

Energy Level Realignment in Weakly Interacting Donor-Acceptor Binary Molecular Networks

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Introduction

Understanding the effect of intermolecular and molecule-substrate interactions on molecular electronic states is key to revealing the energy level alignment mechanism at organic-organic heterojunctions or organic-inorganic interfaces.

In this work, we investigate the energy level alignment mechanism in weakly interacting donor-acceptor binary molecular superstructures, comprising copper hexadecafluorophthalocyanine ($F_{16}CuPc$) and copper phthalocyanine (CuPc), or manganese phthalocyanine (MnPc) on graphite.

The molecular electronic structures have been systematically studied by *in-situ* ultraviolet photoelectron spectroscopy (UPS), low-temperature scanning tunneling microscopy/spectroscopy (LT-STM/STS) experiments and corroborated by density functional theory (DFT) calculations.

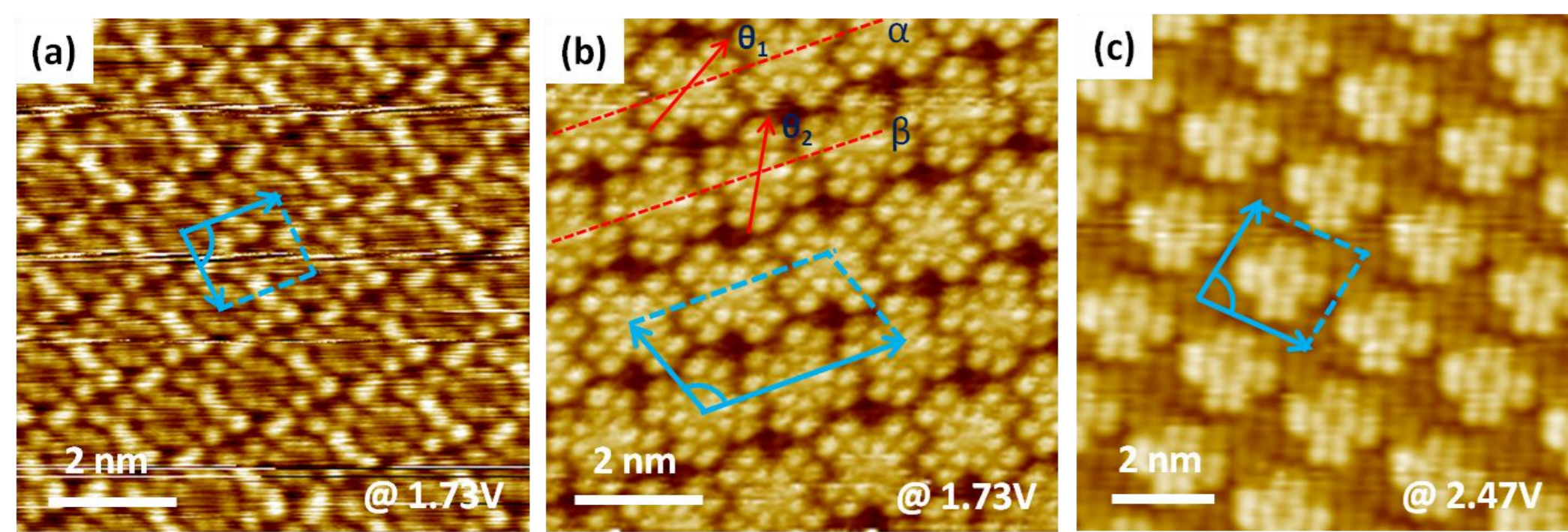


Fig 1. STM images of (a) CuPc monolayer ($V_{tip} = 1.73V$, 8×8 nm²), (b) $F_{16}CuPc$ monolayer ($V_{tip} = 1.73V$, 8×8 nm²) and (c) CuPc- $F_{16}CuPc$ binary network with intermixing ratio of 1:1 ($V_{tip} = 2.47V$, 10×10 nm²) on HOPG substrate. (d)-(f) are the corresponding unit cell based on the STM images with further structure optimization.

