Supplementary materials

Experimental details

Extraction procedures. Aliquots of dye@clay samples were subjected to extraction with DMSO, 90:10 (% v/v) H_2O:DMSO and 50:50 (% v/v) MeOH:DMSO mixtures in closed vials. Prior to the extraction the suspensions were maintained 24 h under magnetic stirring. The resulting extracts were studied conjointly with solutions of indigo and lapachol in the same solvents.

Instrumentation and methods. The extracts were injected into a LC-DAD equipment consisted of an Agilent 1200 Series HPLC system equipped with a UV diode array detector set at 286 nm (Agilent Technologies, Palo Alto, CA, USA). The column was a Agilent Zorbax XDB C18 150x4,6 mm 5 μm particle size (Agilent, Palo Alto, USA) preceded by a Agilent C18 12 mm, 4.6 μm guard cartridge. Signals were processed by Agilent ChemStation software Ver. 10.02 [1757]. Analysis was performed in the gradient mode. The mobile phase used was a mixture of two solvents (solvent A: water - 0.1% formic acid and solvent B: acetonitrile). Gradient conditions were initiated by holding the mobile phase composition for 0.1 min with 7% B, after that it was changed linearly to 75% B during 12 min. The composition was then changed to 98% B in 3 min and maintained for 4.5 min as a cleaning step in order to improve the results. After cleaning, the eluent composition was returned to the initial 7% B. The flow rate of the mobile phase was 1.2 mL/min and injection volume was 10 μL. The column oven was operated at 35 ºC.

UPLC-MS analyses of the extracts obtained from samples from the different reference materials and specimens were performed in an ACQUITY UPLC system (Waters Corp.) with a conditioned autosampler at 4 °C. Liquid samples were prepared by diluting 0.1 mL of the extracts in 1.0 mL of acetonitrile. Typically, 20 μL of the prepared sample was injected into the UPLC system equipped with Phenomenex Kinetex XB-C18 column (100 x 4.6 mm i.d.; 2.6 μm particle size). The column temperature was maintained at 40 °C. The mobile phase, pumped at 1.0 $ml \cdot min^{-1}$, consisted of 0.1% formic acid in water (A) and acetonitrile (B). The gradient applied was the following: 7% B isocratic to 0.1 min, to 75% B (linear) at 12 min, to 98% B (linear) at 15 min, to 98% B isocratic to 19.5 min, to 7% B (linear) at 20.5 min and 7%

B isocratic until 25 min. Separated components of sample mixture were detected by means of a Waters ACQUITY™ XevoQToF Spectrometer (Waters Corp.) connected to the UPLC system via an electro-spray ionization (ESI) interface. The ESI source was operated in positive ionization mode with the capillary voltage at 1.5 kV. The temperature of the source and desolvation was set at 100 °C and 400 °C, respectively. The cone and desolvation gas flows were 100 $L \cdot h^{-1}$ and 800 $L \cdot h^{-1}$, respectively. All data collected in Centroid mode were acquired using Masslynx™ software (Waters Corp.). Leucine-enkephalin was used as the lock mass generating an $[M+H]^+$ ion (m/*z* = 556.2771) at a concentration of 2 $ng \cdot mL^{-1}$ and flow rate of 50 $\mu L \cdot min^{-1}$ to ensure accuracy during the MS analysis.

Voltammetry of microparticles experiments were performed at sample-modified paraffin-impregnated graphite electrodes (PIGEs) using a CH I660 equipment. A standard three-electrode arrangement was used with a platinum auxiliary electrode and a Ag/AgCl (3M NaCl) reference electrode in a cell at 298 K. Experiments in aqueous media were performed with 0.25 M acetic acid/sodium acetate solutions at pH 4.75. For modified electrode preparation, ca. 0.5 mg of the samples were thoroughly powdered in an agate mortar and pestle and extended forming a spot of finely distributed material. The lower end of the graphite electrode was pressed over that spot of sample to obtain a sample-modified surface, as previously described.

SECM experiments were performed on deposits of the dye@clay materials on a graphite plate acting as a substrate electrode in contact with 5.0 mM $K_4Fe(CN)_6$ solution in 0.25 M HAc/NaAc (pH 4.75). Experiments were performed with CH 920c equipment using a microdisk platinum electrode tip (CH 49, diameter 20 μm) and a Pt substrate electrode. The bipotentiostat mode was used to apply potentials to the tip (E_T) and the electrode substrate (E_S). EIS measurements were performed at graphite electrodes covered by a deposit of dye@clay specimens with a CH I660 equipment in the 0.01 to 100000 Hz frequency range with amplitude of 10 mV upon application of different potentials using a 2.5 mM $K_4Fe(CN)_6$ + 2.5 mM $K_3Fe(CN)_6$ solution in 0.25 M HAc/NaAc (pH 4.75) aqueous buffer as a redox probe.

