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Optical and theoretical investigation of Indian yellow (euxanthic acid and euxanthone)

Charlotte Martin de Fonjaudran, Angela Acocella, Gianluca Accorsi, Diego Tamburini, Giovanni Verri, Amarilli Rava, Samuel Whittaker, Francesco Zerbetto, David Saunders

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Textual abstract:

The optical properties and DFT calculations of Indian Yellow are here described and correlated to its chemical composition.
OPTICAL AND THEORETICAL INVESTIGATION OF INDIAN YELLOW (EUXANTHIC ACID AND EUXANTHONE).

Charlotte Martin de Fonjaudran, a Angela Acocella, b* Gianluca Accorsi, c* Diego Tamburini, d Giovanni Verri, a* Amarilli Rava, a Samuel Whittaker, a Francesco Zerbetto b and David Saunders d

a The Courtauld Institute of Art, Somerset House, Strand, WC2R 0RN, London, UK, E-mail: giovanni.verri@courtauld.ac.uk, Tel: +44 (0)29 84 21 64; charlotte.martinde@courtauld.ac.uk, amarilli.rava@courtauld.ac.uk, samuelwhittaker@gmail.com
b Dipartimento di Chimica “G.Ciamician”, Università di Bologna, Via F. Selmi 2, 40126, Bologna, Italy. E-mail: angela.acocella3@unibo.it, francesco.zerbetto@unibo.it
c CNR NANOTEC - Institute of Nanotechnology c/o Campus Ecotekne, University of Salento; Via Monteroni - 73100 Lecce, Italy. E-mail: gianluca.accorsi@nanotec.cnr.it, Tel: +39 0832 319813
d Department of Scientific Research, The British Museum, Great Russell Street, London WC1B 3DG, UK, E-mail: DTamburini@britishmuseum.org, DSaunders@britishmuseum.org

ABSTRACT

The optical properties (photophysics and imaging) of Indian yellow were investigated both in solid state and in aqueous solution and correlated with its chemical composition. The analyses were corroborated by a theoretical study carried out on the different xanthone derivatives that comprise the pigment under investigation, both as isolated molecules and in a polar (protic) solvent, to help the assignment of the excited states involved in the photo-induced process. Knowledge of its relatively high photoluminescence quantum yield (PLQY 0.6%), excitation and emission spectra and lifetime decays enhances the potential for reliable identification using non-invasive photo-induced luminescence imaging techniques. New insights into the chemical composition of the pigment, such as the identification of a sulphonate derivative of euxanthone, and its extensive occurrence on a 17th-century Indian wall painting are also reported for the first time in this study.

Keywords: Indian yellow; Photoluminescence spectroscopy; Time-dependent Density Functional Theory Calculation; Photoluminescence imaging; Indian wall painting
1. INTRODUCTION

Indian yellow, a historic pigment produced in India until the end of the 19th/ beginning of the 20th century, is characterised by its luminous yellow-orange colour and noticeable photoluminescence properties. The main colorant is based on the crystalline mixture of the magnesium and calcium salts of euxanthic acid, EA [1]. One of the most frequently cited accounts of its production method states that the pigment derives from the urine of cows fed solely on mango leaves, a process which allegedly caused their premature death and led to a ban on production [1-3]. Early chemical studies showed that euxanthone (C_{13}H_{8}O_{4}), or its precursor present in mango leaves, can combine with glucuronic acid metabolised by mammals such as cows or rabbits and be excreted as a salt of EA (C_{19}H_{16}O_{10}) [4, 5]. However, some scholars have questioned this production process and the reasons behind its discontinuation [6-9].

Indian yellow has been identified on several miniature paintings dated between the 16th and 19th centuries that are attributed to the Mughal and Rajput schools [1, 10-12]. It was also used by artists in Europe and the United States [13-17]. However, its extensive occurrence on a monumental painting is reported for the first time in this study, following analyses of the yellow pigments used in the wall paintings decorating the Badal Mahal within Garh Palace in Bundi (Rajasthan, India). The painted scheme, dated to 1620–30, is one of the most significant within the palace complex. Depictions of courtly life, unfolding on the walls, are among the earliest and finest in Rajasthan [18]. Other subject matters include a Ragmala series as well as scenes of Hindu mythology on the ceiling.

