

The Fundamental Guest-Host Interactions in Maya Blue Pigments: DFT-CPMD Calculations

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Abstract. – *The color shift of the Maya Blue (MB) inorganic-organic pigment, observed upon moderate heating, reflects fundamental guest-host interactions leading to the unusual stability of Maya Blue. A possible way to shed light on these interactions is to assess the stability and compare the properties of models representative of specific modes of interaction between the palygorskite (P) host and the indigo (In) dye guest. In this work we have employed Car-Parrinello molecular dynamics to obtain and optimize relatively large periodic MB supercells, containing two different P-In modes of interaction: the ab-initio simulations confirm the considerable stability of these inclusion complexes, and reveal specific structural and dynamical features which determine and affect how the organic dye is anchored to the inorganic host.*

Introduction

Maya Blue (MB) is a turquoise-greenish pigment used by the Maya civilization and in central America between the V and XVI centuries: [1] the astonishing property of this pigment is that the color of artefacts painted with MB has survived essentially intact until today, despite centuries of exposure to rain, heat and humidity in tropical environments: MB is in fact stable to chemical attacks by acid, basic, oxidant and reducing agents. [2] This is particularly interesting, considered that MB is made of the organic dye indigo combined with the inorganic clay palygorskite, [1] and does not contain heavy metals, such as copper or cobalt: fundamental studies on the physico-chemical nature of the MB stability can open the way towards a new generation of metal-free colorants, and are in general relevant in the context of hybrid inorganic-organic materials. [3] Experimental and theoretical studies have shown that the indigo molecule is able to penetrate inside the channel structure of the palygorskite clay, especially after applying a moderate thermal treatment to a crushed indigo/palygorskite mixture. [4-6] While it is clear that heating removes some of the water weakly adsorbed in the channels and thus makes room for the bulky indigo molecules, [7] revealing the exact nature of the physico-chemical interactions locking the organic molecule in place has so far resulted a very difficult task. Previous MD and static

simulations using empirical potentials have identified the C=O group of the indigo molecule as the most likely interaction site through which the molecule can be locked within the channels [4,5] and some indications in this sense also came from experimental NMR and vibrational spectroscopy studies. [5,6] A more reliable atomistic probe could be provided by ab-initio calculations; however, a very large periodic supercell of the host clay is needed in order to include the bulky indigo molecule within a channel, and the corresponding very large computer resources required have discouraged the applications of ab-initio techniques to this system so far.

We present the first application to Maya Blue of ab-initio (Car-Parrinello) Molecular Dynamics simulations, which were employed to fully relax a periodic indigo-palygorskite complex where the organic dye was anchored to the host through two different interaction modes. Besides revealing specific structural and dynamical features which can play a key role in stabilizing the palygorskite-indigo adducts, these simulations provide an essential starting point for additional advanced calculations of vibrational and optical properties [11,12] which could unambiguously identify the interactions responsible for shifting the color of the pigment from blue (corresponding to the unheated palygorskite-indigo mixture) to turquoise-greenish (corresponding to the “real” MB pigment, obtained by moderate heating). [8]

