



Hybrid Photonic Antennae Based on Mesoporous Silica Frameworks

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This contribution describes design, preparation and physico-chemical characterization of a new photostable hybrid antenna based on mesoporous SBA-15 silica. Concepts of host-guest chemistry are applied in such a way that one or more photoactive guest molecules are incorporated into the silica channels and on the outer surface, acting as energy harvesting and transferring units. The presented composite system behaves as efficient Förster resonance energy transfer (FRET) pair and shows high photoluminescence and stability towards photodegradation, representing an important step forward in the search for new efficient materials with opto-electronic applications.

Keywords: Mesoporous Silica, Photonic Antenna, Semiconductors, Energy Transfer, Photoluminescence.

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1. INTRODUCTION

Artificial light-harvesting systems represent an important field of research for design and fabrication of energy-storage devices. Taking inspiration from photosynthetic natural systems, many efforts and studies have been carried out to build so-called photonic antennae, in which the chromophoric units are specifically organized in space and energy dimensions so that the harvested light is all channeled through energy transfer steps to a common reaction centre.[1]

In this regard, several systems have been developed and studied that successfully make use of unidirectional energy transfer processes, including metal complexes, dendrimers and quantum dots, to cite some examples.[2] Host-guest assemblies have also received great attention, especially for the possibility they offer in improving the photostability of the chromophores, avoiding their aggregation and conferring high organization by spatial constraints, which is an important requirement for building up more complex nanoarchitectures.[3]

Micro- and mesoporous materials can be employed depending on the chromophore size and the surface properties of the host. Particularly, porous silicas and aluminosilicates are well suited as host materials, because they combine the mechanical strength of their framework with a homogeneous dispersibility of the guests.[4] They can also, in turn, be interfaced with a conductive surface in the case of thin-film deposition or with an organic polymeric matrix to fabricate highly stable opto-electronic devices.[5,6]

2. THE CONCEPT

In our approach for the construction of hybrid photonic antennae, we aim to realize photostable systems, in which encapsulated molecules either harvest or transfer the photoexcitation energy from/to chromophoric units that are linked outside a silica framework through selective functionalisation processes. For this purpose, we started our investigations focusing on semiconductive polymers as guests and mesoporous silica as hosting material (Figure 1a).[7]

Semiconductive polymers are widely used in electroluminescent devices and strongly emerging in this field as they are much less expensive to produce than their inorganic counterparts, easily processable as very thin films (< 100 nm) and their colors can be modulated over the entire visible range by structural modifications.[8] Although much progress has been made in improving the performances of these organic materials in light-emitting and photovoltaic devices, there are still drawbacks associated with their application such as reduced fluorescence quantum yields due to molecular aggregation and the tendency to photobleach in the presence of molecular oxygen.[9]

To overcome these drawbacks, the use of a rigid and spatially constraining matrix can help enhancing both chemical and physical stability by preventing molecules aggregation and degradation.[10] Moreover, whereby the hosting matrix features regular porous structure, like an array of uniform nanochannels or cages, high surface area and optical transparency, the guest units can be homogeneously dispersed and preferentially oriented, giving rise to anisotropic materials. As reported by Corma and coworkers, it is possible to obtain a remarkable increase in the stability of polyphenylenevinylene (PPV) electroluminescent polymer by encapsulation inside the pores of zeolites X and Y.[11]

Our antenna system consists of a PPV derivative (Super Yellow, SY)[12] incorporated into plate-shaped SBA-15 silica, whose surface is functionalized with a cyanine dye (IRIS3). The SBA-15 host structure was chosen since it has, by far, the largest mesochannels, with thick walls and adjustable pore size ranging from 3 to 30 nm, and possesses high hydrothermal and mechanical stability, along with the possibility of tailoring its morphology.[13]

In a so designed system we are able to strongly reduce the polymer leakage out of the mesopores as they are partially hindered by the anchored dye. We also expected favorable energy transfer from the protected polymer to the cyanine dye due to the very good spectral overlap between donor emission and acceptor absorption spectra (Figure 1b).

