Electronic Supplementary Material (ESI) for Chemical Communications
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Supporting Information

Anchoring of self-assembled monolayers of unsymmetrically-substituted chromophores with an oxoporphyrinogen surface clamp

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1.0 General experimental.

Synthesis. Compounds **1** – **4** were prepared and purified as previously reported.[S1-S4]

Scanning Tunneling Microscopy (STM). The STM experiments were conducted at room temperature using a custom-built Unisoku STM at a base pressure below 1×10^{-10} Torr. All the STM experiments were performed in constant current mode with sample at a fixed bias. Electrochemically etched tungsten tips were used for STM imaging. Au(111) films on mica were used as the substrates, which had been cleaned by cycles of Ar^+ sputtering and annealing. Samples of the molecules were prepared by two methods: solvent assisted drop-casting (for **1** – **4**) and thermal evaporation (**3** and **4** only). For drop-casting, a clean Au(111) surface was prepared by sputtering and annealing cycles, then it was placed in the STM load/lock chamber. Acetone solution of the required compound (c = ~1×10^{-4} M) was dropped on the substrate in air and allowed to evaoporate. Then the sample/substrate were transferred into the vacuum chamber and annealed at a relatively low temperature (about 50 ^{o}C) to remove residual solvent. For thermal evaporation method, **3** or **4** were sublimed from a Knudsen cell at approximately 330 ^{o}C and 370 ^{o}C, respectively. **4** was also sublimed at 420 ^{o}C for preparation of a sample to measure at variable tip bias. The vacuum measured during evaporation was ~5×10^{-8} Torr. To obtain well-ordered states of the molecular monolayer annealing (~100°C) was applied, especially for **3** and **4**.

S1. J. P. Hill, *et al*, *J. Org. Chem*., 2004, **69**, 5861.

S2. J. P. Hill, *et al*, *Eur. J. Org. Chem.*, 2005, 2893.

S3. J. P. Hill, *et al*, *J. Porphyrins Phthalocyanines*, 2007, **11**, 390.

S4. J. P. Hill, *et al*, *Eur. J. Org. Chem*., 2006, 595.

2.0. STM Images of 3.

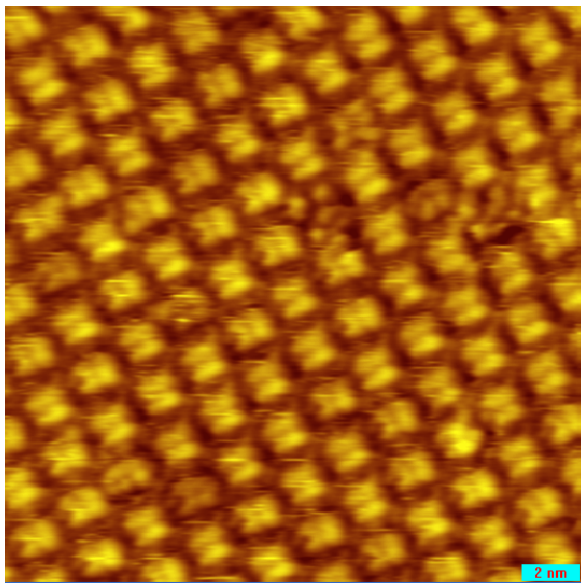

Figure S1. Scanning tunneling microscopy image of bis-2-pyrenyl-substituted-OxP, **3**. Lobes due to the N-substituents are similarly randomly oriented as in **2**. V_s = +2.0V; I_t = 0.1 nA.

