Complex Salts of TCNQ with Substituted Phenyl Pyridines and Their Characterization by Scanning Tunneling Microscopy

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New conductive complex salts of tetracyanoquinodimethane (TCNQ) with substituted phenylpyridines have been prepared and characterized by optical microscopy, conductivity measurements, X-ray powder diagrams and scanning tunneling microscopy (STM). The molecular stacking, which is responsible for the one-dimensional conductivity, was revealed from the diffraction data and STM images. The analysis of the STM images was based on the results obtained on a model compound, the complex salt of TCNQ and quinolinium. Although in STM the surface partial electron density is measured, several crystallographic parameters of the molecular arrangement have been determined from these images.

Introduction

Complex salts of tetracyanoguinodimethane (TCNQ) are typical representatives of organic metals [1]. Specific physical properties such as pronounced one-dimensional conductivity and temperature dependent phase transitions have invoked a considerable interest to such compounds. These salts, inserted in polymer matrices, are used in production of conductive polymer films [2]. An unique packing motif - stacking of TCNQ molecules as well as an amount of electron transfer from donors to TCNQ - is responsible for their physical behavior. In order to understand the structure-properties relationship a variety of TCNQ-based compounds have been prepared and examined [3]. Several structural parameters are important for the characterization of these crystals. The order of the neighbouring donor and acceptor stacks, various types of stack construction (mono-, di-, tri- or tetradic) have been identified in different TCNO complex salts. Unfortunatelly, crystals of some salts are not suitable for the detailed crystallographic analysis.

The new microscopic techniques - scanning tunneling microscopy (STM) and atomic force microscopy - give unique possibilities for the examination of conductive and non-conductive surfaces [4]. Since the first STM results of the TCNQ complex with tetrathiafulvalene (TTF) [5], several other TCNQ complex salts and organic conductors have been examined [6-9]. It was found that the periodical arrangement of STM patterns corresponds to the crystallographic parameters taken from the X-ray bulk data. The interpretation of high-resolution patterns within the unit cell is more difficult and can not be clarified without a theoretical consideration. According to the STM theory the tunneling current (I_{tun}) is proportional to the local density of electronic states at the Fermi level (E_F) , $\rho(E_{\rm F}, r_0)$, determined at the tip position (r_0). Recently it was shown that the STM images can be rationally interpreted on the basis of the $\rho(E_F, r_0)$ maps calculated in the framework of the extended Hückel tight binding method. The images of transition metals layered compounds [10], TCNQ complexes [11] and bis(ethylenedithia)tetrathiofulvalene salts [12-13] have been successfully explained. These findings prove the coincidence of the experimental STM images with the distribution of the partial electron density, which is not necessary identical with the surface topography.

In this contribution new TCNQ complex salts with substituted phenyl pyridines are characterized by STM in addition to other traditional methods. Earlier two modifications of the TCNQ complex salt with N-methyl-4ethylpyridinium cation (4-EP) were found in the combined STM and X-ray diffraction analysis [7]. In the development of this approach several structural parameters of TCNQ complex salts will be determined from the images. Preliminary results were reported elsewhere [14].

Experimental

Before the STM measurements crystals have been characterized by optical microscopy and X-ray diffraction. An optical microscope 'VANOX-T' (Olympus, Japan) and a STADI P (STOE, Darmstadt, Germany) powder diffractometer were used for these purposes. The diffraction experiments at ambient conditions have been conducted with Ge monochromized Cu-K_{a1} radiation (L = 0.15405 nm) in Debye Scherrer geometry. Samples were prepared in glass capillaries, d = 0.3 mm. The data collection was performed with a computer operated scintillation counter with typical parameters of 0.04° for the step width and 20 s/step for a counting time. For data processing STOE software [15] was applied. The electrical conductivities were measured between room temperature and 75 °C by the four-point method. Due to the small size of crystals pressed pellets were used for this purpose [14, 16]. The $TCNQ^{-}/TCNQ^{0}$ ratio was determined by optical absorbance at 395 and 842 nm [16]. The complex salt of TCNQ with quinolinium (QN) was regarded as a model system. Its molecular structure was simulated from the crystallographic data [17] with the program "Schakal" [18].

