

Cite this: *J. Mater. Chem.*, 2012, **22**, 21857

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A luminescent steroid-based organogel: ON–OFF photoswitching by dopant interplay and templated synthesis of fluorescent nanoparticles†Valeria C. Edelsztein,^a Elizabeth A. Jares-Erijman,^a Klaus Müllen,^c Pablo H. Di Chenna^{*b} and Carla C. Spagnuolo^{*a}

Received 24th July 2012, Accepted 12th September 2012

DOI: 10.1039/c2jm34891h

The modulation of the fluorescence emission of a perylene dye between ON and OFF states was achieved with high efficiency by means of a diarylethene photochromic compound in an organogel medium. Fluorescent gels were prepared from a steroidal low molecular weight organogelator doped with the perylene fluorophore. The compatibility of the photochromic compound in this medium and the non-destructive readout capability were demonstrated. The dye doped organogel was further used as a template and an innovative method was employed to grow fluorescent silica spherical nanoparticles with physically and chemically admixed perylene dye.

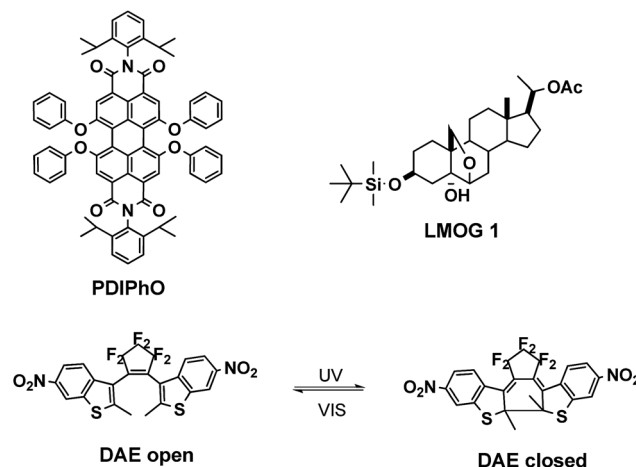
Materials science has found a promising new area of research in the development of low-molecular mass organogelators (LMOGs).^{1,2} The potential applications of such well-defined structures include catalysis, drug delivery, molecular electronics, and so forth.^{3–7} Among the LMOGs, steroid analogues with gelling properties have been used to prepare different soft functional materials.^{8–11} Recently, Edelsztein *et al.* have reported on the synthesis of a novel non-cholesterol steroid LMOG (**1**).¹² This organogelating pregnane steroid possesses a rigid and asymmetric structure due to the presence of a 6 β ,19 oxygen bridge (acting as a hydrogen bond acceptor) and a complementary hydrogen bond donor (hydroxyl group) at position 5 α . These functionalities together with the presence of a 3 β -*tert*-butyldimethylsilyl ether moiety covalently linked at C-3 make the structure unique among the steroidal LMOGs. The gels of LMOG **1** have been used for the *in situ* sol–gel polymerization of tetraethyl orthosilicate (TEOS).

The morphology of the silica nanoparticles so obtained could be controlled by choosing the reaction conditions. In the absence of a catalyst the slow polymerization leads to templated nanotubes of silica while the fast, base catalysed polymerization rendered silica nanospheres with high aspect ratio homogeneity.

On the other hand, perylene dyes are unique fluorophores due to their optical properties as well as high thermal and photochemical stability.¹³ These ultrastable dyes have found applications as organic super-conductors,¹⁴ photovoltaic cells¹⁵ and fluorescent bioprobes,¹⁶ among others. Some perylene structures have been successfully modified in order to get self-assembled organogels.^{17,18} In this study we work with the tetraphenoxylated perylene diimide derivative (PDIPhO, Fig. 1).

Photochromic compounds of the family of diarylethenes (DAEs) have been widely studied during the last few decades as memory materials, switching components in molecular devices and supra-molecular systems.^{19–21} DAEs have remarkable features such as high thermal stability and high fatigue resistance, which make them valuable material as optical components, especially as ON/OFF switches for the emission of fluorophores.^{22–26}

In this article we present a set of interesting results arising from experiments designed to explore the versatility and potentiality of the organogel (OG) from LMOG **1** as a functional material. These investigations include special optical properties such as ON–OFF

Fig. 1 Chemical structures of PDIPhO, LMOG **1** and DAE.

