Supplementary Information

Charge Transfer-Assisted Decyanation Reaction of TCNQ-type Electron Acceptors on Cu(100)

Christian Urban,^a Yang Wang,^{b,c} Jonathan Rodríguez-Fernández,^a Raúl García,^d M. Ángeles Herranz,^d ⁵ Manuel Alcamí,^c Nazario Martín,^{b,d} Fernando Martín,^{b,c} José M. Gallego,^{b,e} Rodolfo Miranda,^{a,b} Roberto Otero*^{a,b}

Experimental and Computational Details.

Experimental Procedures: Film growth and STM and XPS investigations were carried out in ultrahighvacuum (UHV) conditions, with a base pressure of $\sim 2 \times 10^{-10}$ torr. Atomically flat, crystalline Cu(100) surfaces were prepared by standard sputter/anneal procedures (sputter with 1 kV Ar⁺ ions for 15 min followed by annealing to 800 K for another 15 min), resulting in large terraces (~200 nm wide) separated by monoatomic steps. The molecules were deposited from a low-temperature Knudsen cell, heated at 460 K, onto the clean ¹⁵ Cu(100) substrate, which was held at room temperature.

The UHV vacuum chamber was equipped with a variable temperature "Aarhus" type STM purchased from SPECS. STM measurements were performed both at low temperature (100 K) and at room temperature, with tunneling conditions chosen so as not to disturb individual molecules ($V_b \sim 1-2$ V, $I_t < 0.5$ nA). From the STM ²⁰ chamber, the samples were transferred in-situ to the XPS chamber, were photoemission spectra were recorded using Al K α X-rays of 1486.7 eV with an ellipsoidal monochromator, also from SPECS. STM images were taken both before and after the X-ray measurements, to check for any possible influence of the radiation in the sample structure. No damage or structural change was found in any case.

Theoretical calculations: The Cu(100) surface was modeled by a four-layer slab of copper atoms allowing 25 the top two layers to relax. The molecules were placed on the surface in a 3D periodic unit cell, separated by 13 interlayer distances (~25 Å) of vacuum in the surface normal direction. The DFT calculations were carried out with the exchange-correlation functional of Perdew, Burke, and Ernzerhof (PBE)¹ using the Vienna ab-initio simulation package (VASP).² The projector-augmented wave (PAW) method³ was applied to describe the ionic ³⁰ cores. A Methfessel-Paxton smearing⁴ of 0.2 eV was used to calculate the occupation of electronic states. The Monkhorst-Pack scheme⁵ was utilized for the Brillouin-zone integrations. The cut off energy was set to 400 eV for the plane wave expansion. The atomic positions of the whole molecule and the top two surface layers were fully optimized using a conjugated-gradient algorithm until the forces on each ion are smaller than 0.02 eV $Å^{-1}$. At each ionic step of the geometry relaxation, the dispersion corrections following Grimme's DFT-D scheme⁶ $_{35}$ were included, as implemented in the VASP package. The geometry relaxations were performed using Γ -point and then the single-point calculations were performed afterwards using a $3 \times 3 \times 1$ k-point mesh. Atomic charges were computed based on Bader's analysis⁷ of the electron density (including the core charge) using the Bader analysis program for VASP. The constant-current STM images were simulated using the Tersoff-Hamann approximation.⁸

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STM images of the decyanation reaction.

In order to investigate the way in the decyanation reaction takes place, we have carried out a statistical analysis of the morphology of the sample as a function of annealing temperature. This analysis has been carried ⁴⁵ out for samples with different initial coverages. Figure S1 shows four representative images of samples annealed

to different temperatures (a and b have been annealed to 380 K, c to 460 K and d to 490 K) and different coverages. For these image sizes individual molecules can still be distinguished, and the number of missing lobes can be counted. Inspection of the STM images a) and b) reveals that the reaction is not significantly affected by the coverage, implying that the reaction mechanism involves only individual molecules and the substrate with the possible intermolecular interaction playing only a minor role. Subsequent increase in the

- substrate, with the possible intermolecular interaction playing only a minor role. Subsequent increase in the anneling temperature leads to an increased number of missing lobes, until all of them are missing for annealing treatments in excess of 490 K (d). Notice also that at this temperature the radicals are able to diffuse, and they form short oligomeric chains. It is also important to point out that the decyanation process does not seem no proceed by sequential elimination of the cyano groups, since both doubly and single decyanated species can be found at any appealing temperature
- ¹⁰ found at any annealing temperature.



