the chain conduction of doped, high molecular weight conjugated polymers. These attributes include their flat, broad conjugated nature, their ability to form ordered structures, and the fact that they contain a number of large, polarizable atoms such as sulfur which allow for orbital interaction, through short intermolecular S–S distances, from one planar molecule to a nearest neighbor.[9] Some of these charge-transfer salts are shown in Figure 1.[10]

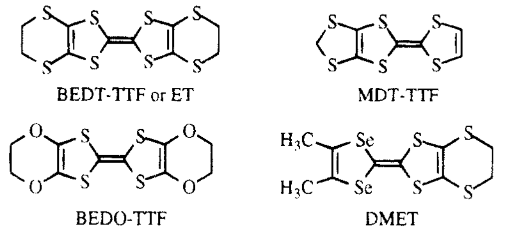

Figure 1. Several representative charge-transfer complexes.

The initial system we have chosen is poly(benzo[1,2-*b*:4,5-*b*′]dithiophene-4,8-diylvinylene) (**1**) since this appears to possess many of the desired characteristics. Since we required a material that could be cast into films, we have synthesized this polymer via a processable precursor polymer. We now report on the preparation, properties, and quantum mechanical calculations of this novel material.

Experimental Section

General Procedures. FT-IR spectra were obtained in KBr with a diffuse reflectance unit. NMR spectra were obtained at 300 MHz for ^{1}H or 75 MHz for ^{13}C in $CDCl_3$ or D_2O (where indicated). Elemental analyses were done on a Perkin-Elmer 2400 CHN analyzer or by Texas Analytical Laboratories, Stafford, TX. TGA was done from 40 to 800 °C with a heating rate of 10 °C/min. UV–vis–near-IR spectra were recorded on polymer thin films cast onto quartz cuvettes. Conductivity of doped polymer films was measured using the four-in-line probe method.[11,12]

1,4-Bis[(2,2-dimethoxyethyl)thio]-2,5-dimethylbenzene (4). In a three-necked flask equipped with a magnetic stirrer, a condenser with a drying tube, an addition funnel, and a nitrogen inlet was put 2,5-dibromo-*p*-xylene (5.28 g, 0.02 mol) and 40 mL of dry THF. The mixture was cooled to −78 °C and 12.5 mL of 1.6 M *n*-BuLi in hexanes (0.02 mol) was added dropwise in about 15 min. The mixture was stirred for 30 min, 2,2,2′,2′-tetramethoxyethyl disulfide (**3**; 4.84 g, 0.02 mol), prepared essentially as reported,[13] in 5 mL of dry THF was added dropwise over about 15 min, and the mixture was stirred for an additional 30 min. The second part of the *n*-BuLi (13.75 mL, 1.6 M, 0.022 mol) was added dropwise in about 15 min, and the mixture was stirred for 30 min. Disulfide **3** (4.84 g, 0.02 mol) in 5 mL of dry THF was added dropwise over about 15 min, and the mixture was stirred for 1 h. The mixture was warmed to room temperature, 15 mL of water was added, and it was extracted with diethyl ether (3 × 100 mL). The combined ether layer was washed with distilled water (3 × 100 mL) and dried ($MgSO_4$), and the ether was distilled. The crude product was purified by flash chromatography [ethyl acetate/hexanes (1:10)] to give 2.29 g of **4** (33% yield): mp 74–75 °C (lit.[14] mp 72–73 °C); ^{1}H NMR δ 7.14 (2H, s), 4.53 (2H, t, J = 6 Hz), 3.37 (12H, s), 3.05 (4H, d, J = 6 Hz), 2.36 (6H, s); ^{13}C NMR δ 136.23, 133.00, 130.73, 102.91, 53.39, 36.04, 19.98. Anal. Calcd for $C_{16}H_{26}S_2O_4$: C, 55.46; H, 7.56. Found: C, 55.33; H, 7.77. Two other products, **7** and **8**, were also obtained in a combined yield of 46%. A total of 1.41 g (22% yield) of 1-[(2-methoxyethenyl)thio]-4-[(2,2-dimethoxyethyl)thio]-2,5-dimethylbenzene (**7**) was obtained as a viscous yellow liquid: ^{1}H NMR δ 7.12 (1H, s), 7.03 (1H, s), 6.86 (1H, d, J = 12 Hz), 5.35 (1H, d, J = 12 Hz), 4.50 (1H, t, J = 6 Hz), 3.72 (3H, s), 3.35 (6H, s), 3.02 (2H, d, J = 6 Hz), 2.37 (3H, s), 2.28 (3H, s); ^{13}C NMR δ 157.02, 136.62, 136.17, 133.13, 131.50, 131.09,

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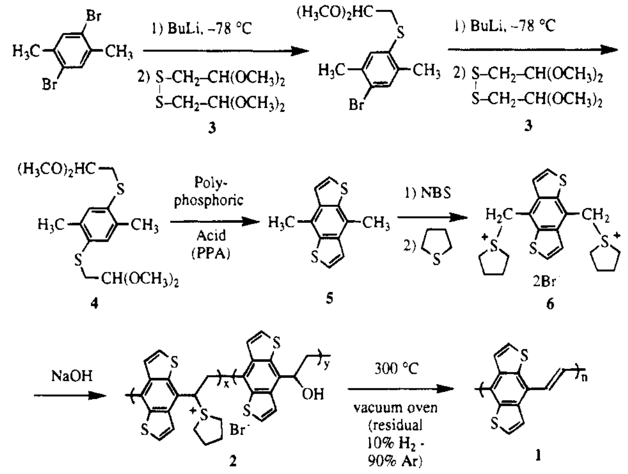
127.05, 102.88, 91.43, 56.92, 53.26, 36.43, 20.03, 19.16; FTIR ($\bar{\nu}$) 3054, 2935, 2832, 1620, 1602, 1456, 1322, 1242, 1211, 1153, 1120, 1093, 1061, 987, 934, 781, 571 cm^{-1}. MS (M$^+$). Calcd for $C_{15}H_{22}S_2O_3$: *m/e* 314. Found: *m/e* 314. Anal. Calcd for $C_{15}H_{22}S_2O_3$: C, 57.29; H, 7.05. Found: C, 57.07; H, 7.18. A total of 1.35 g (24% yield) of 1,4-bis[(2-methoxyethenyl)thio]-2,5-dimethylbenzene (**8**) was obtained as white crystals: mp 126–128 °C; ^{1}H NMR δ 7.00 (2H, s), 6.86 (2H, d, $J = 12$ Hz), 5.35 (2H, d, $J = 12$ Hz), 3.71 (6H, s), 2.30 (6H, s); ^{13}C NMR δ 156.68, 134.26, 133.48, 127.59, 92.10, 56.94, 19.36; FTIR ($\bar{\nu}$) 3044, 3012, 2987, 2933, 2831, 1620, 1598, 1476, 1434, 1382, 1353, 1322, 1207, 1151, 1090, 983, 956, 928, 885, 787, 766, 570 cm^{-1}.

