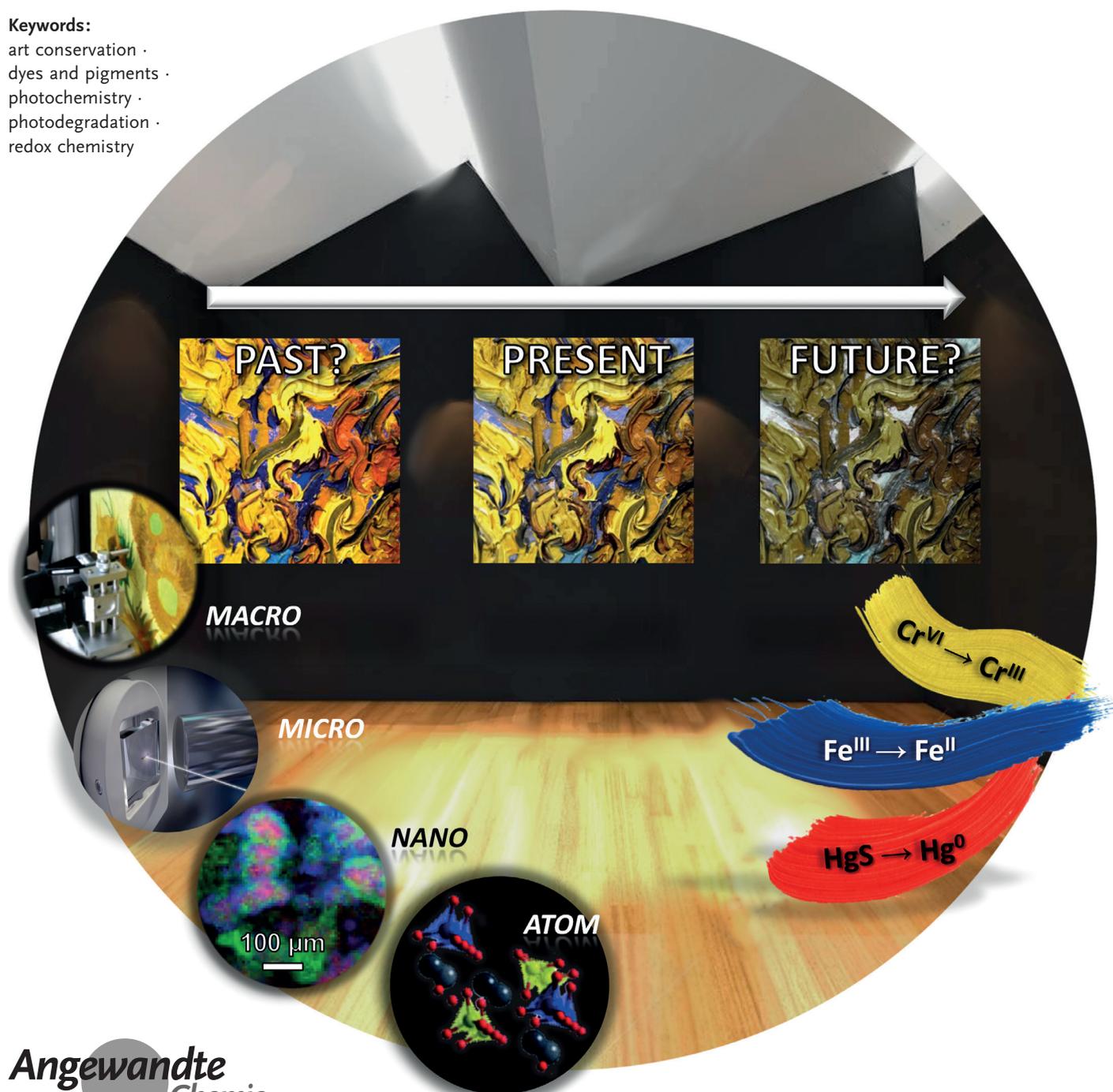


Photochemistry of Artists' Dyes and Pigments: Towards Better Understanding and Prevention of Colour Change in Works of Art

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The absorption of light gives a pigment its colour and its reason for being, but it also creates excited states, that is, new molecules with an energy excess that can be dissipated through degradation pathways. Photodegradation processes provoke long-term, cumulative and irreversible colour changes (fading, darkening, blanching) of which the prediction and prevention are challenging tasks. Of all the environmental risks that affect heritage materials, light exposure is the only one that cannot be controlled without any impact on the optimal display of the exhibit. Light-induced alterations are not only associated with the pigment itself but also with its interactions with support/binder and, in turn, are further complicated by the nature of the environmental conditions. In this Minireview we investigate how chemistry, encompassing multi-scale analytical investigations of works of art, computational modelling and physical and chemical studies contributes to improve our prediction of artwork appearance before degradation and to establish effective preventive conservation strategies.

1. Introduction

The harmful effect of light on artworks has been recognized for centuries. In the late 1880s, following the introduction of artificial lighting in the South Kensington Museum (now the Victoria and Albert Museum, London UK), a public controversy arose over the fading of watercolours in English national collections.^[1] Two preeminent chemists, Dr. W. J. Russell and Capt. W. de W. Abney were commissioned by the Committee of Council on Education “to investigate as a scientific question the action of light on the various pigments used in painting”. Using spectrophotometric measurements, for the first time they assembled compelling evidence that exposure to light was a cause of fading.^[2]

Today modern chemistry has gained a crucial role in heritage science, a research field, spanning humanities and natural sciences, that focuses on the understanding, conservation and management of cultural heritage. In this vivid context, a renewed cross-disciplinary interest for the impact of light on artists’ materials has recently been triggered by technical innovations in museum lighting and artwork restoration.^[3] A deep comprehension of the photochemical processes underpinning changes in artists’ materials is sought to offer: 1) a solid framework to develop preventive conservation strategies through the selection of optimal lighting conditions;^[4] 2) (semi)quantitative compositional data to predict the original artistic intended appearance of an artwork before discoloration and propose its digital reconstructions.^[5] On the other hand, heritage materials with their often unknown and heterogeneous compositions and unmonitored long-term modifications represent highly complex systems. Understanding and disclosing their behaviour under visible-light exposure is an intriguing challenge for chemical sciences.

