Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Assembly of 2D ionic layers by reaction of alkali halides with the organic electrophile 7,7,8,8-tetracyano-p-quinodimethane (TCNQ)

Christian Wäckerlin,[a] Cristian Iacovita,[b] Dorota Chylarecka,[a] Petra Fesser,[c] Thomas A. Jung*,[a] and Nirmalya Ballav*,[d]

[a] *Laboratory for Micro- and Nanotechnology, Paul Scherrer Institute, 5232 Villigen, Switzerland. E-mail: nballav@iiserpune.ac.in; thomas.jung@psi.ch; Fax: +41-56-310-2646; Tel: +41-56-310-4518*
[b] *Department of Physics, University of Basel, 4056 Basel, Switzerland*
[c] *Laboratory for Organic Chemistry, Department of Chemistry and Applied Biosciences, ETH Zürich, 8093 Zürich, Switzerland*
[d] *Indian Institute of Science Education and Research, Pune 411008, India*

Addition of LiCl onto TCNQ/Au(111)

The STM image of the TCNQ+LiCl/Au(111) system (Fig. S1) exhibits a similar arrangement to TCNQ+NaCl/Au(111) system. XPS data for TCNQ+LiCl/Au(111) in submonolayer and multilayer regimes are shown in Fig. S2. In both, the NaCl and LiCl case, a significant decrease in N1s binding energy is observed after deposition of the ionic compound. Furthermore the C1s peak shape is modified consistently, as discussed in the main text for the TCNQ+NaCl/Au(111) sample.

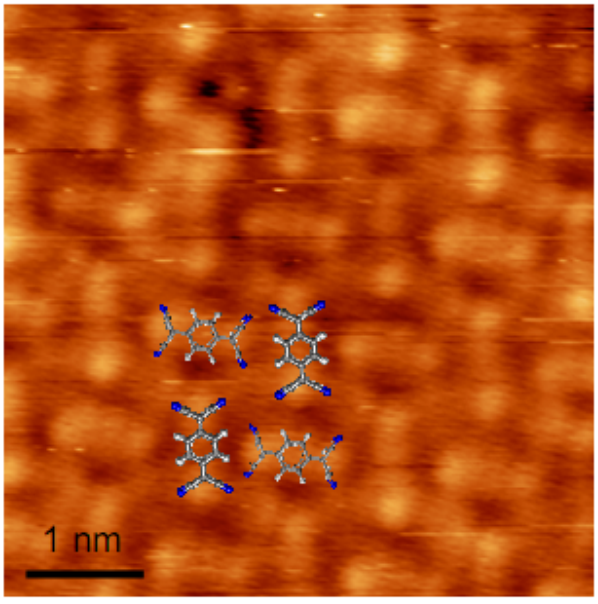

Figure S1: STM image of TCNQ molecules on Au(111) surface with subsequently evaporated LiCl.

