

**Supplementary material for “*Assisted-assembly of coordination materials into advanced nanoarchitectures by Dip Pen Nanolithography*”
by Bellido et al.**

S1. Materials and methods

Materials: $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ (98% ACS reagent), pure dimethylformamide DMF (99%), 1,3,5-benzenetricarboxylic acid H_3BTC (95%), 16-mercaptohexadecanoic acid MHA (90%) and octadecanethiol ODT (98%) were purchased from Aldrich. The solutions were filtrated with a Nylon membrane filter of 0.20 μm pore size, purchased from Chmlab Group. POMs were prepared as previously described.¹

Substrate preparation: The Si/SiO_x substrates were prepared by initially cutting the Si wafers into 0.5 x 0.5 cm² pieces. Then, each Si/SiO_x substrate was washed in an ultrasonic bath for 10 min in acetonitrile, ethanol and Milli Q water, and dried by blowing nitrogen gas. Si/SiO_x substrates prepared in the same way were also used to prepare the Au substrates by thermal evaporation of a 10 nm-thick adhesion layer of Ti on the Si/SiO_x substrate followed by a 40 nm layer of Au at a rate of 1 Å s⁻¹ and a base pressure of around 1 x 10⁻⁷ Torr. Then, the freshly prepared Au substrates were immersed in a 1 mM ethanolic solution of the desired thiol, and left at room temperature for 15 minutes. The SAM-functionalized surfaces were repeatedly washed in ethanol and Milli Q water and dried by blowing nitrogen gas.

DPN experiments: The DPN experiments were performed with a commercial dip-pen writer; NSCRIPTOR™ DPN® System (NanoInk Inc., USA). Commercial silicon nitride Type M Probe Arrays (NanoInk Inc., USA) with a spring constant of 0.5 N m⁻¹ were used for patterning. To coat the tips, a microfluidic ink delivery chip-based system (Inkwell, NanoInk Inc., USA) was used. The inkwells contained several reservoirs that were filled with the solution. This solution was then transferred to microwells through microchannels that connect the reservoirs with the microwells. Finally, the tips were coated with the solution by dipping the tips into the microwells. Then, the nanoarrays were generated by traversing the tip over the surface in the form of the desired pattern. An integrated environmental chamber as part of the NSCRIPTOR™ controlled the environmental conditions (humidity and temperature) during all DPN patterning processes in order to fulfil the requirements needed for each particular experiment.

Characterization: The nanoarrays were studied by SEM (Quanta 200 ESEM-FEG from FEI) operating an acceleration voltage of 10 kV. HR-TEM images were taken with a JEOL JEM-2011 microscope (JEOL LTD, Tokyo, Japan). Energy dispersive X-ray spectroscopy (EDS) was obtained by a MERLIN[®] FE-SEM (Carl Zeiss). Small-angle X-ray scattering (SAXS) data were recorded on a X'PERT PRO MPD de PANalytical using a Cu K α radiation source ($\lambda=1.5406$ Å). 2Theta scan. The diffraction patterns were collected between -0.115 and 5° with a step-size of 0.03 degrees, and scan rate of 50 seconds per step.

S2. FT-IR experiments

Stability of POM architectures grown on the surface was studied by means of FT-IR experiments (see Figures 2-5) and compared with the FT-IR spectra of both, bulk crystalline samples and the FT-IR spectra of the as-synthesized crystals described in the literature.ⁱ The characteristic bands for the Na₉[ErW₁₀O₃₆] crystal as-synthesized sample are: 935(s), 845(s), 786(m), 709(m), 586(w), 545(m), 490 (w). The characteristic bands for the K₁₂[GdP₅W₃₀O₁₁₀] crystal as-synthesized sample are: 1161(s), 1066(s), 1020(w), 939(s), 910(s), 775 (s). IR spectra were recorded on a ATR-IR Bruker Tensor 27 spectrometer. As shown next, the results clearly demonstrated the stability of the material along the whole experimental procedure.

