

Aromaticity in Tropone-Containing Polythiophene

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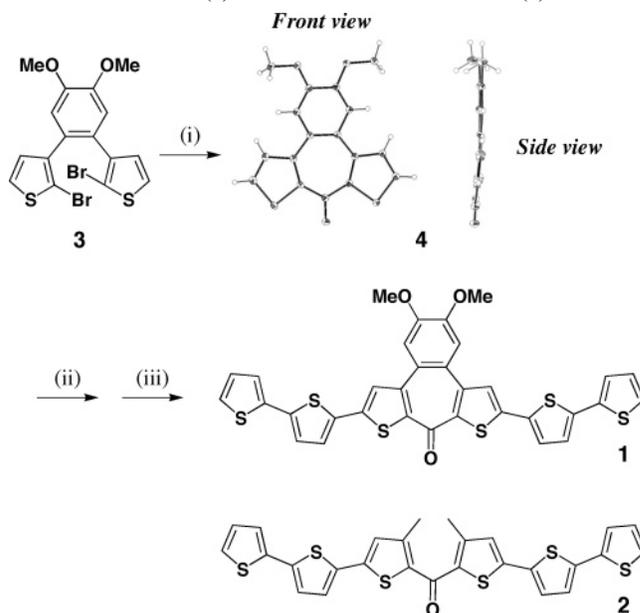
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The ability to control and switch the optoelectronic properties of conjugated polymers (CPs) is of fundamental importance in the areas of materials science and supramolecular chemistry, especially in the context of tailor-made organic electronics and sensory materials.^{1–3} Our group has a continuing interest in the design of conductivity switching systems wherein molecular recognition events within the CP backbone are capable of causing a change in the resistance of the materials in response to a target analyte.^{4–6} In these systems, we utilized *external perturbations* to the CP backbone, such as conformational changes (from planar to twisted),⁴ and electrostatic repulsion between analytes and charge carriers,⁵ etc.⁶ to effect the desired change. To further develop sensory materials, we have designed a conceptually new system based on aromaticity switching, by which the optoelectronic properties of CPs can be *internally* perturbed. Herein we report a polythiophene fused with tropone ring, which can gain aromaticity by protonation.^{7,8,9a} Switching of the tropone moiety between nonaromatic and aromatic forms in the CP backbone is expected to directly affect the electronic delocalization of the CP.⁹

The synthetic route to an electropolymerizable tropone monomer is outlined in Scheme 1. Intermediate 1,2-bis(2-bromo-3-thienyl)-4,5-dimethoxybenzene (**3**) was lithiated and subsequently treated with dimethylcarbamyl chloride to yield the cyclized product, **4**.¹⁰ X-ray crystallographic analysis of compound **4** revealed that the thiophene-fused tropone moiety is completely planar. Iodination at the α -position of thiophene groups using $\text{PhI}(\text{CF}_3\text{COO})_2$ and I_2 , followed by Stille coupling with tributylstannyl-2,2'-bithiophene gave compound **1**. Ketone analogue (**2**) was also synthesized via a similar procedure using 2-bromo-3-methylthiophene as starting material. All new compounds were characterized by ^1H and ^{13}C NMR, ATR-FT-IR, and HR-ESI-MS spectroscopic methods.¹¹

Electrochemical polymerizations were performed under ambient conditions with 2 mM **1** or **2** and 100 mM $n\text{-Bu}_4\text{NPF}_6$ in CH_2Cl_2 .¹¹ Upon repeated potential sweeps between -0.27 and 0.93 V (vs Fc/Fc^+), a quasi-reversible redox wave arising from electrode-deposited polymers gradually increased.¹² The linear scan-rate dependencies of these polymers in a monomer-free electrolyte solution established that the redox processes originate from electrode-bound redox-active species. Spectroelectrochemical studies of these polymers deposited on indium tin oxide (ITO)-coated glass electrodes showed the concomitant appearance of longer wavelength transitions associated with the polaronic (around 700 and >1100 nm) and bipolaronic states (>900 nm) upon oxidation, which are similar to the behavior of other segmented polythiophenes.¹³

The features of the cyclic voltammogram (CV) and the absorption spectrum of poly(**1**) were sharper than those of poly(**2**), as a result of the more regular conformation of the

Scheme 1. Synthetic Route to Tropone-Containing Thiophene Monomer (**1**) and Its Reference Monomer (**2**)^a

^a Key: (i) $n\text{-BuLi}$, dimethylcarbamyl chloride in ether at -78 °C; (ii) $\text{PhI}(\text{CF}_3\text{COO})_2$, I_2 in dichloromethane at room temperature; (iii) tributylstannyl-2,2'-bithiophene, $\text{Pd}(\text{PPh}_3)_4$ in DMF at 90 °C. A single-crystal ORTEP of **4** was generated using 50% probability thermal ellipsoids.