Light microscopy, XRD, SEM-EDX and FTIR were most commonly employed at the end of the 20th century to identify Indian yellow on works of art [1, 12, 13, 17]. More recently, other micro-destructive techniques such as NMR, HPLC-DAD [19] and LC-ESI/MS [15] have been applied to the identification of this unusual pigment. Non-invasive analytical techniques are now favoured for the preliminary study of artefacts and portable XRF and FTIR are more routinely used in the cultural heritage field [20-23]. While such techniques can be combined with imaging [20, 24], the
instruments commonly employed in museums or in the field provide only point analyses, thus limiting the information available on the distribution of pigments of interest over large areas. Photo-induced luminescence (PL) imaging, using ultraviolet (UV) excitation and recording visible emission with a photographic camera, has been used since the late 1980s to highlight the possible presence of Indian yellow [1, 13, 25, 26]. However, several other organic colorants commonly encountered on Asian paintings also show comparable fluorescence when excited with UV radiation [27], thus limiting possible differentiation between original materials. Nonetheless, PL imaging using digital cameras offers an invaluable and affordable tool, which has been successfully applied to the characterisation of several pigments such as Egyptian blue, Han blue, manganese blue and cadmium-based pigments [28-30]. PL spectroscopy presents a necessary complementary technique to corroborate the results and inform PL imaging protocols. The luminescence properties of several pigments, such as lithopone [31], zinc oxide [32], zinc sulphide [33], manganese blue [29], Egyptian blue [34, 35] and cadmium-based pigments [36-38], have been investigated in recent years using both steady-state and time-resolved PL spectroscopy. However, the only published study on Indian yellow presents a limited view of its excitation and emission profiles, with data uncorrected for instrument response [1].

A complete understanding of the photophysical properties of Indian yellow is required for correct interpretation of results obtained with PL spectroscopy and imaging techniques. In this study, the organic chemical components of two samples, from a reference archive at the National Gallery, London (NG) and from the wall painting in Bundi (B64), were identified with HPLC-ESI-Q-ToF. The optical properties of the Indian yellow reference sample, that is the absorbance (total reflection), excitation and emission profiles, as well as the lifetime decay were characterised both in the solid state (as powder) and in solution (water) and compared to the emission profile and lifetime decay of the wall painting sample. PL imaging, using a customised DSLR camera, xenon flashes and bandpass filters, aimed to characterise visible and infrared (IR) emission following UV excitation.
In an attempt to resolve the optical structure of the pigment, a theoretical study at the DFT level of theory was conducted on euxanthic acid (EA), 4-sulphonate euxanthone (SE) and euxanthone (E), both in the gas phase and in water, to support the experimental component. DFT calculations were also run for 1-hydroxy-7-methyl-xanthone (OH-CH$_3$-X) and xanthone (X), to investigate the role of substituents on the UV/Vis spectra and to make a comparative analysis with previous results on X [39-42]. The chemical structures of all the compounds investigated are shown in Scheme 1.

![Chemical structures of xanthone (X), 1-hydroxy-7-methyl-xanthone (OH-CH$_3$-X), euxanthone (E), 4-sulphonate-euxanthone (SE), and euxanthic acid (EA).]

**Scheme 1.** Chemical structure of a) xanthone (X), b) 1-hydroxy-7-methyl-xanthone (OH-CH$_3$-X), c) euxanthone (E), d) 4-sulphonate-euxanthone (SE), and e) euxanthic acid (EA).

## 2. EXPERIMENTAL

### 2.1 Indian yellow samples

A powdered sample (NG) of historic reference material was provided by the National Gallery, London. The wall painting sample (B64) was taken from a yellow paint layer on the south wall of the Badhal Mahal, in Garh Palace, Bundi (Rajasthan, India). An image of the area where the sample was taken and a detail of a cross-section are shown in Figure 1. Yellow paint layers are extensively used for the geometrical and floral patterns unfolding on the walls and for the garments of Krishna and the gopis engaged in a circular dance depicted on the ceiling.
Fig. 1 Location of sample B64 on the south wall of the Badal Mahal, Garh Palace, Bundi (Rajasthan, India). Inset: cross-section illustrating the stratigraphy of the paint layer composed of a white ground and a single yellow layer.

