

## Electronic Supplementary Information (ESI)

### Molecular tectonics based nanopatterning of interfaces with 2D metal-organic frameworks (MOFs)

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### ***1- Characterization techniques***

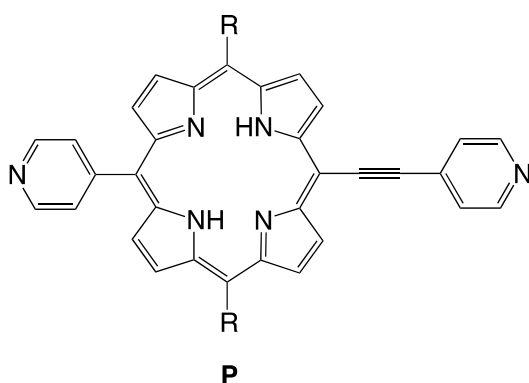
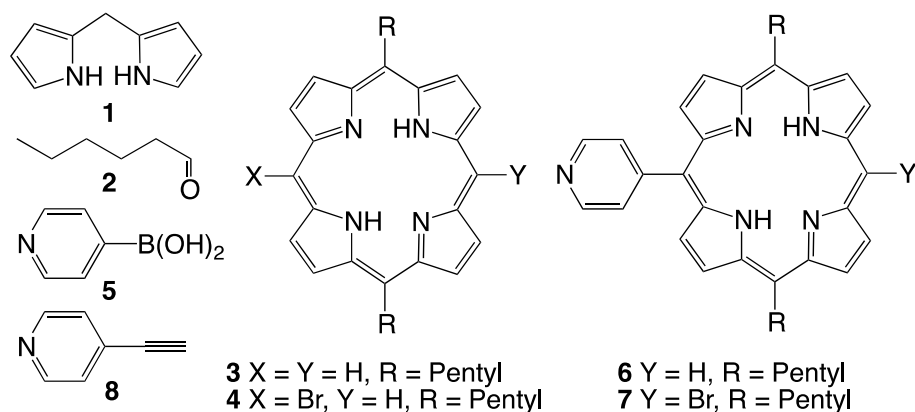
<sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were recorded at room temperature on Bruker NMR spectrometers. UV-Vis absorption spectra were collected at room temperature on a UVIKON XL spectrometer from BIO-TEK instruments. Mass spectra (ESI-MS) were recorded on a microTOF LC spectrometer (Bruker Daltonics, Bremen).

X-ray diffraction: data were collected at 173(2) K on a Bruker APEX8 CCD Diffractometer equipped with an Oxford Cryosystem liquid N<sub>2</sub> device, using graphite-monochromated Mo-K $\alpha$  ( $\lambda$ = 0.71073 Å) radiation. For both structures, diffraction data were corrected for absorption. Structures were solved using SHELXS-97 and refined by full matrix least-squares on  $F^2$  using SHELXL-97. The hydrogen atoms were introduced at calculated positions and not refined (riding model).<sup>1</sup> They can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/datarequest/cif](http://www.ccdc.cam.ac.uk/datarequest/cif). CCDC: 995030

### ***2- Synthesis***

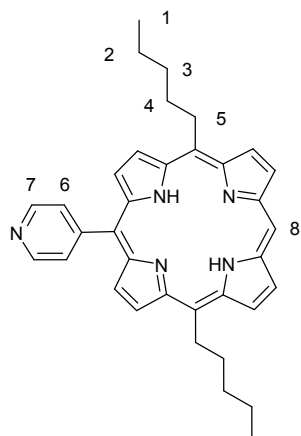
All reagents were purchased from commercial sources and used without further purification, except for pyrrole, NBS, As(PPh<sub>3</sub>)<sub>3</sub> and CuI. The support used for chromatography was Geduran, Silica Gel Si60 (40-63  $\mu$ m) from Merck and Aluminium Oxide 90 standardized from Merck.

Dipyrromethane **1**<sup>2</sup> and 5,15-dipentylporphyrin **3**<sup>3</sup> were synthesized as described in literature.



