APPLICATION NOTE

Photo-Physical Properties of Ancient and Modern Artwork Pigments

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Introduction

The interest in non-invasive investigations for the study and identification of painting materials has greatly increased during the past two decades.[1] The nature of museum objects is such that sampling is always kept to a minimum, thus, a spectroscopic approach is ideal for this purpose. In this respect, an ancient and a modern pigment, cuprorivaite, $CaCuSi_4O_{10}$ (Egyptian blue) and barium manganate (VI) sulphate compound (manganese blue) respectively, have been photo-physically investigated.[2,3] The investigation includes qualitative information, *i.e.* emission and excitation spectra, as well as quantitative that is the photoluminescence quantum yields (PLQY) that have been obtained in the near-infrared (NIR) region.

Methods and Materials

Excitation and emission spectra were measured using an FLS980 Fluorescence Spectrometer equipped with a 450 W Xe lamp with double excitation and emission monochromators. Near-infrared detectors were used for the detection of both samples. PLQY have been calculated by corrected emission spectra obtained by using a barium sulphate coated integrating sphere, following the procedure described by De Mello et al.[4] Experimental uncertainties were estimated to be ±20% for emission quantum yields, ±2nm and ±5nm for absorption and emission peaks, respectively.

Results - Discussion

Figure 1 reports the excitation and luminescence spectra of the two samples.

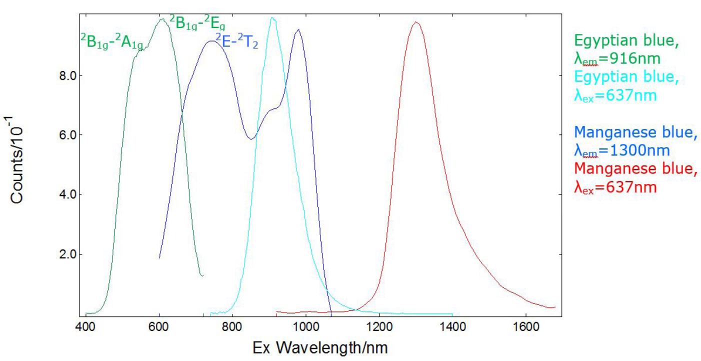

Figure 1: Excitation and emission spectra of ancient, Egyptian blue, and modern, manganese blue, pigments. The energy levels corresponding to each transition are also displayed.

Egyptian blue shows two different electronic transitions ($^2B_{1g}$-^2E_g and $^2B_{1g}$-$^2A_{1g}$) that can be assigned to Cu^{2+} ions, which are expected to be the only luminescent components of cuprorivaite.[1] On the other hand, those of Manganese Blue can be attributed to ligand-field (LF) transitions (^2E-$^2T_2$, c.a 800 nm - 900 nm) and to ligand-to-metal charge-transfer bands (between 600 nm and 800 nm) of the MnO_4^{2-} unit.[5]

The luminescence profiles have peaks at 920 nm and 1300 nm for Egyptian blue and manganese blue, respectively. Consequently, the corresponding PLQYs have been obtained. Manganese blue showed a quantum yield of Φ=0.5% attributed to luminescence quenching factors that occur at lower energy.[6] By contrast, Egyptian blue revealed to be a very strong NIR emitter (Φ=10.5%) that, to the best of our knowledge, has the highest quantum efficiency for a molecule-level chromophore in the 800 nm – 1100 nm range.[1]

Conclusions

The photo-physical properties of an ancient and a modern art pigment were investigated by means of fluorescence spectroscopy. In addition, the PLQY of the pigments has been measured, as a quantitative means of their photoluminescence properties and demonstrate the effectiveness of this method as a minimally invasive means of measuring samples of cultural significance.

References

[1] Accorsi, G.; Verri, G.; Bolognesi, M.; Armaroli, N.; Clementi, C.; Miliani, C.; Romani, A. The exceptional near-infrared luminescence properties of cuprorivaite (Egyptian blue). *Chem. Commun.* 2009, (**23**), 3392-3394.

[2] (a) Artist's Pigments – A Handbook of Their History and Characteristics. Elisabeth West Fitzhugh editor: 1997; Vol. 3; (b) Berke, H. The invention of blue and purple pigments in ancient times. *Chem. Soc. Rev.* 2007, ***36*** **(1)**, 15-30.

[3] Eastaugh, N.; Walsh, V.; Chaplin, T.; Siddall, R. *Barium Manganate (IV) Sulfate.* Butterworth-Heinemann: Oxford (UK), 2008.

[4] De Mello, J. C.; Wittmann, H. F.; Friend, R. H. An improved experimental determination of external photoluminescence quantum efficiency. *Adv. Mater.* 1997, ***9*** **(3)**, 230-236.

[5] Chen, Z. L.; Schmalle, H. W.; Fox, T.; Blacque, O.; Berke, H. NH-functionalized tungsten complexes of 2-(dimethylphosphino)imidazole. J. Organomet. Chem. 2007, ***692*** **(22)**, 4875-4885.

[6] Accorsi, G.; Verri, G.; Acocella, A.; Zerbetto, F.; Lerario, G.; Gigli, G.; Saunders, D.; Billinge, R. Imaging, photophysical properties and DFT calculations of manganese blue (barium manganate(VI) sulphate) - a modern pigment. *Chem. Commun.* 2014, ***50*** **(97)**, 15297-15300.

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