In the following we review recent findings regarding different types of inorganic pigments belonging to the class of semiconductors and charge-transfer compounds of which the photoredox properties in paint layers have been investigated through a phenomenological approach starting from the

identification of secondary products on artificially aged mock-ups and/or original artworks. A specific section is dedicated to natural organic dyes, the degradation issues of which have been addressed by studying the photophysics of parent molecules as a conceptual key to understand their photochemistry and to predict resulting colour changes in artworks.

2. Light-Induced Redox Behaviour of Inorganic Pigments in Paint Layers

2.1. Semiconductor Pigments

Several artists’ pigments are semiconductors, the excited states of which can cause the self-redox reaction of the

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pigment (i.e. photocorrosion) as well as promote redox reactions of other paint components (i.e. photocatalysis).

The n-type semiconductor red cinnabar or vermilion (α -HgS) is known since the Neolithic period. Used worldwide in various kind of artefacts,^[6,7] under certain conditions it tends to develop lilac-gray/black crusts, disfiguring Old Masters' easel paintings^[3,6,8] as well as wall paintings of archaeological sites and cathedrals (Figure 1 a,b).^[9,10] While in the past the α -HgS blackening was ascribed a priori to the photoinduced structural change to black cubic β -HgS,^[6] recent analyses of microsamples from artworks^[8–10,11,12] proved that the process is associated with Hg-Cl secondary products, such as Hg₃S₂Cl₂ polymorphs, Hg₂Cl₂ and HgCl₂ (Figure 1 c,d). In fresco samples, calcium sulfates were also usually detected (Figure 1 c).

Artificial aging of α -HgS mock-ups by UVA-Vis light, NaClO and O₂-rich conditions reproduced the conversion of α -HgS to Hg₂Cl₂ (with α -Hg₃S₂Cl₂ as intermediate) and sulfates.^[11]

Theoretical calculations allowed a scheme for the formation/decomposition paths of Hg-Cl secondary compounds to be proposed (Figure 1 e).^[13] Upon light and humidity expo-

sure, environmental Cl chemisorbs onto the α -HgS surface. The structure of Cl@HgS favours the growth of various Hg-S-Cl phases, before finally ending up as the more stable α -Hg₃S₂Cl₂. At the α -HgS/ α -Hg₃S₂Cl₂ interface, significant lattice mismatch occurs, likely promoting the formation of structural instabilities within α -Hg₃S₂Cl₂, with the release of black Hg⁰ (identified by electrochemistry experiment).^[14] The formation of whitish Hg₂Cl₂/HgCl₂ can take place as well, which may undergo further light-induced alteration (e.g., via disproportionation) providing a second path for Hg⁰ precipitation.

Integrating the information gained through computational modelling studies, artificial aging experiments and phenomenological observations from case studies, the mechanism depicted in Scheme 1 can be proposed.

Cadmium yellows (CdYs) are n-type semiconductor pigments, comprising CdS and Cd_{1-x}Zn_xS in different crystalline structure (hexagonal/cubic).^[15a] For their vibrant hues, 19th–20th century painters often employed CdYs, which only in some of their artworks appear discoloured today. A multi-analytical approach was employed to study three of these masterpieces.^[16–18] In *Flowers in a blue vase* by Van Gogh, amorphous CdSO₄, CdC₂O₄ and PbSO₄ were identified in the grayish alteration crust.^[16] In *Still Life with Cabbage* by Ensor, CdSO₄·nH₂O and (NH₄)₂Cd(SO₄)₂ were revealed in the white globules at the paint surface (Figure 2 a,d).^[17] In *Joy of Life* and *Flower Piece* by Matisse, the blanched CdY paints resulted in products composed of CdSO₄·nH₂O, CdC₂O₄ and CdCO₃, while the darkened areas were enriched with Cd-Cl compounds (Figure 2 b,c,e–g).^[18]

The photo-oxidation of CdS-based compounds to CdSO₄, that is the most likely degradation pathways in the presence of O₂ and moisture,^[19] has been confirmed by electrochemical measurements on CdS powder.^[20]



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Maria João Melo is President and Full Professor at the Department of Conservation and Restoration of the Faculty of Sciences and Technology-New University of Lisbon. Her research interests center on the study of the photodegradation mechanisms of dyes in paints and plastics, for the development of new conservation methodologies of medieval illuminations and of Contemporary Art. Other fields of expertise are colour in nature.



Simona Fantacci is senior research scientist at the CNR-ISTM (Perugia, Italy). She received a PhD in Theoretical Inorganic Chemistry from the University of Perugia in 1999 and was research associate at Princeton University (USA) in 2002–2003. Her research interests range from DFT/TDDFT study of transition metal complexes in the fields of DSSCs, OLED devices and NLO materials to modeling of photophysical properties and degradation processes of dyes and pigments.



Koen Janssens studied Chemistry at the University of Antwerp and obtained his PhD in 1989. Since then, he has been actively making use of focused X-ray micro- and nanobeams, produced in large accelerator complexes, for non-destructive materials analysis. He applies the same suite of techniques for better understanding alteration processes in cultural heritage materials. He is currently vice-dean of the Faculty of Science of the University of Antwerp.