polymer backbone of poly(**1**) imposed by the cyclized tropone moiety (Figure 1). The redox processes of both polymers are shifted to a higher potential by the addition of TFA, probably due to cationic charges of the protonated CP backbones (Figure 1a,b). Spectral changes of these polymers induced by the

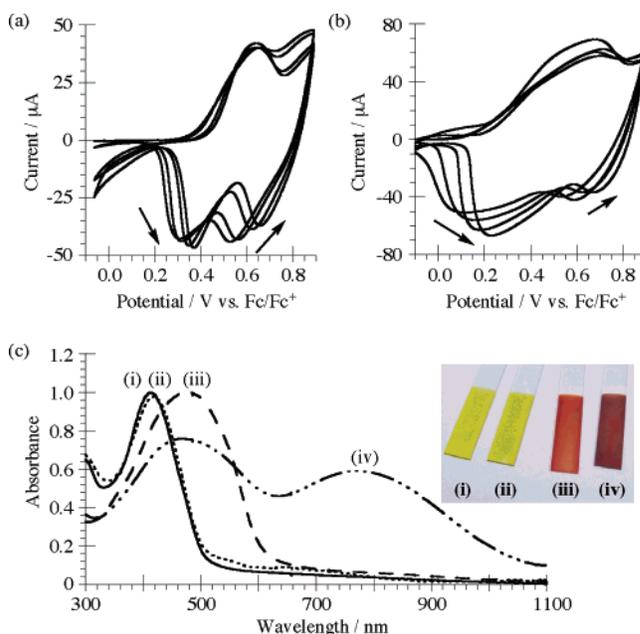


Figure 1. CV and UV-vis-NIR absorption spectral changes of poly(**1**) and poly(**2**) by the addition of TFA. The CV of poly(**1**) (a), and poly(**2**) (b), in response to $[\text{TFA}] = 0, 0.1, 0.5, 1$ M, scan rate = 100 mV/s, Pt button electrode. The UV-vis-NIR absorption spectra are of poly(**1**) (i), poly(**1**) with 1 M of TFA (ii), poly(**2**) (iii), and poly(**2**) with 1 M of TFA (iv) on ITO electrodes. The inset picture shows electrodeposited films prepared on ITO electrodes that correspond to samples i–iv in part c.

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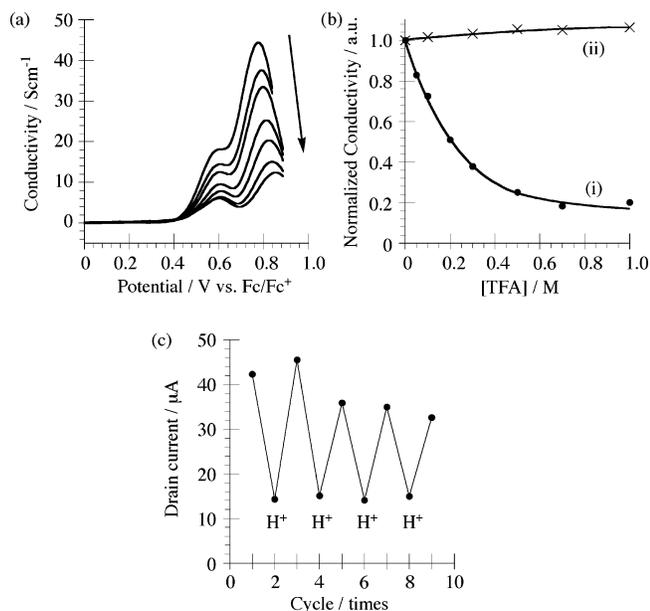


Figure 2. (a) In situ conductivity measurements of poly(1) with increasing TFA concentration: [TFA] = 0, 50, 100, 200, 300, 500, 700 mM. (b) Plots of relative conductivities of poly(1) (i) and poly(2) (ii) as a function of TFA concentration. (c) Drain current switching of poly(1) with TFA addition: [TFA] = 500 mM. The conductivity decreased during the cycling due to a partial delamination of the film from the electrode with washing.

addition of TFA were measured on ITO electrode (Figure 1c). In poly(2), a new absorption peak at longer wavelength ($\lambda_{\max} = 772$ nm) gradually appeared and this spectral change saturates at ca. 1 M of TFA. A similar absorption spectral change was also previously reported with an aromatic polyketone.¹⁴ In contrast to poly(2)'s behavior, the absorption spectrum of poly(1) is scarcely affected by protonation of tropone moieties.

In situ conductivity measurements were performed with interdigitated microelectrodes (5 μm distance, Pt). The maximum

conductivities (σ_{\max}) of poly(1) and poly(2) were $\sim 10^2$ S cm^{-1} , which is comparable with those observed for most polythiophenes. Very interestingly, only poly(1) showed a significant TFA response in conductivity measurements. Figure 2a shows conductivity profiles of poly(1) measured for increasing TFA concentrations. Upon addition of TFA, a significant drop in σ_{\max} was observed along with a slight peak shift to a higher potential. It should be noted that the diminished conductivity of protonated poly(1) is recovered after washing the film with pure electrolyte solution (Figure 2c). In contrast, the conductivity of poly(2) was scarcely affected by the addition of TFA.¹⁵ These results are the opposite of the spectral responses to TFA addition wherein poly(2) displayed a response and poly(1) did not. On the basis of this behavior, we illustrate possible resonance structures of poly(1) and poly(2) in Figure 3.

