

Reversible switching of single dipole molecule imbedded in two dimensional hydrogen-bonded binary molecular networks

Jia Lin Zhang,[†] Tian Chao Niu,[‡] Yun Hao Lu,[†] Wei Chen^{†,‡,*}

[†]Department of Physics, National University of Singapore, 2 Science Drive 3, 117542, Singapore

[‡]Department of Chemistry, National University of Singapore, 3 Science Drive 3, 117543, Singapore

Introduction

Self-assembly of binary molecular systems on inert graphite surface via the formation of multiple intermolecular hydrogen bonding represents a versatile approach to fabricate ordered and robust molecular nanostructures arrays. Here, we demonstrate the reversible switching of single dipole molecule CIAIPc imbedded in two-dimensional (2D) hydrogen-bonded binary molecular networks formed by co-assembly of CIAIPc and perfluoropentacene (PFP) on graphite, as investigated by in-situ low-temperature scanning tunneling microscopy (LT-STM).

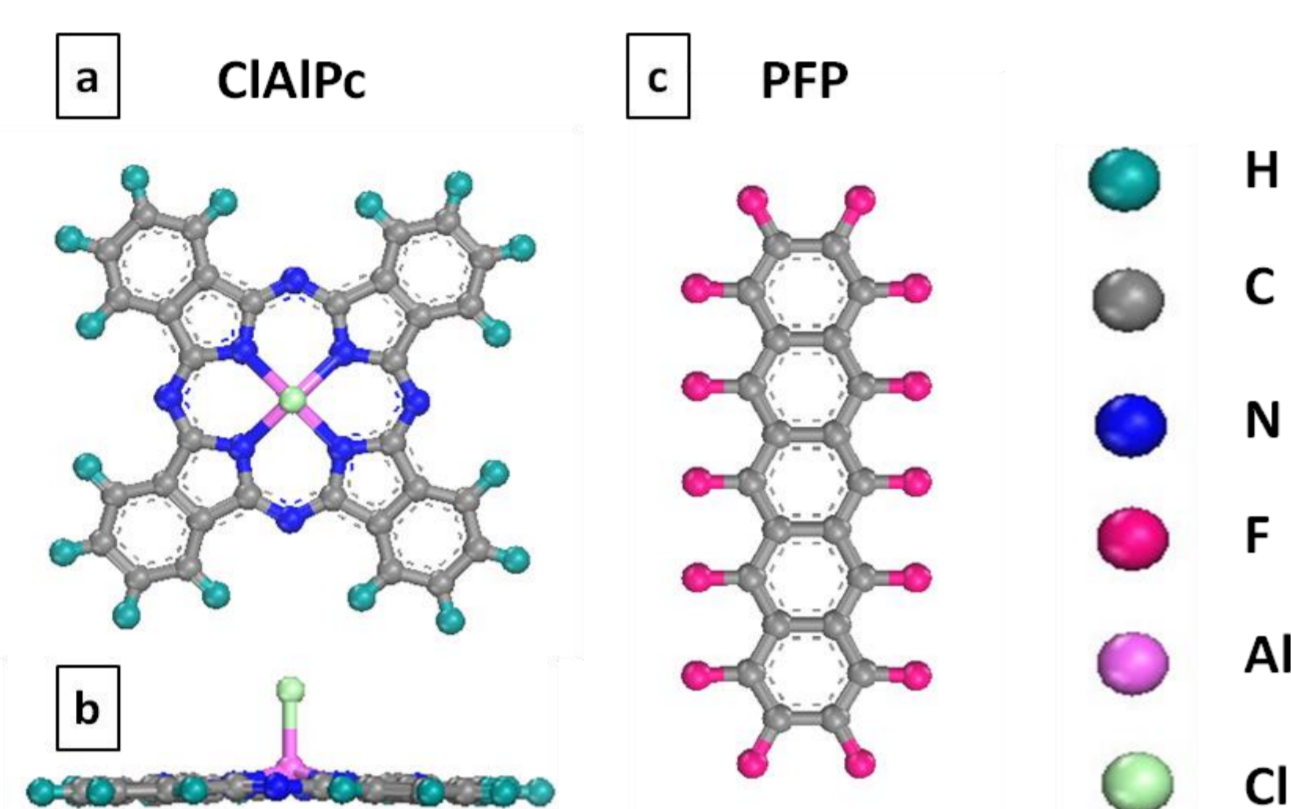


Figure 1. Molecular structure of CIAIPc and PFP molecule

Results and Discussion A

Hexagonal network PFP:CIAIPc 1:2

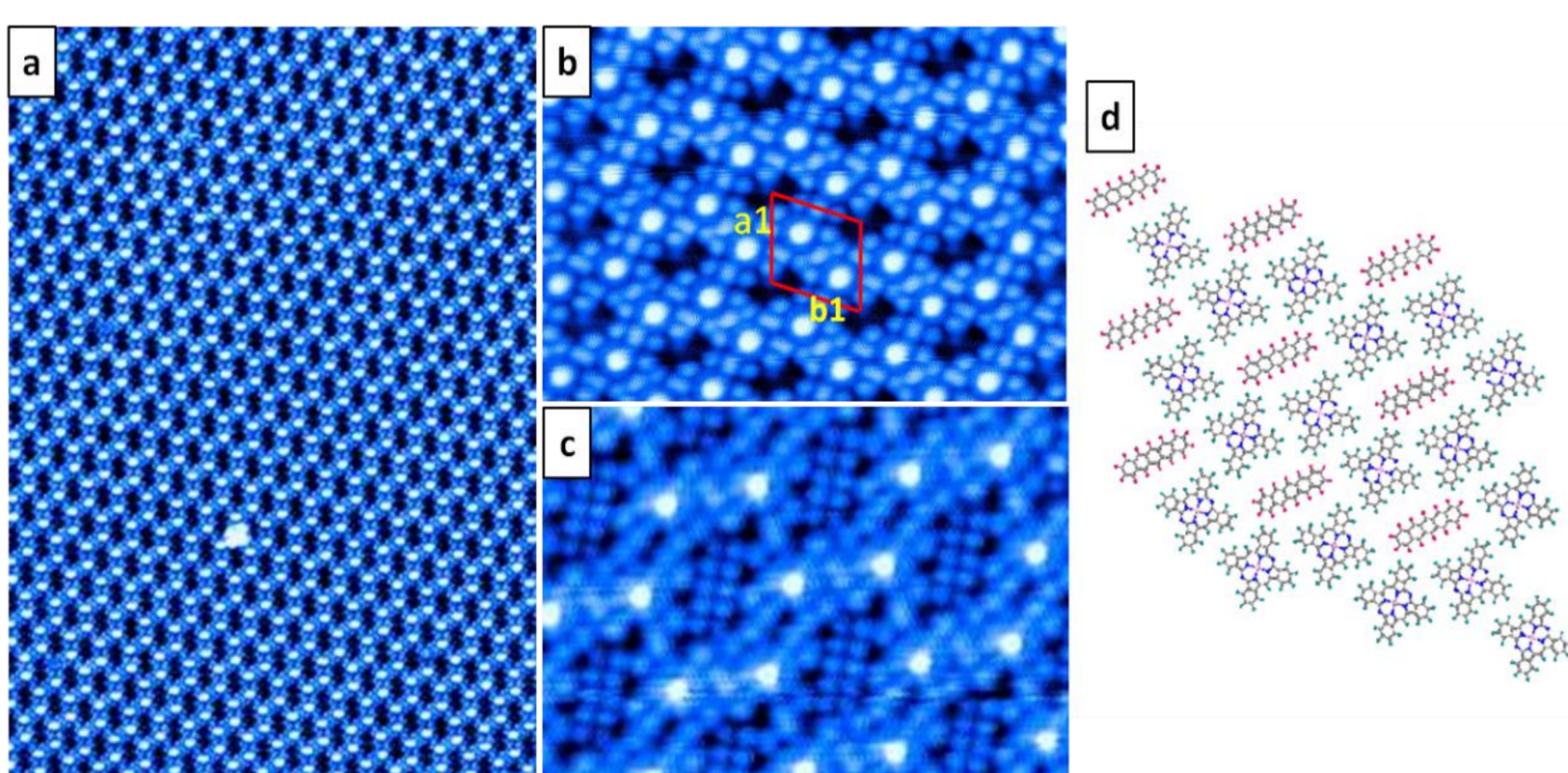


Figure 2.(a) STM image ($45 \times 60\text{nm}^2$, $V_{\text{tip}}=2.205\text{V}$) of long-range ordered hexagonal binary molecular network formed by PFP and CIAIPc with molecular ratio 1:2 on HOPG;(b) ($15 \times 10\text{nm}^2$, $V_{\text{tip}}=1.89\text{V}$)and (c) ($9 \times 6\text{nm}^2$, $V_{\text{tip}}=2.5\text{V}$) the corresponding high resolution STM images of the hexagonal structure;(d) Schematic packing structure for the hexagonal network

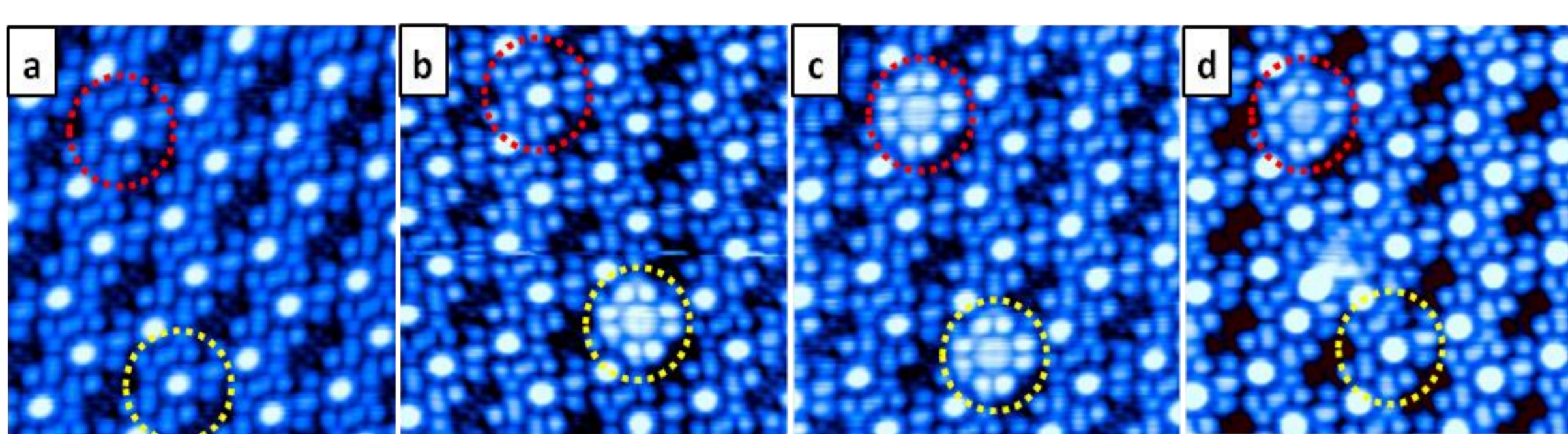


Figure 3.(a-d) Sequential STM images showing the reversible switching between the Cl-up and Cl-down configurations. ($10 \times 10\text{nm}^2$; $V_{\text{tip}}=2.047\text{V}$, $I_{\text{set}}=100\text{pA}$)The molecule indicated