

Supplementary Information of CP-ART-03-2010-000021

**The Influence of Orientations and External Electric Field on Charge Carrier
Mobilities in CuPc and F₁₆CuPc Films on Highly Ordered Pyrolytic Graphite
and Octane-1-thiol Terminated Au(111) Substrates**

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Table of Contents

1. Force Field Parameters for Molecular Dynamic Simulations
2. Calibration of the Consistent-Valence Force Field (CVFF)
3. Test of Simulation Settings
4. Radial Distributions of Intermolecular Distances under the Applied Electric Fields
5. Electrostatics Embedding Model
6. Influence of External Electric Field on Transfer Integrals
7. Distance-Dependent Transfer Integrals
8. CuPc (F₁₆CuPc) Monolayers from Molecular Dynamic Simulations
9. Effects of External Electric Field

1. Force Field Parameters for Molecular Dynamic Simulations

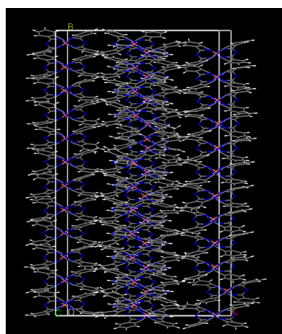
Table S1. Force field parameters adopted in CVFF ^a for molecular dynamic simulations.

Force field types	Atom type description
cp	C in graphene layers or in six membered rings of CuPc/F ₁₆ CuPc molecules
Au	Au in Au layers
s	S in C8-SAM ^b
c2	C in methene of C8-SAM
c3	C in methyl of C8-SAM
h	H in C8-SAM or in CuPc molecules
Cu	Cu in CuPc/F ₁₆ CuPc molecules
np	N in CuPc/F ₁₆ CuPc molecules
c5	C in five membered rings of CuPc/F ₁₆ CuPc molecules
f	F in F ₁₆ CuPc molecules
Cut-off of non-bonded interactions	
vdW	15.5 Å
electrostatics	15.5 Å

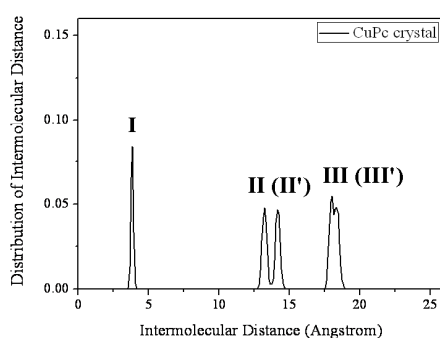
^a CVFF can be found in the reference.^{S1}

^b C8-SAM indicates octane-1-thiol self-assembling monolayer.

2. Calibration of the Consistent-Valence Force Field (CVFF)



(a)



(b)

Types	Intermolecular distance, r (Å)	
	CVFF	Exptl.
I	3.8	3.8
II (II')	13.3 (14.1)	12.1 (13.2)
III (III')	18.0 (18.4)	17.0 (17.5)

Figure S1. (a) Snapshot of CuPc α -phase crystal after about 100-ps MD simulations, and (b) distribution of intermolecular distance for various packing pairs within crystal. The experimental values of intermolecular distances are taken from the references S2-S5.

3. Test of Simulation Settings

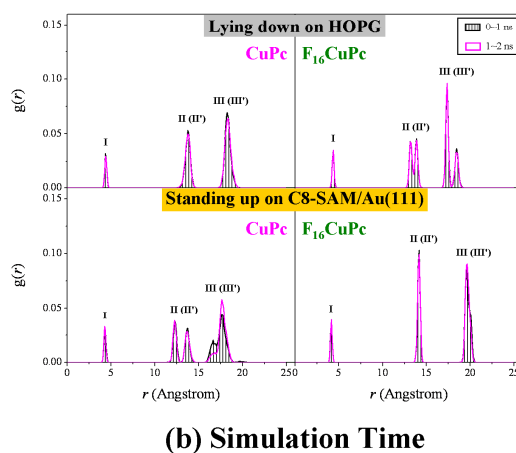
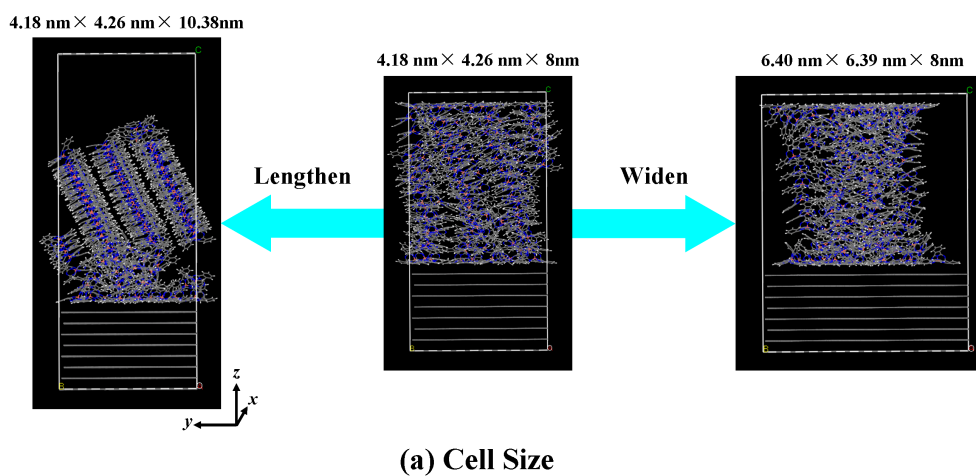


