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ARTICLE TYPE

# Imaging, photophysical properties and DFT calculations of manganese blue (barium manganate(VI) sulphate) – a modern pigment

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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. The photophysical properties of the compound are described as well as the setup needed to record the spatial distribution of the pigment on works of art.

Manganese blue is a modern, synthetic greenish-blue pigment. It is a barium manganate(VI) sulphate compound that, according to Eastaugh *et al.* 2008,<sup>1</sup> has the formula  $x\text{BaSO}_4 \cdot y\text{BaMnO}_4$  (Colour Index, 1971, CI 77112/Pigment Blue 33)<sup>2</sup> and is made by calcining sodium sulphate, potassium permanganate and barium nitrate at about 750–800°C; other recipes for its production are reported by the same authors. While it is first mentioned in the patent literature in 1935 by I.G. Farbenindustrie AG,<sup>1,3,4</sup> Salter mentions in 1869 that ‘an aqueous solution of permanganate of potash yields with baryta-water a violet structure, which afterwards becomes colourless, and deposits a blue precipitate’.<sup>5</sup> He also adds that the precipitate ‘retains its colour after washing and drying, but cannot be recommended as a pigment’.<sup>5</sup> While the compound created by Salter might not correspond exactly to the manganese blue produced since the mid-1930s, his recommendation was not followed and manganese blue was in production and sold as a pigment until the 1990s, when production was interrupted following concerns over its toxicity.<sup>1</sup> At present, copper phthalocyanine blue (PB 15, 74160) is used in preference to manganese blue when a greenish blue is required. According to Eastaugh *et al.* 2008, 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 1990s. 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.<sup>6-9</sup> In the 1980s, manganese blue was recommended to conservators as an excellent non-metameric match for azurite,<sup>10</sup> and the pigment is still used for retouching paintings at, among other places, the National Gallery, London and the Courtauld Institute of Art,<sup>6</sup> despite dwindling supplies, as the pigment is no longer being produced.

This paper discusses the photo-induced luminescence properties of manganese blue in detail and suggests a means by which the pigment can be imaged to record its spatial distribution.

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. 1, while the lifetime decay is showed in the inset.

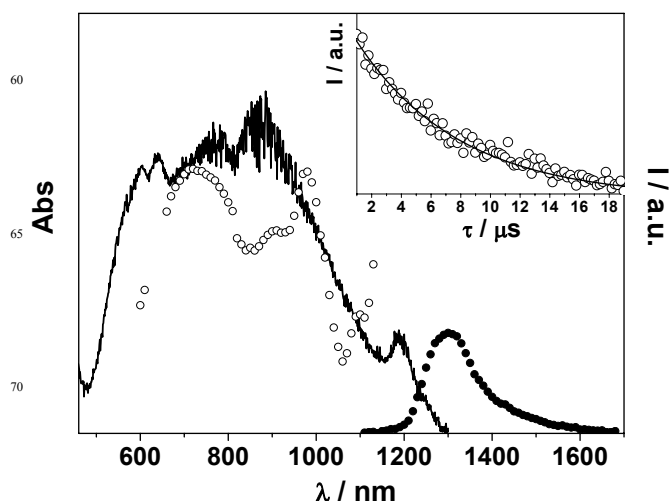


Fig. 1: Absorbance (total reflection, full line), excitation (empty circle,  $\lambda_{em} = 1300$  nm) and emission (full circle,  $\lambda_{exc} = 637$  nm) spectra of powdered synthetic manganese-blue. Inset: luminescence decay (7.1  $\mu\text{s}$ ,  $\lambda_{exc} = 637$  nm).