by the red circle was switched from Cl-up (b) to Cl-down (c) by a positive voltage(+4.5V,5ms),and the molecule indicated by the yellow circle was switched from the Cl-up configuration (a) to the Cl-down configuration (b) by a positive voltage pulse and back to the Cl-up configuration (d) by applying a negative pulse (-3V,5ms).

References

- Joachim, C.; Gimzewski, J. K.; Aviram, A. Nature 2000, 408, 541
- Nitzan, A.; Ratner, M. A. Science 2003, 300, 1384
- Huang, Y. L.; Lu, Y.; Niu, T. C.; Huang, H.; Kera, S.; Ueno, N.; Wee, A. T. S.; Chen, W. Small 2012, 8, 1423
- Niu, T. C.; Huang, Y. L.; Sun, J. T.; Kera, S.; Ueno, N.; Wee, A. T. S.; Chen, W. Applied Physics Letters 2011, 99, 143114
- Fukagawa, H.; Hosoumi, S.; Yamane, H.; Kera, S.; Ueno, N. Physical Review B 2011, 83, 085304
- Barth, J. V.; Weckesser, J.; Cai, C.; Günter, P.; Bürgi, L.; Jeandupeux, O.; Kern, K. Angewandte Chemie International Edition 2000, 39, 1230.

