Electronic Supplementary Information for:

A Luminescent Steroid-based Organogel: ON-OFF Photoswitching by Dopant Interplay and Templated Synthesis of Fluorescent Nanoparticles

Valeria C. Edelsztein, Elizabeth A. Jares-Erijman, Klaus Müllen, Pablo H. Di Chenna and Carla C. Spagnuolo

General

The solvents were dried and purified by standard methods prior to use. All starting materials were purchased from Sigma-Aldrich and were used as received. N,N'-bis(2,6-diisopropylphenyl)-1,6,7,12-tetraphenoxy-perylene-3,4:9,10 acid diimide (PDIPhO) was supplied by BASF AG. Corrected fluorescence emission spectra were obtained on a Cary Eclipse spectrophotometer equipped with two Czerny-Turner monochromators and a 15 W Xenon pulse lamp (pulse width: 2-3 us, power: 60-75 kW). When temperature control was necessary, the cell was thermostated using the Thermal Application of the ADL software. Steady state anisotropy parameters were obtained using manual polarisers methodology. Kinetic anisotropy parameters and fluorescence lifetimes were determined by time-correlated single photon counting (TCSPC) in a HORIBA Jobin Yvon IBH 5000U apparatus. The excitation source was a NanoLED 559 nm and detection was performed with a TBX-PS detector with a long pass emission filter Schott OG590. Fluorescence decays were recorded using an impulse repetition rate of 1 MHz. Acquisition was terminated when the peak signal reached 10000 counts. DAS6v6.2 decay analysis software or Nonlinear ModelFit routine of Mathematica (Wolfram Research) were used for lifetime calculations. The quality of fit was judged by the value of χ^2 and visual inspection of the residuals.

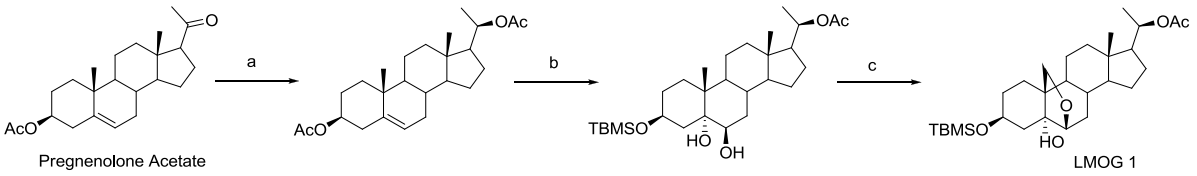
The light source for the photochromic switching was a Lumatec Superlite SUV-DC-P irradiator equipped with a 200 W DC Super Pressure Short Arc Mercury lamp, time selector for irradiation and fiber optic coupled output. Two filters were used for fine wavelength selection. DAE closed form was reached using a UV filter (340 nm) and an ambar filter (590 nm) for the reverse opening reaction. Light source power at 366 nm was approximatedly154 μW and 9 mW at 547 nm.

Microscopy images were obtained with an Olympus IX 81 with a confocal modulus FV 1000. Excitation was applied with a HeNe 543 nm laser with emission filters at 580/40 nm and an objective UPlanSapo 60X W NA 1.20. A Carl Zeiss NTS SUPRA 40 FEG-Scanning electron microscopy spectrometer was used for taking the SEM pictures. A small portion of the solid sample (xerogel or silica) was attached to the holder by using a conductive adhesive carbon tape. Prior to examination the xerogel was coated with a thin layer of gold.

Synthesis of the organogelating pregnane steroid LMOG1

The organogelating pregnane steroid (LMOG 1) was synthetized by us from pregnenolone acetate according to the literature previously reported.[1] The photochemical reaction was carried out using dichloromethane and

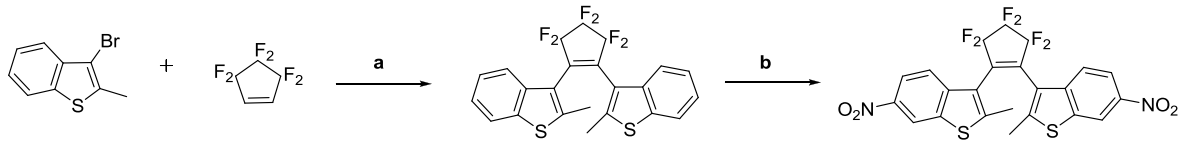
1,2-dichloroethane instead of dichloromethane and carbon tetrachloride as solvents. LMOG 1 was identified by spectroscopic methods.