The STM measurements were carried out at ambient conditions with a commercial scanning probe microscope "Nanoscope II" (Digital Instruments, Inc. Santa Barbara, USA). The samples were fixed to a copper support by a conductive silver glue. Mechanically-sharpened tips were prepared from a Pt(0.8)/Ir(0.2) wire. An approach of the tip to the surface of the tiny crystals was possible only under the control of an optical stereo-microscope. The crystals were positioned with their longest axis being parallel to the y-direction of the microscope stage for convenience of the tip engagement. The STM experiments were carried out on the largest crystal faces. Typical tunneling currents and bias voltages were 1 - 2 nA, 50 - 100 mV for samples, which will be later identified as group I, and 0.2 - 0.5 nA, 0.4 - 1.0 Vfor other compounds (group II). Although the etching of surface layers was observed during the STM measurements of the TCNO complex salts, it was possible to found more perfect surface places where the atomic scale STM images were collected in the current imaging mode. In such a case the image contrast is formed by current deviations from the pre-set value, while the tip is scanning over the surface at an almost constant height. Consequently, the brighter spots in the STM top view current images correspond to places with a higher electron density. In the alternative height imaging mode the contrast presents the z-variations of the piezodrive, which is adjusted to keep tunnelling current at a constant level. Our experience shows, however, that the atomic scale images registered in both modes are similar.

To emphasize the periodical STM features the images have been filtered using the Fast Fourier Transform (FFT). For this purpose the pronounced frequency patterns in the power spectrum were used for the inverse FFT to simulate an idealized image. The geometrical parameters of the STM images were used for the sample characterization. Due to experimental reasons (thermal drift of the sample at ambient conditions, for example) the accuracy of the STM parameters ($100 \pm 5\%$) is inferior than that of the crystallographic data.

Results

Synthesis

The preparation of the N-arylpyridinium TCNQ complex salts has been described shortly in [14]. The reaction of the sodium salt of glutodialdehyde (1) with the appropriate aniline derivative yielded intensively violet coloured dianilide hydrochlorides (2):

$$Na^{+} \xrightarrow{0} 1 \xrightarrow{0^{-}} \frac{R}{Hcl/C_{2}H_{5}OH} \xrightarrow{R} 2 \xrightarrow{H_{+}} x \xrightarrow{H_{+} x \xrightarrow{H_{+}} x \xrightarrow{H_{+}} x \xrightarrow{H_{+} x \xrightarrow{H_{+}} x \xrightarrow{H_{+}} x \xrightarrow{H_{+}} x \xrightarrow{H_{+} x \xrightarrow{H_{+}} x \xrightarrow{H_{+} x \xrightarrow{H_{+}} x \xrightarrow{H_{+} x \xrightarrow{H_{+} x \xrightarrow{H_{+$$

Ring closure occurred during refluxing of 2 in alcoholic hydrochloric acid. Since the chlorides 3 are usually hygroscopic, the iodides 4 were prepared by reaction with an excess of sodium iodide in ethanol:

$$2 \xrightarrow[HC1/C_2H_5OH]{} \xrightarrow{R} \xrightarrow{t} N \xrightarrow{t} C_{1} \xrightarrow{Nal} \xrightarrow{R} \xrightarrow{t} N \xrightarrow{t} C_{2}H_5OH} \xrightarrow{R} \xrightarrow{t} N \xrightarrow{t} N$$

The reaction of **4** with the lithium salt of TCNQradical-anion in aqueous methanol yielded the violet compounds **5**. The black TCNQ-complex-salts **6** were obtained by mixing boiling solutions of **5** and neutral TCNQ in acetonitrile and allowing the reaction mixture to cool slowly to room temperature:



General Procedure for the Preparation of the N-arylpyridinium-TCNQ-Complex-Salts 6

Together with the appropriate aniline (in a molar ratio of 1:3) the sodium salt of glucondialdehyde dihydrate (1-dihydrate) was stirred with a mixture of either ethanol or methanol and a 25% aqueous hydrochloric acid (2:1) at room temperature for three hours. The hydrochloride of the dianilide 2 was isolated, washed with cold methanol and dried over diphosphorpentoxide in vacuum at $50 \,^{\circ}$ C.

2 was refluxed for three hours in 25% aqueous hydrochloric acid, the solution and the solvent evaporated in vacuum. The residue was extracted several times with water at room temperature, whereby the water evaporated in vacuum. The oily product was dissolved in ethanol with an excess of sodium iodide (in the case where a dark brown oily layer appears under addition of charcoal), shortly refluxed, and the hot solution was filtered.

