Amino Acid Semiconductor

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$(Pro_2H^+)_2(TCNQ^{\bullet -})_2 \cdot TCNQ$: An Amino Acid Derived Semiconductor**

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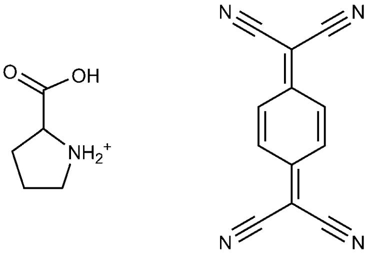
Materials based on TCNQ (tetracyanoquinodimethane) derivatives are of particular interest as they offer promise as biodegradable components for the semiconductor industry. TCNQ itself is a classical electron acceptor with an electron affinity of 2.88 eV[1] so that the anionic radical, $TCNQ^{\bullet -}$ is readily formed by chemical reduction,[2] photoreduction,[3] or electrochemical methods.[4] In the presence of electron donors, the resulting charge-transfer (CT) complexes with $TCNQ^{\bullet -}$ are characterized by an extensive range of electronic and optical properties.[5] To date, $TCNQ^{\bullet -}$ materials have been formed in combination with many cations, including metal ions (Na^+, Mg^{2+}, Cu^{2+}, Gd^{3+}),[6] organometallic complexes (e.g., ferrocene, $[Ru(bpy)_3]^{2+}$),[7] as well as some organic cations (Me_4N^+, NMP^+, TTF^+).[8] Characterization of these materials yields a wide range of 1) stoichiometries,[6d,9] including fractional charge transfer ratios, 2) morphologies,[10] even with the same cation, although the radical anion consistently forms laminar π-stacked columns, and 3) phases,[11] induced by electrochemical, photochemical, or thermal methods. Interestingly, even though TCNQ itself is a semiconductor, the band gap is greater than 2 eV[5b,12] so that the conductivity of pure TCNQ crystals is quite low. $TCNQ^{\bullet -}$-based CT complexes generally have a much higher conductivity,[13] approaching even metallic conductivity[5b,12] or superconductivity[14] under certain conditions.

Amino acids are key building blocks for polymeric macromolecules, especially proteins. The side-chain functionality includes a variety of polar, non-polar, aromatic, and heteroatoms. Proline (Scheme 1) is unique insofar as it does not contain a primary amino group, instead it has a secondary amine thereby raising the pK_a from 9 to >10.5.[15] Unlike the typical cationic TCNQ complexes, amino acids are not obvious candidates for TCNQ CT complexes. However, there is one report whereby solid TCNQ was ground with four different amino acids with the formation of a CT product indicated by IR spectroscopy.[16]



Scheme 1. Molecular structure of proline (left) and TCNQ (right).

Here we report the preparation and characterization of a novel bioorganic TCNQ material $(Pro_2H^+)_2(TCNQ^{\bullet -})_2 \cdot TCNQ$ (ProTCNQ), formed as a CT compound between neutral L-proline and TCNQ. Water was found to be necessary to provide the proton and the redox balance achieved through the oxidation of water (see Supporting Information, Section S3). Subsequently, rational methods of synthesis were introduced. An extensive range of physicochemical methods has been employed to characterize this new biomaterial. This is the first member of a new class of CT biomaterials derived from amino acids with TCNQ.