Scheme S1. a) i) $NaBH_4$, MeOH, DCM, **ii)** Ac_2O, py; **b) i)** HCOOH, H_2O_2, **ii)** MeOH, NaOH, **iii)** TBMSCl, imidazole, DMF; **c)** DIB, DCM, 1,2-DCE, I_2, hυ.

Synthesis of the diarylethene DAE

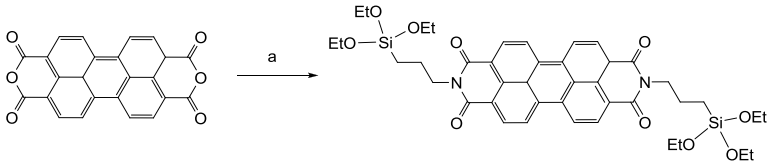
The diarylethene photochromic compound was synthetized by us following the standard procedure.[2]



Scheme S2. a) *n*-BuLi, Et_2O, -78ºC, Ar; **b)** HAcO, Ac_2O, fuming nitrate, 10ºC.

Synthesis of PDI-APTES

The perylene diimide PDI-APTES was synthetized by us following the standard procedure.[3]



Scheme S3. a) APTES, n-propanol/water, reflux

Perylene PDIPhO-doped organogel

Absorption spectra of PDIPhO

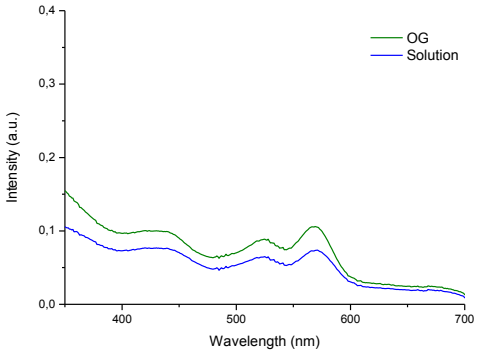


Figure S1. Absorption spectra of PDIPhO in solution and in the OG from TEOS

Optical properties

For the determination of the optical properties of the perylene PDIPhO in solution, 25 μL from a 93 μM solution of PDIPhO in acetone were dissolved in 0.5 mL of the organic solvent (*n*-hexane or TEOS) with a final concentration of 4.7 μM of the PDIPhO. Then, the solution was placed in a cuvette (solution in *n*-hexane or TEOS).

For the determination of the optical properties of the perylene PDIPhO in the organogels, a mixture of the gelator LMOG **1** (5 mg, 1 wt %), the organic solvent (*n*-hexane or TEOS) (0.5 mL) and the perylene (25 μL from a 93 μM solution of PDIPhO in acetone, final concentration: 4.7 μM) in a closed flask was heated and shaken until the solid was dissolved. Then, the hot solution was placed in a cuvette and cooled to room temperature to form a stable gel (OG from *n*-hexane or OG from TEOS).

To determine the gelation temperatures (Tg) of the OG from *n*-hexane and the OG from TEOS the fluorescence intensity of a gelled sample was measured while the temperature of the sample was raised gradually. The Tg values data were taken as the points of largest slope (inflexion points) in plots of fluorescence intensity versus temperature[4] (S5 and S6).

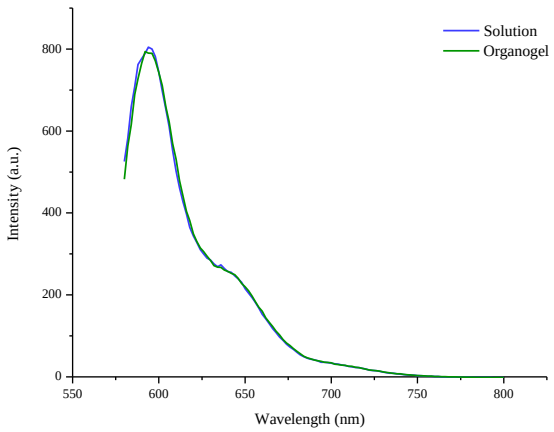


Figure S2. Fluorescence emission spectra of PDIPhO in solution and in the OG from TEOS. λexc = 570 nm

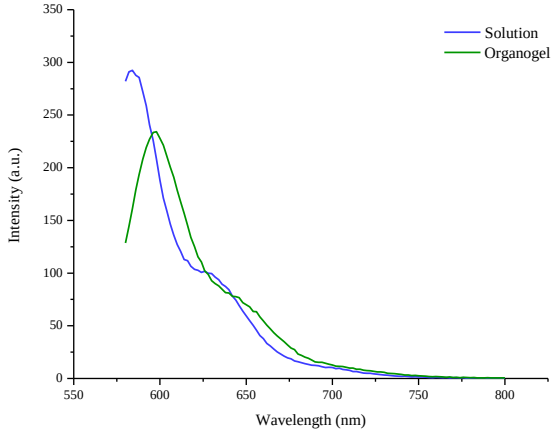


Figure S3. Fluorescence emission spectra of PDIPhO in solution (*n*-hexane) and in the OG from *n*-hexane. λexc = 570 nm

