SCANNING TUNNELING MICROSCOPY AND HIGH-RESOLUTION TRANSMISSION ELECTRON MICROSCOPY OF $C_{16}H_{33}$-Q3CNQ, HEXADECYLQUINOLINIUM TRICYANO- QUINODIMETHANIDE

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ABSTRACT

Scanning tunneling microscopy (STM) of a Langmuir-Schaefer (LS) monolayer film of hexadecylquinolinium tricyanoquinodimethanide ($C_{16}H_{33}$-Q3CNQ, **3**) on graphite shows atomic resolution: the image is ascribed to the atoms in the dicyanomethylene "swallowtail" end of the molecule. The molecule is probably twisted about 20° from the normal to the graphite surface. High-resolution transmission electron microscopy (HRTEM) of a LS monolayer of **3** on a Cu grid shows a spacing of 18 Å between well-defined layers, and a pseudo-hexagonal pattern.

INTRODUCTION

Upon mixing a N-methylpiperidine ($C_6H_{13}N$) solution of TCNQ (**1**) with a N-methylpiperidine solution of N-substituted picolinium and lepidinium halides, one can observe, instead of the precipitation of the usual charge-transfer complex, a slow chemical reaction, with loss of HCN, yielding a zwitterionic molecule [1, 2]:

TCNQ, **1**
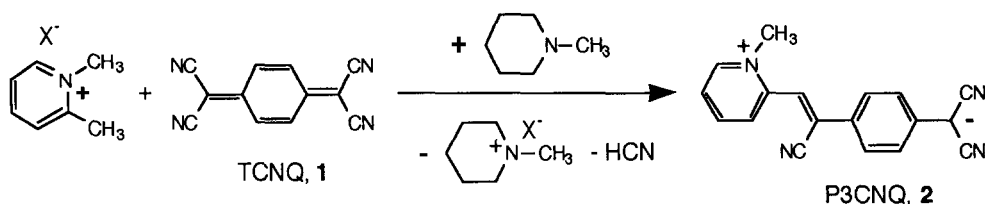
P3CNQ, **2**

The first such molecule, picolyltricyanoquinodimethan (P3CNQ, or Z-β-(1-methyl-2-pyridinium)-α-cyano-4-styryldicyanomethanide, **2**) was crystallized, and its molecular structure was determined [3]. P3CNQ has a huge calculated INDO ground state dipole moment (26.2 Debyes). Crystals of P3CNQ exhibit an intramolecular intervalence band peaked at 538 nm, and an intermolecular charge-

$C_{16}H_{33}$-Q3CNQ, **3**
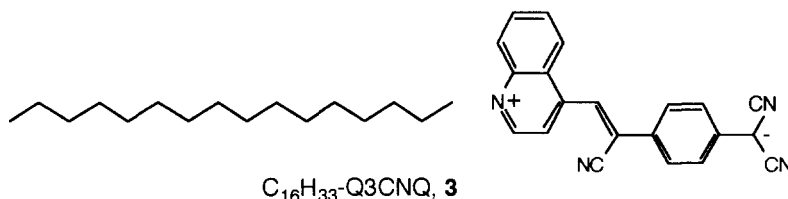
transfer band at 806 nm [4]. We can thus call P3CNQ a zwitterionic D^+-π-A^- molecule (D= one-electron donor, π=pi electron bridge, A=one-electron acceptor).

A series of alkylpyridinium and quinolinium analogs of P3CNQ were also shown to exhibit very sharp absorption bands as Langmuir-Blodgett (LB) multilayer films, which were photochromic [2, 6, 7]. One molecule of the series, N-hexadecylquinolinium tricyanoquinodimethanide ($C_{16}H_{33}$-Q3CNQ, **3**), formed Pockels-Langmuir (PL) monolayer films at the air-water interface with an area A= 47 $Å^2$/molecule at a film pressure of 25 mN/m; the molecular area decreased smoothly with pressure, from about 110 $Å^2$ at 0 mN/m, to about 41 $Å^2$ at 30 mN/m. For the PL nomenclature, see [8]. This molecular area was somewhat larger than the van der Waals cross-sectional areas of the quinolinium ring viewed end-on (about 30 $Å^2$) or of the dicyanomethylene "swallowtail" group (24 $Å^2$) [2]. Other homologs R-Q3CNQ with shorter "greasy tails" ($R=C_6$ to C_{14}) had a relatively smaller area, of about 30 $Å^2$ molecule^{-1}, presumably because of a different molecular tilt: this seems to be corroborated by a shift in the visible spectra of LB multilayers [2].

