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ARTICLE TYPE

Protective Effect of the Mesoporous Host Towards the Photo Oxidation of Fluorescent Guests: a UV-Vis Spectroscopy Study

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The inclusion of fluorescent molecules within the pores of an inorganic host system is one of the most common ways used for the preparation of highly fluorescent nanosystems. The confination of labile molecules, usually lead to better performances mainly due to their protection against environmental parameters which can concur to the deactivation of the fluorescent ones. In this work the protective effect of the siliceous mesoporous host towards photo oxidation of fluorescent guest molecules has been investigated under different experimental conditions, highlighting an outstanding photostability if compared to the performances exerted by the fluorescent dye in solution.

Introduction

Since the early 1990s when the preparation of MCM-41 was first reported,[1] host-guest systems based on such kind of mesoporous materials started attracting increasing interest. In the last decades mesostructured silicas have been studied and tested as hosts for different kind of guest molecules, ranging from drugs and bioactive molecules for drug delivery systems [2,3,4,5] to organic and inorganic luminescent compounds for both technological and biomedical applications. Several kinds of fluorescent moieties have been hosted within the pores and channels of mesoporous materials, ranging from organic dyes [6,7] (e.g. coumarins, fluoresceins, rhodamines, phorphyrins, thionines and cyanines) to organometallic complexes [8,9] (e.g. ruthenium complexes) and semiconductor nanocrystals [10] (e.g. CdSe or silicon quantum dots).

The confinement of an organic molecule within the pores and channels of mesoporous materials should result in its protection against both chemical and photochemical decomposition (e.g. photo oxidation processes), as demonstrated in the case of the hosting of small labile molecules such as drugs [11,12,13]. In the case of organic fluorophores the dispersion within the uniform pores of mesoporous materials should lead to highly homogeneous distribution of the dye within the final hybrid. This induces an improvement in the photophysical properties, mainly due to reduction of side effects such as quenching phenomena, formation of non-luminescent aggregates, and inner filter effects and a consequent enhancement of the fluorescence performances, in term of brightness, quantum yield, photostability, etc.[14,15]

Among the organic fluorophores which could be used for these purposes, indocyanine dyes represent a valid candidate due to their high structural versatility that allows the introduction of functional groups exploitable for the linkage with variously functionalized biomolecules and materials. Moreover, it is possible to tune the absorption and emission features from the visible up to the Near Infra Red region of the electromagnetic spectrum, where the interference from the biological samples (cells, biomolecules, tissues) is negligible. [16,17]

Fluorescent hybrid organic-inorganic mesoporous nanoparticles can be prepared by physical adsorption or grafting of indocyanine dyes within the channels of MCM-41 nanoparticles[18,19,20]. Some authors of the present work have recently demonstrated[21,22,23] that photoactive mesoporous nanoparticles based on indocyanines inserted by physical adsorption into the pores of pure MCM-41 silica can be used as fluorescent tools for imaging and tracking of intracellular events in cell cultures. Previous experiments showed that this kind of architecture provides the highest stability and signal intensity upon specific thermal treatments, if compared to the correspondent indocyanine dye in solution and other kinds of nanoparticles.[24] This gain in performances could be related to the combined beneficial effect of the immobilization of the dye, which lead to an increase in the probability of radiative processes, and protective effect of the dye by the silica matrix towards to photo oxidation processes.

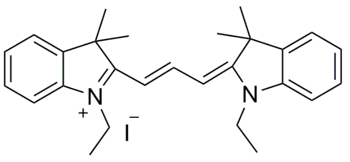
In this contribution the sensitivity of fluorescent hybrid organic/inorganic nanoparticles, prepared as previously reported,[18] to photo oxidation was tested under different experimental conditions and compared to the performances of the correspondent indocyanine dye in solution. Photodegradation experiments were performed under simulated solar illumination and the optical performances of the samples after irradiation were evaluated by UV-Vis absorption and emission spectroscopy, augmented by fluorescence lifetime measurements. The effect of different parameters, such as the absence or the presence of oxygen and the presence of TiO_2 on the photodegradation was also investigated.