Methodology

- $In-situ$ UPS experiments were carried out in a custom designed ultra-high vacuum (UHV) system with a base pressure better than 2×10^{-10} mbar.
- LT-STM/STS experiments were performed in a multi-chamber UHV system housing an Omicron LT-STM. STM imaging was carried out at 77 K in constant current mode with a chemically etched tungsten tip.
- Theoretical calculations were performed using VASP code with the projector-augmented wave (PAW) potentials.

Results 1: UPS, CuPc- $F_{16}CuPc$

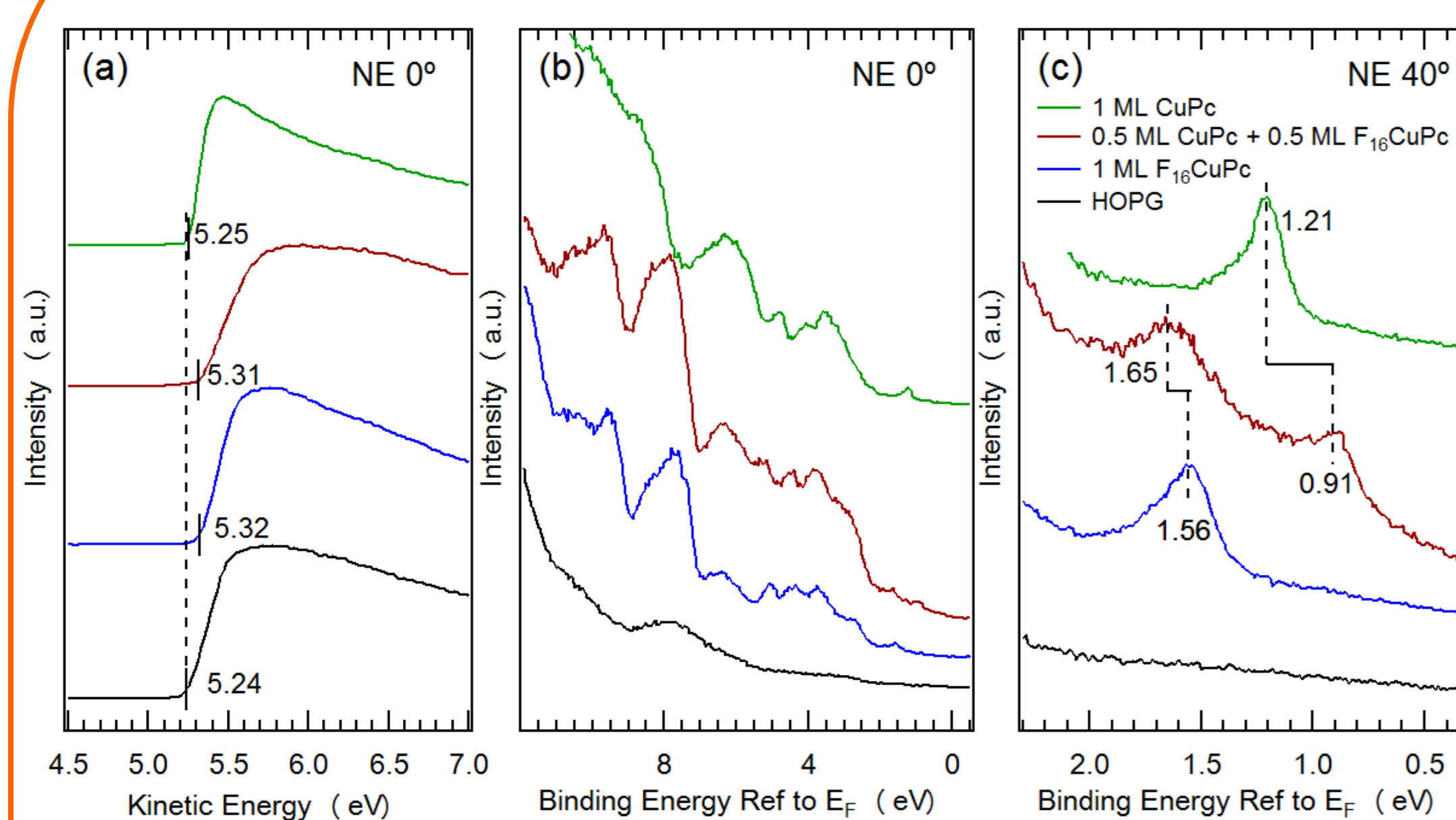


Fig 2. UPS spectra for CuPc and $F_{16}CuPc$ monolayer and their 1:1 mixture on HOPG substrate. (a) UPS spectra at the low-kinetic energy part with a -5 V sample bias (i.e., secondary electron cutoff), (b) valence band spectra at the low-binding energy part and (c) corresponding close up spectra in the HOMO band region. The photoelectron takeoff angle relative to the analyzer are indicated in the figures.