Theoretical calculations predicted a large second-order hyperpolarizability β for $C_{16}H_{33}$-Q3CNQ [3]; this was experimentally confirmed, as a Z-type LB multilayer of $C_{16}H_{33}$-Q3CNQ showed a strong second harmonic output, when irradiated with laser light at 1064 nm [7].

More recently, and surprisingly, a single monolayer of $C_{16}H_{33}$-Q3CNQ, sandwiched between a Pt substrate and a Mg overlayer (shadowed with Ag) exhibited electrical rectification [9]. It may be that the rectification by the Aviram-Ratner mechanism [10], sought in vain by the Organic Rectifier Project [11], had been found in this system [9], as well as in the related system DDOP-C-BHTCNQ [12]. However, other interpretations of the rectification signal are possible. If one assumes that the Pt surface is hydrophobic, then the orientation "Pt | $C_{16}H_{33}$-Q3CNQ | Mg | Ag" is inferred, with the Q3CNQ end closest to the Mg overlayer, and one could ascribe the rectification current to a Schottky barrier effect (formation of a $(Mg^{++})(Q3CNQ^{--})$ complex [13] at the Mg to organic interface). In fact, using differential pulse voltammetry, we have observed a reversible one-electron oxidation of $C_{16}H_{33}$-Q3CNQ in acetonitrile at 0.40 V versus saturated calomel electrode, and a reversible two-electron reduction at 0.54 V versus SCE (to D^0-π-A^{--}), but no one-electron reduction was observed. However, the $C_{16}H_{33}$-Q3CNQ molecules only transfer to the substrate on the upstroke, so a geometry "Ag | Mg | $C_{16}H_{33}$-Q3CNQ | Pt" is possible (unless the molecules invert after transfer and before deposition of the Mg overlayer) [9]: in this case, a Schottky barrier is less obvious, and the Aviram-Ratner mechanism may be operative. However, in the experiment just described [9] there are many interfaces, and this may becloud the issue of what causes the rectification.

We present here recent data obtained by scanning tunneling microscopy (STM) and by high-resolution transmission electron microscopy (HRTEM), which show atomic resolution within a monolayer film on a graphite substrate, and crystalline re-ordering of a monolayer after standing on a copper grid for six months. A full account of these results is in preparation [14].

EXPERIMENTAL PROCEDURES

$C_{16}H_{33}$-Q3CNQ, dissolved in dichloromethane, was carefully spread over a purified water subphase (Millipore Milli-Q, 16 MΩ) at room temperature (20°C) in a Lauda film balance (Langmuir trough) set on a vibration-free table in a room with filtered air. The insoluble PL film of $C_{16}H_{33}$-Q3CNQ collapses at a Π_c=36±1 mN/m, with area A_c = 34±1 Å^2 molecule^{-1}. A monolayer was transferred, with the film pressure held at 25 mN/m, by the quasi-horizontal (Langmuir-Schaefer (LS)) method, to graphite (Union Carbide highly oriented pyrolytic graphite (HOPG), grade ZYA) for the STM studies, and to a 400-mesh copper grid for the HRTEM studies. Also, a drop of $C_{16}H_{33}$-Q3CNQ, dissolved in tetrahydrofuran, was put on a second graphite substrate, and studied by STM after the solvent had evaporated.

