Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Electronic Supplementary Information

Understanding the photophysical properties of coumarin-based Pluronic-Silica (PluS) nanoparticles by means of time-resolved emission spectroscopy and accurate TDDFT/stochastic calculations.

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Combining the counterpoise correction with the polarizable continuum method.

It is well known that molecular orbital calculations on dimeric species are susceptible to basis set superposition error (BSSE) when finite basis set are used. As a consequence, the interaction energy of a dimeric species (let's say AB) is overestimated because of the overlap of the basis functions centered on the atoms of the interacting molecules. Therefore, each monomer effectively increases its basis set leading to a further stabilization of the dimer. This is not the case when the monomer is treated alone, e.g. when a binding or interaction energy is calculated. Therefore, the energy of the whole system is computed lower in comparison to the separated subsystems which do not benefit from the basis functions of their interaction partners.

The counterpoise method (CP) introduced by Boys et al.[14] eliminates the BSSE by including the basis set functions of the whole complex during the calculation of the energy of each monomer.

In the uncorrected interaction energy for the dimer AB is:

$$E_{AB}(Q) = E_{AB}(Q, AB) - E_A(Q_A, A) - E_B(Q_B, B)$$

Where Q denotes the coordinates specifying the geometry of the dimer and E_{AB}(Q,AB) the total energy of the dimer AB calculated with the full basis set of the dimer at that geometry. $E_A(Q_A, A)$ and $E_B(Q_B, B)$ denote the total energies of the monomers A and B, calculated with the appropriate monomer basis sets at the geometry that the monomers A and B occupies in the dimeric species, respectively.

Instead, the counterpoise corrected interaction energy is given by:

$$E_{AB}^{cc}(Q) = E_{AB}(Q, AB) - E_A(Q_A, A,*) - E_B(Q_B,*, B)$$

Where $E_A(Q_A, A,*)$ and $E_B(Q_B,*, B)$ denote the total energies of monomers A and B computed with the dimeric basis set, that is, in the calculation of monomer *A* the basis set of monomer *B* is present at the same location as in dimer *AB*, but the nuclei of *B* are not. In this way, the basis set for each monomer is extended by the functions of the other monomer.

Therefore, the BSSE correction is estimated as:

$$BSSE = E_{AB}(Q) - E_{AB}^{cc}(Q)$$

In the case of PCM calculations one has to choose which cavity shape to use in the calculation of the monomer energies. As suggested by Zawada et al.[15] we employed the dimeric cavities (DC) because this choice is more consistent with the definition of interaction energy, which within the Born-Oppenheimer approximation is the difference between the energy of a complex and those of its constituents estimated at the complex geometry. Moreover, it is worth to note that the choice of monomeric cavities in combination with the dimer centered basis set violates the boundary conditions imposed on Poisson equation in the PCM model[25] because a substantial charge density would lie outside the monomer cavity.