The N-arylpyridinium-iodide 4 formed either a precipitate after cooling the ethanolic solution, or was isolated by evaporation of the ethanol, extraction of the residue with hot chloroform and evaporation of the chloroform. The product was dissolved in ethanol, precipitated by drop-wise addition of ether and dried over diphosphorpentoxide at $50 \,^{\circ}$ C in vacuum.

5 was shortly refluxed with LiTCNQ (molar ratio 1:1) in a methanol/water mixture (10:1). After cooling to $5 \,^{\circ}$ C the N-arylpyridinium-TCNQ-salt 5 was collected, washed with cold methanol and dried over diphosphorpentoxide at $50 \,^{\circ}$ C vacuum.

Two boiling acetonitrile solutions of 5 and neutral TCNQ (molar ratio 1:1) were joined and after allowing the reaction mixture to cool slowly to room temperature the resulting N-arylpyridinium-TCNQ-complex-salt 6 was collected, washed with cold acetonitrile, and dried over diphosphorpentoxide at $50 \,^{\circ}$ C in vacuum.

General Characterization

The main results of samples characterization are collected in Tables 1 and 2 where the appearance of the samples, their

No.	Donor	Structural formula	Conduct. S/cm ⁻³	E _A /eV	TCNO⁰ TCNQ⁻	Abbreviation	Appearance
1	N-Phenylpyridinium		1.6	0.04	1.05	PhPy	needle
2	N-(p-methylphenyl)pyridinium		0.82	0.12	1.15	p-MePhPy	needle
3	N-(p-ethylphenyl)pyridinium		0.81	0.12	1.20	p-EtPhPy	needle
4	N-(p-methoxyphenyl)pyridinium		1.6	0.06	1.25	p-MeOPhPy	needle
5	N-Biphenylpyridinium		0. 62	0.10	1.00	BiPhPy	needle
6	N-(p-nitrophenyl)pyridinium		1.4*10 ⁻³	0.38	1.10	p-NiPhPy	block/needle
7	N-(o-methylphenyl)pyridinium		0.57	0.08	0.55	o-MePhPy	block
8	N-(o-methoxyphenyl)pyridinium		1.3	0.05	1.15	o-MeOPhPy	block
9	N-Naphtylpyridinium		0.62	0.11	1.00	NaPy	block/plate

Table 1

conductivity and the structural parameters, determined from X-ray powder diagrams and from the STM images, are presented. The stoichiometry of the TCNQ complexes was deduced from the $TCNQ^0/TCNQ^-$ ratio. For the majority of the complex salts the corresponding values are close to 1 (Table 1). Thus, the stoichiometric donor/TCNQ ratio in these compounds can be regarded as 2.

The appearance of the prepared TCNQ complexes as well as the structural formula of the donors are presented in Table 1. Their substituents are different in nature and size. Microphotographs of four typical crystals are shown in Figs. 1A-1D. All compounds can be divided into two groups according to their shape. Many of the crystals ap-

Table 2

Main periodicities determined by STM, X-ray and the calculated inclination angle

No.	Period 1 STM	Period 2 STM	X-ray	Inclination angle	
1	1.35±0.05	0.40 ± 0.03	0.65 0.34 0.32	32	
2	1.28 ± 0.03	0.43 ± 0.03	0.63 0.32 0.83	42	
3	1.46 ± 0.06	0.45 ± 0.01	0.64 0.65 0.34	41	
4	1.41 ± 0.3	0.43 ± 0.03	0.64 0.33 0.66	40	
5	3.83 ± 0.03	0.43 ± 0.02	0.63 0.34 0.31	38	
6	1.44	0.43			
7	0.96 ± 0.03	0.89 ± 0.06	0.66 0.32 0.32		
8	0.97 ± 0.09	0.41 ± 0.01	0.68 0.35 0.32		
9	0.89 ± 0.04	0.68 ± 0.05	0.64 0.32 0.32		

pear as thin elongated platelets, needles, (complexes 1-6, group I) with their width being in the range from several to tens of microns, Figs. 1A-1B. The other crystals (complexes 7-9, group II) have the shape of more defined and wider platelets, Figs. 1C-1D. It will be shown below that the appearance of the crystals has a definite correlation with the molecular structure.