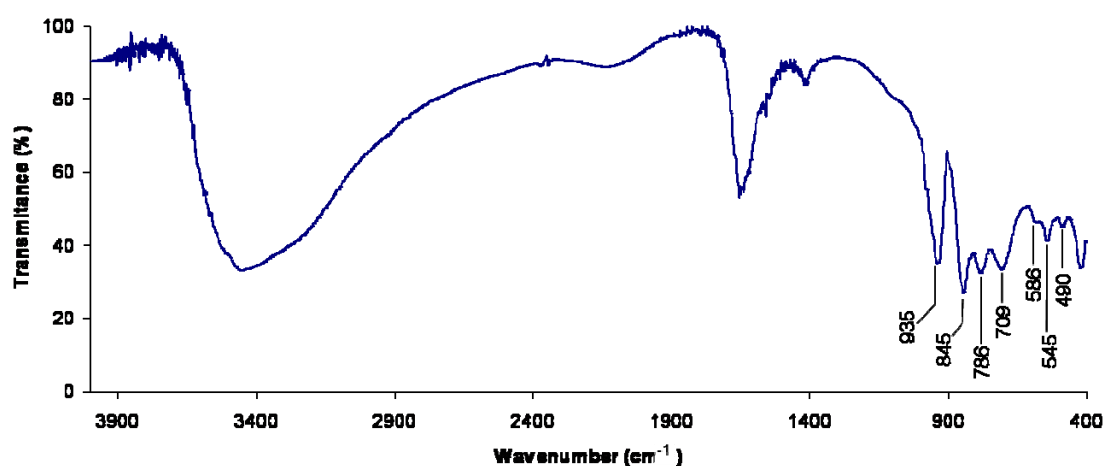


Fig. S1 Infrared spectra of the Na₉[ErW₁₀O₃₆] crystal as-synthesized.ⁱ The characteristic bands of the compound are assigned.

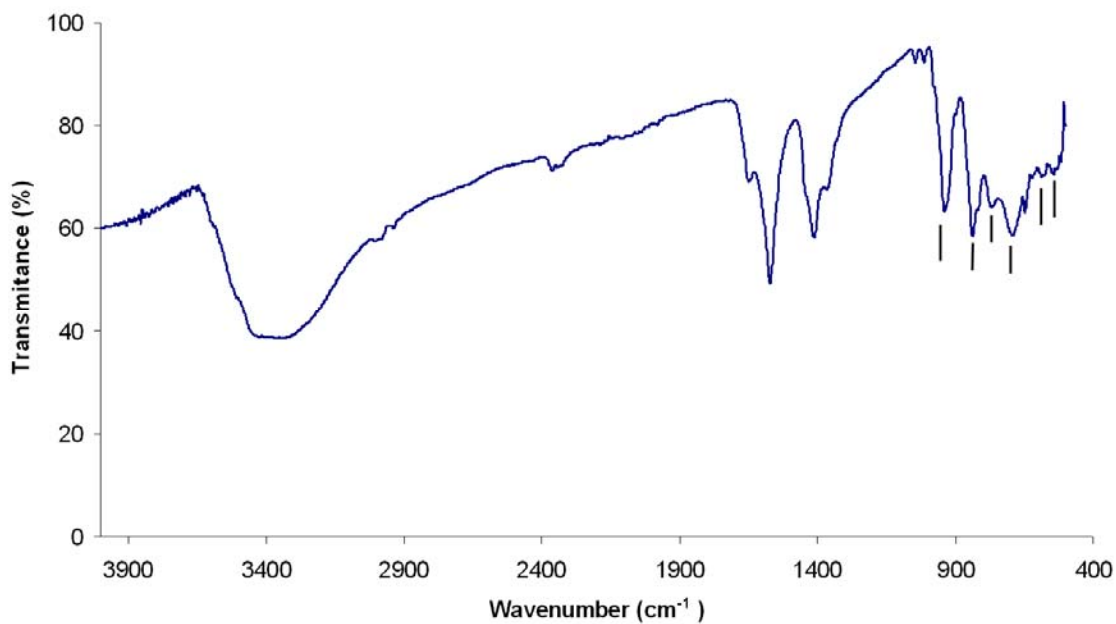


Fig. S2 Infrared spectra of the $\text{Na}_9[\text{ErW}_{10}\text{O}_{36}]$ compound deposited by drop-casting on a SiO_2/Si substrate. The characteristic bands of the compound are assigned.

