

Revisiting Maya Blue and Designing Hybrid Pigments by Archaeomimetism**

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Supplementary Information

1. Supplementary Figures

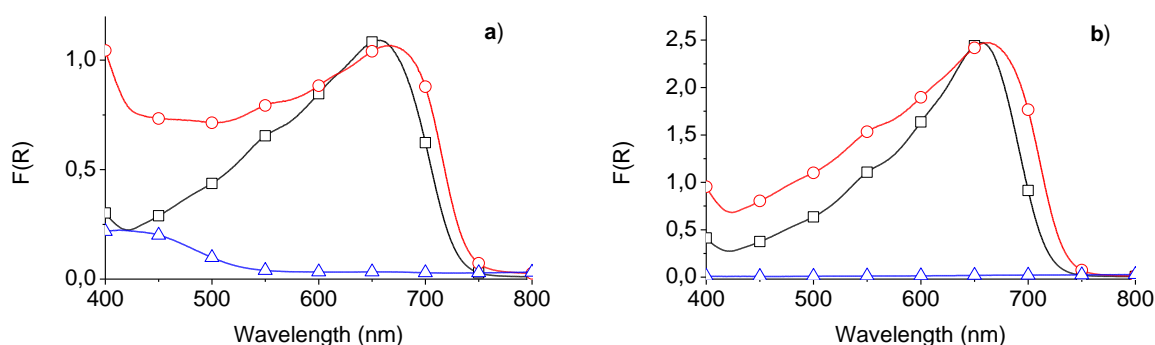


Figure 1. Supplementary to fig. 2 main text: Kubelka-Munk transforms, $F(R)$, of the UV-visible diffuse reflectance of indigo-microporous guest-host systems (2% wt. Indigo): (a) indigo-mordenite, (b) indigo-LTA. (\square) unheated mixtures; (\circ) heated complexes; (Δ) heated complexes after the nitric acid test. The absorption band responsible for the blue colour persists after the nitric acid test only for the palygorskite and the silicalite systems. Spectra are normalised at 665 nm. Screening of the alkene function by internal uptake of indigo (4.8 Å large) is impossible in the narrow pores of LTA (channel section 4.1x4.1 Å²): indeed the material discolours under the acid test, with loss of the characteristic reflectance band of the dye (Fig. 1b). Similarly, indigo in the wider channels of mordenite (channel section 7x6.5 Å²) yellows, with appearance of a new reflectance band at 450 nm (Fig. 1a), attesting conversion of the dye to isatin directly into the channels.

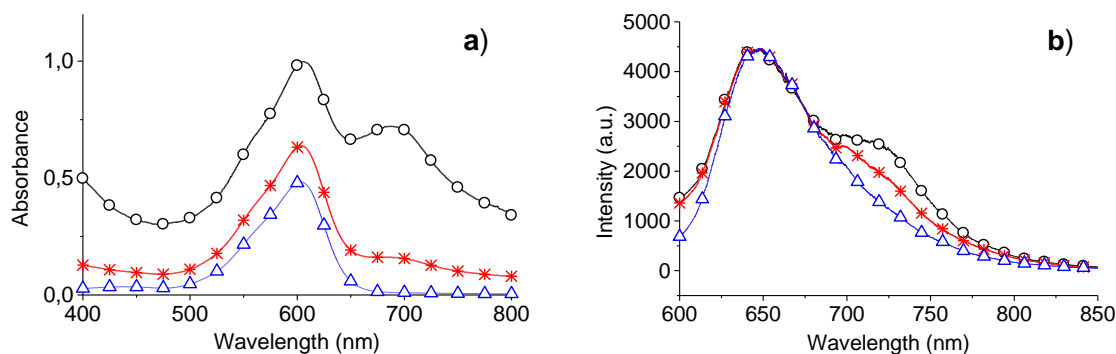


Figure 2. (a) Absorption spectra (path length = 1 cm) and (b) fluorescence spectra of solutions of indigo in chloroform: (Δ) 4.1×10^{-6} M ; (*) 4.1×10^{-5} M ; (\circ) 1.3×10^{-4} M. The 606 nm absorption band and the 650 nm fluorescence band are attributed to indigo monomers whereas the 690 nm absorption band and the 730 nm fluorescence band are characteristic of a dimer form.

