

Supporting Information

Multimodal anti-counterfeiting inks: modern use of an ancient pigment in synergy with a persistent phosphor

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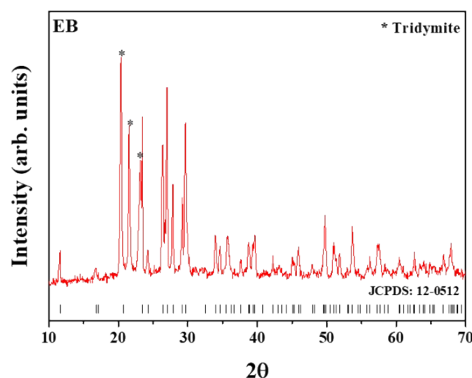
1. Experimental Procedures

1.1 List of reagents

- Copper(II) carbonate hydroxide $\text{Cu}_2\text{CO}_3(\text{OH})_2$ (Sigma-Aldrich, reagent grade CAS 12069-69-1)
- Calcium carbonate CaCO_3 (ACS reagent, $\geq 99.0\%$ CAS 471-34-1)
- SiO_2 Silica gel (Sigma-Aldrich high purity grade CAS 112926-00-8)
- Sodium Carbonate Na_2CO_3 (ACS reagent, $\geq 99.5\%$ CAS 497-19-8)
- Sodium Bicarbonate NaHCO_3 (ACS reagent, $\geq 99.5\%$ CAS 144-55-8)
- Sodium Sulfate Na_2SO_4 (ACS reagent, $\geq 99.5\%$ CAS 7757-82-6)
- Sodium Chloride NaCl (ACS reagent, $\geq 99.8\%$ CAS 7647-14-5)
- Egyptian Blue (Kremer Pigmente GmbH & Co. KG) (EB-COM)
- $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}, \text{Mg}^{2+}, \text{Ti}^{4+}$ (FOSHAN JULIANG PHOTOLUMINESCENT PIGMENT CO. Data Sheet^[11])
- Arabic Gum (Carlo Erba CAS 9000-01-5)
- H_2O deionized (Conductance $< 1,5 \mu\text{S/m}$)
- Calcium Hydroxide $\text{Ca}(\text{OH})_2$ (ACS reagent, $\geq 99.5\%$ CAS 1305-78-8)

1.2 Preparation of Egyptian Blue

The synthesis of Egyptian Blue (EB) was carried out by solid-state method. 0.416 g of CaCO_3 , 0.500 g of $\text{Cu}_2\text{CO}_3(\text{OH})_2$, 2.166 g of silica gel and 0.25 g of Natron were weighed, mixed, and ground in an agate mortar. Natron is a fluxing agent, prepared by mixing 2.08 g of Na_2SO_4 , 1.812 g of Na_2CO_3 , 1.436 g of NaHCO_3 and 1.5 g of NaCl . The resulting powder was thus thermally treated at 950°C for 24 hours in a GEFTRAN 1001 ME320 muffle furnace operating at 220 Volts. The XRD pattern of the obtained powder shows that it is constituted by cuprorivaite together with a few amount of silica tridymite.



¹ RP-A4 MSDS Photoluminescent[1076].Pdf.

1.3 Methods of characterisation

XRD patterns were acquired by a Philips X'Pert PRO diffractometer (now part of Malvern PANalytical, Malvern, U.K.) equipped with a fast detector (X'Celerator) using Cu-K α radiation ($\lambda = 1.5405 \text{ \AA}$) and operating at 40 kV and 40 mA. Each measurement was performed at room temperature in the 5-80° 2 θ range with a step of 0.008° and a time for step of 5 sec. The phase identification was performed by using the X'pert HighScore Plus® Software.

Multispectral Imaging. Photos of in the visible and infrared regions were acquired illuminating the samples with a UV lamp or a 640 nm lamp, to obtain visible and infrared images, respectively, and using a 20.3 MPX NX3300 photcamera equipped with a manual UV-IR lens and a visible filter and an 850 nm filter for IR imaging with NEEWER filters.