With the addition of TFA, the protonated tropone (tropylium cation) gains aromaticity. As a result, the thiophene-fused tropone moiety destabilizes the quinoid resonance form that promotes delocalization (see * in Figure 3). In contrast, protonated poly(2) has enhanced delocalization over the sexithiophene segments. This postulate of a conductivity response is consistent with the absorption spectral changes wherein only poly(2) shows longer wavelength shift by protonation (Figure 1c). These schemes in Figure 3 are illustrated for ground states of poly(1) and poly(2), however, we can also expect that these factors will influence their oxidized (i.e., conducting) states.

To further support the role of the tropylium aromaticity illustrated in Figure 3, we conducted in situ EPR measurements on poly(1) in the absence and presence of TFA (see Supporting Information, Figure S5). A polymer's conductivity is known to be proportional to the product of density (n) and mobility (μ) of charge carriers:¹⁶

$$\sigma = ne\mu \quad (1)$$

For example, the emeraldine base form of polyaniline becomes

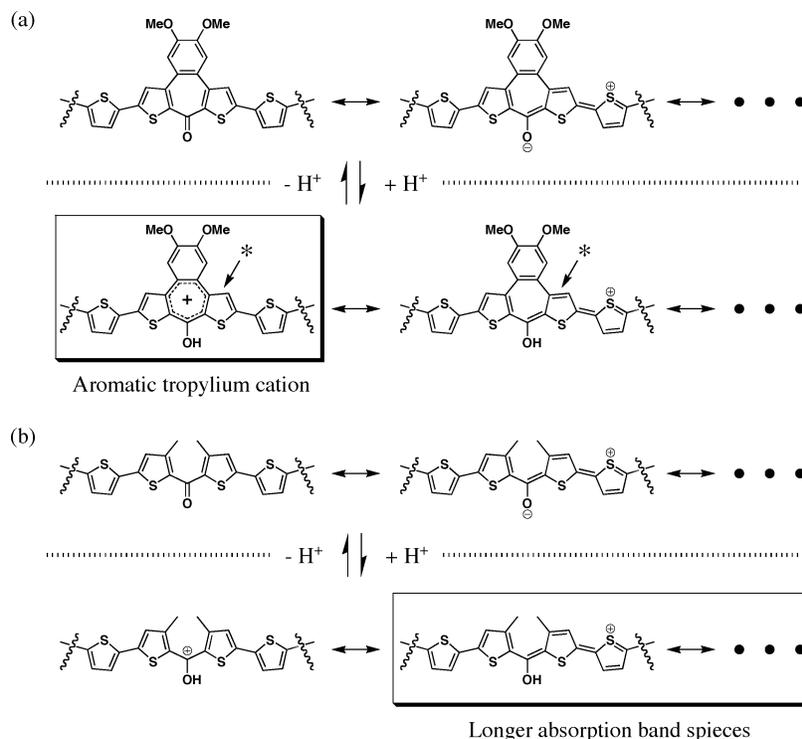


Figure 3. Resonance structures of poly(1) and poly(2). Note the thiophene group fused with tropone ring (*), whose quinoid resonance form is destabilized by aromatic tropylium cation. Enclosed structures are dominant resonance contributors.

highly conductive upon protonation due to the increase of charge carrier density (formation of polysemiquinone radical cation).¹⁷ During the first oxidation process of poly(**1**) (without H⁺), spin densities gradually increased, then decreased throughout further second oxidation. The coincidence of this bell-shaped spin density profile with the conductivity profile demonstrates that charge-delocalized cation radicals (polarons) are the major participants in the charge-carrying mechanism. Interestingly, the EPR intensity of oxidized poly(**1**) was not affected by the addition of TFA, indicating that the densities of charge carriers are constant. These results demonstrate that the decrease of conductivity of poly(**1**) induced by protonation is not due to the decrease of carrier density but due to the decrease of carrier mobility. Hence we assert that the aromatic character of the tropylium cation prevents delocalization along the polymer chain, which in turn limits carrier mobility.

In conclusion, we have demonstrated that the conductivity of tropone-containing polythiophene can be switched reversibly by a protonation/deprotonation process. The conductivity switching mechanism of this polymer is alternative to that of conventional proton dopable polymers such as polyaniline in terms of eq 1.

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Supporting Information Available: Text giving detailed descriptions of experimental procedures, syntheses (including a reaction scheme), and instrumental analysis, figures showing ¹H NMR and ¹³C NMR spectra of compound **1** and **2**, electrochemical polymerization, and spectroelectrochemistry of the polymers, a table of crystallographic data, and X-ray crystallographic information files

in cif format of **4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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