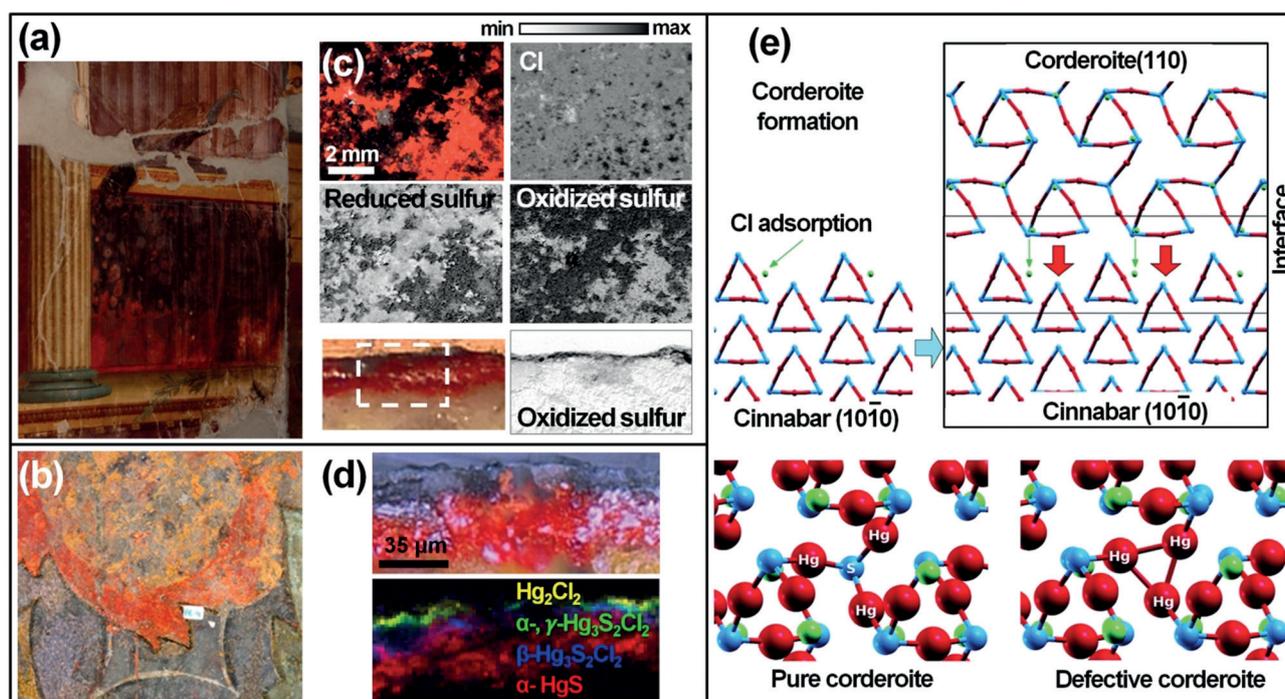
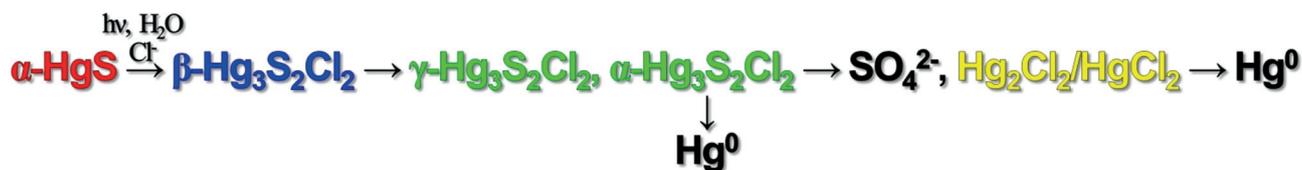


Figure 1. Photographs of discolored α -HgS paints of a) a Roman fresco of *Oplontis* excavation sites (Torre Annunziata, IT) (credits: M. Pagano) and b) a wall painting of Pedralbes Monastery (Barcelona, ES). c) Photomicrograph and Cl and S speciation maps of a (top) fragment and (bottom) cross-section from a Roman fresco of *Villa Sora* (Torre del Greco, IT). d) Photomicrograph and synchrotron radiation (SR) μ -XRD maps of a cross-section from (b). e) (top) Proposed mechanism of α -Hg₃S₂Cl₂ formation; (bottom) local atomic structure for pure α -Hg₃S₂Cl₂ (left) and defective α -Hg₃S₂Cl₂ with a S vacancy (right). Adapted from Refs. [9, 12, 13].



Scheme 1. Overall photodegradation mechanism of α -HgS based on the literature (cf. also Figure 1).^[9–14]

Computational simulations of the interaction of CdS with O₂ and/or H₂O also showed that structural defects (i.e., Cd/S vacancies) at pigment surface are reasonably linked to the more complex photo-oxidation reactions observed in paintings.^[21] Nevertheless, for the following reasons we are still far from a thoroughly understanding of the reactivity of CdS in paint layer: 1) both CdSO₄ and other compounds, identified as secondary products, could instead already be present in the original paint formulations, as synthesis residues or additives;^[15a] 2) it is not clear whether or not Cd–Cl species (likely the residues of the CdS synthesis) can promote self-oxidation; 3) it is not clear how the stability of CdY is affected by their differences in crystal structure and stoichiometry. Moreover, also the possible activity of CdY as photocatalyst deserves further investigation since the chalking phenomenon visible in *Joy of Life*^[18,22] and in CdY mock-ups exposed to light and humidity^[23] might be ascribed to the oxidative degradation of the binding medium.

Minium or red lead (Pb₃O₄) and titanium white (TiO₂) are two other semiconductor pigments both recognized as photo-

catalysts.^[24–26] Investigations of a blanched Pb₃O₄ sample from a Van Gogh's painting led to formulate the following mechanism.^[24] The Pb₃O₄ excited conduction band can both reduce Pb^{IV} to Pb^{II} and induce decarboxylation of the oil binder at the pigment surface with the release of CO₂. The latter in turn reacts with Pb^{II} to form various white lead carbonates as final alteration products.

TiO₂-pigmented oil paints can experience the photo-oxidation of the binder into volatile low-molecular weight species. The process ultimately manifests as chalking, being more pronounced with increasing humidity and in the presence of O₂.^[25,26] Modelling studies of TiO₂ for photocatalysis are a well-established and pointed to the prominent influence of crystal facets and defects on the reactivity of organic pollutants.^[27] The insights obtained here may be directly transferred to the cultural heritage context along with dedicated analyses of different TiO₂ paint formulations and specific reaction media.

