Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Hybrid pigments resulting from several guest dyes onto γ-alumina host: A spectroscopic analysis

Erik Pérez [a], Ilich A. Ibarra [a], Ariel Guzmán [b], Enrique Lima [a,*]

[a] Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Circuito Exterior s/n Ciudad Uiversitaria, Coyoacán, México, DF 04510, Mexico
[b] Instituto Politecnico Nacional, ESIQIE-SEPI-DIQI, Laboratorio de Investigación en Materiales Porosos, Catálisis Ambiental y Química Fina (LiMpCa-QuF), UPALM Edif. 7 P.B. Zacatenco, GAM, México, DF 07738, Mexico

ARTICLE INFO

Article history:
Received 15 November 2015
Received in revised form 1 February 2016
Accepted 8 April 2016
Available online xxxx

Keywords:
Dyes
Alumina
Chromophore
Colour
MAS NMR
Pigments

ABSTRACT

The synthesis of hybrid pigments was made from combination of γ-Al_2O_3 and some organic chromophores such as carminic acid, alizarin, purpurin, curcumin, fluorescein and betacyanins. The γ-Al_2O_3 was obtained through sol-gel synthesis with 2-propanol and aluminium tri-*sec*-butoxide (ATB). This article presents some spectroscopic evidences related to the formation of aluminium complexes between coordinative unsaturated sites (CUS) of aluminium and some organic groups (carboxylic acid, quaternary ammonium and β-keto enol) present in the chromophores structure. The physicochemical properties upcoming from a spectroscopic analysis point out that these materials can be applied in the design of new materials with potential uses in artworks and in the field of cultural heritage.

1. Introduction

In art there is a need of coloured materials, in order to use them as the source of colour to create paintings and in general art works. However, the pigment efficiency clearly depends of the surface where it is applied; in other words, the chemistry of interactions pigment surface should determine the perfection of art work. Evidently the artist plays the most important role, but the tools such as the pigments are also crucial to create, for example, a painting. In this context, the Tuscan painter Cennino Cennini [1] prepared his own pigments for painting on fresco and on panel. He proposed pigments highly specific for a determined surface and described the preparations of pigments from a variety of sources. At present, there is a great variety of sources but even today there is a necessity to find combinations of raw materials, both synthetic and natural, and use them as colourants not only to create art works but to apply them in many other fields such as sensitisation of solar cells and lasers. Thus, a growing application of dye doped materials was established [2]. Several synthesis strategies for the stabilization of chromophores onto surfaces of inorganic materials are established [3]. Composites derived from organic dyes–inorganic compounds combinations have found applications in the fields of optics, art (picture conservation) and food processing, among others [4,5].

A number of factors have been reported to be decisive in the properties of the hybrid dye–inorganic compound. It is comprehensible that, on the one hand, chemical properties such as polarity and acidity of the inorganic receptors, and on the other hand, the arrangement of the attached organic molecules, are key parameters in the stabilization of chromophores in inorganic matrices [6].

Recently the synthesis of new-generation hybrid organic-inorganic pigments has become of great importance to scientific development [7,8]. A major problem of many organic colourants is their poor stabilization against acids, light or temperature [9,10]. In this context, stabilization of organic chromophores is possible by immobilisate them in inorganic matrices [11].

The combinations organic chromophore and inorganic matrix are numerous and the final application is decisive to design a hybrid pigment [12,13]. For instance, a famous organic–inorganic pigment is the Maya blue, which is the molecule indigo incorporated into the channels of palygorskite clay [14–15]. In this case the palygorskite structure shields the indigo molecule against acid attacks.

In this work we have stabilised several dyes, which are attractive from a view of their chromatic properties, onto a same matrix, a gamma alumina. The choice of alumina as the host material is based on a previous work [8] where already is shown the importance of acidity and coordinative unsaturated sites of aluminium to stabilise some organic molecules. In this paper, we focus again on alumina to stabilise different organic dyes in order to elucidate the importance of inorganic host to produce a wide family of hybrid pigments.

* Corresponding author at:Instituto de Investigaciones en Materiales, UNAM, Circuito Exterior s/n Ciudad Uiversitaria, Coyoacán, México, DF 04510, Mexico.
E-mail address: lima@iim.unam.mx (E. Lima).

http://dx.doi.org/10.1016/j.saa.2016.04.017
1386-1425/

2. Experimental

2.1. γ-Al_2O_3

The γ-Al_2O_3 was prepared through sol-gel synthesis with tri-*sec*-butoxide (ATB-97%), 2-propanol anhydrous like organic dissolvent and H_2SO_4 as the acid catalyst, the molar ratio of every reagent was 2-propanol:ATB = 60:1; H_2SO_4:ATB = 0.09:1 and H_2O:ATB = 1:1. The ATB was dissolved in 2-propanol anhydrous, previously heated to 80 °C, after that the mixture was refluxed at 85 °C; after 1 h the water was added into the dissolution, then the mixture was refluxed at 80 °C for 3 h. The solvent was removed by evaporation at 120 °C, the dried solid was thermal treated at 550 °C for 4 h with a heated rate of 4 °C by minute. The final product was characterised by X-ray diffraction. Finally the sample was labelled like 2p97.

