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Photochromic fluorescent diarylethene nanocrystals grown in sol–gel thin films

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ABSTRACT

Nanocrystals of two diarylethene compounds, 1,2-bis(2-ethyl-5-phenyl-3-thienyl)perfluorocyclopentene (D1) and 1,2-bis(3-methyl-2-thienyl)ethene (D2), were grown in sol–gel thin films and their optical properties (fluorescence and photo-conversion) were compared to that of diarylethene microcrystals.

1. Introduction

Organic photochromic materials have attracted much attention because of their potential applications to rewritable optical memory media and photo-optical switches [1]. Among various types of photochromic dyes, diarylethene derivatives are the most promising molecules for these applications because they undergo ring-closing and ring-opening reactions when irradiated with UV and visible light with an excellent thermal stability of both isomers and a high degree of fatigue resistance [2–5]. Moreover, when they are included in supramolecular assemblies, they can exhibit a large number of interesting properties: for instance, photoregulation of luminescence when they are combined to tetraazaporphyrins [6], photoregulation of Lewis acidity when a boron atom is incorporated in the photochromic backbone [7] and in general multiple photoswitching when they are associated to polymers, chiral molecules, liquid crystals or molecular magnets [8,9]. Thus, the potential applications offered by the diarylethenes cover a large field: optical data storage, optical limiters, switches, logic gates, molecular wires or sensors [10]. Photochromic diarylethenes exhibiting large two-photon cross sections are now particularly investigated for 3D optical storage. Indeed, two-photon absorption allows a better localization of excitation volume and a higher discrimination against the surrounding background [11].

However, to design optical devices, photochromic reactions should take place in the solid state, such as dyes dispersed in polymer matrices [12], in amorphous solids [13] or in single crystals [14–16]. Irie and co-workers demonstrated that using single crystals for photochromism was the most favourable approach because side fatigue reactions were strongly suppressed and the reaction efficiency was found to be extremely high [17]. Moreover, various diarylethene derivatives are found to undergo reversible photochromic reactions in the single-crystalline phase [18–20]. Despite of these major advantanges, the industrial development of molecular crystals is limited due to delicate growths and shaping (slicing, polishing..) for the design of optical devices.

In order to overcome the basic mechanical drawbacks of organic crystals, we engineered new hybrid organic-inorganic materials through a simple and generic preparation of stable organic nanocrystals grown in sol–gel thin films [21–23]. We chose the high versatility of the sol–gel chemistry based on silicon alkoxide precursors and also its ability to obtain stable inorganic host-matrices close to the room temperature. Thus, sol–gel process can be involved in the shaping (dispersion, grafting, nanocrystallization…) of a wide variety of organic fluorophores. It has been extensively shown that the sol–gel chemistry can be used to encapsulate organic molecules in inorganic matrices, bulk or thin films [24]. In all these previous works, dyes were dispersed within or grafted onto sol–gel

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networks [25]. Our process is based on the confined nucleation and growth of organic crystals in the pores of sol–gel glasses. The crystalline nature of these nanoparticles was previously evidenced for different dyes by differential scanning calorimetry [26] (presence of a melting point), by advanced spectroscopy techniques [27] and by electron microscopy [28]. These nanocomposite films not only combine the optical properties of organic crystals (luminescence, NLO properties, photochromism [22,29,30]) with those of amorphous inorganic materials (high stability, transparency, convenient processing and shaping), but also the advantages of the crystalline phase. Indeed the small size of the nanocrystals leads to the preparation of non-scattering materials for visible and IR wavelengths; secondly, through the dye nanocrystallisation, the chemical stability and photostability of organic phases are also improved in comparison to isolated molecules dispersed in solutions or in solid matrices such as sol–gel or polymers. Finally, because a nanocrystal is an aggregation of about 10^4 to 10^8 organic molecules organized in a crystalline network, the light excitation can be spread in these nanoparticles that can induce a behaviour of single fluorescent emitter [22]. This paper concerns the preparation and the photophysical properties of two types of diarylethene nanocrystals grown in sol–gel films.

