



Trapping and diffusion of organic dyes inside of palygorskite clay: The ancient Maya Blue pigment



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ABSTRACT

The Maya Blue is an artificial colorant with a remarkable stability to chemical attacks and a characteristic pale blue color, with tonalities going from greenish to turquoise. A systematic study of the energetics, structural, bonding and electronic properties of the unusual stable pigment known as Maya Blue is presented. Total energy calculations based on density functional theory are used. Particular attention is paid to the high stability of the Maya blue pigment. We present a comparative study of the energetic barriers for indigo and dehydroindigo in the tunnels taking into account the presence of aluminum in the palygorskite. A clay-framework dependence for the indigo diffusion and a blocking due to dehydroindigo is shown by the binding energy as the molecules take several positions into the tunnels. In the hybrid dye-clay system, the high binding energy is due to the strong hydrogen bonds of carbonyl and amine functional groups of the dyes with the structural water molecules at the edge of the dioctahedral layer in the clay. The electronic and optical properties near the Fermi level in the nanostructured Maya blue are exclusively due to the slightly modified electronic states from the molecules with no contribution from the clay. Indigo and dehydroindigo show a red- and blue-shifted, respectively.

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1. Introduction

The Maya Blue (MB) pigment is a nanostructured hybrid material with remarkable stability and characteristic hue created by the pre-Colombian Maya civilization [1]. Although the exact preparation method of the MB is unknown, by modern analytical techniques is confirmed that MB consists of two main components: indigo (IND) obtained from the leaves of the *indigofera suffruticosa* plant and palygorskite (PAL) found in the Yucatán Peninsula and Campeche [2,3]. IND is a quasi-planar organic molecule of approximate dimensions $4.8 \times 12 \text{ \AA}$, Fig. 1. PAL is a kind of natural fibrous clay and its idealized structural formula is $(\text{Mg,Al})_4\text{Si}_8\text{O}_{20}(\text{OH})_2(\text{H}_2\text{O})_4 \cdot 4\text{H}_2\text{O}$ [4], where $(\text{H}_2\text{O})_4$ refer to tightly bound (structural) water molecules (labeled as OH_2 in specialized literature) completing the coordination of the (Mg,Al) atoms, while $4\text{H}_2\text{O}$ refer to weakly (zeolitic) water filling the pores. There are two polymorphs: monoclinic ($C2/m$) and orthorhombic ($Pbmn$)

[5]. This synthetic colorant is a polyfunctional mineral-organic complex with high resistance to chemical and thermal treatments. MB is not faded by boiling acid or alkaline agents at moderate times or biodegradation. The unprecedented stability of MB is due to its placement at hollow regions (tunnels) having a transversal area of $3.7 \times 6.4 \text{ \AA}$, which are able to allocate and protect the organic molecules like IND and dehydroindigo (DHI, see Fig. 1) an oxidized form of IND [6], or other molecules such as methyl red, methyl orange and acetone with similar size [7–9]. For several years, the chemical nature of MB has been the subject of great controversy. As a result, several extensive synthesis and mainly characterization studies have been developed to understand and explain the physico-chemical process involved the MB stabilization.

Several questions arise about the MB pigment, some of them have been tackled in papers already published. For example, Van Olphen [1] suggested that IND molecules are undoubtedly too big to enter in the PAL tunnels. As consequence, the turquoise-blue color in the MB should be IND molecules adsorbed only on the external channels of the clay surface. However, Kleber et al. [11] pointed out one year later that; the possible IND penetration

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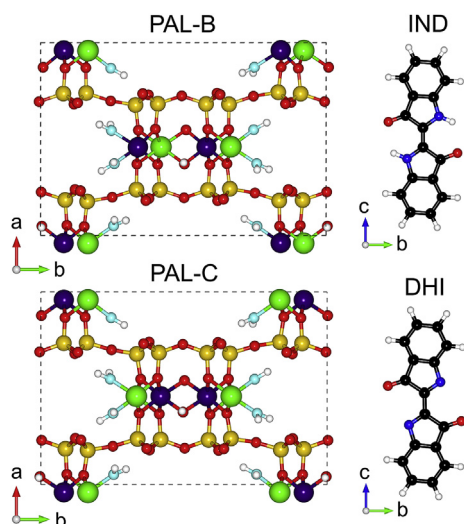


Fig. 1. Left side: Ball-stick representations of the equilibrium PAL-B and PAL-C. Right side: Optimized molecular indigo (IND) and dehydroindigo (DHI) geometries. Color code: dark-blue, green, red, yellow, white, black and blue represent Al, Mg, O, Si, H, C, N atoms. The light blue means O atom in the structural water molecules (OH_2). We have removed the zeolitic water molecules from the tunnel for clarity. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

should not be discarded taking into account the size of the PAL channels [10]. Most recently, Chiari et al. suggested that IND form strong hydrogen bonds with carbonyl group mediated by the structural water, based on synchrotron radiation data and molecular modeling [12]. Thermogravimetric, solid-state nuclear magnetic resonance (NMR), X-ray, synchrotron diffraction and Raman spectroscopy were used in Refs. [13,14] to suggest that IND molecules block the pores of the PAL clay.