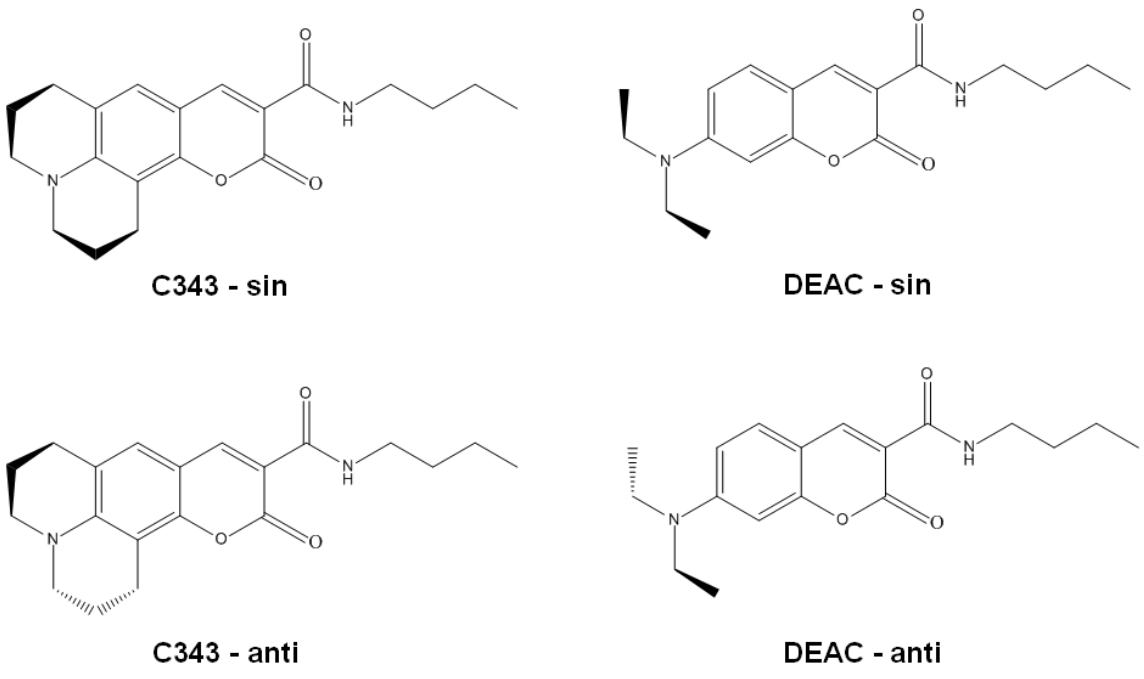


Figure S1. Conformations of the two coumarin molecules investigated.

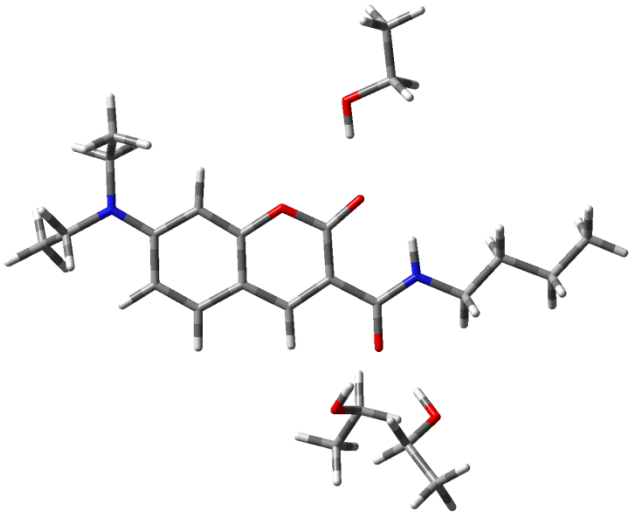


Figure S2. B3LYP optimized structure of the **D** molecule with three explicit ethanol molecules.