The compound absorbs radiation in the visible and near-infrared regions between *c.* 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,<sup>11</sup> it mainly consists of a near-IR band system, between 800 and nearly 900 nm, that can be attributed to  ${}^2E \rightarrow {}^2T_2$  ligand-field (LF) transitions, and ligand-to-metal charge-transfer bands between 600 and 800 nm, as also predicted by DFT calculations performed in the present work (see

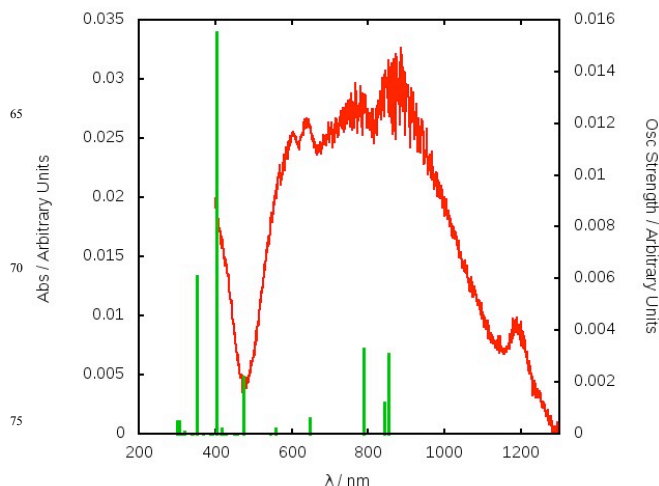
below).

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. The photoluminescent quantum yield (PLQY) of the luminescence centred at *c.*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  $\mu$ s have been found. In the attempt to resolve the  $\text{MnO}_4^{2-}$  optical structure, quantum mechanical DFT calculations were conducted on the  $3d^1$  electron configuration of the manganate(IV) anion in order to assist the interpretation of the absorption spectrum. Brunold's previous studies on  $\text{MnO}_4^{2-}$  ion doped in the  $\text{BaSO}_4$  host lattice<sup>11</sup> indicate a geometry distortion of the crystal sites from a Cs to a quasi- $C_{2v}$  symmetry, and provide a crystal-field analysis in terms of the angular overlap model (AOM) for the  $\text{MnO}_4^{2-}$  anion.

Time-dependent density functional calculations were run with the 'Gaussian09' suite of programs,<sup>12</sup> on the anion geometry in its  $C_{2v}$  symmetry in order to analyse the optical spectra of  $\text{MnO}_4^{2-}$ -doped  $\text{BaSO}_4$  in the approximate  $C_{2v}$  group. Ground and electronic state calculations were performed with different sets of DFT-functions and ECP-pseudopotentials on manganese(VI) electrons (see Table S2)†, with the aim of reproducing the experimental absorption bands accurately. The UB3LYP level of theory<sup>13</sup> with a set of 6-31+G\* basis functions on the oxygen atoms, combined with a modified LAN2LZ pseudopotentials version (optimized for the first row transition metals)<sup>14</sup> for the manganese(VI), provided the best computational performance. Table S1† lists the TD-UB3LYP theoretical transition energies for the  $C_{2v}$  anion geometry, the experimental absorption bands obtained in the present study and Brunold's previous literature data, which extended the spectral region below 500 nm. To assist interpretation, Figure 2 shows a comparison between the experimental and the theoretical stick spectrum. Our calculations, in agreement with Ligand Field Theory predictions, allow to properly assign near-IR band system (extended from 800 to 900 nm, according to Brunold *et al.*<sup>11</sup>) to be assigned properly to  $^2E \rightarrow ^2T$  LF transitions, split in three nearly-overlapping d-d bands as a consequence of Jahn-Teller  $T_d \rightarrow C_{2v}$  distortion. The molecular orbital analysis of the DFT electronic wavefunction also reveals the  $C_{2v}$  transformation properties of the d orbitals involved in the three LT transitions (in brackets in Table S1),† with the symmetry state ordering switched, due to their close DFT energies. As also indicated in the literature, the MO analysis confirms the charge transfer nature of involved orbitals in the region below 600 nm, thus assigned to LMCT transitions.

