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Conjugated dye-intercalated fluoromica hybrids displaying tunability of optical properties through packing variation

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ABSTRACT

Conjugated dye-intercalated fluoromica hybrids involving three different cationic organic dyes, i.e. oxazine, rhodamine and ter-fluorene derivatives, have been characterized by synchrotron X-ray diffraction (XRD) in combination with optical spectroscopy. The results show the tunability of the dye packing, hence of the absorption and emission properties, as a function of both type and amount of intercalated molecule. Suitable molecular models compatible with XRD findings, accounting for the observed optical behavior, are proposed and discussed.

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1. Introduction

Hybrid composites constitute a milestone in the development of functional and structured materials displaying peculiar properties and improved performances. Typically, these assembled materials combine the intrinsic features of both organic and inorganic components, leading to enhanced mechanical, physical and thermal properties [1–3]. Among the hybrid composites, those comprising π-conjugated organic chromophores have gained considerable interest for the possibility of developing materials with specific optical and electronic properties [4–7]. In fact, over the decades scientists focused their efforts towards the synthesis of hybrid multifunctional assemblies for different optoelectronic applications such as waveguide laser cavities [8], optical memory systems [9], artificial antenna systems [10], and for the manufacturing of optical sensors [11] and light emitting diodes [12]. In these systems, the inorganic component is arranged into ordered nano-scale architectures embedding photofunctional organic π-conjugated dyes.

Among the inorganic nano-structured materials, layered silicates have been widely used as hosts owing to their ion-exchange capability, large specific surface area, and unique two-dimensional expandable intra-layer space [13,14]. These specific features enable the tuning of the interaction between the embedded organic dyes in a sandwich-type intercalation by surface chemistry (i.e., ion-exchange and grafting reactions).

Recently, we have synthesized different SOMASIF 100 (**SME**) hybrids based on an intercalated organic dye and a polymer matrix wrapping the inorganic nanostructure, and we have shown that the **SME** interlayer spacing can be varied by changing the type of intercalated dye and its loading [14–17]. The main goals achieved, besides the enhanced processability imparted by the polymer, are the improvement of the dye photo-, thermo-, and chemical-stability, and the control of the accommodation of the guest to realize efficient dye assemblies, thus allowing the tuning of the hybrid's photo-functions.

Because of the great interest for the applications of these polymer hybrids in optoelectronic devices [18], a deeper structural characterization of the crystalline dye-intercalated **SME** precursors is desirable. Quite recently three contributions concerning the complete crystal structure of hybrids constituted by layered silicate and organic molecules have been reported [19–21]; in these

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studies the molecules taken into consideration were either not conjugated or small, and no significant optoelectronic properties could be conceived.

In this work, aiming to gain a deeper insight into the dye arrangement within the interlayer spacing, the salts of three prototypal π-conjugated dyes appealing for optoelectronic applications, were studied by means of synchrotron XRD investigations. The chemical structure of three dyes differing in their size, shape, and stiffness are all shown in Scheme 1, i.e. oxazine-1 chloride (**Ox1**$^+$), rhodamine 6G chloride (**R6G**$^+$), and 2,7-bis(9,9-dioctylfluorene-2-yl)-9,9-bis[6-(trimethylammonium)hexyl]fluorene dibromide (**TF**$^{2+}$).

Moreover, suitable molecular models compatible with XRD findings are proposed and the agreement with the optical properties of the hybrids is discussed.

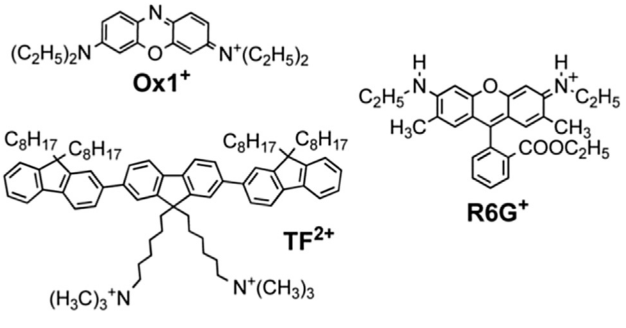
2. Experimental

2.1. Hybrid preparation

The materials were synthesized following the procedures developed for each specific case, detailed in Refs. [14], [16], and [17], for **Ox1**$^+$, **TF**$^{2+}$ and **R6G**$^+$, respectively. A general procedure however is reported in Supplementary data.

