

Poly(acenaphtho[1,2-*b*]thieno[3,4-*e*]pyrazine): a new low band gap conjugated polymer†

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The preparation of a new conjugated polymer with a low band gap of ~ 0.5 eV has been accomplished via the electropolymerization of acenaphtho[1,2-*b*]thieno[3,4-*e*]pyrazine.

Conjugated polymers continue to attract significant attention due to their desirable optical and electronic properties, which has led to their application in light-emitting diodes, photovoltaic devices, sensors, electrochromic devices and field effect transistors.¹ The advantage of utilizing conjugated polymers in these applications is the ability to tune the material properties at the molecular level. In particular, many of the properties of interest are dependent on the energetic width of the material's band gap (E_g), the energy between the filled valence and empty conduction bands, corresponding to the HOMO–LUMO gap of the solid-state material. The E_g therefore determines the lowest energy absorbance of the material and the energy of any potential emission. Low E_g values result in enhanced thermal population of the conduction band, increasing the number of intrinsic charge carriers. In addition, the lower oxidation potential associated with low E_g values results in a stabilization of the corresponding doped (*i.e.* oxidized) state.¹ Thus, control of the polymer E_g is an important factor in the production of technologically useful materials.

One method of tuning polymer properties is the annulation of aromatic rings to the repeat units, which has been found to be a powerful approach for the production of low E_g materials.² This was first demonstrated in 1984 with poly(isothianaphthene) (PITN, **1**, R = H).² In addition to various functionalized derivatives,^{1d,e} other fused variants soon followed, including poly(thieno[3,4-*b*]pyrazines) (pTPs, **2**)³ and poly(thieno[3,4-*b*]thiophenes) (**3**).⁴ In further attempts to lower the E_g of these systems, analogs with more extended ring fusions were also investigated (**4–7**) (Chart 1).^{5–9}

While extended analogues of thieno[3,4-*b*]pyrazines (TPs) have been utilized in polymers derived from mixed terthienyls,^{1d,e} the instability of the extended thieno[3,4-*b*]pyrazine units have prohibited the production of the corresponding homopolymeric materials. Reported herein is the synthesis of acenaphtho[1,2-*b*]thieno[3,4-*e*]pyrazine (**10**), a stable extended TP that can be produced *via* a simple condensation,

as shown in Scheme 1.¹⁰ Monomer **10** can then be easily electropolymerized to give the resulting poly(acenaphtho[1,2-*b*]thieno[3,4-*e*]pyrazine) (pATP, **11**), exhibiting a band gap of ~ 0.5 eV.

As with previous TPs,¹¹ **10** is readily produced from 3,4-diaminothiophene (**8**), obtained from the reduction of 2,5-dibromo-3,4-dinitrothiophene.¹² Condensation of **8** with commercially available acenaphthenequinone (**9**) gives a yellow crystalline solid in yields of 50–55%. Monomer **10** is surprisingly stable, with solid samples stored at room temperature exhibiting no detectable oxidation or decomposition over periods exceeding one month.

The cyclic voltammograms (CVs) of **10** and 2,3-dimethylthieno[3,4-*b*]pyrazine (**12**)¹¹ are shown in Fig. 1. Monomer **10** exhibits an irreversible oxidation at 1.12 V and a quasi-reversible reduction at -1.73 V. The nature of both redox waves are consistent with **12**,¹¹ although both occur at decreased potential in **10** due to increased conjugation. As acenaphthene does not exhibit oxidation below 2 V and calculations of the radical cation of **10** predict the highest spin density at the thiophene α -positions, the oxidation of **10** is believed to be thiophene-based and analogous to simple TPs.¹¹

Polymeric films of pATP were produced by applying a constant potential of 1.5 V (*vs.* Ag wire quasi reference) to saturated solutions of **10** in CH₂Cl₂. The neutral films were burgundy in color and exhibited little to no solubility in organic solvents. A CV of the resulting pATP film is shown in Fig. 2, which exhibits a single well-defined oxidation at ~ -25 mV. In comparison, the previously electropolymerized pTPs exhibited two oxidations, a smaller peak occurring at ~ -250 mV, followed by a more significant oxidation at

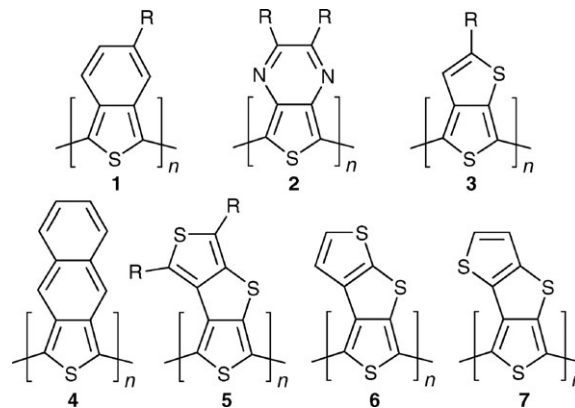
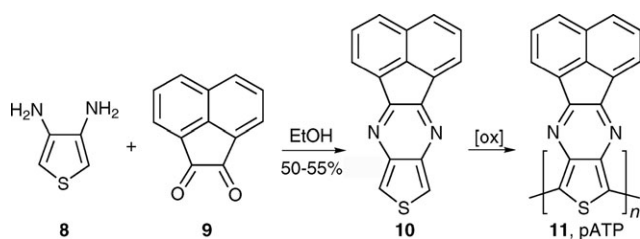


Chart 1

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Scheme 1 Synthesis of poly(acenaphtho[1,2-*b*]thieno[3,4-*e*]pyrazine).