Photoluminescence emission (PL) and excitation (PLE) spectra were measured using the FLS980 Fluorescence Spectrometer from Edinburgh Instruments. The 450 W Xenon lamp for both PL and PLE were used as an excitation source. The R928P side window photomultiplier tube from Hamamatsu was used as a detector. The excitation arm was supplied with a holographic grating of 1800 lines/mm, blazed at 300 nm, while the emission arm was supplied with ruled grating, 1800 lines/mm blazed at 500 nm in Czerny Turner configuration. The scanning range was from 250 nm to 600 nm for PLE spectra and from 460 nm to 820 nm for PL spectra. All spectra were corrected for the sensitivity of the detection channel (PL) and the intensity of incident radiation (PLE).

The *lifetime measurements* were carried out using the same instrument while a 150 W Xe pulsed lamp was used as the excitation source. A mono-exponential decay curve as described in Equation (1) was fitted to the decay curves.

$$I(t) = I_0 + e^{-(t-t_0)/t_1} + I_{\text{offset}} \quad (\text{eq.1})$$

The *rise time* was estimated from the relaxation profile graphs as the time coinciding with the maximum value of the counts.

Thermoluminescence (TL) curves were measured by Lexsyg research – Fully Automated TL/ OSL Reader from Freiberg Instruments GmbH. As irradiation sources were used laser diodes (LDs). The TL glow curves were collected with an R13456 photomultiplier tube from Hamamatsu Photonics. *PersL decay curves* were collected using the same instrument with one minute delay after irradiation. Before measurements, all samples were preheated up to 350 °C and kept for 60 s for cleaning (removing) traps. All modules were operated using LexStudio 2 software dedicated to the TL/OSL Reader operation and supplied by the manufacturer. Obtained data were analyzed with the Origin 9.0® software.

The *PersL spectra* were collected via Si CCD spectrometer (USB2000+, Ocean Optics) with 1 s integration time. The detected spectrum intensity was calibrated by a standard halogen lamp.

SUPPORTING INFORMATION

Sedimentation kinetics. The kinetic stability of the inks was evaluated by turbidimetric measurements using a double beam UV-Vis spectrophotometer (Beckman DU-800) operating in the wavelength range between 200 and 800 nm with a resolution of 1.0 nm. The wavelength selected for the acquisition is 750 nm since at this wavelength the absorbance of the components present in dispersion is negligible. Measurements were conducted at 5-minute intervals for a time of 60 minutes.

2 Figures and Tables of Results and Discussion section

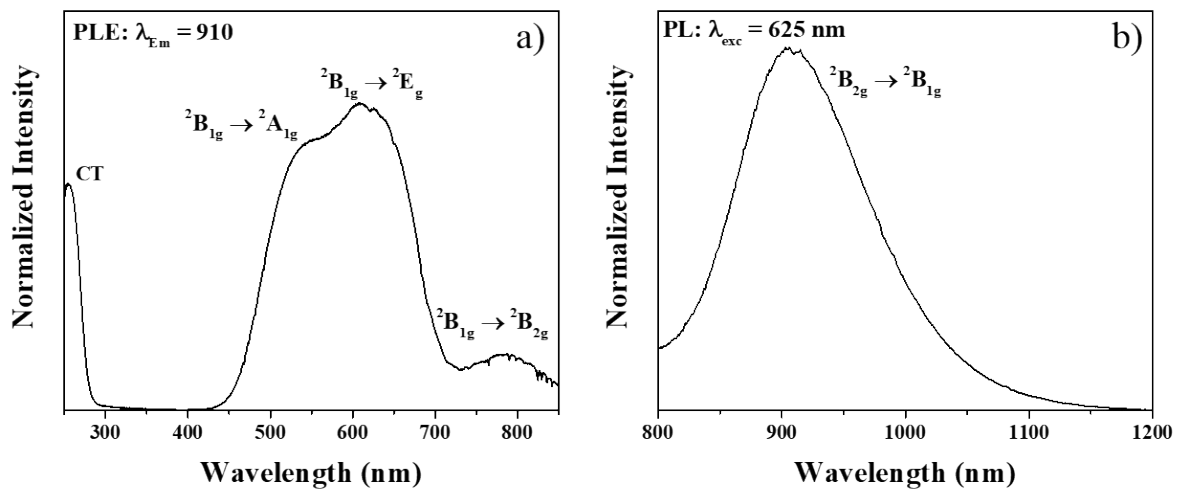


Figure S2. Excitation (a) and emission (b) spectra of EB; PLE: 910 nm; PL: 625 nm.