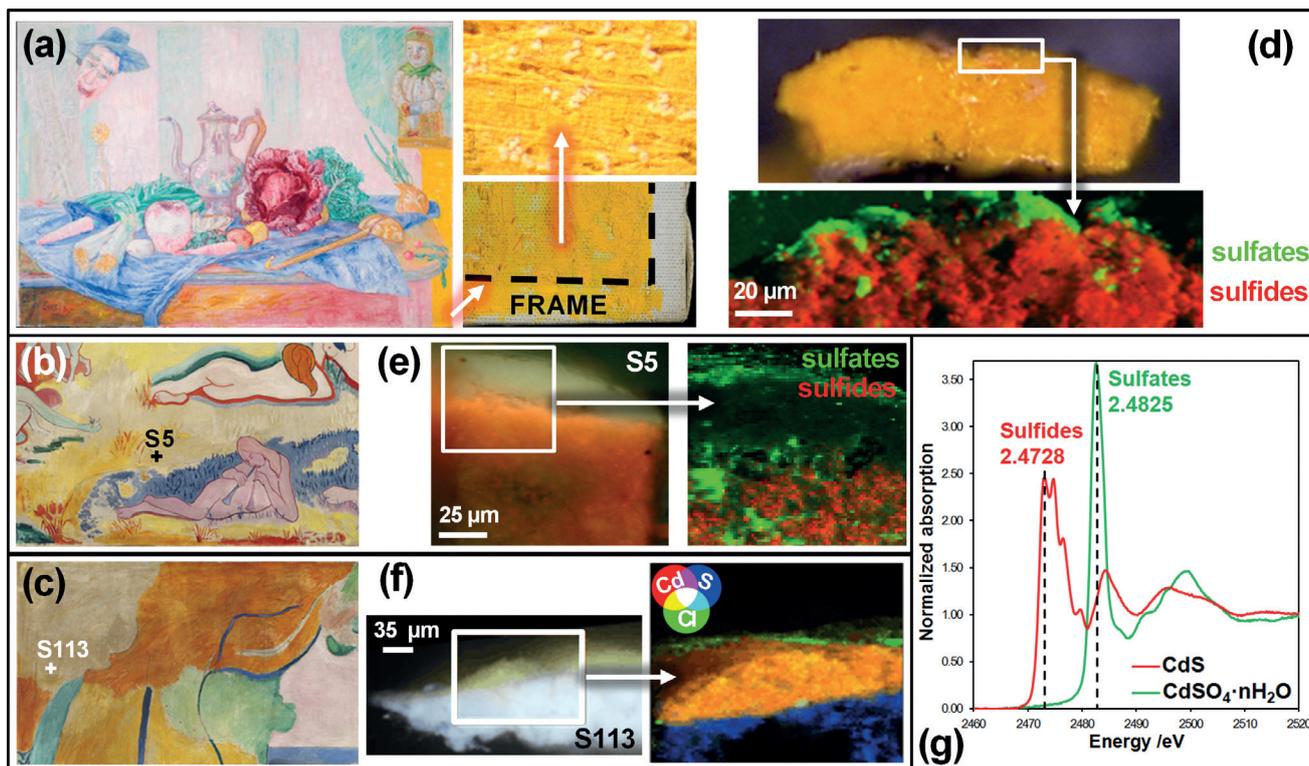


Figure 2. Photographs of discolored CdY paints of: a) *Still Life with Cabbage* (James Ensor, ca. 1921; Kröller-Müller Museum, Otterlo, NL) and (b,c) *Joy of Life* (Henri Matisse, 1905–1906; The Barnes Foundation, Philadelphia, USA). d–f) Photomicrographs of cross-sections taken from (a–c) and corresponding RGB SR μ -XRF sulfides/sulfates and Cd/Cl/S maps. g) S-K edge XANES spectra of CdS (red) and $\text{CdSO}_4 \cdot n\text{H}_2\text{O}$ (green). Adapted from Refs. [17, 18].

2.2. Charge-Transfer Pigments

The colour of many artists' pigments arises from charge transfer (CT) optical transitions of metal–ligand complexes, which, differently from d–d transitions, are not spin-forbidden and are thus very intense. Depending on the direction of CT, they are classified as either ligand-to-metal (LMCT) or metal-to-ligand (MLCT) charge transfer; the metal center can be photoreduced by the first and photo-oxidized by the second charge-transfer process.

Frequently used among impressionist and postimpressionist masters,^[15b] chromate-based yellows are characterized by an intense absorption band, due to a LMCT from the oxygen nonbonding to unoccupied Cr antibonding d orbitals.

The origin of the darkening of zinc yellow ($\text{K}_2\text{O} \cdot 4\text{ZnCrO}_4 \cdot 3\text{H}_2\text{O}$) observed in *A Sunday at La Grande Jatte* by Seurat was studied by investigating both microsamples obtained from the painting and artificially aged mock-ups using Cr-speciation methods.^[28, 29] Here light and sulfur gaseous pollutants promote the formation of Cr^{III} and dichromate compounds as secondary products.

An extended multi-technique study on microsamples from Van Gogh's paintings^[30–33] as well as historical and in-house synthesized powders^[34–38] allowed the stability of various chrome yellows (CYs) to be assessed (Figure 3). It has been proved that the darkening is due to a $\text{Cr}^{\text{VI}} \rightarrow \text{Cr}^{\text{III}}$ photoreduction with long-lived Cr^{V} -species that are thermally formed through the interaction with the oil binder.^[36, 37] Cr^{III} -

alteration products were usually found as a 3–5 μm thick layer (Figure 3 b,c) and/or micrometric particles at the surface.^[30–38] A series of aging experiments on oil mock-ups allowed the following information to be gained: 1) monoclinic and/or orthorhombic $\text{PbCr}_{1-x}\text{S}_x\text{O}_4$ ($0 < x \leq 0.8$) more readily undergo darkening than monoclinic S-free PbCrO_4 ;^[35] 2) the degradation path depends on the environmental conditions: the formation of Cr^{V} -compounds is favoured under exposure to moisture, while that of Cr^{III} -species upon light irradiation;^[37] 3) different lighting sources have different effects on the CY stability (Figure 3 c).^[36]

In recent investigations of *Sunflowers* (Figure 3 a),^[33, 39] the sensitivity of reflection FTIR spectroscopy to detect at the painting surface not only different CY types but also Cr^{III} oxides (Figure 3 b, left) was exploited, opening up the possibility of using this technique, along with Raman and MA-XRPD mapping, as a non-invasive tool for monitoring the CY stability at the macroscale length.