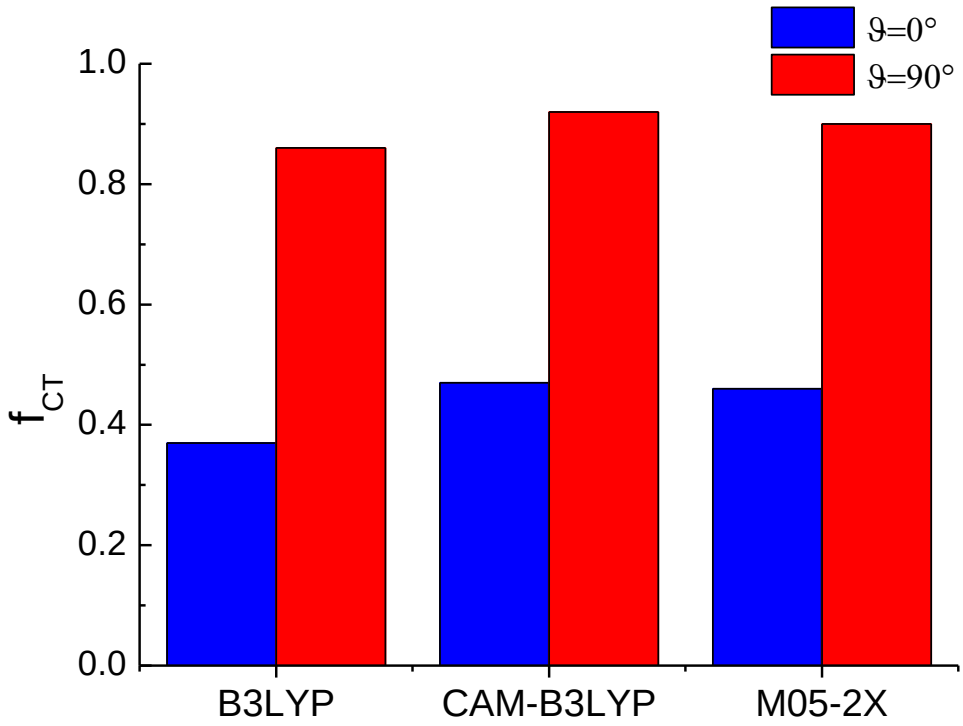


Figure S3. Charge transfer parameter f_{CT} computed with different functional by using the LRPCM approach for two different values of the twisting angle (θ) in the excited state of D molecule. $f_{CT}=\Delta q_D-\Delta q_A$, where Δq_i is the charge difference in the donor or acceptor unit between ground and excited state. The donor and acceptor groups are the N,N-dialkyl group and the benzopyrone moiety. If the excitation really corresponds to a CT from donor to acceptor f_{CT} will be large and positive since Δq_D is large and positive while Δq_A is large in absolute value but negative.

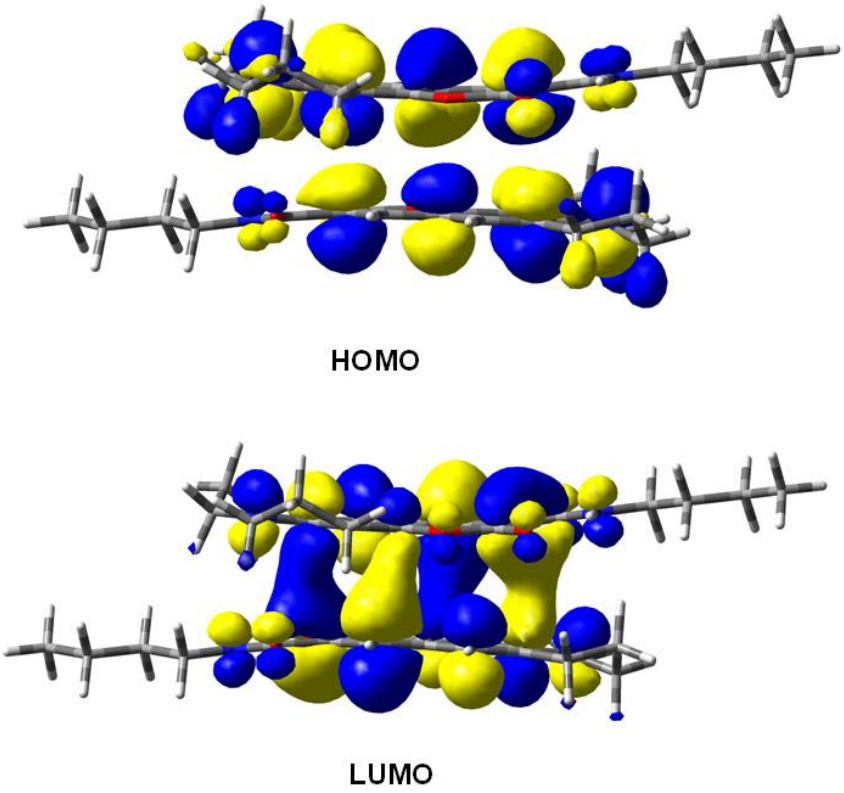


Figure S4. Kohn-Sham HOMO and LUMO molecular orbitals charactering the CT state of the C343 excimer.