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† Electronic supplementary information (ESI) available: Synthesis of LMOG **1** and DAE. Description of steady-state and time resolved experiments. See DOI: 10.1039/c2jm34891h

fluorescence photoswitching achieved by dopant interplay in gels of LMOG **1** and the characterization of fluorescent silica nanospheres prepared from the luminescent organogel. We report on the photophysical studies of a donor–acceptor system comprising a perylene dye PDIPhO and a DAE derivative²⁷ as dopants in an optically transparent organogel of LMOG **1** in TEOS and *n*-hexane. We studied the changes in the optical properties of the perylene dye in the gel, the dependence of fluorescence emission with temperature, the influence of the dopant on the morphology of the gel and the modulation of the emission of the dye by the photochromic compound, through steady state and time resolved fluorescence techniques. The study of such a switching system, especially the photochromic behavior of DAE in the organogel matrix, is presented as a proof of principle for the development of an organogelator composed of a perylene derivative covalently bound to **1**, to build sensor systems and other photonic devices based on soft materials. We include in this communication a related application of the fluorescent organogel as a template for the preparation of emissive inorganic nanoparticles. This type of nano-structures have found extensive use in bioanalysis and biodetection and could be easily miniaturized for portable devices.²⁸ We envision future investigations on this gel–nanoparticle transformation with luminescent organogels highly pre-organized, *e.g.* with covalently bound dye.

The structure and morphology of the doped organogel

LMOG **1** was synthesized according to ref. 12 (see also the ESI†). Perylene doped organogels from TEOS and *n*-hexane were prepared by heating the suspensions until the solid dissolved and the solutions were cooled to room temperature. The morphology of the perylene doped organogel was analyzed by SEM observations of the xerogel fibers obtained from *n*-hexane. The images showed an entangled fibrillar network identical to that of the xerogel of **1** with fibers of the same length and width (Fig. S18†). This observation indicates that perylene does not intercalate between the steroid molecules and must be distributed in the liquid phase that is immobilized within the 3D self-assembled fibrillar structure of the gel.

Optical properties of the dye-doped organogel

The fluorescence emission maximum of PDIPhO in the OG from TEOS matched exactly the spectrum of the dye in solution while it was slightly shifted in the gel from *n*-hexane for comparison (Fig. S2 and S3†). The fluorescence intensity was similar in the OG compared to that in solution, suggesting that no aggregate formation of the dye takes place in the gel medium. The fluorescence lifetime of PDIPhO was determined to be 5.82 ns in solution and 5.77 ns in the neat OG. The fluorescence intensity of the perylene doped OG from TEOS decreased 35% when the temperature was raised from 10 °C to 100 °C (Fig. 2). T_g was estimated to be 68 °C from this measurement which is in accordance with the value determined from the DSC experiment (72 °C (ref. 12)). This experiment was also performed for a gel of LMOG **1** 1% in *n*-hexane with similar results: T_g (flu.) = 45 °C and T_g (DSC) = 52 °C.

The variation of the excitation spectrum with the temperature was also measured and no change was observed. This suggests that PDIPhO exists as monomers in the gel state similar to the sol state.

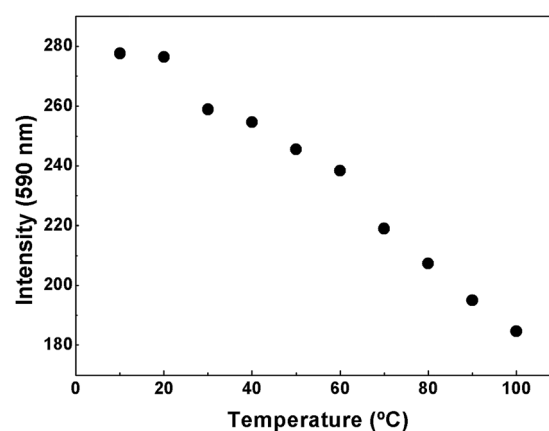


Fig. 2 Variation of the fluorescence intensity with temperature for a PDIPhO doped TEOS gel.

For the subsequent optical experiments we decided to work with OG from TEOS because it is far more stable than the OG from *n*-hexane, given the volatility of this solvent and the lower T_g .

For the OG 1% from TEOS doped with PDIPhO a value of steady state anisotropy (r_{ss}) of 0.045 was determined while it was 0.00 for the dye in solution, at 610 nm. When the gel was heated from 10 °C to 100 °C, r_{ss} decreased, indicating higher mobility of PDIPhO in the sol phase compared to that in the gel phase (Fig. S9†).