Synthesis of the ProTCNQ complex was achieved using four different synthetic routes involving either TCNQ or LiTCNQ[13a] as a starting material (Section S1). Astonishingly, all methods resulted in the same product, which suggests that the stoichiometry found for ProTCNQ is thermodynamically favored. Dark blue, single crystals of ProTCNQ were obtained by diffusion of diethyl ether into a methanol solution of L-prolineH·BF_4[13a] and LiTCNQ. The asymmetric unit contains two crystallographically independent proline residues and three halves of TCNQ species (Figure 1a, namely TCNQ-A, TCNQ-B, and TCNQ-C, respectively). From the analysis of the mean bond lengths for each TCNQ (Table S1), TCNQ-A and TCNQ-C are regarded as $TCNQ^{\bullet -}$ radical anions, whereas TCNQ-B is a neutral TCNQ molecule. The structure consists of alternating layers of proline cations and TCNQ moieties (Figure 1b). In each case, the planar TCNQ molecules form three separate 1D chains defined by weak H-bonding interactions between CN and H groups of each TCNQ (Figure 1c). These TCNQ chains run parallel to the *b* axis (the TCNQ molecules themselves lie parallel to the *ab* plane), and stack along the *c* axis to create a 2D layer (Figure 1b). There are strong π–π interactions between the chains containing the TCNQ-A and TCNQ-C

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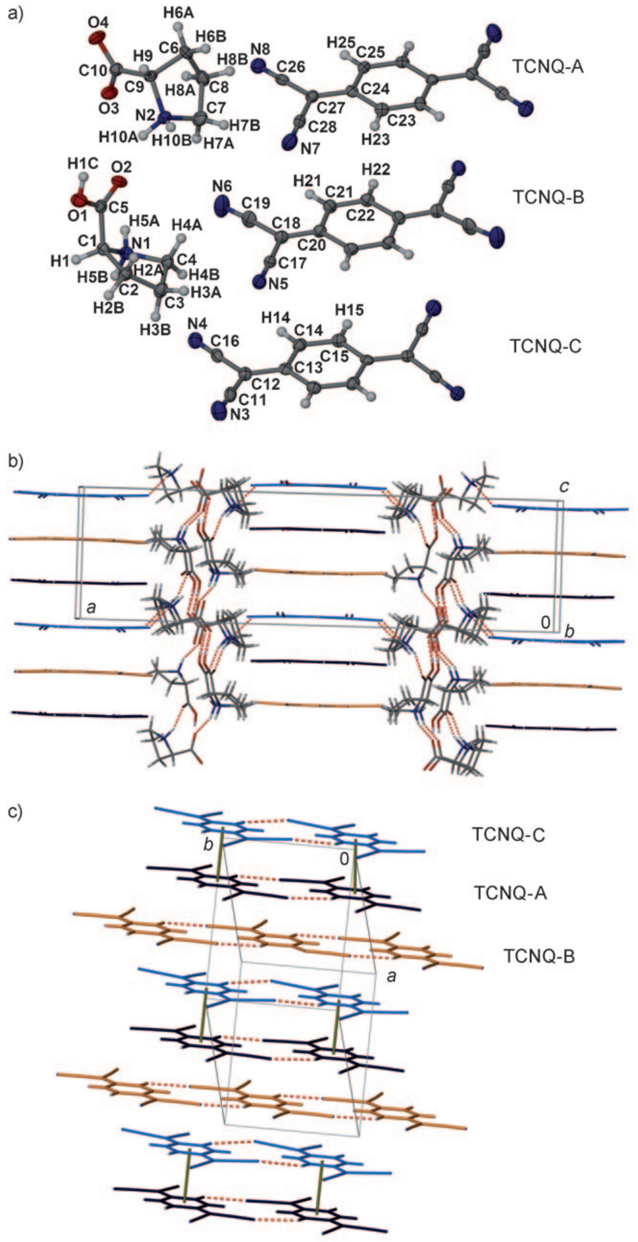

Figure 1. Crystal structure of $(Pro_2H^+)_2(TCNQ^{\bullet-})_2{\cdot}TCNQ$. a) Asymmetric unit of the complex. b) Packing viewed down the *b* axis (dark blue for TCNQ-A, orange for TCNQ-B, blue for TCNQ-C). c) TCNQ anion packing (green line indicates a π–π stacking dimer, red: hydrogen bonding).

