Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for the Article “Structural origins of the cohesive energy in metal-terpyridine oligomer thin-films”

Velimir Meded,[§*] *Nikolaus Knorr, Tobias Neumann,*[§] *Wolfgang Wenzel,*[§] *Florian von Wrochem*[*]

Materials Science Laboratory, Sony Europe Ltd, Zn Deutschland,

Hedelfinger Strasse 61, 70327 Stuttgart, Germany

[§]*Institute of Nanotechnology, Karlsruhe Institute of Technology, 76021 Karlsruhe, Germany*

Content:

Chemicals. Chloroform (≥99.5%), ethanol (≥99.8%), mercaptobenzene (MB), 1,4-di(2,2',6',2''-terpyridine-4'-yl)benzene (TPT) (96%), 2,2′:6′,2″-Terpyridine (tpy) (98%), 4′-(4-Methylphenyl)-2,2′:6′,2″-terpyridine (ttpy) (98%) were purchased from Sigma-Aldrich and used without further purification. Iron triflate (98%) was purchased from Strem Chemicals. MPTP (4'-(4-mercaptophenyl)-2-2':6'2''-terpyridine) was synthesized and purified as described previously.[1]

AFM measurements. AFM scans for film thickness evaluation are performed with a Multimode Nanoscope IIIa (Digital Instruments) on bottom electrode structures as shown in Figure S1, i.e. on the electrodes after being grafted with the MCO oligomers. The scans are done along the direction perpendicular to the bottom electrodes, such that the height of the electrodes plus that of the MCO layers relative to the silicon wafer is measured. Knowing the thickness of the as-prepared Au electrodes from reference samples, the thickness of the films is deduced by means of AFM sections, yielding values as shown in Fig. S1. A complete set of Nanowear scans with center-line cuts for all the data points shown in Figure 4 can be found in Figure S2.

Theory: morphology generation. The electrostatic model is extracting positions of Fe^{II} and the counter ions from our atomistic calculations, as performed in Ref. [7]. In brief, as an input for the molecular mechanics simulations we use the 4'-(4-mercaptophenyl)terpyridine (MPTP) moiety with the sulfur atom located at the origin of the coordinate system (the sulfur is connected to the Au substrate in the experiment). The MPTP unit coordinates to a Fe^{II} redox center, which is again coordinating to a 1,4-di(2;2';6';2''-terpyridine-4'-yl)benzene (TPT) ligand (oligomer unit, see Fig. 1a). Both the geometry of the TPT unit and the triflate counter-ions are optimized with DFT using the BP86 exchange-correlation functional [2, 3] and the def-SV(P) basis set [4] with TURBOMOLE program package.[5] Atomistic point charges are fitted to optimally reproduce the quantum mechanical electrostatic potential of the system around the compound using the Kollman [6] fit, for details see Ref. [7].

The MCO layer structure is obtained from a Metropolis Monte Carlo[7] simulation as implemented in simulation package SIMONA[8] consisting of 10 Simulated Annealing (SA) cycles from 4000K to 200K, each consisting of 50000 MC steps. During the relaxation procedure, the only constraint was to fix the wire center of geometry in z direction (z=0) as to mimic the bond to the surface. More explicitly, the wires are allowed for rigid body rotations in all three dimensions as well as 2D translation in the xy-plane. The resulting structure shows a tight packing of the three wires (three being the minimum for a definition of the lattice parameters in xy-plane) with almost parallel orientation (the average angle between the molecular axis and the z-axis being 46.6±0. 6°) and lattice constants in the xy-plane of a = 1.64 nm and b = 1.17 nm, with the unit cell angle between them being 41º (see Ref.[9]). Notably, the angle of 46.6±0. 6° between the molecular axis and the z-axis is in excellent agreement with the experimental value obtained from the AFM height profiles (Fig. S1).

In Fig. S3 we present the dependence of the cohesive energy as function of the number of layers (number of oligomer units) and the displacement of the counter ions obtained within the electrostatic model. The graph displays robustness of the cohesive energy to both the length of the wire (lines with different colors) and the maximum displacement of the counter ions.