Chemicals: All the following reagents and solvents were used as received without further purification: non ionic surfactant Pluronic® F127, tetraethyl orthosilicate (TEOS, 99.99 %), chlorotrimethylsilane (TMSCl, ≥ 98 %), acetic acid (≥ 99.7 %), triethylamine (TEA, ≥ 99.5%), 1-hydroxybenzotriazole hydrate (HOBt ≥ 99.0 %), 4-(Dimethylamino)pyridine (DMAP, ≥ 99.0%), *N*-(3-dimethylaminopropyl)-*N*-ethylcarbodiimide hydrochloride (EDC·HCl, ≥ 98.0%), *N*-(3-dimethylaminopropyl)-*N*-ethylcarbodiimide (EDC, ≥ 98.0 %), (3-aminopropyl)triethoxysilane (APTES, ≥ 98.0 %), Butylamine (≥ 99.5 %), Coumarin 343 (97 %) and 7-(diethylamino) coumarin-3-carboxylic acid (DEAC, ≥ 98.0 %), reagent grade dichloromethane, cyclohexane, ethyl acetate, NaCl, DMF and n-eptane.

A Milli-Q Millipore system was used for the purification of water (resistivity ≥ 18 MΩ).

Dialysis was performed vs. water at room temperature under gentle stirring with regenerated cellulose dialysis tubing (Sigma, mol wt. cut-off > 12 KDa, avg. diameter 33 mm). Filtration of particles solutions was made when necessary using Millipore Durapore filters (0.22, 0.45 µm).

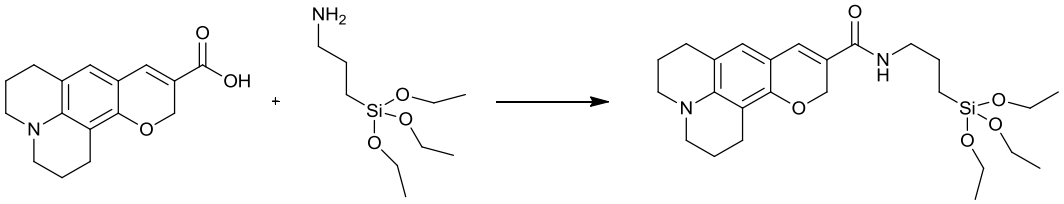
Fluorophore Synthesis

DS: Fluorophore **DS** was synthetized using reported procedures (DOI: 10.1002/anie.201301155 and 10.1002/ange.201301155)

Triethoxysilane derivative of Coumarin-343 (11-oxo-*N*-(3-(triethoxysilyl)propyl)-2,3,5,6,7,11-hexahydro-1*H*-pyrano[2,3-*f*]pyrido[3,2,1-*ij*]quinoline-10-carboxamide), **CS:**

A 10 mL two-necked flask is dried with a heat gun under a flow of nitrogen. Then 3-aminopropyltriethoxysilane (APTES, 2 eq., 0.136 mmol, 32.5 µL), coumarin 343 (1 eq., 0.068 mmol, 20 mg), triethylamine (TEA, 2 eq., 0.136 mmol, 19.1 µL), *N*-(3-dimethylaminopropyl)-*N'*-

ethylcarbodiimide (EDC, 2 eq., 0.136 mmol, 24.8 µL,) and 1-hydroxybenzotriazole hydrate (HOBt, 2 eq., 0.136 mmol, 18.9 mg) are dissolved in dichloromethane and stirred overnight at room temperature.



Scheme S1: (a) APTES, TEA, EDC, HOBt, dichloromethane; (b) purification by silica flash chromatography (cyclohexane : AcOEt, gradient 6:4 – 1:1, v/v)

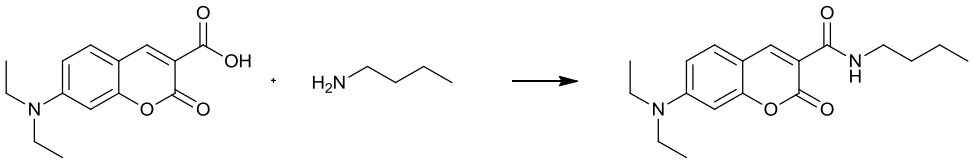
The reaction mixture is then concentrated under reduced pressure and purified by means of flash chromatography on silica using a cyclohexane/ethyl acetate gradient (6:4 – 1:1, v/v) as eluent, obtaining the product as a light orange solid (22.8 mg, 69%).