4,8-Dimethylbenzo[1,2-*b*:4,5-*b*′]dithiophene (5). The procedure was somewhat modified from that in the literature.[14] A solution of 3.50 g of **4** in 60 mL of benzene was added to 20 g of poly(phosphoric acid), the mixture was refluxed for 24 h and cooled to room temperature, and the benzene layer was decanted. Another portion of benzene (40 mL) was added, the mixture was refluxed for another 12 h and cooled to room temperature, and the benzene again was decanted. The residue was washed with benzene (2 × 10 mL), the combined benzene layers were washed with distilled water (3 × 20 mL) and dried ($MgSO_4$), and the benzene was distilled. The yellow crude product was purified by either silica gel chromatography (hexanes) or sublimed under vacuum to give faint yellow product **5**; yield, 57% of crude product, 45% sublimed; mp 157–159 °C (lit.[14,15] mp 164, 169 °C); ^{1}H NMR δ 7.45 and 7.47 (4H, AB-q, $J = 5$ Hz), 2.80 (6H, s); ^{13}C NMR δ 137.53, 136.03, 125.98, 123.46, 121,95, 17.99; FTIR ($\bar{\nu}$) 3092, 2908, 2851, 1757, 1616, 1564, 1439, 1382, 1297, 1194, 1093, 1028, 915, 881, 801, 736, 665, 641, 513, 454 cm^{-1}. Anal. Calcd for $C_{12}H_{10}S_2$: C, 66.05; H, 4.62. Found: C, 65.67; H, 4.40.

4,8-Bis(tetrahydrothiopheniumylmethyl)benzo[1,2-*b*:4,5-*b*′]dithiophene Dibromide (6). To a stirred solution of 218 mg of **5** (1 mmol) in 10 mL of dry benzene was added 8 mg of benzoyl peroxide and 374 mg of *N*-bromosuccinimide (2.1 mmol; NBS), under N_2, at room temperature. The mixture was stirred at room temperature for 15 min, warmed to 50 °C, and stirred for an additional 5.5 h. After cooling the mixture to room temperature, the precipitate was filtered and washed with benzene (3 × 2 mL), $CHCl_3$ (3 × 2 mL), and water (3 × 5 mL). The crude product was put in 40 mL of $CHCl_3$, boiled for 10 min, cooled, filtered, and washed with $CHCl_3$. Finally, the purified yellow product, 4,8-bis(bromomethyl)benzo[1,2-*b*:4,5-*b*′]dithiophene, was dried under vacuum overnight; yield 316 mg (84%); mp 277–279 °C (lit.[16] mp 280 °C); ^{1}H NMR δ 5.08 (s) and 7.6 (AB-q). Anal. Calcd for $C_{12}H_8Br_2S_2$: C, 38.32; H, 2.14. Found: C, 38.45; H, 2.23. To a suspension of 376 mg of this dibromide (1 mmol) in 12 mL of CH_3CN was added 1.76 g of tetrahydrothiophene (20 mmol). The mixture was warmed to 75 °C, stirred for 24 h, and cooled to room temperature. The white precipitate was filtered, washed with CH_3CN (3 × 5 mL), and dried under vacuum overnight. The crude product was dissolved in 30 mL of H_2O, to which 200 mL of acetone was added and cooled in an ice bath. The precipitate was filtered and washed with acetone to afford 450 mg of **6** in 81% yield: mp >300 °C (dec); ^{1}H NMR (D_2O) δ 7.97 (2H, d, $J = 6$ Hz), 7.76 (2H, d, $J = 6$ Hz), 5.07 (4H, s), 3.52 (4H, m), 3.41 (4H, m), 2.57 (4H, m), 2.36 (4H, m); ^{13}C NMR (D_2O) δ 142.85, 140.43, 133.27, 124.00, 120.83, 46.17, 45.61, 31.38. Anal. Calcd for $C_{20}H_{24}S_4Br_2$: C, 43.48; H, 4.38; S, 23.21; Br, 28.93. Found: C, 43.29; H, 4.29; S, 23.03; Br, 28.81.

Precursor Polymer 2. To a solution of 295 mg of the freshly prepared bis-sulfonium salt **6** (0.534 mmol) in 25 mL of water at room temperature was added a solution of 21.4 mg of NaOH (0.534 mmol) in 1 mL of water under N_2. The mixture was stirred for 6 h, during which time the color changed as follows: yellow → green → greenish-yellow → golden → orange. The orange solution was dialyzed (MW cutoff 3500) against a 0.1% aqueous pyridine solution for 2 days. The resulting orange solution could be used to cast yellow films. Removal of water gave an orange powder: FTIR ($\bar{\nu}$) 3552, 3280 (OH), 3099, 3080, 2925, 2858, 1655, 1625, 1539, 1515, 1473, 1438, 1381, 1239, 1199, 1161, 1095, 1053 (C–O), 801, 741, 642, 470 cm^{-1}. Anal. Calcd for $C_{16}H_{15}S_3Br$ (repeat unit): C, 50.13; H, 3.94; S, 25.09. Anal. Calcd for $C_{12}H_8S_2O$ (repeat unit): C, 62.04; H, 3.47; S, 27.60. Found: C, 52.43; H, 3.54; S, 21.65.

