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**Mayan inspired nanocomposite materials: an overview**

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**Abstract**

*Maya Blue* is a famous blue pigment, used by the ancient Mayas in Central America (especially in the *Yucatàn* peninsula, Mexico) from the V to the XVI Century AD, mostly for mural paintings and decorations on ceramics and statues. Once re-discovered in modern times (circa 1930), it quickly grabbed the interest of the Scientific Community due to its amazing stability: this pigment, in fact, is known to resist the attack of acids, alkalis and solvents, with no fading in colour nor loss of structural features. Around the turn of the millennium, it was acknowledged – following seminal studies – that *Maya Blue* forms after to a heating-induced encapsulation and bonding of indigo – an organic dye – into the channels that permeate the structure of palygorskite and sepiolite – microporous clay minerals [1,2]. As a matter of fact, *Maya Blue* can therefore ‘legally’ be considered the ancestor of modern nanocomposite materials (though the Mayans hardly knew that!). The incorporation and shielding of the guest indigo dye in the host palygorskite framework *de facto* stabilizes the organic molecule – frail and decomposable when isolated – thus gifting the resulting hybrid nanocomposite with its renowned invulnerability.

These achievements raised new aspirations: “*Mayas made it Blue; what if someone else makes it … any other colour*?” To do that, several dye molecules were ground and heated with palygorskite, so to check whether one of the ensuing compounds might have represented an innovative nanocomposite material, endowed by the very same stability of its renowned blue predecessor.

Curiously, a stable red ‘Mayan-inspired’ hybrid composite was obtained by ‘marrying’ palygorskite with methyl red – an azo dye used as an indicator, whose colour changes after pH fluctuations (red at pH ≤ 4.4, yellow at pH ≥6.2 and orange in between). Once fixated on palygorskite, however, methyl red undergoes no colour change consequent to pH variation, and the resulting ***palygorskite@methyl red*** **hybrid composite** maintains a vivid and brilliant red-purplish hue in spite of severe acid or alkali attacks, with no appreciable fading.

The fixation of methyl red inside the palygorskite framework and the nature of the mutual host/guest interactions were investigated with a multi-analytical approach, including both molecular mechanics simulations and experimental techniques (i.e., UV-visible, FT-IR, SER and FT-Raman spectroscopies, synchrotron XRPD and TGA coupled with GC-MS). As well as in *Maya Blue*, the palygorskite@methyl red composite forms after incorporation of the guest dye inside the tunnels that cross the host framework. Different topological methyl red forms (neutral, zwitterionic and/or mono- and di-protonated) coexist inside these tunnels, causing the palygorskite@methyl red complex to be suitably considered a poly-functional organic/inorganic hybrid composite – a definition fitting also for its famed blue predecessor [3]. Supramolecular interactions occur between the host and the guest, responsible for the composite outstanding stability. These bonds – mainly involving the dye COOH group and the clay framework – show an atypical evolution, whose reversibility depends on the temperatures reached during synthesis. Sheltering inside the host pores, however, enhances the thermal stability of the guest dye with respect to the isolated molecule.

The palygorskite@methyl red hybrid composite represents a valid, ecological surrogate to other synthetic pigments used in the Materials Science and Cultural Heritage fields. Future perspectives aim at synthesizing similar composites with different hues, as well as testing the suitability of palygorskite as a valid carrier for different kinds of organic guests (e.g., active principles of drugs).

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