Pigment reconstructions following 19th century methods of synthesis used by Winsor & Newton colourmen were also spectroscopically characterized and photochemically aged allowing a better understanding of its manufacturing processes and how they impact on CY stability.^[40]

More recently the relationship of structure and electronic properties of different CY varieties have been examined by computational methods for better understanding their behaviour.^[41–43] DFT methods have been employed to describe the electronic structure of PbCrO_4 and $\text{PbCr}_{1-x}\text{S}_x\text{O}_4$ (Fig-

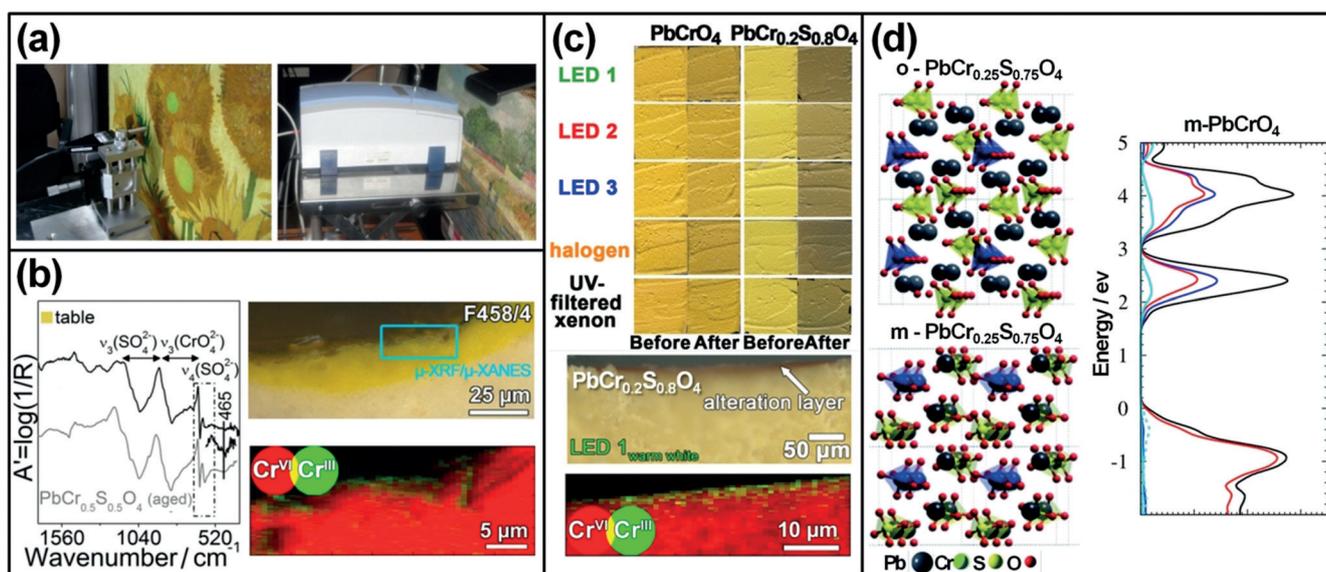


Figure 3. a) Portable devices in front of *Sunflowers* and *Bank of the Seine* by Van Gogh (Van Gogh Museum, Amsterdam, NL). b) (left) Reflection FTIR spectrum (black) with reference (gray) obtained from the table area of *Sunflowers* and (right) photomicrograph of a cross-sections obtained from the same region where SR μ -XRF/ μ -XANES analysis were performed. c) (from top) CY mock-ups before and after exposure to various white lamps, microphotograph of a LED-exposed CY thin section and corresponding RG Cr^{VI}/Cr^{III} maps. d) (left) Optimized structures of orthorhombic (o) and monoclinic (m) $\text{PbCr}_{0.25}\text{S}_{0.75}\text{O}_4$ and electronic structure for *m*- PbCrO_4 . Adapted from Refs. [33, 36, 42].

ure 3d, left). All theoretical investigations have shown that the valence band (VB) of PbCrO_4 is mainly constituted of O 2p states, while its conduction band (CB) is mainly due to Cr 3d states (Figure 3d, right). The optical, electronic and structural modifications occurring within $\text{PbCr}_{1-x}\text{S}_x\text{O}_4$ solid solutions have revealed a general trend of increasing band gap upon increasing the SO_4^{2-} content. Since the increase in band gap is generally attributed to a lower photoreactivity, additional explanations for the SO_4^{2-} -induced pigment degradation have been put forward. Munoz-Garcia et al.^[41] described that PbCrO_4 and PbSO_4 tend to segregate into separate phases, with the PbCrO_4 -rich phase mainly undergoing degradation. Amat et al.^[42] proposed degradation due to the release of CrO_4^{2-} anions into the paint matrix, thus pointing at an extrinsic degradation pathway. Rahemi et al.^[43] instead reported that Cr reduction increased in SO_4^{2-} -rich phases, in relation to the calculated photoabsorption current. Although these three theoretical studies reached different conclusions, in this context modelling was shown to provide valuable insights into the pigment properties, which may represent the basis for future targeted experimental investigations.

The intense blue colour of Prussian blue (PB; $\text{KFe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6] \cdot x\text{H}_2\text{O}$ and $\text{Fe}^{\text{III}}_4[\text{Fe}^{\text{II}}(\text{CN})_6]_3 \cdot x\text{H}_2\text{O}$) arises from a metal-to-metal charge transfer (MMCT) between Fe^{II} and Fe^{III} mediated by the CN moiety.^[44] The fading of PB endangers various heritage artefacts, including textiles, prints, blueprints, watercolours, and oil paintings (Figure 4a).^[45, 46] The extension of the phenomenon is variable and depends on the presence of white extenders,^[47, 48] the type of environment and substrate,^[49] as well as the PB manufacture procedures.^[44, 50] The presence of Fe^{III} oxyhydroxide as by-product of eighteenth century PB-synthesized powders (Figure 4c,d) may contribute to enhance the tendency of the paint layer towards discoloration (Figure 4b).^[50] Studies on photochemically aged

mock-ups by different spectroscopic techniques have proved that the PB fading is due to a $\text{Fe}^{\text{III}} \rightarrow \text{Fe}^{\text{II}}$ photoreduction,^[48–50] most likely activated through the LMCT $\text{Fe}^{\text{III}}\text{--CN}$ transition.

