

Supporting information

Templated Assembling of Phthalocyanine Arrays along a Polymer Chain

Shengbin Lei,^{*a} Ke Deng,^b Zhun Ma,^c Wei Huang^c and Chen Wang^{*b}

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1. Experimental section

Experimental section: PPE 1 and 2 were synthesized as reported. CuPcBu8 and toluene (HPLC) were purchased from Acros and used as received. For sample preparation the compounds were dissolved in toluene with concentration less than 1 mg/g and drop casted on freshly cleaved HOPG surface. For preparation of the composite film PPE and CuPcBu8 were either deposited sequentially or premixed before deposition, these procedures give out the same results. STM characterization was carried out with a Nanoscope IIIa system (Veeco Instruments Co., Ltd.) operating with constant current mode. STM tips were mechanically formed from Pt/Ir (80%/20%) wires.

2. Fundamental informations of the polymers

The degree of polymerization and polydispersity index of PPE 1 and 2 were determined by GPC. The GPC measurements were performed on a Shimadzu LC10A chromatograph equipped with Shim-pack GPC-803, 804 and 8025 columns and refractive index detector, using seven kinds of polystyrenes (MW from 1000 to 240'000 Da) as external standards and THF as an eluent at a flow rate of 1.0 ml/min and 35 °C. The sample solution concentrations are around 10 mg/ml and 20 µl solutions were injected for each example.

Molecular structures and GPC analysis of the PPE polymers. PPE 1: $M_n=7300$, $M_w=12100$, $DI=1.66$; PPE 2: $M_n=9700$, $M_w=22000$, $DI=2.27$.

3. Assembling structures and models of CuPcBu8 and CuPc

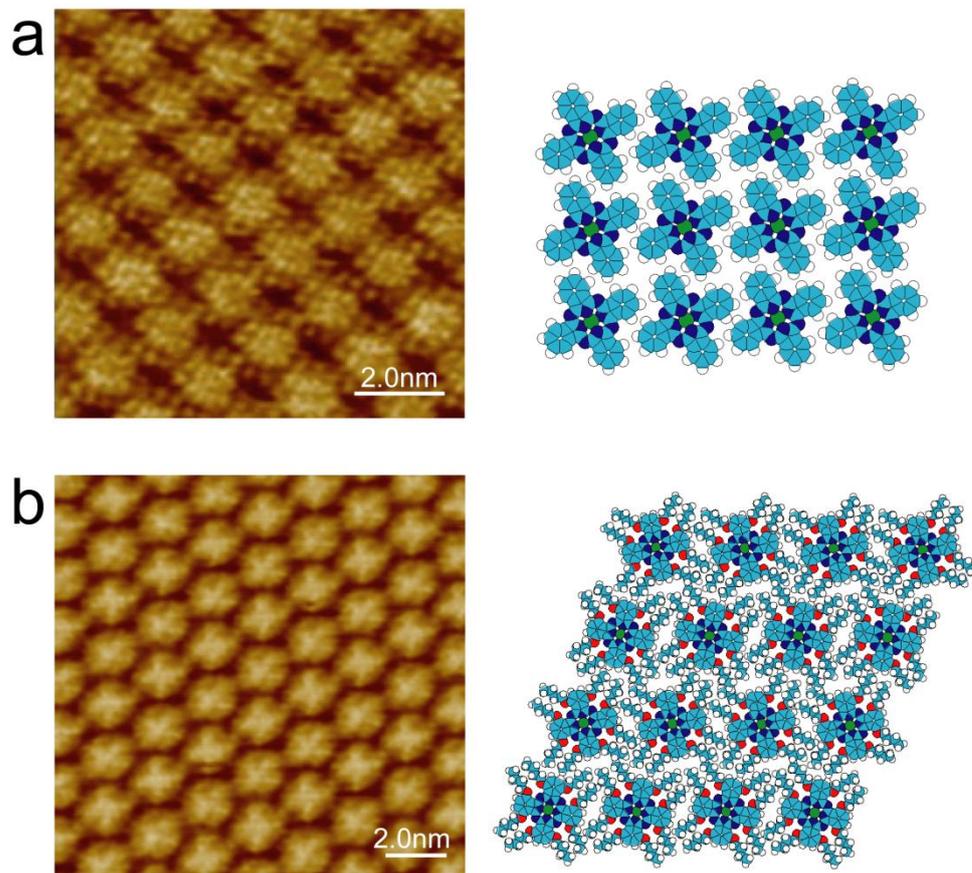


Figure S1. Assembling structures and proposed models of CuPc (a) and CuPcBu8 (b) on the graphite surface. The compounds were deposited onto the surface from a toluene solution and imaged with STM after evaporation of the solvent.