The conductivity measurements show that most of the complex salts have an electrical conductivity of about 1 Scm^{-1} and an activation energy of lower than 0.1 eV, calculated by the equation

$$\sigma = \sigma_0 \mathrm{e} \frac{-E_\mathrm{A}}{2kT} \ .$$

Some compounds (e.g. No 6 and some other substituted complex salts [16]) have a value of σ of around 10^{-3} Scm⁻¹ and an activation energy of $E_A \approx 0.4$ eV [16]. The plot of log σ against 1/T follows an exact linear function.

A precise X-ray determination of the crystalline structure was impossible for the tiny crystals of the prepared salts. In such cases X-ray powder diagrams give a definite structural information, being in many respects a "finger print". Typical diagrams of the compounds of groups I and II are presented in Fig. 2. They show definite similarities in the positions of the most pronounced crystallographic reflexes.



Optical microphotographs of several TCNQ complex salts with substituted biphenyl pyridinium cations: A - BiPhPy, B - p-MeoPhPy, C - o-MePhPy, D - o-MeOPhPy

A detailed interpretation of the diagrams is difficult, and in many respect ambiguous due to several non-controlled experimental factors such as scattering and reflection effects. The most prominent peaks are collected in Table 2. The correlation of the powder diagram peaks with the structural parameters and the STM data will be discussed below.

STM Images

The complex salt of TCNQ with quinolinium, $QN/TCNQ_2$, is one of the first discovered organic conduc-

tors. The crystallographic structure of QN/TCNQ₂ is known [17], the chemical structure of the donor and the stoichiometry are similar to those of the discussed compounds. Fig. 3 A shows the structure of QN/TCNQ₂ within one unit cell viewed along the *b* axis. These crystals have a monoclinic structure (a = 2.8468 nm, b = 0.3838 nm, c = 2.5704 nm, and $\beta = 113.64^{\circ}$) and a needle-like shape similar to the compounds of group I. The structure consists of columns of donors and acceptors aligned along the *b* axis. In bulk each quinolinium column is surrounded by six TCNQ columns. In these columns the molecules are stacked







in a plane-to-plane manner. The molecular planes of the TCNQ and QN molecules are differently inclined with respect to the bc plane, the corresponding angles are 32.9° and 24.3°, respectively. The interplanar spacing within the TCNQ and QN stacks is 0.322 and 0.350 nm, respectively. The peak in the X-ray diagram of QN/TCNQ₂ (0.3226 nm) is related to the interplanar distance in the TCNQ stack. Consequently, the short intermolecular distance indicates on the strong electronic interactions within a TCNQ stack. The same correlation has been found in other TCNQ complex salts [7]. This means that the reflexes around 0.32 nm found in the powder diagrams of the TCNQ complex salts can be assigned to molecular stacks. Among different molecular sheets, which can appear in the topmost layer of the bc plane, the structure of the TCNQ layer (Fig. 3B) is the most relevant for the STM image [11]. Since QN/TCNQ₂ is a single chain conductor we believe the conducting TCNQ layer to be probed by STM. Moreover, a surface made up of QN cations is expected to be less stable because of its loose packing.

The STM image of QN/TCNQ₂ is shown in Fig. 3 C. The bright rows of patterns along the longest crystal direction correspond to molecular stacks. The periodicities along the stack (0.38 nm) and in the perpendicular direction (2.5 nm) are close to the crystallographic b and c constants, confirming the assignment of this surface to the bc plane. The inclination of the TCNQ plane, estimated from the X-ray reflex (0.322 nm) and the repeat distance along the stack, 32°, is close to the crystallographic value. The $\rho(r_0, E_F)$ plot of the TCNQ layer in the bc plane (Fig. 3D), calculated in the framework of the extended Hückel tight binding method, is similar to the image. The calculation details were reported elsewhere [10-12]. Thus, the STM patterns correspond to the "hills" of electron density localized on the

TCNQ stack. Similar "triplets" on two N atoms of the cyanogroups and between them were found in the STM image and the $\rho(r_0, E_F)$ plot of TTF/TCNQ [11].