2.2 HPLC-DAD-ESI-Q-ToF

For analysis with High-Performance Liquid Chromatography coupled to Electrospray Ionisation and Quadrupole Time-of-Flight, samples (c. 100 µg) were admixed with 200 µL DMSO and heated at 80°C for 10 minutes. After centrifugation, the supernatant was transferred into another vial. The residue was admixed with 200 µL of methanol/acetone/water/0.5M oxalic acid 30:30:40:1 (v/v/v/v) and heated at 80°C for 15 minutes. The solution was evaporated under N₂ and reconstituted using 200 µL of MeOH/H₂O 1:1 (v/v). The DMSO extract was combined with the oxalic acid extract and the solution was centrifuged for 10 minutes. The supernatant was transferred to a fresh 250 µL insert and 5-10 µL of the solution were injected into the HPLC system.

Analyses were carried out using a 1260 Infinity HPLC (Agilent Technologies), coupled to a Quadrupole-Time of Flight tandem mass spectrometer 6530 Infinity Q-ToF detector (Agilent Technologies) by a Jet Stream ESI interface (Agilent Technologies). The HPLC conditions were: Zorbax Extend-C18 column (2.1 mm × 50 mm, 1.8 µm particle size); 0.4 mL/min flow rate; 5 µL injection volume for MS experiments and 10 µL for MSMS experiments; 40°C
column temperature. Separation was achieved using a gradient of water with 0.1% formic acid (eluent A) and acetonitrile with 0.1% formic acid (eluent B). The elution gradient was programmed as follows: initial conditions 95% A, followed by a linear gradient to 100% B in 10 min, then held for 2 min. Re-equilibration time for each analysis was 10 min. The ESI operating conditions were: drying gas (N\textsubscript{2}, purity >98%): 350°C and 10 L/min; capillary voltage 4.0 kV; nebulizer gas 276 kPa; sheath gas (N\textsubscript{2}, purity >98%): 375°C and 11 L/min.

High resolution MS and MS/MS spectra were acquired in negative mode in the range 100-1700 m/z. The fragmentor was kept at 150 V, nozzle voltage 1000 V, skimmer 65 V, octapole RF 750 V. For the MS/MS experiments, different voltages in the collision cell were tested for Collision Induced Dissociation (CID), in order to maximise the information obtained from the fragmentation. The collision gas was nitrogen (purity 99.999%). The data were collected by targeted MS/MS acquisition with an MS scan rate of 1.0 spectra/sec and a MS/MS scan rate of 1.0 spectra/sec. MassHunter® Workstation Software was used to carry out mass spectrometer control, data acquisition, and data analysis.

2.3 Optical measurements

The photophysical properties of Indian yellow, in both solid state and solution, were investigated using a Perkin-Elmer Lambda 1050 UV-Vis-NIR equipped with an integrating sphere (total reflection measurements). The emission and excitation spectra were recorded by an Edinburgh FLS980 spectrometer equipped with a Peltier-cooled Hamamatsu R928 photomultiplier tube (185-850 nm) and a xenon lamp (450 W) as light source. To determine the luminescence quantum yield, the method proposed by De Mello et al. was followed [43]. The emission lifetimes in the pico- to nanosecond timescale were measured using a single photon counting system (Edinburgh FLS980 spectrometer) with a 1 MHz laser diode as excitation source coupled with a Hamamatsu MCP R3809U-50, time resolution 20 ps, as detector.
2.4 Imaging

The PL luminescence of the paintings in the Badal Mahal was recorded using a customised Nikon D7000. The removal of the camera’s internal IR blocking filter and replacement with a quartz filter, allows detection of emission from c.350-1100 nm. The excitation source consisted of two Quantum Instruments T5dR xenon flashes, equipped with Xnite 330C and Xnite CC1 bandpass filters (c.280-400 nm). The camera was fitted with a cut-on Schott KV418 ultraviolet-blocking filter (50% transmission at 418 nm) and an IDAS-UIBAR bandpass filter (c.400-700 nm) to record emission in the visible, and Xnite 715 filter (50% transmission at 715 nm) to record emission in the IR. A white board covering the entire field of view, a Gretag-Macbeth ColorChecker chart, and a set of lambertian reflectance standards (Spectralon® 99, 75, 50 and 2%) were inserted in all images to allow for post-capture processing and correction (light distribution, colour correction, removal of ambient stray light) using Nip2 software and following the protocol described in Dyers et al. [44].