#### 5,15-dipentyl-10-bromoporphyrin **4**

To a solution of 5,15-dipentylporphyrin **3** (100 mg, 0.22 mmol, 1 eq) in  $\text{CHCl}_3$  (75 ml) and pyridine (0.1 ml) NBS (32 mg, 0.18 mmol, 0.8 eq) was added at  $0^\circ\text{C}$ . After 1h, the reaction mixture was quenched using acetone (4.2 ml) and solvents removed under reduced pressure. The poorly soluble solid mixture thus obtained was washed with methanol (3 x 10 ml) affording a purple solid (100 mg) containing a mixture of three porphyrins: of 5,15-dipentylporphyrin (12%), 5,15-dipentyl-10-bromoporphyrin **4** (70%) and 5,15-dipentyl-10,20-dibromoporphyrin (18%). The mixture was directly used in the subsequent step without further purification.



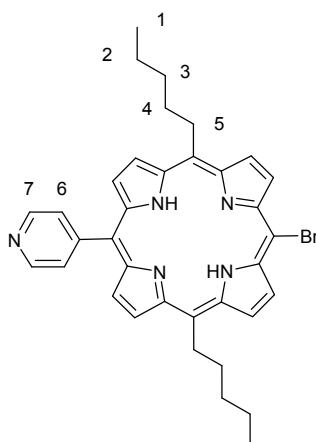
#### 5,15-dipentyl-10(4-yl-pyridine)porphyrin **6**

The mixture of **3**, mono- (**4**) and di-brominated porphyrins (100 mg, 0.189 mmol, 1eq),  $\text{K}_2\text{CO}_3$  (522 mg, 3.7 mmol, 20eq) and pyridine-4-ylboronic acid **5** (232 mg, 1.89 mmol, 10eq) were dissolved in 15 ml of a 10/5/1 mixture of THF/MeOH/ $\text{H}_2\text{O}$ . After flushing argon for 15 min,  $\text{Pd}(\text{PPh}_3)_4$  (22 mg,  $19\mu\text{mol}$ , 0.1eq) was added and the reaction mixture was stirred and heated at  $60^\circ\text{C}$  for 72 h. Solvents were

removed under vacuum and the black solid was dissolved in 100 ml of  $\text{CHCl}_3$  and washed with 100 ml of water, dried over  $\text{MgSO}_4$  and filtered. The mixture was evaporated to dryness under reduced pressure and the mixture was purified by column chromatography ( $\text{SiO}_2$ ,  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  (1.5%)) affording the desired compound **6** as a purple solid (70 mg, 60%, Based on compound **3**).

$^1\text{H-NMR}$  (400 MHz, 25 °C,  $\text{CDCl}_3$ )  $\delta$ (ppm): -2.90 (2H, br s, NH), 0.97 (6H, t,  $J = 7.2$  Hz,  $\text{H}_1$ ), 1.51 (qt, 4H,  $J = 7.2, 7.8$  Hz,  $\text{H}_2$ ), 1.75 (4H, tt,  $J = 7.8, 7.8$  Hz,  $\text{H}_3$ ), 2.52 (4H, tt,  $J = 7.8, 7.8$  Hz,  $\text{H}_4$ ), 4.94 (4H, t,  $J = 7.8$  Hz,  $\text{H}_5$ ), 8.11 (2H, d,  $J = 5.4$  Hz,  $\text{H}_6$ ), 8.80 (2H, d,  $J = 4.8$  Hz,  $\text{H}_\beta$ ), 8.98 (2H, d,  $J = 5.4$  Hz,  $\text{H}_7$ ), 9.34 (2H, d,  $J = 4.7$  Hz,  $\text{H}_\beta$ ), 9.45 (2H, d,  $J = 4.8$  Hz,  $\text{H}_\beta$ ), 9.52 (2H, d,  $J = 4.7$  Hz,  $\text{H}_\beta$ ), 10.06 (s, 1H,  $\text{H}_8$ ).  $^{13}\text{C-NMR}$  (400 MHz, 25 °C,  $\text{CDCl}_3$ )  $\delta$ (ppm): 14.2, 22.8, 32.7, 34.9, 38.4, 104.5, 115.5, 119.8, 127.9, 128.3, 129.4, 131.0, 132.0, 143.7, 144.9, 147.2, 147.6, 148.0, 151.4. UV-Vis ( $\text{CH}_2\text{Cl}_2$ , 25 °C)  $\lambda_{\text{max}}$  (nm) ( $\epsilon \times 10^{-4}/\text{L mol}^{-1}\text{cm}^{-1}$ ): 411 (34.3), 480 (0.3), 510 (1.6), 543 (0.4), 586 (0.5), 642 (0.3).  $m/z$  ( $\text{ESI}^+$ ) calculated for  $\text{C}_{35}\text{H}_{38}\text{N}_5$ : 528.312 ( $\text{M}+\text{H}^+$ ), found 528.310.