4. Assembling structure of PPE 1

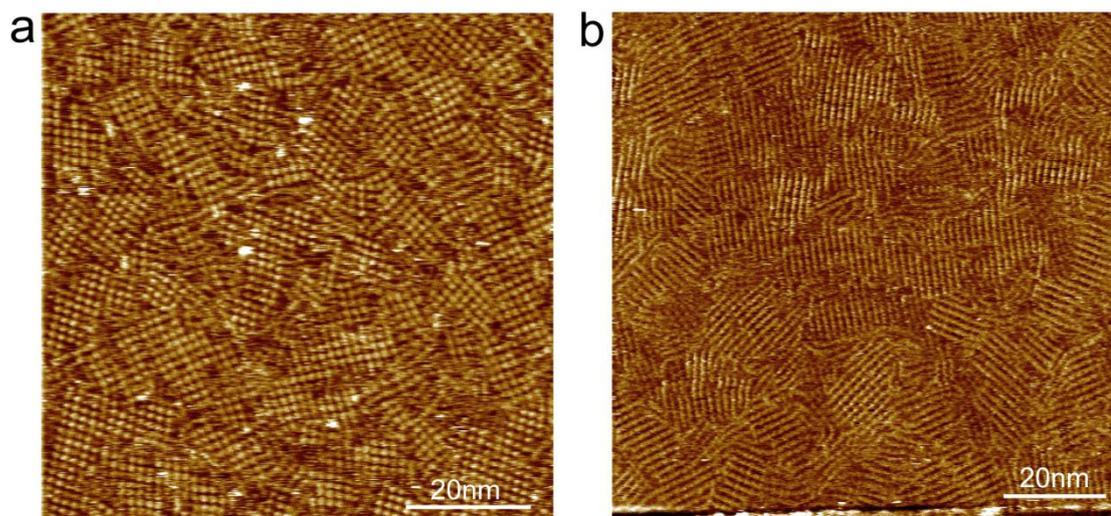


Figure S2. Assembling structure of PPE 1. (a) $V_{\text{bias}} = -1.19\text{V}$, $I_{\text{set}} = 277\text{ pA}$, (b) $V_{\text{bias}} = -820\text{ V}$, $I_{\text{set}} = 440\text{ pA}$. Noticably PPE 1 shows different contrast under different tunneling conditions, possibly due to the spatial distribution of the electron density along the z direction.