130 mV (Fig. 3A).⁷ Thus, the oxidation exhibited by the pATP film falls roughly between the two oxidative peaks of the previous pTP films and is significantly lower in potential than the more significant oxidation of the pTPs.

More noteworthy, however, are the very large differences in the reduction potentials of pTPs vs. pATP. Not only does the pATP reduction exhibit considerably more reversible character than the analogous pTP reductions, but pATP reduction occurs at ~ -970 mV, much lower than the corresponding reductions observed in the pTPs.^{3h} This is important, as the band gap of a material is usually reduced by destabilizing the top of the valence band (HOMO), which leads to oxidatively unstable materials.^{1d,e} In this case, the additional ring fusion to the repeat unit has little effect on the resultant polymer HOMO level, but significantly stabilizes the bottom of the conduction band (LUMO), resulting in a reduction in E_g without decreasing the polymer stability.

A comparison of the oxidation and reduction onsets of the pATP film gives a conservative estimate of the electrochemical band gap to be ~ 0.45 eV (Fig. 2). While there is some debate as to the most appropriate way to determine E_g by CV, the use of onset potentials is more common as they would be most representative of the band edges of the ideal polymer structure, free from conjugation limiting defects.¹³ In order to determine more accurate values for the redox onsets, the pATP films were also investigated *via* differential pulse voltammetry (DPV, Fig. 3B). The advantage of DPV over CV is that contributions from capacitive current are minimized, resulting in a more sensitive current measurement.¹⁴ The DPV-determined onsets agree well with the previous CV values, although the oxidation onset was found to be slightly more positive, giving a slightly higher E_g value of ~ 0.5 eV. Both electrochemically-determined pATP values are in close agreement, and are considerably lower than the E_g values of ~ 0.70 – 0.80 eV determined from the CVs of the previous pTPs.^{3h} This

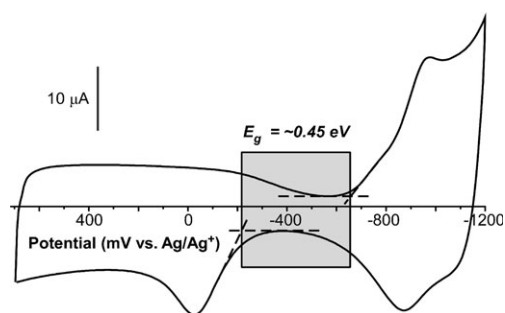


Fig. 2 Cyclic voltammogram of pATP.

reduction in E_g for pATP is consistent with the reduced HOMO–LUMO gap of **10**.

While low E_g materials typically undergo oxidative doping at lower potentials, such materials have also been shown to be more sensitive to over-oxidation. This is a common problem among conjugated polymers at higher potentials, resulting in destruction of the polymer electroactivity. This process is evidenced by a large anodic current response that is usually about seven times that of a typical doping response.¹⁵ It has been reported that PITN undergoes oxidative degradation above ~ 1.3 V,² and it has been found that over-oxidation begins as low as ~ 0.9 V in pTPs.^{3h} Due to the known oxidative sensitivity of pTPs, it was expected that pATP would exhibit similar difficulties, perhaps undergoing degradation at even lower potentials. Thus, it was surprising to find that over-oxidation did not seem to be a factor for pATP, and no such processes were observed within the solvent window of CH_2Cl_2 (~ 1.8 V). While the reason for this improved oxidative stability is unclear, it provides another significant advantage of pATP over typical pTPs.

In order to investigate the optical properties of the pATP films, samples were also grown on ITO (indium tin oxide) slides. The visible-NIR spectrum of pATP is shown in Fig. 4, which exhibits a λ_{max} at ~ 910 nm. Although this λ_{max} is a bit higher in energy than the previously studied pTPs, it exhibits a long tailing-down below 2700 nm (the spectra exhibit significant noise below 2700 nm due to additional intense ITO absorption processes). Within this tailing, there appears to be a second lower energy transition centered around 2000 nm, which may be indicative of partial oxidation. Treatment of the film with iodine vapor resulted in a shift of the λ_{max} to ~ 1140 nm, with an enhancement of the low energy absorption, further suggesting partial oxidation of the initial film.