ATR-FTIR spectra of sample-modified electrodes were obtained with a Bruker Vertex 70 Fourier-transform infrared spectrometer with an FR-DTGS (fast recovery deuterated

triglicine sulphate) temperature-stabilised coated detector and an MKII Golden Gate Attenuated Total Reflectance (ATR) accessory. A total of 32 scans were collected at a resolution of 4 cm^{-1} and the spectra were processed using the OPUS/IR software. UV-Vis absorption spectra of the liquid extracts and diffuse reflectance spectra of powdered samples were obtained with a Perkin-Elmer lambda35 spectrometer, slit width 1 nm, scan speed 480 nm/min. ^{1}H and ^{13}C NMR measurements were acquired on a Bruker Advance 400 spectrometer operating at 399.91 MHz in deuterated DMSO.

XRD measurements were made using a Bruker-AXS D8-Discover diffractometer equipped with parallel incident beam (Göbel mirror), vertical θ-θ goniometer, XYZ motorized stage and with a GADDS (General Area Diffraction System). Samples were placed directly on a low background sample holder (Si(510)) and the area of interest was selected with the aid of a video-laser focusing system. An X-ray collimator system allows to analyze areas of 500 μm. The X-ray diffractometer was operated at 40 kV and 40 mA to generate CuKα radiation. The GADDS detector was a HI-STAR (multiwire proportional counter of 30x30 cm with a 1024x1024 pixel).

Samples were examined with a Jeol JSM 6300 scanning electron microscope operating with a Link-Oxford-Isis X-ray microanalysis system (SEM/EDX). The analytical conditions were: accelerating voltage 20 kV, beam current $2x10^{-9}$ A, and, working distance 15 mm. Samples were carbon coated to eliminate charging effects. TEM images were obtained with a Philips CM10 transmission electron microscope equipped with Keen view camera: Soft imaging system was used operating voltage 100 kV. Samples were prepared by grinding a few micrograms in an agate mortar and then dispersing them by the help of an ultrasons bath in dichloroethane. A drop of the dispersion was poured on TEM grids pretreated with a polymer film layer with holes to improve the quality of the images.

Figure S.1. ATR-FTIR spectra of lapachol, palygorskite and LA@PL_{25}. In view of the low amount of dye, the spectrum of the dye@clay specimens are dominated by the clay absorption bands.

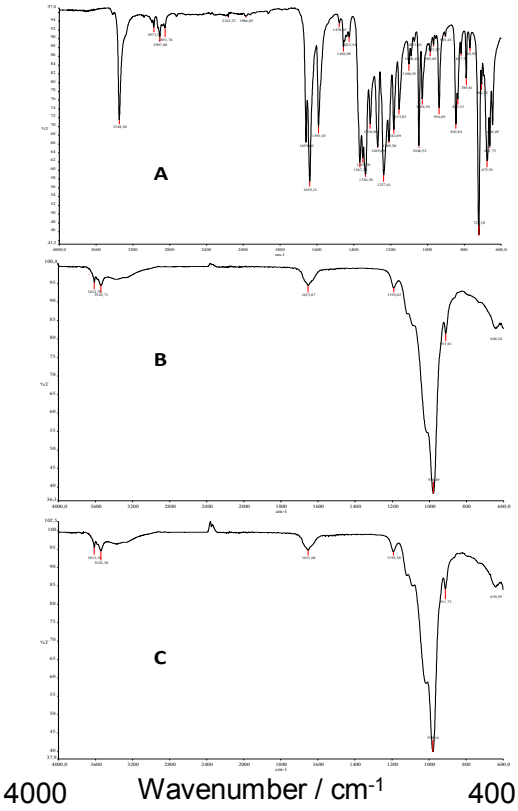
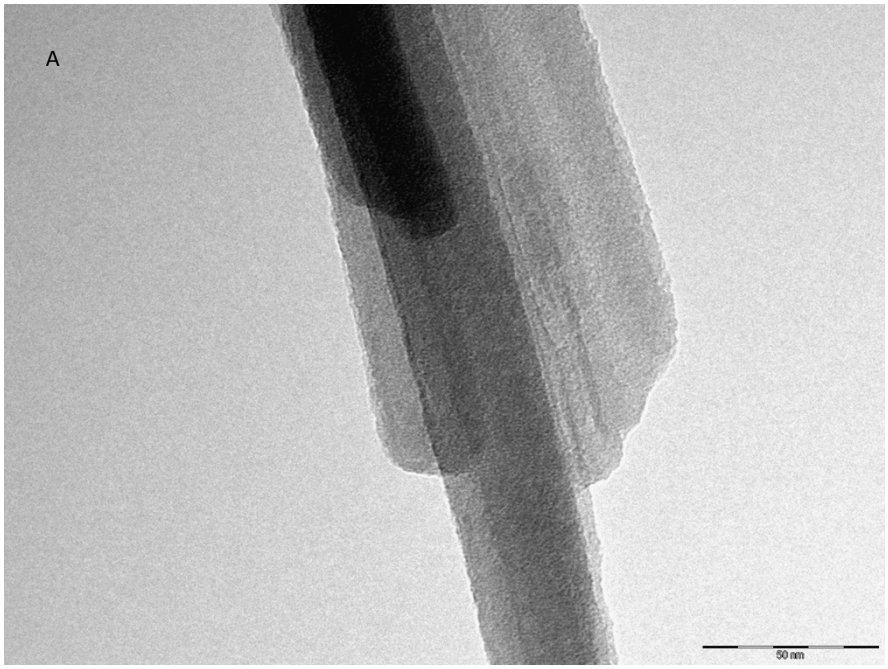


