Electronic Supplementary Material (ESI)

Reversible Photoswitching of dye-doped core-shell nanoparticles

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Chemicals: All reagents and solvents were used as received without further purification: non ionic surfactant Pluronic® F127, tetraethyl ortosilicate (TEOS, 99.99%), chlorotrimethylsilane (TMSCl, ≥98%), and Acetic acid (≥99.7%) were purchased from Aldrich. Reagent grade dichloromethane, and NaCl were purchased from Fluka. A Milli-Q Millipore system was used for the purification of water (resistivity ≥18 MΩ).

Photoswitch synthesis

0.424 g (1.0 mmol) of 1,2-Bis(5-formyl-2-methylthiophen-3-yl)perfluorocyclopentene,[1] 1.250 g (3.0 mmol) (Ethoxycarbonylmethyl)triphenylphosphoniumbromide and a spatula tip of 18-crown-6 were dissolved in 20 ml dichloromethane. 0.360 g (6.0 mmol) freshly ground potassium hydroxide was added. The reaction mixture was stirred for 3 h at room temperature, filtered and evaporated. The resulting syrup was dissolved in cyclohexane/ethyl acetate 7:3 and filtered over silica gel and evaporated to yield 340 mg (0.63 mmol) 1,2-Bis(*E*-3-ethylacrylato)thiophen-3-yl)hexafluorocyclopentene.

Synthesis of the triethoxysilane derivative R: Triethoxysilane derivative of rhodamine B R was synthesized as previously reported.[2]

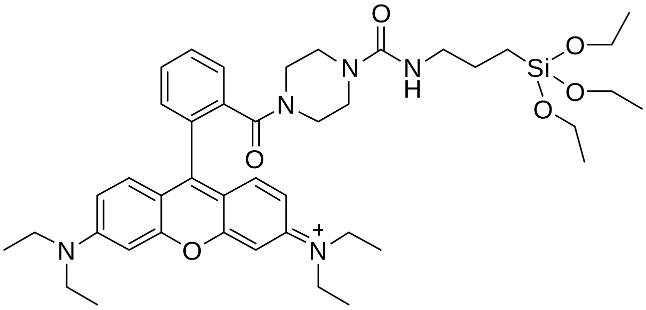

Figure S1 Chemical structure of triethoxysilane derivative of rhodamine B **R**.

Nanoparticles Synthesis. We synthesized core-shell silica-PEG (polyethylene glycol) NPs by adapting previously reported procedures. [2]

In a typical preparation, 200 mg of Pluronic F127 and the desired amount of dye (0.004 mmol) were carefully solubilized with 1-2 mL of dichloromethane in a 20 mL glass scintillation vial. The solvent was evaporated from the homogeneous solution by means of a gentle nitrogen flow and subsequently under vacuum at room temperature. NaCl (137 mg) was added to the solid residue, and the mixture was solubilized at 25 °C under magnetic stirring with 3200 µL of acetic acid 1.00 M. TEOS (360 µL, 1.61 mmol) was then added to the resulting aqueous homogeneous solution, followed by TMSCl (20 µL, 0.16 mmol) after 180 min. The mixture was kept under stirring for 20 h at 25 °C before dialysis/UF treatments. The dialysis purification steps were carried out versus water on a precise amount of NPs solution (1500 µL) finally diluted to a total volume of 5 mL with water.

Ultrafiltration and Dialysis Experiments. Nanoparticle UF was carried out by means of Amicon Ultra 0.5 mL centrifugal filters (RC 100 KDa, 10000 rpm / 10 min).

Dialysis was performed versus water at room temperature under gentle stirring with regenerated cellulose dialysis tubing (Sigma, mol wt cutoff > 12 KDa, av. diameter 33 mm).

Dynamic Light Scattering. The determination of the NP hydrodynamic diameter distributions was carried out through DLS measurements employing a Malvern Nano ZS instrument with a 633 nm laser diode. Samples were housed in disposable polystyrene cuvettes of 1 cm optical path length using water as suspendant. The width of DLS hydrodynamic diameter distribution is indicated by PdI (polydispersion index). In the case of a monomodal distribution (Gaussian) calculated by means of cumulant analysis, PdI=$(\sigma/Z_{avg})^2$, where σ is the width of the distribution and *Z*avg is average diameter of the particles population, respectively.