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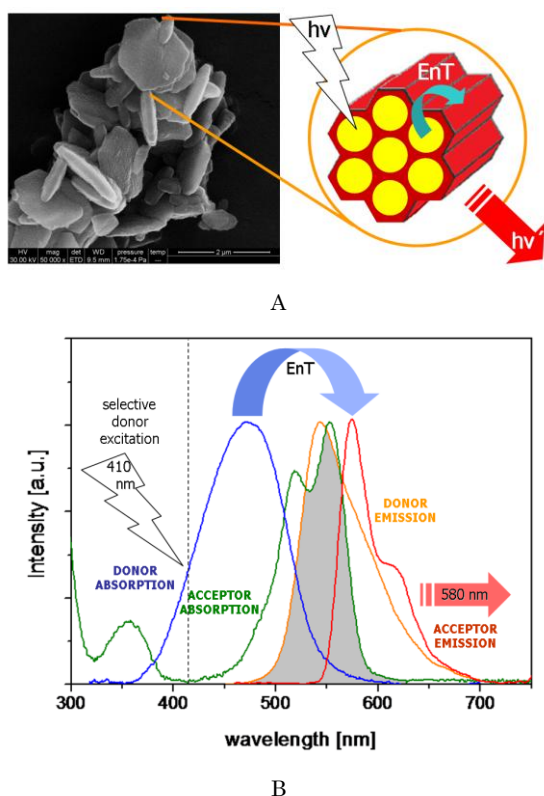


Fig. 1 – A) SEM image and schematic representation of SBA-15 silica platelets loaded with SY polymer and functionalised with IRIS3 dye; B) absorption and emission spectra of both donor and acceptor chromophores: the overlap area is highlighted in grey

3. RESULTS

XRD analysis confirmed that the silica samples maintain their structural properties upon IRIS3 functionalization, because all the profiles display the characteristic main reflection peak at $0.9^\circ 2\theta$ along with the secondary reflections at 1.5° and $1.7^\circ 2\theta$, which can be indexed, respectively, as the (100), (110) and (200) planes related to the hexagonal pore array of SBA-15. The obtained hybrid composite IRIS3-SY@SBA-15 was then characterized by nitrogen physisorption analysis and compared to the reference systems SY@SBA-15 and IRIS3@SBA-15 (Table 1). No significant differences between the pore volume and specific surface area of SY@SBA-15 and the composite IRIS3-SY@SBA-15 sample were observed indicating that, when the internal pore surface is previously functionalised with the polymer, the dye is selectively localized on the external surface of SBA-15 support.

Table 1 – Textural data of the hybrid materials measured by N_2 adsorption/desorption isotherms

	S_{BET} [m^2g^{-1}]	Pore volume [cm^3g^{-1}]	Pore size [\AA]
SBA-15	798	1.02	85
SY@SBA-15	587	0.80	81
IRIS3@SBA-15	610	0.88	81
IRIS3-SY@SBA-15	589	0.79	81

In the polymer-loaded silica, the size of the anchored dye (ca. 12 \AA), although small when compared to the mean pore diameter of SBA-15, is sufficient to

play an important role in blocking the encapsulated polymer. Leaking tests, carried out on IRIS3-SY@SBA15 and compared with SY@SBA15 sample, show that SY extraction is strongly impeded in toluene, in which the polymer is soluble, even after ultrasonic treatment of the suspensions.

To observe a photoinduced energy transfer process from the excited SY to IRIS3, specific requirements have to be met by the donor-acceptor pair: the donor unit must have efficient light absorption along with high photostability, the electronic transition dipole moments of donor and acceptor must be oriented in a favourable way, and a good spectral overlap between donor emission and acceptor absorption spectra is essential. Moreover, the transfer process should be fast enough to compete with other deactivation processes, such as donor emission or thermal relaxation pathways.[14] All the above mentioned conditions are satisfied in the IRIS3-SY@SBA-15 system, since both chromophores display a good spectral overlap and SY donor photostability is significantly enhanced by inclusion into the SBA-15 platelet crystals, which also confers higher rigidity to the polymer chains, reducing thermal deactivation of its excited state.[7]