Results and Discussion B

Square network PFP:CIAIPc 2:1

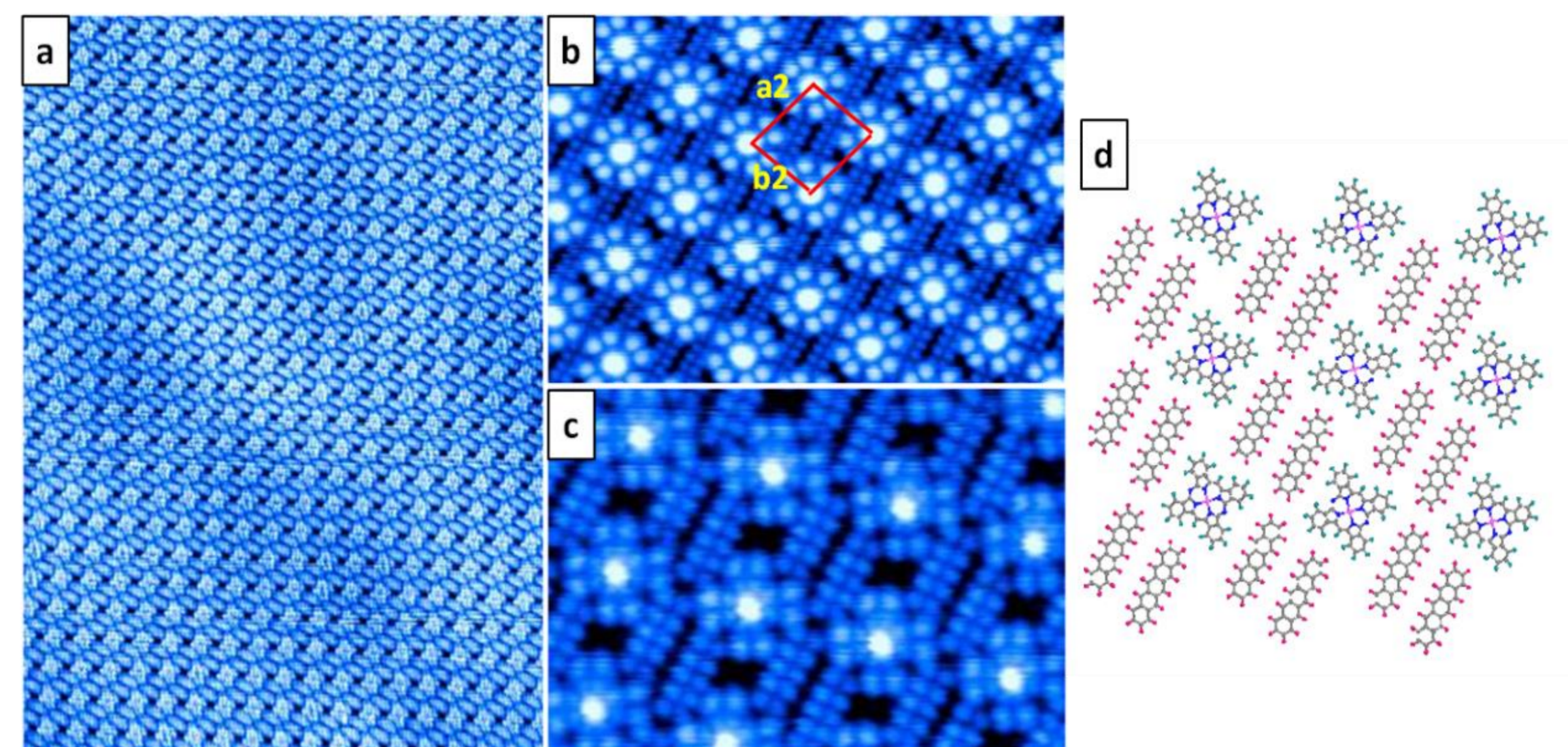


Figure 4.(a) STM image ($45 \times 60\text{nm}^2$, $V_{\text{tip}}=1.969\text{V}$) of long-range ordered square binary molecular network formed by PFP and CIAIPc with binary molecular ratio 2:1 on HOPG;(b) ($15 \times 10\text{nm}^2$, $V_{\text{tip}}=2.5\text{V}$)and (c) ($9 \times 6\text{nm}^2$, $V_{\text{tip}}=2.5\text{V}$) high resolution STM images of the square structure;(d) Schematic packing structure for the square network.