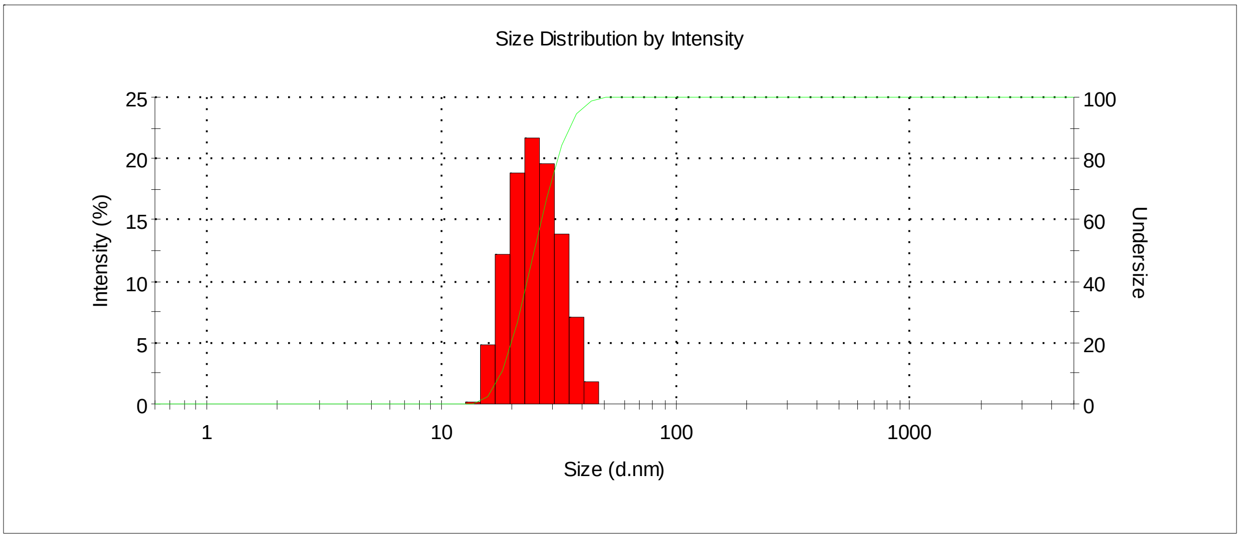

Figure S2 Hydrodinamic diameter distribution of core-shell silica-PEG nanoparticles d_H= 25 nm, PdI=0.03, (water, 25°C).

Transmission Electron Microscopy Experiments. A Philips CM 100 transmission electron microscope operating at 80 kV was used. For TEM investigations a 3.05 mm copper grid (400 mesh) covered by a Formvar support film was dried up under vacuum after deposition of a drop of nanoparticles solution diluted with water (1:50).