Figure S.2. TEM images of palygorskite crystals of: a) LA@PL_{25}; b) LA@PL_{150} specimens. In agreement with previous observations for Maya Blue samples,[4] acicular palygorskite crystals exhibit textural changes with appearance of pores due to the evacuation of zeolitic water after thermal treatment.



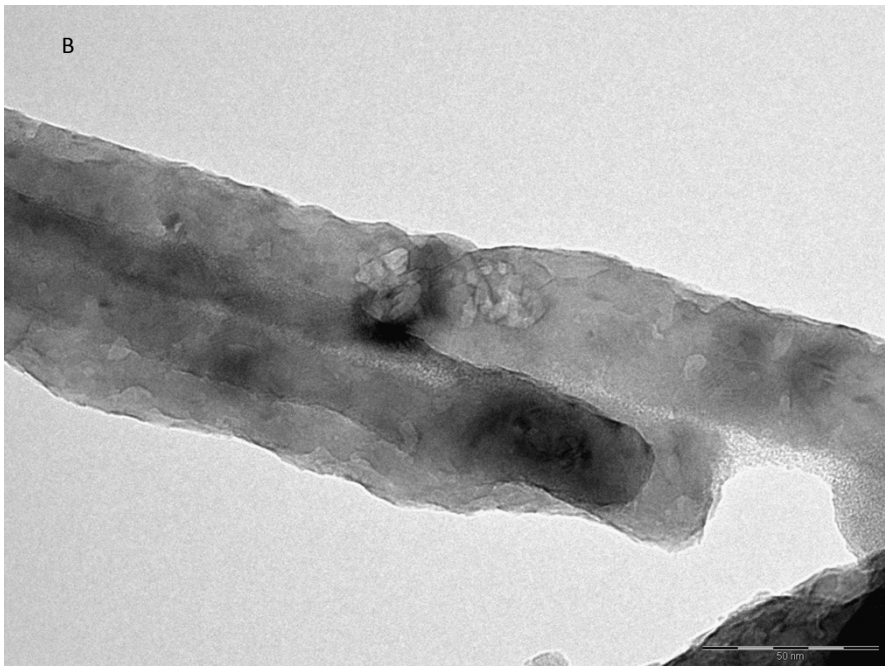


Figure S.3. LC-DAD chromatograms for methanolic extracts of: A: LA@KA_{25}; B: LA@KA_{150}.

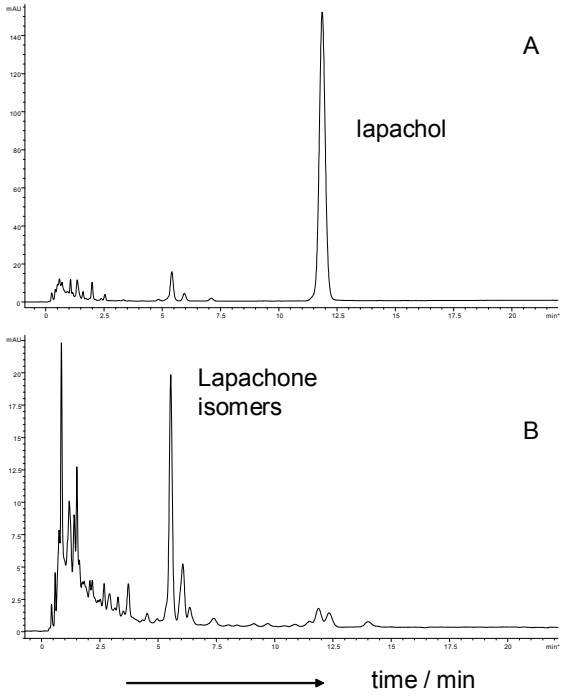


Table S.1. Majority components identified using HPLC-DAD, UPLC-MS and Py-GC-MS analysis of MeOH extracts in dye plus palygorskite specimens in this study.

Dye/treatment	**Compounds identified in the extracts**	**$[M+H]^+$ (m/*z*)**	**$[\underline{M+Na}]^+$ (m/*z*)**
LA@PL_{25}	Lapachol	243.1030	
LA@PL_{150}	α-Lapachone	243.1032	
	Lapachone isomer 1		265.0831
	Lapachone isomer 2	243.1022	
	Lapachone isomer 3	243.1027	
	4-Hydroxy-α-lapachone		281.0490
	Dihydro-4-hydroxy-α-lapachone	261.1117	
	Dehydro-α-lapachone		263.0694