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Conducting Probe-Mediated Electrochemical Nanopatterning of Molecular Materials

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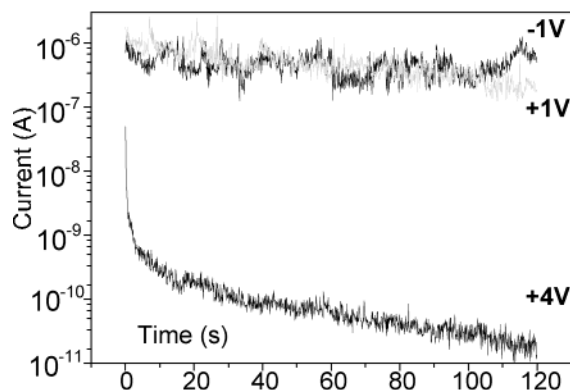


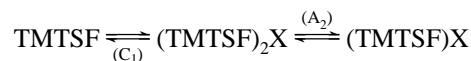
Figure 2. Probe-sample currents as a function of time for different bias potentials.

creation of smooth nanometer-scale insulating barriers onto the (001) *ab* face of a (TMTSF)₂PF₆ single crystal¹⁸ chosen as an example,¹⁹ by an ambient-air operated (CP) AFM instrument²⁰ working in the oxidative mode.

The results of the present surface reactions are summarized in Figure 1, emphasizing the unique possibility offered by (CP)AFM to visualize simultaneously the topographical features *and* the local electrical surface properties of the substrate. At zero bias there is no surface modifications (Figure 1c, d), in striking contrast to the surface modifications achieved when the tip–substrate bias is applied. The measurements are not symmetric: the disconnection of conducting fragments for a quite low negative potential (−0.5 V) (Figure 1e, f) is not detected in the opposite direction. This clearly excludes an electric-field effect as a source of these modifications and indicates the occurrence of electrochemical reactions. Increasing the negative bias above −0.5 V results in much greater surface damage and even in probe degradation for *V* = −4 V. In contrast, for positive substrate bias up to +4 V, smooth lines are obtained which increase in width with potential (Figure 1a, b). Keeping the probe fixed with a bias of +4 V results in an *outgrowth* of an insulating powdery solid of lower density (Figure 1, yellow arrows), whereas the insulating lines have a hollow appearance, probably because the probe *partly* sweeps out the new oxidized microcrystalline material. Both processes are found to be strongly sensitive to other parameters such as scanning speed, probes sharpness,²¹ and load. The corresponding currents (at fixed probe) measured for both processes (Figure 2) are also very different. Thus, for positive bias the Faradaic current rapidly stops after a sharp decrease, reflecting the formation of un-interrupted insulating areas (Figure 2, +4 V). On the other hand,

for negative bias which results in detachment of conducting fragments (−1 V in Figure 2), the current is not significantly reduced over time. Similarly, for moderately positive potentials involving almost no surface reactions (Figure 1, +1 V), the measured current is fairly stable over the same period of time.

The observed solid-state modifications are ascribed to the following electrochemical reactions:



with peak potentials $E_{p\text{C}_1} = -0.03$ V and $E_{p\text{A}_2} = +0.47$ V (vs SCE) corresponding respectively to the cathodic C₁ and the anodic A₂ processes (i.e., for X = PF₆ or ClO₄).^{16b} The large difference (almost 2 V) between threshold voltages for the present probe-mediated Faradaic processes, as compared to the voltage range (0.5 V) where these materials are electrochemically inactive, clearly reflects the influence of associated water redox reactions (see Figure 1 caption).

The structures of the oxidized insulating (TMTSF)X solids are unknown,^{22a} and require additional efforts to be fully characterized. However, they could be expected to result in smaller structural changes of the (TMTSF)₂X conducting materials structures^{22b} than those involved in the back reaction to the neutral parent TMTSF.^{22c} Hence, the significant structural changes coupled with the anion expulsion phenomenon, associated with the crystal reduction reactions, could account in this case for the coarse surface damage²³ (Figure 1a, b) observed for negative bias, as compared to the regular surface modifications obtained by oxidation (Figure 1c, d).

In summary, these preliminary results show that useful solid-state modification of molecular (super)conducting material¹⁹ can be obtained using scanning probe-mediated electrochemical reactions and that these reactions are locally confined in the tens-of-nanometers range. Although the precise thickness of the insulating regions, created within the conducting organic substrate, has not yet been determined, the resulting barriers match the magnitude of the coherence length values ξ_a and ξ_b , of around 75 and 35 nm, respectively,²⁴ for (TMTSF)₂ClO₄ the superconducting member of the series. The dimensions of present modifications could also be decreased, using established relative-humidity lowering procedures,²⁵ thereby opening the way to the not-yet available organic Josephson tunnel junctions. Work is in progress in our laboratories toward these objectives.

Supporting Information Available: Details on experimental setup and commercial-probes performance evaluation and optimization (sharpness and electrical behavior) (PDF). This material is available free of charge via the Internet at <http://www.pubs.acs.org>.

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(18) See ref 17c for the indexing of these crystal faces.

(19) The solid-state electrochemical properties of Bechgaard salts do not depend significantly on the nature of the constituent anions, see ref 16 b.

(20) A homemade system for local contact resistances and current measurements (Resiscope) derived from a Nanoscope III AFM instrument (Veeco) was utilized. When a bias voltage *V* (−10 < *V* < 10) is applied between the probe and the sample, the Resiscope allows currents ranging from 1 mA to almost 1 pA to be measured. For electrical image acquisitions, the sample was positively biased (*V* = +1 V). For the surface modification reactions, distinct voltage values (−0.5 to +4 V) were applied. One-legged diamond coated Si cantilevers (Nanosensors, spring constant ~2 N/m.) were used (see ref 21 for tip performance improvements). Platinum-coated silicon cantilevers (Nanosensors, spring constant ~0.1 N/m) were rapidly damaged and consequently yielded nonreproducible results. The reported surface modifications, obtained with low tip-applied forces, have been investigated in ambient air with a 45% relative humidity (at 25 °C).

(21) See Supporting Information Available.

(22) (a) Only a single (solvent-containing) TMTSF cation-radical 1/1 perchlorate salt has ever been described, see: Kobayashi, H.; Kobayashi, A.; Sasaki, Y.; Saito, G.; Inokuchi, H. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2894. (b) See, for example: Thorup, N.; Rindorf, G.; Soling, H.; Bechgaard, K. *Acta Crystallogr.* **1981**, *B37*, 1236. (c) Kistenmacher, T. J.; Emge, T. J.; Shu, P.; Cowan, D. O. *Acta Crystallogr.* **1979**, *B35*, 772.

(23) This surface cracking is reminiscent of the behavior of Ti films damage, obtained at higher potentials (*V*_a = −5 V), by STM tip scans (see Figure 6 in ref 12a); however, in the latter case specific chemical reactions are not identified, and the film damage was curiously assigned to the pressure of hydrogen bubbles evolving from water when the sample is biased negatively.

(24) Ishiguro, T.; Yamaji, K. *Organic Superconductor*; Springer-Verlag: Berlin, 1990.

(25) See, for example a very nice illustration of this phenomenon in: Hong, S.; Mirkin, C. A. *Science* **1999**, *286*, 523; Supplementary Information available at www.sciencemag.org/feature/data/1044170.shl.