Scheme 1



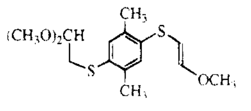
Poly(benzo[1,2-*b*:4,5-*b*′]dithiophene-4,8-diylvinylene) (1). Thermal elimination of the yellow precursor polymer film **2** was at 300 °C for 2–3 h in a vacuum oven where the oven was evacuated and filled five times with a mixture of 10% H_2 and 90% Ar and finally evacuated to ca. 3 Torr. The polymer **1** was burgundy and upon doping became light blue–green. Thermal elimination of the orange precursor polymer powder **2** under the same conditions gave what appeared to be a black polymer powder **1**: FTIR ($\bar{\nu}$) 3100, 3081, 2924, 2853, 1660, 1612, 1513, 1466, 1435, 1383, 1326, 1233, 1190, 1173, 1095, 959, 881, 813, 735, 662, 634, 624, 461 cm^{-1}. Anal. Calcd for $C_{12}H_6S_2$: C, 67.26; H, 2.82; S, 29.92. Found: C, 67.08; H, 2.69; S, 29.85.

Doping and Electrical Conductivity. The polymer films were doped with $FeCl_3$, $NOBF_4$, and I_2. For $FeCl_3$ and $NOBF_4$ doping, the polymer films were soaked at room temperature in a 1% nitromethane solution. The doped films were washed with fresh nitromethane and dried, before the electrical conductivity was measured using the standard four-in-line probe method.[11,12] For I_2 doping, the polymer films were exposed to iodine vapor at room temperature for 24 h and then excess iodine was removed under vacuum for 1 h. The degree of doping was calculated from the weight uptake.

Results and Discussion

The synthesis of poly(benzo[1,2-*b*:4,5-*b*′]dithiophene-4,8-diylvinylene) (**1**) via the soluble precursor polymer **2** is shown in Scheme 1. 2,2,2′,2′-Tetramethoxyethyl disulfide (**3**) was prepared essentially as reported by reaction of chloroacetaldehyde dimethyl acetal with sodium disulfide in the presence of potassium iodide, although the potassium iodide, which is reported to be used as a catalyst,[13] appeared not to be required. 1,4-Bis[(2,2-dimethoxyethyl)thio]-2,5-dimethylbenzene (**4**) was prepared by reacting 2,5-dibromo-*p*-xylene with 1 equiv of *n*-butyllithium followed by reaction with 2,2,2′,2′-tetramethoxyethyl disulfide (**3**) and repeating this procedure a second time (using a slight excess of *n*-BuLi) to incorporate both (dimethoxyethyl)thio groups. Preparation of 2,2-(dimethoxyethyl)thio aromatic compounds by this procedure was first reported in 1959.[17] In addition to the desired product 1,4-bis[(2,2-dimethoxyethyl)thio]-2,5-dimethylbenzene (**4**) produced in 33% yield, two other products were identified as 1-[[(*E*)-2-methoxyethenyl]thio]-4-[(2,2-dimethoxyethyl)thio]-2,5-dimethylbenzene (**7**) and 1,4-bis[[(*E*)-2-methoxyethenyl]thio]-2,5-dimethylbenzene (**8**) in 22% and 24% yield, respectively. These products were identified by ^{1}H and

^{13}C NMR spectroscopy, infrared spectroscopy, elemental analysis, and, in the case of **7**, mass spectrometry. These products can be explained simply as methanol elimination products of **4** formed by reaction of **4** (or its precursor) with butyllithium. The assignment of the trans configuration to the double bonds is based on the observation that the vicinal $H{-}C{=}C{-}H$ NMR coupling constants, $^3J_{HCCH}$, in both **7** and **8** are 12 Hz. A previous study of the coupling constants in a series of cis and trans alkenes containing ethoxy and alkythio groups, **9a** and **9b**, demonstrated that $^3J_{HCCH}$ for the cis compounds were 5.5–5.6 Hz while those for the trans compounds were 12.0–12.2 Hz,[18] the same as in **7** and **8**.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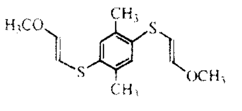
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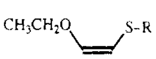
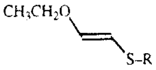

9a

R = Me, Et, *i*-Pr, *t*-Bu


9b

In addition to the NMR spectral data, confirmation for the trans stereochemistry comes also from the infrared spectra. Both compounds **7** and **8** show a double peak for the double bond stretch at 1602 and 1620 cm^{-1} for **7** and 1598 and 1620 cm^{-1} for **8**. A previous infrared spectral study by Turecek and Prochazka demonstrated that the trans series of compounds **9b** showed two double bond stretching bands at around 1600 and 1625 cm^{-1} while the cis series **9a** showed only a single absorption at about 1630 cm^{-1}.[19] In addition, for both compounds **7** and **8** the absence of any peaks between 600 and 750 cm^{-1} and the presence of peaks between 900 and 1000 cm^{-1} are also consistent with trans disubstituted alkenes.[20]