Figure S2. Test of MD-simulation settings: (a) influence of the cell size on trajectories of 1-ns MD simulations, as exemplified by the CuPc/HOPG system, and (b) radial distributions $g(r)$ of lying-down and standing-up CuPc and F_{16} CuPc films obtained from 1ns and 2ns-simulations, respectively.

4. Radial Distributions of Intermolecular Distances under the Applied Electric Fields

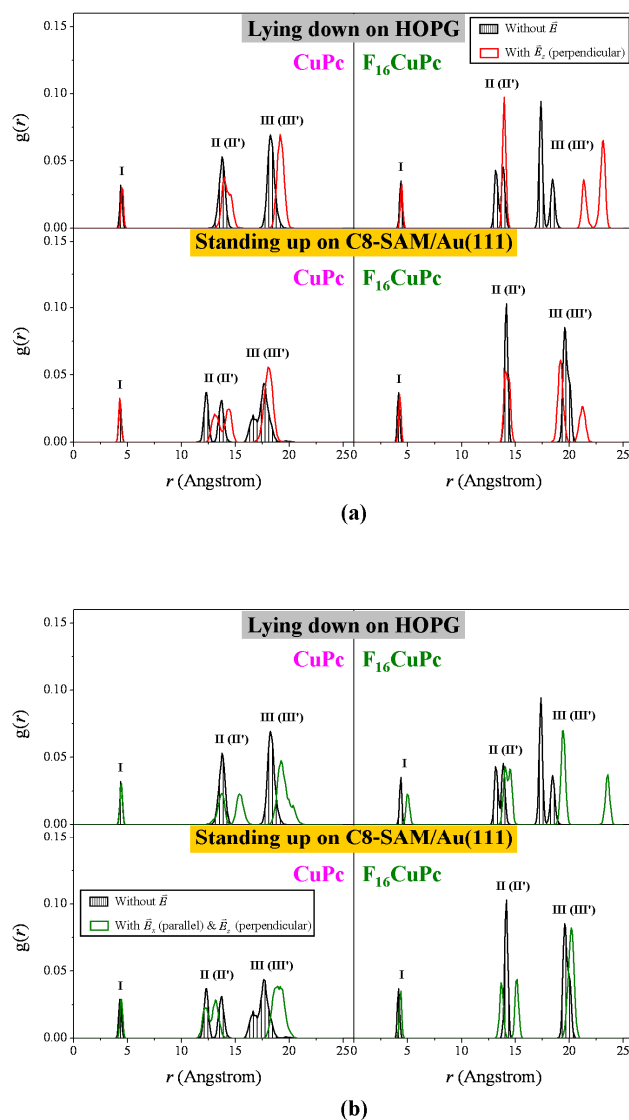


Figure S3. Radial distributions $g(r)$ of lying-down and standing-up CuPc and F₁₆CuPc films without/with applied electric field, respectively. $\vec{E}$ stands for the external electric field. $\vec{E}_x$ and $\vec{E}_z$ indicate the electric fields parallel and perpendicular to the substrates (with the strength of 10^4 and 10^7 V·cm⁻¹), respectively.