The experimental absorption spectrum in Fig. 2 shows additional bands in the region between 620 and 820 nm compared to previously reported spectra for  $\text{MnO}_4^{2-}$ . DFT calculations also predict two different sets of peaks in this region, at 787 and 646 nm, respectively, whose nature can be regarded as lower energy LMCT states, or as a redistribution of the electron density between oxygen and the Mn(VI) ion, due to the modest ionic character of the Mn-O bond. The photo-induced luminescence properties of manganese blue can be used to image the spatial distribution of the pigment non-invasively.<sup>15</sup> Photo-induced luminescence imaging has already been used extensively to

identify and map the distribution of other inorganic pigments, such as Egyptian blue, Han blue and Han purple,<sup>16, 17</sup> and cadmium-based reds and yellows.<sup>18, 19</sup>

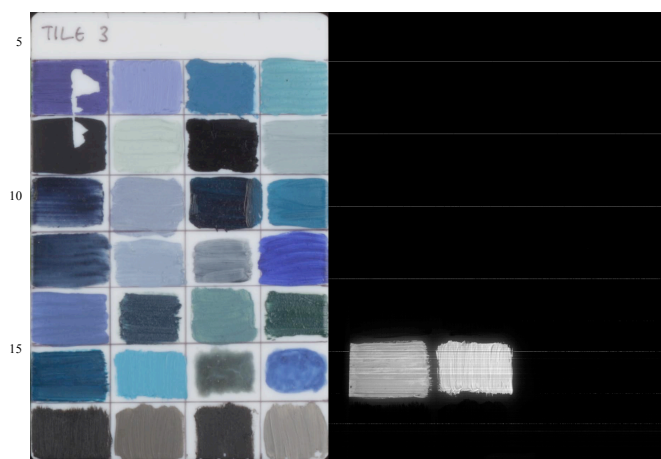


**Fig. 2:** The experimental Mn-doped  $\text{BaSO}_4$  absorption spectrum (red line) and the stick theoretical TD-UB3LYP/631+G\* spectrum (green line); on the right y-axis, theoretical oscillator strengths are reported.

Figure 3 shows the visible (left) and visible-induced luminescence (right) images of a tile painted with a variety of blue pigments, including manganese blue§. To the right of the panel in the visible-induced luminescence images is a 99% Spectralon reflectance standard, which shows no luminescence and is thus used as a reference standard. Any grey values greater than those for the reference standard can be attributed to luminescence. In the visible-induced luminescence image, manganese blue appears as 'glowing white' against a dark background. The visible-induced image was made using a combination of blue, green and red LEDs<sup>17</sup> sources for excitation and an InGaAs camera (Osiris, Opus Instruments, sensitivity *c.*700–1700 nm), equipped with a Schott RG850 cut-on emission filter (50% transmission at 850 nm). The white/grey horizontal lines on the visible-induced luminescence image are due to noise caused by the long integration time. The two swatches painted with indigo show a very weak luminescence, already reported by Ajo *et al.*<sup>20</sup>, but rarely observed in real cases. This luminescence is only visible if the contrast is strongly enhanced and cannot be observed in Fig. 3.

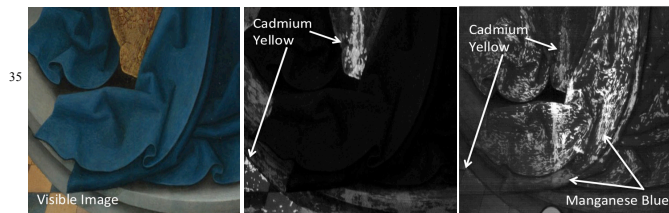
The same equipment was used to image a painting depicting *The Coronation of the Virgin*, by the Master of Cappenberg in the collection of the National Gallery London (NG 263).<sup>21</sup> This panel, which is dated to around 1520, is one of a number of surviving fragments from the Liesborn alterpiece. Manganese blue and cadmium yellow were used during the restoration of the painting in 1984 to retouch the historic losses of paint, particularly those along the vertical join between two of the constituent wooden boards that made up the panel. Manganese blue was used to retouch the blue (azurite) mantle of the Virgin and the grey plinth on which she is kneeling, while cadmium yellow was used on the golden brocade of her garment. Cadmium yellow, as mentioned above, shows a strong luminescence emission in the 800-1000 nm range when excited in the visible range.<sup>19</sup> Figure 4 shows the visible (left), visible-induced luminescence in the 800-1000 nm range (middle) and visible-

induced luminescence in the 700–1700 nm range (right) images of a detail from *The Coronation of the Virgin* (excitation wavelength at 450–650 nm).<sup>17</sup>



**Fig. 3** Visible (left) and visible-induced (right) luminescence image in the 700–1700 nm range for a variety of blue pigments, including manganese blue, which is the only blue pigment that emits infrared radiation with a peak at about 1300 nm when irradiated with visible light.

