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Synthesis of Low-Bandgap Zwitterionic and Planar Conjugated Pyrrole-Derived Polymers. Reversible Optical Absorptions from the UV to the Near-IR

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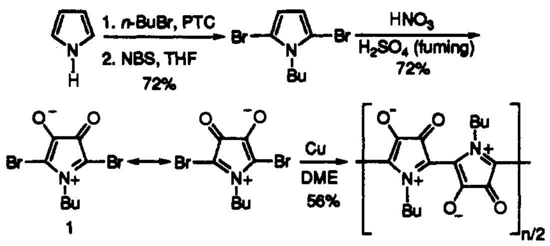
In an effort to maximize the extended π-conjugation in polymers and to study their corresponding electronic and optical properties, several have undertaken the synthesis of new conjugated organic polymers that have a planar or near-planar conformation between the consecutive repeat units.[1,2] Described here is the synthesis of a unique zwitterionic pyrrole-derived polymer that can reversibly convert to a linear and planar conjugated polymer with a solution bandgap of approximately 1.1 eV. The material possesses a reversible and enormous pH-dependent or solvent-dependent absorption spectral range from the UV to the near-IR spectral region. Soluble polymeric materials that can respond dramatically and reversibly to external stimuli could have importance in the development of organic-based optical and electronic sensors,[2] while polymers with absorbances in the near-IR can serve as dyes for optical data discs.[3]

The synthesis of the new pyrrole-derived zwitterionic polymer is described in Scheme 1. Pyrrole was N-alkylated under standard phase-transfer conditions.[4] Bromination[5] and vigorous oxidation yielded the zwitterionic monomer **1**, a carbonyl-stabilized azomethine ylide, in an overall 52% yield for the three steps. The FTIR (KBr, 1718 cm^{-1}, with no hydroxyl absorbance), mass spectrum (calcd for $C_8H_9Br_2NO_2$, 311, found, 311), elemental analysis (Calcd for $C_8H_9Br_2NO_2$: C, 30.89; H, 2.92; Br, 51.39; N, 4.50. Found: C, 30.90; H, 2.92; Br, 51.25; N, 4.48.), UV spectrum (CH_2Cl_2, λ = *248*, 322; NMP, λ = *281*, 320 (sh); there was little change in the UV spectra in the presence of aqueous NaOH or aqueous HCl), ^1H NMR [(300 MHz, $CDCl_3$) δ 3.59 (t, J = 7.3 Hz, 2 H), 1.57 (p, J = 7.1 Hz, 2 H), 1.30 (sext, J = 7.3 Hz, 2 H), 0.91 (t, J = 7.3 Hz, 3 H)], and ^{13}C NMR [(75 MHz, $CDCl_3$) δ 163.85, 129.24, 39.48, 30.39, 19.82, 13.52] were all consistent with the proposed structure. Note that two resonance forms exist for **1**; therefore, there are only six peaks in the ^{13}C NMR spectrum.

Scheme 1



We then sought to polymerize **1** using a variety of coupling methods.[6] $(COD)_2Ni(0)$,[7] copper(II) triflate,[8] and Rieke copper[9] failed to afford any polymeric product. Classical Ullmann[10] coupling using copper-bronze (Aldrich) also failed when utilizing the common solvents (DMF, quinoline, tetramethylurea, or pyridine); however, in DME, copper-bronze-promoted polymerization (200 °C, screw cap tube, 18 h) of **1** afforded the desired polymer **2** (Scheme 1) in 56% yield after fractional precipitation (CH_2Cl_2, CH_3OH). The precipitation dramatically sharpened the polydispersity (PD) to 1.15–1.25 with M_n = 3910 (SEC, PS standards).[11] If the reaction was run for 40 h, the molecular weight peaked at M_n = 4980, with PD = 1.54. Continued heating caused no increase in the molecular weight. Spectral analysis again confirmed the proposed structure: FTIR (film, 1697 cm^{-1}, with no hydroxyl absorbance), elemental analysis (Calcd for $C_8H_9NO_2$: C, 63.56; H, 6.00; N, 9.26. Found: C, 63.40; H, 6.71; Br, <0.5; Cu, <0.02; N, 8.06.), ^1H NMR [(300 MHz, $CDCl_3$) δ 3.40 (br s, 2 H), 1.55 (br s, 2 H), 1.27 (br s, 2 H), 0.89 (br t, J = 7 Hz, 3 H)], and ^{13}C NMR [(125 MHz, $CDCl_3$) δ 169.16, 131.07, 39.26, 30.58, 20.08, 13.92]. No detectable bromide content was observed since the excess Cu(0) carries out oxidative additions on nearly all aryl bromide locations with subsequent end group protonations on workup, a commonly observed feature of Ullmann reactions.[10b] A macrocyclic structure cannot be ruled out; however, to have a pyrrole ring system with all the nitrogen atoms pointing inward would require 10 pyrrole units to complete the ring.[6c] A macrocycle with all the oxygen atoms pointing inward would require far more pyrrole units, therefore excluding a monomeric Cu-templation driven macrocyclization.