The STM instrument was a Digital Instruments Nanoscope II, used in air with a type A head (0.6 μm maximum range); the probe was a 0.010 inch Pt-Ir alloy wire, formed with an atomically sharp tip (Digital Instruments Nanotip); the conducting substrate was HOPG. If the graphite is hydrophobic, then the alkyl chain of the molecule should be closest to the graphite, and the negatively charged dicyanomethylene end of the molecule should be closest to the STM tunneling tip:

Graphite | $C_{16}H_{33}$-Q3CNQ | Pt-Ir tip.
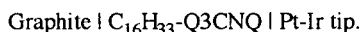
The STM experiments were repeated twice, several months apart, and the same images were observed both times. Current-voltage (IV) profiles were also collected, using the Nanoscope II scanning tunneling spectroscopy (STS) software in the constant height mode (s=c) mode. The IV plots often showed asymmetries, but these would occur, at both forward bias and reverse bias, at different times: no clear signature of molecular rectification was seen.

The HRTEM studies were carried out with a Hitachi H-800 transmission electron microscope. The $C_{16}H_{33}$-Q3CNQ LS film on a Cu electron microscope grid was dried for 15 days in a desiccator, then examined using an accelerating voltage of 75 kV: some small regions of the self-supporting film had crystallized, and a very complex diffraction pattern was observed: these data are not reported here. The
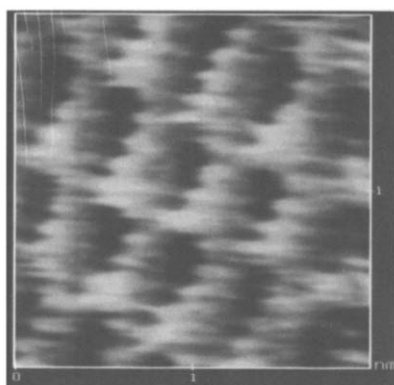

Fig. 1. Scanning tunneling micrograph of Langmuir-Schafer monolayer of $C_{16}H_{33}$-Q3CNQ on HOPG graphite, at room temperature, in air, using a Pt-Ir Nanotip. Bias voltage=0.093 V, setpoint current =1.3 nA, scan area=2.0 x 2.0 nm^2, constant current mode, vertical scan scale =0.5 nm. Shown previously as Fig. 3 of Ref. [15].
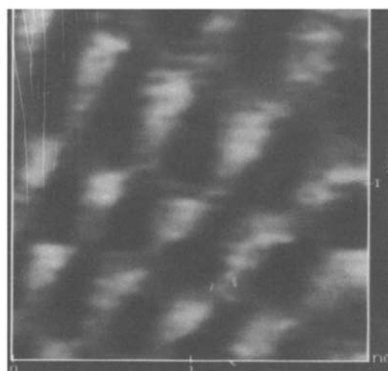
Fig.2. Scanning tunneling micrograph at room temperature, in air, using a Pt-Ir Nanotip, of a dried solution droplet of $C_{16}H_{33}$-Q3CNQ on HOPG graphite. Bias voltage= 0.067 V, setpoint current=0.96 nA, scan area=2.0 × 2.0 nm^2, constant current mode, vertical scan scale=0.5 nm.

same sample on the Cu grid was examined six months later, using a 200 kV electron beam: this time a large crystallized area had formed.

RESULTS AND DISCUSSION

Fig. 1 shows the STM image for $C_{16}H_{33}$-Q3CNQ, while Fig. 2 shows the STM image for a dried solution droplet of $C_{16}H_{33}$-Q3CNQ. The STM image of the "dried droplet" (Fig. 2) is essentially identical to that of the LS film (Fig. 1), except for the slightly lower resolution: this suggests that the
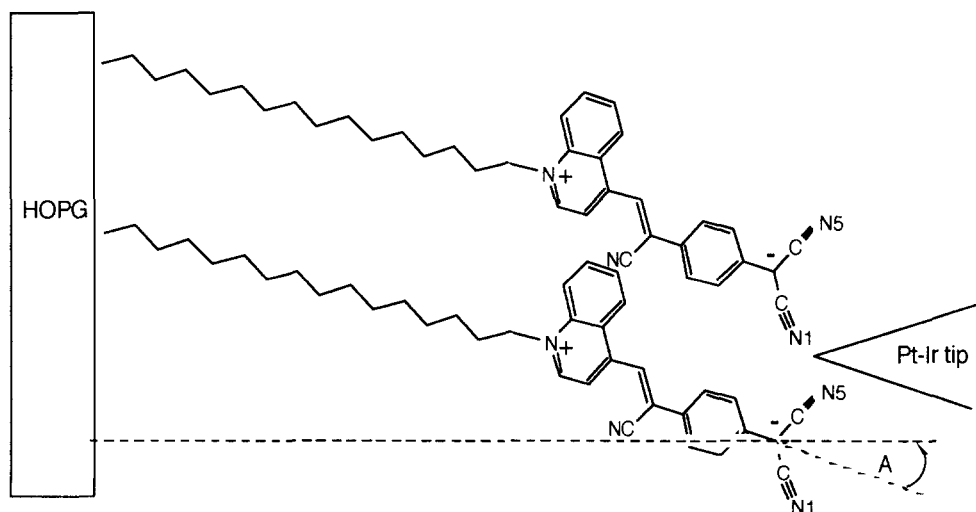