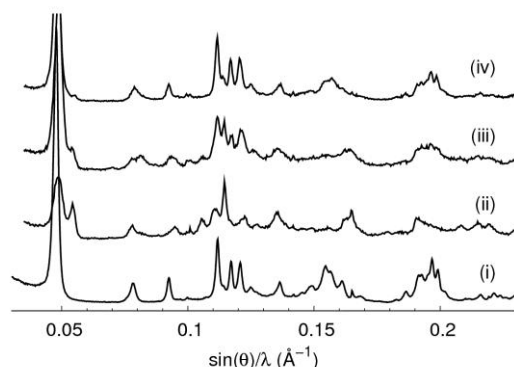


Figure 3. X-ray diffraction on palygorskite based complexes. Palygorskite at 25°C, (i) and at 250°C, (ii); 2% wt. indigo-palygorskite at 250°C, (iii) and 9% wt. indigo-palygorskite at 250°C, (iv). Note the absence of significant differences between (i) and (iv), which proves that folding is hindered in presence of high loading of indigo.

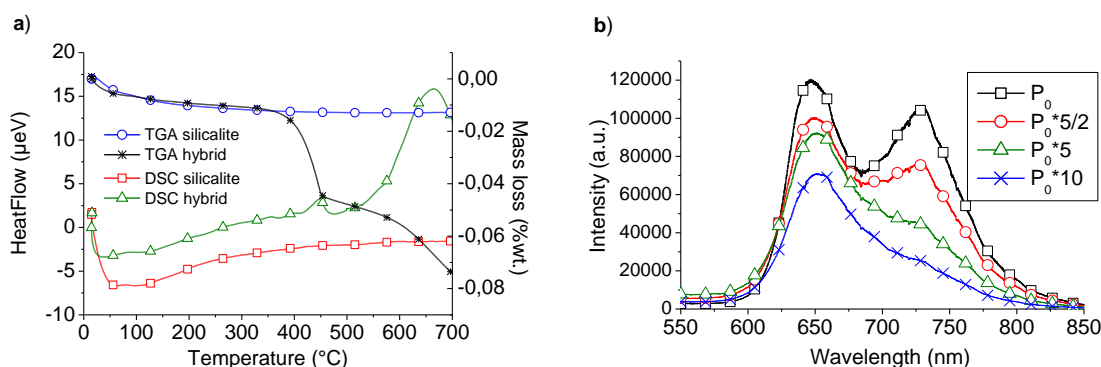


Figure 4. Thermal and photo-resistance of indigo@MFI: a) TGA/DSC curves recorded on the raw silicalite and an indigo@silicalite (5%wt.) sample. These curves show that indigo molecules become very stable once incorporated inside the silicalite channels (decomposition observed in the 550-700°C range). Note that the first exothermic reaction associated to the first TGA mass loss is attributed to the decomposition of indigo powder aggregated on the silicalite surface [ref. 7 of the main text] b) Fluorescence spectra of an indigo@silicalite (2%wt.) sample after 5 minutes laser irradiation ($\lambda_{\text{ex}} = 488 \text{ nm}$, P_0 corresponds to a power of ca. 3 kW cm^{-2}). Emission bands: 730nm = surface indigo, 650nm = internal monomer indigo. The 650nm band is not notably affected whereas the 730nm band disappears progressively with the increase of the irradiation power.

2. Adsorption capacity of palygorskite

The shape and size of the channels and surface grooves in palygorskite are taken from the crystal data of ref. 18 of the main text. Typical shapes and sizes of palygorskite fibres are taken from ref. 20 of the main text: 30-100 nm broad and *ca.* 1 μm long. These dimensions determine the total length of channels or grooves available in a typical fibre and the number of bridge sites at the fibre ends. The size of the indigo molecule is taken from ref. 1. The length relevant to packing into the channels or surface grooves is $l_1 \sim 13.5 \text{ \AA}$, including allowance for the van der Waals radii. The maximum possible mass % concentrations of indigo accommodated in either the channels or the surface grooves then follow readily, assuming at best head to tail packing of the guest. Loading of the stable site at the fibre ends is restricted on steric grounds to one molecule per channel opening.