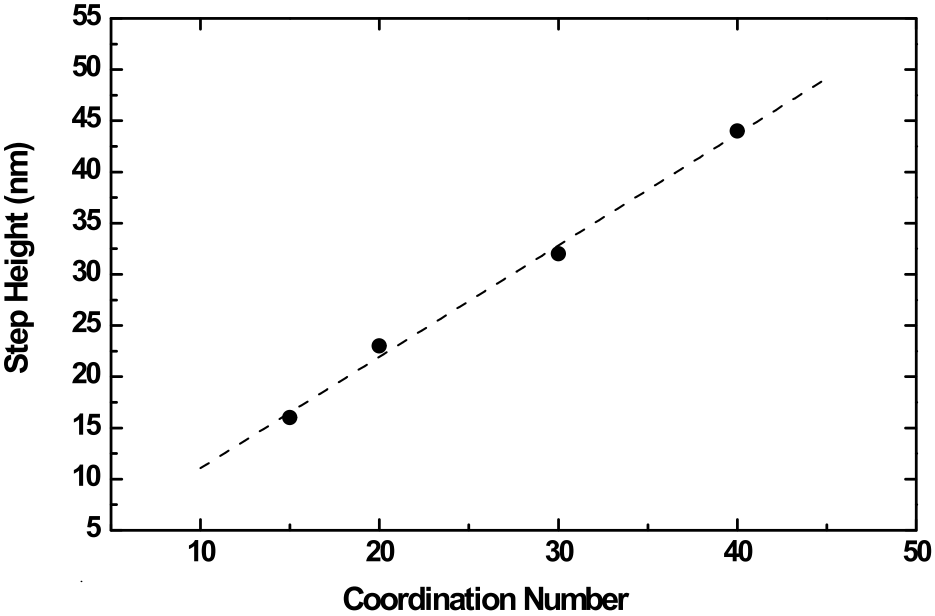

Figure S1: Dependence of step height on the number of deposition cycles determined from AFM height measurements. As samples, MCO oligomer layers with 4 different lengths, i.e. with 15, 20, 30, and 40 MC units are used in order to provide an accurate estimation of the topographic height increment/MC deposition by means of a linear fit to the AFM data. A linear fit to the data results in an increase of the MCO layer thickness by 1.08 nm/coordination number.

