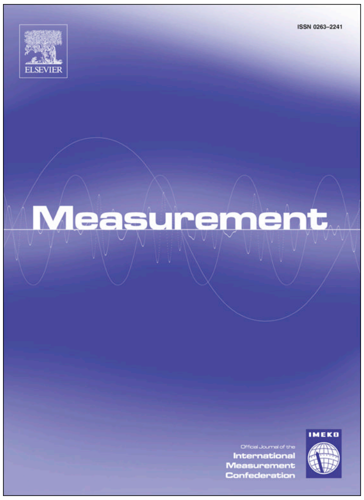


Photophysics of Artist's Pigments

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

PII: S0263-2241(18)30275-6
DOI: https://doi.org/10.1016/j.measurement.2018.03.082
Reference: MEASUR 5401

To appear in: *Measurement*

Received Date: 15 February 2018
Revised Date: 30 March 2018
Accepted Date: 31 March 2018

Please cite this article as: G. Accorsi, G. Verri, A. Acocella, D. Saunders, C. Martin de Fonjaudran, D. Tamburini, A. Rava, S. Whittaker, F. Zerbetto, Photophysics of Artist's Pigments, *Measurement* (2018), doi: https://doi.org/10.1016/j.measurement.2018.03.082

Photophysics of Artist’s Pigments

Gianluca Accorsi[1], Giovanni Verri[2], Angela Acocella[3], David Saunders[4], Charlotte Martin de Fonjaudran[2], Diego Tamburini[4] Amarilli Rava,[2] Samuel Whittaker[2] and Francesco Zerbetto[3]

[1] CNR NANOTEC - Institute of Nanotechnology c/o Campus Ecotekne, Via Monteroni, 73100 Lecce, Italy, gianluca.accorsi@nanotec.cnr.it
[2] The Courtauld Institute of Art, Somerset House, Strand, WC2R 0RN, London, UK, giovanni.verri@courtauld.ac.uk, charlotte.martinde@courtauld.ac.uk
[3] Dipartimento di Chimica “G.Ciamician”, Università di Bologna, Via F. Selmi 2, 40126, Bologna, Italy, angela.acocella3@unibo.it
[4] Department of Scientific Research, The British Museum, Great Russell Street, London, WC1B 3DG, UK, DSaunders@britishmuseum.org

Abstract

Among analytical techniques, photophysics represents a non-invasive method suitable for the study of artefacts in the cultural heritage field. Thanks to this technique, many useful data can be collected on the pigments in order to get information on their identification and aging status. This represents a powerful tool for restores and scholars with the aim of preservation and fruition of artefacts. Here, we report the optical properties of i) Cuprorivaite (Egyptian Blue) exhibiting an exceptionally high emission quantum efficiency in the near-infrared region (λ_{max}=910 nm, P□□□=10.5%) that makes it also appealing for several technological applications; ii) Manganese blue, a synthetic barium manganate(VI) sulphate compound, used both as a blue pigment in works of art and by conservators in the restoration of paintings and iii) Indian yellow, a historic pigment produced in India that is characterised by its luminous yellow-orange colour and noticeable photoluminescence properties. The choice of the above-mentioned pigments has been mainly driven by the availability of real *case studies* in different worldwide regions.

1. Introduction

During the past decades, interest in non-invasive investigations for the characterisation and identification of painting materials has greatly increased.[1] In general, the nature of museum objects is such that sampling is always kept to a minimum and is often completely unacceptable. Therefore, such analyses are more routinely used in the cultural heritage field. Photoinduced luminescence spectroscopy (PL) can provide quantitative information on a small area (e.g. emission properties, PLQY and lifetime). By contrast, photoinduced luminescence imaging provides information on the distribution of materials of interest over large areas. When supported by theoretical (DFT) calculations for the interpretation of the photophysics involved in the luminescence processes, luminescence investigations can provide useful information for heritage specialists. Moreover, photoluminescence investigations of painting materials have proven useful to fields well beyond cultural heritage. In fact, as recently demonstrated, Egyptian Blue exhibits a remarkable emission intensity in the near-infrared region and has a future in a variety of hi-tech applications including bio-medicine, lasers and telecommunications.[2]