The preparation of 4,8-dimethylbenzo[1,2-*b*:4,5-*b*′]dithiophene (**5**) was carried out by a procedure similar to that described in the literature.[14] In our case we used poly(phosphoric acid) (PPA) directly, while Beimling and Kossmehl prepared the PPA in situ by mixing phosphoric acid and phosphorus pentoxide.[14] It should also be pointed out that the eliminated products **7** and **8** also produce **5** upon treatment with poly(phosphoric acid). Bromination of **5** twice with *N*-bromosuccinimide (NBS) produced the corresponding dibromide,[16] which, upon treatment with tetrahydrothiophene, afforded 4,8-bis(tetrahydrothiopheniumylmethyl)benzo[1,2-*b*:4,5-*b*′]dithiophene dibromide (**6**). This was converted into the precursor polymer **2** by reaction with aqueous NaOH. Infrared spectral analysis of **2** clearly showed the presence of hydroxyl groups and hence the formulation of **2** as a random copolymer of units containing sulfonium salt and hydroxyl groups. An approximate composition, that is the ratio of *x* to *y* in **2**, was obtained from the TGA curve shown in Figure 2. Given that loss of tetrahydrothiophene and HBr represents a 44% weight loss from a sulfonium-containing repeat unit and loss of H_2O represents an 8% weight loss from an OH-containing repeat unit and that the weight loss (from 100–350 °C) in **2** is about 30%, the ratio of *x*:*y* is calculated as 61:39 or about 61% sulfonium and 39% hydroxyl groups. Thermal conversion of cast films of the precursor polymer **2** to films of the desired conjugated polymer poly(benzo[1,2-*b*:4,5-*b*′]dithiophene-4,8-diylvinylene) (**1**) was effected in a vacuum oven and was studied at a number of temperatures by following the UV–vis absorption. It was found that the optimum conditions were 300 °C for 2–3 h where $\lambda_{max} = 503$ nm. Shorter reaction times gave a shorter wavelength absorption maximum, while longer reaction times and higher temperatures produced some polymer degradation and also gave a shorter wavelength absorption maximum. Our initial experiments provided a polymer **1** which gave an acceptable elemental analysis but showed a small OH band in the infrared spectrum independent of the time or temperature for the elimination. Recently, however, a group at Bell Telephone Laboratories found that pyrolysis of the precursor polymer **10** to give poly(phenylenevinylene) (**11**) typically gave product which contained small amounts of oxygen-containing functionalities as shown by the infrared spectra. If, however, the vacuum oven used in the pyrolytic elimination was purged with forming gas, which is a reducing mixture of 15% H_2 and 85% N_2, then these oxygen-containing groups were either eliminated or reduced significantly and the polymer showed better properties.[21,22] After purging our vacuum oven five times by pulling vacuum and allowing a mixture of 10% H_2 and 90% Ar to be admitted after each evacuation and finally evacuating to about 3 Torr and then heating precursor polymer **2**, the poly(benzo[1,2-*b*:4,5-*b*′]dithiophene-4,8-diylvinylene) (**1**) which was produced no longer showed any OH absorption in the infrared spectrum. Further, the conductivity was also improved. It should also be noted that aqueous solutions of the precursor polymer **2** were unstable even though they were stored in a refrigerator. Within days, the polymer formed a gel which could not be redissolved in water. However, a stable precursor polymer solution was obtained when a small amount of pyridine was added to the solvent. This stable solution remained precipitate- and gel-free for several months. Han and Elsenbaumer discovered that, in general, small amounts of a variety of weak bases, especially pyridine, substantially stabilized aqueous and nonaqueous polyelectrolyte solutions of the precursor polymers to both poly(dialkoxyphenylenevinylenes) and poly(heteroaromatic vinylenes).[23] Thus, the current polymer provides another example that the presence of a weak base in the solvent

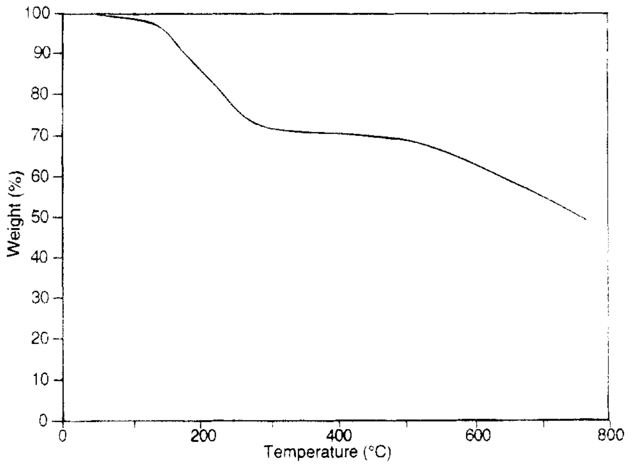
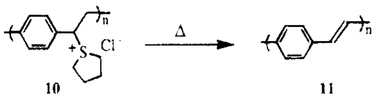


Figure 2. TGA curve of precursor polymer **2**, 10 °C/min under N_2.



10 11

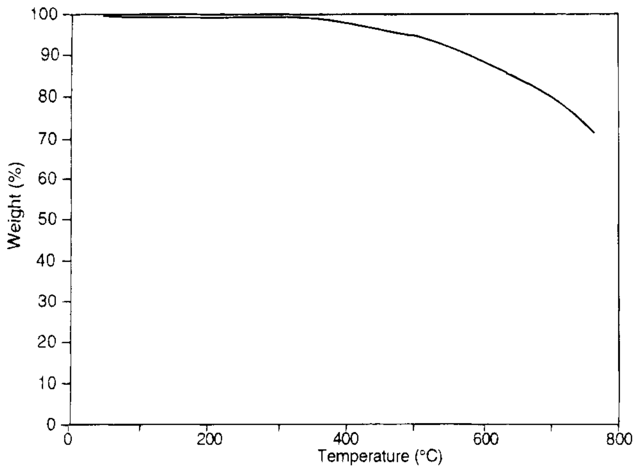


Figure 3. TGA curve of polymer **1**, 10 °C/min under N_2.

can prevent the polyelectrolyte polymer from precipitating or forming gels.

Upon thermal elimination the alcohol absorptions in the IR spectrum of **1** at 3552 and 3280 cm^{-1} and the C−OH stretch 1053 cm^{-1} disappeared, while the *trans*-vinylene CH=CH out-of-plane wagging band appeared at 959 cm^{-1}.[24] Further, elemental analysis was consistent with the completely eliminated structure **1**. From the band edge of the 503-nm absorption a band-gap of 1.89 eV is obtained. This value is between that of poly(*p*-phenylenevinylene), 2.5 eV,[25] and that of poly(2,5-thienylvinylene), 1.8 eV,[26] and is below that of poly(2,5-dimethoxy-1,4-phenylenevinylene), 2.1 eV,[27] which also has two electron-donating atoms, in this case oxygen rather than sulfur, attached to the benzene ring.

