Time resolved spectroscopy of indigo and Maya Blue simulant

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Introduction

Indigo is a natural dye extracted from a plant belonging to the genus *Indigofera* widely known for its intense blue color still used in textile dyeing. Besides its use in textile, it is also found in the Maya blue (MB) pigment, an organic/inorganic hybrid prepared by mixing clay (typically palygorskite or sepiolite) with indigo. Despite the expressive number of publications on MB [1], some questions concerning the dye structure inside the clay are yet to be answered. Time resolved spectroscopic techniques (Transient Absorption – TA and Time Resolved Infrared – TRIR) are able to probe molecular excited states and other dynamic processes, using dephased pulsed radiation (lasers) to pump and probe these states. The aim of this work is, therefore, the study of the vibrational and electronic excited energy levels of indigo and the evaluation of the effect of confinement in the palygorskite structure using Time Resolved Spectroscopic techniques.

Results and Discussion

TA and TRIR spectroscopies of indigo and indigo with palygorskite (ind+paly – MB simulant) were obtained at Ohio State University and the experimental setup was described elsewhere.[2] Fig. 1 shows the TA spectra of indigo in DMSO and ind+paly in nujol in several delay times.

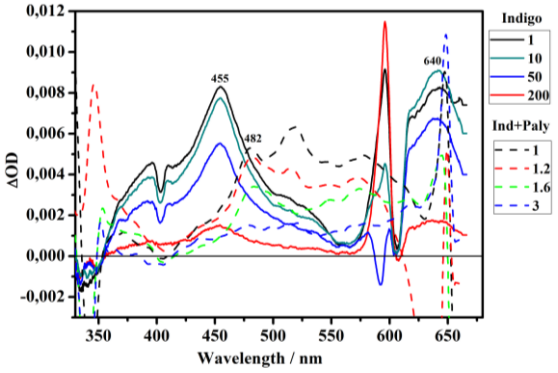

Figure 1. TA spectra of indigo in DMSO solution (line) and ind+paly (dash line) at different delay times.

It is possible to observe two absorbance maxima at 455 and 640 nm, related to different electronic excited states of indigo. Regarding the ind+paly spectra it can be observed the band at 482 nm related to the 455 nm in pure indigo. The kinetics of these bands (Fig. 2) reveal that the 455 nm and 482 nm kinetics have significantly different lifetimes (ca. 117 ps for indigo and 3 ps for ind+paly). The lifetime of indigo agrees with the reported for time resolved fluorescence. [3] The shorter lifetime of ind+paly can be associate with the stability of Maya Blue, since the indigo inside the clay has a very efficient excited state deactivation to the ground state. TRIR spectroscopy were also performed for indigo and ind+paly and the vibrational modes of the indigo excited state were observed at 1530 cm^{-1} of ν C=O and 1362 cm^{-1} of δ N-H, whereas for ind+paly the bands were at 1475 cm^{-1} (ν C=C) and 1387 cm^{-1} (δ N-H). The kinetics agree with the observed to TA experiments.

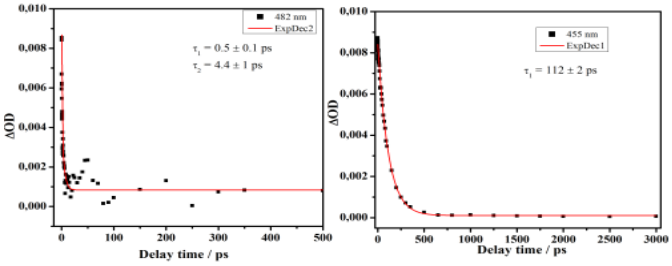

Figure 2. TA kinetics of (A) 455 nm band of indigo and (B) 482 nm band of ind+paly.

Conclusões

The results here reported for indigo in different environments (DMSO and clay) shows that the dye photochemistry is altered indicating a strong interaction with palygorskite. The red shift observed in the TA of ind+paly is in agreement with the observed behavior in the ground state (from 620 nm in DMSO to 670 nm in paly), what can be associated with the excited states stabilization.

Acknowledgment

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