2.2. Dyes

2.2.1. Synthetic chromophores

Carminic acid, alizarin, purpurin, curcumin and fluorescein were purchased from Aldrich and used without any further purification. These dyes were labelled as Cac, Aliz, Purp, Curc and Fluo, respectively. The chemical structure of the dyes is drawn in Fig. 1.

2.2.2. Natural chromophore

Betacyanin fraction was obtained as follows: 50 g of dry bracts of purple *Bougainvillea glabra* flowers were ground with 200 mL of deionized water, the mixture was filtered and the aqueous extract was centrifuged at 20,000 rpm for 30 min at 4 °C, the recovered supernatant was stored. In order to obtain a betacyanin fraction, the extract was separated by chromatographic column (40 × 3 cm) packed with silica-gel C_{18}, where the eluent was a mixture of methanol and water

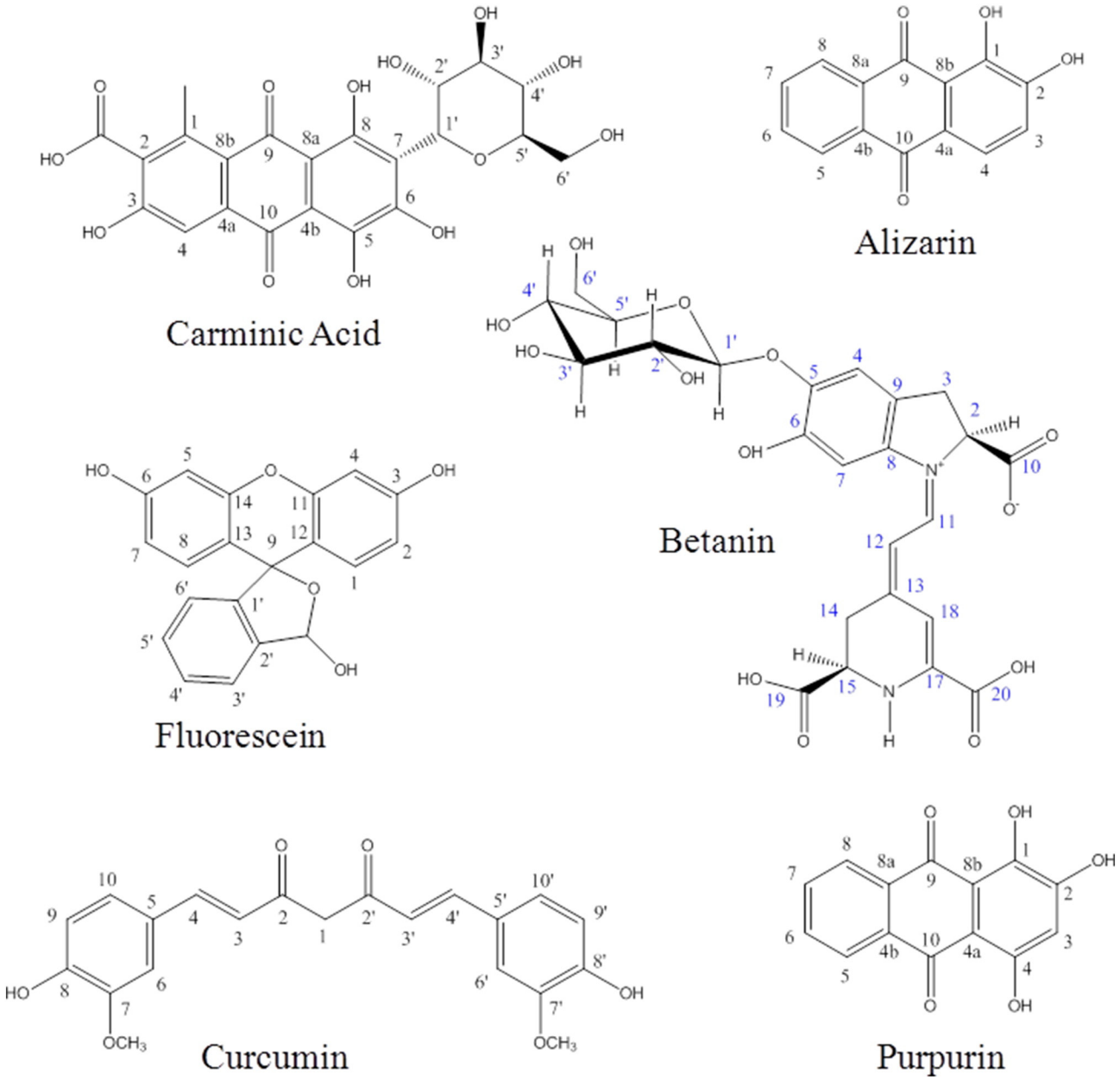

Fig. 1. Chromophore structure of different dyes used as a source of colour in this work.

Please cite this article as: E. Pérez, et al., Hybrid pigments resulting from several guest dyes onto γ-alumina host: A spectroscopic analysis, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy (2016), http://dx.doi.org/10.1016/j.saa.2016.04.017