Results 2: MnPc- $F_{16}CuPc$

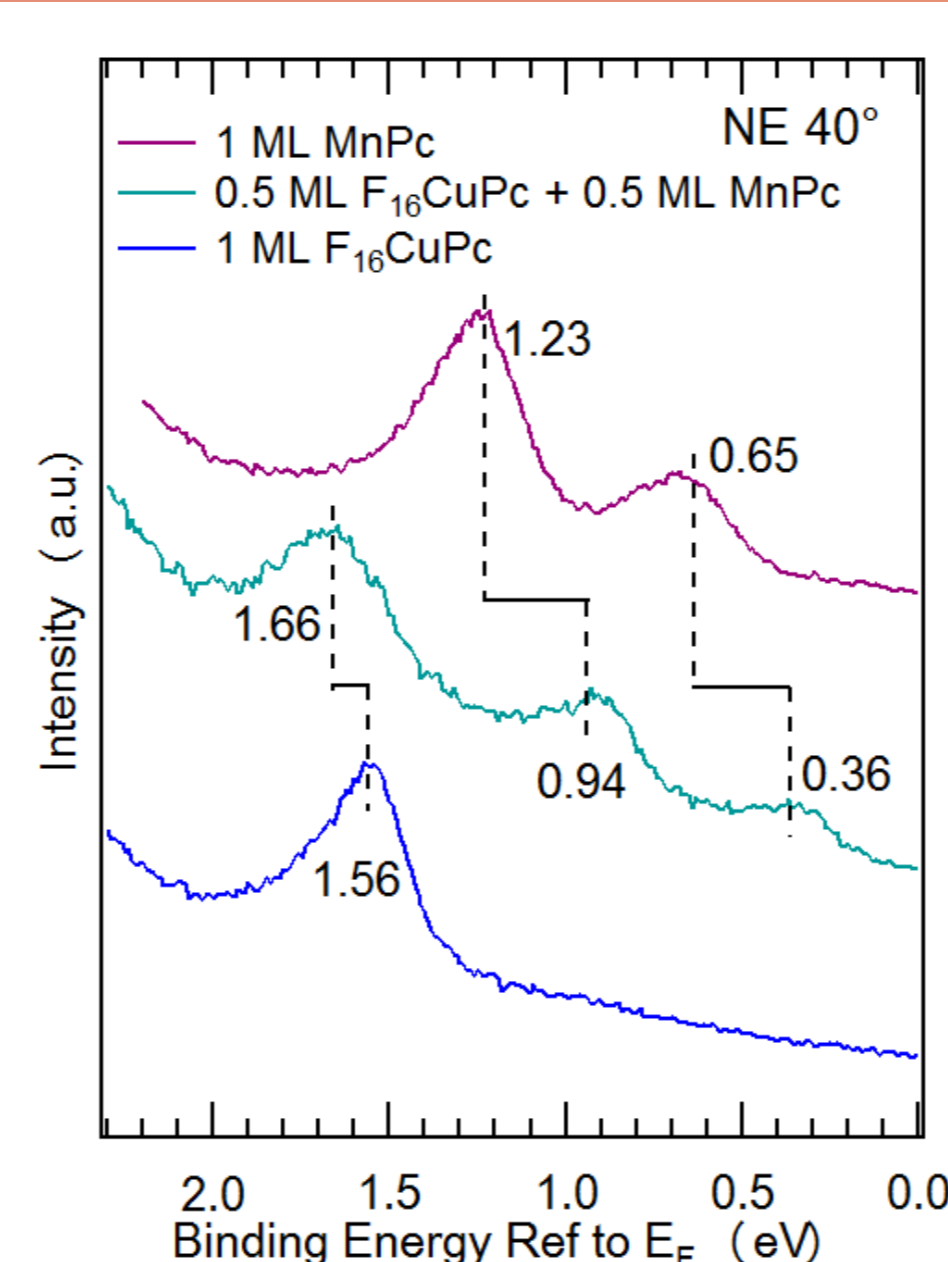


Fig 3. UPS spectra in the HOMO band region for MnPc and $F_{16}CuPc$ monolayer and their 1:1 mixture on HOPG substrate, respectively. Both Mn 3d derived HOMO state (0.65 eV) and ligand π orbital induced HOMO state (1.23 eV) shift to the low binding energy region by 0.29 eV in the binary network.