2. Experimental section

We selected two organic dyes, 1,2-bis(2-ethyl-5-phenyl-3-thienyl)perfluorocyclopentene and 1,2-bis(3-methyl-2-thienyl) ethene respectively named D1 and D2 in this paper which exhibit photochromic properties in the crystalline state. The organic synthesis of these two diarylethenes was previously described [19,20].

D1 and D2 nanocrystals grown in sol–gel thin films were obtained by spin-coating. We first prepared solutions containing solvent, dye, silicon alkoxides and water, which are inserted in airtight flasks. In this work, solutions were obtained from an equimolar mixture of two alkoxide precursors: TMOS (tetramethoxysilane) and MTMOS (methyltrimethoxysilane). The sols were prepared under neutral conditions ($pH \approx 7$) to avoid protonation that can induce an optical properties changing of organic molecules. The process was a one-step hydrolysis and condensation of alkoxide precursors, which was performed during 15 h at 80 °C for D1 and 15 h at 60 °C for D2 with one water molecule per alkoxide function $-OR$ ($h = [H_2O]:[-OR] = 1$). THF (analytical grade) was used to dissolve the organic dyes and to mix the hydrolysis water with alkoxide precursors, the molar ratio [solvent]:[alkoxide], s, was equal to 5. Heating allowed to rapidly dissolve the organic powder and to enhance the hydrolysis and condensation kinetics leading to the formation of silicate chains dispersed in the solution. This sol ageing was necessary to control the sol viscosity, around 10–20 cps, to obtain high quality films, to ensure the control of the sol–gel coating thickness and the particle growth and to avoid the nanocrystal coalescence. The resulting sols, which were stable during several weeks, were deposited at room temperature by spin-coating onto thin microscope slides with a rotation speed of 4000 rpm during 10 s. Thus, films of around 0.5 μm thick were prepared. These nanocomposite coatings were then stabilized by annealing at 80 °C. Dye concentration, expressed as the molar ratio $d = [\text{dye}]:[\text{Si}] \approx 5 \times 10^{-3}$, where [Si] is the concentration of alkoxide molécules, depends on the dye solubility in THF, the nature of the host matrix and on particles sizes which are necessary to be achieved. The latter was targeted here between 200 and 500 nm in diameter to favour nanocrystals characterizations by epifluorescence microscopy.

All the optical characterizations were done at room temperature. UV irradiation on D1 sol–gel films was performed using a 150 W xenon lamp with a power density of 2 mW/cm^2 applied during 30 s. The lamp was associated to a glass filter of 100 nm bandwidth, centered at 335 nm. The corresponding absorption spectra were recorded with a Lambda-9 Perkin–Elmer spectrophotometer. Spatially resolved fluorescence experiments on an individual nanocrystal were performed using a Zeiss Axiovert 200 microscope in which an optical fibber of 50 μm diameter joined the optical image plane of an ×100 objective (numerical aperture 1.3) to an Ocean Optic spectrometer. D2 crystals and sol–gel films were irradiated with a mercury lamp filtered at the wavelength of 365 nm (4 mW/cm^2 on sample). They were probed with an unpolarized halogen lamp of sufficiently low energy to avoid the photo-induced back reaction. The whole spectrum is recorded within less than 2 s after the end of the irradiation process. The spectral window is [400–800 nm] and the point spread function is 250 nm.

3. Results and discussion

We define by D1A the open-ring isomer of D1 and by D1B the closed-ring one (Fig. 1, top scheme). Same notation was used for D2 (Fig. 1, bottom scheme). D1 was found to undergo a thermally reversible photochromic reaction in solution as well as in the single-crystalline phase [20]. Upon irradiation with ultraviolet light, solution containing D1A molecules and single-crystal D1A turned blue along with the formation of closed-ring isomer D1B (Fig. 1, top scheme). The blue solution and single crystal returned colourless by irradiation with visible light ($\lambda > 500$ nm) or by heating above 100 °C. The bleaching is due to the cycloreversion of D1B to D1A. The D2 single crystal undergoes the same photochromic reaction (Fig. 1, bottom scheme) in the single-crystalline phase and emits fluorescence only from the open-ring form isomer D2A. Upon ultraviolet light irradiation, the colourless solution or the corresponding crystal change to yellow D2B. Thus, the formed close-ring isomer is non-fluorescent.