The interaction in the hybrid IND@PAL system is strongly dependent on the IND location in the PAL. When the IND is adsorbed at the PAL surface, the main interaction occurs between PAL silanol (Si-O-H) groups and IND carbonyl group through hydrogen bonding. On the other hand, if the encapsulation process is favorable, the hydrogen bonds of the IND carbonyl groups and the structural OH_2 molecules in the PAL could stabilize the MB. Another scenario is when the IND dye interact directly with Mg or Al cations at the edge of the octahedral [15] or in the tetrahedral layer of SiO_4 [16].

An interesting issue about MB is its greenish color provided by the DHI molecule, as reported after electrochemical analysis [6,17]. The possibility of the presence of both molecules (IND and DHI) shows the importance to perform an energetic comparison of DHI and IND in MB studies. The comparison of binding energy profiles of these systems can provide information about the relative behavior for both molecules. Total energy Density Functional Theory (DFT) calculations can help to understand the physico-chemical processes and the interactions in the nanohybrid mineral-organic IND/DHI@PAL system. In this study we paid attention on the IND and DHI molecules interacting solely with the dehydrated PAL clay (zeolitic water has not been considered). The main interactions in these dyes are C=O and N-H groups with the structural OH_2 molecules tightly bonded to the edge of the dioctahedral sheet in the PAL clay. Here, four PAL models have been considered according to the ordering of Al atoms.

This paper presents a systematic and comparative study of IND/DHI interacting with the internal walls of the PAL clay tunnels. The next section presents the computational details and models. Then, we present results of the structural, bonding and stability

properties of four PAL models. After that, a discussion on the molecular binding energies at several positions along the tunnel considering two dehydrated PAL models is presented. Finally, a detailed analysis of the most stable structures is shown as well as their structural, bonding and electronic properties. Conclusions are presented at the end.

2. Computational details and models

Total energy DFT calculations were performed using the SIESTA computational code [18]. The exchange-correlation energy was described by a functional (vdW-DF) that takes into account the van der Waals forces dispersion effects. The reparameterized version of the vdW-DF functional of Dion et al. [19] as proposed by Klimes-Bowler-Michelides (KBM) [20] was adopted, with the implementation by Roman-Pérez et al. [21] The electron-ion interaction was treated with norm-conserving pseudopotentials [22,23] in their non-local form [24]. A linear combination of pseudoatomic orbitals (LCAO) was utilized for the expansion of the electronic states, with an optimized double- ζ polarized (DZP) basis set [25]. A mesh-cutoff energy of 600 Ry is applied to sample the electronic density in real space. The structural optimization was carried out with the FIRE (Fast Inertial Relaxation Engine) algorithm [26], with a maximum value in the interatomic forces of 0.025 meV/Å together with a value of 0.5 GPa in the stress components. The electronic relaxation was converged to 1.0×10^{-5} . The Monkhorst-Pack scheme [27] was used for the Brillouin zone sampling with a Γ -centered kgrid-cutoff of two times the largest lattice vector of each system, following the Moreno and Soler scheme [28]. A Fermi-Dirac smearing of 0.1 eV is adopted because the PAL is an insulator. Energy cutoff and k-grid convergence tests were performed on $1\mathbf{a} \times 1\mathbf{b} \times 5\mathbf{c}$ supercell for the IND/DHI@PAL where \mathbf{a} , \mathbf{b} and \mathbf{c} are the lattice vectors for the palygorskite. For IND and DHI molecules in a gas phase calculations, we use a vacuum distance in each direction of around 15 Å conducting to a supercell of $15 \times 20 \times 30$ Å.

The PAL-B and PAL-C models in Fig. 1 have the Al (Mg) ordering Al-Mg-Al-Mg and Mg-Al-Al-Mg projected on the (001) plane, respectively. Meanwhile, the PAL-A (Mg-rich) and PAL-D have the next configuration, Mg-Mg-Mg-Mg and Al-Mg-Mg-Al. Thus, a Mg/Al ratio equal to 1 was adopted based on the ideal formula by García-Romero [4] and Artioli [5]. Previously, this ratio has been used by Tilocca et al. in the theoretical study of the Maya complex with time-dependent DFT [15]. In this theoretical study, it is neglected the aluminum atoms as impurities in the SiO_2 sheet. Güven et al. [29] showed an Al/Si ratio smaller than 0.05, and K, Na impurities have similar ratios too. In this theoretical study, we neglected the effect of such impurities. Since a PAL unit cell (u.c.) has two tunnels only one molecule was placed in one tunnel meanwhile the other one is empty during all calculations. This leads to a 3.36 wt % of IND (DHI) in dye@clay system. For the binding energy profiles obtained for dye in PAL, the atomic positions, volume and lattice vectors were set free to relax. A C (Mg) atom was fixed in the \mathbf{c} direction (all directions) as a constraint. Steps of 0.25 Å were employed to displace the molecules along the tunnel. Visualization of atomic models and isosurfaces are performed using the VESTA program [30].

3. Results and discussion

3.1. Palygorskite clay

In the first set of calculations, structural optimization of four hydrated PALs with a $Pbmn$ space group was done. The resulting lattice parameters are reported in Table 1. Mg and Al cations are commonly located in the octahedral M1 and M2 sites, forming a

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