Manganese blue was used as artists’ pigment from its first industrial production until the 1900s. It must, therefore, have been used by a number of artists, but apart from a brief mention of its use by Diego Rivera, there is, to the knowledge of the authors, no published scientific evidence of the use of manganese blue in works of art.[3] In the 1980s, manganese blue was recommended to conservators as an excellent non-metameric match for azurite,[4] and the pigment is still used for retouching paintings. This photo-induced luminescence properties of manganese blue suggests a means by which the pigment can be imaged to record its spatial distribution.

Finally, indian yellow is an historic pigment produced in India until the end of the 19th/beginning of the 20th century and it is characterised by bright yellow-orange colour and noticeable photoluminescence properties. The main colorant is given by the crystalline mixture of the magnesium and calcium salts of euxanthic acid acid, EA[5]. Early chemical studies showed that euxanthone (C13H8O4), 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 ($C_{19}H_{16}O_{10}$) [6]. 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 [5, 7]. It was also used by artists in Europe and the United States [8]. Here, a description of the optical properties of these dyes used in paintworks is given.

2. Discussion

Egyptian Blue, Cuprorivaite ($CaCuSi_4O_{10}$) is rare in nature but well known to Egyptologists and museum scientists as the synthetic blue pigment. The earliest known use of the pigment is in the late Nagada II period and the early Nagada III A-B period in Egypt (around 3350-3200 BC).[9]
It was widely used in Egypt and in the Mediterranean basin until the end of the Roman period and beyond.

The first qualitative analyses of the pigment were undertaken by Chaptal and Davy. On the basis of the X-ray diffraction data, the currently accepted chemical formula for Egyptian blue is that of the naturally occurring mineral cuprorivaite. The coloured crystal can be synthesised by heating together, at 850–1000 °C, a calcium compound (typically calcium carbonate), a copper-containing compound (metal filings or malachite: CuCO3_Cu(OH)2), silica sand and soda or plant-derived potash as a flux.[10] The compound has been photophysically investigated both as a pure powder and mixed with potassium bromide (around 80% KBr) with identical results. Fig. 2 (top) shows the absorption (total-reflectance) spectrum, the emission (λ_{exc} = 637 nm) spectrum and the luminescence decay profile of synthetic cuprorivaite. Absorption and excitation spectra show three different electronic transitions ($^2B_{1g}$-$^2B_{2g}$, ^2E_g and $^2A_{1g}$) attributable to Cu^{2+} ions, which are expected to be the only photoluminescent components of cuprorivaite.[11]