5. Electrostatics Embedding Model

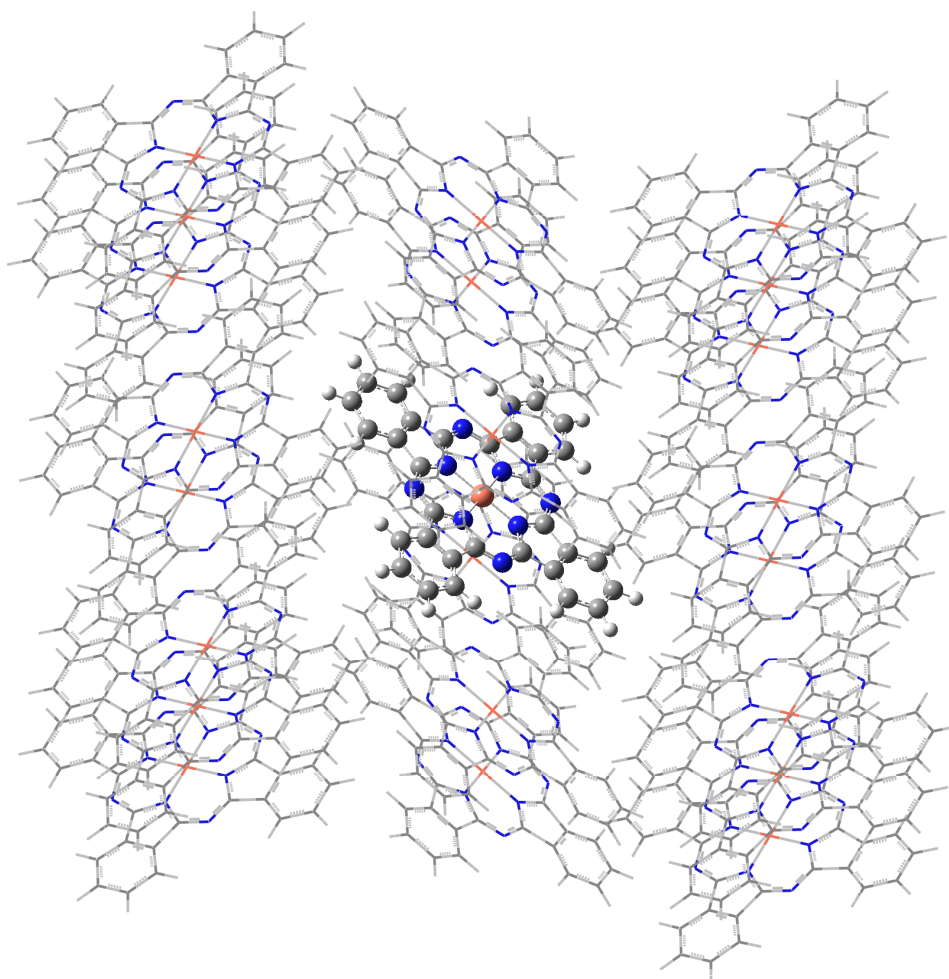


Figure S4. The CuPc ($F_{16}\text{CuPc}$) molecule is embedded in the background of point charges (NBO partial charges taken from natural bond orbital analysis) localized at the atomic centers of distant molecules. Details are also shown in our recent works.^{S6,}

S7

6. Influence of External Electric Field on Transfer Integrals

Table S2. Transfer integrals of eclipsed dimers without and with the electric field,^a respectively.

Distance (Å)	<i>t</i> (eV)			
	Hole		Electron	
	Without E	$E_z = 10^7 \text{ V}\cdot\text{cm}^{-1}$	Without E	$E_z = 10^7 \text{ V}\cdot\text{cm}^{-1}$
CuPc dimers				
3.05	0.613	0.613	0.657	0.657
3.45	0.214	0.214	0.223	0.223
3.85	6.32×10^{-2}	6.32×10^{-2}	6.46×10^{-2}	6.46×10^{-2}
4.25	1.30×10^{-2}	1.30×10^{-2}	1.27×10^{-2}	1.27×10^{-2}
4.65	8.74×10^{-4}	8.79×10^{-4}	1.69×10^{-3}	1.68×10^{-3}
F₁₆CuPc dimers				
3.05	0.585	0.585	0.574	0.574
3.45	0.202	0.202	0.181	0.181
3.85	5.91×10^{-2}	5.91×10^{-2}	4.49×10^{-2}	4.49×10^{-2}
4.25	1.24×10^{-2}	1.24×10^{-2}	4.37×10^{-3}	4.37×10^{-3}
4.65	2.72×10^{-4}	2.75×10^{-4}	4.82×10^{-3}	4.81×10^{-3}

^a E stands for the external electric field, and E_z indicates the electric field perpendicular to the substrates.