Fig S1. Representative STM images at different annealing temperatures and initial coverages. a) and b) are STM images ($14.7 \times 17.2 \text{ nm}^2$ and $24.6 \times 29 \text{ nm}^2$ respectively) corresponding to samples with different coverages that have been annealed to the same temperature (380 K). Notice that the fraction of missing lobes does not seem to depend very strongly on the coverage. c) and d) ($9.5 \times 10.5 \text{ nm}^2$) show how the number of missing lobes increases with annealing temperature until they finally dissapear.

Estimation of the decyanation barrier from annealing experiments.

Table S1 shows the fraction of missing lobes after different annealing treatments have been applied to the TCPQ/Cu(100) sample. Information about the energy barrier has been obtained as follows: If r(T) is the (temperature-dependent) reaction rate, then annealing to temperature T for a time t must have affected s (statistically) to $1-e^{-r(T)t}$ molecules. Following Transition State Theory, the reaction rate can be assumed to show an Arrhenius dependence with temperature $r(T) = v_0 e^{-U/kT}$, where v_0 is the attempt frequency, U is the energy barrier for decyanation of the adsorbed TCPQ molecules and k is the Boltzmann constant. For each annealing procedure, an energy barrier can be estimated using these formulae for different values of the prefactor, which we choose between 10^{11} and 10^{13} s⁻¹. The results of such analysis are shown in Table S1. It can be observed that the choice of the prefactor does not significantly affect the obtained energy value, since a variation of two orders of magnitude only affects the value of U less than 0.2 eV. All the obtained values of U fit within such uncertainty. From our experimental data, the energy barrier for decyanation can thus be estimated as 1.2 ± 0.2 eV.

Sample	Т(К)	t(min)	Fraction of Missing Lobes	<i>r</i> (s⁻¹)	$v_0 (s^{-1})$	<i>U</i> (eV)
1	300	1440	< 10 ⁻²	< 10 ⁻⁷	10 ¹³	> 1
		(1day)			10 ¹²	> 1
					10 ¹¹	> 1
2	375	15	0.30	$4.0 imes 10^{-4}$	10 ¹³	1.18
					10 ¹²	1.11
					10 ¹¹	1.04
3	390	20	0.17	1.6×10^{-4}	10 ¹³	1.26
					10 ¹²	1.18
					10 ¹¹	1.11
4	395	20	0.36	$3.7 imes 10^{-4}$	10 ¹³	1.25
					10 ¹²	1.17
					10 ¹¹	1.09
5	455	20	0.68	$9.5 imes10^{-4}$	10 ¹³	1.40
					10 ¹²	1.31
					10 ¹¹	1.22
6	490	20	> 0.99	> 3.8 × 10 ⁻³	10 ¹³	< 1.45
					10 ¹²	< 1.36
					10 ¹¹	< 1.26

- ¹⁵ Table S1. Experimental values for the fraction of missing lobes for different annealing treatments, from which the reaction rates can be straightforwardly calculated. From the rates, estimations for the energy barrier can be obtained by assuming different prefactors, which are usual for surface dynamic processes. The lower bound for the energy barrier is obtained by noticing that no changes were found in the surface morphology within our statistical sample after waiting for one day at room temperature. The upper bound is estimated by
- noticing that no molecules were found to retain any lobe within our statistical sample by annealing to 490 K for 20 minutes.

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