3. Photophysics of Organic Dyes: A Key for Understanding Their Colour Change in Artworks

Indigo blues and anthraquinone reds are among the most important natural dyes used in various works of art, such as textiles, woods, or paints.^[51] As other natural dyes, they are generally considered prone to photodegradation, and yet in many cases they display an almost pristine aspect. For instance, anthraquinone reds may undergo fading in paintings,^[3] while they may be incredibly resilient as showcased in millenary Andean textiles or medieval illuminated manuscripts.^[52] In order to be lightfast, a molecule must absorb damaging radiation and safely dissipate it before irreversible chemical reactions can take place. The excess of absorbed energy may be dissipated through radiative or non-radiative decay pathways. These safe processes for returning to the ground state compete with unsafe electron-transfer reactions that usually are responsible of irreversible photochemistry.

3.1. Indigo

Indigo's intense blue colour is an intriguing feature for a relatively small molecule.^[53, 54] Resonance cannot explain it,^[55] thus the chromophore is best described as a donor–acceptor dye, where the amino groups act as the electron donors, while the carbonyl groups as the electron acceptors. DFT calculations supported this description, showing that the HOMO is essentially located in the central C=C bond and the

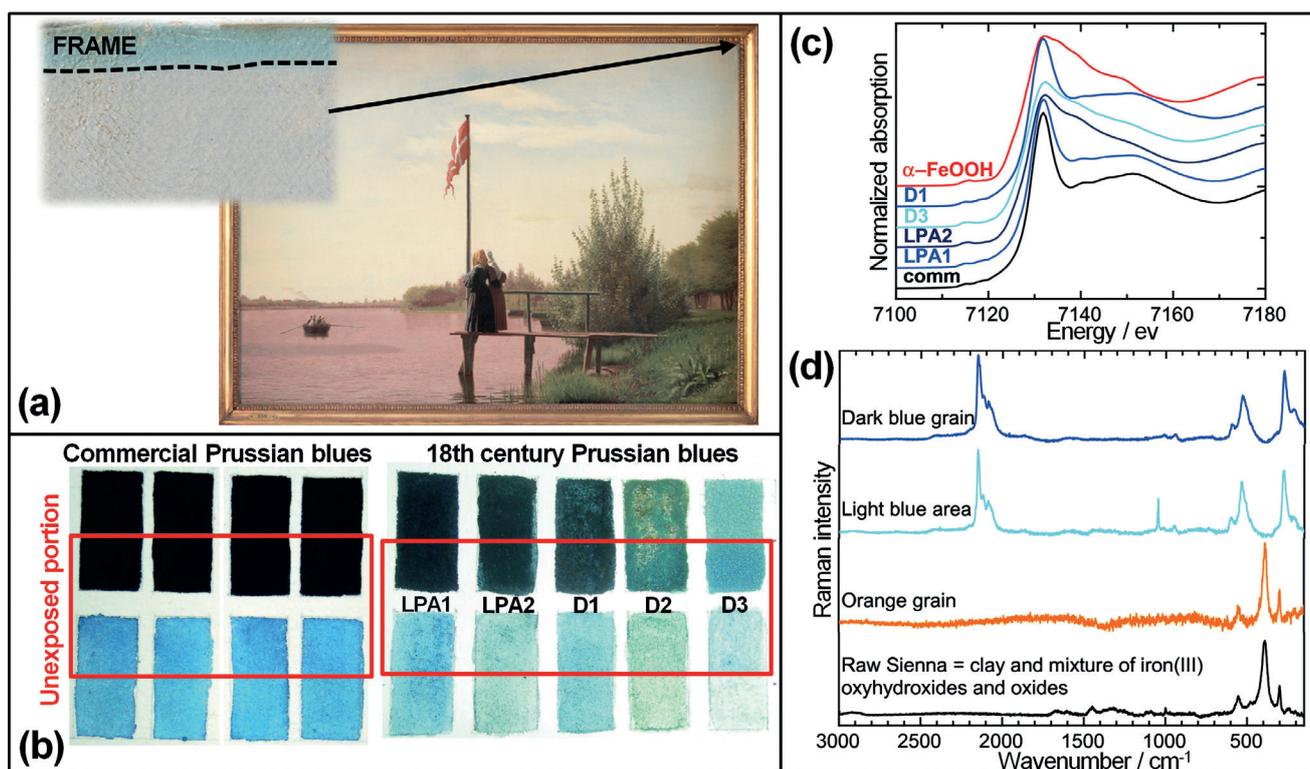


Figure 4. a) Photograph and detail of a faded PB area of *View of Lake Sortedam from Dosseringen Looking Towards the Suburb Nørrebro outside Copenhagen* (Christen Købke, 1838; Statens Museum for Kunst, Copenhagen, DK). b) Photochemically aged PB watercolor mock-up paints and c) corresponding Fe K-edge XANES spectra compared to that of α -FeOOH. d) Raman spectra recorded from a cross-section of the *Guardian angel* (polychrome linden wood sculpture, Assumption church, La Gleize, BE) and a raw Sienna reference. Adapted from Refs. [45, 50].

nitrogen atoms, whereas the LUMO is located in the central C=C bond and the oxygen atoms.^[56] In a simplified approximation, the absorption of visible light may be explained by a narrow HOMO–LUMO separation;^[56] the donor groups raise the π orbital (HOMO) of the C=C double bond, while the acceptor groups lower the π^* orbital (LUMO). This favours an efficient coupling between the S_0 and S_1 vibrational modes, offering efficient radiationless conversion of the absorbed energy. In the excited state, the excess of energy of indigo may also be dissipated through excited-state proton transfer (ESPT, Figure 5a).^[53,57,58,59] These two very efficient deactivation channels allow for 99.99% of the quanta to be lost, protecting indigo from chemical modification.^[53,58,59]