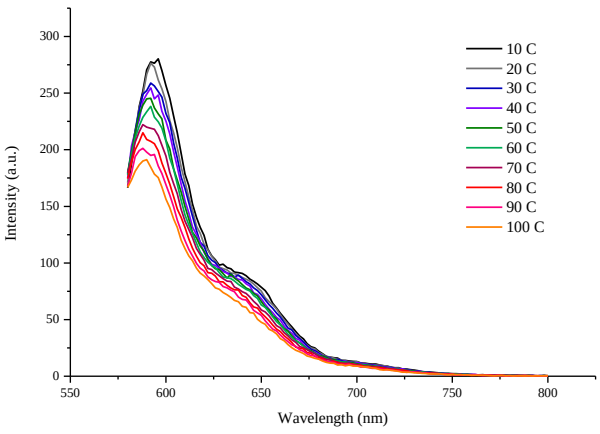


Figure S4. Fluorescence emission spectra of PDIPhO in the OG from TEOS. Temperature was raised from 10 to 100ºC. λexc = 570 nm

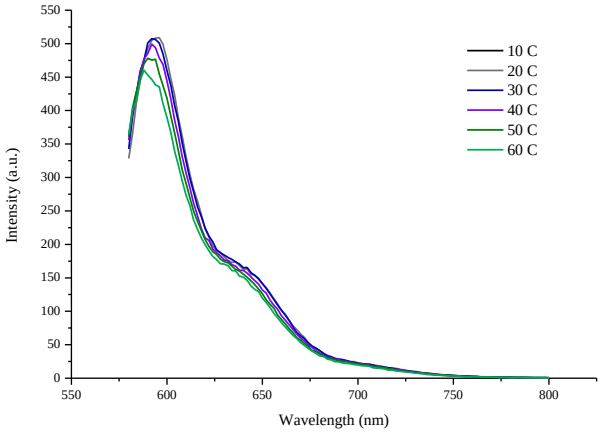


Figure S5. Fluorescence emission spectra of PDIPhO in the OG from *n*-hexane. Temperature was raised from 10 to 100ºC. λexc = 570 nm

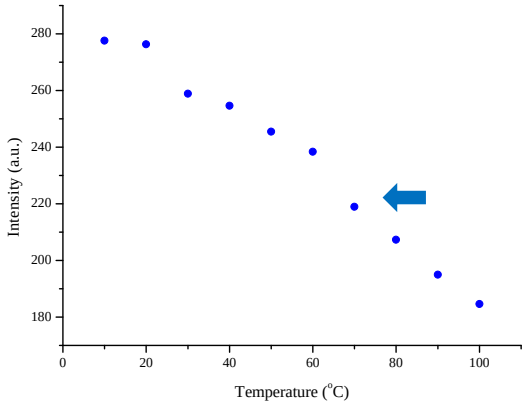


Figure S6. Estimated Tg (68°C) of PDIPhO in the OG from TEOS.

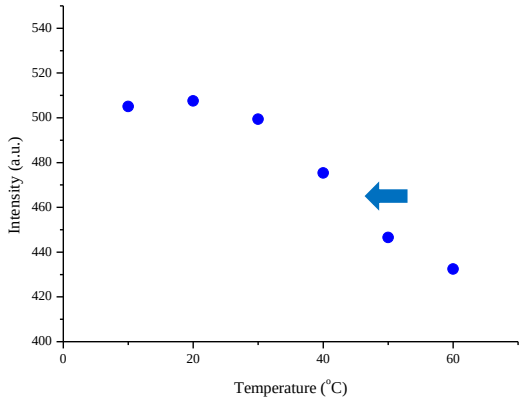


Figure S7. Estimated Tg (45°C) of PDIPhO in the OG from *n*-hexane.