Results 4: Projected DOS

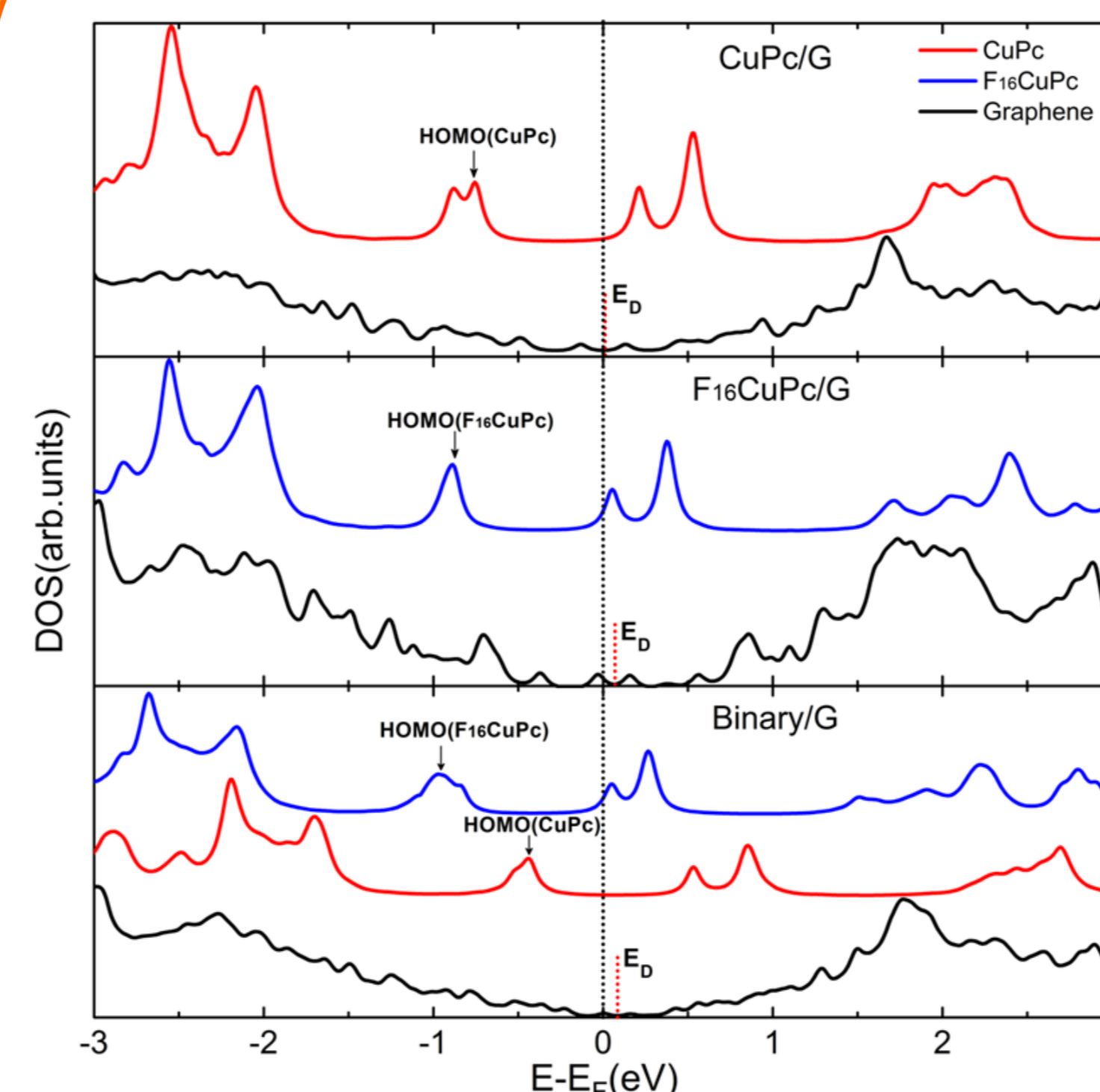


Fig 5. Projected DOS for the monolayer of CuPc, $F_{16}CuPc$ and their 1:1 mixture absorbed on graphene substrate. The Fermi level is set to zero, and the red dotted lines mark the Dirac point of graphene.