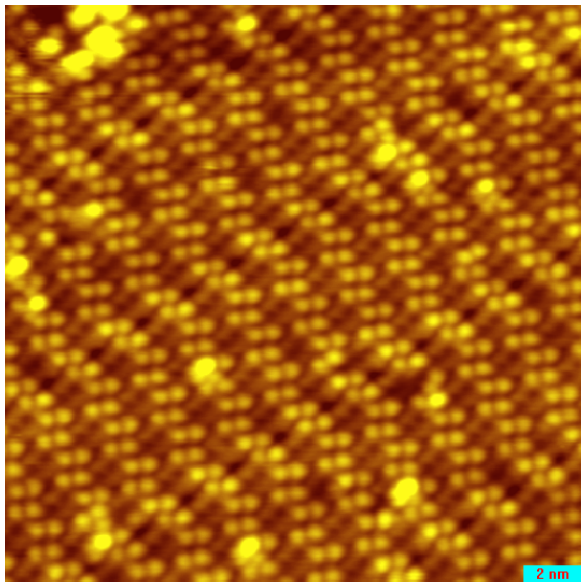

Figure S2. Scanning tunneling microscopy image of bis-2-pyrenyl-substituted-OxP, **3**, after annealing. V_s = +1.5 V; I_t = 0.1 nA.

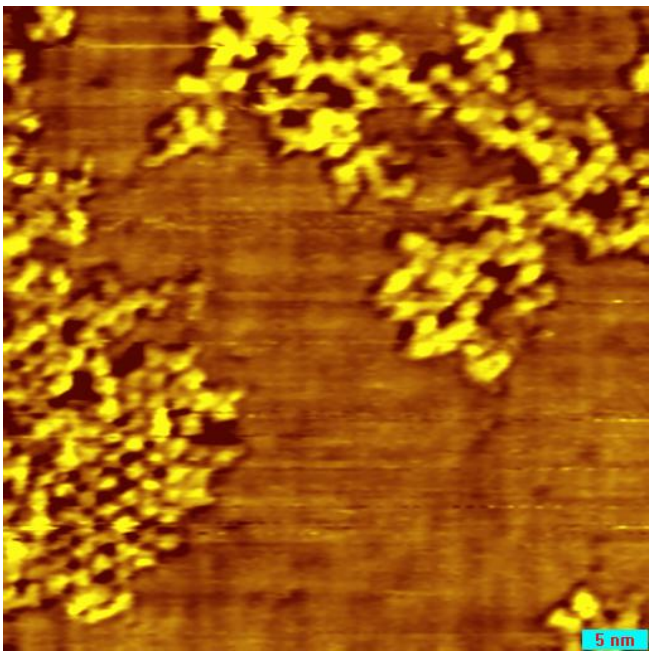

Figure S3. Scanning tunneling microscopy image of **3** deposited by heating in Knudsen cell. V_s = +2.5V; I_t = 0.1 nA.

3.0. Additional STM Image of 2. Bright/Dark Contrast

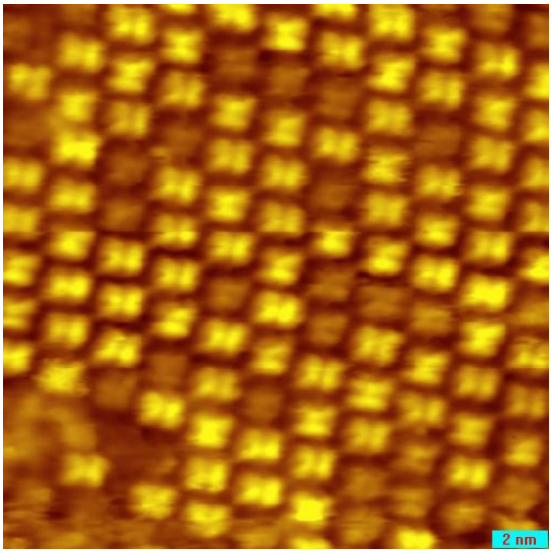

Figure S4. Scanning tunneling microscopy image of **2** deposited from solution. Several molecules appear brighter than others. This is speculated to be due to electronic interaction with the substrate during scanning. V_s = +2.0 V; I_t = 0.1 nA.