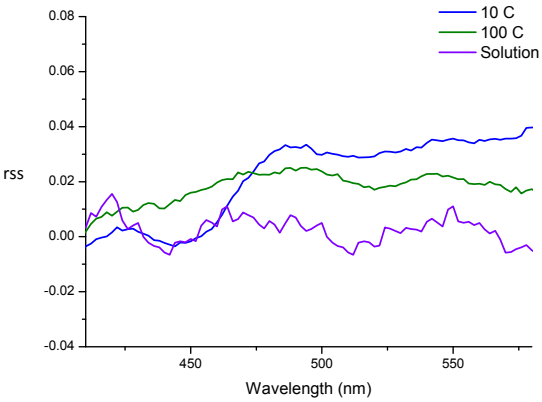


Figure S8. Steady state anisotropy of PDIPhO in the solution and in the OG from TEOS at 10ºC and 100ºC. λem = 600 nm

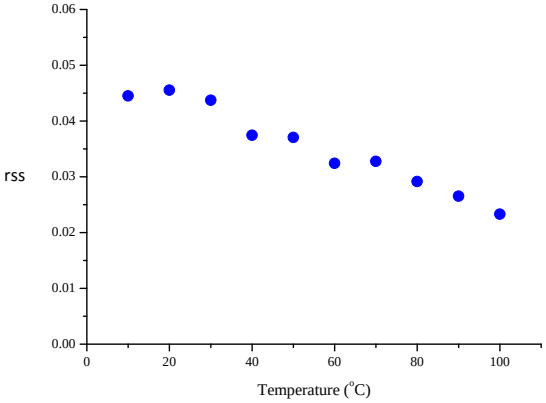


Figure S9. Steady state anisotropy of PDIPhO in the OG from TEOS as a function of temperature

Modulation of the fluorescence emission of the perylene dye by DAE

Absorption spectra of DAE

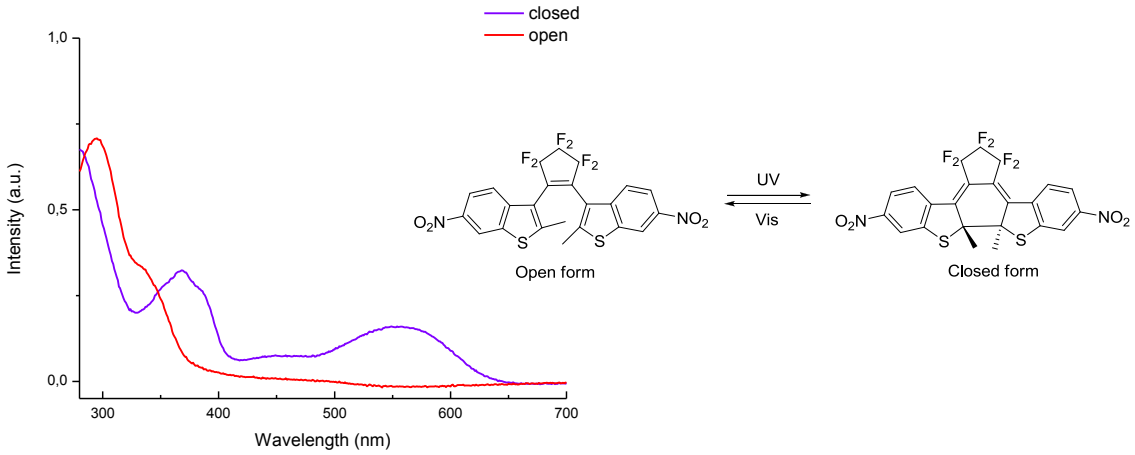


Figure S10. Absorption spectra of DAE closed and open form in the OG from TEOS

Photochromism in *n*-hexane solution and in the OG from *n*-hexane

For the analysis of the modulation of the fluorescence emission of PDIPhO by the DAE in solution, 25 μL

from a 93 μM solution of PDIPhO in acetone and DAE (amount required for each experiment) were dissolved in 0.5 mL of *n*-hexane with a final concentration of 4.7 μM of the PDIPhO. Then, the solution was placed in a cuvette.

For the analysis of the modulation of the fluorescence emission of PDIPhO by the DAE in the organogel, a mixture of the gelator LMOG 1 (5 mg, 1 wt %), *n*-hexane (0.5 mL), the perylene (25 μL from a 93 μM solution of PDIPhO in acetone, final concentration: 4.7 μM) and DAE (0.7 mg, 2.5 mM) in a closed flask was heated and shaken until the solid was dissolved. Then, the hot solution was placed in a cuvette and cooled to room temperature to form a stable gel (OG from *n*-hexane).