Experimental

Materials

Fluorescent hybrid organic/inorganic mesoporous nanoparticles (fMSNP) were prepared by physical adsorption of indocyanine dye IRIS3 (Scheme I) (hereafter dye) within the channels of MCM-41 mesoporous nanoparticles, as reported elsewhere.[18] IRIS3 dye was kindly provided by Cyanine Technologies S.p.A. (Settimo Torinese, Italy). The uncoated TiO_2 Aeroxide P 25 (ca. 80% anatase, 20% rutile, BET area ca. 50 m^2g^{-1}) and Aerosil300 were from Evonik; all the other reagents were purchased from Sigma Aldrich and used as received, without any further purification.

Scheme I Chemical structure of indocyanine dye used in the present study



IRIS3

Methods

UV-Vis absorption and Diffuse Reflectance UV-Vis spectroscopy

UV-Vis absorption spectroscopy measurements were carried out on a Varian-Cary300 BIO instrument.

DR-UV-Vis spectra were taken with a Varian-Cary 5000 instrument equipped with an integrated sphere for measurement on solid samples in the diffuse reflectance mode. The reflectance spectra were then elaborated by using the Kubelka-Munk function.

Fluorescence

Photoemission and excitation steady-state spectra were acquired using a Horiba Jobin Yvon Fluorolog3 TCSPC spectrofluorimeter equipped with a 450 W Xenon lamp and a Hamamatsu R928 photomultiplier. The spectral response was corrected for the spectral sensitivity of the photomultiplier. Solutions and suspensions were kept in contact with air, because dissolved oxygen was expected to be quite ineffective as quenching agents toward fluorophores with lifetimes shorter than 5 ns[25] as typically exhibited by indocyanine dyes. Fluorescence lifetimes were measured using a time-correlated single photon counting (TCSPC) technique (Horiba Jobin Yvon) with an excitation source, NanoLed, at 455 nm (Horiba) and at an impulse repetition rate of 1 MHz at 90° to a TBX-4 detector. The detector was set to 570 nm with a 5 nm band pass. The instrument was set in the Reverse TAC mode, where the first detected photon represented the start signal by the time-to-amplitude converter (TAC), and the excitation pulse triggered the stop signal. DAS6 decay analysis software was used for lifetime calculation.

Photodegradation tests

Photodegradation experiments were performed on IRIS3 water solutions (2.00 μM concentration) and fMSNP water suspensions (1.5 mg/mL, corresponding to ca. 2.8 μM IRIS3 concentration, on the basis of 1mg/g IRIS3/fMSNP loading) under solar illumination. Irradiation was carried out using a solar light simulator MASTER TL-D90 Graphica 36W/956 ISL, Philips. The lamp had 0.9 Wm^{-2} power emission of radiation, measured, in the same experimental conditions, with CO.FO.ME.GRA. power meter.

An aliquot (10.0 mL) of each sample was introduced in Pyrex® glass cells closed with a screw cap and irradiated for different time intervals (0, 1, 2, 3, 4 hours) under magnetic stirring (RO 5, IKA, Staufen, Germany) at a distance of 2.75 cm from the solar simulator.

In order to study the influence of TiO_2 photocatalytic activity on cyanine degradation, TiO_2 (0.025% w/w with respect to dye content) was added to the fMSNP suspensions upon sonication. Irradiation was carried out under the same conditions previously adopted for the samples without TiO_2.

In order to evaluate the influence of oxygen on photodegradation processes, all the experiments were also performed in nitrogen atmosphere. The samples were de-aerated by bubbling/insufflating high purity N_2 gas into the glass cells for 15 s in dark; the cells were then hermetically sealed and irradiated. The estimation of the photodegradation was made on the basis of both DR-UV-Vis measurements (performed on solid sample, after centrifugation and drying in the dark) and steady-state fluorescence measurements (performed on suspension).