Fig. 2 shows optical transmission images of D1 nanocrystals in sol–gel films. Before irradiation (Fig. 2a), nanocrystals appeared colourless. D1 nanocrystals turned clearly blue upon irradiation with 335 nm light (Fig. 2b). In previous work, Irie and co-workers [20] showed that light could penetrate the crystal as deep as 400 μm and change the color. To confirm this photo-induced conversion in nanocrystals, absorption spectra of sol–gel films (Fig. 2c) were recorded. The absorption maximum in the visible region was found at 650 nm. The residual absorption found in this

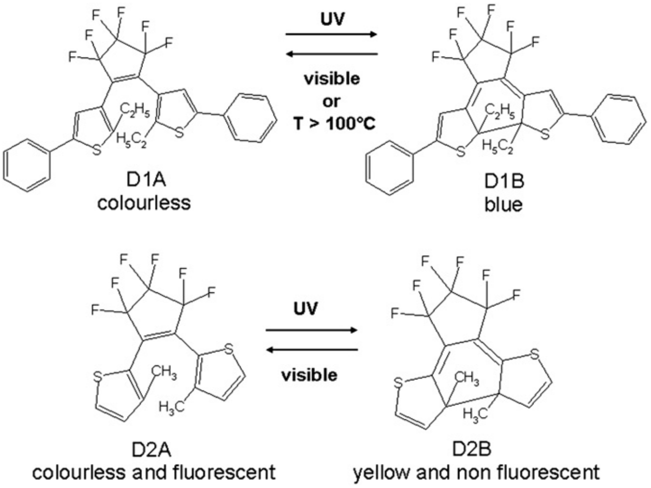

Fig. 1. Photochromic reactions for 1,2-bis(2-ethyl-5-phenyl-3-thienyl)perfluorocyclopentene (D1A-D1B) and for 1,2-bis(3-methyl-2-thienyl)ethene (D2A-D2B).

