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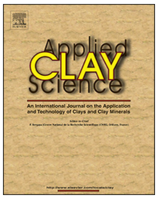

Research paper

Organic/inorganic hybrid pigments from flavylium cations and palygorskite

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A R T I C L E I N F O

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A B S T R A C T

Features such as color, brightness and fluorescence are extremely important in applications of pigments. Hybrid materials inspired by the ancient Maya Blue pigment are a promising alternative to improve the properties and applicability of natural and synthetic dyes. In this work, we report the preparation, photophysical properties, and stability of several fluorescent hybrid pigments based on flavylium cations (FL) adsorbed on palygorskite (PAL). Five flavylium cations were investigated, viz., the 3′,4′,7-trimethoxyflavylium (FL1), 7-hydroxy-4′-methoxy-flavylium (FL2), 7-hydroxy-4-methylflavylium (FL3), 5,7-dihydroxy-4-methylflavylium (FL4) and 7-methoxy-4-methylflavylium (FL5) cations. Only FL1 and FL2, without a methyl substituent at the 4-position that could hinder inclusion in palygorskite channels, adsorbed strongly on PAL, producing fluorescent hybrid pigments with attractive colors. The spectroscopic and fluorescence properties of the FL1/PAL and FL2/PAL hybrid pigments were characterized. The color of the adsorbed dyes was somewhat more resistant to changes in external pH, photochemical stability was maintained and the thermal lability was markedly improved in the FL/PAL hybrid pigments, pointing to flavylium cations as promising chromophores for the development of fluorescent hybrid pigments with attractive colors.

1. Introduction

Hybrid materials prepared by the combination of dyes with inorganic substrates have been extensively studied in search of materials with unique properties and color attributes (preferably bright and/or fluorescent) that are chemically, thermally and light stable (Laguna et al., 2007; Teixeira-Neto et al., 2009, 2012; Dejoie et al., 2010; Giustetto et al., 2014; Lin et al., 2014). One of the oldest and perhaps the most famous example of an organic-inorganic hybrid material is the Maya Blue pigment, which was widely used in murals, codices, ceramics and sculptures by the Maya civilization in the Pre-Columbian era. Maya Blue is extremely stable, able to resist the attack of concentrated nitric acid, bases and organic solvents without losing its color (Sánchez Del Río and Martinetto, 2006; Arnold and Branden, 2008; Chiari et al., 2008; Giustetto et al., 2011). The amazing chemical and photochemical stability of Maya Blue is presumably due to its unique structure, which consists of the dye indigo protectively (and apparently irreversibly) inserted into the channels of palygorskite or sepiolite clay (Giustetto et al., 2005, 2006, 2011; Chiari et al., 2008; Tilocca and Fois, 2009).

Palygorskite (PAL) is a hydrated magnesium and aluminum phyllosilicate clay mineral. Unlike most clays, PAL has fibrous morphology, consisting of a layer structure of ribbons of tetrahedral silica and central magnesium octahedra oriented along the fibers. The octahedral sheet is sandwiched between two tetrahedral sheets that have periodic inversion of the apical oxygen, resulting in well-defined one-dimensional cavities or tunnels (Sánchez Del Río et al., 2009; Doménech et al., 2011) with dimensions 3.7 × 6.4 Å (Brigatti et al., 2006) and, on the external surface of the clay fibers, partially open grooves or channels (as denominated for sepiolite by, e.g., Ruiz-Hitzky (2001) and Martínez-Martínez et al. (2011)). Several studies have shown that palygorskite has two main types of acidic sites, sites of stronger acidity with an effective pK_a in the range of 5–5.5 and more weakly acidic sites with a pK_a around 9–9.5 (Frini-Srasra and Srasra, 2008; Acebal and Vico, 2017). The porous structure of this clay allows the insertion and/or adsorption of organic molecules and ions, making it a good adsorbent (Giustetto et al., 2014; Mu and Wang, 2016). Recent studies involving dyes and PAL clay have obtained several novel Maya Blue-like pigments (Lima et al., 2012; Fan et al., 2014; Zhang et al., 2015a, 2015b; Zhang et al., 2015c, 2015d), some of which are materials with interesting self-cleaning properties (Zhang et al., 2016a, 2016b).

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Adsorption of dyes onto PAL and PAL composites (Mu and Wang, 2016) and biomedical applications of clay-drug hybrid materials (Kim et al., 2016) have been recently reviewed and the use of PAL as an adsorbent for environmental remediation continues to be of interest (Ugochukwu et al., 2014; Boudriche et al., 2015; Yang et al., 2018).

The chromophoric group of anthocyanins, which are responsible for most of the purple, blue and red colors of flowers and fruits, is a 7-hydroxyflavylium cation. The chemical and photochemical reactivity of synthetic flavylium cations mimics that of natural anthocyanins, with the advantage of the facility and versatility of modifying the substituents on the flavylium chromophore and consequently their reactivity. Although anthocyanins and synthetic flavylium cations have great potential for practical applications as dyes or antioxidants, these applications are limited by their chemical reactivity, which is affected by several factors including pH, temperature, light, oxygen, among others (Ferreira da Silva et al., 2005; Castañeda-Ovando et al., 2009; Quina et al., 2009; Cavalcanti et al., 2011; Silva et al., 2016).