Photochromism in the organogel

The absorption spectra of the open and closed form of DAE were not affected by its inclusion in the gel matrix of the OG from TEOS (Fig. S10†). Upon irradiation of the gel using UV light (band pass filter of 340 nm) the photochromic conversion was observed and an absorption band around 560 nm appeared, which corresponds to the closed form of DAE along with a change in the colour of the gel from colourless to purple. Subsequent irradiation with visible light (long pass filter of 550 nm) decoloured the gel raising the absorption band of the open form at 313 nm.

Modulation of the fluorescence emission of the perylene dye

An OG 1% from TEOS doped with PDIPhO and DAE was prepared to study the quenching of the fluorescence emission of the dye by the presence of DAE in its closed form. The photochromic compound was embedded in the gel in its open form. Once the gel was formed, the sample was irradiated with UV light for 180 seconds. Increasing the irradiation time led to an increase in the amount of DAE closed form, with an absorption maximum at 560 nm, thus matching the emission of perylene. As a consequence an efficient overlap takes place yielding a high degree of quenching. The loss of fluorescence emission at 590 nm was 98.6%. As is shown in Fig. 3, the emission intensity can be gradually switched off by increasing the irradiation time with UV light. Once the OFF state was reached, the gel was irradiated with visible light for 30 seconds to recover the full emission intensity. This UV-Vis irradiation cycle between the two isomers of the DAE compound was repeated more than 20 times rendering reproducible ON–OFF states (Fig. 4).

A rather similar system can be tracked in the literature where a diarylethene compound is used to modulate the fluorescence emission

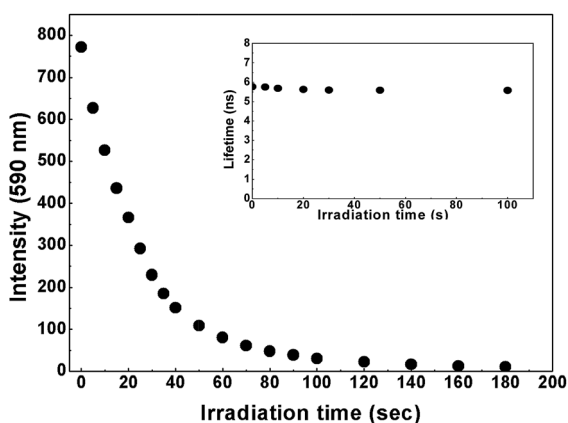


Fig. 3 Decrease of the fluorescence intensity of PDIPhO and fluorescence lifetime changes (inset) upon increasing irradiation times of the DAE open form with UV light.

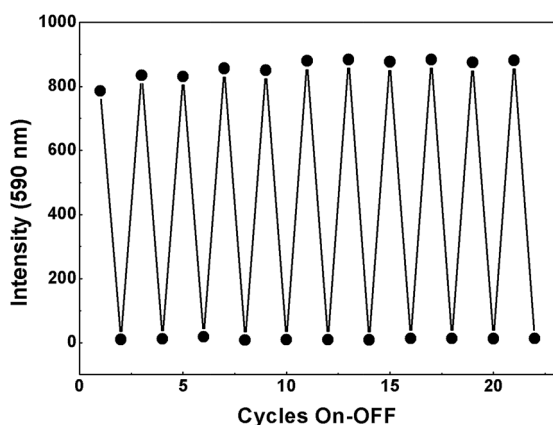


Fig. 4 ON-OFF photoswitching of the fluorescence of PDIPhO in the gel.

of an organogel but in this case the organogelator itself has an emissive behaviour, with absorption and emission activity in the UV and Vis region, respectively.²⁹ A significant quenching is also demonstrated although no further confirmation on the energy transfer mechanism is reported, such as time-resolved determinations. To investigate in our system whether the quenching was due to a radiative or non-radiative energy transfer process, we performed the quenching of the fluorescence by increasing the irradiation time with UV light and measured the fluorescence lifetime (τ) of PDIPhO in the gel. As can be seen from Fig. 3 (inset), τ is practically unmodified thus indicating the prevalence of a trivial radiative energy transfer between PDIPhO and DAE (closed form).

Non-destructive fluorescence readout

The fluorescence intensity at 590 nm did not change under continuous irradiation for more than 2 hours within the fluorimeter ($4 \mu\text{W cm}^{-2}$) (Fig. 5).

A very promising non-destructive readout capability is achieved in this system and the fluorescence emission modulation in the gel is good enough to achieve an efficient logic operation.