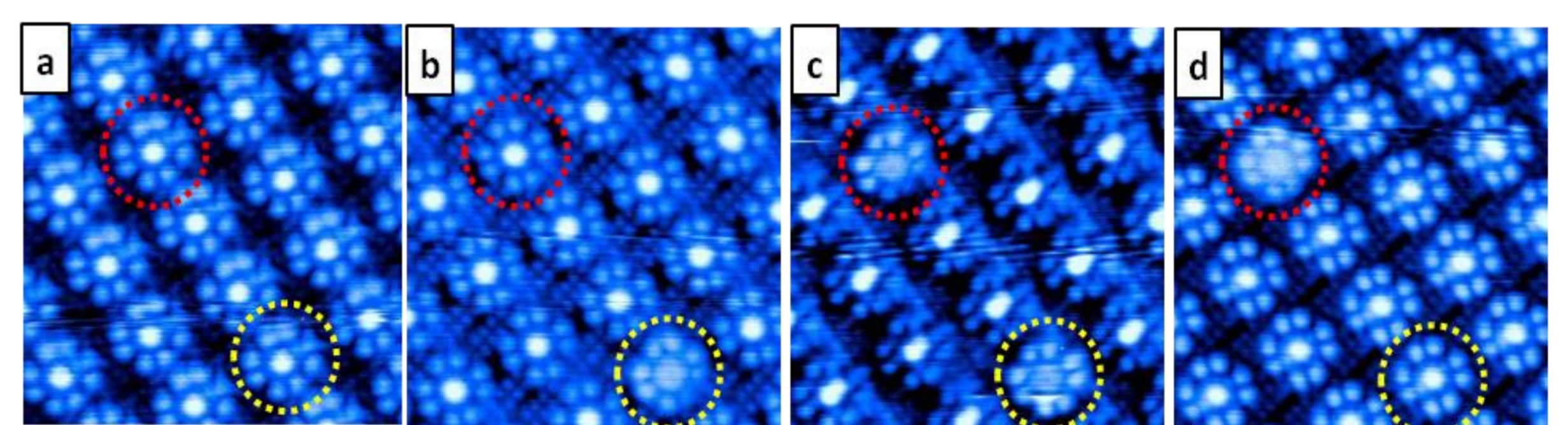


Figure 5.(a-d) Sequential STM images showing the reversible switching between the Cl-up and Cl-down configurations. ($10 \times 10\text{nm}^2$; V_{tip} : 2.126V, 2.047V, 2.047V, 2.205V; $I_{\text{set}}=100\text{pA}$) The molecule indicated by the red circle was switched from Cl-up (b) to Cl-down (c) by a positive voltage (+4.5V,5ms),and the molecule indicated by the yellow circle was switched from the Cl-up configuration (a) to the Cl-down configuration (b) by a positive voltage pulse and back to the Cl-up configuration (d) by applying a negative pulse (-3.5V,5ms).

