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In-solution patterning of standing up porphyrin based nanostructures within hydrogen bonded porous networks – Structural effect of host matrix on guest entities

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1) Network and SAM elaboration – solution process

a. Chemicals

N,N–Dimethylformamide (DMF) was purchased from Sigma-Aldrich (CHROMASOLV® Plus for HPLC, purity ≥99.9%) and it was used without further purification.

Dichloromethane (DCM) GPR Rectapur® (purity 99% assay, 0.02% water) was purchased from VWR Chemicals. An extraction with a sodium carbonate (Na_2CO_3) at 50 g/L in ultrapure water was performed. Before use, a distillation on column under ambient pressure has been realized.

Perylene–3,4,9,10–tetracarboxylic–3,4,9,10–diimide (PTCDI) was purchased from Alfa Aesar (purity > 98%) and has been used as received.

1,3,5–triazine–2,4,6–triamine (melamine) was purchased from Fluka, Sigma-Aldrich (HPLC, purity ≥ 99.0%) and has been used as received.

b. Au(111) substrate preparation

Au(111) slides were purchased from Phasis, Geneva. They consist in a 200 nm thick gold layer evaporated on mica. They were cleaned by immersion in 1/1 ultrapure water/ethanol mixture for 2 minutes and blown dry under an argon flow. An annealing step was then performed with 10 short passages in a hydrogen flame immediately before the immersion of the sample in solution.

c. PTCDI-melamine network elaboration

A suspension of PTCDI at 50 $mg.L^{-1}$ in DMF was prepared and then diluted to a concentration of 3.2×10^{-6} $mol.L^{-1}$. In parallel, a solution of melamine at 4×10^{-3} $mol.L^{-1}$ in DMF was also prepared. The mixing of equal volumes of those two solutions resulted in a PTCDI melamine solution at 1.8×10^{-6} $mol.L^{-1}$ and 2×10^{-3} $mol.L^{-1}$ respectively. Such a solution was heated at 100°C for 45 minutes before dipping a clean Au(111) slide for 1.5 minutes at the same temperature. The slide was then briefly rinsed in purified DMF and blown dry under an argon flow.

d. SAM elaboration

Intrinsic PNiSAc SAM. A solution of PNiSAc at 10^{-5} $mol.L^{-1}$ was prepared in purified DCM and a freshly prepared gold slide was immersed inside for 5 minutes at room temperature. The sample was then rinsed by dipping twice the sample for 1.5 minute in purified DCM followed by drying under argon.

Patterned PNiSAc SAM. The back-filling of PTCDI melamine networks with PNiSAc was performed by immersing the templated Au(111) slide in a solution of PNiSAc following the protocol described above.

2) STM experimental procedure

STM studies were performed under ambient conditions using a Molecular Imaging PicoScan® microscope. STM image acquisition was done in the constant current mode with the following typical parameters:

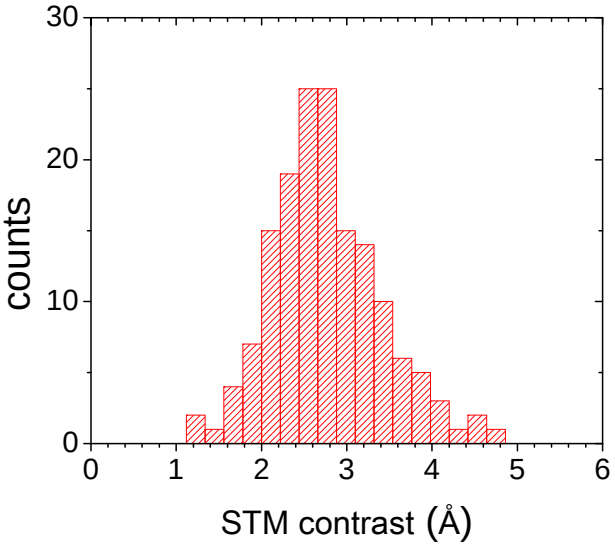
PTCDI melamine host network: current set point ranging from 100 pA to 300 pA; bias voltage ranging from 100 mV to 300 mV.

PNiSAc SAMs and host guest networks: current set point ranging from 1 pA to 5 pA; bias voltage ranging from 200 mV to 500 mV.

Image processing was carried out with the free WSxM software.[1]

3) Apparent height histogram of porphyrin derivatives in the intrinsic SAM

The height histogram of PNiSAc in the intrinsic SAM has been measured over 160 protrusions attributed to single molecules in the STM image presented in Fig. 1b). STM contrast has been evaluated from a single reference area located at a domain wall. The distribution is relatively broad but exhibits a single peak, showing a single preferential adsorption of PNiSAc in that case.



In addition, the STM contrast of bright protrusions, assigned to high density domains of PNiSAc, lies around 7 Å.

[1] Horcas, I.; Fernandez, R.; Gomez-Rodriguez, J.; Colchero, J.; Gómez-Herrero, J.; Baro, A. WSXM: A Software for Scanning Probe Microscopy and a Tool for Nanotechnology. *Rev. Sci. Instrum*. **2007**, 78, 013705.

4) PM–RAIRS experimental procedure and band assignment

PM–IRRAS spectra were taken using a Nicolet 8700 spectrometer along with a photo–elastic modulator PEM–90 (Hind Instruments). Due to the typically weak signal of the samples, each spectrum resulted from the sum of at least 2000 scans with a resolution of 4 cm^{-1} and an optical velocity 0.47 cm^{-1}.

IR Absorption band attribution of PNiSAc:

Wavenumbers cm^{-1} TPP[a] / TPPNi[b]	Wavenumbers cm^{-1} PNiSAc in KBr pellet	Assignment and ***polarisation*** of PNiSAc in KBr pellet
1597 / 1600	1598	ν –C=C– phenyl, phenyl
1575 / 1576	1578	phenyl–pyrrole ***L***
1556 / 1550	1552	ν –C=C– pyrrole ***M***
1492 / 1492	1490	ν –C=C– phenyl $\boldsymbol{M_{ph}}$
1460 / 1452	1460	–C=N–
1443 / 1443	1441	δ C–H pyrrole ***M***
1350 / 1351	1350	ν ---C–N–
1007	1018	ρ C–H pyrrole ***M***
1003 / 1023	1004	ρ C–H pyrrole ***M***
966		ρ C–H rocking pyrrole ***M***
799 / 794	792	γ C–H pyrrol ring ***N***
752 / 752	755	γ C–H phenyl $\boldsymbol{N_{ph}}$
699 / 695	702	γ C–H phenyl $\boldsymbol{N_{ph}}$

ρ: rocking, ν: stretching, δ: bending, γ: out of plane bending

[a] TPP: Tetraphenyl Porphyrin

[b] TPPNi: Nickel Tetraphenyl Porphyrin