

Perylene Dye@SiO₂ Core-Shell Nanoparticles with Intense Fluorescence

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– ELECTRONIC SUPPORTING INFORMATION – (ESI)

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1. Analytical Techniques

Dynamic light scattering (DLS) was performed to determine the hydrodynamic diameter of the PD/CC@SiO₂ core-shell nanoparticles in suspension. To this concern, suspensions were analyzed in polystyrene cuvettes using a Nanosizer ZS (Malvern Instruments, United Kingdom). The same instrument was also used for *zeta potential measurements* to evaluate surface charging and the colloidal stability of the nanoparticles.

Scanning electron microscopy (SEM) was used to determine the particle size, using a Zeiss Supra 40 VP (Zeiss, Germany). Samples were prepared small by dapping droplets of the nanoparticle suspension in water onto a silicon wafer, which was left to dry for at least 8 h at room temperature. At least 150 nanoparticles were statistically evaluated to determine mean particle diameter. The same device was also used for *scanning transmission electron microscopy (STEM)* to confirm particle size and examine inner cavity and shell of the SiO₂ core-shell nanoparticles.

Transmission electron microscopy (TEM) and *high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM)* were performed with a FEI Osiris microscope (FEI, Netherlands) at 200 kV. TEM samples were prepared by evaporating small droplets of an aqueous nanoparticle suspension on Lacey-film carbon copper TEM grids.

Energy dispersive X-ray spectroscopy (EDXS) was applied to gain information about the core-shell structure and to obtain element mappings. To this concern, a Bruker Quantax system (XFlash detector, Bruker, Germany) was used, which was installed at the FEI Osiris TEM.

Fourier-transformed infrared (FT-IR) spectra were recorded with a Bruker Vertex 70 FT-IR spectrometer (Bruker, Germany). For this purpose, 300 mg of dried KBr were mixed with 2 mg of the core-shell nanoparticles, pestle, and pressed into pellets thereafter. The pellets were then measured in transmission mode in the range of 4000-450 cm⁻¹.

UV-Vis spectra were recorded on a Shimadzu UV-2700 (Shimadzu, Japan), equipped with a deuterium discharge lamp (180-360 nm) and a quartz halogen lamp (360-800 nm). UV-Vis spectroscopy was used to quantify the amount of FR in the FR/CC@SiO₂ core-shell nanoparticles according to the Kubelka-Munk formalism. The respective concentrations were quantified in comparison to reference solutions with known FR concentration by applying a

calibration curve. UV-VIS spectra were recorded with an UV2700 from Shimadzu. Nanoparticle suspensions with 25 $\mu\text{g/mL}$ were measured in quartz glass cells (Starna, type Q, 170-2700 nm, spectral quality 6) in an integrating sphere in diffuse transmission geometry against the corresponding pure solvent as a reference. For solutions of freely dissolved FR in ethanol, a double-beam setup was used for transmission measurements with the corresponding pure solvent as a reference.

Photoluminescence (PL) was recorded with a Horiba Jobin Yvon Spex Fluorolog 3 (Horiba Jobin Yvon, France) equipped with a 450 W Xe lamp and double grating excitation and emission monochromators. Either powder samples or suspensions (5 mg/mL) were examined in quartz cuvettes. Pure FR as a reference was as well analysed as powder sample or as solution in ethanol (0.50 mg/mL). Excitation/emission spectra were recorded with a slit width of 1 nm. Emission spectra were corrected for the emission characteristics of the Xe lamp.

Elemental analysis (EA) (C/H/N/S analysis) of dried samples was performed via thermal combustion with an Elementar Vario Microcube device (Elementar, Germany) at a temperature of about 1100 °C.

2. Material Characterization

The density of the as-prepared FR/CC@SiO₂ core-shell nanoparticles is lower than the density of water, which can be related to the presence of FR and CC. After centrifugation, therefore, the FR/CC@SiO₂ core-shell nanoparticles are collected in the top-phase (Figure S1). For purification, the bottom phase was removed with a syringe to remove all salts and excess starting materials.

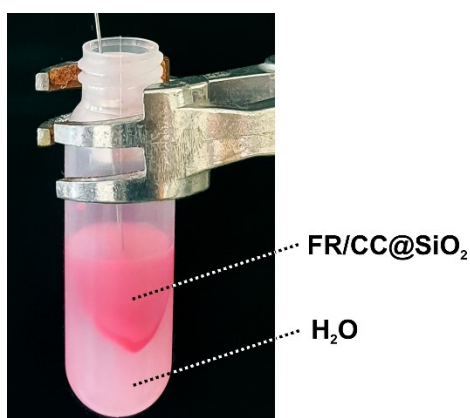


Figure S1. Photo of FR/CC@SiO₂ core-shell nanoparticles occurring as top phase after centrifugation due to a density lower than the density of water.

To determine the concentration of encapsulated FR in the FR/CC@SiO₂ core-shell nanoparticles, UV-VIS spectroscopy was applied. For this purpose, a calibration curve of FR dissolved in ethanol at known concentration was measured (Figure S2). This calibration curve shows an almost ideal linear dependence of absorbance (recorded at 567 nm) and FR concentration in a range of 0-10 µg/mL (Figure S2). Thus, using the Lambert-Beer equation is appropriate to determine the FR-concentration in FR/CC@SiO₂ core-shell nanoparticles. In this regard, the molar extinction coefficients of ethanol and water were considered to be similar, which is liable since the absorption of both solvents in the visible regime is very low. Moreover, the absorption spectra of FR in ethanol (solution) and FR/CC@SiO₂ core-shell nanoparticles (suspension) are identical (*see main paper: Figure 5a*). Since the measurements were performed with a reflecting sphere (Ulbricht sphere), finally, the scattering of the nanoparticles is not an issue. As a result of the photometrical quantification FR/CC@SiO₂ suspensions with a load of 25 µg/mL core-shell nanoparticles contain FR with a concentration of 2.7 µg/mL (10.8 wt-%).