^{1}H NMR ($CDCl_3$, Me_4Si, 200 MHz, 25 °C) δ (ppm): 0.72 (2 H, t, J = 8.4 Hz, -CH_2-CH_2-Si,), 1.24 (9 H, t, J = 7.0 Hz, CH_3-CH_2-O-), 1.79–1.67 (2 H, m, -CH_2-CH_2-CH_2-Si), 2.05–2.00 (4 H, m, -CH_2-CH_2-CH_2-N-CH_2-CH_2-CH_2-), 2.91–2.76 (4 H, m, -CH_2-CH_2-CH_2-N-CH_2-CH_2-CH_2-), 3.38–3.23 (4 H, m, -CH_2-N-CH_2-), 3.50–3.40 (2 H, m, CO-NH-CH_2-), 3.84 (6 H, q, J = 7.0 Hz, CH_3-CH_2-O-), 7.02 (1 H, s, H_{arom}), 8.63 (1 H, s, H_{arom}), 8.9 (1 H, t (broad), -CO-N*H*-).

Synthesis of D: 7-(Diethylamino)coumarin-3-N-butyl-carboxamide (N-butyl-7-(diethylamino)-2-oxo-2H-chromene-3-carboxamide)

A 10 mL two-necked flask is dried with a heat gun under a flow of nitrogen. Then, 7-(diethylamino)coumarin-3-carboxylic acid (DEAC, 1 eq., 0.095 mmol, 25 mg), HOBt * xH_2O (2 eq., 0.19 mmol, 25.7 mg), EDC*HCl (6.0 eq., 0.057 mmol, 110 mg), DMAP (0.55 eq., 0.053

mmol, 6.5 mg) and 5.0 mL of dry DMF are mixed together and stirred at room temperature for 1 h, to obtain a yellow-green fluorescent solution; after that, n-butylamine (5.3 eq., 0.51 mmol, 50 µL), is added. After 12 h, the presence of unreacted DEAC is checked through an extraction procedure (brine : Na_2CO_3 5% = 1:1) carried on a small sample of the reaction mixture. Finally, additional 100 mg of EDC*HCl are added and the reaction mixture is stirred for other 12 h. The reaction mixture is finally diluted with 100 mL of AcOEt and is subjected to the following extraction steps: 3 x 50 mL (brine: Na_2CO_3 5% = 4:1), 3 x 50 mL (brine: citric acid 5% = 4:1) and 2 x 50 mL (brine: Na_2CO_3 5% = 4:1).



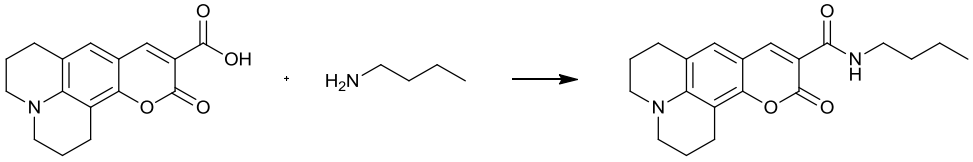
Scheme S2: (a) HOBt*xH_2O, EDC*HCl, DMAP, DMF, 12 h; (b) purification by silica flash chromatography (AcOEt : n-eptane = 1:1).

The organic layer is treated with anhydrous Na_2SO_4, filtered and the solvent is removed under reduced pressure with a rotary evaporator. The crude solid is purified by means of flash chromatography on silica gel (AcOEt : n-eptane = 1:1; v/v); the appropriate fractions of the eluate are then concentrated with the rotary evaporator and desiccated in vacuum, affording a yellow solid (28.8 mg, quantitative yield).

