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Defining Space around Conducting Polymers: Reversible Protonic Doping of a Canopied Polypyrrole

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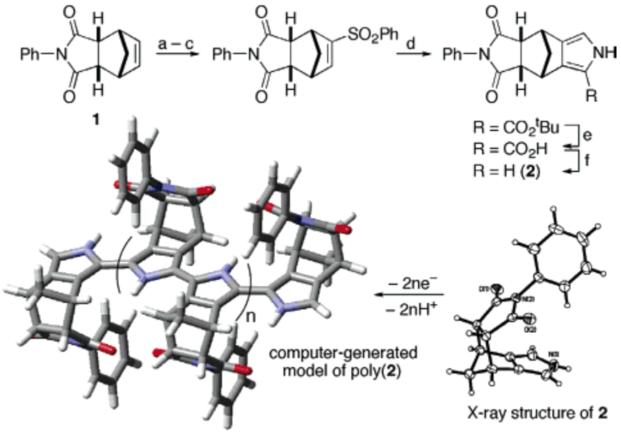
Molecular wires built on π-extended organic frameworks have proven useful for sensory signal amplification.[1] In such functional solids, binding of analytes can elicit either deconjugation of the conducting polymer (CP) backbone or an energy mismatch between juxtaposed redox-active sites.[1a] An important prerequisite for CP-based sensing scheme is the presence of well-defined charge transporting pathways, the stereoelectronic perturbation of which translates into measurable changes in collective properties such as conductivity. Equally crucial in this context is the availability of a highly porous internal structure that facilitates passive diffusion of analytes across the bulk material. In this communication, we report a synthetic strategy targeting these two objectives. Here, a sterically hindered canopy was integrated into the polypyrrole backbone to provide free volume and to minimize cross-communication between adjacent polymer strands. The reduced dimensionality of the charge-transporting pathways in such constructs translates into a different conductivity profile than is observed in the parent polypyrrole. Notably, this porous polypyrrole derivative still retains high conductivity, which can be reversibly modulated by protonic doping.[2]

A synthetic strategy has been implemented that allows access to a new class of sterically hindered pyrrole derivatives (Scheme 1). The prototypical molecule **2** features a C-shaped cavity defined by the pyrrole ring and a phenyl canopy. Such an architectural consideration is expected to minimize $\pi-\pi$ stacking interactions between adjacent CP strands in poly(**2**) (Scheme 1). Substitutions on the β-positions of the pyrrole unit in **2** are also expected to enhance structural homogeneity as well as chemical stability by preventing interchain linkages and nucleophilic attack on the polypyrrole backbone. Compound **2** was prepared in seven steps from readily available materials (overall yield = 32%) and characterized by various methods including X-ray crystallography (Scheme 1).[3] Utilizing modified Barton−Zard approach,[4] the pyrrole fragment in **2** was synthesized from the olefinic double bond of the kinetic Diels−Alder adduct of *N*-phenylmaleimide and cyclopentadiene, **1**.

Anodic polymerization of **2** was carried out under ambient conditions. Upon repeated potential sweeps between −500 and +1000 mV vs Ag/AgNO$_3$ (0.01 M) in MeCN, a quasi-reversible redox wave arising from electrode-deposited poly(**2**) gradually builds up. The scan rate dependence of poly(**2**) in monomer-free electrolyte unambiguously establishes that the redox process at $E_{1/2}$ = −95 mV originates from an electrode-bound redox-active species.[5] Spectroelectrochemical studies of poly(**2**) revealed properties reminiscent of those associated with the parent polypyrrole. Specifically, the build-up and decay of the $S = {}^1/_2$ paramagnetic species as well as spectral shifts in the UV−vis spectra induced by gradual oxidation of poly(**2**) could be explained by invoking the polaron−bipolaron model of charge-delocalized π-platforms (vide infra).[3,6]

Scheme 1 [a]



[a] (a) PhSH, NCS, CH$_2$Cl$_2$, −78 °C to rt. (b) mCPBA, CHCl$_3$. (c) DBU, CH$_2$Cl$_2$. (d) CNCH$_2$CO$_2$^{t}Bu, ^{t}BuOK, THF, reflux. (e) TFA, rt. (f) LiCl, H$_2$O, ethylene glycol, 190 °C. Structure of **2** was generated using 50% probability thermal ellipsoids.

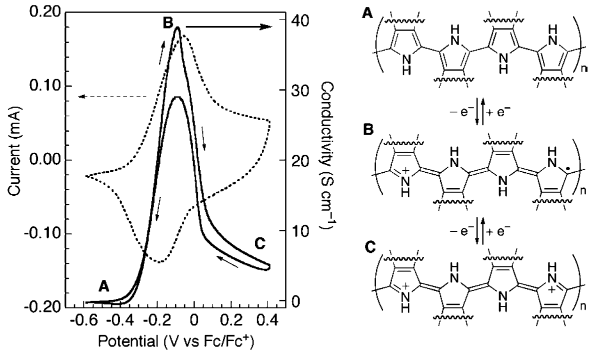


Figure 1. Cyclic voltammogram (25 mV/s; dotted line) and in situ conductivity measurement[7] (5 mV/s, offset potential of 40 mV; solid line) of poly(**2**) on 5-μm interdigitated Pt electrodes in MeCN with 0.1 M (Bu$_4$N)PF$_6$ as supporting electrolyte (left), and qualitative representations of neutral (A), polaronic (B), and bipolaronic (C) states of the polypyrrole backbone (right).