Results and Discussion

General properties of the fMSNPs

fMSNPs were prepared by physical adsorption of indocyanine dye IRIS3 within the pores of MCM-41 nanoparticles (see ESI for details); the obtained hybrid material exhibited a quasi-spherical particle morphology with an average particle size of ca. 100±23 nm and regular and ordered cylindrical channels with hexagonal symmetry. A representative High Resolution Transmission Electron Microscopy (HRTEM) image of the sample is reported in figure 1. According to the results from gas-volumetric analyses (N_2 adsorption/desorption isotherms at liquid nitrogen temperature), as expected fMSNP showed a type IV isotherm, typical of mesoporous materials with one-dimensional cylindrical channels[26,27] and a SSA (Specific Surface Area) of ca. 900-1000 m^2/g with average pore diameter of ca. 3.4 nm (see ESI for details). IRIS3 dye molecules were inserted within the pores of MCM-41 nanoparticles at a low loading (1.0 mg/g) which ensure the maintenance of the photophysical properties of the dye without occurring of aggregation or self quenching phenomena.[18,21]

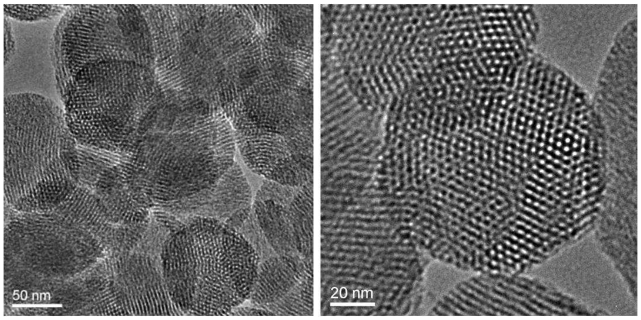


Fig.1 HRTEM images of the fMSNP sample

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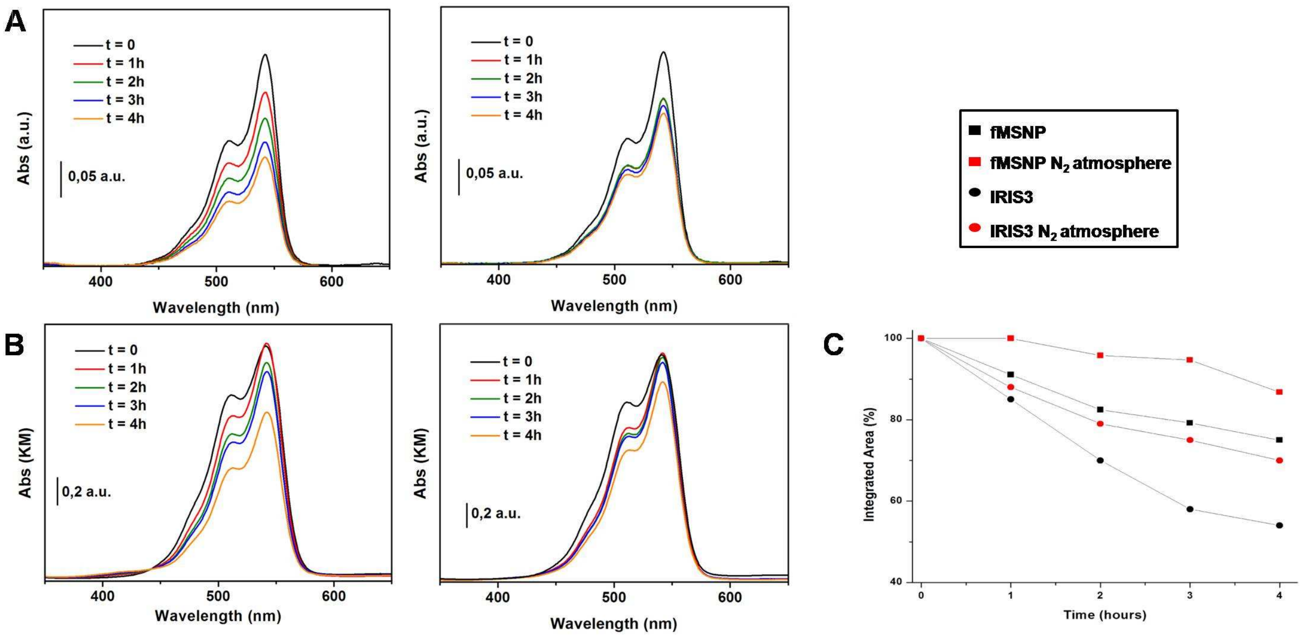