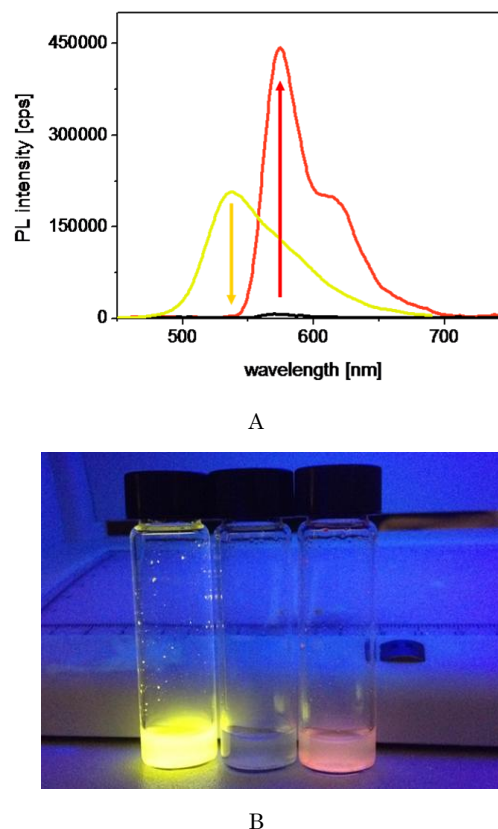


Fig. 2 – A) photoluminescence emission spectra of the IRIS3-SY@SBA-15 system (red line) compared with SY@SBA-15 (yellow line) and IRIS3@SBA-15 (black line), all recorded from 0.5 mg/ml 2-propanol suspensions upon excitation at 410 nm; B) digital photographs under UV light of, from left to right, SY@SBA-15, IRIS3@SBA-15 and IRIS3-SY@SBA-15 in 2-propanol suspensions

The photoluminescence spectra of the three systems were then recorded by using an excitation wavelength where the acceptor absorption is almost negligible (see

Fig. 1b) and are shown in Figure 2a. It is possible to observe that in IRIS3-SY@SBA-15 the donor emission is nearly all quenched compared with SY@SBA-15 spectrum and sensitization of IRIS3 emission occurs. Digital photographs of the three samples in 2-propanol suspension, collected under UV irradiation ($\lambda_{\text{exc}} = 320\text{--}400\text{ nm}$) confirm that light is absorbed by the copolymer and transferred to the dye (Figure 2b).

In order to gain further insight into the energy transfer dynamics, the three systems were also studied by means of time resolved confocal microscopy. This allowed us to obtain the luminescence lifetimes of the donor unit in absence (3.5 ns) and in presence (2.1 ns) of the acceptor, lifetimes that are needed for estimating the transfer efficiency and the donor-acceptor distance.^[15] The efficiency of the process turns out to be 40% while the mean distance between donor and acceptor is about 40 Å. This is consistent with the silica wall thickness of SBA-15 reported in literature (*ca.* 33 Å)^[16], and confirms that the IRIS3 dye is anchored essentially on the external surface of the crystal platelets.

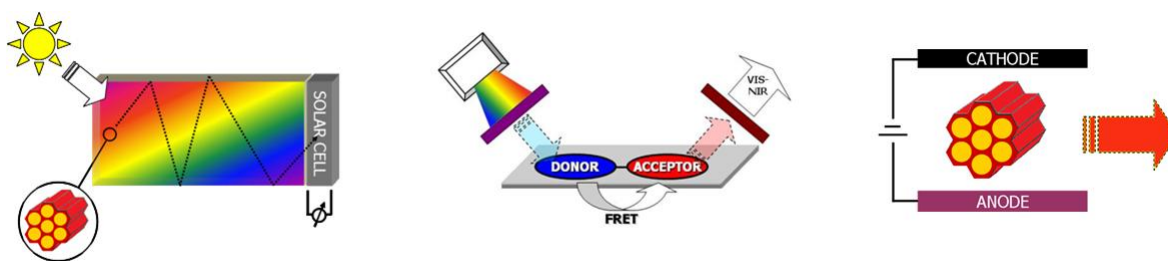


Fig. 3 – Schematized applications of hybrid photonic antennae: luminescent solar concentrators (left), FRET imaging probes (middle) and light-emitting diodes (right)

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