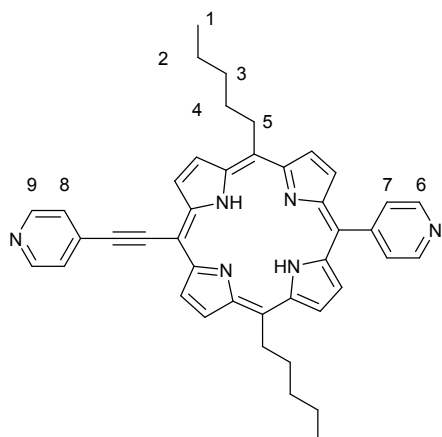
### 5,15-dipentyl-10(4-yl-pyridine)-20-bromoporphyrin **7**



A solution of compound **6** (65 mg, 0.12 mmol, 1 eq) in  $\text{CHCl}_3$  (75 ml) and pyridine (0.1 ml) was treated with NBS (22 mg, 0.12 mmol, 1 eq) at 0 °C. After 2h, the reaction was quenched with acetone (4 ml). The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography ( $\text{SiO}_2$ ,  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  (5%)) and washed with methanol (3 ml) to yield the bromoporphyrin **7** as a brown product (70 mg, 96%).

$^1\text{H-NMR}$  (300 MHz, 25 °C,  $\text{CDCl}_3$ )  $\delta$ (ppm): -3.00 (s, br, 2H, NH), 0.96 (6H, t,  $J = 7.2$  Hz,  $\text{H}_1$ ), 1.51 (4H, qt,  $J = 7.2$  Hz,  $J = 7.8$  Hz,  $\text{H}_2$ ), 1.69 (4H, tt,  $J = 7.8, 7.8$  Hz,  $\text{H}_3$ ), 2.40 (4H, tt,  $J = 7.8, 7.8$  Hz,  $\text{H}_4$ ), 4.66 (4H, t,  $J = 7.8$  Hz,  $\text{H}_5$ ), 8.05 (2H, dd,  $J = 4.3, 1.5$  Hz,  $\text{H}_6$ ), 8.67 (2H, d,  $J = 4.9$  Hz,  $\text{H}_\beta$ ), 9.01 (2H, dd,  $J = 4.3, 1.5$  Hz,  $\text{H}_7$ ), 9.24 (2H, d,  $J = 4.5$  Hz,  $\text{H}_\beta$ ), 9.26 (2H, d,  $J = 4.5$  Hz,  $\text{H}_\beta$ ), 9.58 (2H, d,  $J = 4.9$  Hz,  $\text{H}_\beta$ ).  $^{13}\text{C-NMR}$  (500 MHz, 25 °C,  $\text{CDCl}_3$ )  $\delta$ (ppm): 14.3, 22.9, 32.8, 35.3, 38.6, 94.7, 102.9, 115.8, 119.0, 120.3, 120.8, 128.3, 128.5, 129.2, 131.0, 132.7, 143.7, 148.5, 150.6. UV-Vis ( $\text{CH}_2\text{Cl}_2$ , 25 °C)  $\lambda_{\text{max}}$  (nm) ( $\epsilon \times 10^{-4}/\text{L mol}^{-1}\text{cm}^{-1}$ ) ( $\text{CH}_2\text{Cl}_2$ ): 419 (45.2), 488 (0.4), 520 (1.6), 555 (1.0), 599 (0.4), 658 (0.6).  $m/z$  ( $\text{ESI}^+$ ) calculated for  $\text{C}_{35}\text{H}_{37}\text{N}_5\text{Br}$ : 606.2227 ( $\text{M}+\text{H}^+$ ), found 606.2263.