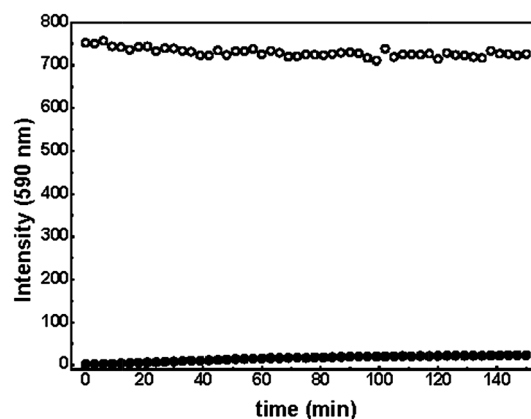


Fig. 5 Non-destructive fluorescence readout capability of both open (○)- and closed (●)-DAE isomers.

Templated synthesis of fluorescent silica nanoparticles

Organogels from LMOG **1** have been previously used as a template for the synthesis of high aspect ratio inorganic materials as silica nanotubes and nanospheres.¹² Fluorescent dye-doped silica nanoparticles have demonstrated excellent potential for use in advanced bioanalysis to facilitate deeper understanding of biology and medicine at the molecular level. In particular, silica nanoparticles have been applied to diagnostic and therapeutic applications in cancer and gene/drug delivery.²⁴ Integration of fluorescent dye-doped silica nanoparticles (FSNPs) with functional molecules using various surface modification techniques can bring about great improvements in bioapplications such as selective recognition, sensitive imaging, and reporting.

Regarding this aspect, we aimed at the preparation of fluorescent silica nanospheres by the *in situ* sol-gel polymerization process using the fluorescent organogels of LMOG **1** and PDIPhO described previously. Gels of LMOG **1** from TEOS doped with PDIPhO produced, after 5 days of base catalyzed sol-gel polymerization conditions, emissive spherical particles of silica with homogeneous size (200–300 nm) (Fig. 6a). The nanoparticles were exhaustively washed with methanol until no fluorescence emission was observed at 610 nm in the supernatant.

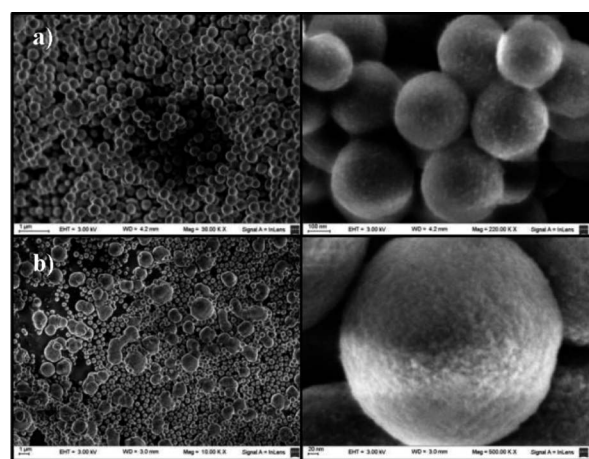


Fig. 6 SEM images of silica nanoparticles prepared by template synthesis from organogel. (a) PDIPhO doped silica Np; (b) PDI-APTES silica Np.

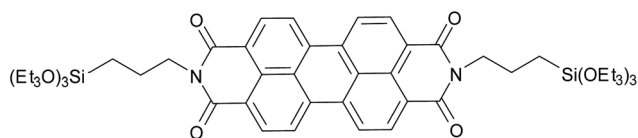


Fig. 7 PDI-APTES.

The fluorescence spectrum of the silica nanoparticles showed an emission band at 610 nm (Fig. S20†). The perylene dye successfully survived the conditions of the polymerization process. Schneider and Mu reported that alkoxy-silane modified perylene derivatives that could attach covalently to the silica matrix during the polymerization of TEOS enhance the solubility resulting in a higher concentration of the dye as well as its photostability.³⁰ As a first approximation to covalently bound fluorophore-silica nanoparticles, a simple alkoxy-silane-PDI (PDI-APTES, Fig. 7) was prepared from 3,4:9,10-perylenetetracarboxylic dianhydride and APTES, which as expected had lower solubility than the phenoxy-substituted perylene-tetracarboxydiimides. However, its solubility sufficed to incorporate it homogeneously in the sol-gel process under the same conditions as for the physically admixed PDI-PhO.