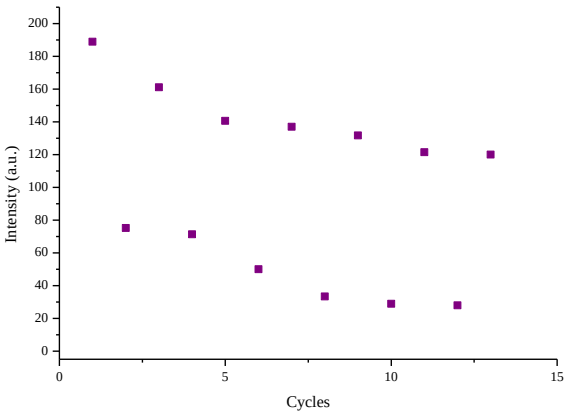


Figure S11. Modulation of the fluorescence emission intensity of PDIPhO in *n*-hexane solution through UV-Vis irradiation cycles (180 s) between the DAE closed and open form at λmax = 598 nm

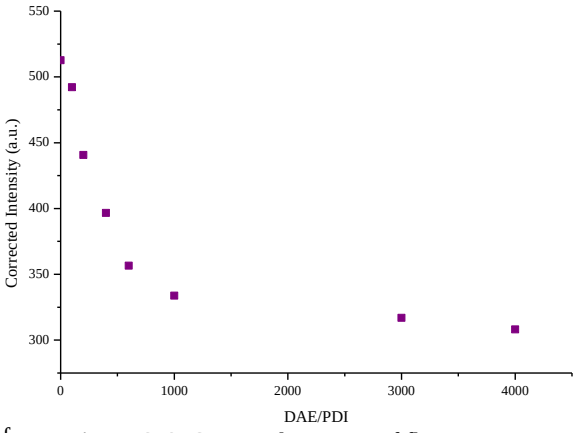


Figure S12. Corrected intensity of fluorescence emission of PDIPhO in *n*-hexane solution. Titration with increasing concentrations of the closed form of the DAE; λexc = 570 nm

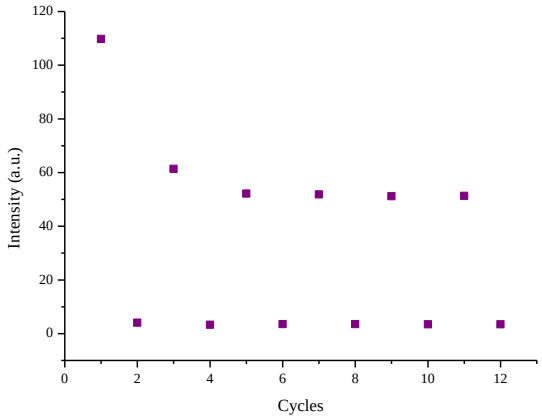


Figure S13. Modulation of the fluorescence emission intensity of PDIPhO in the OG from *n*-hexane through UV-Vis irradiation cycles (180 s) between the DAE closed and open form at λmax = 606 nm

The quenching efficiency was calculated as follows:

$$\% \text{ quenching} = (1 - I/Io) * 100\%$$

where Io= fluorescence intensity of PDIPhO at λmax without UV irradiation of the DAE (100% open form)

I = fluorescence intensity at λmax after UV irradiation of the DAE during 180 s (100% closed form)

The quenching percentage for the fluorescence emission of PDIPhO by the DAE in solution of *n*-hexane was 60.1% while in the OG from n-hexane this percentage raised up to 97%. Besides, when the PDIPhO was in the OG fibrillar network the modulation of its fluorescence emission by the DAE resulted more stable.

Photochromism in TEOS solution and in the OG from TEOS

For the analysis of the modulation of the fluorescence emission of PDIPhO by the DAE in solution, 25 μL from a 93 μM solution of PDIPhO in acetone and DAE (0.7 mg, 2.5 mM) were dissolved in 0.5 mL of TEOS with a final concentration of 4.7 μM of the PDIPhO. Then, the solution was placed in a cuvette.

For the analysis of the modulation of the fluorescence emission of PDIPhO by the DAE in the organogel, a mixture of the gelator LMOG 1 (5 mg, 1 wt %), TEOS (0.5 mL), the perylene (25 μL from a 93 μM solution of PDIPhO in acetone, final concentration: 4.7 μM) and DAE (0.7 mg, 2.5 mM) in a closed flask was heated and shaken until the solid was dissolved. Then, the hot solution was placed in a cuvette and cooled to room temperature to form a stable gel (OG from TEOS).