## 5,15-dipentyl-10-(4-yl-pyridine)-20-ethynylpyridin-porphyrin P



Solvents used were used distilled and degassed. Compound **7** (80 mg, 0.13 mmol, 1eq), Pd<sub>2</sub>(dba)<sub>3</sub> (30 mg, 0.03 mmol, 0.25eq), 4-ethynylpyridine **8** (20 mg, 0.20 mmol, 1.5 eq) and As(Ph)<sub>3</sub> (40 mg, 0.13 mmol, 1eq) were dissolved under argon in 15 ml of a 7:3 mixture of THF/Et<sub>3</sub>N. The mixture was stirred at 66 °C for 4h. Solvents were removed under reduced pressure and the crude product was purified by chromatography (Al<sub>2</sub>O<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>/MeOH (0.5 %)) and washed with ether (2ml) to

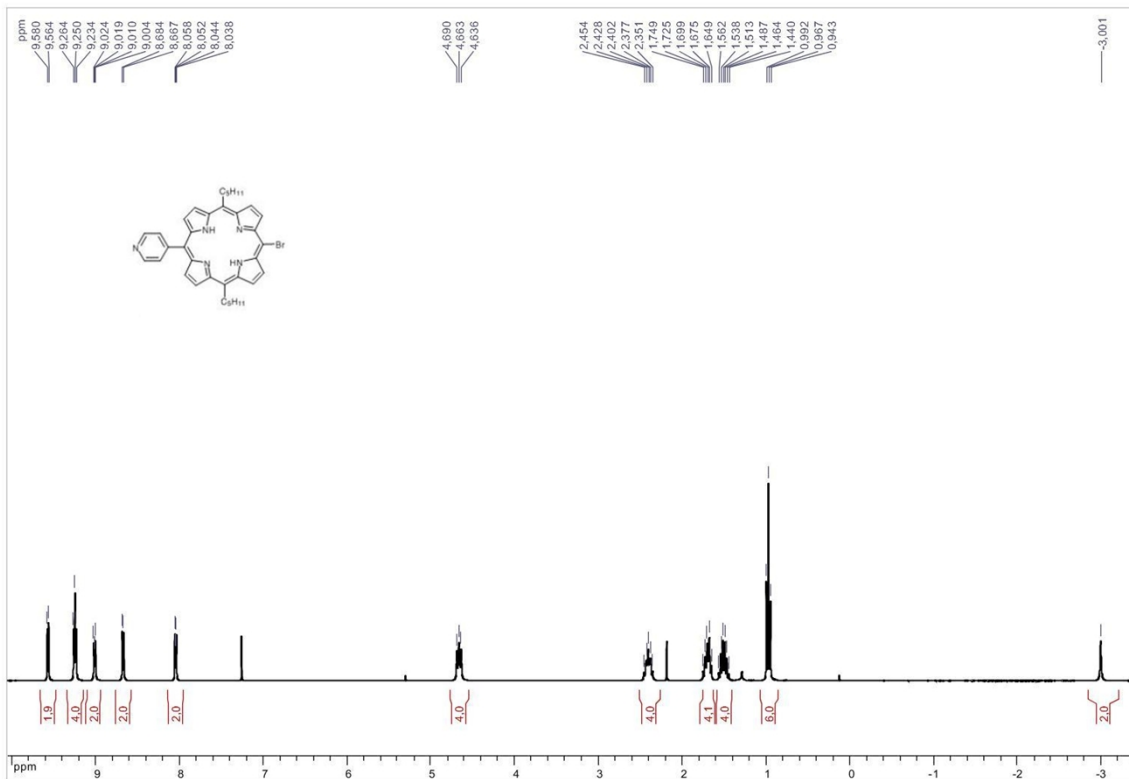
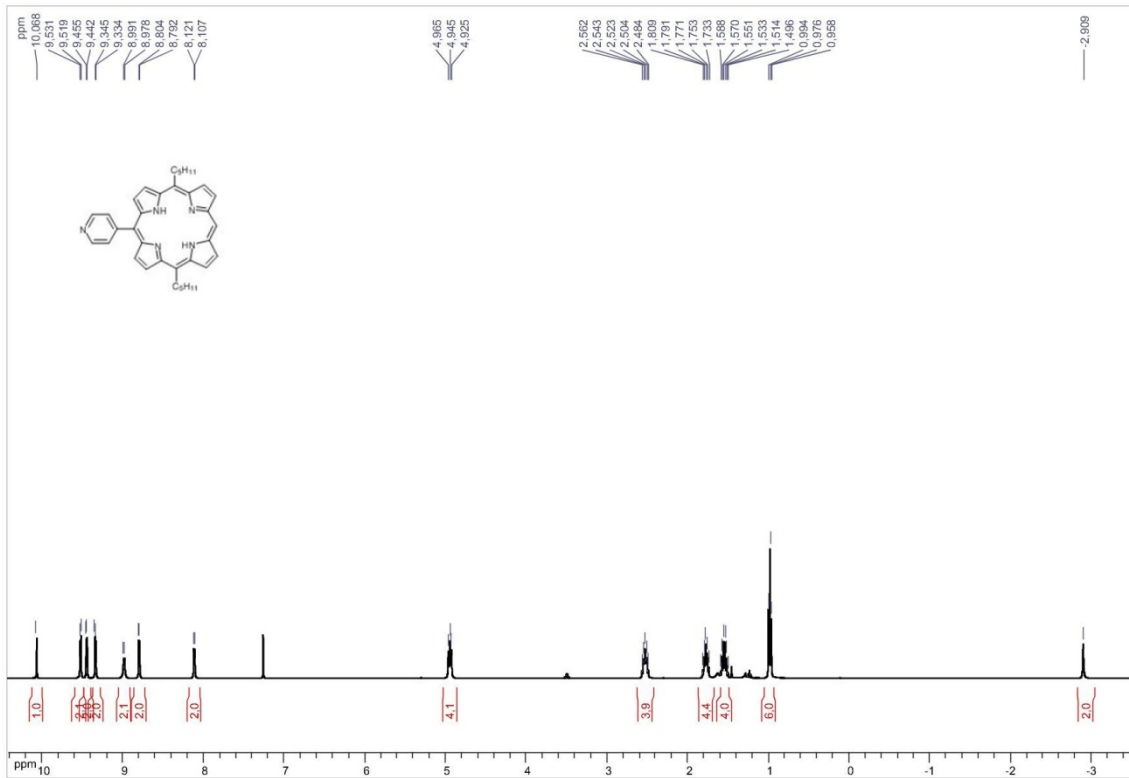
yield the desired compound **P** as a purple solid (60.1 mg, 73%).