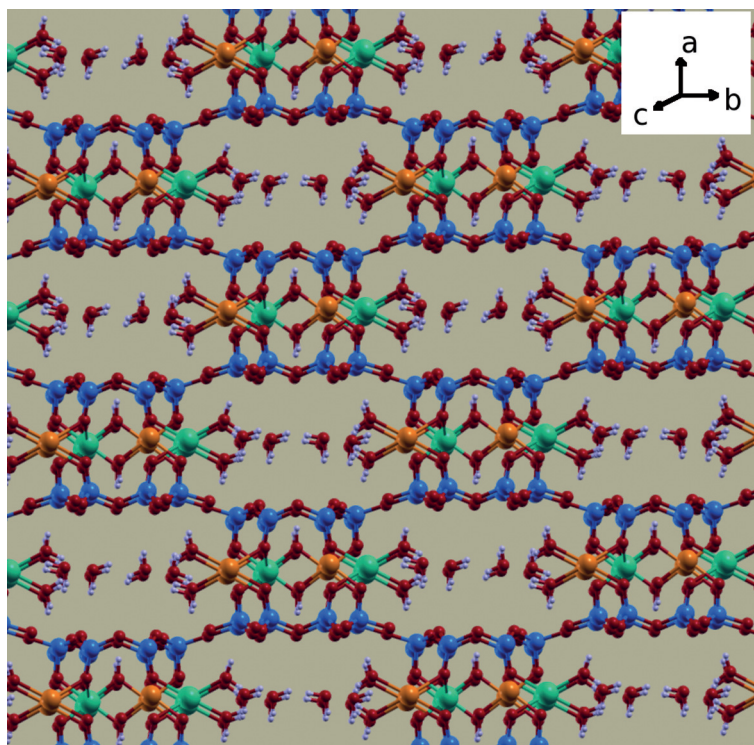


FIGURE 1. – *The experimental structure of monoclinic palygorskite. Color codes are blue, red, green, yellow, gray for Si, O, Al, Mg and H atoms, respectively.*

Details of the calculations

Palygorskite (Figure 1) is a silicate clay, comprised of Mg/Al octahedral layers sandwiched between two tetrahedral silicate sheets; the octahedral layers are discontinuous, leading to the formation of channels running along the c crystallographic axis. Mg and Al ions at the edge of the channels complete their octahedral coordination by bonding two structural water molecules, and other weakly bound water molecules are usually found further towards the centre of the channels (Figure 1). A periodic supercell, including $1 \times 1 \times 3$ monoclinic palygorskite (P) unit cells was created from the experimental P coordinates, [13] leading to a $[\text{Si}_{48} \text{Al}_{12} \text{Mg}_{12} (\text{OH})_{12} \text{O}_{120} (\text{H}_2\text{O})_{24}] \cdot (\text{H}_2\text{O})_{24}$ composition, with structural (coordinated to Mg/Al) water molecules inside the brackets and zeolitic (loosely bound) water outside. The supercell contains two parallel tunnels, each one extending approximately 15 \AA along the c direction; an indigo molecule was then arranged along one of these two channels (Figure 2), after removing zeolitic (and also structural where needed, see below) water, using the exact location of the In molecule highlighted in our previous classical MD simulations. [4] In particular, we have focused on the modes of interaction where: (i)