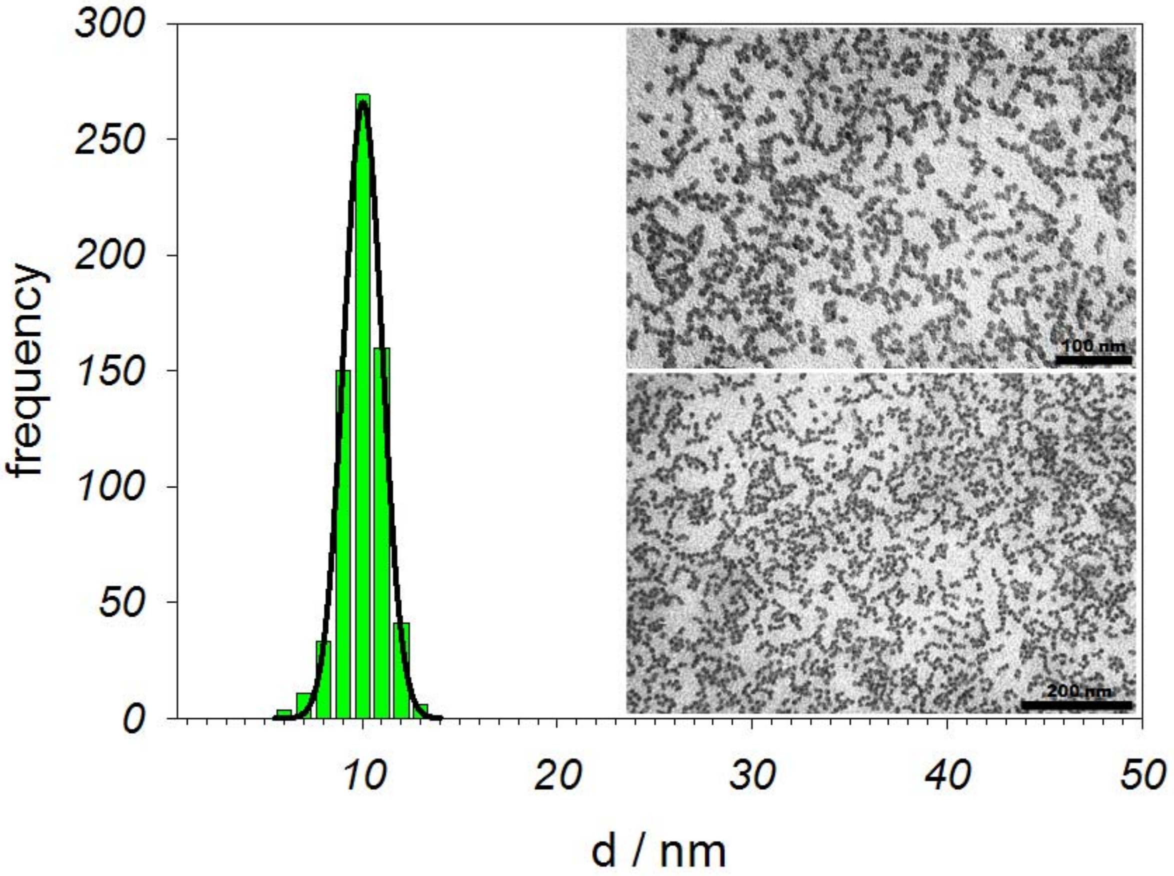

Figure S3 TEM images of Core-shell silica-PEG nanoparticles, and silica core size distribution, d = (11±3) nm, (scale bars 100 nm and 200 nm).

Photophysical Measurements. All NP solutions show very weak light scattering and can be treated from the photophysical point of view as any solution of molecular species. DLS measurements show no aggregation of the NPs, even after several months. UV-vis absorption spectra were recorded at 25 °C on a Perkin-Elmer Lambda 45 spectrophotometer. Disposable polystyrene cuvettes with optical path length of 1 cm were used. The fluorescence spectra were recorded with an Edinburgh FLS920 equipped photomultiplier Hamamatsu R928P. Luminescence quantum yields (uncertainty 15%) were determined using rhodamine 101 solution in ethanol as a reference (Φ = 1.0). Fluorescence intensities were corrected for inner filter effects according to standard methods.

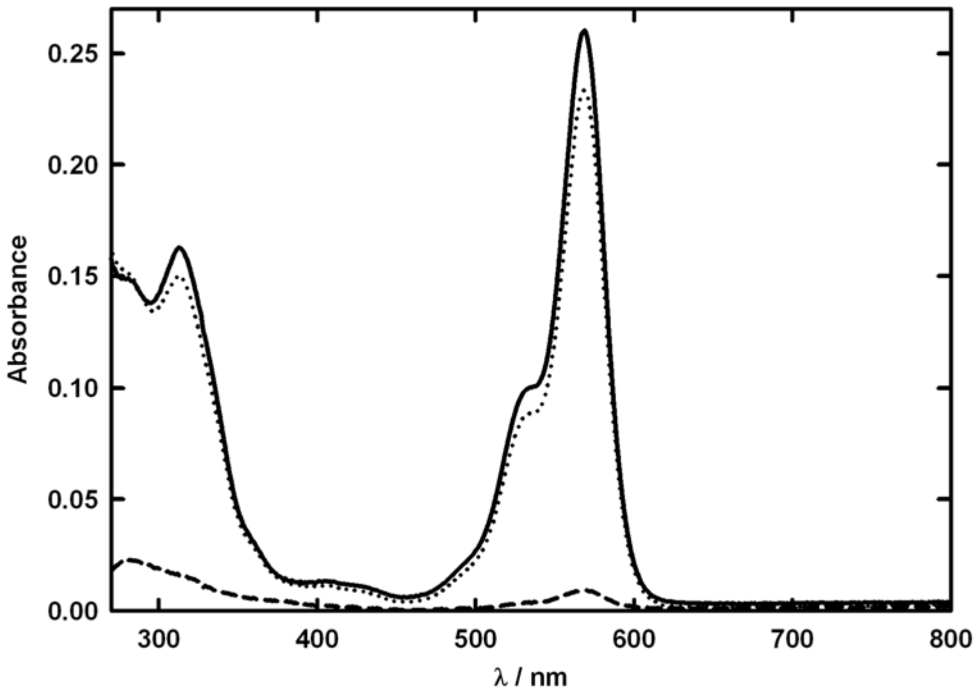

Figure S4. Absorption spectra of a water suspension of **R@NPs** and **PS** before (solid line) and after ultrafiltration through a regenerated cellulose membranes (100 kDa cutoff): the retentate (dotted line) displays both absorption bands of **R@NPs** and **PS**, while the filtrate solution (dashed line) only displays negligible traces of the two components. Both retentate and filtrate solutions were diluted to the initial total volume.