Fig. 3. Intepretation of the STM images: the N1, N5 designations for the cyano nitrogen atoms are from the crystal structure of P3CNQ, Ref. [3]. The tilt angle A= 20° refers to the angle between the normal to the graphite plane and the long axis of the 3CNQ moiety.
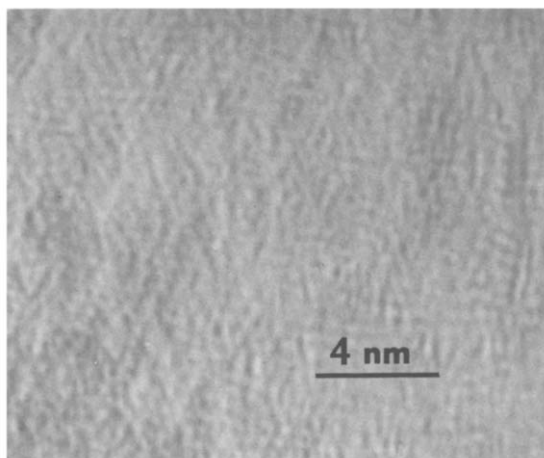
Fig. 4. HRTEM of a monolayer of $C_{16}H_{33}$-Q3CNQ,transferred by LS technique onto a Cu grid, and dried for 6 months. Regions of high order (not shown here) exhibit a pseudo-hexagonal diffraction symmetry and interspot spacings of about 18 Å.

same ordering occurs spontanously on the graphite surface in both cases (LS film, and dried solution droplet). The STM pictures clearly do not represent the graphite surface. Also, it is easy to exclude the possibility that the molecules are lying flat on the graphite substrate: a monolayer of cadmium arachidate on graphite has been seen [16], and looks not at all like the micrographs shown here.

Since there is atomic resolution in Figs. 1 and 2, we may estimate the area per molecule, and identify the orientation of the molecules. The cartoon of Fig. 3 should be helpful. The bright regions of Fig. 1 are probably the negatively charged $C(CN)_2$ groups at the right-hand end of the molecule in Fig. 3, while the dark regions of Fig. 1 are probably where the STM tip cannot penetrate to "see" the second aromatic ring of the quinolinium moiety. The repeating feature is about 7.9 ± 0.1 Å long and 4 Å wide, for a molecular area of about 32 Å^2: this is close to the measured molecular area at film collapse, $A_c=34\pm1$ A^2. The striations in Fig. 1 are about 1.1 Å apart, and may be due to aromatic C-C or C≡N bonds. From the solved crystal structure of P3CNQ [3], we remember the N1-N5 interatomic distance (4.385 Å, between the two swallowtail N atoms). There is a 4.12 Å distance between evey fifth spot, that could be ascribed to the two cyano nitrogens: this implies a tilt angle $A = \cos^{-1}(4.12/4.385) = 20°$. We thus suggest that the brightest spots of Fig. 1 correspond to atom N5.

The HRTEM image of a $C_{16}H_{33}$-Q3CNQ monolayer, after six months of "crystallization", is shown in Fig. 4. In some regions of the image, a regular spacing of 18 Å between spots is seen; also, a selected-area diffraction pattern shows a pseudo-hexagonal symmetry, which is being analyzed.

ACKNOWLEDGEMENTS

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