4.0. Expanded model structure of 4 monolayer packing

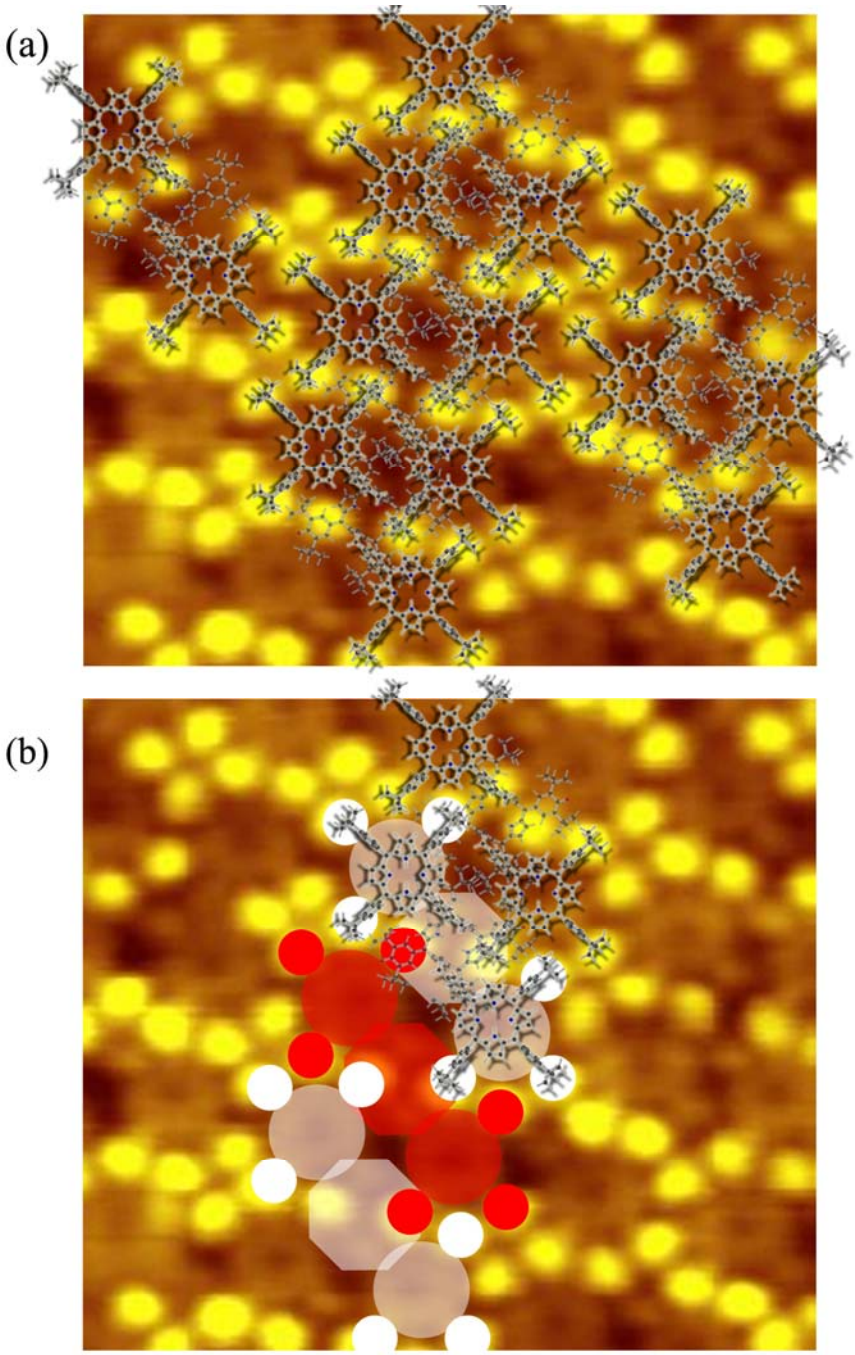

Figure S5 Model structure of **4** packing. (a) In a regular portion of the monolayer structure porphyrins are effectively packed under the influence of their *t*-butyl substituents. (b) Individual molecules are highlighted to illustrate their relative positions (hexagon + two large circles = one molecule of **4** with *t*-butyl groups as small circles; single molecule is all white or all red). Note that porphyrin groups overlap underlying OxP groups.