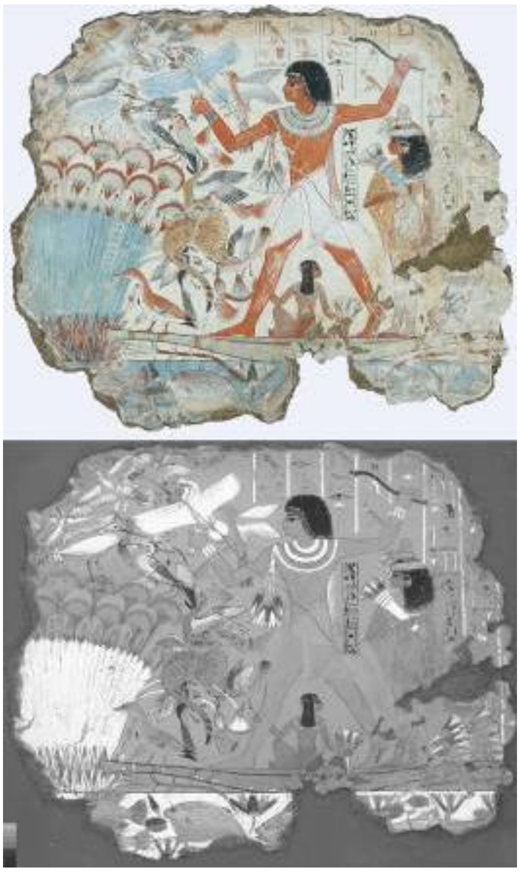


Fig. 1 Fowling in the marshes (EA 37977), Nebamun wall painting fragment, British Museum, London, U.K.: visible (top) and infrared photoluminescence (bottom) images. Bright white areas, which correspond to the presence of Egyptian blue, are caused by luminescence from the pigment. © The Trustees of the British Museum

The emission spectrum is centred at 910 nm and is related to the lowest energy electronic transition ($^2B_{2g}$ - $^2B_{1g}$). This transition is symmetrically prohibited, as suggested by the very long luminescence decay (107 μs; inset Fig. 2). The compound shows an exceptionally high luminescence quantum yield for an infrared emitter, PLQY (Photoluminescence quantum yield) = 10.5%. The strong emission can be observed in Fig. 2 (bottom), which shows the visible and visible-induced luminescence images of powdered synthetic cuprorivaite. The long luminescence lifetime and the unusually intense infrared emission make cuprorivaite an excellent candidate as a luminescent label for a number of applications. In the bio-medical field, for instance, the greater penetration by infrared photons of human tissue with respect to the penetration of UV or visible photons offers the possibility of attaining more detailed and highly resolved images. Materials that emit between about 700 and 950 nm or around 1050 nm are preferred as this minimizes absorption by the tissue. Thus, excitation between about 650 and 900 nm is required. Moreover, the relatively long-lived luminescence makes it possible to cut off short-lived background emission from biological matrices.

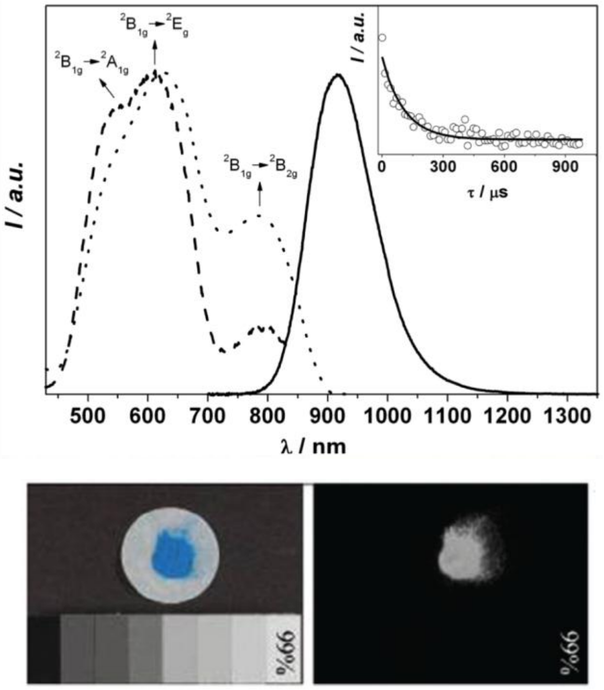


Fig. 2. (Top) Absorbance (dotted line), excitation (dashed line, λ_{em}= 916 nm) and emission (solid line, λexc = 637 nm, corrected for the detector response) spectra of powdered synthetic cuprorivaite. Inset: luminescence decay (107 μs, λ_{exc} = 637 nm). (Bottom) Visible (left) and visible-induced luminescence (right) digital images (λ_{exc} = 629 nm) of a synthetic cuprorivaite sample captured in the 800–1000 nm range. The 99% reflectance standard is non luminescent and allows quantification of ambient stray infrared radiation.