The inclusion and/or adsorption of anthocyanins and flavylium cations in/on inorganic substrates such as mesoporous materials (Kohno et al., 2008a, 2011, 2015; Gago et al., 2017) and clays (Lima et al., 2007; Kohno et al., 2007, 2009, 2010; Ogawa et al., 2017; Ribeiro et al., 2018), may represent promising alternatives for preventing the undesirable chemistry of these dye molecules. In the present work, we have investigated the preparation of flavylium cation/palygorskite (FL/PAL) complexes as prototypes for fluorescent hybrid anthocyanin/palygorskite pigments. The complexes that retained the more intense colors and fluorescence after exhaustive washing with acidic methanol were chosen for evaluation of the thermal, photochemical and pH stability of their color and fluorescence.

2. Experimental section

2.1. Materials

The flavylium cation salts 3′,4′,7-trimethoxyflavylium chloride (FL1), 7-hydroxy-4′-methoxy-flavylium chloride (FL2), 7-hydroxy-4-methylflavylium chloride (FL3), 5,7-dihydroxy-4-methylflavylium chloride (FL4) and 7-methoxy-4-methylflavylium chloride (FL5) used in this work (Scheme 1) were available from previous studies of the group and the syntheses have been previously reported (Freitas et al., 2013; Held et al., 2016; Silva et al., 2018). The palygorskite used in this work was the Source Clay PFl-1 from the Clay Minerals Society. The chemical composition, characterization and properties of this clay have been described (Shariatmadari et al., 1999; Borden and Giese, 2001; Chipera and Bish, 2001; Guggenheim and Koster Van Groos, 2001; Madejová and Komadel, 2001; Mermut and Cano, 2001; Li et al., 2003; Dogan et al., 2006; Frost et al., 2010). Hydrochloric acid (HCl, Vetec) was used as received, methanol (Merck) was treated with sodium and ultrapure water was used for the preparation of all aqueous solutions.

2.2. Preparation and physical characterization of the FL/PAL hybrid pigments

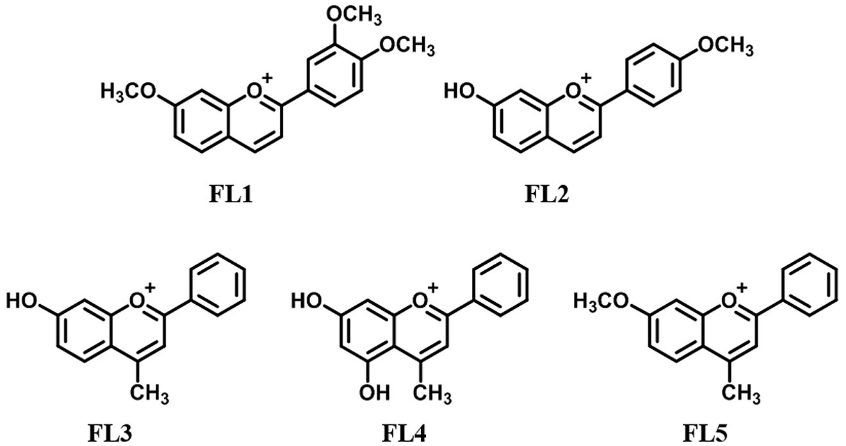
Aliquots of solutions of the FL in methanol (in which FL cations are highly soluble) containing 1% 1.0 mol dm^{-3} HCl (in order to suppress proton transfer and hydration of the flavylium cations) were added to the appropriate amount of PAL clay powder. The initial FL/PAL ratios utilized were 0.050, 0.075, 0.100 and 0.125 mmol g^{-1}. The resulting dispersions were stirred for 24 h in the dark at room temperature, centrifuged and the solid washed exhaustively with HCl-acidified methanol and dried at 45 °C under vacuum for 2 h. The amount of flavylium cation adsorbed was estimated from the decrease in the absorbance of the supernatant employing the known molar attenuation coefficient of each FL.

Powder X-ray diffractograms of PAL and FL1/PAL were determined with a Bruker D2 Phase diffractometer using Cu-K$_\alpha$ radiation (1.5418 Å, 30 kV, 15 mA) employing a scan step of 0.05°. Nitrogen adsorption/desorption isotherms were determined at −196 °C using a Quantachrome volumetric adsorption analyzer (Model 100E). The samples were outgassed for 24 h under reduced pressure at 80 °C. The specific surface areas (S_{BET}) and total pore volumes (V_{tot}) of the samples were determined by the BET (Brunauer et al., 1938) and BJH (Barrett et al., 1951) methods, respectively. Surface areas of the micropores (S_{micro}), the external surface areas (S_{ext}),the micropore volumes (V_{micro}) and the sum of meso- and macropore volumes ($V_{meso+macro}$) were estimated by the *t*-plot method (Lippens and de Boer, 1965).

2.3. Spectroscopic measurements

For the infrared measurements, about 1.50 mg of solid sample was added to approximately 150 mg of dry KBr in a small agate mortar and mixed by grinding. The resulting powder was pressed into a pellet using a hydraulic press (Caver, model 3912, Wabash). Infrared spectra of the pellets were collected using a Bruker Vector 22 FTIR spectrophotometer in the frequency range of 4000–500 cm^{-1}, 32 scans at 0.5 cm^{-1} digital resolution.

The UV–Vis-diffuse reflectance (DR) spectra were measured with a Varian Cary 50 UV–vis Bio spectrophotometer equipped with a *Barrelino*™ diffuse reflectance probe (Harrick Scientific Products, Inc.). Samples with greater amounts of adsorbed flavylium (FL1 and FL2) were diluted in barium sulfate. The diffuse reflectance spectra were converted to the corresponding reemission function, F(R), employing the Kubelka-Munk equation (Tomasini et al., 2009):



Scheme 1. Structures of the flavylium cations (FL) used in this work.