5.0. Additional STM Images of 4. Disordered monolayer structure.

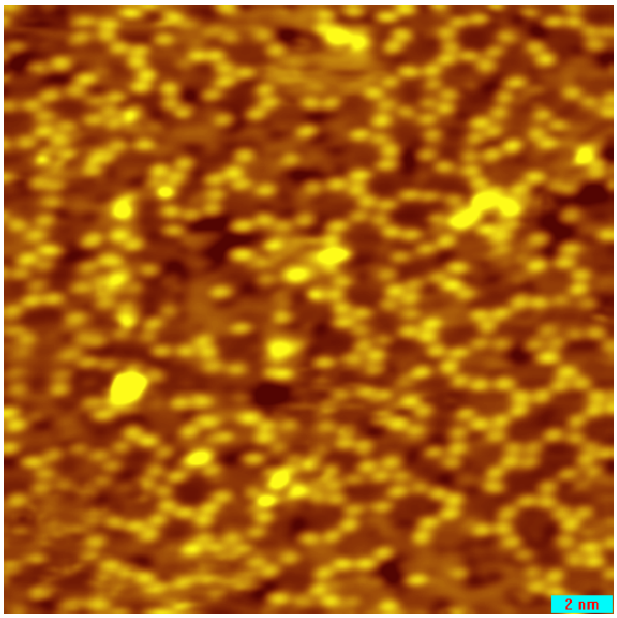

Figure S6. Scanning tunneling microscopy image of **4** deposited from solution revealing a disordered structure although single molecules can still be discerned. V_s = +2.5 V; I_t = 0.1 nA.

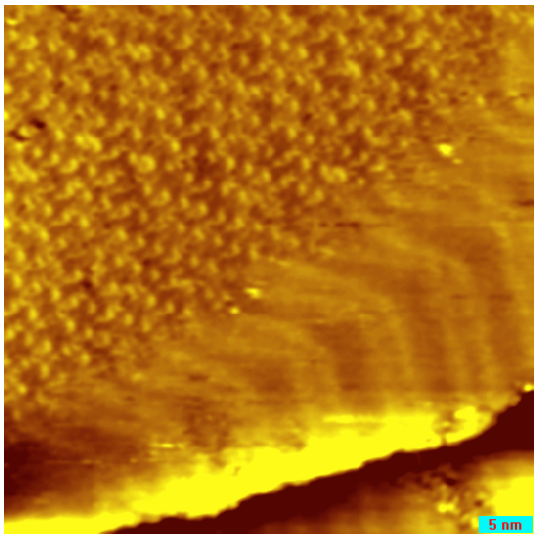

Figure S7. Scanning tunneling microscopy image of **4** deposited by sublimation revealing an ordered monolayer structure (top) adjacent to unresolved area due to molecular 'gas phase' (lower region). V_s = +2.5 V; I_t = 0.1 nA.