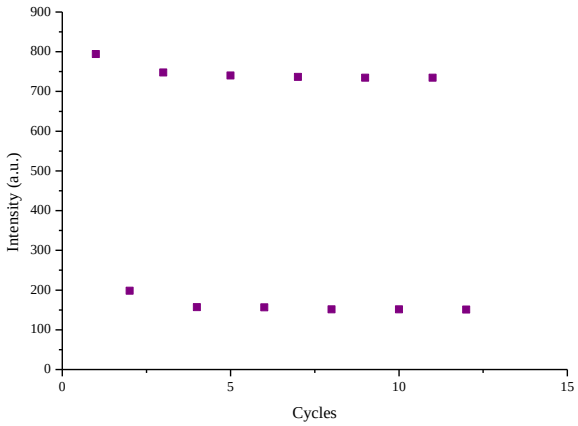


Figure S14. Modulation of the fluorescence emission intensity of PDIPhO in TEOS solution through UV-Vis irradiation cycles (180 s) between the DAE closed and open form at λmax = 592 nm

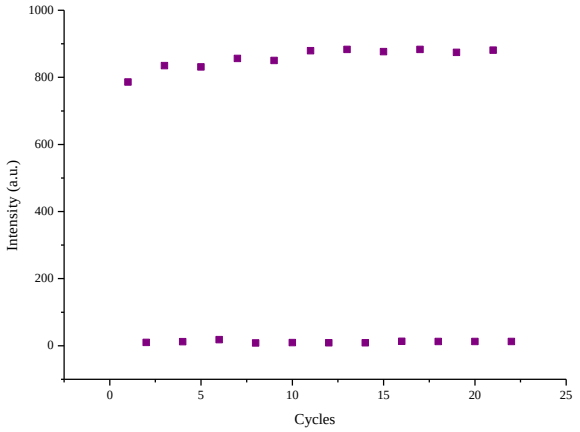


Figure S15. Modulation of the fluorescence emission intensity of PDIPhO in the OG from TEOS through UV-Vis irradiation cycles (180 s) between the DAE closed and open form at λmax = 596 nm

Similarly to the *n*-hexane situation the quenching percentage for the fluorescence emission of PDIPhO by the DAE in solution of TEOS was 75.0% while in the OG from TEOS this percentage raised up to 98.6%. Besides, when the PDIPhO was in the OG fibrillar network the modulation of its fluorescence emission by the DAE resulted even more stable than in *n*-hexane.

The quenching efficiency in stationary state and resolved in time was calculated as follows

$$\% \text{ quenching} = (1 - It/Io) * 100\%$$

Where Io= fluorescence intensity of PDIPhO at λmax without UV irradiation of the DAE (100% open form)

It = fluorescence intensity at λmax after UV irradiation of the DAE during t seconds (t from 5 to 180)

The quenching efficiency resolved in time was calculated as follows

$$\% \text{ quenching} = (1- \tau_t/\tau_o) * 100\%$$

where τ_t = PDIPhO lifetime without UV irradiation of the DAE (100% open form)

It = PDIPhO lifetime after UV irradiation of the DAE during t seconds (t from 5 to 100)

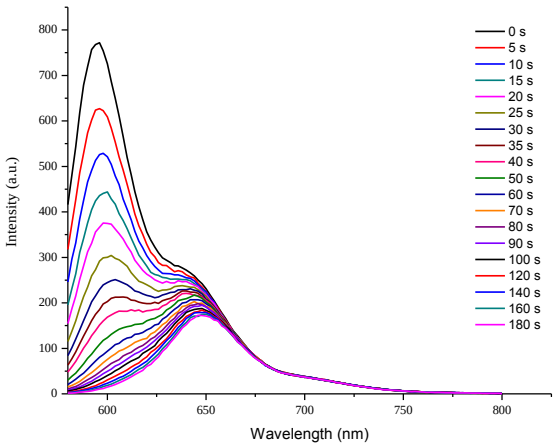


Figure S16. Fluorescence emission spectra of PDIPhO gradually switched off by increasing the irradiation time with UV light of the DAE in the OG from TEOS.

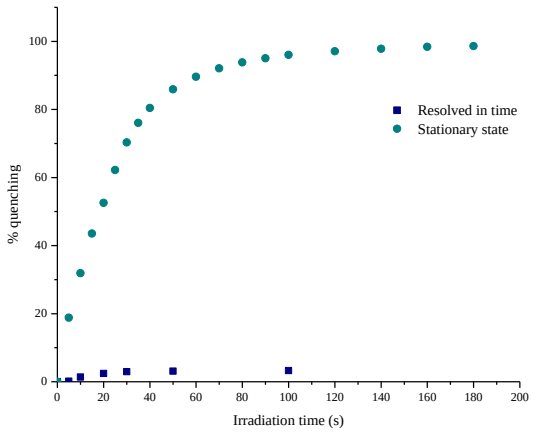


Figure S17. Comparison of the quenching efficiency of the DAE closed form in the OG from TEOS as a function of irradiation time in stationary state and resolved in time.