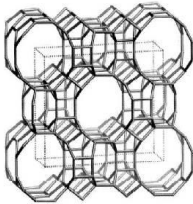
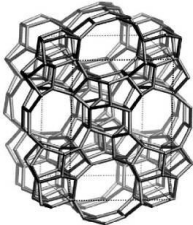
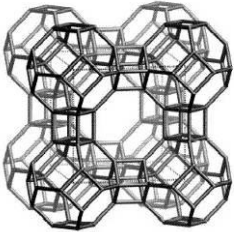
3. Analysis of the TGA data

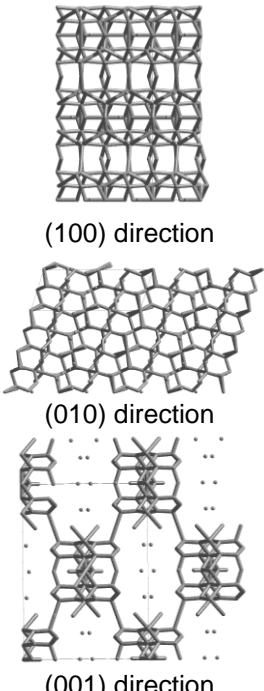
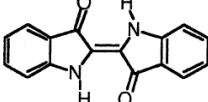
The solid line curves in figure 3 of the main text are deduced from the TGA data of raw palygorskite assuming: (i) Surface water and indigo are negligible compared to the internal capacity of the fibres (*cf* shape and size of typical fibres); (ii) Steric considerations and the hydrophobicity of indigo imply that water may pass indigo in the channels but should not lastingly occupy the same channel sections as indigo. The amount of channel water in a complex therefore follows from the channel length left over by indigo. In raw palygorskite, there are $N_w = 8$ channel water molecules per unit cell [ref 18 of the main text], in two channel sections along (001) (*i.e.* $8/2c$ water molecules per unit channel length, where c is the unit-cell length). Hence we assume that each internal indigo molecule excludes $Z=8l_f/2c \sim 10.3$ water molecules, on average. Finally, we need the number of indigo molecules per palygorskite unit cell, Y , corresponding to a mass fraction X (% total mass): $Y= X/(1-X)M_{cell}/M_I$, where M_{cell} and M_I are the molar masses of the (hydrated) unit cell of palygorskite and of the indigo molecule. Let $\delta\mu/\mu(T)$ be the TGA mass loss for a rehydrated MB sample. It is related to the weight loss of the raw palygorskite, $\delta m/m(T)$, by:

$$\delta\mu/\mu(T) = \delta m/m(T) \times (N_w - ZY)/N_w$$

This formula accounts well for the data for rehydrated MB at $X=2\%$, but not at $X=10\%$, where we must assume $X=5\%$ to obtain agreement with experiment, implying only partial filling.

4. Inorganic matrices and indigo

Matrix	Pore structure	Chemical formula	Channel dimensions (\AA^2)
Mordenite (MOR)	 (001) direction	$[\text{Na}_8(\text{H}_2\text{O})_{24}][\text{Al}_8\text{Si}_{40}\text{O}_{96}]$	1-D channel structure 7.0x6.5
Silicalite (MFI)	 (100) direction	$(\text{SiO}_2)_{96}$	2-D channel structure Sinusoidal : 5.3x5.1 Straight : 5.3x5.6
LTA zeolite		$\text{Na}_{96}[(\text{AlO}_2)_{48}(\text{SiO}_2)_{48}], 215\text{H}_2\text{O}$	Cage structure 4.1x4.1

Palygorskite	 <p>(100) direction</p> <p>(010) direction</p> <p>(001) direction</p>	$[\text{Mg}_2(\text{OH})_2(\text{H}_2\text{O})_4](\text{Al}_2\text{Si}_8\text{O}_{20})_4\text{H}_2\text{O}$	1-D channel structure 6.4x3.7
Indigo		$\text{C}_{16}\text{H}_{10}\text{N}_2\text{O}_2$	12.3x4.8

Zeolite model sketches from the database of the International Zeolite Association². Palygorskite model sketch from ref. 15 in main text.

Mordenite powder was crystallized according to the protocol of Sano et al.³, with addition of 1-butanol (BuOH) to enhance the crystallinity⁴. LTA zeolite was purchased from E.J. Lima Munoz (Mexico). Chemical composition was checked by EDX analysis.

References

¹ P. Susse, M. Steins, V. Kupick, *Z. Kristall.* **1988**, *184*, 269-73.

² Ch. Baerlocher and L.B. McCusker, <http://www.iza-structure.org/databases/>

³ T. Sano, S. Wakabayashi, T. Uozumi, *Microporous and Mesoporous Mater.* **2001**, *46 (1)*, 67-74.

⁴ F. Porcher, E. Borissenko, M. Souhassou, M. Takata, K. Kato, J. Rodriguez-Carvajal, C. Lecomte, *Acta Cryst. B* **2008**, *64*, 713-724.