Results 3: LT-STM/STS

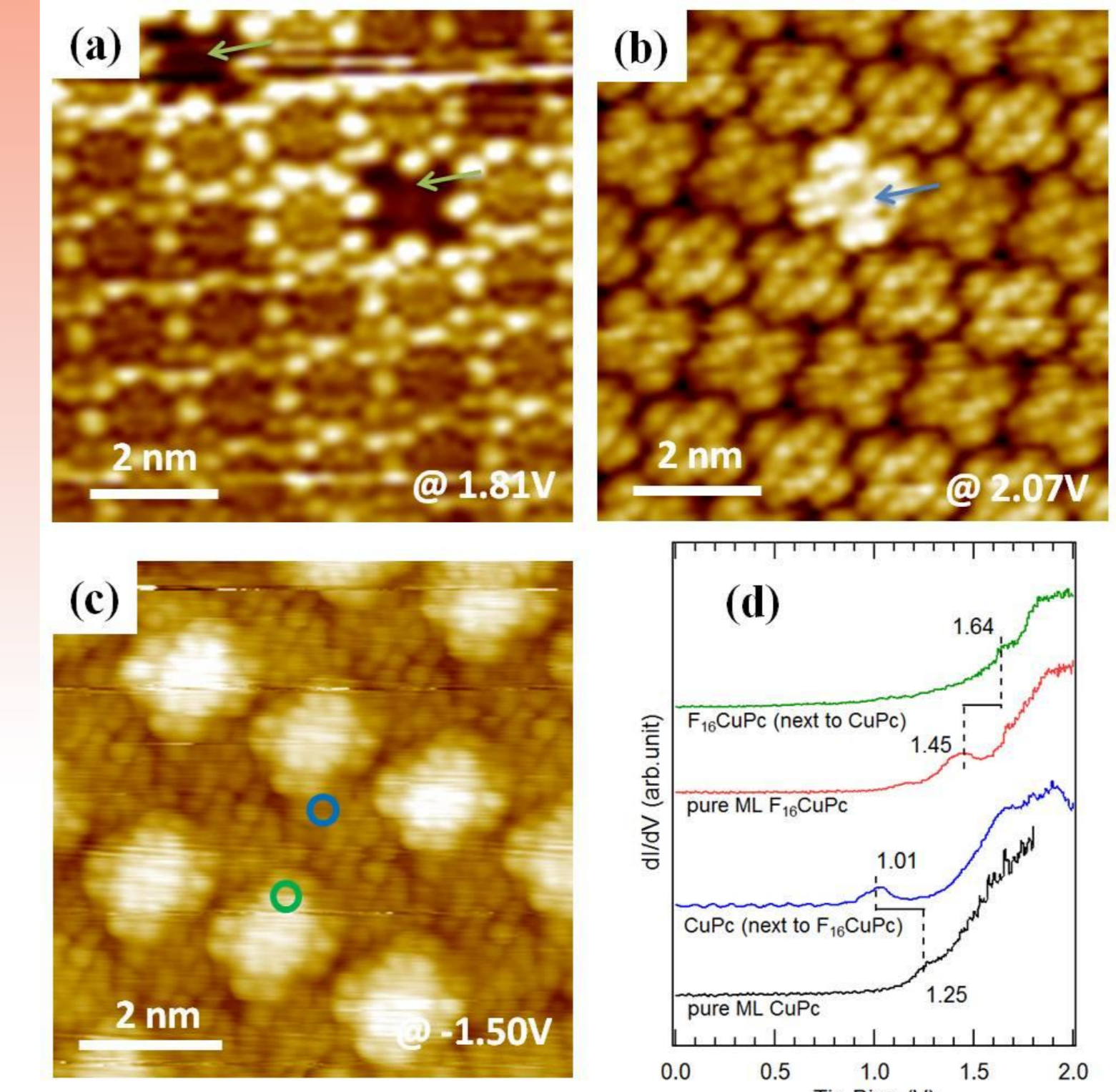


Fig 4. STM images

- (a) two $F_{16}CuPc$ molecules embedded in the CuPc monolayer on HOPG (the dark features refer to the $F_{16}CuPc$ molecules)
- (b) one CuPc molecule embedded in the $F_{16}CuPc$ monolayer on HOPG (the bright feature refers to the CuPc molecule).
- (c) supramolecular packing structure of CuPc- $F_{16}CuPc$ binary network with intermixing ratio of 2:1. (here, the dark and bright features refer to the CuPc and $F_{16}CuPc$ molecules respectively).
- (d) STS spectra taken at the lobe of $F_{16}CuPc$ molecules and CuPc molecules for both pure and mixed molecular layer.