2.2. X-ray diffraction

Powders loaded into a sealed capillary were examined at 25 °C. GIWAXS measurements were performed at the X-ray diffraction beamline 5.2 at the Synchrotron Radiation Facility Elettra in Trieste (Italy). The X-ray beam emitted by the wiggler source on the Elettra 2 GeV electron storage ring was monochromatized by a Si(111) double crystal monochromator, focused on the sample and collimated by a double set of slits giving a spot size of 0.2 × 0.2 mm. The beam was monochromatized at energies from 6.2 keV to 10.34 keV ($1.2 \leq \lambda \leq 2$ nm) both for films and powders. Samples were oriented by means of a four-circle diffractometer with a motorized goniometric head. The X-ray beam direction was fixed, while the sample holder could be rotated about the different diffractometer axes, in order to reach the sample surface alignment in the horizontal plane containing the X-ray beam by means of laser light reflection. Subsequently it was possible to rotate it around an axis perpendicular to this plane or, alternatively, vary the angle between beam and surface (angle of incidence). Bidimensional diffraction patterns were recorded with a 2M Pilatus silicon pixel X-ray detector (DECTRIS Ltd., Baden, Switzerland) positioned perpendicularly to the incident beam, at 200 mm distance from the sample, to record the diffraction patterns in reflection geometry. Sample and detector were kept still during the measurements. The sample inclination to the beam was changed from $\omega = -0.05°$ to $\omega = 0.25°$, in steps of 0.05° yielding seven diffraction images. The q resolution of the 2D collected images was estimated by means of Lanthanum Hexaboride powder (NIST standard reference material 660a) and was evaluated ranging from 0.2 to 0.3 nm^{-1} both for q_z and q_{xy}, in agreement with other synchrotron measurements [22,23]. The same calibration standard allowed for the integration of 2D patterns using the software Fit2D [24] yielding powder-like patterns of intensity vs. diffraction angle, corrected for geometry, Lorentz, and beam polarization effects. Peaks positions were extracted by means of the program Winplotr [25]. Powders, when available in sufficient amount, were also examined using an Anton&Parr Camera under nitrogen flux and Siemens D-500 diffractometer (Cu Kα radiation, $\lambda = 0.154$ nm). The operating voltage and current were 40 kV and 40 mA, respectively. Data were collected from 3° to 33° 2θ at 0.05° 2θ intervals.



Scheme 1. The chemical structure of the organic dyes considered in the study.

2.3. Optical analysis

Due to the extremely low solubility of the hybrids, the optical characterization of the composite crystalline powders was performed on ground samples in KBr pressed pellets.

UV–visible absorption measurements were carried out via PerkinElmer Lambda900. The continuous wave photoluminescence (PL) spectra were recorded by a charge-coupled device cooled with liquid nitrogen, combined with monochromator. The excitation source was a monochromated xenon lamp. The spectra were corrected for the instruments response [10]. The PL spectra were acquired by exciting with a wavelength slightly shorter than the main absorption maxima of the compounds.

3. Results and discussion

3.1. General considerations

Depending on the nature of the components used (i.e., layered silicate and organic cation) and the preparation method, different types of hybrid can be obtained [7]. Phase-separated microcomposites (conventional composites) are obtained when the organic counterpart is unable to intercalate: silicate lamellae remain stacked in structures often referred to as tactoids as in the pristine mineral. Otherwise, when the organic cations penetrate in between the silicate layers, an intercalative system is obtained. In this case the composite shows, at least in principle, a well ordered multilayer morphology built up by alternating organic and inorganic layers. The most interesting and technologically promising materials are those belonging to this latter type, so that the understanding of the organic guest arrangement in between silicate lamellae is desirable, and XRD investigation is an irreplaceable technique to this aim.

In intercalated hybrids, the repetitive multilayer structure is well preserved, allowing the intra-layer spacing to be determined. Such an intercalation increases the intra-layer spacing with respect to the spacing of the pristine silicate, leading to a shift of the corresponding diffraction peak towards lower angle values. Moreover, the π-conjugated organic molecules accommodate within the lamellae and form peculiar ordered patterns, allowing for intermolecular interactions which can provide unique optical properties to the composites. Hence absorption and photoluminescence spectroscopy can be exploited as a complementary techniques to XRD analysis to give, beside the structural details about guest uptake in fluoromica layers, information on the intra-layer molecular arrangements as a function of both the dyes molecular species and their loading level.

The choice of **SME** fluoromica host, described by the formula $Na_{0.66}Mg_{2.68}(Si_{3.98}Al_{0.02})O_{10.02}F_{1.96}$, stems from its high aspect ratio ($L/W \cong 6000$, where L and W are length and thickness of silicate

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