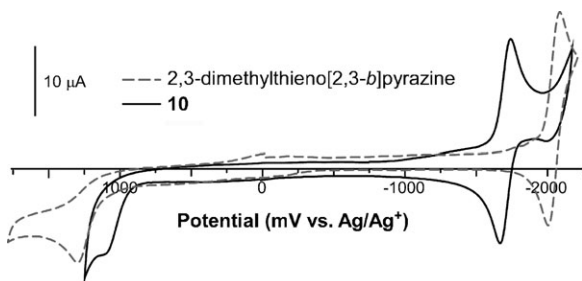


Fig. 1 Cyclic voltammograms of acenaphtho[1,2-*b*]thieno[3,4-*e*]pyrazine and 2,3-dimethylthieno[3,4-*b*]pyrazine.

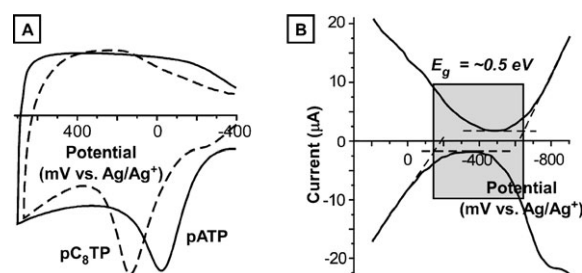


Fig. 3 (A) Comparison of pATP and pTP ($R = \text{C}_8\text{H}_{17}$) oxidation processes (ref. 7). (B) Differential pulse voltammetry of pATP.

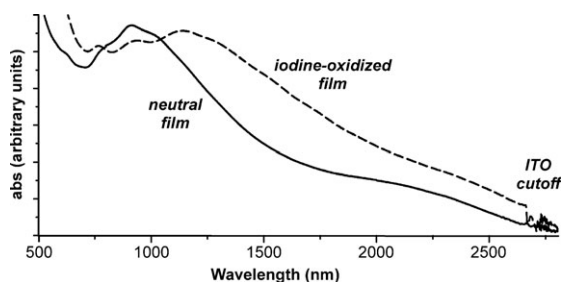


Fig. 4 The solid-state visible-NIR spectrum of pATP on ITO.

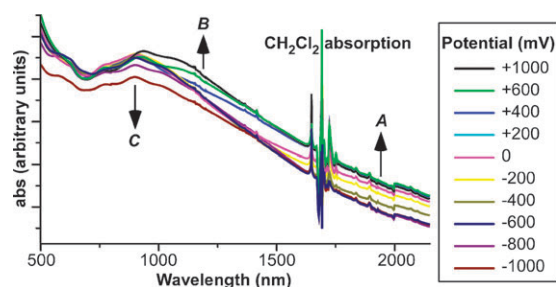


Fig. 5 Spectroelectrochemistry of pATP.

In order to determine if this low energy absorption was the result of partial oxidation, films were further characterized *via* spectroelectrochemistry, as shown in Fig. 5. This study verified that the absorption near 2000 nm (feature A) is indeed potential dependent, with the transition beginning to grow-in at potentials more positive than -600 mV and maximizing at ~ 0 mV. At increased positive potentials, a second absorption begins to grow-in near 1200 nm (feature B), which agrees well with the iodine-oxidized spectrum shown in Fig. 4. Reducing potentials were also applied, resulting in a bleaching of the neutral film's primary absorption (feature C) at potentials more negative than -600 mV. The lack of more significant bleaching of the spectra during redox processes may be due to significant transitions resulting from the pendent acenaphtho[1,2-*b*]pyrazine units of the pATP backbone. ZINDO calculations of model oligomers have shown that these pendent chromophores do not contribute significantly to the HOMO and LUMO, but do contribute to a number of transitions at higher energy that would not necessarily undergo bleaching upon oxidation of the polymer backbone. The lack of stronger low energy absorptions from charge carrier transitions are most likely due to the fact that such transitions occur beyond the ~ 2600 nm cutoff of the ITO electrode.

The spectra of the neutral material given in Fig. 5 exhibit an onset below 2200 nm, corresponding to an optical band gap of ~ 0.55 eV. This value is in good agreement with the electrochemical values of ~ 0.45 and 0.50 eV discussed above. As with the electrochemical values, the optical E_g value is reduced in comparison to the pTP optical gaps of ~ 0.7 eV.^{3h}

In conclusion, acenaphtho[1,2-*b*]thieno[3,4-*e*]pyrazine can be easily produced to give the first stable extended analogue of simple thieno[3,4-*b*]pyrazines. This new fused ring species can then be simply electropolymerized to give polymer films exhibiting band gaps of ~ 0.5 eV, as determined by cyclic voltammetry, differential pulse voltammetry and optical spec-

troscopy. This value is reduced in comparison to previous pTPs,³ and represents the lowest known reported band gap for a simple homopolymeric conjugated polymer. The development of soluble pATP derivatives is currently under way.

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