2.5 Calculations

In order to select the most suitable functional to gain meaningful results, the ground state geometries of EA, SE and E were optimised in the gas phase with the Gaussian09 suite of programs [45] at different hybrid and long-range corrected DFT functionals (namely, B3LYP [46], pure PBE [47], PBE0 [48], HSE06 [49], CAM-B3LYP [50] and LC-wPBE [51]) at the TZVP basis set level of theory. This set of functionals was selected to encompass a wide number of parameters, such as, corrections (or not) for dispersion effects and global or range-separated hybrids. Relative vertical electronic excitations, (transitions) dipole moments and oscillator strengths were obtained, at the corresponding level of theory, with the Time Dependent Density Function Theory (TDDFT) [52], generally used to reproduce the UV/Vis spectra of most organic [53-56] and inorganic dyes [57, 58]. The energetic positions of the triplet states are here analogously investigated, since X and some of its analogues are largely used as triplet sensitizers.
To mimic the solvent environment, the CPCM polarisable conductor model implemented in Gaussian09 [59, 60] with the Pauling cavity set [61] and combined with a TD-DFT scheme, has proven to be appropriate to reproduce the experimental absorption/excitation spectra for EA, SE and E in water, with a high level of accuracy. B3LYP/CPCM and TDDFT(B3LYP)/CPCM calculations were carried out to obtain optimised geometries and vertical excitation energies of EA, E and SE in water.

Additional TDDFT calculations at the same level of theory were run on OH-CH$_3$-X and X molecules to obtain complete information about the effect that substituents on the main xanthone structure have on the position of the absorption bands, and to compare results with previous literature data available on X.

3. RESULTS AND DISCUSSION

3.1 Chemical composition

HPLC-ESI-Q-ToF analysis revealed that both samples were composed of euxanthone (E) and euxanthic acid (EA), in agreement with the literature [15]. Nevertheless, a third component was also detected, and identified as a sulphonate derivative of euxanthone (SE), (C$_{13}$H$_8$O$_7$S). The identification of SE was based on the high resolution mass data and the MSMS fragmentation spectrum. The mass obtained for the molecular ion was [M]$^-$ = 306.9922 uma and it showed a -1.21 ppm difference from the calculated mass (calculated [M]$^-$ = 306.9918 uma). The MSMS spectrum showed a main fragmentation peak at m/z 227.0353, corresponding to euxanthone (ppm difference -1.39) and derived from the loss of a SO$_3$ moiety. Although the exact position of the sulphonate group was not ascertained, we hypothesise that the C$_4$ position is that undergoing reaction, based on the structure of other natural sulphonated xanthones [62].

Semi-quantitative calculations were performed to evaluate differences in the distribution of E, EA and SE between sample S64 and the reference sample (NG). Chromatographic area ratios were calculated by considering the sum of the chromatographic areas of E, EA and SE as 100%. Using
this method the percentage areas were EA = 77.4 ± 0.8%, SE = 14.7 ± 0.6% and E = 7.9 ± 0.2% for sample NG and EA = 65.4 ± 0.4%, SE = 28.9 ± 0.4% and E = 5.6 ± 0.1% for sample S64 (standard deviation refer to triplicate measurements). It is important to underline that these values do not necessarily correspond to the actual percentage contents of the three components in the samples, because the ionisation yield of each compound may vary. Nevertheless, the results can be used to compare the samples and a higher relative abundance of SE was observed for sample B64 compared to NG.

Although Indian yellow has been characterised by LC-MS analysis previously [15], this work presents the first identification of euxanthone-4-sulphonate. Its presence in the wall painting sample (B64) makes it unlikely to result from a synthetic production process and would rather point towards a natural occurrence. In fact, sulphonation and glucoronidation are two competitive mechanisms in the metabolism of mammals, especially for phenolic molecules, and sulphonation usually occurs in parallel to glucoronidation, but to a lesser extent [63, 64]. This could be taken as further evidence that a metabolic pathway is involved in the production of the pigment, supporting the hypothesis of its manufacture through ingestion, digestion and urination by cows. However, sulphotransferase enzymes are also present in plants, and sulphonated xanthones [62] and flavonols [65] have been isolated. Accordingly, the identification of this compound cannot alone validate the animal-based production process described above.