Fig.2A) Absorption spectra of dye water solution and B) DR-UV-Vis spectra of fMSNP water suspension taken at different time intervals during the irradiation, in the presence (left) and in the absence (right) of O_2; C) Plot of the abs/DR-UV-Vis intensity vs time of irradiation

Photodegradation tests

The evaluation of photodegradation extent was carried out on both the sample suspension by steady-state fluorescent measurements and the dried samples by DR-UV-Vis spectroscopy. Steady state measurements were carried out on the fMSNP water suspensions after the photodegradation experiments, without any dilution. As a consequence, the IRIS3 concentration range investigated was similar both in IRIS3 solutions and in fMSNP suspensions. It was not possible to measure absorption spectra of fMSNP suspensions because the contribution of scattering of silica nanoparticles was severely affecting the goodness of transmission measurements, so absorption profile of fMSNP samples were derived by DR-UV-Vis measurements on dry samples.

The estimations obtained by the two methods are in good agreement, hence for the sake of comparison with the data recorded on dye solution, only the data obtained by DR-UV-Vis measurements are reported within the text whilst steady-state fluorescence data are reported in the ESI file.

The absorption spectra of dye solutions, under both air and N_2-saturated conditions, recorded at different time intervals during the visible light irradiation are shown in figure 2, section A.

In the same figure, section B, DR-UV-Vis spectra recorded on fMSNP irradiated in the same time-frame are reported.

The dye absorption maximum is observed at ca. 540 nm both in water solution and in fMSNP, indicating a negligible effect of the confination within the pores of MCM-41 on the UV-Vis absorption features of the dye.[18,28] In both cases the intensity of the absorption/DR-UV-Vis band decreases along with the increase in time of irradiation. In figure 2C the absorbance/DR-UV-Vis taken at any time interval is plotted against the time; the absorbance/DR-UV-Vis values are normalized with respect to the non irradiated sample.

Concerning the dye in solution, in the presence of air (O_2) ca. 18%, 30%, 41% and 48% of the dye degrades after 1, 2, 3 and 4 hours, respectively. On the other hand, when irradiation is carried out in N2-saturated conditions the loss of substance registered after 4 hours of irradiation corresponds only to the 30% ca. In the case of the fMSNP suspension, we registered a total loss of substance after 4 h of irradiation of the 34% in presence of air, whilst the photodegradation is strongly reduced when the suspension is de-aerated before irradiation: ca. the 87% of the dye is preserved at the end of the irradiation.

It is worth noting that the protective effect obtained by the encapsulation within the pores of MCM-41 NPs is higher than the effect of the absence of molecular oxygen dissolved in the indocyanine dye solution.

In order to investigate the effect of the TiO_2 photocatalytic activity on the photodegradation of the cyanine dye in solution and encapsulated into fMSNP, photodegradation tests were performed in the presence of 0.025% w/w TiO_2. As shown in figure 3A, in the presence of TiO_2 an irradiation time of 4 minutes is enough to have a complete degradation of the dye in