7. Distance-Dependent Transfer Integrals

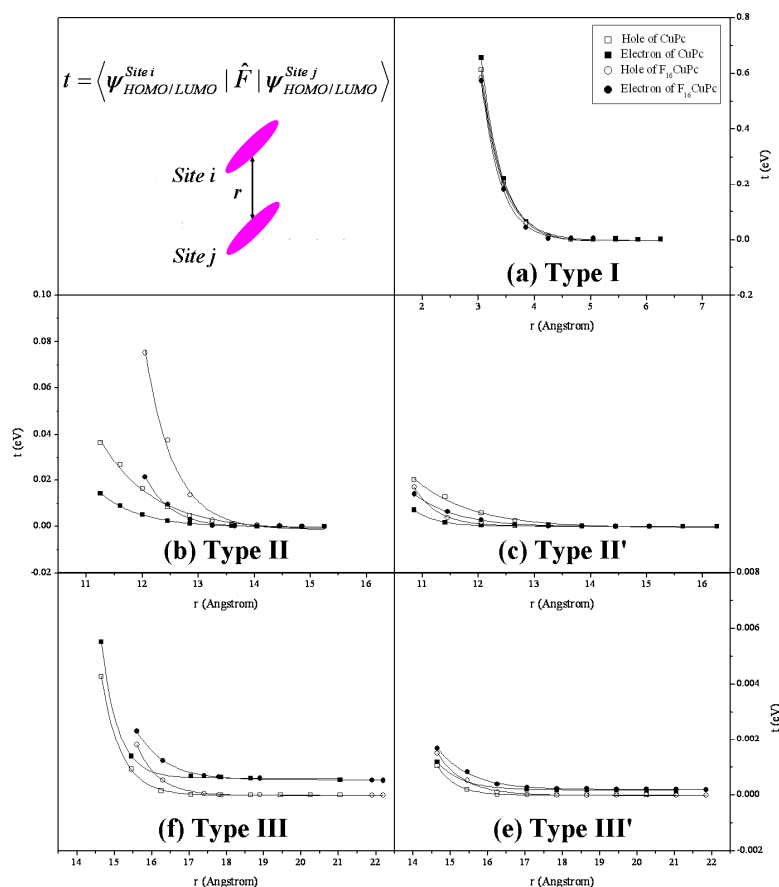
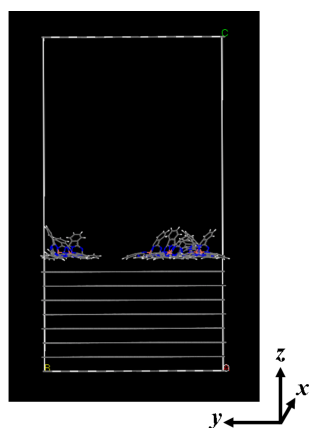


Figure S5. Transfer integrals for CuPc (F₁₆CuPc) dimers as a function of interpair distance, r . Solid lines represent the fitting curves of transfer integrals by using the exponential decay formula $t(r) = a \cdot \exp(-r/b) + c$. The corresponding parameters (a , b , and c), and statistic analysis are shown in Table 2 and Table S3.

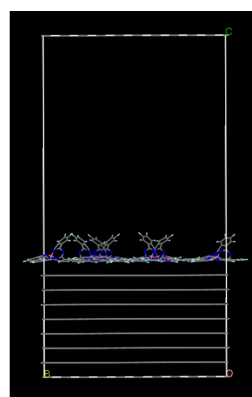
Table S3. Standard derivation and correlation coefficient of the fitting curves of transfer integrals of CuPc and F₁₆CuPc dimers.