Morphologically, the nanoparticles obtained with the covalently attached dye are bigger (300–600 nm). After successive washings with methanol/ethanol, the particles showed an emission peak at 610 nm (Fig. S22†). Table 1 lists the main photophysical properties of both fluorescent nanoparticles in comparison with the free dyes. The fluorescence lifetimes of the dyes in the nanoparticles, whether covalently bound or physically admixed, had almost no change compared with the free dyes in solution. On the other hand, the steady state anisotropy (r_{ss}) rendered significant values for the dyes in the inorganic matrix, which reflects the difference in polarization between bound and non-bound states. This property has potential applications to use the nanoparticle as a probe for studying local viscosity in different media. Both types of fluorescent nanoparticles with perylene dye physically or chemically attached were also observed in a confocal microscope. Fig. 8 shows images of these nanospheres adsorbed onto a microscope slide. It can be seen that for doped nanoparticles, the image shows darker nanoparticles accounting for the loss of fluorescent molecules during the washes (Fig. 8b). In the case of PDI-APTES Nps the higher number of bright particles indicates the presence of covalent bonded PDI molecules that could not be eliminated by washing the material.

The biocompatibility of silica makes them promising for *in vivo* imaging applications. A further increase of the dye concentration in the nanoparticle could be reached by adding substituents at the bay position of perylene-3,4:9,10-tetracarboxydiimides, which is known to enhance even more the solubility. Such a derivative is under

Table 1 Photophysical properties of silica nanoparticles

	λ_{max}/nm	τ/ns	r_{ss}
PDI-APTES	567	4.3	0.00
PDIPhO	615	5.8	0.00
PDIPhO doped Np	611	5.5	0.36
PDI-APTES Np	611	4.9	0.20

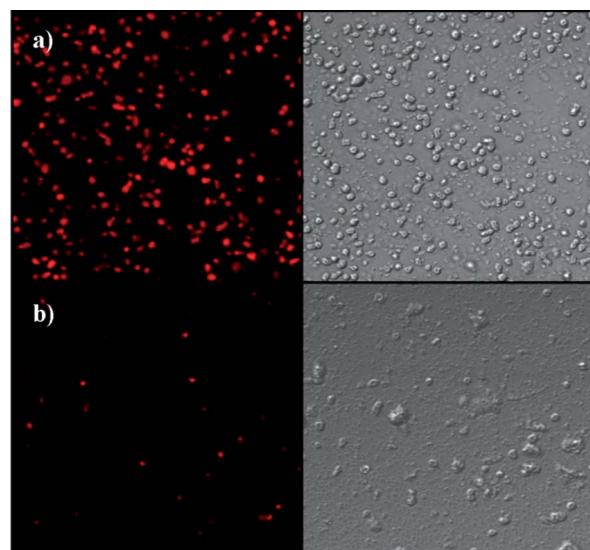


Fig. 8 LSM images of silica nanoparticles. (a) PDI-APTES silica Np; (b) PDI-PhO silica Np. Left: fluorescence; right: transmission.

preparation along with variations of the precursors of the inorganic matrix in order to achieve smaller nanoparticles.

Conclusions

We have established a simple photoswitchable system with ultrastable optical components such as a perylene dye and a diarylethene photochromic compound, integrated in an organogel matrix. A highly efficient energy transfer process occurs between PDIPhO and DAE included in the organogel. The ON-OFF photoswitching process is performed by alternative cycles of irradiation of the gel with UV-Vis light. The organogel based on LMOG **1** offers a suitable medium for optical applications. These results provide the proof of principle for further studies on more controlled and complex systems. The preparation of a compound which combines perylene dye linked covalently to the steroid fragment is currently under progress. Such a compound will be studied as a single organogelator molecule in order to develop soft materials with optoelectronic functions. We have established a method for the preparation of doped and covalently bound perylene-silica nanoparticles by the *in situ* sol-gel polymerization of TEOS gels of LMOG **1**. The nanospheres so obtained were fluorescent and stable proving the presence of the fluorophore unit in the nanoparticles. These results are the first step toward the preparation of functionalized, highly fluorescent photostable nanomaterials from organogels of LMOG **1** with promising biomedical and biotechnological applications.

Acknowledgements

This work is dedicated to Elizabeth Jares, in her memory and in acknowledgment of her passion for life and work, inspired leadership and unflinching support. We thank Francisco Guaimas for the microscopy images and Guillermo Menéndez for advice on time resolved measurements. The authors are grateful to ANPCyT (Argentina), CONICET (Argentina), University of Buenos Aires and Max Planck Society for financial support. V.C.E. is also grateful to CONICET for a post-doctoral fellowship.

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