Despite the apparent similarities, the potential−conductivity profiles of poly(**2**) are markedly different from those of the parent polypyrrole system. As shown in Figure 1, the conductivity of poly(**2**) increased upon oxidation and maximizes at −90 mV ($\sigma_{max} \approx$ 40 S cm^{-1}). Further oxidation resulted in a rapid drop, defining finite potential windows of high conductivity. A similar potential−conductivity profile was obtained upon return sweep. This buildup and decay of the charge-transporting species in poly(**2**) matches closely with the potential-dependent changes in the intensity of the $g = 2$ EPR signal,[3] corroborating the notion that charge-delocalized radical cation species (B, Figure 1) is the major participant in the charge-transporting mechanism of poly(**2**). In contrast, the con-

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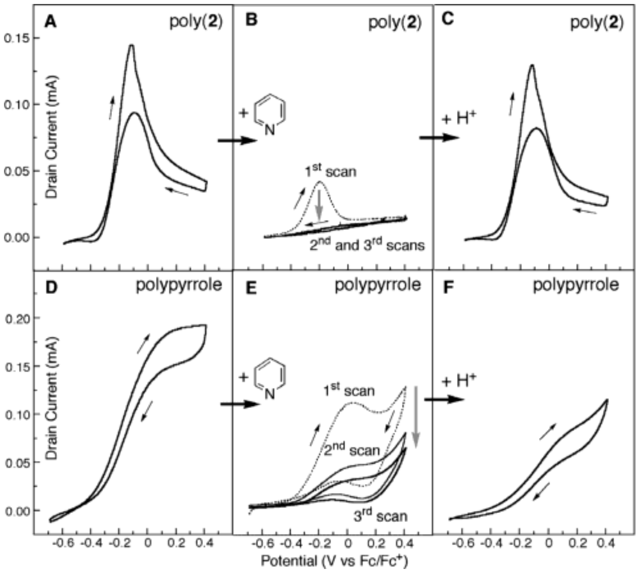

Figure 2. Conductivity profiles (5 mV/s, offset potential of 40 mV) of poly(**2**) (A−C) and polypyrrole (D−F) on 5-μm interdigitated Pt electrodes in MeCN electrolyte solutions ([Bu_4N)PF_6] = 0.1 M) of either TFA (10 mM, A, C, D, and F) or pyridine (10 mM, B and E). See the text for experimental details.

ductivity of parent polypyrrole system increases upon oxidative doping of the polymer and maximizes at the potential range dominated by the EPR-silent bipolaronic states (C, Figure 1; Figure 2D).[6,7b,c,8] An efficient interstrand charge hopping promoted by close contacts between planar π-extended platforms facilitates charge delocalization within polypyrrole, providing three-dimensional electronic connectivity for bipolaron migration.[9,10] In contrast, limited interstrand electronic coupling in poly(**2**) apparently strengthens localization of the charge carriers and affords finite potential windows of high conductivity dominated by polaronic charge carriers (B, Figure 1).

Oxidation of the polypyrrole backbone of poly(**2**) formally generates iminium functional groups (B and C, Figure 1). Deprotonation of these fragments would result in oxidized poly(**2**) having varying degrees of deprotonation and contributions from quinonoid resonance structures.[11] Migration of polaronic charge carriers should thus be significantly hampered across the polymer backbone embedded with such local energy barriers. This postulation was probed experimentally. When poly(**2**) was placed in an MeCN electrolyte solution of trifluoroacetic acid (TFA, 10 mM), a well-defined bell-shaped conductivity profile was obtained (Figure 2A). Upon exposure to pyridine (10 mM), however, a significant (>70%) drop in $\sigma_{\max}$ was observed, followed by a featureless return sweep (Figure 2B). The material remains insulating upon subsequent sweeps. The conductivity profile of poly(**2**), however, was regenerated upon reexposure to TFA (Figure 2C). A similarly rapid and reversible switching was effected when a sterically demanding analogue of pyridine such as 2,3-cyclododecenopyridine was used, demonstrating the highly porous nature of poly(**2**) accessible to bulky analytes.

Polypyrrole subjected to similar conditions, however, displayed a significantly different behavior. Although the $\sigma_{\max}$ ($\sim$75 S cm^{-1}) observed at the positive end of the potential scan (Figure 2D) decreased substantially upon deprotonation (Figure 2E), polypyrrole still retained significant conductivity (ca 35%) even after three scans in a MeCN solution of pyridine (10 mM). Reprotonation by TFA resulted in a partial increase in conductivity (Figure 2F), but it failed to reproduce the original profile prior to deprotonation (Figure 2D). A suppressed cross-communication between adjacent polymer strands within poly(**2**) apparently limits the number of pathways available for charge transport, facilitating a rapid and reversible conductor-to-insulator transition. The sluggish response of polypyrrole can be due to the slower diffusion of acids and bases in its thin films and may also be due to its delocalized interchain charge carriers that can potentially take alternative pathways upon encountering locally introduced energy barriers. If strong interstrand electronic coupling in such a $\pi-\pi$ stacked system attenuates the perturbation introduced to the energy landscape of CP, it is a liability for resistivity-based sensing. A preliminary experiment established that the conductivity of poly(**2**) could be similarly modulated in aqueous electrolyte solutions between pH = 3 and pH = 9. The compatibility of the present system with aqueous media as well as the potential for further elaborating the canopy module in the prototypical monomer **2** offers opportunities for biologically and environmentally important sensing applications.

In summary, by defining space around CP, we lowered the dimensionality of the electronic structures responsible for charge transport. A conceptual linkage can be drawn to a strategy recently adopted for polymer light-emitting devices, in which luminescent CP strands are encapsulated within insulating organic sheaths.[12] Limited interstrand electronic interactions between such site-isolated π-conjugated platforms facilitate an efficient exciton-to-photon conversion, while high mobilities of charge-carrying species are still being maintained.

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Supporting Information Available: Crystallographic data of **2** (CIF) and spectroelectrochemical data of poly(**2**) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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