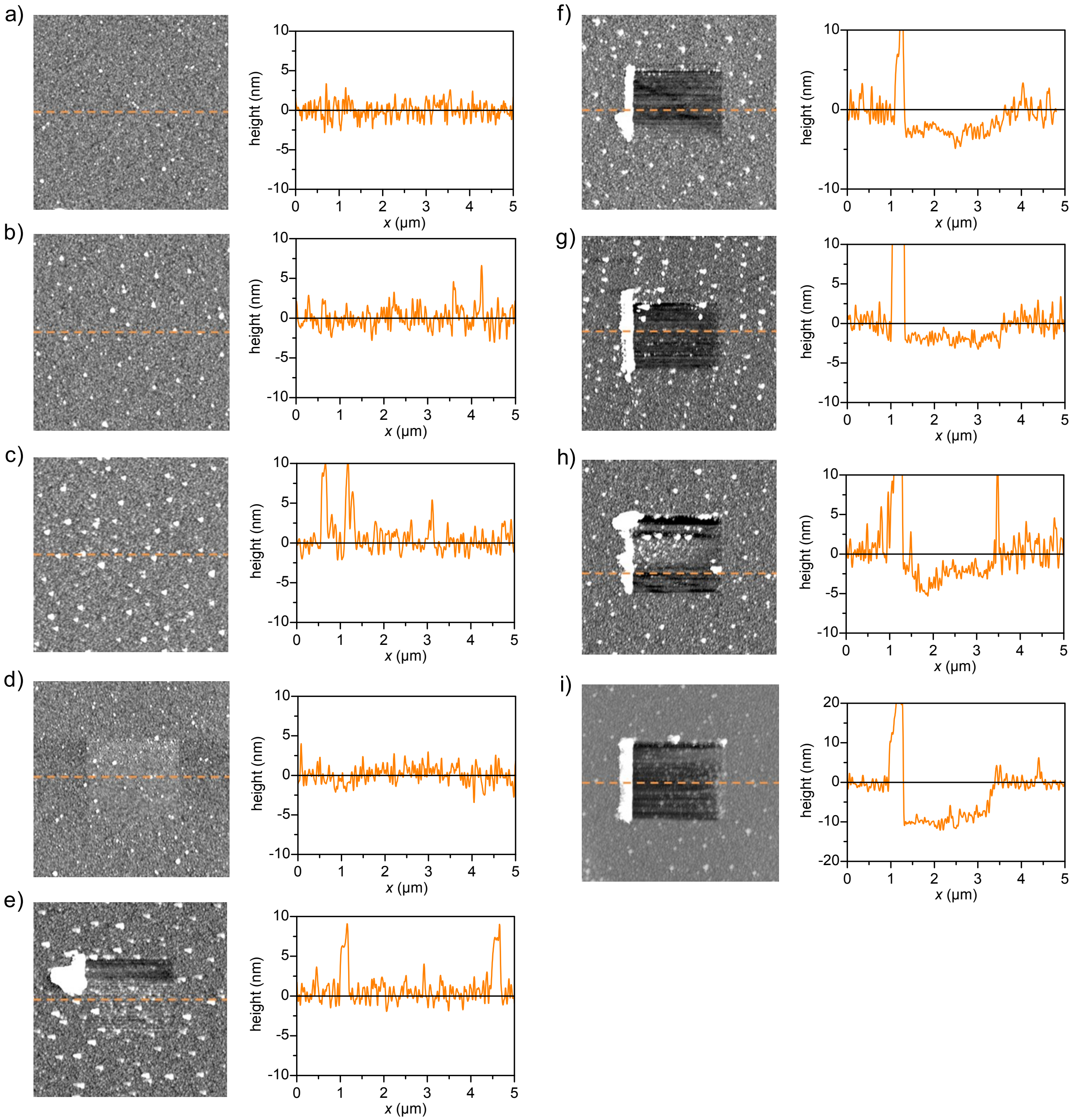

Figure S2: Complete series of topographic AFM surface scans (5 µm x 5 µm, left) and horizontal center line cuts of the pristine MCO surface (a) and of a 2 µm x 2 µm area subjected to wear with the load forces employed in this study, namely, 40 nN (b), 200 nN (c), 400 nN (d), 600 nN (e), 800 nN (f), 1 µN (g), 1.2 µN (h), and 2 µN (i). Grayscales: ±5 nm (from a to h) and ±15 nm (i).

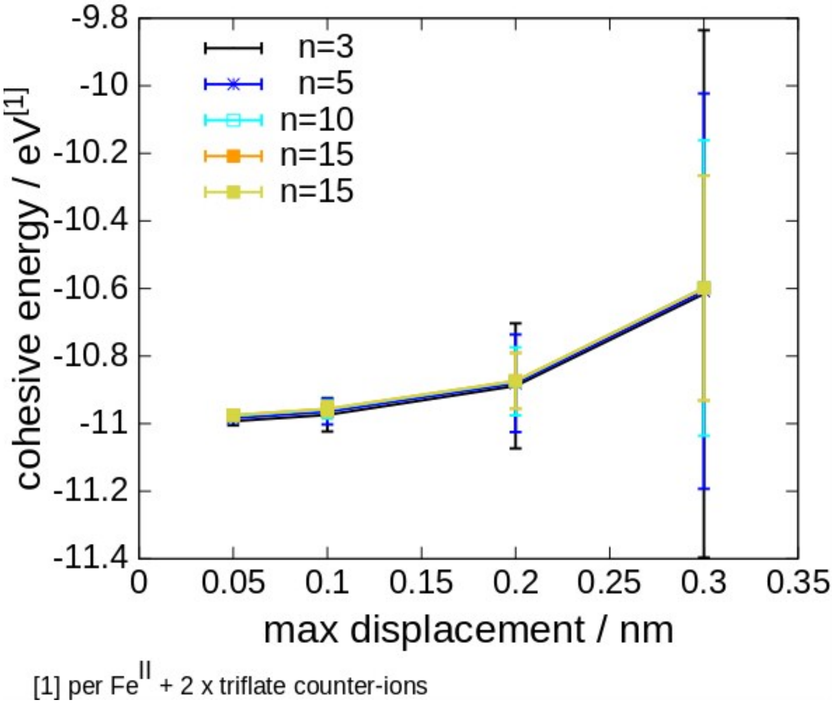

Figure S3: Cohesive energy in the electrostatic model (ESM) for different numbers *n* of layers (*i.e.* monomers, or lengths of MCMWs). Periodic boundary conditions are applied in the *xy*-plane. To test the energetic stability, the counter ions are shifted randomly from the initial position between the two Fe^{II}-redox centers. The resulting cohesive energy is averaged over 10^4 random initial configurations. For better comparison, resulting energies are divided by the number *n* of layers. We obtain a cohesive energy of E_{coh} = 10.98 eV. For the lowest maximal displacement with decreasing cohesion energy, indicating that the counter ion position between two redox centers represents the most stable configuration.

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