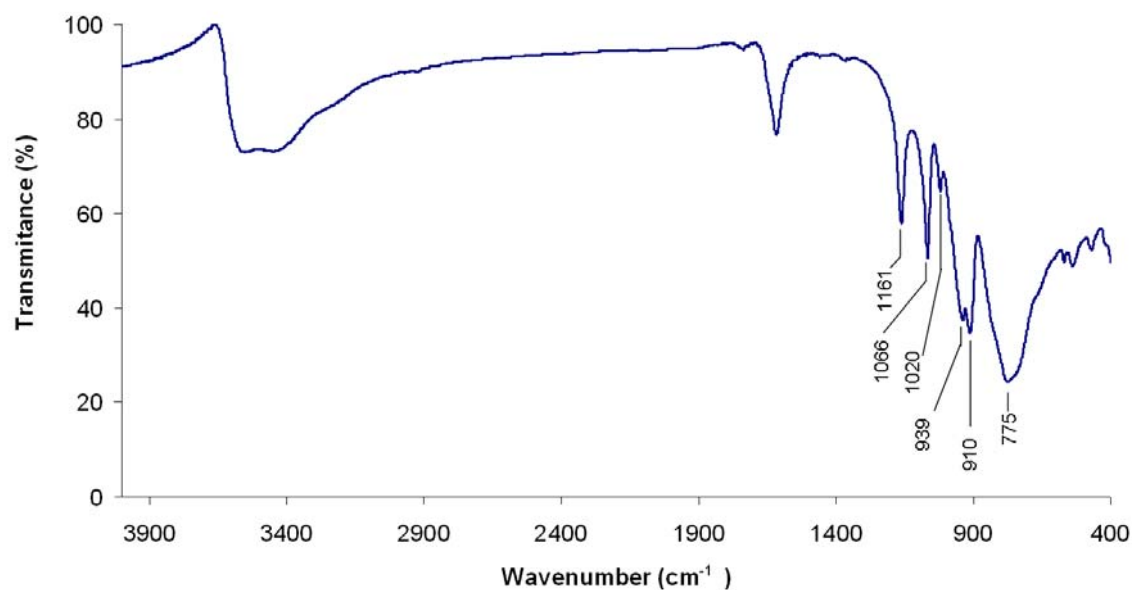


Fig. S3 Infrared spectra of the $\text{K}_{12}[\text{GdP}_5\text{W}_{30}\text{O}_{110}]$ crystal as-synthesized.ⁱ The characteristic bands of the compound are assigned.

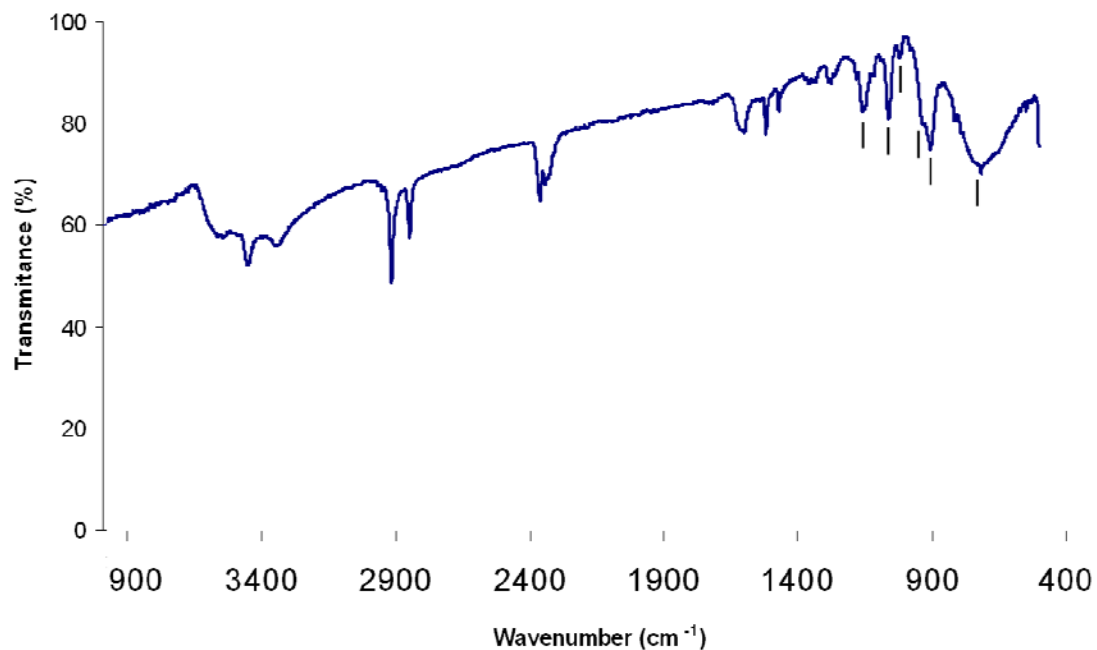


Fig. S4 Infrared spectra of the $K_{12}[GdP_5W_{30}O_{110}]$ compound deposited by drop-casting on a SiO_2/Si substrate. The characteristic bands of the compound are assigned.

ⁱ (a) M. AlDamen, S. Cardona-Serra, J.M. Clemente-Juan, E. Coronado, A. Gaita-Ariño, C. Martí-Gastaldo, F. Luis and O. Montero, *Inorg. Chem.*, 2009, **48**, 3467-3479. (b) I. Creaser, M. C. Heckel, R. J. Neitz and M. T. Pope, *Inorg. Chem.*, 1993, **32**, 1573-1578.