molecules lying in an eclipsed arrangement with an interplanar distance of 3.237 Å. Thus, the TCNQ-A and TCNQ-C chains form a tight π stacked pair. The neutral TCNQ-B chains are located between neighboring pairs of TCNQ-A and TCNQ-C chains, however no π–π interactions are formed. Two crystallographically independent proline residues adopt a half-chair conformation, and are linked by extensive hydrogen bonding into 2D sheets. Analysis of the bond lengths revealed that a hydrogen atom (H1C) is equally shared between both proline residues.[17] Finally, the TCNQ layers interact with the cationic proline sheets through hydrogen bonds between CN groups of TCNQ/$TCNQ^{\bullet-}$ and proline ammonium groups.

Physicochemical characterization provided independent support for the composition of ProTCNQ. In particular, Raman spectroscopy is a powerful tool to distinguish between neutral $TCNQ^0$ and anionic $TCNQ^{\bullet-}$.[18] $TCNQ^0$ exhibits four expected diagnostic bands (Figure 2a): the C≡N stretch at 2227 cm^{-1}, the C=C stretch at 1601 cm^{-1}, the exo-ring C=C stretch at 1454 cm^{-1} and the C–H bending band at 1205 cm^{-1}. The ProTCNQ crystal (Figure 2b) shows two additional bands at 2194 cm^{-1} and 1387 cm^{-1}, consistent with the presence of $TCNQ^{\bullet-}$.[18b] Interestingly, the spectrum shows the TCNQ exo-ring C=C stretch at 1454 cm^{-1} and the C–H bending band at 1205 cm^{-1} shifts to 1466 cm^{-1} and 1187 cm^{-1}, respectively, in ProTCNQ. This was not expected as the shift of the exo-ring C=C stretch and C–H bend was not observed previously for TCNQ-based CT complexes. We attribute this shift to the hydrogen bonding interactions between the CN nitrogen and a CH hydrogen on the TCNQ/$TCNQ^{\bullet-}$, in the same plane (Figure 1c), apparent from the X-ray structure. Proline is Raman active, however, when incorporated in the ProTCNQ crystal, its resonance bands appeared to be too weak to be detected. FT-IR spectra supported the coexistence of $TCNQ^{\bullet-}$ (2179 cm^{-1} for ν(C≡N) and 824 cm^{-1} for δ(C-H)) and TCNQ (2207 cm^{-1} and 857 cm^{-1}) in the complex. The proline moieties were also identified at 1723 cm^{-1} ν(C=O) in the IR spectrum, albeit shifted to higher wavenumbers by ca. 100 cm^{-1}, compared with L-proline (1617 cm^{-1}), due to the addition of a proton. X-ray powder diffraction (XRD) patterns were obtained from the dark blue bulk materials confirmed that the bulk material was polycrystalline with the main diffraction peaks matched well to the simulated pattern based on the X-ray crystal structure.

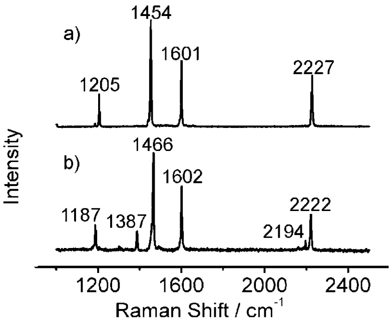

Figure 2. Raman spectra obtained for a) TCNQ crystal adhered to a gold substrate, b) ProTCNQ single crystal on a gold substrate.

In solution, the UV/Vis spectrum of ProTCNQ supported the coexistence of both $TCNQ^0$ and $TCNQ^{\bullet-}$ (Figure S1). Steady-state voltammetry of ProTCNQ dissolved in acetonitrile at a microdisk electrode showed the position of zero current lies 2/3 through the TCNQ/$TCNQ^{\bullet-}$ process (Figure 3a), which suggests the TCNQ moieties have a composition of two $TCNQ^{\bullet-}$ to one $TCNQ^0$. Also, solution conductivity of ProTCNQ in acetonitrile was measured to be 2.0 $mS\,cm^{-1}mol^{-1}$ (KCl 140 $mS\,cm^{-1}mol^{-1}$), consistent with some dissociation of ions.