Compound **2** is an intrinsic semiconductor exhibiting an undoped conductivity of $1.4 \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$ and an iodine-doped conductivity of $4.2 \times 10^{-4}\ \Omega^{-1}\ cm^{-1}$ (4-point probe, pellet). The low doped conductivity of the system may be due to the presence of the carbonyl functionality which can retard polaronic or bipolaronic migrations.[1j] Thermogravimetric analysis (TGA, 10 deg/min, N_2) showed 10% weight loss at 318 °C with a rapid weight decrease at 400 °C.

The absorption maximum of **2** exhibits a strong bathochromically shifted absorbance, relative to polypyrrole, that may be due to ionic interactions that force a diminution in the interunit twist angle.[2] Solvatochromic effects are consistent with this proposal in that the following trend of S_0–S_1 (π–π^*) absorption maxima are present for **2**: CCl_4, 520 nm; THF, 512 nm (Figure 1); EtOH/THF (1:1), 503 nm; acetone, 482 nm; H_2SO_4, 498 nm (with strong hypochromicity that is indicative of a protonic substitution effect). Thus, when the charges can be solvent stabilized, interunit stabilization/planarization is retarded and the absorption shifts hypsochromically. Likewise, stabilization of the polar ground state increases the energy gap of the π–π^*

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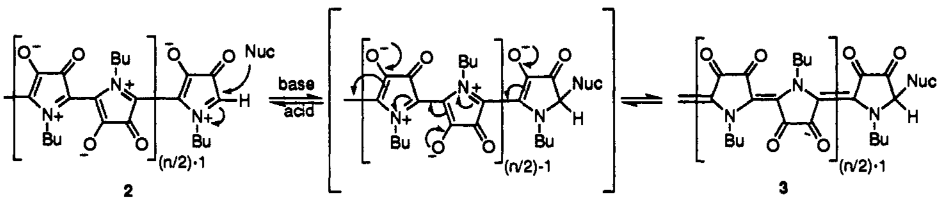
Scheme 2



2

3

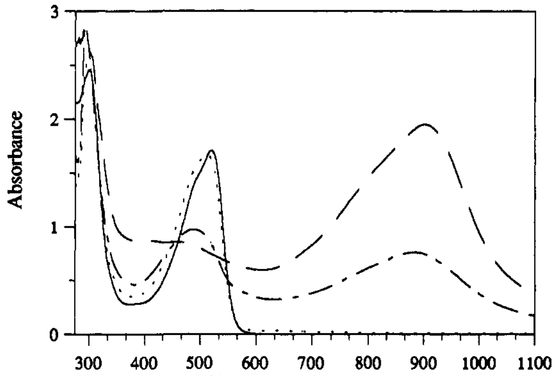


Figure 1. (a) Spectrum of **2** in CCl_4 (—) and THF (· · ·). (b) Dissolution of **2** in THF/aqueous NaOH (- - -) and HMPA (— — —) to form **3**.