Fluorescence microscopy and data analysis. The fluorescence images were obtained with an inverted microscope (Olympus IX71) equipped with a cooled CCD camera (Princeton Instruments, Photon Max 512) and using as excitation light the 488nm laser emission of an Ar^+ ion laser (Melles Griot, IMA1 – Multiwavelength, 43 series ion laser). A portable UV lamp (UVP, UVGL-15 lamp, 365nm, 4W) was placed 2 cm over the sample to irradiate it from the top. Image analysis with Matlab homemade routines provided traces in time of single particle fluorescence intensity. We used the Matlab version of the IDL code by Crocker and Grier[3] to find the particles coordinates; particles intensity was then tracked in time upon UV irradiation cycles, and averaged over all particles in the field of view.

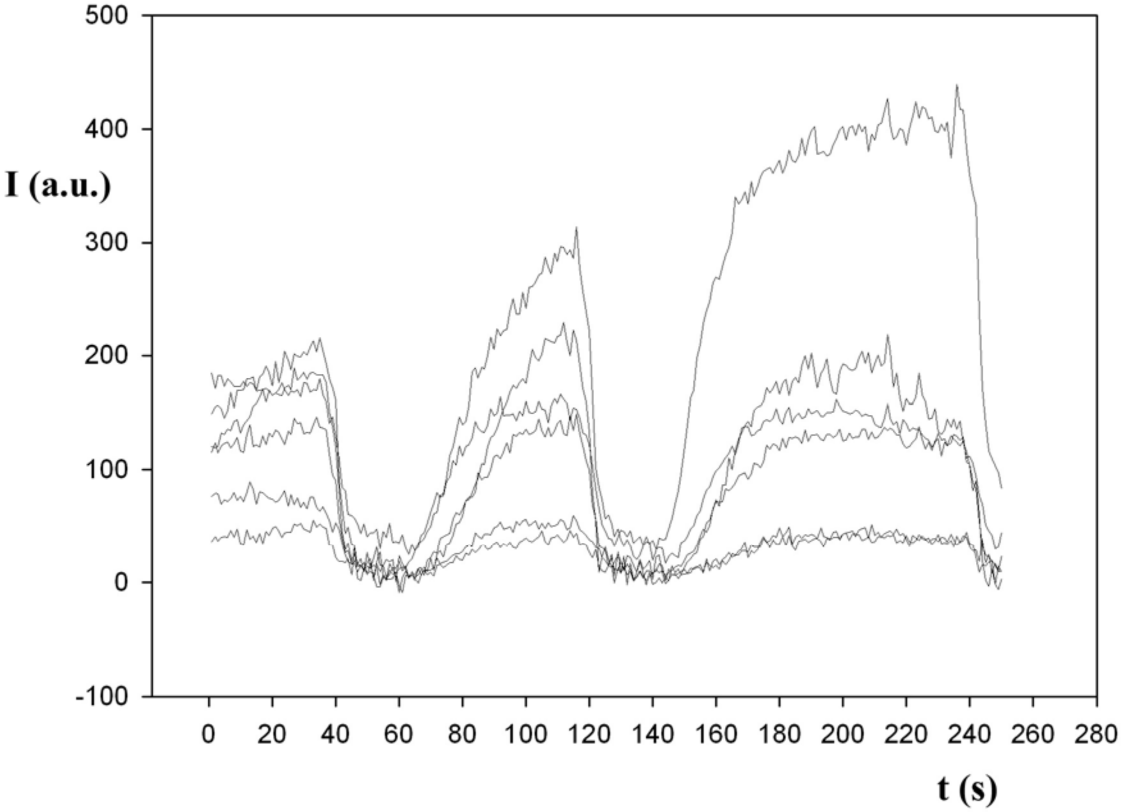

Figure S5. Fluorescence intensity of single particles in the field of view upon turning on and off the UV irradiation, under constant 488 nm laser excitation.

References

1 A. Osuka, D. Fujikane, H. Shinmori, S. Kobatake and M. Irie, *J Org. Chem*. **2001**, *66*, 3913-3923.

2 E. Rampazzo, S. Bonacchi, R. Juris, M. Montalti, D. Genovese, N. Zaccheroni, L. Prodi, D. C. Rambaldi, A. Zattoni and P. Reschiglian, *J. Phys. Chem. B*, 2010, **114**, 14605-14613.

3 J. C. Crocker and D. G. Grier, *J. Colloid Interface Sci.*, 1996, *179*, 298.