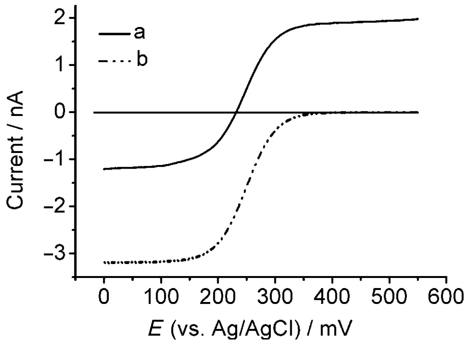

Figure 3. Steady-state voltammetry obtained with a 10 μm diameter Pt electrode at a scan rate of 50 mV s^{-1} for a) 0.33 mM ProTCNQ or b) 1.0 mM TCNQ in acetonitrile solution containing 0.1 M Bu_4NPF_6 as the supporting electrolyte.

The solid-state conductivity of the compressed ProTCNQ disk was measured as 2.5 mS cm^{-1} at 295 K using the standard four-probe technique. This lies well within the semiconductor range (10^{-5} to 10^{6} mS cm^{-1}), and is significantly higher than that of most 1:1 cation^{+} TCNQ$^{\bullet -}$ configurations (≈ 0.01 mS cm^{-1})[13a] and close to Cs_2TCNQ_3 (2.0 mS cm^{-1}).[13a] The resistivity (Ω m) showed an increase as the temperature is lowered (Figure 4). The linear ln(Ω m) vs. $1/T$ relationship (Arrhenius plot) shows that ProTCNQ behaves as an intrinsic semiconductor with an activation energy (E_a) of 11.3 ± 0.1 kJ mol^{-1} over temperature range of 300 to 130 K.

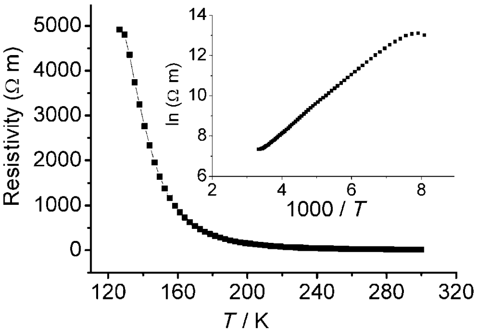

Figure 4. Temperature dependence of the resistivity (Ω m) for ProTCNQ (solid). Inset shows an Arrhenius plot of ln (Ω m) vs 1000/T.

The temperature dependence of the EPR and magnetic susceptibility (Figures S3, S4) and the magnetic field dependence of the latter (Figure S4) indicate the presence of antiferromagnetic ordering and spin-flop behavior with the spins in the TCNQ sublattice, as commonly found in quasi-one-dimensional $S = \frac{1}{2}$ Heisenberg chain systems.[1,11,19] These materials also show conducting or semiconducting behavior at higher temperatures, as in the present case.

In summary, we have reported the first example of an amino acid/TCNQ derived semiconductor. The X-ray structure for the proline derivative shows a novel and unpredicted structure. $(Pro_2H^+)_2(TCNQ^{\bullet -})_2\cdot TCNQ$ is derived from sheets of cations and anions in the two-dimensional lattice supported by extensive H-bonding interactions resulting in unusual electronic properties. The extensive physicochemical characterization of this material is in complete accord with the crystal structure. The likelihood that the composition is the thermodynamically stable one is supported by several different methods for synthesis, including a solid–solid transformation, that all result in the same ProTCNQ product. Access to an amino acid derived charge transfer compound offers substantial potential for development of other biomaterials with semiconducting properties. We envisage that these CT complexes may provide suitable supports for "tethering" biomolecules which can be employed in biosensing and bioreactor applications.

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