3.2 Photophysical properties

The absorbance spectrum of sample NG covers the range between $c.250$ and $550$ nm, imparting the dark yellow colour to the powder. The bands in the UV region can be attributed to $\pi-\pi^*$ transitions, while those at longer wavelengths (> $400$ nm) are of $n->\pi^*$ ($S_0 > S_1$) nature [39] (see also the TDDFT calculations in section 3.4). The excitation spectrum, obtained by monitoring the emission at $600$ nm, closely matches the absorption profile, pointing to a lack of intermediate photo-induced processes between absorption and emission. Both samples (NG and B64) emit in the
yellow-orange region with a maximum around 600 nm (Figure 2). The corresponding lifetime
decays (Figure 2, inset) are in good accordance with a bi-exponential model (B64: $\tau_1 = 510$ ps
(73%), $\tau_2 = 1.50$ ns (27%); NG: $\tau_1 = 530$ ps (75%); $\tau_2 = 1.49$ ns (25%)), suggesting the presence of
different packed domains (driven by the $\pi-\pi$ stacking and hydrogen bonds), which commonly occur
in solid-state organic samples [66]. For the first time, it was possible to measure the
photoluminescence quantum yield (PLQY) of a solid sample of Indian yellow: PLQY(NG) = 0.6%.
Unfortunately, the sub-millimetric sample from the wall panting was too small to measure its
PLQY. The $< 10$ nm hypsochromic shift between the emission maxima of the two samples can be
attributed to the different ratios of EA and E.

Fig. 2 Absorbance (total reflection, full line), excitation (dashed line, $\lambda_{em} = 600$ nm) and normalised
emission (full line, $\lambda_{exc} = 407$ nm) spectra of powdered NG (dark green line) and B64 (dark red
line). Inset: sample luminescence decays and instrument response (black full line).

3.3 Imaging

Figure 3 shows the visible (top), UV-induced visible (middle) and UV-induced IR (bottom)
luminescence images of the overall area from which sample B64 was taken (as illustrated in Figure 1). Indian yellow is characterised by a yellow-orange fluorescence, in keeping with the emission maximum at 600 nm following excitation at 407 nm revealed by PL spectroscopy. The emission of Indian yellow also occurs in the IR range (c.700-800 nm range, Figure 2), and it can be observed in the UV-induced IR imaging (c.700-1000 nm range) as 'glowing white', against a grey-black background. Areas in the UV-induced visible image that show a paler yellow fluorescence may indicate the presence of other compounds and further investigation and analysis is ongoing.

Because of the relatively high PLQY of Indian yellow, it was possible to image a large section (c.10 m²) of the ceiling in a single frame from a distance of about 5 m, by firing the flashes many times during a 30s exposure (Figure 4).

![Fig. 3 Area from which sample B64 was taken; visible image (top), UV-induced visible (middle) and UV-induced IR (bottom) luminescence images. Indian yellow is characterised by a yellow-orange fluorescence. Areas showing a paler yellow fluorescence may contain other compounds.](image-url)
Fig. 4 Ceiling of the Badal Mahal, Garh Palace, Bundi (Rajasthan, India) depicting Krishna dancing with the gopis; (top) visible image and (bottom) UV-induced luminescence image, showing the yellow-orange emission of Indian yellow. Due to the distance between the camera and the ceiling, the use of a white board and Spectralon® reflectance standards was impossible, thus precluding correction for inhomogeneous light distribution and ambient stray light.

3.4 TDDFT calculations

Results of benchmarks of the present study for EA, SE and E are presented in Tables S1, S2 and S3 in the Supplementary Material. Although pure PBE better estimates the positions of the first two singlet states for all the three species with respect to the experimental reference spectrum (dark green line in Figure 2), it gives a mismatch in the order of the lowest two singlet and four triplet states with respect to all the other functionals investigated and previous literature data on X, which found four triplet states below the optically-active $S_2$, where the first triplet was determined to have a $^3(n_0\rightarrow\pi^*_L)$ character in a vacuum [39]. Long-range corrected hybrid functionals, known to give a
A comprehensive comparison shown in Table 1 between the lowest triplet and singlet states in a vacuum, obtained at TDDFT(B3LYP)/TZVP level of theory for: i) EA, ii) SE, iii) E, iv) OH-CH$_3$-X and v) X, allows the identification of a bathochromic effect induced by hydroxyl groups and glucuronic acid added to the benzene rings in X to form E and EA, respectively, leading to a final excitation spectrum of EA moderately red-shifted with respect to X. The presence of the sulphonate substituent in SE barely affects the absorption spectrum profile with respect to EA, as expected.