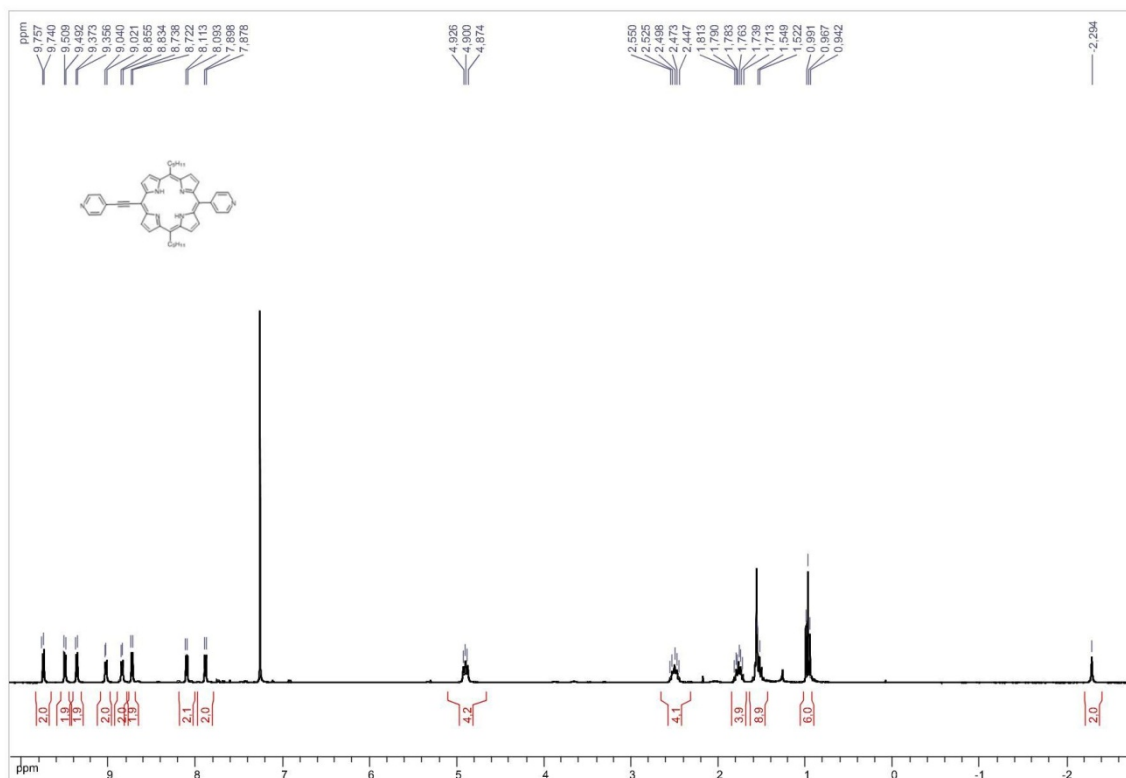
<sup>1</sup>H-NMR (300 MHz, 25 °C, CDCl<sub>3</sub>) δ(ppm): -2.29 (2H, br s, NH), 0.97 (6H, t, J = 7.4 Hz, H<sub>1</sub>), 1.54 (4H, qt, J = 7.4, 7.6 Hz, H<sub>2</sub>), 1.76 (4H, tt, J = 7.6, 7.8 Hz, H<sub>3</sub>), 2.50 (4H, tt, J = 7.8, 7.8 Hz, H<sub>4</sub>), 4.90 (4H, t, J = 7.8 Hz, H<sub>5</sub>), 7.88 (2H, d, J = 6.0 Hz, H<sub>8</sub>), 8.10 (2H, d, J = 5.9 Hz, H<sub>7</sub>), 8.73 (2H, d, J = 4.9 Hz, H<sub>β</sub>), 8.84 (2H, d, J = 6.0 Hz, H<sub>9</sub>), 9.03 (2H, d, J = 5.9 Hz, H<sub>6</sub>), 9.36 (2H, d, J = 4.9 Hz, H<sub>β</sub>), 9.50 (2H, d, J = 4.9 Hz, H<sub>β</sub>), 9.75 (2H, d, J = 4.9 Hz, H<sub>β</sub>). <sup>13</sup>C-NMR (500 MHz, 25 °C, CDCl<sub>3</sub>) δ(ppm): 17.0, 22.8, 32.7, 35.1, 38.4, 93.5, 96.7, 97.3, 117.8, 121.7, 125.4, 127.6, 128.1, 129.1, 130.8, 131.5, 148.2, 150.1, 150.6. UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>, 25 °C) λ<sub>max</sub> (nm) (εx10<sup>-4</sup>/L mol<sup>-1</sup>cm<sup>-1</sup>) (CH<sub>2</sub>Cl<sub>2</sub>): 433 (34.9), 504 (0.7), 534 (1.0), 576 (2.6), 612 (0.4), 671 (1.5). m/z (ESI<sup>+</sup>) calculated for C<sub>42</sub>H<sub>41</sub>N<sub>6</sub>: 629.339 (M+H<sup>+</sup>), found 629.338.