Polymer **1** is quite thermally stable as shown by TGA (N_2 atmosphere; Figure 3). The onset of decomposition is at about 370 °C with 10% weight loss at 585 °C and 20% at 700 °C. Poly(benzo[1,2-*b*:4,5-*b*′]dithiophene-4,8-diylvinylene) (**1**) could be readily doped to the conducting state with $FeCl_3$, $NOBF_4$, or I_2. This should be contrasted with poly(*p*-phenylenevinylene) which shows rather low conductivity when doped with mild oxidizing agents such as I_2.[28] There are a number of reports that poly(*p*-phenylenevinylene) doped with the mild oxidizing agent $FeCl_3$ gives low-conductivity material,[28] but one group has recently reported a conductivity of 35 S cm^{-1} for this material.[29] On the other hand, poly(2,5-dimethoxy-1,4-phenylenevinylene) with electron-donating groups on the phenylene ring readily dopes with I_2 or $FeCl_3$,[29,30] as does polymer **1**. Upon doping with 1% $FeCl_3$ in nitromethane, two new UV−vis−near-IR absorption bands grew in at 860 and 1860 nm (bipolaron formation), while the undoped polymer absorption at 503 nm decreased and the film went from a burgundy color to a light blue−green. The doping process was clean and reversible as shown by two isosbestic points, shown in Figure 4, and the observation that the doped polymer could be dedoped by reducing with ammonia and the original UV−vis−near-IR spectrum regenerated. The conductivity, measured by the usual four-in-line probe method,[11,12] was 60 S cm^{-1} for the $FeCl_3$-doped material. In addition, samples which had previously been prepared at 0 °C and without a residual H_2 reducing atmosphere showed conductivities of 15 S cm^{-1} for $FeCl_3$, 4 S cm^{-1} for $NOBF_4$, and 16 S cm^{-1} for I_2 doping. The extent of doping, measured by weight gain, was about 20%, 30%, and 20% for the three dopants, respectively. It should be pointed out that this value of 60 S cm^{-1} is considerably higher than that of the as-prepared poly(*p*-phenylenevinylene) doped with AsF_5,[31,32] modestly higher than that doped with $FeCl_3$,[29] and compares favorably with other poly(*p*-phenylenevinylenes) with electron-donating groups doped with $FeCl_3$.[30,33,34]

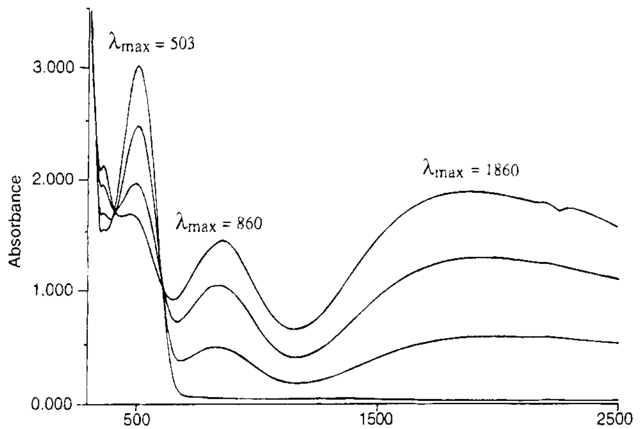
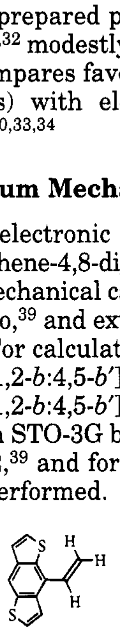


Figure 4. Visible−near-infrared spectra of **1**, before doping and after doping with $FeCl_3$ for 5, 10, and 15 s in a 1% $FeCl_3$ solution in CH_3NO_2.

Quantum Mechanical Calculations

The electronic structure of poly(benzo[1,2-*b*:4,5-*b*′]-dithiophene-4,8-diylvinylene) was calculated using quantum mechanical calculations based on the PRDDO,[35−38] ab initio,[39] and extended Hückel[40−42] (MEH) methodologies. For calculations on the monomeric units, 4-vinylbenzo[1,2-*b*:4,5-*b*′]dithiophene (**12**) and 4-ethylidene-8*H*-benzo[1,2-*b*:4,5-*b*′]dithiophene (**13**), ab initio calculations with an STO-3G basis set were performed with GAUSSIAN 92,[39] and for both **12** and **14** PRDDO calculations were performed.



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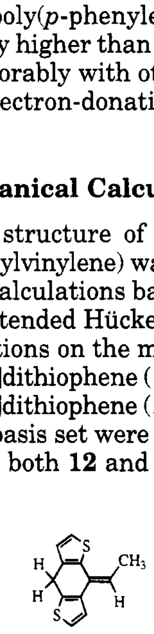

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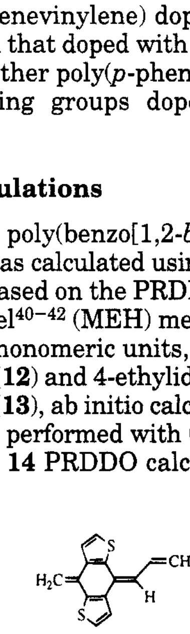

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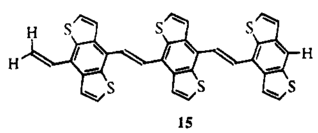
Because the degree of coplanarity of conjugated aromatic polymers is an important factor which affects the π electron delocalization and band structure of the system, detailed conformational analyses of the trimers of the aromatic and quinoid forms were also performed using PRDDO and ab initio (GAUSSIAN 92) calculations with an STO-3G basis set, followed by modified extended Hückel[43] calculations to obtain the band structures. The relative stability of aromatic vs quinoid chains of structure **1** was calculated by the following extrapolation method.[7,44] First the trimer of both forms was optimized to obtain the geometry of the repeating monomer unit. The two molecules which were used are shown in structures **15** and **16**. Second, the energies of the oligomers up to the hexamer were calculated. Then the energy difference between the two forms as a function of chain length, *N*, was estimated using eq 1

$$\Delta E_{qa}^{\ N} = E_{q}^{\ N} - E_{a}^{\ N} + 2E_{H} + 2E_{CH} \qquad (1)$$



