Electronic Supplementary Information

Precise tuning of single molecule conductance in electrochemical environment

L. -L. Peng[a], F. Chen[a], Z.-W. Hong[a], J.-F. Zheng[a], L. Fillaud[b], Y. Yuan[c], M. -L. Huang[a], Y. Shao[a], X.-S. Zhou*[a], J.-Z. Chen*[c] and E. Maisonhaute*[b]

[a] Key Laboratory of the Ministry of Education for Advanced Catalysis Materials, Institute of Physical Chemistry, Zhejiang Normal University, Jinhua, Zhejiang 321004 China. e-mail: xszhou@zjnu.edu.cn

[b] Sorbonne Université, CNRS, Laboratoire Interfaces et Systèmes Electrochimiques, LISE, F-75005, Paris, France. e-mail: emmanuel.maisonhaute@upmc.fr

[c] Department of Physics, Shanghai University, Shanghai 200444, China. e-mail: jingzhe@shu.edu.cn

Table of content

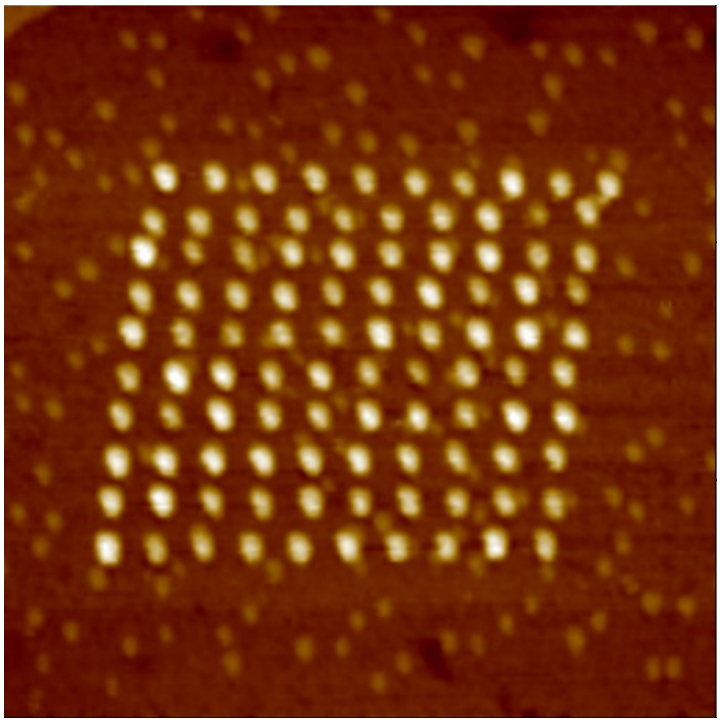

Fig. S1 Image of an array of Cu clusters realized during the EC-STMBJ experiment (150x150 nm^2).

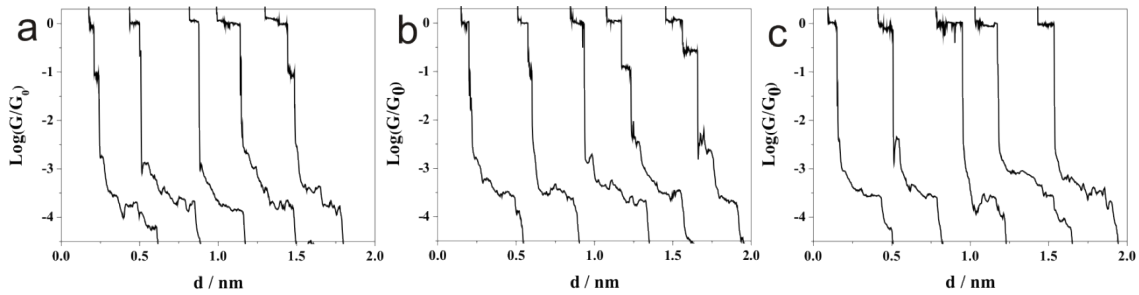

Fig. S2. Representative conductance curves obtained for [Cu^{2+}] = 10 mM (a), 1 mM (b) and 0.1 mM (c).