Results 5: CDD

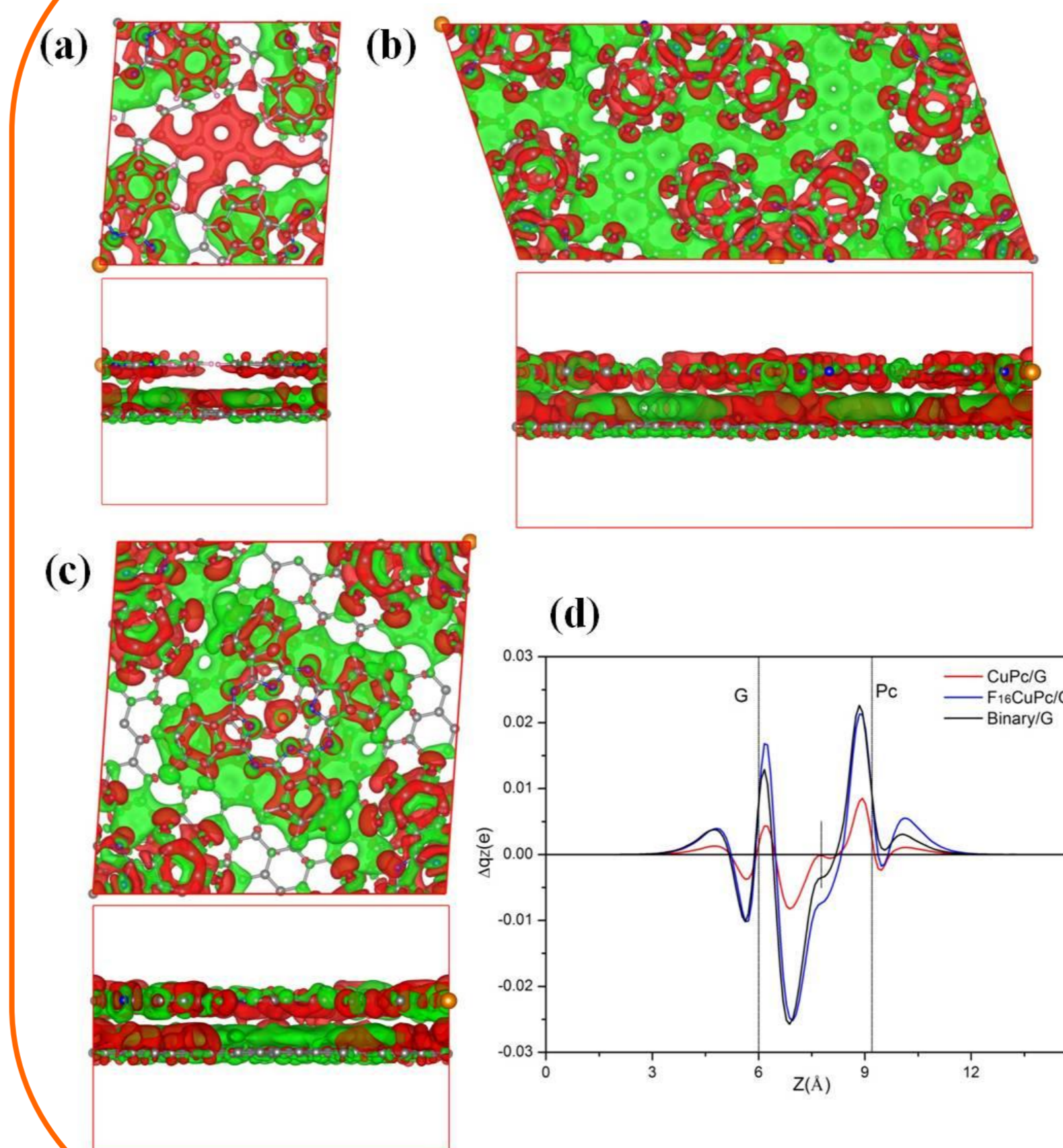


Fig 6. Top view and side view of the charge density difference for (a) CuPc/Graphene (b) $F_{16}CuPc$ /Graphene (c) Binary/Graphene (d) 1D charge density difference along the surface normal direction of graphene