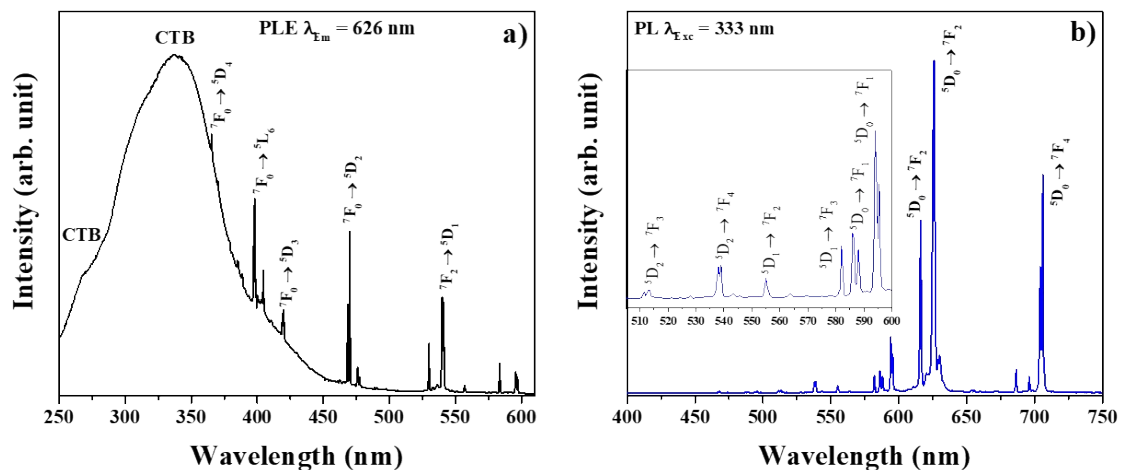


Figure S3. Excitation (a) and emission (b) spectra of YOS; PLE: 626 nm; PL: 333 nm.

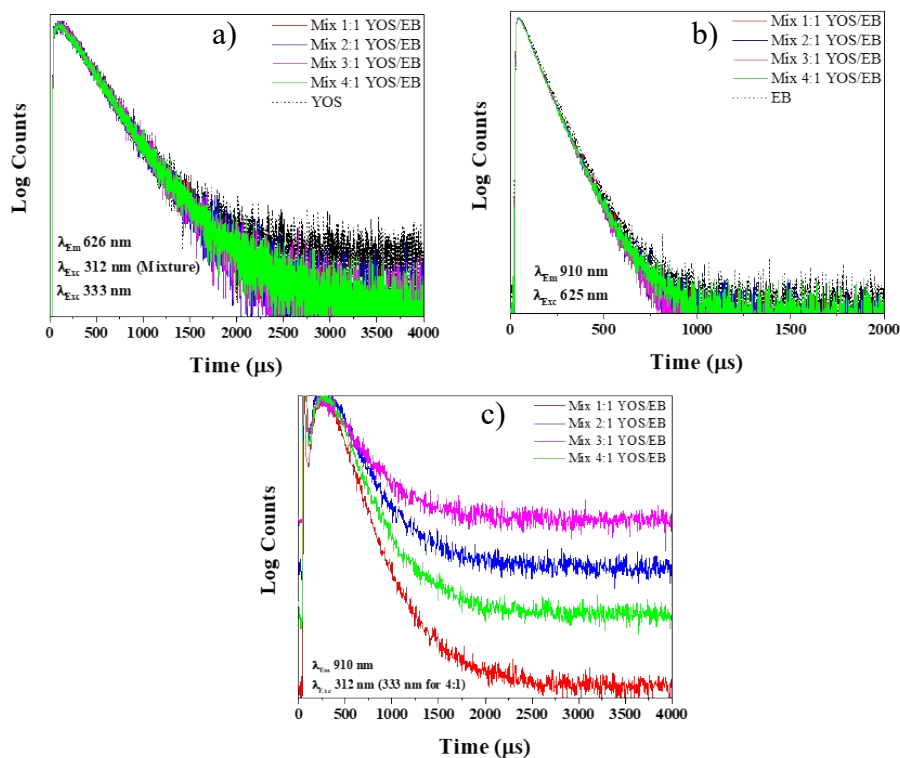


Figure S4. Relaxation profiles of YOS in mixtures (a), of EB in mixtures (b) and of EB following YOS-stimulated excitation (c).