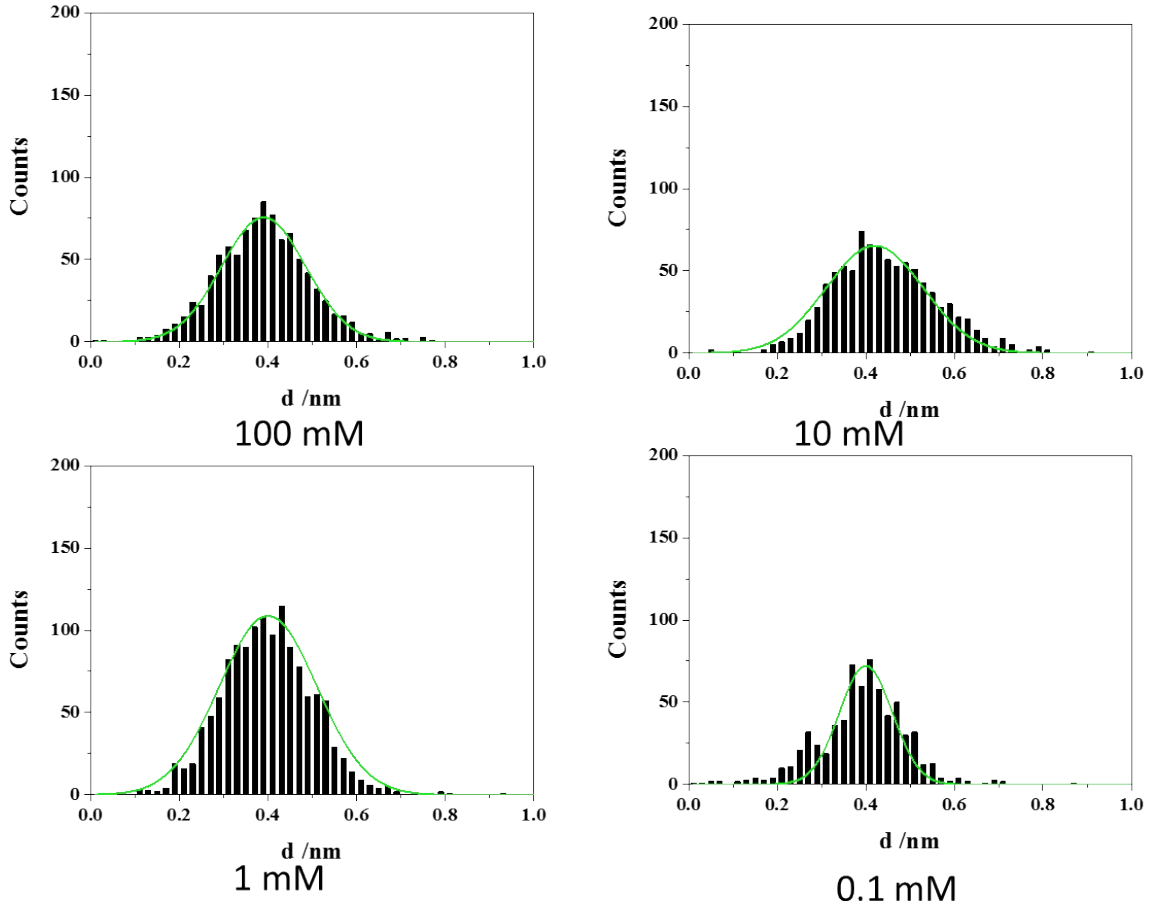

Fig. S3 Estimation of the breaking off distance obtained from conductance value of $10^{-4.8}$ G_0 to $10^{-0.3}$ G_0 (0.5 G_0) in every conductance curves at different concentrations. E_{tip} = -5 mV, $E_{substrate}$ = 45 mV.

Evaluation of the Nernst potential of Cu^{2+}/Cu (E_{Nernst})

E_{Ref} needs to be accurately defined in order to evaluate the average Fermi level $E_{F,\,av}$. For that, two possibilities were exploited:

1) In order to apply equation (4) of the main text, the activity coefficient γ^+ of Cu^{2+} ions needs to be calculated. For that, several theoretical approaches are available. Using Davies equation S1 we obtained the different values of $\log(\gamma^+)$ reported in Table S1.[1]

$$\log\left(\gamma^{+}\right) = -0.51 \times 4\left(\frac{\sqrt{I}}{1 + 3.29 \times 0.215 \times \sqrt{I}} - 0.3I\right) \qquad \text{(S1)}$$

Where I is the ionic strength. Table S1 provides the calculated $E_{Ref,\,calculated}$.

2) As described in the main text, E_{Nernst} may be also directly measured versus a true reference electrode, here a saturated calomel electrode. Table S1 evidences that $E_{Ref,\,calculated}$ and $E_{Ref,\,measured}$ are very close, which further demonstrates that no complexation of Cu^{2+} ions by the BDA that would also alter the potential occurs.