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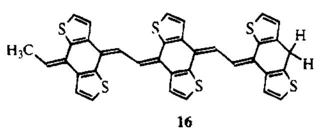

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Table 1. Optimized Structure of Monomer 12 (and Monomer 13 in Parentheses)

bond	STO-3G//3G	bond angle	STO-3G//3G
S1−C2	1.74 (1.73)	C2−S1−C5	90.4 (90.8)
S1−C5	1.75 (1.74)	S1−C2−C3	114.3 (112.9)
C2−C3	1.33 (1.33)	C3−C4−C5	110.5 (111.8)
C3−C4	1.47 (1.46)	S1−C5−C4	112.0 (112.0)
C4−C5	1.41 (1.50)	C5−C11−C10	118.2 (112.5)
C6−C7	1.33 (1.33)	C4−C5−C11	121.3 (123.4)
C7−S8	1.75 (1.73)	C3−C4−C12	128.4 (125.4)
S8−C9	1.76 (1.74)	C4−C12−C9	117.0 (112.5)
C9−C10	1.41 (1.35)	C5−C4−C12	121.1 (122.8)
C6−C10	1.47 (1.46)	C7−S8−C9	90.8 (90.8)
C10−C11	1.39 (1.50)	C9−C12−C13	123.3 (126.5)
C5−C11	1.38 (1.49)	C4−C12−C13−C14	−142.1 (−178.9)
C4−C12	1.40 (1.50)	C4−C12−C13−H16	36.3 (0.9)
C9−C12	1.40 (1.49)	C9−C12−C13−C14	38.6 (0.0)
C12−C13	1.50 (1.33)		
C13−C14	1.31 (1.52)		

where E_q and E_a are the total energies of the quinoid and aromatic forms, respectively. E_H is the hydrogen atomic energy, −0.4712 au, and E_{CH} is the average C−H bond dissociation energy, 90.3 kcal/mol. Finally, the calculated $\Delta E_{qa}^N/N$ values were fitted to a three-parameter equation (eq 2) to extrapolate the energy difference per chain length. The relative stability of the infinite

$$\Delta E_{qa}^N/N = a_0 + a_1/N + a_2/N^2 \tag{2}$$

chains of the two forms is equal to a_0. The optimized central unit of trimers obtained from the calculation described above was then used for the band calculations. The atomic valence state ionization potentials (VSIP) of carbon 2s and 2p orbitals are −21.4 and −11.4 eV and of sulfur 3s and 3p orbitals are −20.0 and −13.3 eV, respectively. The corresponding valence shell exponents are 1.625[40] for carbon 2s and 2p and 2.217[42,43] for sulfur 3s and 3p orbitals.

Monomers

The structure of 4-vinylbenzo[1,2-*b*:4,5-*b*′]dithiophene (**12**) was investigated via optimization at the ab initio (STO-3G) level. The optimized structural parameters are given in Table 1. The values in parentheses are those of the quinoid form **13**. The C−C distances within the phenylene ring of **12** are between 1.39 and 1.41 Å, and the C−C vinylene double bond length is 1.31 Å. The quinoid form shows alternating C−C distances along the carbon backbone with a bond length range of 1.35−1.50 Å. The bond angles around the sulfur atoms are 91°. Torsion angle C9−C12−C13−C14 is 38.6°; however, the calculated barrier to internal rotation of the aromatic form is only 1.5 kcal/mol. This suggests that the planar form of this polymer may well be dominant in the solid state. The quinoid form optimized to a planar geometry which is 36.5 kcal/mol less stable than the aromatic form. The bond angle C9−C12−C13 in **12** is 126.5°, whereas that of **13** is 123.3°. This difference is attributed to the repulsion between a sulfur lone pair and the hydrogen atom of the adjacent vinyl group. The distances S8−H17 and H15−H16 are 2.74 and 2.34 Å, respectively, in the aromatic form. The corresponding contacts in the quinoid form are 2.39 and 1.97 Å. The optimized structures of **12** and **13** are shown below.

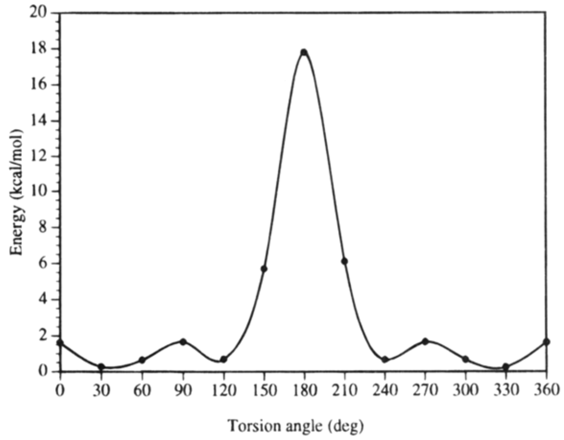
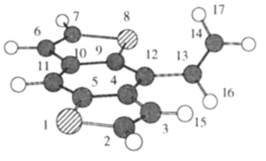


Figure 5. Torsion angle potential curve for 4,8-divinylbenzo-[1,2-*b*:4,5-*b*′]dithiophene (**17**).