It is reasonable to predict the existence of molecular stacks of donor and acceptor molecules in the TCNQ complex salts with substituted phenyl pyridinium cations. In addition to the high conductivity and the low activation energy [16] this proposal is based on the crystallographic data. The prominent peaks corresponding to the periodicities in the range of 0.321 - 0.326 nm, were found in the X-ray powder diagrams. They might be assigned to the interplanar distances in the TCNQ stacks. In the STM images of several salts these stacks have been observed, Figs. 4-6. By analogy to the shape of the crystals these images can be separated in two groups according to the main features and their repeat distances. Linear rows of patterns are the main features observed in the STM images of compounds of group I, Figs. 4-5. The images of the other salts (Figs. 6A - 6C) do not show a pronounced direction in the arrangement of the atomic-scale patterns, with one exception (Fig. 6b). The classification of the examined compounds into two groups according to their appearance and the STM images correlates with the chemical structure of the donors. The donors of the salts of group I have a linear molecular structure, while those of the other compounds are non-linear due to the positions of the substituents. The variations of the bulk conductivities of the pressed samples of both groups are not so evident. Their images, however, were recorded at different tunneling conditions that indicates on a higher surface conductivity of the elongated crystals.

All images can be characterized by two-dimensional lattice parameters. The main periodicities were chosen in orthogonal directions. Their values are presented in Table 2.



Figs. 3A-3D

(A) Perspective view of the crystal structure of QN/TCNQ₂ along the b direction (B): The crystallographic structure of the bc plane of QN/TCNQ₂, calculated from the X-ray data. The uppermost atoms lying in a layer of 0.4 nm thickness are shadowed by a bright contrast. (C): Atomic scale STM image of QN/TCNQ₂. Some of the STM patterns are emphasized by opened circles. The grey-coded contrast indicates variations in the z-direction perpendicular to the examined surface which are proportional to ln (I_{tun}). (D): $\rho(r_0, E_F)$ plot calculated for the TCNQ layer of the bc plane of QN/TCNQ₂. The contour values used are 300, 200, 100, 50, 10, 5 and 1×10^{-5} electrons/au³. The N atoms of the TCNQ molecule are represented by the large circles, and the C atoms by the small circles

Images of the salts of group I are shown in Figs. 4A - 4Cand Figs. 5A - 5D. The repeat distances along the stack direction are in the range of 0.40 - 0.45 nm, whereas the periodicities along the almost perpendicular directions are in the range of 1.3 nm - 1.4 nm, with one exception. These parameters can be regarded as the crystallographic constants of the corresponding TCNQ complex salts. As in the case of QN/TCNQ₂ we can expect that the conducting TCNQ layers have been imaged because the non-conducting cations sheets are usually more easily removed from the surfaces during scanning [12, 13]. Following the idea that the rows of the most pronounced "hills" in the STM images show the local density of electronic states, $\rho(r_0, E_F)$, of the TCNQ stacks, the different stack periodicities indicate on



the various inclinations of the TCNQ planes with respect to the examined surface. The inclination angles were calculated from the STM periodicities and X-ray reflexes in the powder diagrams, Table 2. The separation between the TCNQ stacks is related to the geometry and the orientation of the donor molecules in this plane. This parameter is responsible for the conductivity in the direction perpendicular to the stack, and it determines the degree of anisotropy.

The first three images (Figs. 4A-4C) are similar in details, with bright stacks consisting from two or one patterns (Fig. B). This arrangement is similar to that found in the STM images of the complex salt of TCNQ with 4EP [7]. The STM patterns along a stack are different from the



triplets of the $\rho(r_0, E_F)$ "hills" observed in the TTF/TCNQ and QN/TCNQ₂ images. Variations of the electron density distribution along a stack can be related with slight differences in the positions of the TCNQ molecules.

The STM images presented in Figs. 5A - 5D belong to compounds, which seem to be rather interesting for further investigations. The observed dimerization of patterns along the stacks in the STM image of the complex salt of TCNQ with p-MeOPhPy can be explained by specific electronic interaction between neighbouring TCNO molecules. We have observed similar effects in the case of the fluoranthenyl radical cation salt with PF_6^- [8]. It appears that this effect is more pronounced in the distribution of the electron density than in the crystallographic structure. In addition to the dimerization, variations of configuration of the patterns between the most pronounced stacks were found in the image (Fig. 5A). A tentative explanation of this effect might be based on the possibility of two different conformations of the methoxy group in the donor molecule. Both findings should be checked by other methods.

The STM image of the TCNQ-BiPhPy complex salt (Fig. 5B) shows well resolved features with separations of 0.15-0.35 nm. In this image the periodicity between the stacks (3.8 nm) is bigger than in the other compounds and correlates with the double length of a donor. Probably, two donor molecules are lying perpendicular to the TCNQ stack. Due to the correlations found, this salt is most suitable for molecular modeling calculations of its crystal structure.