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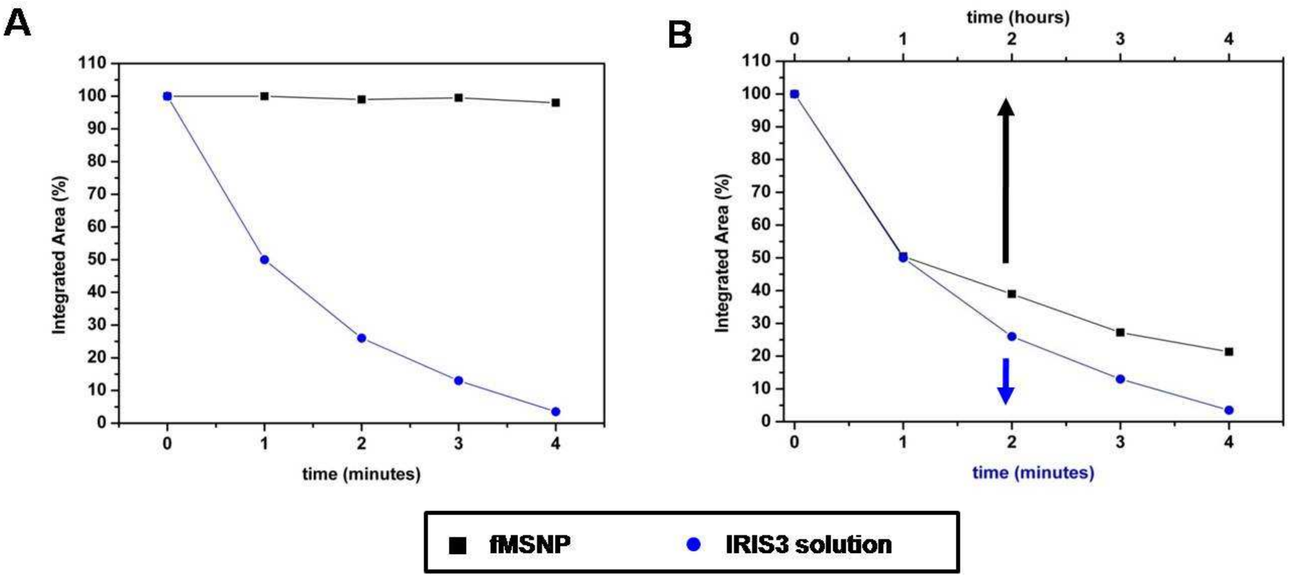

Fig.3 Plot of the abs/DR-UV-Vis intensity vs time of irradiation in the presence of TiO_2 and O_2: A) in a 4 minutes time-frame; B) comparison of 4 minutes (circles) and 4 hours (squares) time-frame

solution. In the same time-frame no degradation of the dye is detectable in fMSNP; only after 4 hours of irradiation a significant photodegradation is achieved (figure 3B).

Fluorescence lifetimes of the dye molecule in solution and of the fMSNP in suspension were measured at any time interval during the irradiation (0, 1, 2, 3, 4 h). Lifetime data are reported in table 1. For the sake of clarity only the values taken at the beginning and at the end of irradiation are reported; the complete list of lifetime data is provided in the ESI material.

The fluorescence decay of the dye in solution followed monoexponential kinetics, characterized by a lifetime of 0.24 ns. On the contrary, fMSNP are characterized by emission decay traces well fitted by biexponential decay function. The cyanine dye entrapped within the pores of MCM-41 NPs are therefore characterized by two different lifetime values (τ_1=0.60 ns; τ_2=1.70 ns). Both the lifetimes of the fMSNP are longer than the value that characterizes the correspondent dye in solution. This is due to the fact that the interaction with the silica surface restricts the vibrations and rotations of the dye molecules, thus reducing their non-radiative transitions. Furthermore, due to the dispersion within the channels of the inorganic host, the energy loss caused by the dye molecule collisions and dye-solvent molecule interactions is reduced and the fluorescence lifetime prolonged.[18,30]