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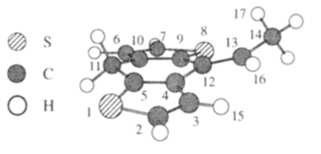

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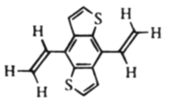
Torsion Energy

Preliminary calculations demonstrated that the conformation of **12** is affected significantly by steric factors between the thiophene ring and the neighboring vinyl group. Therefore, we investigated the species in which the para positions of the phenylene ring are substituted with vinyl groups (see: **17**, aromatic type; **18**, quinoid type). For the calculations of torsion energies, one of the vinyl groups of the phenylene ring was fixed and the other was rotated in 30° increments of the torsion angle (*θ*). These calculations employed the PRDDO method since it has been proven to be a very useful tool for predicting conformations as well as geometries of relatively large molecules.[7,44,45] Since detailed intraring structures should not significantly affect the relative energetics of the rotational conformers, the intraring parameters for the monomer optimized by PRDDO were used throughout the calculations. The optimized structures for **17** and **18** are shown below.



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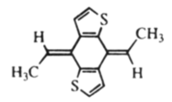

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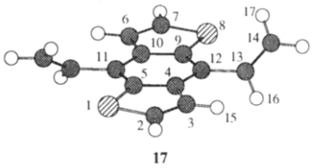

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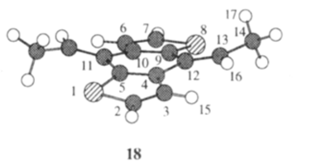

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In Figure 5 the torsion energy surface for **17** is shown. The torsion angles from 0 to 180° represent the *cisoid* form in which two vinyl groups are oriented in the same direction with respect to the aromatic moiety, and those from 180 to 360° represent the *transoid* form in which two vinyl groups are oriented in opposite directions. The optimized distances between the S8 and H17 atoms and between H15 and H16 of **17** are 2.74 and 2.34 Å, respectively. The small barriers in the potential surface at 90° and 270° arise from the breaking of conjugation along the backbone. The structure with 180° torsion angle is very unstable due to the steric hindrance between the *β*-hydrogen of the thiophene moiety and the

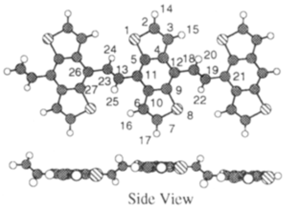
Table 2. Optimized Structure (STO-3G) of Trimer 15 (and Trimer 16 in Parentheses)

bond	distance	bond angle	angle
S1–C2	1.74 (1.73)	C2–S1–C5	90.7 (90.8)
S1–C5	1.76 (1.74)	S1–C2–C3	114.2 (112.9)
C2–C3	1.33 (1.33)	C2–C3–C4	112.8 (112.5)
C3–C4	1.47 (1.46)	C3–C4–C5	110.9 (111.9)
C4–C5	1.41 (1.36)	C3–C4–C12	127.6 (125.5)
C4–C12	1.40 (1.49)	C5–C4–C12	121.6 (122.6)
C5–C11	1.40 (1.48)	S1–C5–C4	111.4 (111.8)
C6–C7	1.33 (1.33)	S1–C5–C11	126.8 (125.1)
C6–C10	1.47 (1.46)	C4–C5–C11	121.8 (123.0)
C7–S8	1.74 (1.73)	C7–C6–C10	112.8 (112.5)
S8–C9	1.76 (1.74)	C6–C7–S8	114.2 (112.9)
C9–C10	1.41 (1.36)	C7–S8–C9	90.7 (90.8)
C9–C12	1.40 (1.48)	S8–C9–C10	111.4 (111.8)
C10–C11	1.40 (1.49)	S8–C9–C12	126.8 (125.1)
C11–C13	1.50 (1.34)	C10–C9–C12	121.8 (123.0)
C12–C18	1.50 (1.34)	C6–C10–C9	110.9 (111.9)
C13–C23	1.32 (1.47)	C6–C10–C11	127.6 (125.5)
C18–C19	1.32 (1.47)	C9–C10–C11	121.6 (122.6)
C19–C21	1.50 (1.34)	C5–C11–C10	116.7 (112.4)
C23–C26	1.50 (1.34)	C5–C11–C13	123.7 (127.2)
C26–C27	1.40 (1.49)	C10–C11–C13	119.6 (120.4)
		C4–C12–C18	119.7 (120.4)
C5–C11–C13–C23	40.1 (5.1)	C9–C12–C18	123.8 (127.2)
C5–C11–C13–H25	−141.1 (−179.0)	C11–C13–C23	125.7 (127.7)
C10–C11–C13–H25	37.6 (1.7)	C12–C18–C19	125.7 (127.7)
C10–C11–C13–C23	−141.2 (−174.3)	C18–C19–C21	125.8 (128.5)
C4–C12–C18–C19	−141.2 (−174.3)		
C4–C12–C18–H20	37.6 (1.7)		

vinylene hydrogen (H15–H17; 1.17 Å). There are two local minima at $\theta = 40.50°$ (*cisoid*) and 320.50° (*transoid*) which arise from a compromise of two effects: conjugation along the backbone (maximized in the planar conformation) and steric effects (minimized in the perpendicular conformation). The energy difference between the two structures is only 0.03 kcal/mol at the PRDDO level.

Oligomers

The band gap of a nondegenerate conjugated polymer in the ground state is related to the geometry of the repeat unit.[44,46] Thus, the relative stability of the aromatic vs quinoid forms is a critical issue for designing new conducting polymers.[7] As mentioned earlier, trimers **15** and **16** were optimized at the ab initio level (GAUSSIAN 92) with an STO-3G basis set. The optimized parameters are given in Table 2. The differences in geometry between **15** (aromatic) and **16** (quinoid) are obvious. C–C distances within the phenylene ring in **15** have values of 1.39–1.41 Å, whereas alternating average values of 1.34 and 1.49 Å are found in **16** (see Table 2). The average dihedral angle of **15** is 38.6°, very similar to that found in the monomeric structure. Closest contacts between sulfur atoms and hydrogen atoms in neighboring vinyl groups are 2.69–2.70 Å in **15** and 2.47–2.51 Å in **16**. The structures of **15** and **16** are shown below. The optimized geometry for **16** has a very interesting structure. It is predicted to have a spiral chain along the propagation direction, with average dihedral angles of 5.4°. The slight twist is due to the steric repulsion between the vinylene hydrogen atoms and the sulfur lone pair electrons on both sides of the vinyl group. This steric hindrance is reduced by the twisting of the monomer plane. By calculating the energy differences of the aromatic and quinoid forms for a series of oligomers up to the hexamer, **19** and **20**, the energy difference, per repeat unit, for the infinite chain can be obtained by extrapolation. The calculated energy differences are shown in Table 3. For the infinite chain the aromatic form is more stable than the quinoid form by 24.1 kcal/mol per repeat unit.