This can be easily achieved by setting the instrument to detect the luminescent output after a suitable delay. Another potential application of this strong NIR emitter is in silica-based optical amplifiers and fibre optic systems for telecommunications. For long distance communication it is necessary to compensate for losses in the fibre by regenerating the signal, typically every 50–150 km (depending on the data rate). At present, this is achieved using optical amplifiers, which are typically pumped at 1480 or 980 nm (standard telecommunication window) with commercially available semiconductor diode lasers coupled into the amplifier with a wavelength multiplexer. NIR emitting species are also useful in laser technology, where the generation of coherent low energy light beams can form the basis of tunable solid-state lasers over a wide spectral range.[2]

Manganese blue is a synthetic barium manganate(VI) sulphate compound that was produced from 1935 to the 1990s and was used both as a blue pigment in works of art and by conservators in the restoration of paintings. According to Eastaugh et al. (1998),[12] manganese blue was used as a colorant in cement and therefore known as ‘cement blue’. In addition to its use in the cement industry, manganese blue was also sold as an artists’ pigment from its first industrial production until the 1900s. It must, therefore, have been used by a number of artists, but apart from a brief mention of its possible use by Diego Rivera, there is, to the knowledge of the authors, no published scientific evidence of the use of manganese blue in works of art. In the 1980s, manganese blue was recommended to conservators as an excellent non-metameric match for azurite,[4] and the pigment is still used for retouching paintings at, among other places, the National Gallery, London, and the Courtauld Institute of Art, despite dwindling supplies, as the pigment is no longer being produced. The photophysical properties of manganese blue were investigated both as a pure powder and mixed with potassium bromide (to refine the absorbance value for the quantitative determination of the luminescence). The absorption (total reflectance), excitation and emission profiles, obtained in the solid state as a powder, are reported in Fig. 3, while the lifetime decay is shown in the inset. The compound absorbs radiation in the visible and near-infrared regions between ca. 500 and 1250 nm; this absorption pattern is responsible for the blue colour of the material. The absorption spectrum is characterized by a broad band structure, due to the very strong coupling between electronic transitions and lattice phonons, typical of transition metal crystal systems. According to previous assignments,[13] it mainly consists of a near-IR band system, between 800 and nearly 900 nm, that can be attributed to ^{2}E- ^{2}T$_2$ ligand field (LF) transitions, and ligand-to-metal charge-transfer bands between 600 and 800 nm, as also predicted by DFT calculations.[14] The excitation spectrum, obtained by monitoring the emission output at 1300 nm, matches the energy position of the absorption profile, indicating that the emitting levels are directly populated by the absorbing states mentioned above.

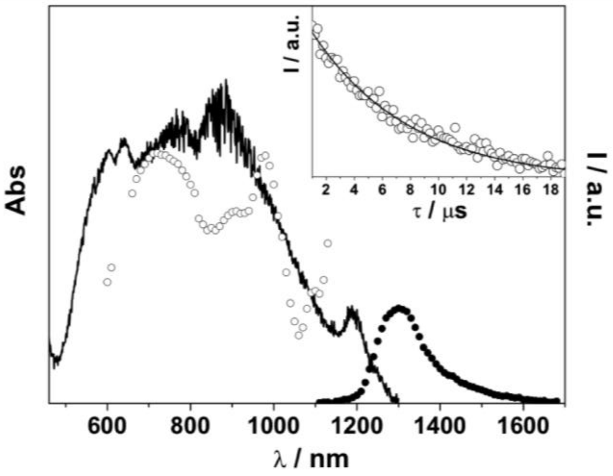


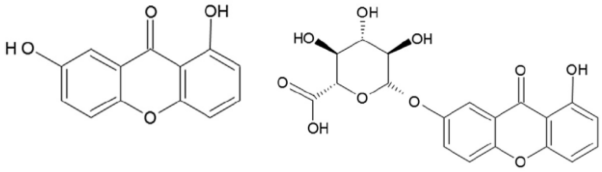
Fig.3: Absorbance (total reflection, full line), excitation (empty circle, λ_{em} = 1300 nm) and emission (full circle, λ_{exc} = 637 nm) spectra of powdered synthetic manganese-blue. Inset: luminescence decay (7.1 µs, λ_{exc} = 637 nm).