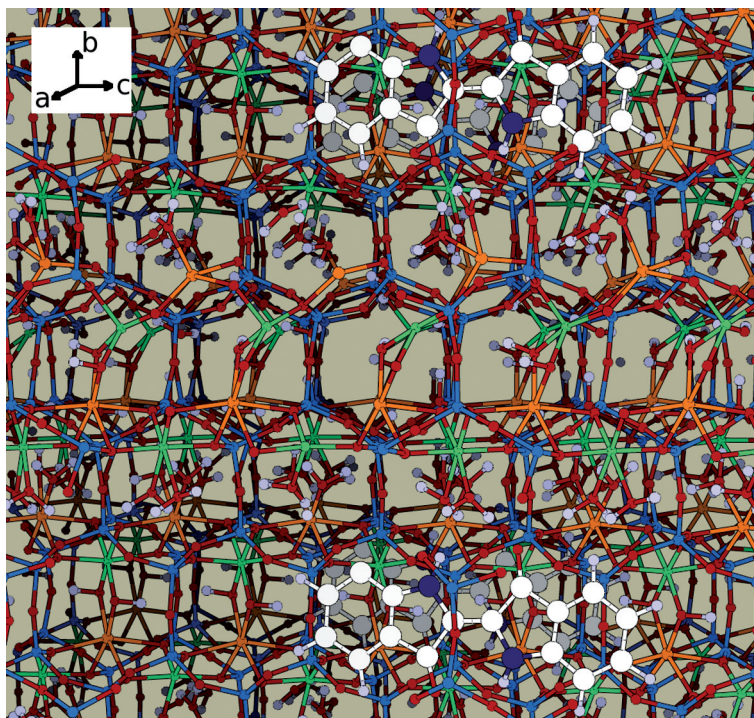


FIGURE 2. – *Indigo inclusion in palygorskite. Color codes are turquoise, red, green, yellow, gray, blue and white for Si, O, Al, Mg, H, N and C atoms, respectively; the atoms of the indigo molecule are highlighted as ball-and-stick.*

the carbonyl group of the indigo molecule is hydrogen bonded to a structural water molecule in the octahedral coordination shell of a Mg^{2+} ion; (ii) the carbonyl group of the indigo molecule is directly coordinated to a Mg^{2+} ion, left exposed after removal of bound structural water on one side of the channel. These two relatively large systems, containing approximately 350 atoms and 1500 electrons, were structurally optimized through damped MD in the Car-Parrinello-DFT scheme, [9] using ultrasoft pseudopotentials, PBE exchange-correlation functional and plane wave basis sets with 25 and 200 Ry cutoffs for the smooth part of the wavefunctions and the augmented density, respectively. [10] The calculations were carried out on the IBM SP5-512 at CINECA, using the parallel CP code of the Quantum-Espresso package. [14]

Results

A short initial CPMD run without temperature control led to a moderate increase in the ionic temperature (up to 300-400 K) for both systems, showing that the starting configurations, adapted from previous classical MD runs, represent reasonable

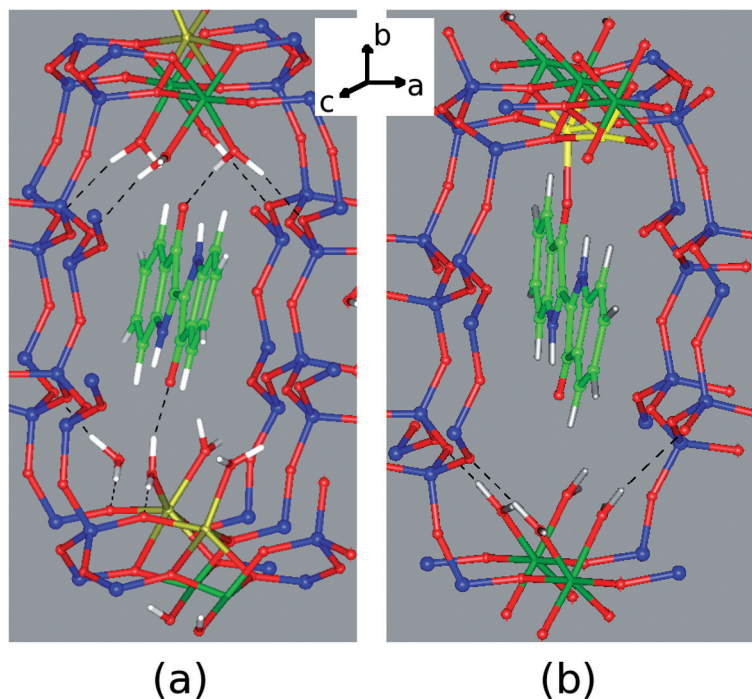


FIGURE 3. – (a) Optimized Maya Blue structure with indigo accepting H-bond from structural (bound to Mg/Al ions) water; (b) Optimized Maya Blue structure with indigo directly anchored to an Mg^{2+} ion exposed on the upper channel wall. Si, O, Al, Mg, C, N and H are colored in blue, red, dark green, yellow, green, dark blue and white, respectively. Only the atoms closest (within $\sim 6 \text{ \AA}$) to the indigo dye are shown.