Furthermore, the calculated junction potential is less than 2 mV and can thus also be neglected.[2]

Table S1. Comparison between measured and calculated Nernst potentials

$[Cu^{2+}]$ (mol.L^{-1})	I (mol.L^{-1})	$\log(\gamma^+)$	$E_{Ref,\,calculated}$ (V *vs* SCE)	$E_{Ref,\,measured}$ (V *vs* SCE)
10^{-4}	0.1504	-0.529	-0.039	-0.031
10^{-3}	0.154	-0.532	-0.009	-0.008
10^{-2}	0.190	-0.563	0.019	0.022
10^{-1}	0.550	-0.656	0.046	0.045

Details about the NEGF-DFT quantum calculations

The first principle calculation part, including structural optimization and transport properties of the molecular junction is finished using SHINE (Shanghai Integrated Numeric Engineering) package, where a theoretical framework combining non-equilibrium Green's function method (NEGF) with density functional theory (DFT) is implemented.[3, 4] In this work, the initial structural configuration is set so that the molecule is attached to two small tips stretching from copper Fcc111 surfaces on both sides. The molecular junction is relaxed using DFT with LDA (local density approximation) functional. Because of the lack of periodicity along the transport direction, three copper buffer layers and a large vacuum region are added on each side of the junction, a (4,4) K-sampling is adopted for the transverse plane, with 12(3*4) atoms on each layer. The structure is relaxed until the maximum force on each atom is less than 0.05 eV/Å. The transport properties are calculated by the NEGF+DFT module with the same functional and K-sampling. LCAO (linear combination of atomic orbital) basis is used in both optimization and transport calculations. To achieve both accuracy and efficiency, double-zeta polarized (DZP) basis set is adopted for organic molecule and superficial copper atoms and single-zeta polarized (SZP) basis set is adopted for inner layers of the electrodes.

In these calculation, the bulk copper with a Fermi level of -4.65 eV below vacuum level is taken as a reference. E_{LUMO} stands 0.14 eV above this level, therefore at -4.51 eV vs vacuum. Otherwise, conversion between electrochemical potentials measured versus a reference electrode and Fermi energies measured versus vacuum is possible through equation (3) of the main text. This allows to compare experimental data to theoretical ones.

Fig. S4 presents the calculated transmission factor over a larger energy range compared to Fig. 6b of the main text. The electron densities at the LUMO (+0.14 eV vs Fermi level of Cu, -4.51 eV vs vacuum), for the transmission channel (0 eV vs Fermi level of Cu, -4.65 eV vs vacuum) and at the HOMO (-1.35 eV, vs Fermi level of Cu, -6.00 eV vs vacuum) levels are provided in Figs. S5a-c.

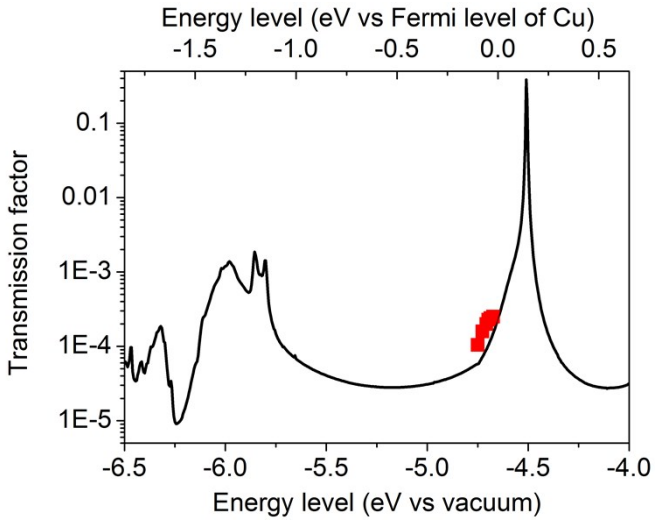

Fig. S4. Calculated (black line) and experimental (red squares) transmission factors as a function of the energy level.