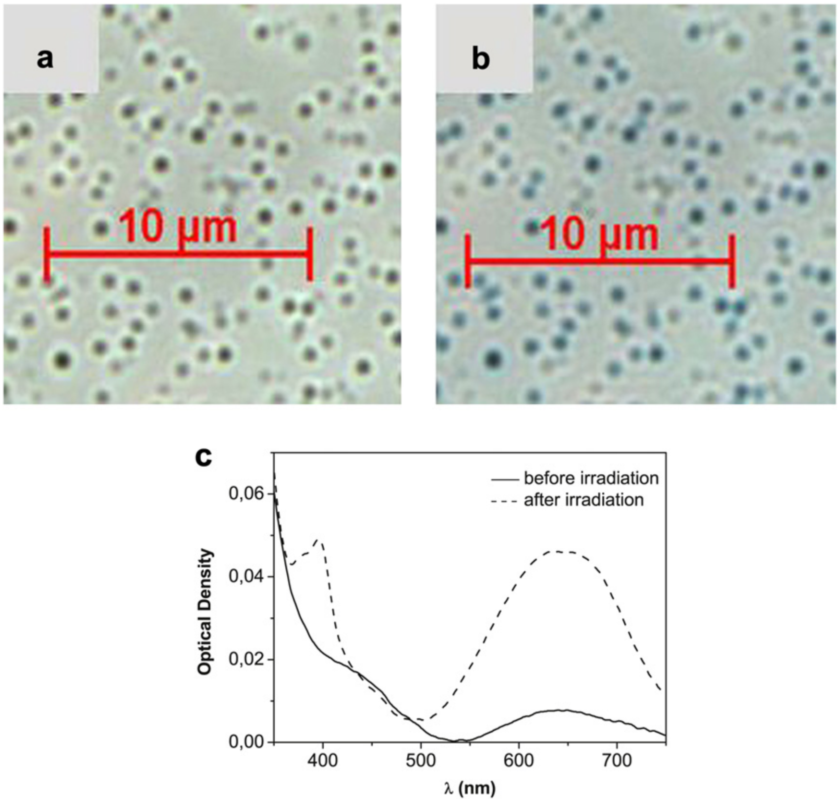

Fig. 2. Optical transmission images of D1 nanocrystals grown in sol–gel film (a) before irradiation, (b) after irradiation and (c) corresponding absorption spectra.

region before irradiation was due to spontaneous irradiation during samples preparation. The absorption apex was the same as that of D1B registered for single crystal [20]. This confirms that the blue color is due to the formation of D1B isomer nanocrystals. Furthermore, sol–gel films returned colourless by irradiation with visible light ($\lambda > 500$ nm). Absorption spectra of D2 nanocrystals are not presented because of their small optical densities in the blue, that were to difficult to measure with our spectrometer.

D2 individual nanocrystals in sol–gel film were observed by epifluorescence microscopy (Fig. 3a). When excited at 365 nm, the open-ring isomer D2A in single crystal is fluorescent, and the close-ring D2B is not fluorescent [18,19]. Thus, we can assume the formation of D2A fluorescent isomer nanocrystals in sol–gel matrix. Particles size distribution was found to be between 200 nm and 350 nm. The fluorescence spectrum of one individual D2 nanocrystal was compared with that of one single D2 microcrystal (Fig. 3b). The fluorescence maximum was observed at 525 nm for the individual nanocrystal. A slight shift to longer wavelengths was thus observed compared to the fluorescence maximum of the single microcrystal (515 nm). This is due to the matrix polarity effect in the case of D2 nanocrystals in sol–gel film. To confirm this result, the fluorescence maximum of the D2 molecule dissolved in THF, which is the polar solvent used in the preparation of the sol–gel thin films, was also measured (Fig. 3b). In this case, the apex was also found at 525 nm. For comparison, the fluorescence maximum in 3-methylpentane (non-polar solvent) was measured at 500 nm [18]. These results are consistent with the fluorescence red-shift of the open-ring isomer D2A when the environment

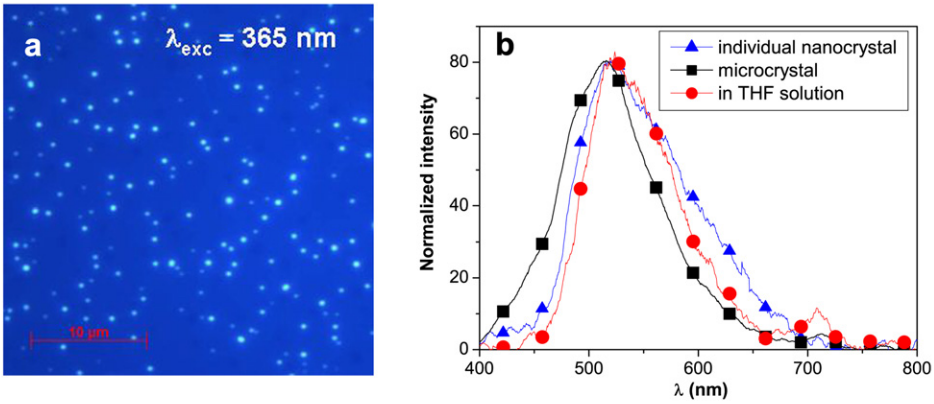

Fig. 3. (a) Fluorescence image of D2 nanocrystals in sol–gel film and (b) normalized fluorescence spectra of an individual nanocrystal compared to the fluorescence emission of a single microcrystal and of D2 powder dissolved in THF solution.