The bathochromic shift observed in the solid state optical response for both the $S_1$ and $S_2$ state energies, with respect to the calculated absorption wavelengths in a vacuum, can be ascribed to a combined effect of intermolecular interactions ($\pi-\pi$ stacking and hydrogen bonds) occurring between packed molecules. The deprotonation of the hydroxyl group, with the resulting formation of calcium and magnesium salts, could be also partially responsible for the spectral red shift.

Table 2 lists the principal TDDFT(B3LYP)/CPCM singlet vertical excitation energies (in nm) calculated in water, with their electronic structure characterisation, for EA, SE and E,
compared with the corresponding experimental main peaks (in nm). Figure 5 shows a comparison
between the experimental absorption spectrum (solid black line) and theoretical stick spectra
obtained in water for EA (solid red lines), SE (solid green line) and E (solid blue line), scaled for
their relative abundance in the NG sample (see Section 3.1) and, also, with their convoluted
Gaussian spectrum (FWHM of 0.05 eV), as a solid thin grey line. The related frontier orbitals
involved in the main vertical transitions are depicted in Figures S1, S2 and S3 for EA, SE and E. As
shown in Table 2, the molecular orbital analysis of the DFT (B3LYP) electronic wavefunction
reveals, in agreement with the literature, electronic transition assignments identified for the X
moiety, with the order of the first two singlet states \(1(n_O -> \pi_L^*)\) and \(1(\pi_H -> \pi_L^*)\) inverted between
vacuum and water, due to the solvatochromic effect of the polar solvent. Indeed, in water, the
combined effects of polarity and hydrogen bond formation become strong enough to trigger a
reversal of the order of singlet states with respect to a vacuum. In our calculations, the \(1(n_O -> \pi_L^*)\)
state experiences a blue shift of about 0.34 eV, with respect to a moderate red shift of about 0.28 eV
of the \(1(\pi_H -> \pi_L^*)\) state for EA. As can be easily seen in the diagram in Figure S4, this variation in
the energy leads to a crossing between the two singlet states. The energy blue shifts of the \(1(n_O->\pi_L^*)\)
state observed in water for SE and E are 0.30 eV and 0.10 eV, respectively, while, the
corresponding red shifts of the \(1(\pi_H -> \pi_L^*)\) state are 0.19 eV and 0.17 eV. Moreover, the order of the
lowest \(3(n_O -> \pi_L^*)\) and \(3(\pi_H -> \pi_L^*)\) triplet states found in water for EA, SE and E by the
TDDFT(B3LYP) calculations is in agreement with the results of Rai-Constapel et al. for X in water
[39].

Our TDDFT(B3LYP) vertical excitation energies calculated on X both in the gas phase and in water
are in good agreement with previous theoretical and experimental data, as shown in Table 3,
although TDDFT predicts the lowest state in the triplet manifold with a \(3(\pi_H-\pi_L^*)\) character in
water, which differs from the DFT/MRCI results reported by Rai-Constapel et al. [39].
Furthermore, TDDFT(B3LYP) optimisations of the first two triplet states of X, \(3(\pi_H-\pi_L^*)\) and
\(3(n_O\pi_L^*)\), in a vacuum, provide adiabatic excitation energies of, respectively, 433 and 428 nm, in
agreement with experimental phosphorescence data in 3-methylpentane [68] or in hexane solution at room temperature [69].

**Fig. 5** The experimental absorption spectrum (solid black tick line) in water of NG Indian yellow, with stick theoretical TD-B3LYP/TZVP/CPCM spectra for EA (red line), SE (green line) and E (blue line) calculated in water and scaled for their relative abundance in the NG sample and their corresponding Gaussian convoluted theoretical spectrum, with FWHM of 0.05 eV (grey solid thin line).

**Table 1.** TDDFT(B3LYP/TZVP) lowest singlet and triplet vertical excitation energies, nm, in a vacuum for euxanthic acid (EA), 4-sulphonate-euxanthone (SE), euxanthone (E), 1-hydroxy-7-methyl-xanthone (OH-CH$_3$-X) and xanthone (X) molecules.
Table 2. TDDFT(B3LYP/TZVP)/CPCM principal singlet vertical excitation energies of euxanthic acid (EA) 4-sulphonate-euxanthone (SE) and euxanthone (E), nm, in water, oscillator strengths, corresponding electronic structure and experimental main peaks in water, nm.

