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

Gianluca Accorsi, Giovanni Verri, Angela Acocella, Francesco Zerbetto, Giovanni Lerario, Giuseppe Gigli, David Saunders and Rachel Billinge

The chemical characterisation of the pigment in the safety data sheet dated 04/1999 and provided by Kremer Pigmente reports “mixed crystals of barium sulphate and barium manganate”. Furthermore, as reported by T.C. Brunold et al (1997, Ref.11 text), given the high temperatures occurring in the production process, a precise control of the ratio between the involved ions in the final product is not possible. Traces of compounds with different oxidation states of the Mn cation were found in the pigment (Brunold et al, Chem. Phys. Lett. 1996, 257, 123).

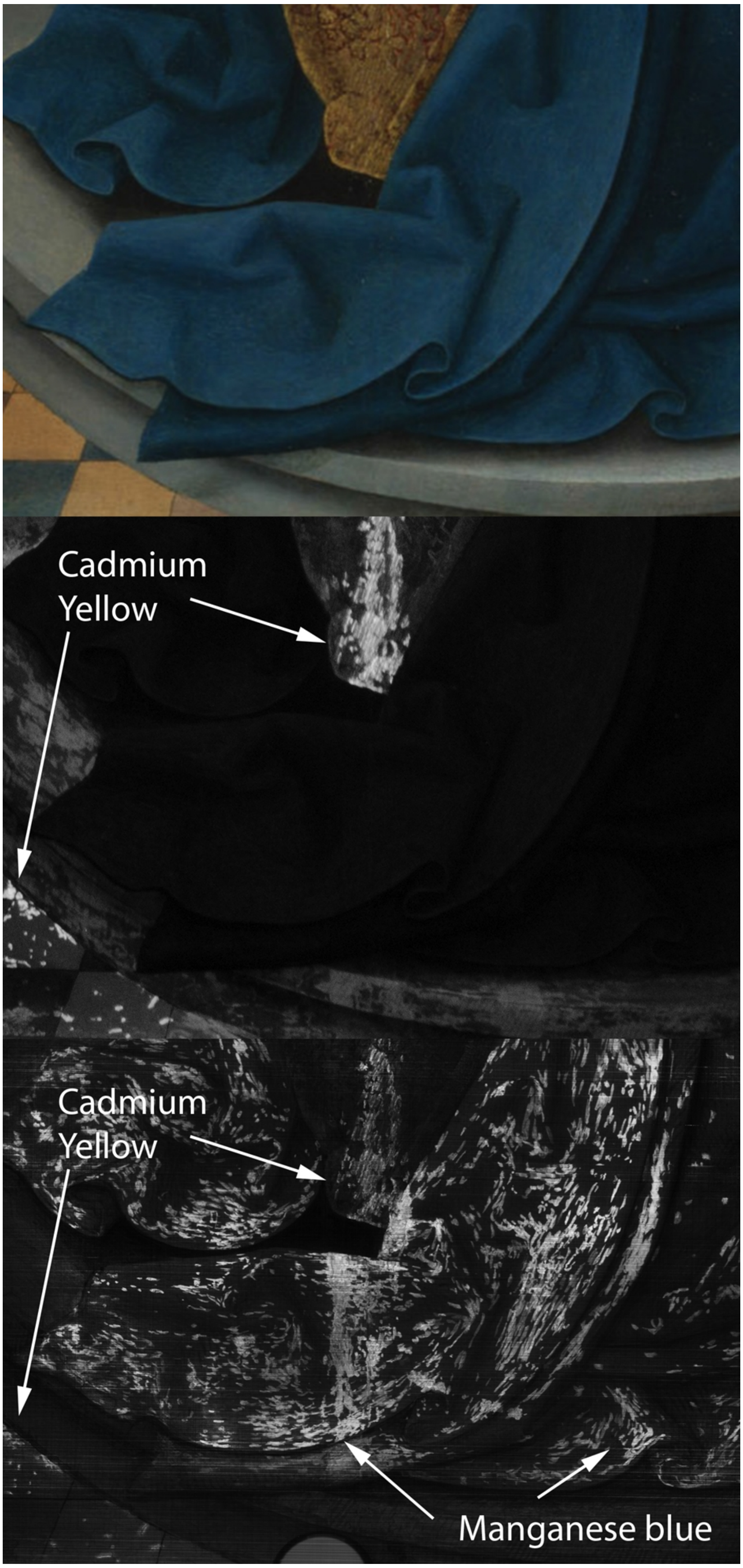

Fig.1-ESI Visible (top), visible-induced luminescence in the 800-1000 nm range (middle) and visible-induced luminescence in the 700-1700 nm range (down) images of a detail from *The Coronation of the Virgin* by the Master of Cappenberg (NG 263).

