Supporting Information

Temperature-Induced Transitions of the Self-Assembled Phthalocyanine Molecular Nanoarrays at Solid-Liquid Interface: from Randomness to Order

Fangyun Hu,[a,b,‡] Yunnan Gong, [c,‡] Xuemei Zhang,[a] Jindong Xue,[a,b] Bo Liu,[b] Tongbu Lu,[c,] Ke Deng,[a,*] Wubiao Duan,[b,*] Qingdao Zeng[a,*] and Chen Wang[a,*]

[a]*CAS Key Laboratory of Standardization and Measurement for Nanotechnology, National Centre for Nanoscience and Technology, Beijing 100190, China.*

E-mail: zengqd@nanoctr.cn; kdeng@nanoctr.cn; wangch@nanoctr.cn

[b]*Department of Chemistry, School of Science, Beijing Jiaotong University, Beijing, 100044, China.*

E-mail: wbduan@bjtu.edu.cn

[c]*MOE Key Laboratory of Bioinorganic and Synthetic Chemistry, State Key Laboratory of Optoelectronic Materials and Technologies, School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou, 510275,China.*

‡ *These authors contributed to this work equally.*

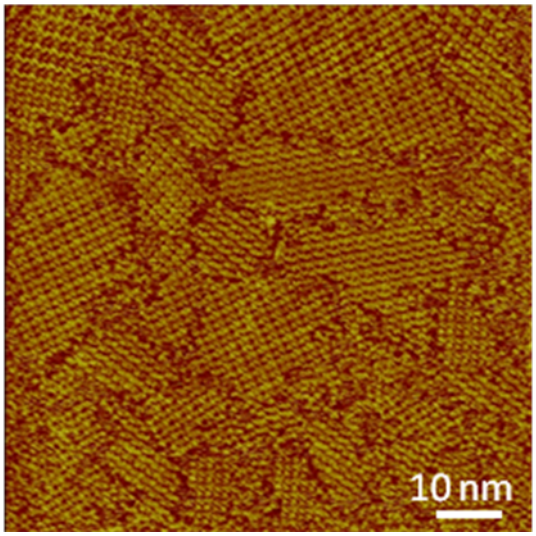

Figure S1. For 100% saturated solutions, the densely packed row structure on HOPG with striped appearance was a dominated structure. I = 280.0 pA, V = 600.9 mV.

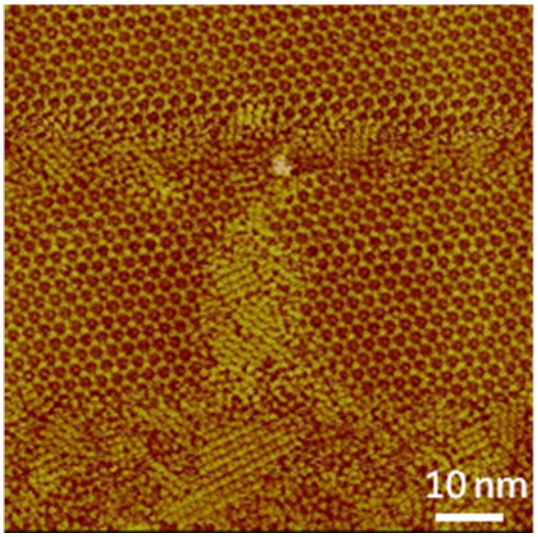

Figure S2. For 50% saturated solutions, a network structure started to appear on the surface, yet in coexistence with the densely packed row structure on the surface. I = 300.1 pA, V = 594.9 mV.