5. Assembling structure of PPE 2

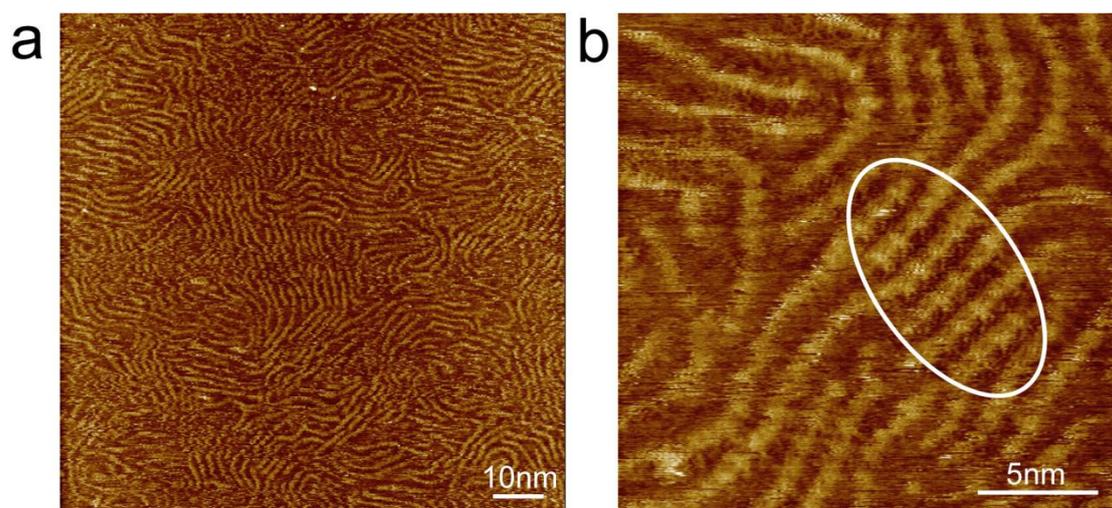


Figure S3. Assembling structure of PPE 2 on graphite. In the high resolution image in (b) a crystalline domain was highlighted with a white ellipse. Within these crystalline domains the side chains can form interdigitation either orientated perpendicular (upleft corner in (b)) or with a $\sim 60^\circ$ angle with respect to the PPE backbone. However, the high density of the side chains prohibits the interdigitation to propagate and only small crystalline domains can be formed.

6. Extra images of the PPE 1/CuPcBu8 assembly

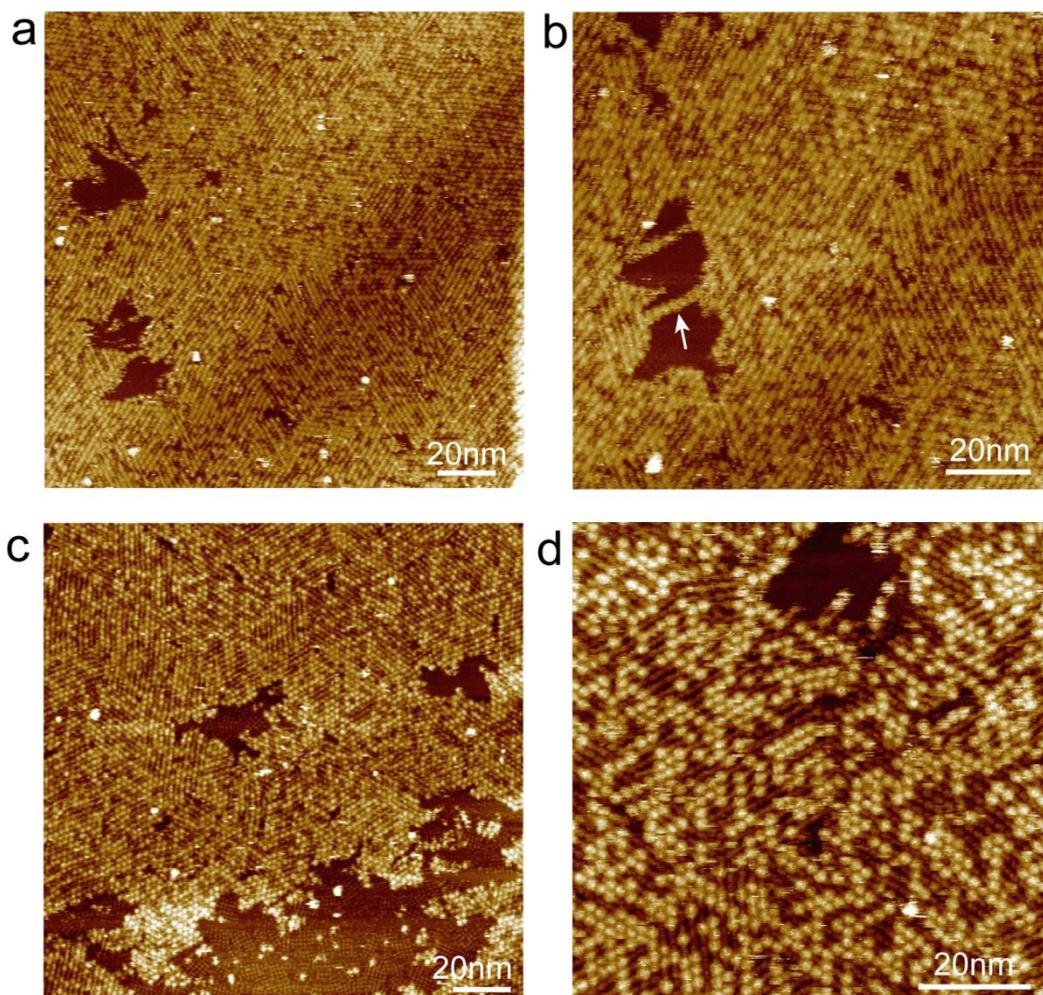


Figure S4. Large (a, c) and medium scale (b, d) STM images of the PPE 1/CuPcBu8 assembly, before (a, b) and after (c, d) partial removal of the atop CuPcBu8 molecules. The white arrow in (b) points to a single CuPcBu8 array assembled along a PPE chain.