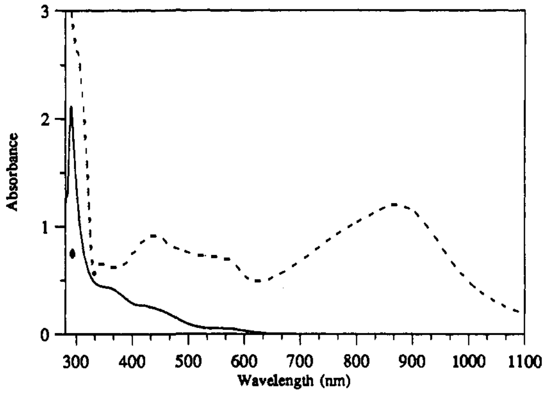


Figure 2. Spectrum of the reduction product of **2** (a) in THF (—) and (b) in DMSO (- - -).

transition, which may exhibit charge-transfer character.[3,12] Remarkably, when aqueous NaOH (0.05 M) was added dropwise to **2** in THF, the initial red-colored solution (λ_{max} = 512 nm) became pale-orange and then finally brown (λ_{max} = 881 nm) as more base was added (Figure 1). This pH-dependent shift in the absorption spectrum was reversible, but polymer decomposition was detected after a few hours in the hydroxide-containing medium. Equally impressive solution effects occurred upon the dissolution of **2** in strongly Lewis basic solvents[12] such as HMPA (λ_{max} = 901 nm) (Figure 1) or NMP (λ_{max} = 746 nm) (**2** was insoluble in DMSO).[13] No polymer decomposition was detected in these Lewis basic solvents, and there was no spectral difference with the strict exclusion of air. Upon the addition of aqueous HCl, the HMPA and NMP solutions once again became red with no absorption bands present above 600 nm. The ^{13}C NMR spectrum of **2** in HMPA (with 10% $CDCl_3$ added for the lock) showed the butyl signals as well as a broad resonance from 176 to 163 ppm. In accord with the dramatic and reversible optical absorbance shifts, Brønsted or Lewis bases might be promoting a cascade of π-electron migrations in **2** to afford the planar conjugated polymer **3** (Scheme 2). **3** is similar to indigo and related indigo-like compounds that possess cross-conjugated vinyligous amides with extraordinarily large values of λ_{max}.[3]

We attempted to get a conductivity of **3** as the diethylamine adduct, λ_{max} (Et_2NH solution) = 783 nm. Removal of the excess amine and press-formation afforded pellets that were repeatedly too brittle for 4-point probe analysis.

Another interesting feature of **2** is that it could be partially reduced with H_2 (1 atm) over Pd/C (24 h, 23 °C) to afford a system that is very similar to the starting polymer by FTIR and SEC analysis, while the ^1H NMR and ^{13}C NMR showed peak broadening; therefore, some of the units were hydrogenated. Although the reduced polymer cannot attain the degree of extended conjugation of **3** (as determined by the optical absorbances), its response range to different solvents can be from the UV region, with weak tailing into visible, to the near-IR (DMSO, λ = 886 nm) (Figure 2). Thus the reduced polymer is soluble in DMSO, and it responds most dramatically to solvent changes. When aqueous NaOH (0.05 M) was added dropwise to the reduced polymer in THF, the initial yellow-colored THF solution became green, blue-green, and finally blue as more base was added and a new absorption band appeared at 618 nm. The absorbance could be stabilized at any color along this transition depending on the amount of hydroxide added, and it was reversed with aqueous HCl addition. Unlike **3**, the reduced polymer undergoes no noticeable hydroxide-induced decomposition upon the reversible pH shifts. Furthermore, we dissolved the reduced polymer (0.05 wt % relative to PVC plus plasticizer) in a solution of THF, poly(vinyl chloride) (PVC), and the plasticizer di(2-ethylhexyl) phthalate (DOP). Evaporation of the THF resulted in the formation of a dark green (possibly resulting from a mixture of yellow and blue),[3] transparent, flexible film since DOP was acting as a Lewis base. Suspension of the film (250 μm thickness) in aqueous HCl (3 N, no organic solvent was present) caused the film to become bright yellow-orange, while suspension in aqueous NaOH (0.5 M) caused the film to become dark blue-brown, and this process was reversible.

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Supplementary Material Available: Detailed synthetic procedures and characterization data for the synthesis and reduction of **2** (3 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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