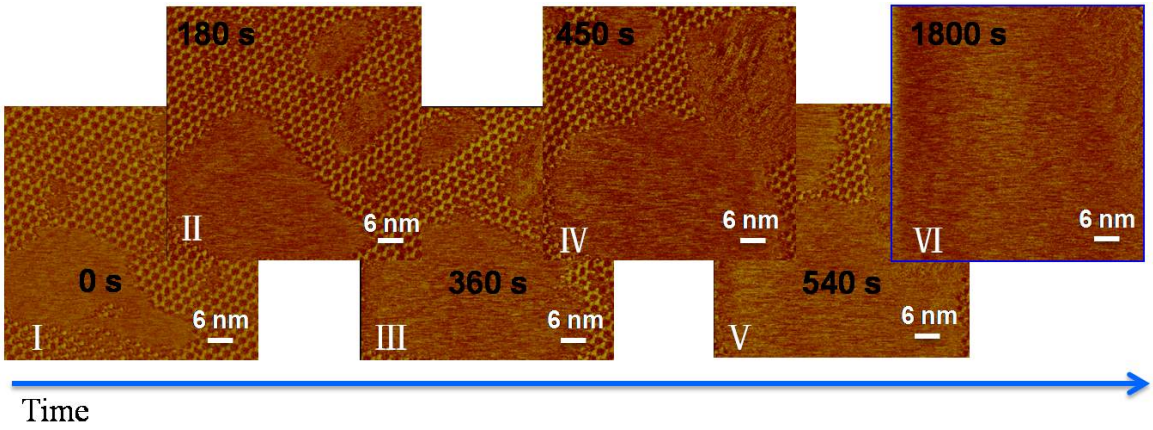

Figure S3. At concentration around 1% of saturation, a considerably unstabled self-assembled monolayer was even captured. STM images were obtained from repeated scanning cycles for about half an hour. I = 296.0 pA, V = 594.9 mV.

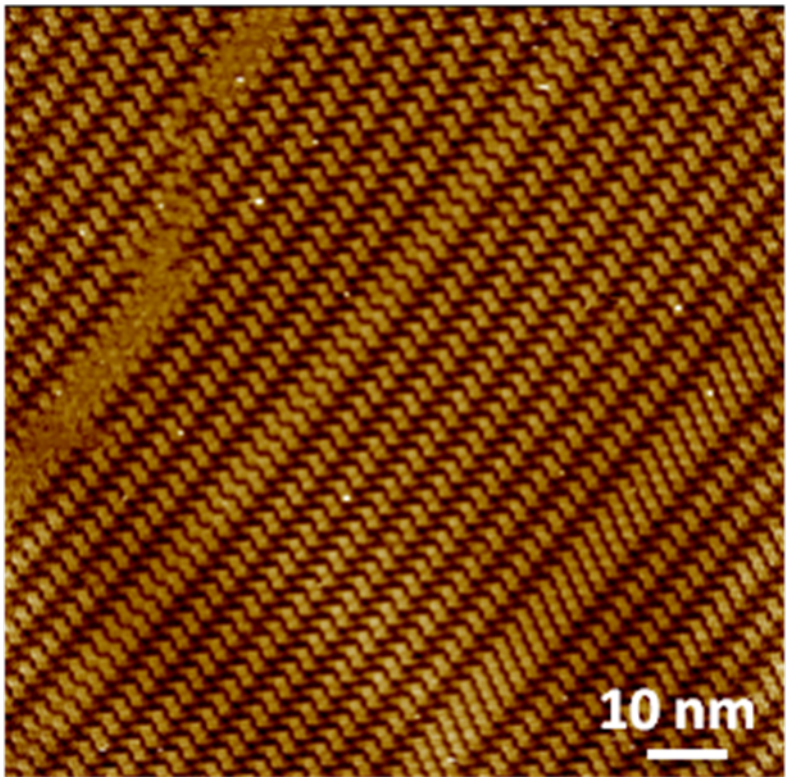

Figure S4. A typically large-area STM image showed some unordered assembled nanoarrays with different shapes, only including $2H_2Pc@H_3TTCA$, $3H_2Pc$ $@H_3TTCA$, $4H_2Pc$-zigzag$@H_3TTCA$, and $5H_2Pc$-line$@H_3TTCA$. I = 405.9 pA, V = 692.1 mV. The concentrations of all the solutions used are less than 10^{-3} M, and H_3TTCA: H_2Pc = 1:1.