Acquiring knowledge about indigo's photophysics is relevant for understanding its light-induced degradation. Experiments have shown that the central double bond is at the same time a photoprotector and a weak point.^[52a] Based on the behaviour of indigo in *N,N*-dimethylformamide (DMF) solutions and solid matrixes, it was proposed that the major colourless degradation product, isatin (Figure 5b), is produced from a reaction between indigo and a radical, resulting from an attack to the central double bond. The double bond and, in turn, indigo may be very stable under certain conditions, displaying photodegradation quantum yields with values either below 10^{-6} (reflecting stable environments) or ranging from 10^{-4} to 10^{-3} (that are representative of media where oxygen-based radicals or reducing species are present). Stable environments are represented by the blues

from Andean textiles, dated from BC 200 to 200 AD (Figure 5b). These objects were kept for millennia in a very dry environment in Paracas (a region in South Peru).^[52a] In the blue indigo-coloured fibres, isatin was found as main photodegradation product, but in low-moderate relative amounts ($\leq 10\%$ – 20%). The mechanism of disruption of the central double bond connecting the two indole moieties is based on a two-step reduction and the reduction potential is pH-dependent.^[52a,60,61] First, a radical is formed in one of the carbon atoms of the central double bond, that, in turn, reacts very promptly with other radicals present in solution. The destruction of the double bond creates a species that is like the *leuco* form (Figure 5c). The comparison between the photophysical properties of the *leuco* and *keto* forms revealed that the radiationless rate constants of all the studied *keto* forms are lower by about one order of magnitude than those found for the *leuco* forms.^[53] Consequently, fluorescence and triplet-state formation are, in the case of the *leuco* forms, alternatives to the internal conversion deactivation channels for the singlet excited state. In fact, it seems reasonable to associate the larger fluorescence quantum yield (ϕ_F) values in the *leuco* forms with some degree of rotation around the central C=C bond. The remarkable stability of indigo is, in part, the result of intramolecular hydrogen bonding between the two-adjacent carbonyl and N–H groups, which keeps the molecule in a *trans* planar configuration, preventing the photochemical *cis*–*trans* isomerization, that in turn will lead to irreversible photochemical fading. The differences observed

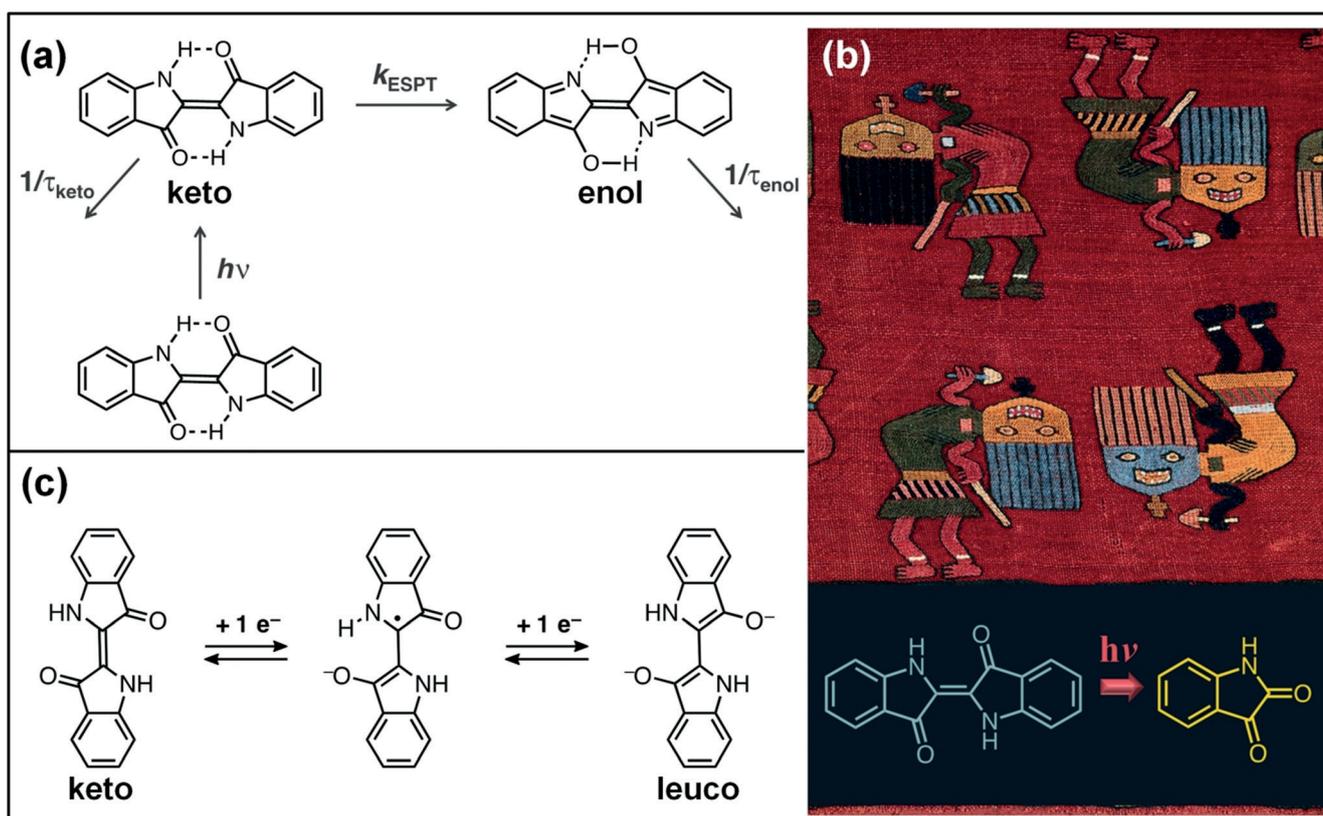


Figure 5. a) The high stability of indigo has its mechanism associated with a fast ESPT: the keto excited species is converted into its enol isomer. b) (top) Photographic detail of an Andean textile (Man's poncho mfa31.496, 100B.C.-0; Museum of Fine Arts, Boston, USA) and (bottom) photoconversion reaction of indigo (blue, keto form) to isatin (yellow, leuco species). c) Scheme for the reduction of indigo in non-acidic media. Adapted from Ref. [60].

between the two forms suggest that the well-known photostability of the *keto* forms of indigo is not present with the reduced species, *leuco*.^[53] These same redox properties of indigo have been used in the past to dye textiles, by converting the insoluble *keto* species into the water-soluble *leuco* species. Indigo photophysics is shared with two other important historic dyes, Maya blue and Tyrian purple, being central for the understanding of their reactivity.