7. Extra images of the PPE 2/CuPCBu8 assembly

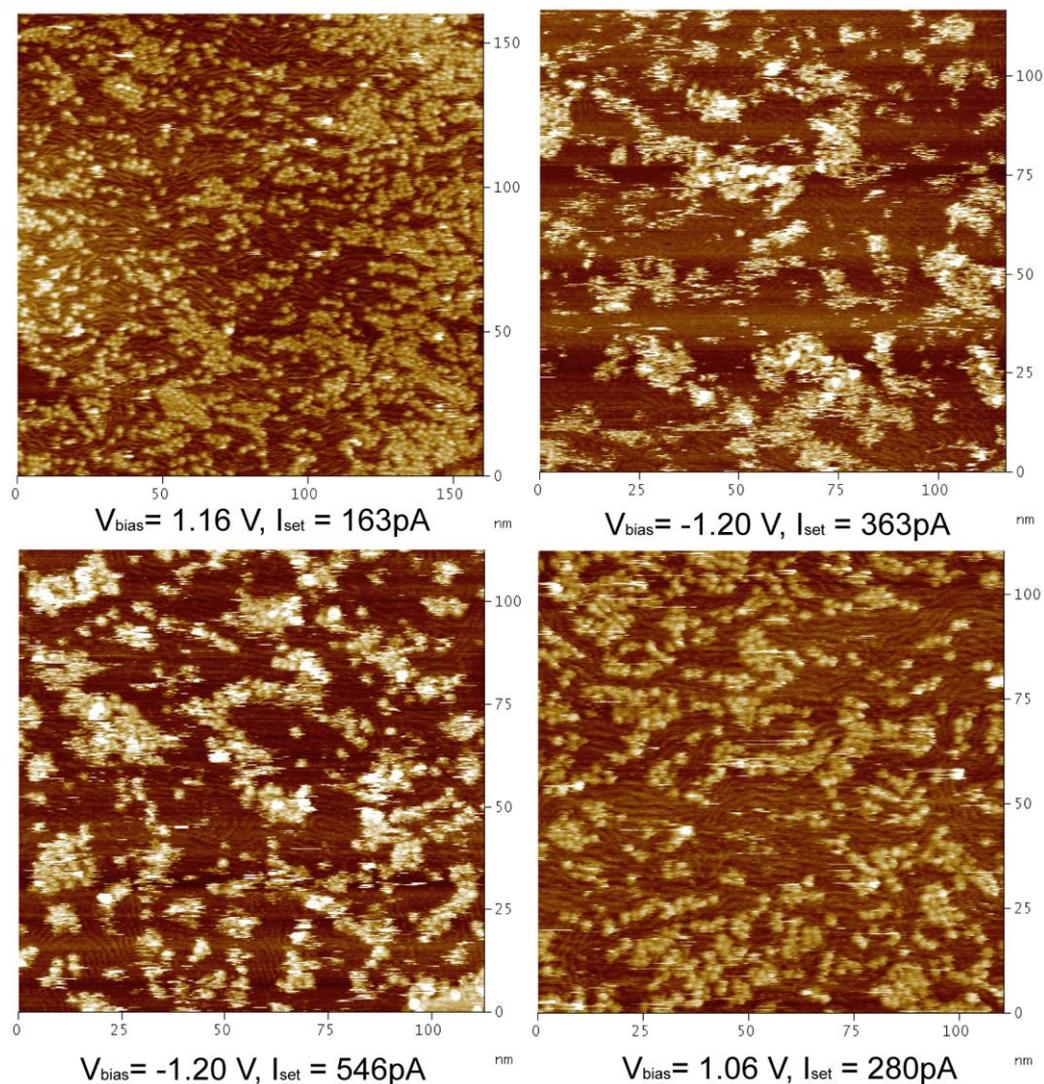


Figure S5. Extra images of the PPE 2/CuPCBu8 assembly. The tunneling conditions were shown underneath the images.