Hopping paths		Exponential decay formula $t(r) = a \cdot \exp(-r/b) + c$			
		CuPc		F ₁₆ CuPc	
		Std. Deriv.	Cor. Coeff.	Std. Deriv.	Cor. Coeff.
Hole					
Type	I	6.09×10^{-3}	99.85%	5.09×10^{-3}	99.92%
	II	7.89×10^{-4}	99.45%	1.91×10^{-3}	99.19%
	II'	4.49×10^{-4}	99.40%	2.75×10^{-4}	99.64%
	III	1.60×10^{-5}	99.98%	1.29×10^{-5}	99.94%
	III'	3.55×10^{-6}	99.98%	2.14×10^{-5}	99.72%
Electron					
Type	I	4.97×10^{-3}	99.91%	4.18×10^{-3}	99.93%
	II	1.22×10^{-4}	99.91%	4.35×10^{-4}	99.46%
	II'	2.33×10^{-5}	99.98%	1.43×10^{-4}	99.86%
	III	3.90×10^{-5}	99.92%	1.76×10^{-5}	99.88%
	III'	6.86×10^{-6}	99.94%	2.28×10^{-5}	99.67%

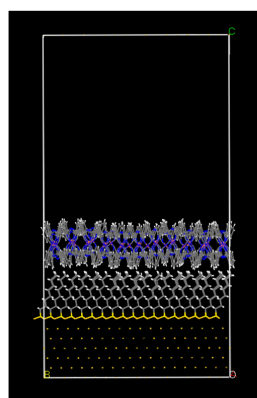
8. CuPc (F_{16} CuPc) Monolayers from Molecular Dynamic Simulations



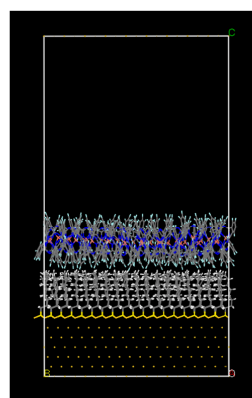
(a) CuPc monolayer on HOPG



(b) F_{16} CuPc monolayer on HOPG



(c) CuPc monolayer on C8-SAM/Au(111)



(d) F_{16} CuPc monolayer on C8-SAM/Au(111)

Figure S6. Snapshots of (a) CuPc and (b) F_{16} CuPc monolayers on HOPG, (c) CuPc and (d) F_{16} CuPc monolayers on C8-SAM/Au(111) after about 3-ns MD simulations.

9. Effects of External Electric Field

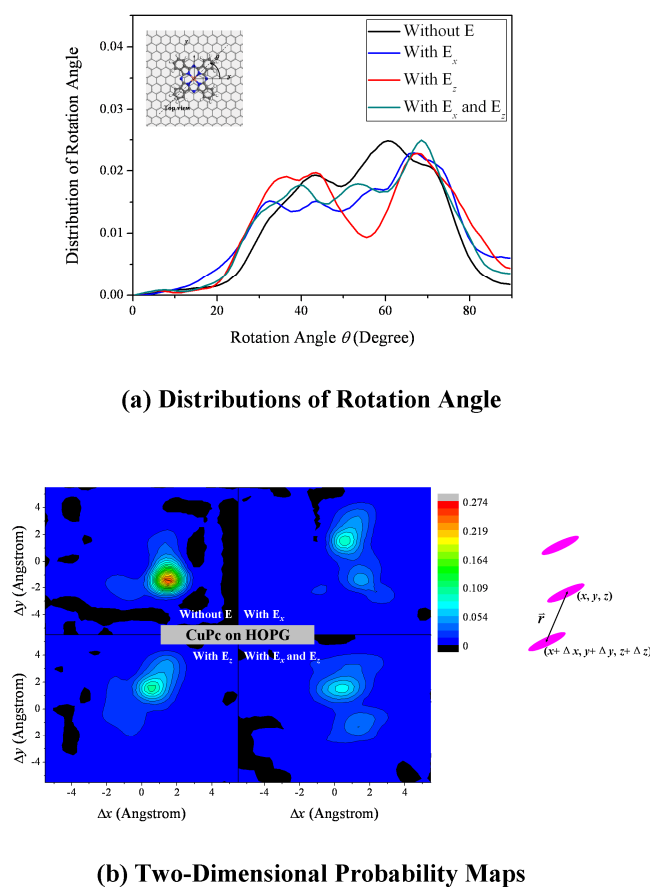


Figure S7. Effects of external electric field: (a) distributions of rotation angle, θ , defined as the azimuthal angle of the vector Cu-N of CuPc molecules to the x direction, and (b) two-dimensional probability maps of horizontal displacements along the x and y directions of the interpair vector $\vec{r}$ within one-dimensional CuPc stacks, for CuPc film on the HOPG surface under different conditions. E stands for the external electric field. E_x and E_z indicate the electric fields parallel and perpendicular to the substrates, with the strength of 10^4 and 10^7 V·cm⁻¹, respectively. The horizontal displacements (Δx , Δy) along the x and y directions are indicated by the inset.

References

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