

Metal-Mediated Self-Assembly of Tetrapyrrolyl Porphyrins by Na⁺ Ions

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ELECTRONIC SUPPORTING INFORMATION

Experimental Details.

Chemicals. 5,10,15,20-Tetra(4-pyridyl)porphyrin (TPyP(4)) was purchased from Aldrich Chemical co. and used as received. Mono(4-pyridyl)-triphenyl porphyrin (4'MpyP) was kindly gifted by Prof. Enzo Alessio (University of Trieste). The sodium salt of tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB), 5,10,15,20-Tetra(3-pyridyl)porphyrin (TPyP(3)) and Cu(II), Zn(II), and Mn(III) derivatives of TPyP(4) were prepared according literature procedures,¹⁻⁴ Porphyrins stock solutions were prepared from the solids in spectrophotometric grade dichloromethane (Sigma), previously filtered on activated alumina to remove any trace of acid and reduce the water content. Solution concentrations were determined from known molar extinction coefficient at the Soret maxima (TPyP(4): $4.54 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$, $\lambda = 416 \text{ nm}$; TPyP(3): $5.59 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$, $\lambda = 419 \text{ nm}$)⁵ while saturated solutions were used in the case of the three metallo-derivatives. In order to increase solubility of Zn(II) and Cu(II) derivatives some methanol (Aldrich, 2% v/v) was added to CH₂Cl₂.

All the other chemicals and solvents were used without any purification.

Methods. Titration experiments on TpyP(3) solution in CH₂Cl₂ were carried out at room temperature in a quartz cuvette by stepwise addition of a saturated NaTFPB solution (4.3 mM) by means of positive-displacement pipettes (Gilson mod. Microman) under stirring. Salt solution has been filtered through 0.22 μm Millipore filters to remove any particulate from solution, and their concentrations were determined from known molar extinction coefficient ($4570 \text{ M}^{-1} \text{ cm}^{-1}$).⁶

In order to obtain porphyrin/NaTFPB deposits suitable for morphological analyses, glass slides were cleaned by immersion in an acid piraña solution, thoroughly rinsed with bidistilled water and finally dried under N₂. These slides were then dipped in intensely colored porphyrin solutions (absorbance ca. 4 AU at λ_{max}) added of an excess of saturated NaTFPB solutions (porphyrin: NaTFPB=4:1 v/v), and left standing overnight. The reagents excess was finally removed by washing the slides with neat CH₂Cl₂, then these were dried under N₂. Samples for EDS analyses were prepared by collecting the deposited solids from the slides onto a carbon conductive double tape, to increase the materials density per unit surface.

Techniques. UV-vis extinction spectra were recorded on a HP diode- array spectrophotometer (mod. 8452). An UV filter (Hoya glass type UV-34, cut off: 340 nm) was used in order to cut off the UV component of the spectrophotometer lamp and avoid the formation of hydrochloric acid by photodecomposition of the halogenated solvent.⁷

Scanning Electron Microscopy analyses of selected samples were carried out using a ESEM-FEI Inspect-S, Electron Microscope coupled with Oxford INCA PentaFETx3 EDX spectrometer which is a Si(Li) detector, nitrogen cooled and equipped with an ultra thin window ATW2. Its resolution is of 137 eV at 5.9 keV (Mn K α 1). The spectral data were acquired at working distance of 10 mm with an acceleration voltage of 20 kV and spot size of 5, integrating times of 60 seconds, approximately 3000 cps and dead time below 30%. The results were processed by INCA software Energy that uses the XPP matrix correction scheme developed by Pouchou and Pichoir.^{8, 9} This type of correction matrix has a better performance compared with ZAF and Phi-Rho-Z widespread used, allowing quantitative analysis for samples that are slightly tilted respect to the incident electron beam.

Atomic force microscopy (AFM) measurements were performed by a NanoSurf easyScan2 microscope operating in non-contact mode at room temperature, with a resolution of 512 x 512 pixels and a moderate scan rate (1- 2 lines/s). Commercial Si-N-type tips (AppNano mod. ACLA) with resonance frequencies of 145-230 kHz were used.

NMR measurements were performed on a Varian 500 spectrometer operating at 500.1 MHz (¹H). All chemical shifts were reported in parts per million (δ / ppm), downfield to tetramethylsilane (Me₄Si) as an internal standard (δ = 0.0 ppm), or referenced to the proton resonance resulting from incomplete deuteration of the NMR solvents such as CD₂Cl₂ (5.32 ppm). ¹H NMR peak assignments follow from COSY and NOESY experiments.