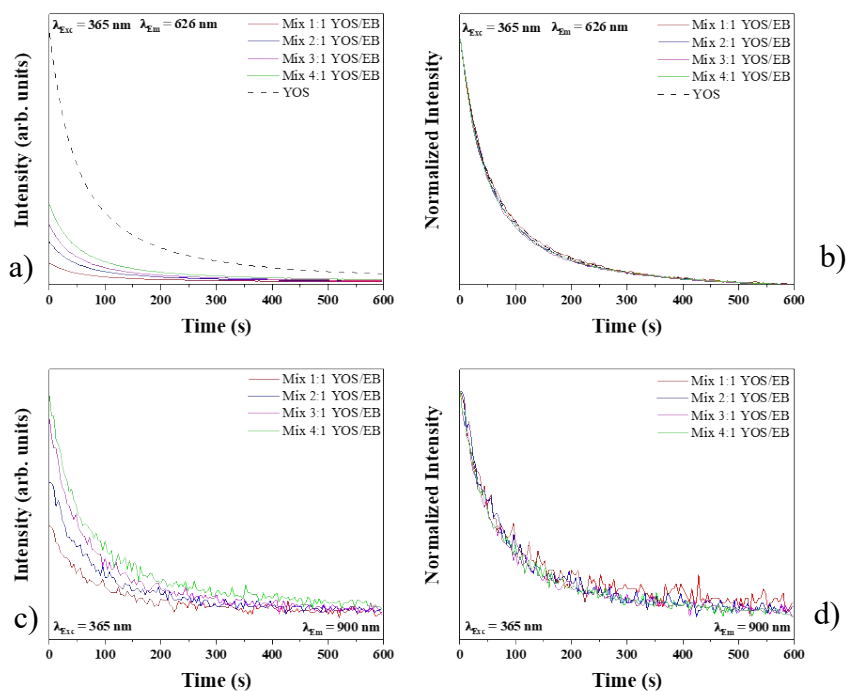
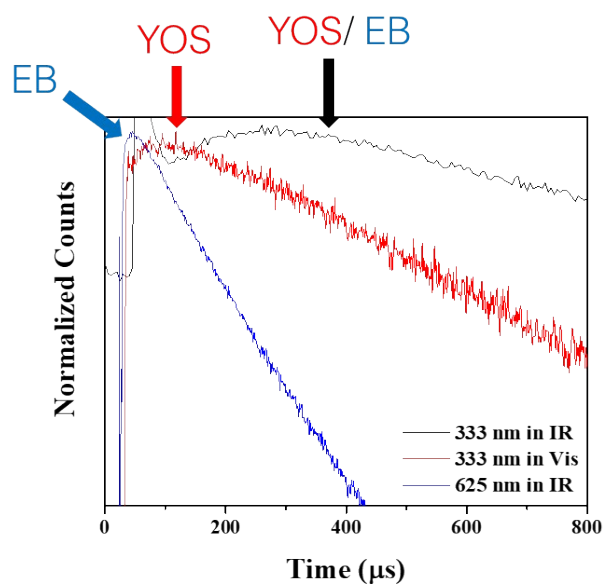


Figure S5. Afterglow decay's spectrum at 626 nm for YOS/EB mixtures (a) and the same spectrum normalized (b); Afterglow decay's spectrum at 900 nm for YOS/EB mixtures (c) and the same spectrum normalized (d).

Table S1. Relaxation time of YOS/EB mixtures (λ_{Emi} 626 nm and λ_{Exc} 312 nm).

	$\lambda_{\text{Exc}} ; \lambda_{\text{Emi}}$	$\lambda_{\text{Exc}} ; \lambda_{\text{Emi}}$	$\lambda_{\text{Exc}} ; \lambda_{\text{Emi}}$
	312 nm ; 626 nm	625 nm ; 910 nm	312 nm ; 910 nm
YOS/EB	$t_{\text{dec}} (\mu\text{s})$	$t_{\text{dec}} (\mu\text{s})$	$t_{\text{dec}} (\mu\text{s})$
1:1	446 \pm 1	140.5 \pm 0.3	471 \pm 4
2:1	440 \pm 2	137.6 \pm 0.3	464 \pm 7
3:1	435 \pm 2	137.2 \pm 0.3	490 \pm 12
4:1	447 \pm 2	137.2 \pm 0.3	478 \pm 5
YOS	433 \pm 3		
EB		145.2 \pm 0.3	

**Figure S6.** Rise time of EB, YOS and YOS/EB mixture.