Table S1. TD-UB3LYP/6-31+G*/LAN2LZ symmetry, excited state energies (nm) and relative oscillator strengths of c2v-optimized $MnO4^{2-}$ anion structure, compared with experimental and literature band positions of Mn-doped BaSO4 absorption spectrum.

State Symm	**B3LYP/631+G* Energy [nm]**	**Osc Strength**	**Exp Bands [nm]**	**Lit Bands [nm]**
^{2}A1	851.95	0.0031	807-932, **846**	903 [^{2}B1 (yz)]
^{2}B2	842.61	0.0012		864 [^{2}A1 (x^2-y^2)]
^{2}B1	842.5	0.0012		848 [^{2}B2 (zx)]
^{2}A1	787.22	0.0033	607-817, **763**	
^{2}B2 ^{2}B1	646.58 646.56	0.0006 0.0006	614-667, **644**	
^{2}B2 ^{2}B1	473.97 473.92	0.0022 0.0022	470-620, **604**	543
^{2}A1	403.73	0.0155		404

^{2}B1	352.29	0.0061		357
^{2}B1	288.10	0.0020		288

Table S2. A comparison between absorption peaks obtained with different combinations of funcionals and ECP-pseudopotentials on manganese(VI) atom, namely: UB3LYP/LAN2LZ, UB3LYP/STUTTGART, UCAM-B3LYP/LAN2LZ, UCAMB3LYP/STUTTGART, UPW3/LAN2LZ and UPW3/STUTTGART. All units are in nm.

UB3LYP/631+G*		**UCAM/631+G***		**UPW3/631+G***	
/LAN2LZ	**/STU**	**/LAN2LZ**	**/STU**	**/LAN2LZ**	**/STU**
851.95	977.74	964.03	1345.20	870.73	906.82
842.61				870.66	
842.5				867.46	
787.22	681.09	687.10	663.24 663.11	798.79	665.24
646.58	654.26	632.09	505.48		641.74
646.56	654.26	632.07	505.34		641.65
	507.89	475.10			490.30
	507.72	475.06			490.26
473.97	430.88	437.42	431.41	472.32	
473.92				472.26	

403.73	379.92	402.39	383.59		416.90
	329.89		383.58		
352.29	357.00	360.10	360.43		364.60
			360.35		
	356.93				364.60
288.10	293.47		301.79		343.13

NOTE TO THEORETICAL CALCULATIONS

Time-dependent density functional theory methodology has proved to be a reliable method for calculating excitation energies for many organic and inorganic molecules, both for closed and open-shell systems. Cramer and Truhlar in 2009 deeply reviewed density functional theory, a large set of different functionals, and their accuracy for the study of transition metal chemistry [Phys. Chem. Chem. Phys., 2009, 11, 10757-10816]. They showed that the application of DFT to transition metal systems has become a well-established approach. In particular, as far as the linear-response TD-DFT method is concerned they proved that it provides a useful model for reproducing and understanding the optical spectra of transition-metal complexes. However, as was emphasized by Sousa et al. [J. Phys. Chem. A 2007, 111, 10439-10452], it is not easy to know *a priori* which functional can be applied to a given case. Furthermore, for transition metal complexes, it is also important the choice of the proper basis set for the description of the heavy atoms. Despite the introduction of even more sophisticated and performing functionals in recent years, none of them has been shown to systematically overshadow all the others. A benchmark over a set of different functionals is required to obtain the best performance in reproducing both the structural and electronic properties of the system under investigation, and to understand how much the correlation contribution is important in the computational description. For such reasons, we carried out calculations with different DFT functionals, in combination with both Stuttgart and LAN2DZ basis sets for Mn atom, also including a range separated functional (CAM-B3LYP), in order to include the non-local charge transfer character in the excited state energies and wavefunctions. The tests revealed that the TD-UB3LYP/6-31+G(d,p)/LAN2LZis level of theory provides the best description of the absorption properties for the manganate anion. Recent benchmark studies showed that B3LYP is the best performer in the prediction of transition metal chemistry properties [J. Comp. Chem. 2014, 35, 1; J. Chem. Phys., 2007, 126, 014103; J. Phys. Chem. A, 2009, 113, 5170; J. Phys. Chem. A, 2007, 111, 11908; J. Phys. Chem. A, 2008, 112, 12792.; J. Phys., 2008, 10, 063020]. In conclusion, of the plethora of different functionals, B3LYP is still one of the most popular and widely used DFT approach, and remains a very good compromise between accuracy and computational cost.