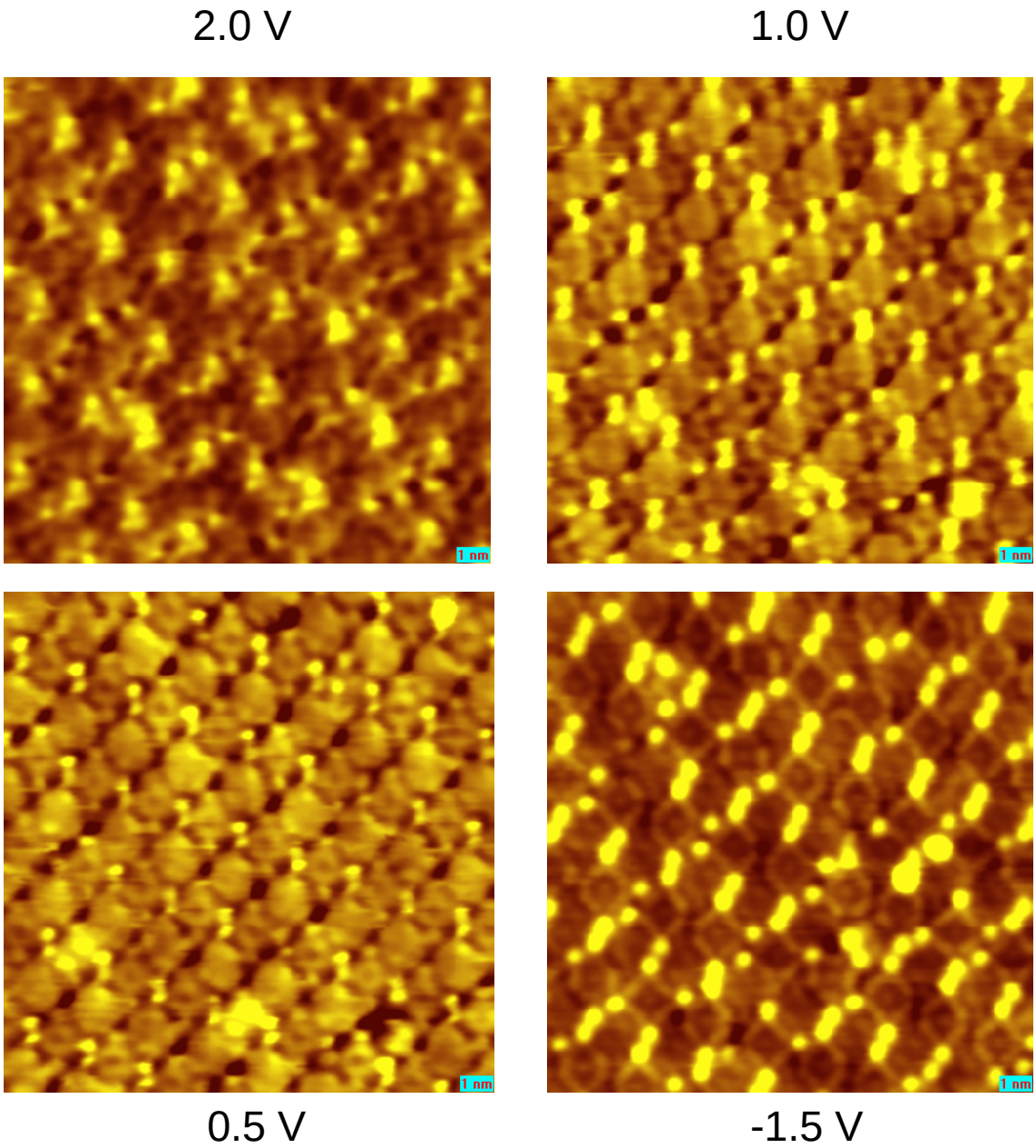

Figure S8. Scanning tunneling microscopy image of **4** deposited by sublimation revealing an ordered monolayer structure and measured at various substrate biases (as indicated). I_t = 0.1 nA.