Morphology

A Carl Zeiss NTS SUPRA 40 FEG-Scanning electron microscopy spectrometer was used for taking the SEM pictures. A small portion of the solid sample (xerogel from *n*-hexane) was attached to the holder by using a conductive adhesive carbon tape. Prior to examination the xerogel was coated with a thin layer of gold.

The xerogel was prepared by drying under high vacuum a frozen thin film of the gel (0.2 wt % 1 in n-hexane) over liquid nitrogen for 12 h and then allowed to reach slowly to room temperature.

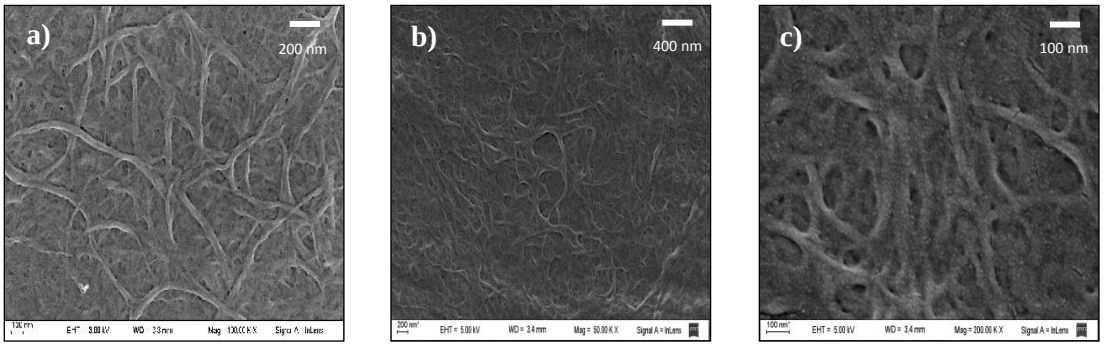


Figure S18.SEM images of the **a)** Xerogel fibers obtained from *n*-hexane **b), c)** perylene doped xerogel from *n*-hexane

Perylene PDIPhO-doped nanoparticles

LMOG 1 (5 mg) was dissolved in *n*-hexane (0.35 mL), TEOS (0.15 mL) and PDIPhO (25 μL from a 93 μM solution of PDIPhO in acetone, final concentration: 4.7 μM) with addition of benzylamine (3 μL) and water (3 μL) as catalysts by heating and shaking. The solution was cooled to room temperature until gelation was observed and then left at room temperature for 5 days. Subsequently, the sample was dissolved in dichloromethane, the precipitated solid was centrifuged, and washed once with dichloromethane.

Morphology

The SEM images of the product showed spherical particles of silica with a very homogeneous size (200 nm) larger than the non-doped nanoparticles (40-45 nm).

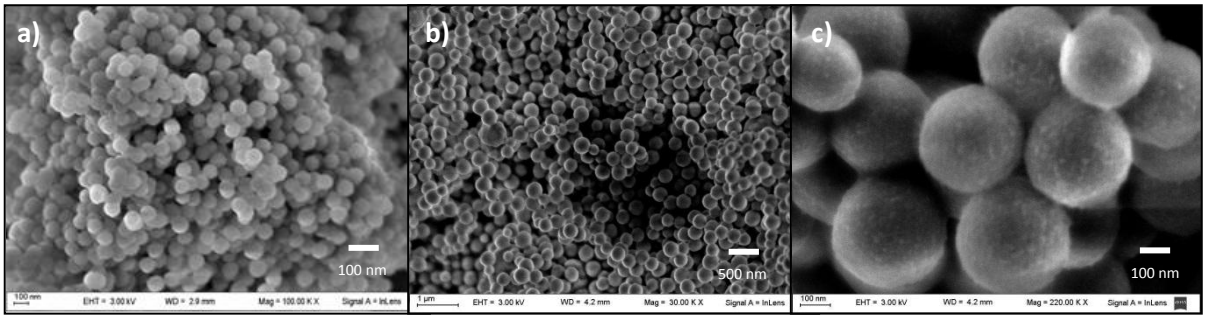


Figure S19.SEM images of **a)** nanoparticles obtained from *n*-hexane/TEOS **b), c)** perylene doped nanoparticles obtained from *n*-hexane/TEOS

Optical properties

For the determination of the optical properties the perylene PDIPhO doped nanoparticles (2 mg) were suspended in methanol (500 μL), centrifuged and the supernatant was discarded. Then, the pellet was suspended in ethanol (500 μL), centrifuged and the supernatant solution fluorescence was measured. This sequence was repeated until no fluorescence emission was detected in the supernatant. Then, the pellet was suspended in ethanol (200 μL) and its fluorescence emission was measured. All measures were taken using a long pass emission filter of 590 nm (λexc: 550 nm).