^{1}H NMR ($CDCl_3$, Me_4Si, 400 MHz, 25 °C) δ (ppm): 0.92 (3H, t, J = 8 Hz, C*H*$_3$-CH_2-CH_2-), 1.18 (6H, t, J = 8 Hz, C*H*$_3$-CH_2-N), 1.36-1.41 (2H, m, CH_3-C*H*$_2$-CH_2-), 1.53-1.59 (2H, m, -CH_2-C*H*$_2$-CH_2-), 3.38-3.44 (6H, m, -C*H*$_2$-N-C*H*$_2$- and -NH-C*H*$_2$-), 6.45-6.46 (1H, d, J = 4 Hz, H_{arom}), 6.59-6.62 (1H, dd, J = 8 Hz, 4 Hz, H_{arom}), 7.39 (1H, d, J = 8 Hz, H_{arom}), 8.67 (1H, s, H_{arom}), 8.75 (1H, t (broad), CO-N*H*-).

Synthesis of C: Coumarin 343-N-butyl-carboxamide (N-butyl-11-oxo-2,3,5,6,7,11-hexahydro-1H-pyrano[2,3-f]pyrido[3,2,1-ij]quinoline-10-carboxamide)

The procedure is similar to the one used in the synthesis of **D**. The following quantities of reagents and solvent were used: Coumarin 343 (1 eq., 0.089 mmol, 25.4 mg), HOBt * xH_2O (2 eq., 0.18 mmol, 24.0 mg), EDC*HCl (1.6 eq., 0.144 mmol, 27.6 mg), DMAP (0.5 eq., 0.045 mmol, 5.5 mg), n-butylamine (5 eq., 0.445 mmol, 44 µL), 5.0 mL of dry DMF. A green-yellow solid was obtained (19.8 mg, 68 %).



Scheme S3: (a) HOBt*xH_2O, EDC*HCl, DMAP, DMF, 12 h; (b) purification by silica flash chromatography (AcOEt : n-eptane = 1:1).

^{1}H NMR ($CDCl_3$, Me_4Si, 400 MHz, 25 °C) δ (ppm): 0.92 (3H, t, J = 8 Hz, C*H*$_3$-CH_2-O-), 1.38 (2H, m, CH_3-C*H*$_2$-CH_2-), 1.55 (2H, m, NH-CH_2-C*H*$_2$-CH_2-), 1.92 (4H, m, -CH_2-C*H*$_2$-CH_2-NH-CH_2-C*H*$_2$-CH_2-), 2.74 (2H, t, J = 8 Hz, N-CH_2-CH_2-C*H*$_2$-), 2.85 (2H, t, J = 8 Hz, N-CH_2-CH_2-C*H*$_2$-), 3.29 (4H, q, J = 12 Hz, 4 Hz, -C*H*$_2$-N-C*H*$_2$-), 3.40 (2H, m, -NH-C*H*$_2$-), 6.97 (1H, s, *H*$_{arom}$), 8.57 (1H, s, *H*$_{arom}$), 8.67 (1H, s, *H*$_{arom}$), 8.82 (1H, t (broad), CO-N*H*-).

Table S1: amount of the silanized dye(s) used in PluS NPs preparation.

NPs sample	***Coumarin derivative***	% mmol **dye** vs mmol TEOS	mmol	mg
$D_{0.1}$	**DS**	0.1	0.0008	0.36
$D_{0.4}$	**DS**	0.4	0.0032	1.44
$C_{0.1}$	**CS**	0.1	0.0008	0.38
$C_{0.4}$	**CS**	0.4	0.0032	1.52

DLS Experiments:

Dynamic Light Scattering measurements were done employing a Malvern Nano ZS instrument equipped with a 633 nm laser diode. Samples were housed in disposable polystyrene cuvettes of 1 cm optical path length, using water as solvent. The width of DLS hydrodynamic diameter distribution is indicated by PdI (Polydispersion Index). In case of a mono-modal 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.