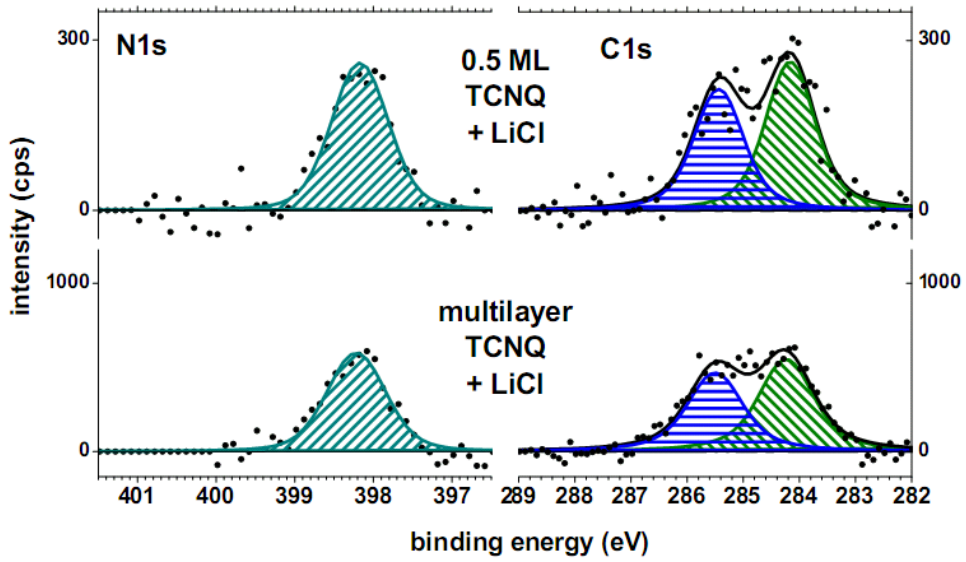

Figure S2: XPS data for TCNQ+LiCl/Au(111) in a submonolayer and multilayer regime.

Bias dependent STM of TCNQ+NaCl/Au(111)

Fig. S3 shows STM images of TCNQ+NaCl/Au(111) obtained at three different bias voltages. Intra-molecular resolution as shown in Fig. 1c was obtained with bias voltages close to -1.45 V.

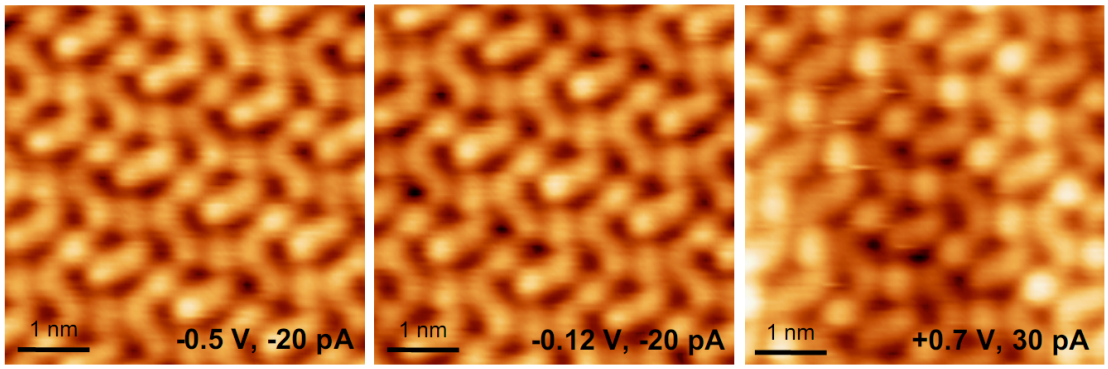

Figure S3: STM images of TCNQ+NaCl/Au(111) at different tunneling parameters

Dynamic vacancies in TCNQ/Ag(111)

Fig. S4 shows two subsequently taken STM images of TCNQ/Ag(111). By superposition of these two images the mobility of interstitial Ag can be visualized. Overlay data taken on the TCNQ/Ag(111) system displayed in Fig. 3. The numbers of vacancies are given in Tab. S1.