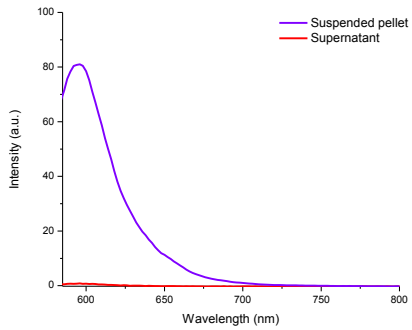


Figure S20. Fluorescence emission spectra of the perylene PDIPhO doped nanoparticles suspended in ethanol and the final supernatant.

Nanoparticles with perylene PDIPhO covalently attached

OG1 (10 mg) was dissolved in n-hexane (0.7 mL) and PDI-APTES (40 μL from an oversaturated solution of PDI-APTES in acetone and 0.3 mL of an oversaturated solution in TEOS) with addition of benzylamine (6 μL) and water (6 μL) as catalysts by heating and shaking. The solution was cooled to room temperature until gelation was observed and then left at room temperature for 5 days. Subsequently, the sample was dissolved in dichloromethane; the precipitated solid was centrifuged, and washed once with dichloromethane.

Morphology

The SEM images of the product showed spherical particles of silica with non-homogeneous size (variation between 150 and 600 nm) and clusters of larger size.

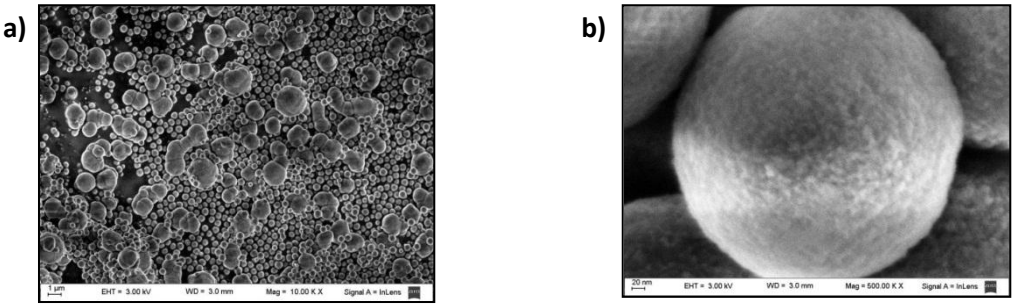


Figure S21.SEM images of **a)** nanoparticles obtained from *n*-hexane/TEOS with PDI-APTES **b)** close-up of one of the smaller nanoparticles

Optical properties

For the determination of the optical properties the perylene PDIPhO covalently attached nanoparticles (2 mg) were suspended in methanol (500 μL), centrifuged and the supernatant was discarded. Then, the pellet was suspended in ethanol (500 μL), centrifuged and the supernatant solution fluorescence was measured. This sequence was repeated until no fluorescence emission was detected in the supernatant. Then, the pellet was suspended in ethanol (200 μL) and its fluorescence emission was measured. All measures were taken using a long pass emission filter of 590 nm (λexc: 550 nm).

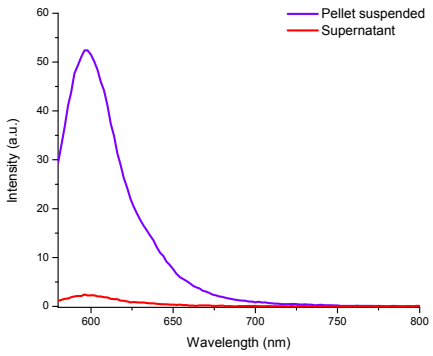


Figure S22. Fluorescence emission spectra of the PDIPhO covalently attached nanoparticles suspended in ethanol and the final supernatant.

References

1. V. C. Edelsztein, G. Burton and P. H. Di Chenna, *Tetrahedron*, 2010, **66**, 2162-2167.
2. S. Kobatake, M. Yamada, T. Yamada and M. Irie, *J. Am. Chem. Soc.*, 1999, **121**, 8450-8456.
3. M. Schneider and K. Mu, *Chem. Mater.*, 2000, **12**, 352-362.
4. L. Lu, T. M. Cocker, R. E. Bachman and R. G. Weiss, *Langmuir*, 2000, **16,** 20-34.