Summary

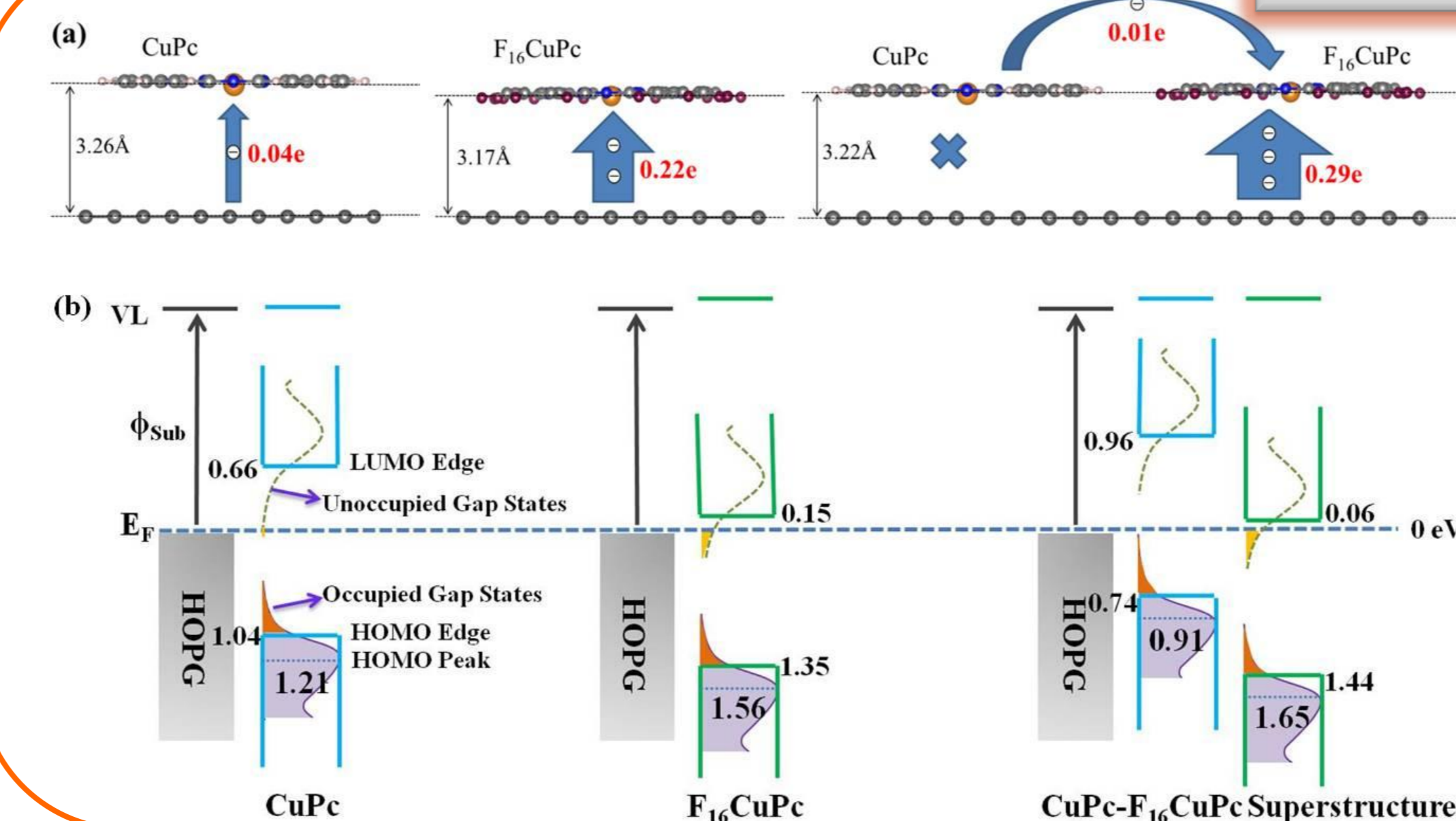


Fig 7. Schematic illustrations of gap states mediated weak interface charge transfer behaviors in explaining the significant energy level shift in weakly interacted binary molecular systems.

The unoccupied and occupied gap states are indicated by the purple arrows in the figure, which are extended from the LUMO and HOMO edge respectively and decayed exponentially into the band gap

Conclusions

- Our studies elucidated the effects of balanced intermolecular and molecule-substrate interactions on the interface charge transfer behaviors and local electronic states.
- The molecular energy levels can be significantly affected and mediated through the gap states mediated interfacial charge transfer via weak hydrogen bonding interactions.
- Reveal the importance of weak intermolecular interactions on the molecular electronic states.

Reference & Acknowledgements

J.Q. Zhong, X.M. Qin, J.L. Zhang, S. Kera, N. Ueno, A.T.S. Wee, J.L. Yang, W. Chen, *ACS Nano*, 8, 5941-5951 (2014)



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