3.2. Anthraquinone Reds

The most common reds used in antiquity to dye textiles are based on hydroxy anthraquinone chromophores (Figure 6).^[51,62] They were extracted from the roots of a variety of plant from the *Rubiaceae* family, being alizarin and purpurin the major occurring species in *Rubia tinctoria* L.^[51] The red extracts were also prepared for use as a pigment for painting, by precipitation with aluminium salts (known as madder lake pigments). The structure of these metal–dye complexes is still a matter of controversy. Systematic phenomenological studies on the fading of various anthraquinone-lake paints, including cochineal lake pigments, indicated differences in colour fading.^[62,63] Considering the lack of knowledge about accurate structures of lake pigments, we will focus on the photophysics

of alizarin and purpurin and how it relates to their photostability.

During the last decades of the 20th century there has been a comprehensive body of published articles on the physico-chemical and chemical properties of hydroxy, amino and acylamino derivatives.^[64–66] The acidochromic effects in the excited state properties of purpurin and alizarin have been more recently studied.^[67,68] From these studies it has been concluded that the substitution pattern of hydroxy anthraquinones is determinant for their excited state properties, where efficient radiationless processes play a determinant role in the overall stability of the molecules. The excited-state surface can be sensitively controlled by substituents, permitting the formation of a 1,10-keto tautomer, the ratio of which (compared to the excited 9,10) can be varied at least by two orders of magnitude (Figure 6a).

Advances in the fundamental photophysical processes enabled to gain further insights into the stability of this dye by single-molecule spectroscopy.^[69] Authors proposed that the existence of a dark radical cation state formed by electron transfer (ET) would promote irreversible chemical transformation of the molecule when returning to the ground state, resulting in the colour fading. In the excited state there will be a kinetic competition between an unsafe ET deactivation pathway and a safe ESPT process that will decay with

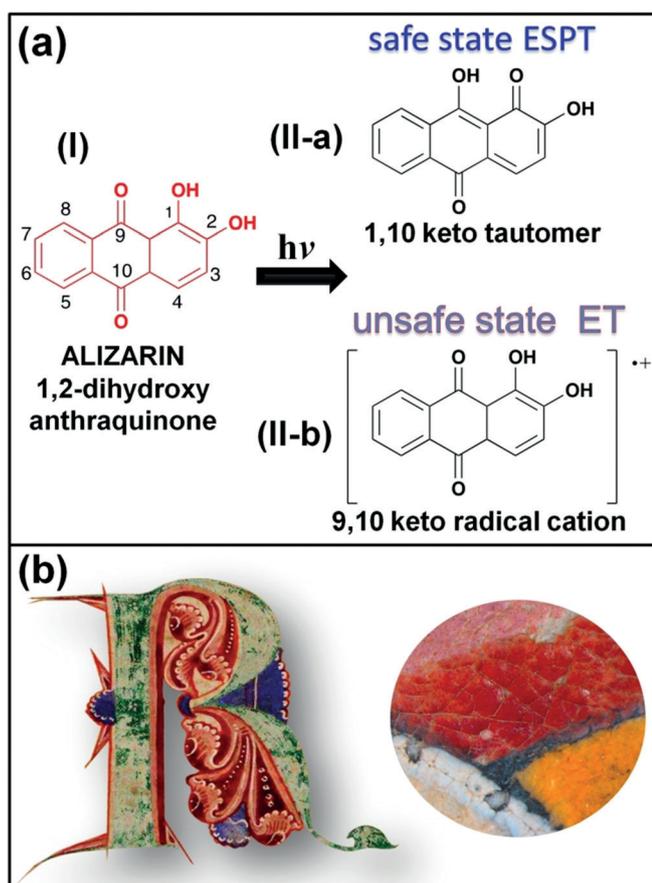


Figure 6. a) Photoconversion pathways of (I) alizarin either into (II-a) 1,10-keto tautomer form or (II-b) a semioxidized 9,10-keto radical cation. The first species is formed through ESPT and will allow a safe return into the ground state. The latter is the result of an ET and will react, converting into degradation products. b) 12th century illuminated initial, where the anthraquinone-based red (lac dye) has preserved its original colour, whereas the Cu-based green is almost completely lost.

recovery of the initial ground-state molecule (Figure 6a). Since the relative stabilities of alizarin and purpurin are best understood in the context of this kinetic competition in the excited state, we anticipate that the relative photostability of alizarin and purpurin–Al^{III} complexes will be maintained.^[70]

4. Summary and Outlook

The understanding and prevention of light-induced colour change in artworks are depending on the chemical comprehension of the excited-state behaviour of pigments and dyes in relation with the matrix and the environmental surrounding.

We have described how a phenomenological approach based on the identification of secondary products on a series of paintings has been pivotal in enabling us to understand the colour change of some pigments. The approach relies on the exploitation of advanced analytical methods which need to range from the nano- to the macro-scale yet ensuring high chemical speciation.

The use of computational modelling as interpretative tool of data from case studies and accelerated aging experiments has proved successful. The access to excited state properties through the time-dependent extension of DFT further opens up the possibility of simulating the evolution of the artists' materials after light absorption while interacting with chemicals possibly related to the degradation process. This is still a challenge, though potentially similar to related modelling studies in photocatalysis.

As for organic dyes, a more conceptual approach has been discussed which relies on fundamental knowledge on ultrafast reactions in the excited state of parent molecules. The comprehension of how the kinetic competition between safe proton transfer and disruptive electron transfer is affected by the substitution pattern of hydroxy anthraquinones as well as by chemistry of the support and the environmental surrounding may give an explanation of different lightfastness properties of anthraquinone reds in artworks.

As a necessary trend in chemistry for heritage science, we can envision physicochemical research addressing the structural, electronic and reactive properties of cultural heritage materials nourished by phenomenological studies unravelling the rich information enclosed in a work of art.

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Conflict of interest

The authors declare no conflict of interest.

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