The photoluminescent quantum yield of the luminescence centred at ca. 1300 nm has been quantitatively determined as well as the corresponding lifetime decay. By exciting manganese blue with radiation at 637 nm, a PLQY of 0.5% and a corresponding decay of 7.1 µs have been found.

Finally, Indian Yellow is a historic pigment produced in India until the end of the 19th/beginning of the 20th century. It has been identified on several miniature paintings dated between the 16th and 19th centuries that are attributed to the Mughal and Rajput schools [5, 7]. It was also used by artists in Europe and the United States[8]. 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.[15]. Other subject matters include a *Ragmala* series as well as scenes of Hindu mythology on the ceiling.

Fig. 4. Detail of Blue Managanese on "The Coronation of the Virgin" by the Master of Cappenberg (NG 263).

It is characterised by luminous yellow-orange colour and noticeable photoluminescence properties. 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 (Scheme 1), the presence of a sulphonate derivative of euxanthone ($C_{13}H_8O_7S$) was identified for the first time.[16]



Scheme.1 Chemical structures of Euxanthone (E, left) and euxanthic acid (EA, right).

A complete understanding of the photophysical properties of Indian yellow is required for correct interpretation of results obtained with PL spectroscopy and imaging techniques. Here, 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.

Fig.5 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.

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 (Fig. 6). 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 π-π* transitions, while those at longer wavelengths (> 400 nm) are of n-> π* ($S_0 > S_1$) nature [17] (see also the TDDFT calculations).[16] 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 6).

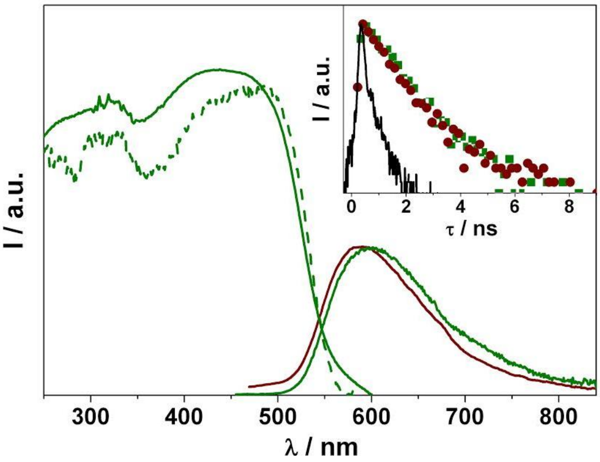


Fig. 6 Absorbance (total reflection, full line), excitation (dashed line, λ_{em} = 600 nm) and normalised emission (full line, λ_{exc} = 407 nm) spectra of powdered NG (dark green line) and B64 (dark red line). Inset: sample luminescence decays and instrument response (black full line).

The corresponding lifetime decays (Figure 6, inset) are in good accordance with a bi-exponential model (B64: τ_1 = 510ps (73%), τ_2 = 1.50 ns (27%); NG: τ_1 = 530ps (75%); τ_2 = 1.49ns (25%)), suggesting the presence of different packed domains (driven by the π-π stacking and hydrogen bonds), which commonly occur in solid-state organic samples[18]. For the first time, it was possible to measure the photoluminescence quantum yield 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 (Euxanthic acid) and E (Euxanthone).[16]

3. Conclusions

In this work, we reported the photophysical studies made on three modern and ancient artist's pigments used in different world regions. Some showed interesting properties potentially useful in technological field. For instance, Egyptian Blue exhibiting a remarkable emission intensity in the near-infrared region that revealed to be particularly useful in a variety of hi-tech applications including bio-medicine, lasers, telecommunications and as crime scene investigation (CSI) tool. Others have been found to be composed by a mix of molecules influencing the chemical structure of the pigment itself and its optical output, according to the preparation method such as Indian Yellow. It has, as main components, euxanthic acid and euxanthone with smaller amounts of a sulphonate derivative of euxanthone ($C_{13}H_8O_7S$) identified for the first time. Information on the presence of organic and inorganic materials and their distribution on a work of art can help in the understanding of their making and history. Importantly, it may also inform conservation intervention, in an attempt to design and implement appropriate treatments, which will contribute to the long-term preservation of art for future generations.