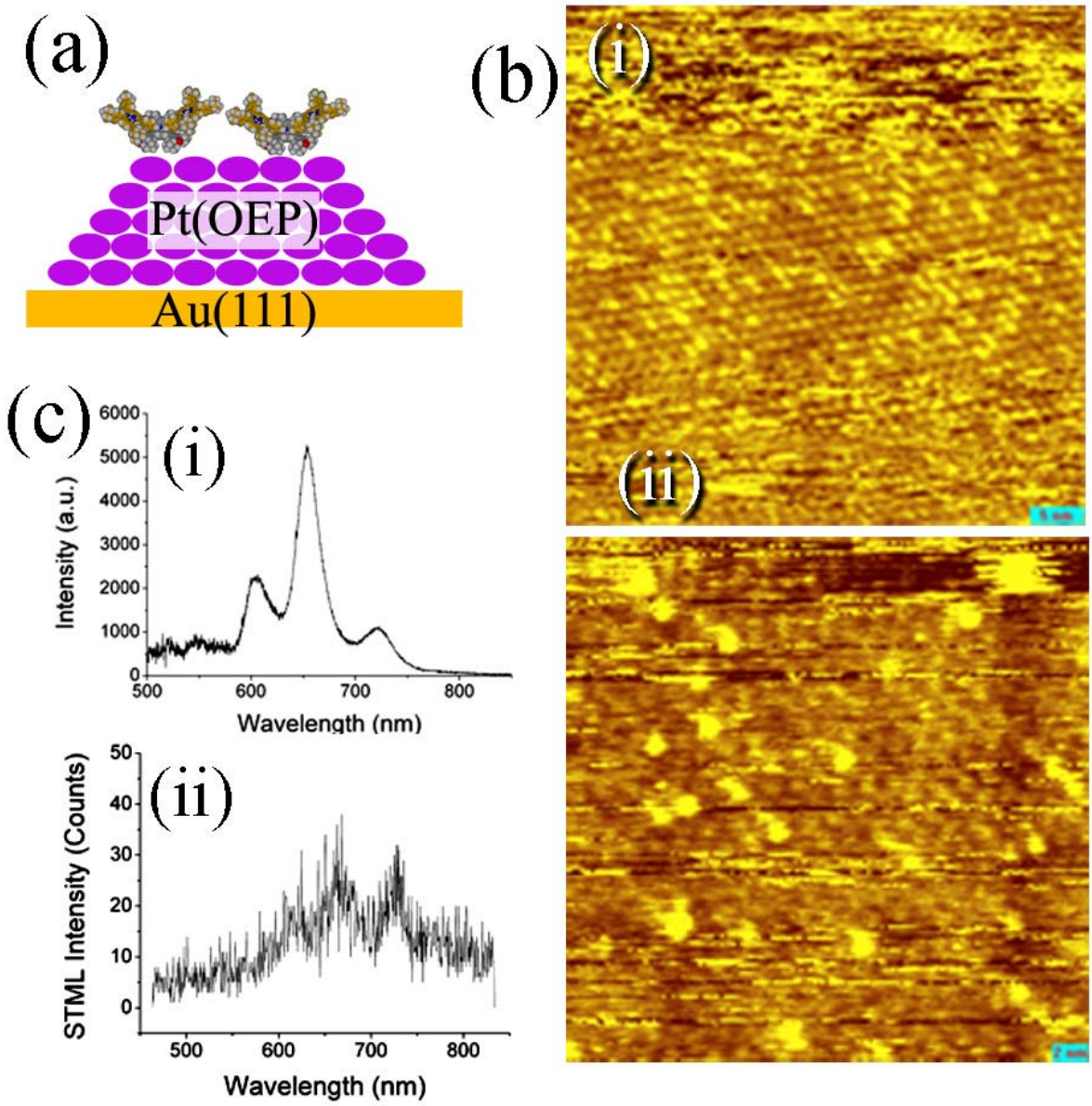

Figure S9. Measurements of molecular fluorescence. (a) A monolayer of **4** was deposited on a thin film (~5 monolayers) of octaethylporhinatoplatinum(II) (PtOEP). (b) STM images of (i) PtOEP thin film, (ii) PtOEP thin film with **4** monolayer deposited on top. (c) Fluorescence emission spectra of **4** in (i) toluene solution, (ii) ellicited from the monolayer in (b)(ii).