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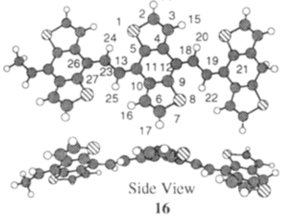

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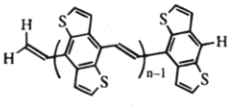
Table 3. Relative Stabilities (kcal/mol) of the Aromatic (19) vs Quinoid (20) Oligomers as a Function of the Chain Length

chain length (n)	ΔE_{qa}	chain length (n)	ΔE_{qa}
1	36.54	5	24.59
2	28.19	6	24.21
3	25.90	∞	24.10
4	25.53		



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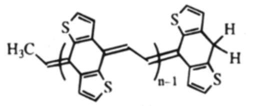

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Band Structure

Modified extended Hückel (MEH) theory[43] was employed for the investigation of electronic properties of poly(benzo[1,2-*b*;4,5-*b*′]dithiophene-4,8-diylvinylene) (**1**). MEH theory is specifically parametrized to reproduce band gaps of conjugated polyheterocycles, with the band gap being defined as λ_{max} for the $\pi \rightarrow \pi^*$ transition in the optical spectrum (as opposed to the band edge). Because the planar geometry of the aromatic monomer **12** is calculated to be only 1.5 kcal/mol higher in energy than the nonplanar ground-state structure, we have calculated the band structure of both forms. Figure 6 shows 14 π bands of optimized geometry (a) and planar geometry (b) of **1**. Since the planar geometry (C_i) is

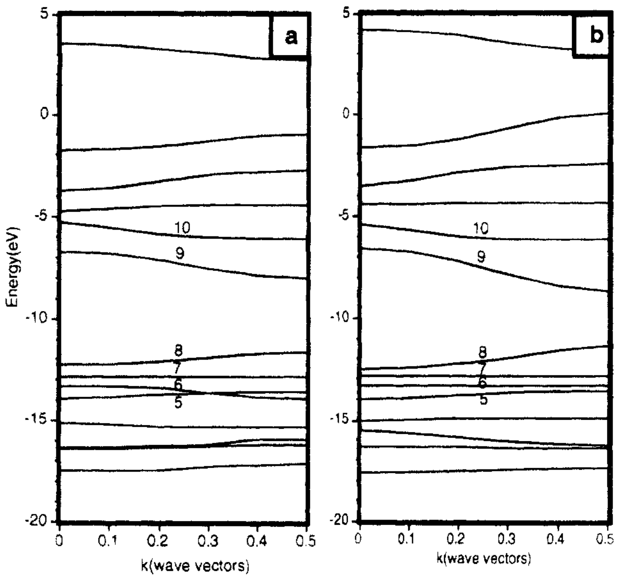
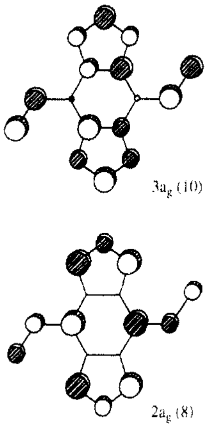
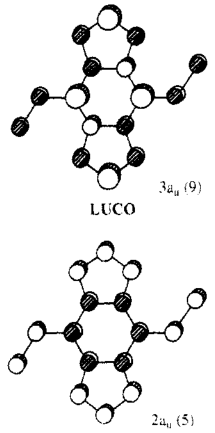


Figure 6. Band structure of (a) the optimized geometry of **1** and (b) planar **1**.

more favorable than the optimized geometry (C_1) for band interactions, bands in Figure 6b are more dispersive than those in Figure 6a. The bandwidth of the highest valence band is 1.1 eV and that of the lowest conduction band is 2.0 eV for the planar structure, whereas the corresponding values are 0.6 and 1.3 eV, respectively, for the optimized structure. The bands around the Fermi level are labeled by numbers from 5 to 10. Band 8 ($2a_g$) is the highest occupied valence band, and 9 ($3a_u$) is the lowest unoccupied conduction band. Bands 6 and 7 are nondispersive since they have nodes on carbon atoms along the phenylenevinylene backbone. Band 9 ($3a_u$) mixes with 5 ($2a_u$), and 8 ($2a_g$) mixes with conduction band 10 ($3a_g$). The orbital interaction of the important crystal orbitals are illustrated in **21** and **22**.



HOCO
21



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The interaction between the vinylene group and the aromatic moiety is π bonding in the highest occupied crystal orbital (HOCO) and π antibonding in the lowest unoccupied crystal orbital (LUCO). The π interactions between the aromatic moiety and the vinyl group will increase with a decrease of the vinyl group torsion angle. Therefore, the HOCO (see **21**: $2a_g$) is stabilized by 0.3 eV, while the LUCO is destabilized by 0.1 eV (see **22**: $3a_u$) at $k = 0$, along with the change of torsion angle from 38.6° to 0.0°. However, the HOCO is destabilized by 0.2 eV, whereas the LUCO is stabilized by 0.7 eV at the Brillouin zone edge ($k = 0.5$). The band gap of the optimized structure is 3.6 eV, while the planar structure was calculated to have a band gap of 2.7 eV. The experimental UV–vis measurement of λ_{max} was 503 nm (2.47 eV) which agrees quite well with the calculated value of 2.7 eV. Thus, the calculations taken together with the UV–vis absorption strongly suggest that the planar form dominates in the solid state.

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