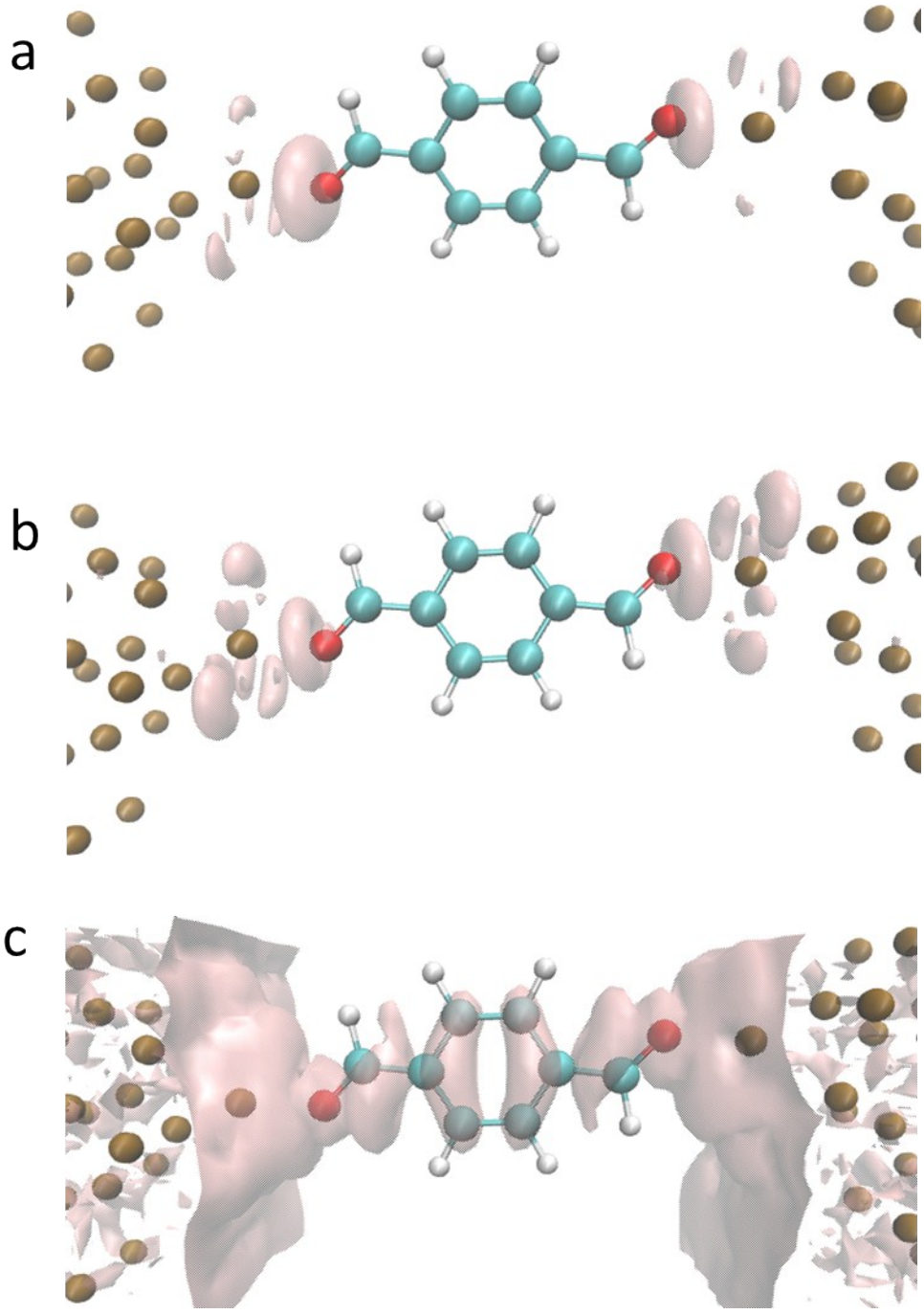

Fig. S5. a) Density distribution at E = 0.0 eV with an isodensity value of 0.006 electron.Bohr^{-3}, corresponding to the Fermi level of bulk copper (-4.65 eV vs vacuum). b) Density distribution at E = 0.14 eV with an isodensity value of 0.04 electron.Bohr^{-3}, corresponding mainly to the LUMO of BDA (-4.51eV vs vacuum level). c) Density distribution at E=-1.35 eV with an isodensity value of 0.016 electron.Bohr^{-3}, corresponding mainly to the HOMO of BDA (-6.00 eV vs vacuum level).

References

1. C. W. Davies, *Ion association*, Butterworths, London, 1962.
2. A. J. Bard and L. R. Faulkner, *Electrochemical Methods*, Wiley, New York, 2001.
3. J. Taylor, H. Guo and J. Wang, *Phys. Rev. B*, 2001, **63**, 13.
4. J. Z. Chen, K. S. Thygesen and K. W. Jacobsen, *Phys. Rev. B*, 2012, **85**, 9.