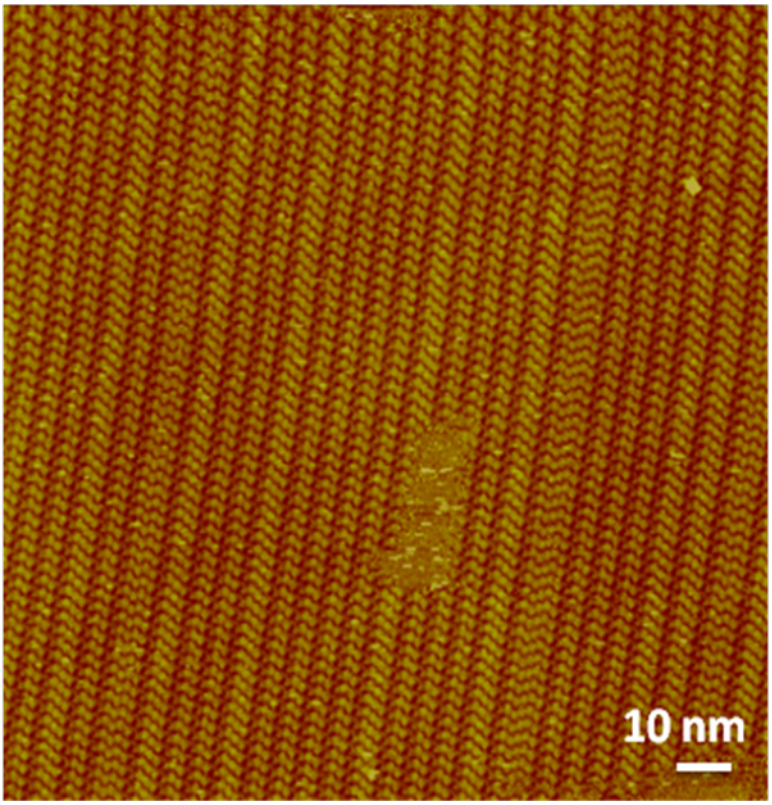

Figure S5. A typically large-area STM image shows some unordered assembled nanoarrays with different shapes, including $2H_2Pc@H_3TTCA$, $3H_2Pc$ $@H_3TTCA$, and $5H_2Pc$-zigzag$@H_3TTCA$. I = 405.9 pA, V = 692.1 mV. The concentrations of all the solutions used are less than 10^{-3} M, and H_3TTCA: H_2Pc = 1:1.

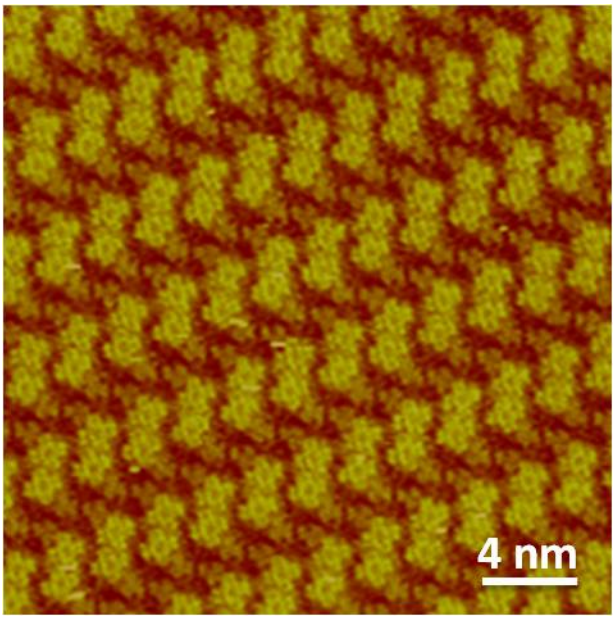

Figure S6. A high resolution STM image of ordered $2H_2Pc@H_3TTCA$ array structures for the $H_2Pc@H_3TTCA$ binary system after the samples were annealed at ~323 K for 10 minutes. I = 380.9 pA, V = 600.1 mV. The concentrations of all the solutions used are less than 10^{-3} M, and H_3TTCA: H_2Pc = 1:1.

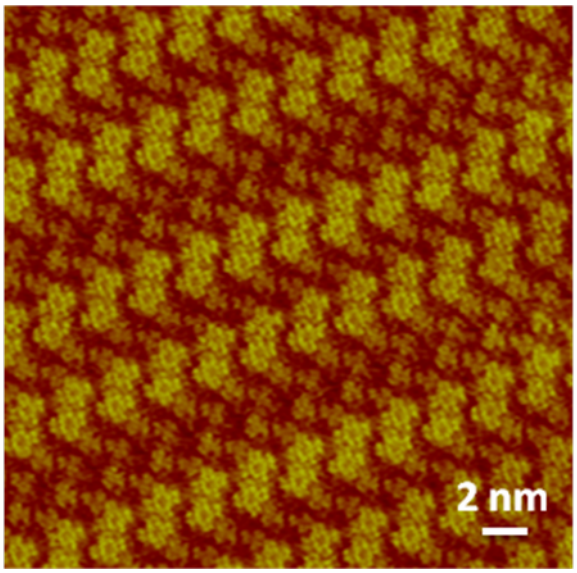

Figure S7. The binary solution of H_3TTCA and H_2Pc leaded to a co-adsorbed monolayer just in a few seconds at room temperature. Arrays of $2H_2$Pc@H_3TTCA structures occur with the deformed H_3TTCA networks. The concentrations of all the solutions used are less than 10^{-3} M, and H_3TTCA: H_2Pc = 1:1.