8. Details of DFT simulation

We performed theoretical calculation using density functional theory (DFT) provided by the DMol3 code.^[a] The Perdew and Wang parameterization^[b] of the local exchange-correlation energy are applied in the local spin density approximation (LSDA) to describe exchange and correlation. We expand the all-electron spin-unrestricted Kohn-Sham wave functions in a local atomic orbital basis. In such double-numerical basis set polarization is described. All calculations are all-electron ones, and performed with the Extra-Fine mesh. Self-consistent field procedure is done

with a convergence criterion of 10^{-5} a.u. on the energy and electron density.

We have simulated the rotated CuPcBu8 molecules adsorb atop the different sites along the PPE backbone between two phenyl groups. For the orientation of CuPcBu8, our simulation indicates that the optimized orientation is CuPcBu8 oriented with the edge parallel to the axis of PPE backbone (as shown in Figure S5a). With this optimized orientation, we have equally divided the distance between two phenyl rings into ten parts and calculated the system energy with CuPcBu8 adsorbed on these sites, and the results are shown in Figure S5b. It should be noted that the orientation shown in Figure S5a is not good for close packing of CuPcBu8 as the butyl side chains point directly to that of the neighboring molecules. This is probably the origin of the increased intermolecule distance.

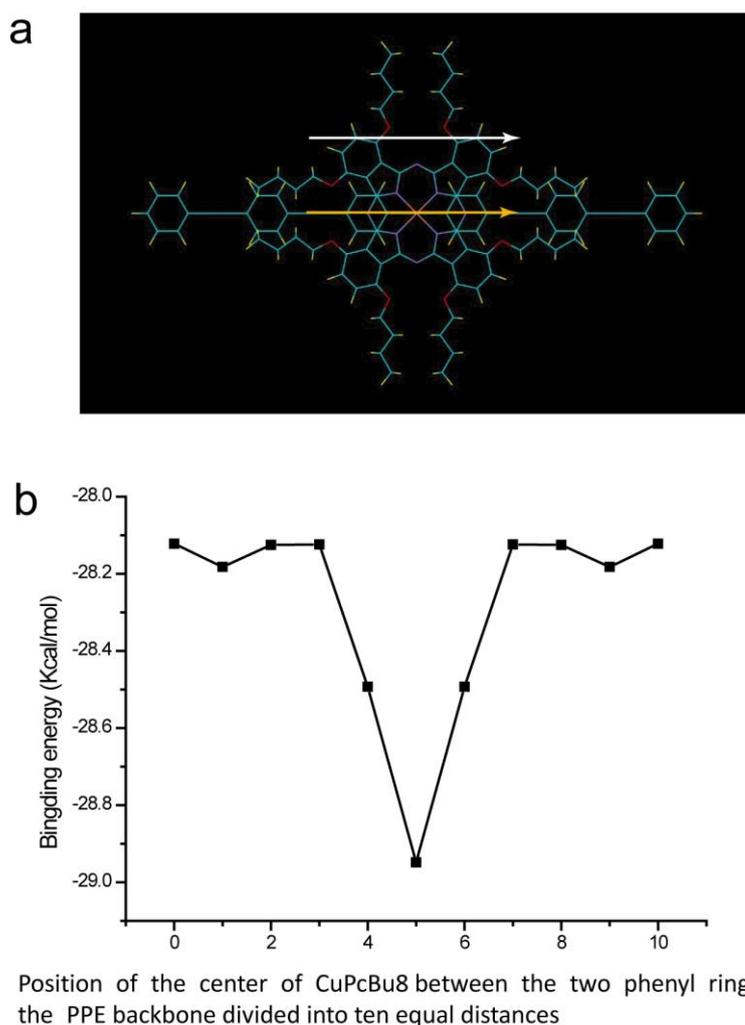


Figure S6. (a) Optimized conformation of the CuPcBu8 adsorbed on a PPE backbone. (b) The adsorption energy of CuPcBu8 along a PPE backbone at different sites. The white and yellow

arrows indicate the molecular edge of CuPcBu8 and the axis of PPE backbone, respectively.

As for CuPc, our simulation also indicates a registered adsorption along the PPE backbone, however, the orientation and optimized adsorption sites are different: CuPc prefers to adsorb on PPE with its molecular edge rotated 40° with respect to the PPE backbone axis and with the copper ion located in the center of phenyl ring (Figure S6). Since the multiples of the distance between phenyl rings (0.69 nm) do not match with the intrinsic intermolecule distance between CuPc (1.45 nm), if CuPc form an array along the PPE backbone not all CuPc molecules can adsorb with the optimized adsorption site, this might be the reason for the low efficiency of templated growth of CuPc by PPE 1.