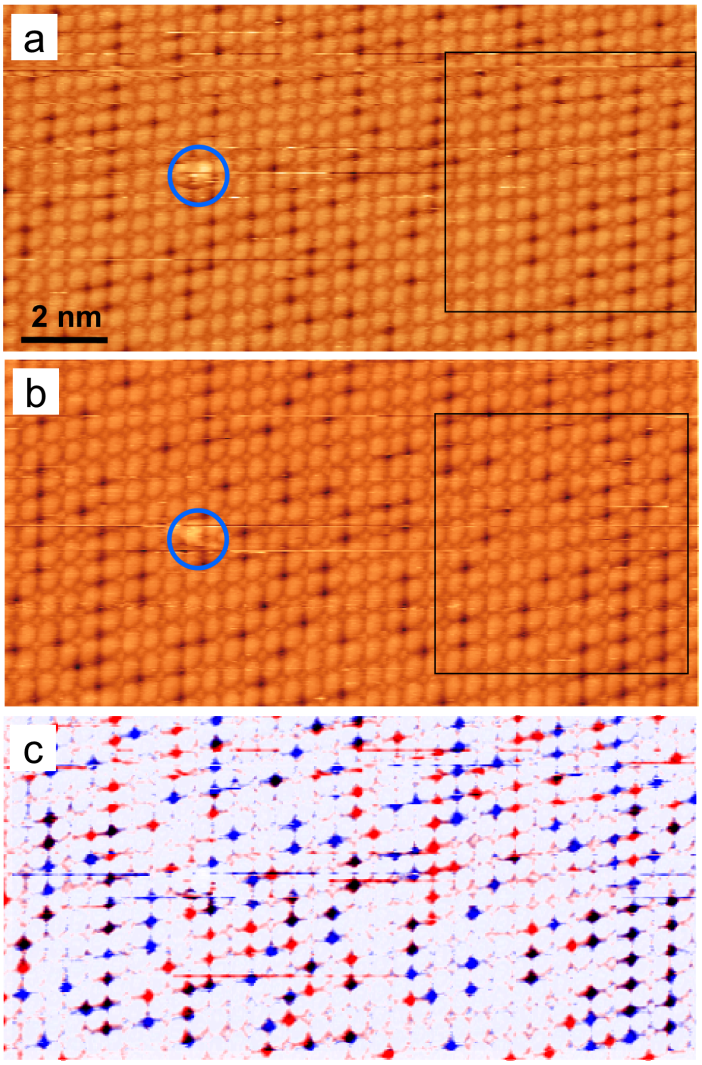

Figure S4: STM data of TNCQ/Ag(111). The two images a) and b) were recorded within 2 minutes. A differential visualization of the vacancies is shown in c). Black dots correspond to vacancies observed in both images, red dots indicate the vacancies appearing in the second image, while blue dots reveal the vacancies visible in the first image and disappearing in the second image. A prominent defect is marked (blue circle) to illustrate that the same sample area has been measured. The rectangular black frames denote the section of the data chosen in preparation of Fig. 3 in the main text to support the frustrated dynamics of the ionic layer.

	Number	Percentage
Total (vacant + full)	421	100 %
vacancies in a)	122	29.0 %
vacancies in b)	123	29.2 %
vacancies observed in both a) and b)	53	12.6 %

Table S1. Numbers of occupied and vacant sites in TCNQ/Ag(111) from Fig. 3

Experimental conditions

The experiments have been performed in ultra-high vacuum environment in a multi-chamber system with a base pressure in the order of 10^{-10} mbar. Au(111) and Ag(111) single crystals were cleaned by repeated sputtering / annealing cycles until no O1s and C1s peaks were observable in the XP spectrum. TCNQ and NaCl/LiCl (Sigma-Aldrich) were sublimed consecutively (first TCNQ and then NaCl) in a 1:2 molar ratio onto single crystals kept at room temperature. The deposition rate was monitored by a quartz crystal microbalance and the monolayer coverage was confirmed by XPS and STM. XPS has been measured using monochromatic Al Kα line. The full with half maximum of the $Au4f_{7/2}$ peak was 0.8 eV.

Valence spectra have been acquired using UV light generated by He I excitation (21.22 eV) and with an applied sample bias of ~-9 V. STM measurements have been performed at room temperature in constant current mode using electrochemically etched and in-situ sputtered tungsten tips. The respective tunneling parameters are given in Tab. S2.

Figure	**Sample**	**Bias voltage (V)**	**Tunnel current (pA)**
1a	TCNQ/Au(111)	-0.7	-10
1a (inset)	TCNQ/Au(111)	1.95	50
1b	TCNQ+NaCl/Au(111)	-1.3	-30
1c	TCNQ+NaCl/Au(111)	-1.45	-20
3; S4	TCNQ/Ag(111)	-0.5	-50
S1	TCNQ+LiCl/Au(111)	-0.9	-10
S3a	TCNQ+NaCl/Au(111)	-0.5	-20
S3b	TCNQ+NaCl/Au(111)	-0.12	-20
S3c	TCNQ+NaCl/Au(111)	0.7	30

Table S2 Tunneling parameters used in the generation of the STM images shown.