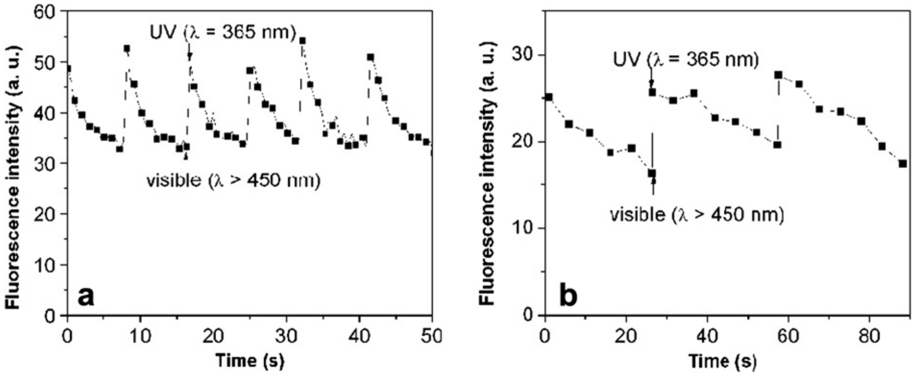

Fig. 4. Evolution of fluorescence signal during coloring-bleaching steps of (a) one D2 microcrystal and (b) one individual D2 nanocrystal.

polarity increases. The evolution of the fluorescence emission during coloring and bleaching cycles for one single D2A microcrystal and an individual D2A nanocrystal were studied (Fig. 4). The mercury lamp was used to excite the nanocrystal fluorescence as well to induce the photochromic reaction. During the coloring step, nanocrystals or single crystals were irradiated by UV light, and then were bleached with visible light. The fluorescence decrease is due to the conversion of D2A isomer to non-fluorescent closed-ring isomer (D2B) in single-crystalline phase. Indeed, upon irradiation with 365 nm light, colourless crystals of D2A form turn yellow and are not any more fluorescent [19]. In the case of the single microcrystal, the fluorescence emission reached a plateau (Fig. 4a) around 34 (a.u.) and the maximum of intensity was of 50 (a.u), thus we obtain a conversion rate of D2A to D2B isomer of 30%, in the single crystal. This is similar to the 20% decrease obtained previously by CW light irradiation, and to the 50% decrease obtained by confocal laser microscopy [19]. Fig. 4b confirms that the photoeffect is also present in the nanocrystalline phase and is reversible. Indeed, D2A was found to undergo a reversible photochromic reaction in nanocrystals as well as in the single microcrystalline phase as previously shown. In this case, the fluorescence decrease was close to 40%. The recovery time is much faster than the writing time. Thus, the ring-opening process is much more efficient than the ring-closing process.

The photo-conversion speed measured for nanocrystals is lower than for free microcrystals. Indeed, for nanocrystals, the confinement effect of the sol–gel matrix may delay the photochromic reaction of diarylethene molecules. This confinement is due to strong hydrogen bonds formed between the dye molecules of the nanocrystal surface with sol–gel matrix, particularly between fluorine atoms and silanol groups (C–F···H–O–Si hydrogen bonds).

4. Conclusions

Our generic process used to prepare nanocrystals of organic dyes in sol–gel thin films was successfully extended to diarylethenes compounds which are photochromic in the crystalline phase. Thus, we obtained nanocrystals of D1 and D2 molecules grown in sol–gel thin films. The sol–gel host matrix was found to maintain photochromism properties of nanocrystals. We clearly attempted to identify nanocrystals under their D1A, D1B, D2A and D2B forms depending on lightening conditions. Indeed, upon UV irradiation, D1A and D1B nanocrystals in sol–gel films underwent reversible photochromic reactions. On the other hand, the host matrix plays the crucial role of a one-step and easy shaping of optical devices compared to large organic crystals while keeping their photochromic properties. This advantage is also coupled to the strong improvement of dye stability: higher mechanical properties of the silicate thin films compared to brittle molecular crystals and better dye photostability through its crystallization referred to dispersed molecules in sol–gel or polymer thin films. Furthermore, size effect of nanocrystals on photochromic properties would lead to interesting filtering properties or three dimensional optical recording developments.

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