### 3- Crystallographic data

Single crystal of the porphyrin **P** were obtained at room temperature upon slow diffusion of methanol into a CHCl<sub>3</sub> solution of the porphyrin in (0.5 mL, 10<sup>-3</sup>M)

Crystallographic data: C<sub>42</sub>H<sub>40</sub>N<sub>6</sub>, M = 626.80, *triclinic*, group spatial *P-1*, *a* = 9.8125(3), *b* = 14.2149(5), *c* = 14.3580(6) Å, *α* = 81.339(2)°; *β* = 71.164(2)°; *γ* = 86.240(2)°, *V* = 1873.53(12) Å<sup>3</sup>, *T* = 173 K, *Z* = 2, *D<sub>c</sub>* = 1.115g/cm<sup>3</sup>, *μ* = 0.067 mm<sup>-1</sup>, 10117 collected reflections, 10117 independent, (*R*<sub>int</sub> = 0.0675), *GooF* = 1.028, *R*<sub>1</sub> = 0.0661, *wR*<sub>2</sub> = 0.1792 for *I* > 2σ(*I*) and *R*<sub>1</sub> = 0.1394, *wR*<sub>2</sub> = 0.2005 for all data. Disordered solvent molecules could not be refined and thus the SQUEEZE command was used.<sup>4</sup>