adsorption structures. As a matter of fact, no significant translation of the indigo molecule along the channel axis were observed in the finite-temperature CPMD run, and after switching to the damped dynamics minimization the molecule rapidly settled in a local minimum in about 1000 CPMD steps. The optimized structures of the two indigo-palygorskite complexes are illustrated in Figure 3: in (a), the organic dye is firmly held in place by two strong hydrogen bonds donated by a pair of structural water molecules bound to the opposite channel walls ($R(\text{O}_{\text{In}}-\text{O}_{\text{W}}) = 2.75 \text{ \AA}$ and $R(\text{O}_{\text{In}}-\text{H}_{\text{W}}) = 1.75\text{-}1.83 \text{ \AA}$). The strong directionality of these H-bonds, combined with the low internal flexibility of the molecule arising from the central double $\text{C} = \text{C}$ bond, is such to align the molecule with its plane almost entirely in the bc crystallographic plane: during the room-temperature CP dynamics, the molecule performs small-amplitude, slow swinging motions about the c axis, rigidly shifting the molecular plane back and forth, so that on average the molecule lies in the bc plane, but it is generally found slightly tilted towards $+a$ or $-a$. These shifts appear correlated with (and induced by) dynamical changes to the H-bond pattern linking indigo to palygorskite through bound water: not only the orientation, but also the *identity* of the structural water molecule donating a H-bond to the indigo carbonyl is frequently changed during the dynamics. Figure 3(b) highlights another possible mode of interaction anchoring indigo to the inner clay walls: removal of structural water molecules (which is known to be the main effect of moderate thermal treatment used in the MB manufacturing process [1, 7]) leaves some of the Mg and Al ions in the octahedral layer exposed (and undercoordinated). The indigo carbonyl oxygen can act as Lewis base and partially restore the Mg/Al coordination. The CP dynamics shows that, once formed, the $\text{Mg}-\text{O} = \text{C}(\text{In})$ bond is rather stable ($R(\text{Mg}-\text{O}) = 1.996 \text{ \AA}$ in the optimized structure), and is indeed maintained along the whole room-temperature trajectory. Compared to the water-mediated interaction mode, in this case the indigo molecule is constantly kept closer to the upper channel wall to which it is directly bonded, and no interactions with the structural water molecules on the opposite side are recorded. This stronger direct interaction appear to markedly perturb both the organic dye and the inorganic host, inducing slight undulations of the T-O-T clay ribbons which were not observed in the other case, as well as more significant deviations from planarity for the organic molecule.

Conclusions

The ab-initio calculations of large periodic models of the palygorskite-indigo inclusion complex have started to shed some new light on the fundamental interactions anchoring the molecule to the clay, and leading to the very high thermal and chemical stability of Maya Blue pigments. The ab-initio calculations fully confirm that the bulky indigo molecule is rather stable inside the palygorskite channels at room temperature. On one hand, the interaction between the organic dye and the clay can be mediated by structural water molecules which are coordinated to the octahedral layer of the clay and also donate a H-bond to the indigo carbonyl: changes to the geometry of these H-

bonds appear to induce re-orientational motions of the indigo molecule, whose molecular plane smoothly swings around the c direction at room temperature. On the other hand, removal of structural water can favor a stronger interaction involving the indigo carbonyl oxygen and an exposed undercoordinated Mg^{2+} ion. This mode of interaction also appears rather stable at room temperature, despite somewhat marked mutual perturbations of both the clay structure and the molecular planarity. Having established the stability of these periodic models of Maya Blue at the ab-initio level, they will enable further atomistic investigations of other properties: for instance, vibrational and optical signatures of each specific mode of interaction can be directly investigated and used to make further progress in solving the intriguing puzzle of the Maya Blue stability. [15]

Acknowledgements. The work has been performed at University of Insubria (Italy) and CINECA, under the HPC-EUROPA project with the support of the European Commission Capacities Area - Research Infrastructures Initiative.

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