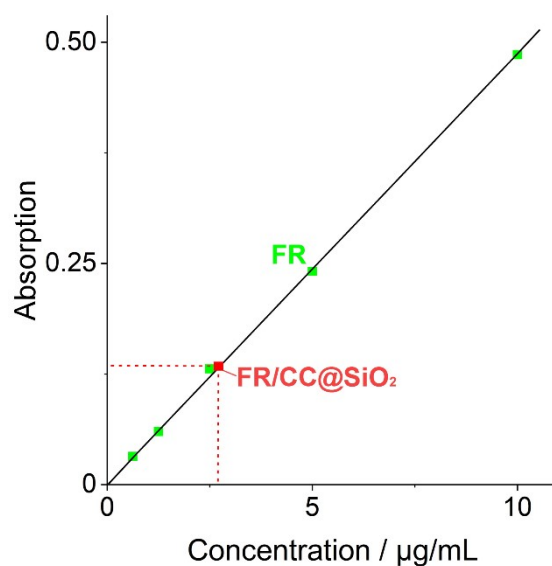


Figure S2. Photometrical analysis of FR/CC@SiO₂ core-shell nanoparticles: calibration curve for FR (solutions in ethanol) with the absorbance measured at $\lambda = 567$ nm (green squares represent the measured values; black line represents the linear fitting function).

To prove the role of CC on the luminescence properties of FR/CC@SiO₂ core-shell nanoparticles, absorption and photoluminescence of CC-containing nanoparticles were compared to CC-free nanoparticles, which – despite the presence or absence of CC – were prepared similarly and contain identical amounts of nanoparticles (5.0 mg/mL) and FR (0.5 mg/mL). UV-Vis spectra of FR/CC@SiO₂ core-shell nanoparticles and FR@SiO₂ core-

shell nanoparticles are predominately identical despite of a significantly stronger absorption below 400 nm (Figure S3). The different absorption intensity already points to a reduced π -stacking of FR in FR/CC@SiO₂ core-shell nanoparticles. Similarly, excitation spectra of FR/CC@SiO₂ core-shell nanoparticles and FR@SiO₂ core-shell nanoparticles are more-or-less identical in regard of their shape, but the intensity of the FR/CC@SiO₂ core-shell nanoparticles is about 10-times higher as compared to the FR@SiO₂ core-shell nanoparticles (Figure S4a). The emission spectra are also significantly different and show a dramatic difference with an about 10-times higher emission of the FR/CC@SiO₂ core-shell nanoparticles (Figure S4b), which clearly points to the importance of CC to avoid the π -stacking of the perylene-type dye.

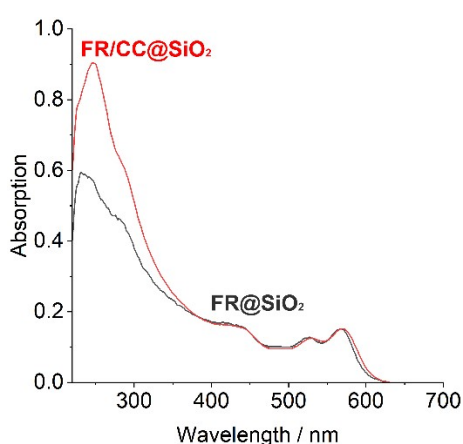


Figure S3. UV-Vis spectra of FR/CC@SiO₂ core-shell nanoparticles and FR@SiO₂ core-shell nanoparticles.

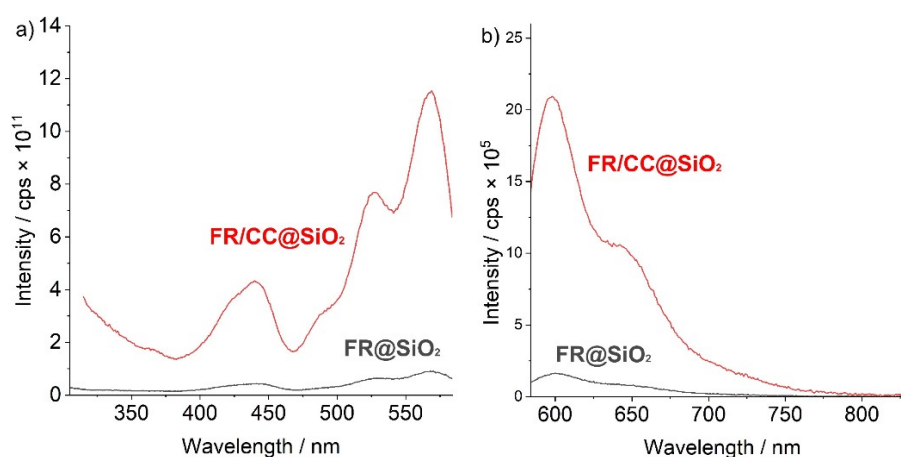


Figure S4. Photoluminescence of FR/CC@SiO₂ core-shell nanoparticles and FR@SiO₂ core-shell nanoparticles: (a) excitation spectra (recorded at $\lambda = 600$ nm), (b) emission spectra (with excitation at $\lambda = 567$ nm).