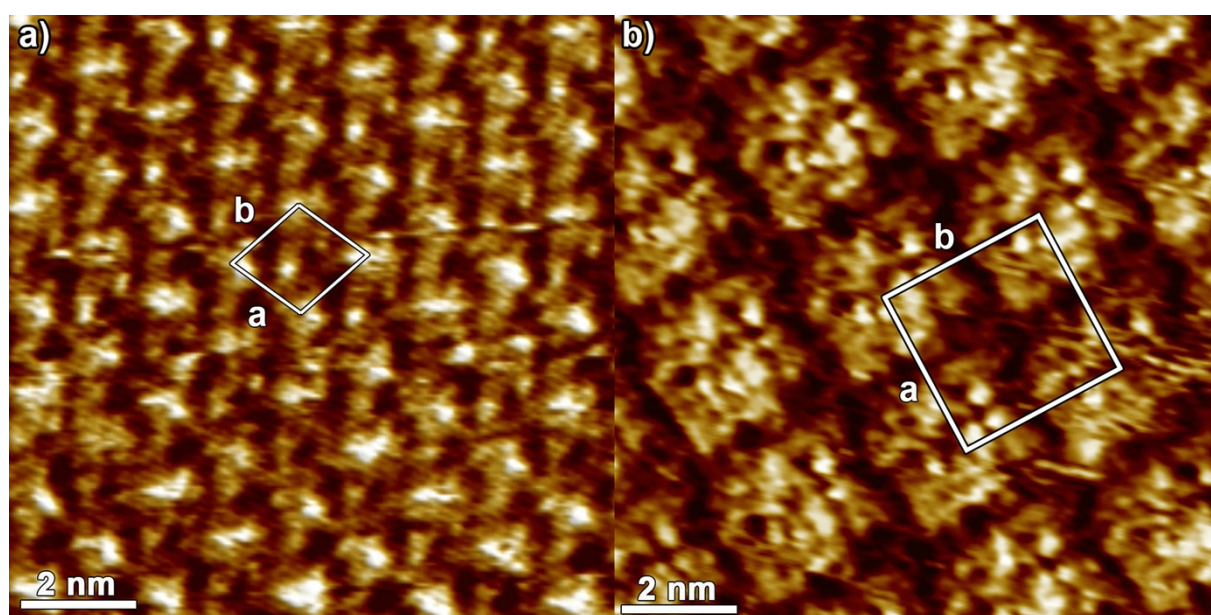
#### 4- Scanning Tunnelling Microscopy experiments

##### 4.1 Experimental details

Scanning Tunneling Microscopy (STM) measurements were performed using a Veeco scanning Tunneling microscope (multimode Nanoscope III, Veeco) at the interface between a highly oriented pyrolytic graphite (HOPG) substrate and a supernatant solution, thereby mapping a maximum area of  $1 \mu\text{m} \times 1 \mu\text{m}$ . Solution of molecules were applied to the basal plane of the surface. For STM measurements, the substrates were glued to a magnetic disk and an electric contact was made with silver paint (Aldrich Chemicals). The STM tips were mechanically cut from a Pt/Ir wire (90/10, diameter 0.25 mm). The raw STM data were processed through the application of background flattening and the drift was corrected using the underlying graphite lattice as a reference. The lattice was visualized by lowering the bias voltage to 20 mV and raising the current up to 65 pA. STM imaging was carried out in constant height mode without turning off the feedback loop, to avoid tip crashes. The STM images were recorded at room temperature once achieving a negligible thermal drift. Solutions of 5,15-dipentyl-10-(4-yl-pyridine)-20-ethynylpyridin-porphyrin were prepared by

dissolving the molecules in  $\text{CHCl}_3$  and diluting with 1-phenyloctane to give 1 mM solution (solvent composition 99 % 1-phenyloctane + 1 %  $\text{CHCl}_3$ ). All of the molecular models were minimized with MMFF and processed with QuteMol visualization software (<http://qutemol.sourceforge.net>). On the other hand,  $\text{CoCl}_2 \times 2\text{H}_2\text{O}$  were dissolved first in isopropanol and diluted in 1-phenyloctane to give 2 mM solution (solvent composition 99 % 1-phenyloctane + 1 % isopropanol).

#### 4.2 *STM current images of free P and [P(CoCl<sub>2</sub>)]<sub>n</sub>*



S1. a) STM current image of 2D free P. b) STM current image of 2D  $[\text{P}(\text{CoCl}_2)]_n$ . Tunneling parameters  $I_t = 25$  pA,  $V_t = 650$  mV

#### 5- References

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