4. Experimental section

Absorption spectra were recorded with a Cary Uv-Vis 4000□spectrophotometer. For luminescence experiments, the samples were placed in fluorimetric 1-cm path cuvettes while the solid state samples (powder) were placed in between two quartz disks fixed by a dedicated metal pincer. Uncorrected emission spectra were obtained with an Edinburgh FLS980 spectrometer equipped with a peltier-cooled Hamamatsu R928 photomultiplier tube (185-850 nm). The steady-state NIR luminescence spectra were obtained with an Edinburgh FLS980 spectrometer equipped with Hamamatsu R5509-72 supercooled photomultiplier tube (400-1700 nm) at 193 K and a TM300 emission monochromator with NIR grating blazed at 1000 nm. An Edinburgh Xe900 450 W Xenon arc lamp was used as exciting light source. Corrected spectra were obtained *via* a calibration curve supplied with the instrument. Luminescence quantum yields (Φ_{em}) in solution obtained from spectra on a wavelength scale (nm) were measured according to the approach described by Demas and Crosby (Demas, J. N.; Crosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991-1024) using air-equilibrated $[Ru(bpy)_3Cl_2$ in water solution□□$\Phi_{em} = 0.028]$ as standard.

Emission lifetimes in the ps-μs range were determined with the single photon counting technique by means of the same Edinburgh FLS980 spectrometer using a laser diode as excitation source (1 MHz repetition rate) and an Hamamatsu MCP R3809U-50 (time resolution 20 ps) as detector. Or, with an IBH single photon counting spectrometer equipped with a thyratron gated nitrogen lamp working in the range 2–40 kHz (0.5 ns time resolution) the detector was a red-sensitive (185–850 nm) Hamamatsu R-3237-01 photomultiplier tube. Analysis of the luminescence decay profiles vs time was accomplished with the DAS6 Decay Analysis Software provided by the manufacturer.

For the emission in the visible region, the luminescence lifetimes in the microsecond-millisecond scales were measured by using a Perkin-Elmer LS-50 spectrofluorimeter equipped with a pulsed xenon lamp with variable repetition rate and elaborated with standard software fitting procedures. For solid samples, Φ_{em} have been calculated by corrected emission spectra obtained from an apparatus consisting of a barium sulphate coated integrating sphere (4 or 6 inches), a He-Cd laser (λ_{exc}: 325 nm, 5mW) or a 450W Xe lamp (λ_{exc} = tunable by a monochromator supplied with the instrument) as light sources, and a R928 photomultiplier tube or a CCD AVA-Spec2048 as signal detectors, following the procedure described by De Mello et al. (J. C. De Mello, H. F. Wittmann and R. H. Friend, Adv. Mat., 1997, 9, 230.)

Experimental uncertainties are estimated to be ± 8% for τ determinations, ± 20% for PLQYs, ± 2 nm and ± 5 nm for absorption and emission peaks, respectively.

5. Acknowledgments

This work was generously supported by the Leverhulme Trust (LuminArt Project). Gianluca Accorsi wishes to thank the project MAAT (MIUR- PON02_00563_3316357 e CUP B31C12001230005).

