

On shuttling mechanism of the chlorine atom in chloroaluminum phthalocyanine based molecular switch

Huanjun Song,^a Cenfeng Fu,^b Na Li,^c Hao zhu,^a Zhantao Peng,^a Wenhui Zhao,^a Jingxin Dai,^a Lingbo Xing,^a Zhichao Huang,^a Wei Chen,^d Yongfeng Wang,^{*c} Jinlong Yang,^{*b} and Kai Wu^{*a}

^a BNLMS, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China. E-mail: kaiwu@pku.edu.cn

^b Department of Chemical Physics, School of Chemistry and Materials Science, University of Science and Technology of China, Hefei 230026, China. E-mail: jlyang@ustc.edu.cn

^c Key Laboratory for the Physics and Chemistry of Nanodevices, Department of Electronics, Peking University, Beijing 100871, China. E-mail: yongfengwang@pku.edu.cn

^d Department of Chemistry, National University of Singapore, Singapore 117543, Singapore

Fig. S1 shows surface mobility of the U1 and U2 molecules during image scanning. Fig. S1a shows the initial positions of individual CIAIPc molecules at a sample bias of 1.0 V. The bias voltage was afterwards decreased to 0.1 V, which means the tip approached closer to the imaged molecules in Fig. S1a. Fig. S1b shows that the U1 and U2 molecules in the lower right area in the image have moved with respect to Fig. S1a. If the bias changed to 1.0 V again, the U1 and U2 molecules in the lower right area in the image also moved, as shown in Fig. S1c. As a reference, all D molecules were immobile during the whole scanning process, indicating that the D molecules are more stable than the U1 and U2 molecules.

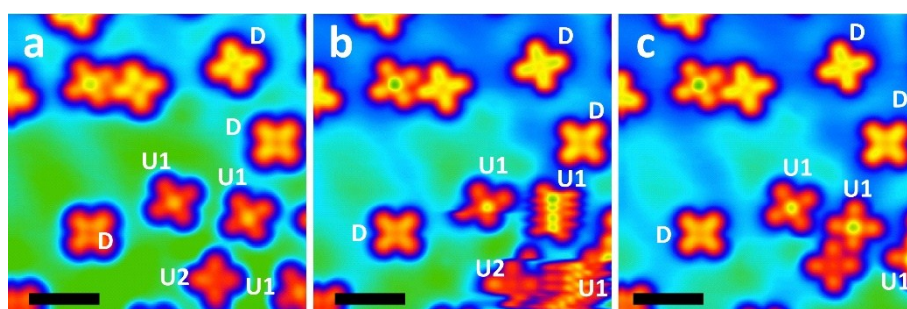


Fig. S1. Motions of the U1 and U2 molecules during the scanning at different sample biases. (a) STM image of the initially adsorbed molecules at surface. $V_{\text{bias}} = 1.0$ V $I_{\text{set}} = 100$ pA; (b) STM image of the monitored molecule during scanning when the STM is brought closer to the molecule. $V_{\text{bias}} = 0.1$ V $I_{\text{set}} = 100$ pA. (c) STM image of the monitored molecule after a period of time. $V_{\text{bias}} = 1.0$ V $I_{\text{set}} = 100$ pA. Scale bars: 2 nm.

Fig. S2 shows the switching process of a monitored CIAIPc molecule on Au(111). The Cl-up molecule in U1 configuration highlighted by the dashed circle in Fig. S2a is

switched into the D configuration (Fig. S2b) by an applied tip pulse. The generated D molecule was then switched back to the U1 configuration again, verifying that the CIAIPc molecule was not damaged by the applied tip pulse, and the Cl atom did not leave the CIAIPc molecule.

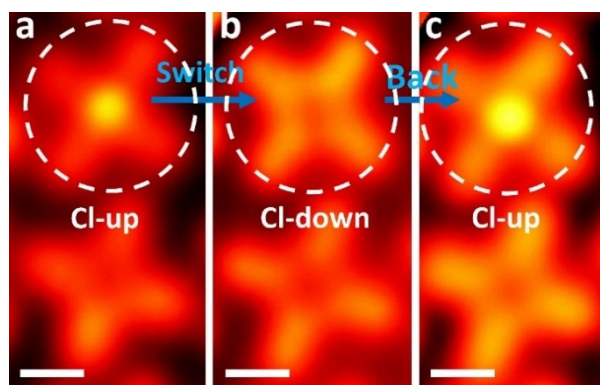


Fig. S2. STM images showing the shuttling process of the Cl atom through the Pc plane. The monitored Cl-up CIAIPc molecule (U1 configuration in the dashed circle) in (a) switches to the Cl-down configuration (b) and back to the Cl-up configuration again (c). Blue arrows refer to the switching sequence. Imaging conditions: constant height mode, $V_{\text{bias}} = 0.1\text{V}$. Scale bars: 0.5 nm.

Fig. S3 shows that the tip-pulse-generated N intermediate from U2 molecule switches back to the U2 configuration again by a sample bias of -1.6 V applied on the center of the N intermediate. Again, this experiment demonstrated that the CIAIPc molecule did not break during the forced conformational transition process from the U2 configuration to the N intermediate.

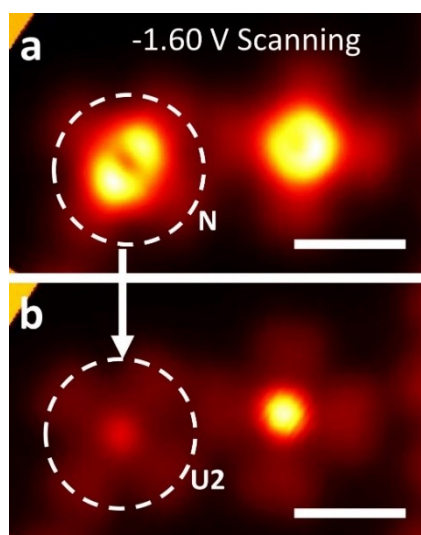


Fig. S3. STM image showing the forced switching process of the generated N molecule back to its original U2 configuration. (a) STM image of the targeted N molecule in white dashed circle. $V_{\text{bias}} = 1.6\text{V}$; (b) STM image of the U2 molecule restored from the N intermediate in (a). $V_{\text{bias}} = -1.2\text{V}$. Both images are acquired in constant height mode. Scale bars: 1 nm.