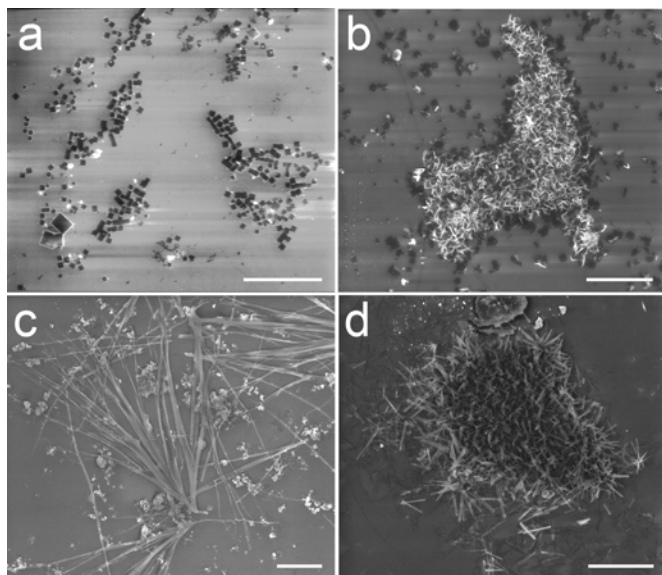


Fig. S1 SEM images of the MTPyP(4) films (M=2H, a; Cu, b; Zn, c; Mn, d) spontaneously formed on interaction of the porphyrins with Na⁺ ions. Scale bars: 15 μ m.

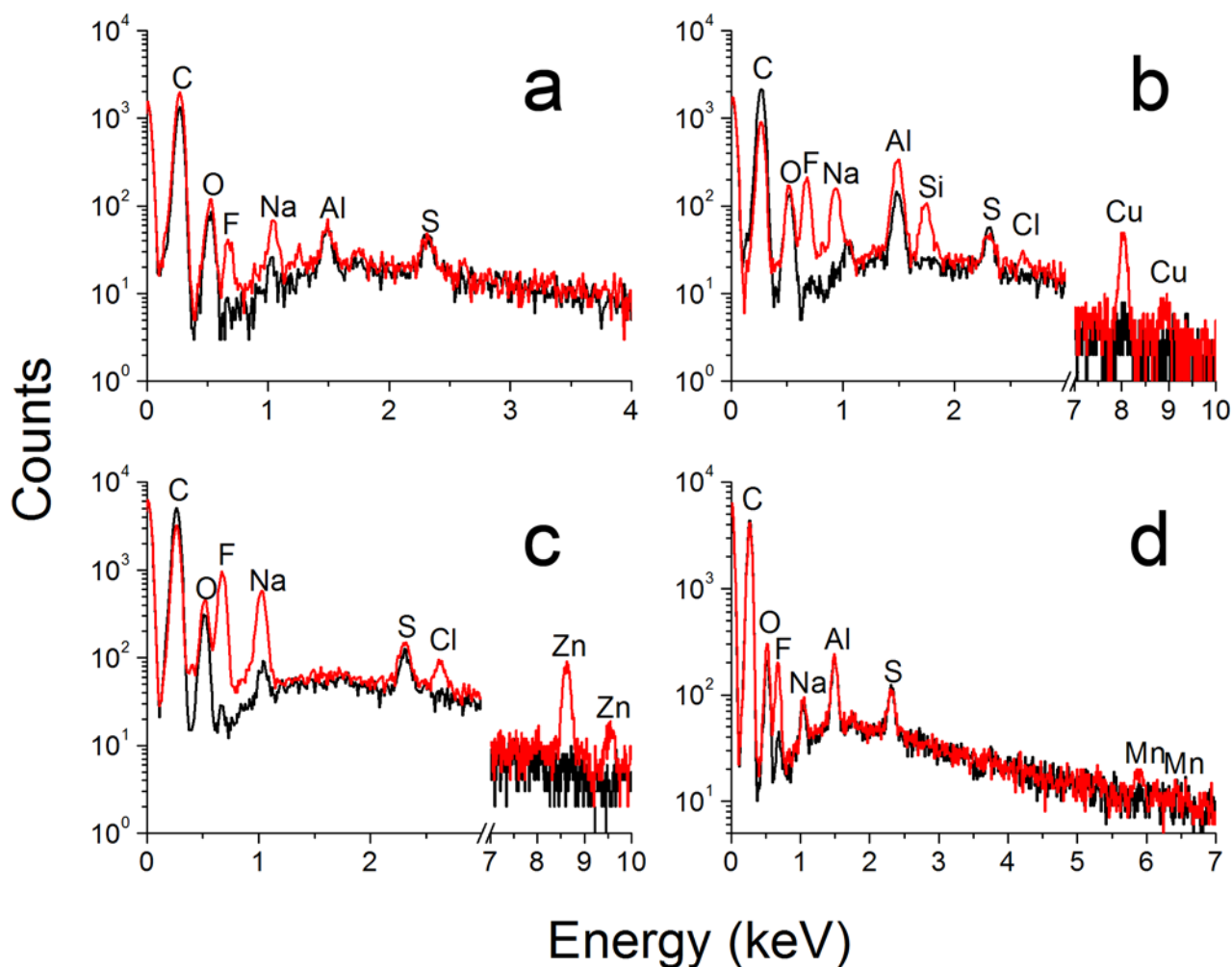


Fig. S2 EDS spectra of the MTPyP(4) films (M=2H, a; Cu, b; Zn, c; Mn, d) spontaneously formed on interaction of the porphyrins with Na⁺ ions, black lines representing the signal from the background (conductive carbon tape).

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