<table>
<thead>
<tr>
<th>Elect. structure</th>
<th>TDDFT(B3LYP/TZVP)/CPCM ΔE (nm)</th>
<th>Osc. Strength</th>
<th>Exp. maximum peaks (nm)</th>
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<tbody>
<tr>
<td></td>
<td>EA</td>
<td>SE</td>
<td>E</td>
</tr>
<tr>
<td>(π_H-&gt;π_L*)^b,^c</td>
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<td>(π_H,5-&gt;π_L+3)*^b,^c</td>
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- ^a^ electronic configuration of EA, ^b^ electronic configuration of SE, ^c^ electronic configuration of E
Table 3. Vertical lowest singlet and triplet excitation energies, nm, from the ground state of xanthone in a vacuum and in water calculated at the TDDFT(B3LYP)/CPCM level of theory with TZVP basis set, compared with available theoretical (DFT/MRCI) and experimental literature data.

<table>
<thead>
<tr>
<th>state</th>
<th>Electronic structure</th>
<th>TDDFT(B3LYP/TZVP) $\Delta E$ (nm)</th>
<th>DFT/MRCI (nm) literature(^a)</th>
<th>Experimental literature (b,c,d)</th>
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<td>vacuum</td>
</tr>
<tr>
<td>$S_0$</td>
<td>ground state</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>$S_1$</td>
<td>$n_O \rightarrow \pi_L^*$</td>
<td>341</td>
<td>315</td>
<td>360</td>
</tr>
<tr>
<td>$S_2$</td>
<td>$\pi_H \rightarrow \pi_L^*$</td>
<td>315</td>
<td>331</td>
<td>319</td>
</tr>
<tr>
<td>$T_1$</td>
<td>$n_O \rightarrow \pi_L^*$</td>
<td>394</td>
<td>410</td>
<td>380</td>
</tr>
<tr>
<td>$T_2$</td>
<td>$\pi_H \rightarrow \pi_L^<em>; \pi_{H-2} \rightarrow \pi_L^</em>$</td>
<td>384</td>
<td>347</td>
<td>373</td>
</tr>
<tr>
<td>$T_3$</td>
<td>Multiconfigurational triplet state</td>
<td>359</td>
<td>359</td>
<td>346</td>
</tr>
<tr>
<td>$T_4$</td>
<td>Multiconfigurational triplet state</td>
<td>353</td>
<td>358</td>
<td>338</td>
</tr>
</tbody>
</table>

\(^a\) Ref. 39; \(^b\) Ref. 40; \(^c\) Ref. 42; \(^d\) Ref. 41

CONCLUSION

For the first time the optical properties of Indian yellow were determined quantitatively in the solid state and correlated with its chemical composition. Although the main components of the pigment — euxanthic acid and euxanthone — were known, the presence of a sulphonate derivative of euxanthone (C\(_{13}\)H\(_8\)O\(_7\)S) was identified for the first time in both samples analysed in this study. A theoretical analysis carried out on euxanthic acid, 4-sulphonate-euxanthone and euxanthone, both as isolated molecules and in a polar (protic) solvent, helped assign the origin of the excited states involved in the photo-induced processes and their electronic configurations. Additional calculations on differently substituted xanthone molecules provide information on the role of substituents in the absorption band positions. In depth characterisation of the photophysical properties of pigments with PL spectroscopy and confirmation by theoretical calculations allow a more reliable interpretation of PL imaging results and the selection of optimum excitation and emission.
wavebands to differentiate pigments based on their luminescence properties. Further research on the topic is ongoing and will be reported in more detail in due course. The extent to which this pigment was used on a wall painting was previously unknown. The widespread occurrence of organic pigments and colorants on Asian murals remains overlooked. Such materials are inherently susceptible to damage during conservation interventions and when exposed to unfavourable environmental conditions, including exposure to electromagnetic radiation or pollution, and changes in relative humidity. Therefore, spatial information on their presence in works of art is of paramount importance for the effective design, implementation and monitoring of appropriate conservation management plans.

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REFERENCES


disasters and confronting the unexpected in conservation, AIC joint 44th annual meeting and 42nd annual conference, May 13-17, 2016, Montreal, Canada: AIC; 2016.


- Photophysics, imaging and theoretical study of Indian yellow, both in solid state and in aqueous solution.

- Correlation between optical properties and chemical composition.

- Identification of a sulphonate derivative of euxanthone in 17th-century Indian wall painting.