Results and Discussion C

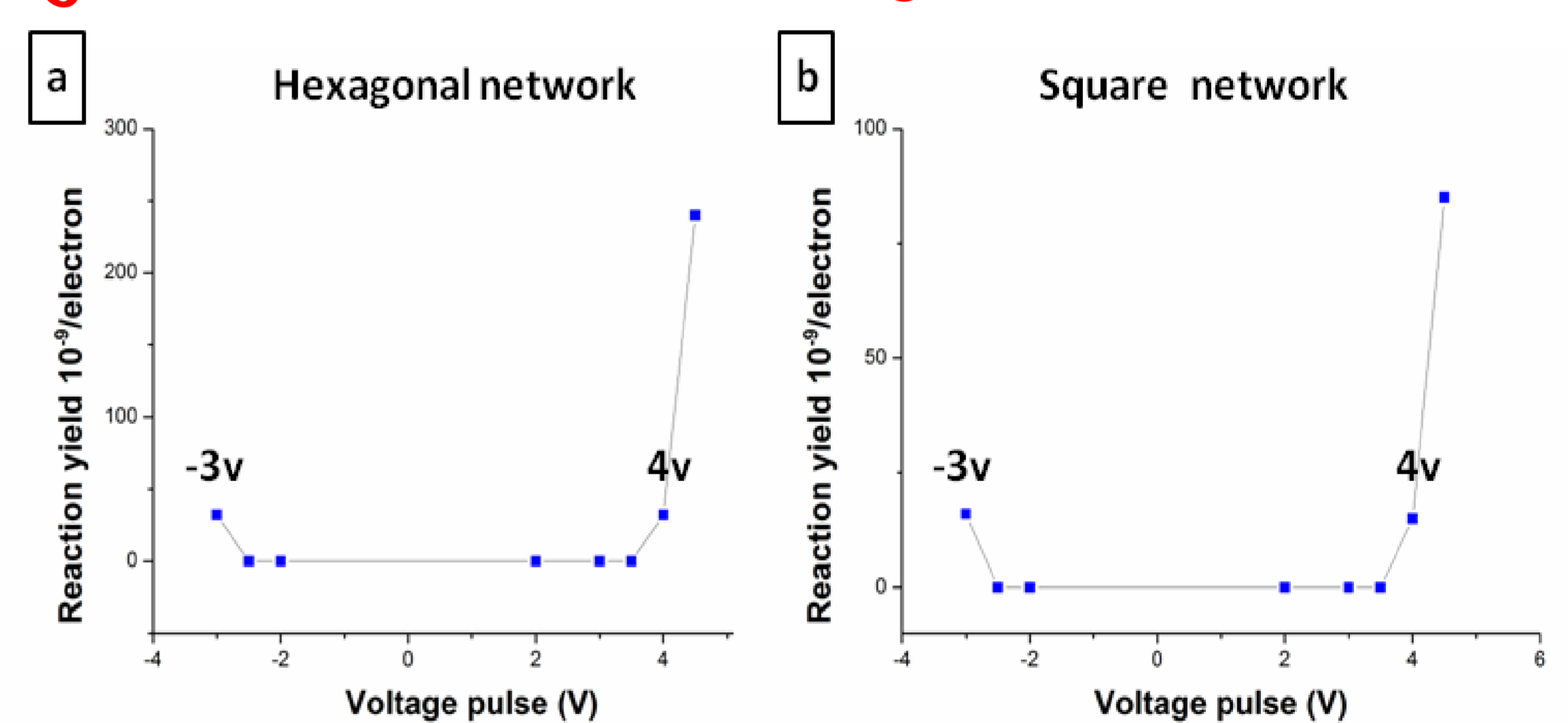


Figure 6.Reaction yield as a function of voltage pulse ($V_{\text{tip}}=2.5\text{V}$, $I_{\text{set}}=100\text{pA}$, feedback loop off).(a) is the plot for the CIAIPc imbedded in the hexagonal network and (b) is for the square network. The threshold voltage for switching from Cl-up to Cl-down configuration (positive voltage pulse) or Cl-down to Cl-up configuration (negative voltage pulse) can be extracted from the plot.

Conclusion

In summary, we have demonstrated reversible switching of single dipole molecule imbedded in 2D hydrogen-bonded binary CIAIPc:PFP molecular networks on HOPG. The CIAIPc molecule can be switched between the Cl-up and Cl-down configurations by controlling the polarity of the voltage pulse applied to the STM tip. We propose that the inelastically tunneled electrons induce the reversible switching of the CIAIPc dipole molecule imbedded in the binary molecular networks between the Cl-up and Cl-down configurations. The switching is spatially confined to the addressed molecule, reversible, intrinsic to the molecule and leaves the binary molecular network unaffected. This shows the great potential for applications in a high density data storage device, where reversible and highly selective memory storage processes are desired.