Crystals of two various shapes (needles and platelets) were found after the preparation of complex salts of TCNO with p-NtPhPy. It is reasonable to assume the existence of two different crystallographic modifications in this compound. The corresponding STM images show different periodicities, and in addition, a superstructure was found in the image of the platelet-like crystal (Figs. 5C - 5D). In the image of the needle-like crystal the periodicity in the direction orthogonal to the stack was the smallest among the compounds of group I. The variation in contrast of every fourth pattern along the stack in the STM image (Fig. 5D) might be associated with charge density waves. This proposal should be checked by other technique. The proposed classification of the examined complex salts and their STM images into two groups is not very strict. The image of o-MeOPhPy (Fig. 6B, group II) can be assigned to both groups. There is one pronounced direction in this image, however, the intensity of neighbouring patterns along this stack varies, and the unit cell parameters are different from those found in the images of the group I. Several local defects are distinguished in this image. They can be related to missing molecules in the surface layer and the correspon-

Figs. 4A-4C

STM top view images of the main planes of (A): PhPy, (B): p-EtPhPy and (C): p-MePhPy. Tunneling conditions: (A) $U_{tun} = 119.6 \text{ mV}$, $I_{tun} = 3.1 \text{ nA}$; (B) $U_{tun} = 73.5 \text{ mV}$, $I_{tun} = 1.2 \text{ nA}$; (C) 202 mV, $I_{tun} = 0.4 \text{ nA}$. The upper left corners of the images are shown after 2D-FFT



Figs. 5A-5D

STM top view images of (A): p-MeOPhPy, (B): BiPhPy, (C and D): p-NiPhPy. Tunneling conditions: (A) $U_{tun} = 66.2 \text{ mV}$, $I_{tun} = 0.8 \text{ nA}$; (B) $U_{tun} = 100.1 \text{ mV}$, $I_{tun} = 1.0 \text{ nA}$; (C) $U_{tun} = 50.0 \text{ mV}$, $I_{tun} = 2.0 \text{ nA}$ and (D) $U_{tun} = 446.8 \text{ mV}$, $I_{tun} = 0.76 \text{ nA}$. The upper left corners of the images are shown after 2D-FFT

ding disturbances in the electron density nearby vacancies. Such defects are the most frequent on the surfaces of organic conductors [20]. The studies of surface defects is an important issue in the field of organic conductors, however, they were beyond the scope of this contribution, and for this presentation images of more perfect surface areas were chosen.

The STM images of the crystals of the group II, Figs. 6A-6C, do not show the existence of molecular stacks on the largest faces. The presence of molecular stacks can be assumed from the X-ray powder diagrams, where periodicities around 0.32 nm were found. In these compounds they are probably hidden within the crystals. This might explain the lower surface conductivity in the group II compounds. A similar situation, when molecular stacks are not on the surface, was found in one of the 4EP/TCNQ_2 crystal modifications and in complex salt of TCNQ with triethylammonium [6, 7]. In these cases the STM patterns and calculated $\rho(r_0, E_F)$ patterns coincide with positions of surface atoms [11].

Conclusions

In addition to traditional methods (optical microscopy, conductivity measurements and X-ray diffraction) STM was applied for the characterization of new conductive complex salts of TCNQ with substituted phenyl pyridines. STM provides the surface maps of the electronic density at the Fermi level, which determines the chemical ability to accept and donate electrons. We have shown that this tech-







Figs. 6A – 6C

STM top view images of the main planes of (A): o-MePhPy, (B): o-MeOPhPy and (C): NaPhPy. Tunneling conditions: (A) $U_{tun} = 467.8 \text{ mV}$, $I_{tun} = 0.3 \text{ nA}$; (B) $U_{tun} = 300.0 \text{ mV}$, $I_{tun} = 0.89 \text{ nA}$; (C) $U_{tun} = 150.1 \text{ mV}$, $I_{tun} = 0.61 \text{ nA}$. The upper left corners of the images are shown after 2D-FFT

nique can be also used for structure characterization of conducting crystals, for which a detailed crystallographic analysis was not possible. In particular, the surface partial electron density associated with the stacks of TCNQ has been imaged and structural parameters have been determined.

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