The presence of two different lifetime values is a clear evidence that the dye molecules in the composite system have experience of two distinct microenvironments which affect in different extent their performances. The longer lifetime (τ_2=1.70 ns) could be assigned to a family of dyes which are much more constrained, whereas the shorter lifetime (τ_1=0.60 ns) could be due to cyanine molecules which are more exposed to the external environment. Previous work[28] carried out on non porous silica nanoparticles demonstrated that for dyes having structure and polarity similar to the IRIS3 dye used in the present study, two distinct dye molecules fractions were identified on the basis of the fluorescence lifetime distribution, one of which was located at the surface of non porous silica nanoparticles. In that case the location at the surface was demonstrated by means of solvatochromism experiments. Due to the non homogeneous distribution of silanol groups in MCM-41 type materials[31], different silica microenvironments (and then different cyanine dye populations) can be distributed in different manner in the nanoparticles, e.g at the entrance of the pores and more deeply into the pores, on the external surface and inside the pores, etc. Hence, in the present case, the spatial distribution of the cyanine molecules within the composite system cannot be determined univocally. In order to have a better insight into the distribution of dye molecules in the fMSNP system we investigated a composite system in which IRIS3 molecules were physically adsorbed on the surface of non porous silica particles (Aerosil300, Evonik; see ESI for details). This situation should mimic that of the dye eventually attached to the outer surface of MCM-41 nanoparticles. The fluorescence lifetime profile of this sample is well fitted by a monoexponential decay function, with a lifetime value of 0.67 ns (χ^2=1.09); this value is consistent with the shorter lifetime found in the fMSNP sample and can be considered as a confirmation of the possible location of a fraction of the cyanine molecules on the outer surface of MCM-41 nanoparticles. This results are in agreement with the behaviour described by Cohen and co-workers in the case of similar systems in which a phtalo-cyanine derivative was studied in interaction with MCM-41 and Al-MCM-41.[32,33]

When looking at the lifetime data reported in table 1 for the fMSNP sample irradiated in suspension in presence of air it can be noted that before the irradiation the fraction of dye molecules characterized by the shorter lifetime value accounts for ca. the 60% of the whole luminescent molecules (the longer lifetime values being characteristic of the remaining 40% of dye molecules). After 4 hours of continuous irradiation the populations are inverted, with the shorter lifetime associated with only the 42% of the whole cyanine dye molecules, whilst the 58% of the dyes are characterized by longer lifetime. This behaviour can be explained as a selective photodegradation of the cyanine molecules more exposed to the external environment and to the reactive species formed in solution after irradiation, which are those characterized by a shorter lifetime, as previously stated.

Table 1. Fluorescence lifetime data

Sample	Irradiation time	τ_1 (ns)	%	τ_2 (ns)	%	χ^2
Dye	-	0.24	100	-	-	1.12
fMSNP (air)	0h	0.60	60	1.70	40	1.09
	4h	0.62	42	1.75	58	1.05
fMSNP (N_2)	0h	0.60	60	1.70	40	1.11
	4h	0.60	58	1.70	42	1.09
fMSNP (TiO_2)	0h	0.60	60	1.70	40	1.08
	4h	0.60	47	1.74	53	1.04

Furthermore, no changes in the lifetime absolute values were registered, thus confirming the good dispersion of the dye molecules within the pores/on the external surface without occurrence of quenching phenomena or aggregation.[18] In the case of quenching phenomena or aggregation, in fact, the removal of dye molecules (by either washing or degradation) should lead to an enhancement of the lifetime values for the remaining dye molecules as a consequence of the reduced probability of deactivation through interaction between neighbouring dye molecules. A similar trend is exhibited also in the case of the fMSNPs suspension kept in suspension in the presence of TiO_2. On the contrary, the irradiation of the fMSNP sample in suspension in N_2-saturated conditions does not cause any significant variations in the fluorescence lifetime values, mainly because, as stated before, the amount of dye which undergoes photodegradation is low.

Conclusions

In summary, the protective effect of the siliceous mesoporous host matrix towards photo oxidation of fluorescent guest molecules was investigated under different experimental conditions. fMSNP prepared by physical adsorption of IRIS3 indocyanine dye within the pores of preformed MCM-41 NPs exhibited an outstanding photostability. In particular, the stability of the dye in the presence of TiO_2 was increased from minutes to hours due to the confination within the siliceous mesoporous host. Furthermore, the analysis of the fluorescence lifetime data evidenced a higher sensitivity to photo oxidation of the cyanine molecules characterized by shorter lifetime, which resulted to be more exposed to the external environment and to the reactive species formed in solution after irradiation.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [Emission spectra of dye molecule in solution and of fMSNP suspensions, complete set of fluorescence lifetime data, other characterization data of fMSNP.]. See DOI: 10.1039/b000000x/

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Table of Contents artwork