References

[1] *R. Mazzeo, Analytical Chemistry for Cultural Heritage, Vol. 375, Springer, **2017**.*

[2] *G. Accorsi, G. Verri, M. Bolognesi, N. Armaroli, C. Clementi, C. Miliani, A. Romani, Chemical Communications **2009**, 3392-3394.*

[3] *aA. Burnstock, The Courtauld Institute of Art, email dated 7 June, **2009**; bM. de Keijzer, Instituut Collectie Nederland, email dated 1 May **2013**; cT. Learner, Getty Conservation Institute, email dated 19 April, **2013**; dJ. Townsend, Tate Modern, email dated 9 September, **2013**.*

[4] *S. Staniforth, Studies in Conservation **1985**, 30, 101-111.*

[5] *N. S. Baer, A. Joel, R. L. Feller, N. Indictor, in Artists' pigments: a handbook of their history and characteristics (Ed.: R. L. Feller), National Gallery of Art, Washington DC, **1986**, pp. 17-36.*

[6] *aN. E. Artz, E. M. Osman, Biochemistry of glucuronic acid, Academic Press, New York, **1950**; bR. Nietzki, A. Collin, W. Richardson, Gurney & Jackson, London, **1892**.*

[7] *aT. R. Ravindran, A. K. Arora, S. Ramya, R. V. Subba Rao, B. Raj, J. Ram. Spect. **2011**, 42, 803-807; bI. Reiche, R. Britzke, G. Bukalis, U. Reinholz, H. P. Weise, R. D. Gadebusch, X-Ray Spect. **2005**, 34, 42-45; cN. Purinton, R. A. Newman, in Pride of the Princes: Indian art of the Mughal era in Cincinnati Art Museum (Ed.: D. S. Walker), Cincinnati Art Museum, **1985**, pp. 107-113.*

[8] *aJ. H. Townsend, Stud. in Cons. **1993**, 38, 231-254; bR. Ploeger, A. N. Shugar, in Emergency: preparing for disaters and confronting the unexpected in conservation, AIC joint 44th annual meeting and 42nd annual conference, May 13-17, 2016, Montreal, Canada, AIC, **2016**; cO. Otlowska, M. liwka-Kaszynska, M. lebioda, M. Wachowiak, RSC Adv. **2015**, 5, 48786-48792; dK. Stonor, R. Morrison, Nat. Gal. Tech. Bul. **2012**, 33, 50-72; eR. A. Newman, C. Weston, E. Farrell, JAIC **1980**, 19, 103-105.*

[9] *L. H. Corcoran, The Color Blue as an 'Animator' in Ancient Egyptian Art Essays in Global Color History, Interpreting the Ancient Spectrum ed., NJ, Gorgias Press, **2016**.*

[10] *S. Pages-Camagna, S. Colinart, Archaeometry **2003**, 45, 637-658.*

[11] *G. Pozza, D. Ajò, G. Chiari, F. De Zuane, M. Favaro, Journal of Cultural Heritage **2000**, 1, 393-398.*

[12] *N. Eastaugh, V. Walsh, T. Chapman, R. Siddall, The Pigment Compendium, Oxford, UK, **1998**.*

[13] *T. C. Brunold, H. U. Gudel, Inorg. Chem. **1997**, 36, 1946-1954.*

[14] *G. Accorsi, G. Verri, A. Acocella, F. Zerbetto, G. Lerario, G. Gigli, D. Saunders, R. Billinge, Chemical Communications **2014**, 50, 15297-15300.*

[15] *M. C. Beach, Bundi Fort : a Rajput world, Marg Publications, Mumbai, India, **2016**.*

[16] *C. M. d. Fonjaudran, A. Acocella, G. Accorsi, D. Tamburini, G. Verri, A. Rava, S. Whittaker, F. Zerbetto, D. Saunders, Dyes and Pigments **2017**, 144, 234-241.*

[17] *V. Rai-Constapel, E. Mihajlo, C. M. Marian, J. Phys. Chem. A **2013**, 117, 3935-3944.*

[18] *A. K. Srivastava, A. Singh, L. Mishra, J. Phys. Chem. A **2016**, 120, 4490-4504.*