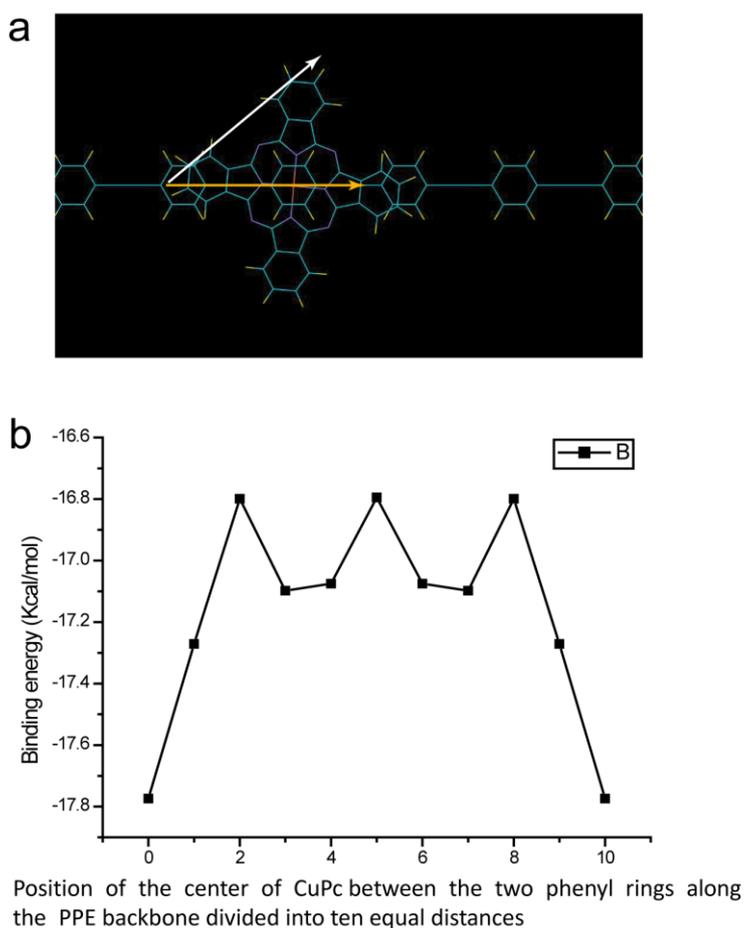


Figure S7. (a) Optimized conformation of the CuPc adsorbed on a PPE backbone. (b) The adsorption energy of CuPc along a PPE backbone at different sites. The white and yellow arrows indicate the molecular edge of CuPcBu8 and the axis of PPE backbone, respectively.

[a] J. P. Perdew, Y. Wang, *Phys. Rev. B* 1992, 45, 13244.

[b] A. Becke, *J. Chem. Phys.* 1988, 88, 2547.

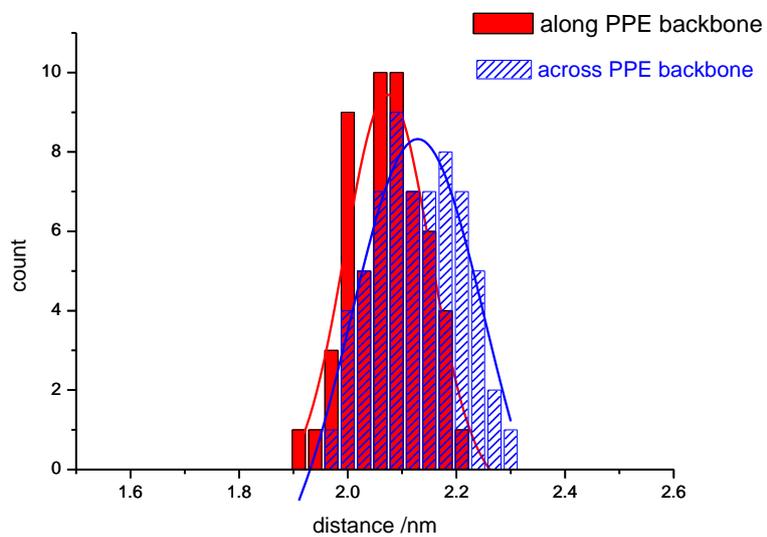


Figure S8. A statistic of the intermolecular distance between CuPcBu8 along and across PPE backbones.