Fig. 4 (middle) shows the luminescence of cadmium yellow on the brocade, while Fig. 4 (right) shows the luminescence of both the cadmium yellow on the brocade and the manganese blue in the blue mantle. The grey appearance of the white Spectralon reference standard below the painting indicates that there is some stray infrared radiation in the latter image. This technique is rather sensitive and even small amounts of the blue pigment show clearly.



**Fig. 4** Visible (left), visible-induced luminescence in the 800–1000 nm range (middle) and visible-induced luminescence in the 700–1700 nm range (right) images of a detail from *The Coronation of the Virgin* by the Master of Cappenberg (NG 263). A larger image is reported in Fig. 1-ESI

In conclusion, in this work we report a comprehensive optical investigation of the inorganic compound manganese blue, which was produced and employed as a blue pigment in works of art from 1935 to the 1990s. The photophysical properties show a broad light absorption (*c.* 500–1200 nm) and a NIR photoluminescence (1300 nm,  $\Phi_{PL} = 0.5\%$ ) originating from  $^2E \rightarrow ^2T_2$  ligand-field (LF) transitions, according to the theoretical calculations. This non-invasive and portable imaging technique could be used within a museum context to identify the spatial distribution of the pigment both when used as a primary colorant or as a retouching pigment by conservators. Because of the well-documented history of the production of the pigment, its identification as an original or added material on a work of art

would provide a *terminus post quem* to assist in dating an object or an intervention on an object, and to assess condition.

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## Notes and references

§ The pigment studied in this work and reported in Fig. 1 was purchased from Kremer Pigmente GmbH & Co. KG (Article No. 45300) by the National Gallery in London in the late 1990s. It was sold until 1999 and, at present, the company still retains small amounts of the pigment, which can only be purchased for conservation-related purposes.

‡ Reflectance spectra were collected using a JASCO V-670 spectrophotometer equipped with an integrating sphere setup. Emission and excitation spectra were recorded by a laboratory-constructed setup with a laser at 532 nm or a W lamp and a PbS photodiode (Hamamatsu P4638) as detector. Both excitation sources were frequency modulated using a chopper and signals were recorded by a lock-in amplifier (SR 830 Stanford Research System). To determine the luminescence quantum yield in the NIR spectral window, the method proposed by De Mello et al.<sup>22</sup> has been followed. The emission lifetime in the microsecond timescale was measured using a single photon counting system (Edinburgh FLS920 spectrometer, 1 MHz laser diode as excitation source, and B&H GmbH MSA-300 acquisition card coupled with the above-mentioned PMT as detector).

§ From top-left, row-wise: cobalt blue, cobalt blue and lead white, Prussian blue, cerulean blue, cerulean blue and lead white; Prussian blue, Prussian blue and lead white, indigo, indigo and lead white; smalt, smalt and lead white, Monastral blue, Monastral blue and white; high quality ultramarine, high quality ultramarine and lead white, mid-quality ultramarine, French ultramarine; French ultramarine and lead white, azurite, azurite and lead white, low quality azurite; manganese blue, manganese blue and lead white, high quality ultramarine in egg, ultramarine in acrylic; ivory black, ivory black and lead white, charcoal, charcoal and lead white. All the pigments were bound in drying linseed oil, unless otherwise stated.

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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

Table S1 shows a comparison between the TD-UB3LYP theoretical transition energies for the C<sub>2v</sub> anion geometry with i) the experimental absorption bands obtained in the present study and ii) the Brunold's previous literature data, which extended on spectrum region below 500 nm. Table S2 lists a comparison between absorption peaks obtained with different combinations of functionals and ECP-pseudopotentials on manganese(VI) atom, namely: UB3LYP/LAN2LZ, UB3LYP/STUTTART, UCAM-B3LYP/LAN2LZ, UCAMB3LYP/STUTTART, UPW3/LAN2LZ and UPW3/STUTTART.

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