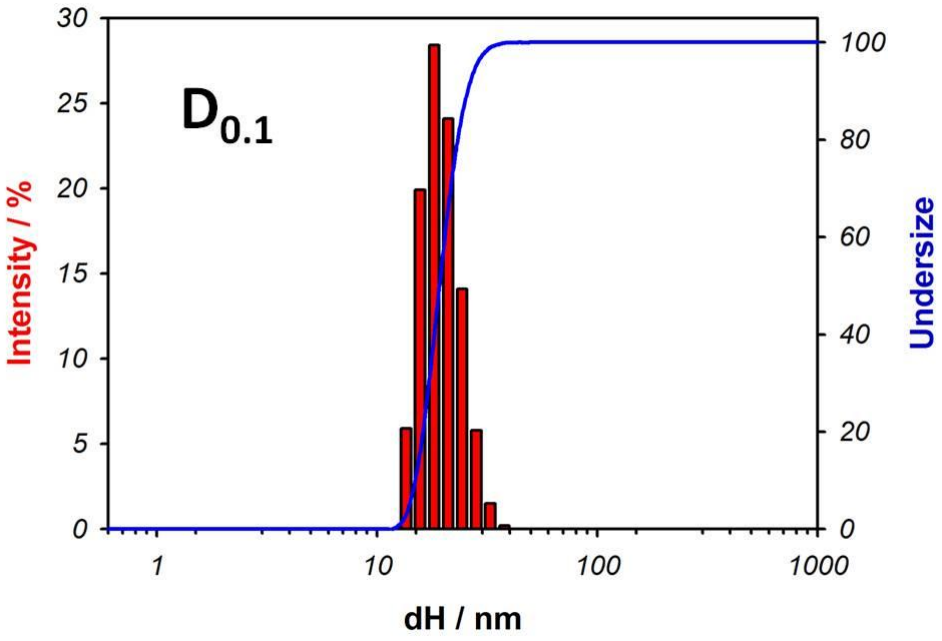


Figure S4: Intensity DLS distribution of sample **$D_{0.1}$** in water, 25°C. d_H = 21.5 nm (PdI = 0.10).

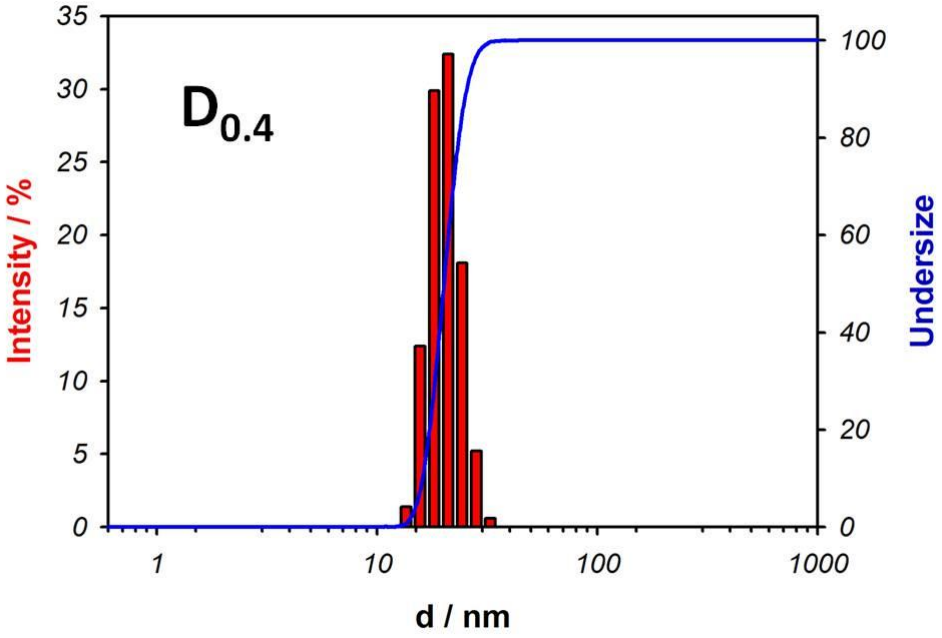


Figure S5: Intensity DLS distribution of sample $\mathbf{D_{0.4}}$ in water, 25°C. d_H = 22 nm (PdI = 0.14).

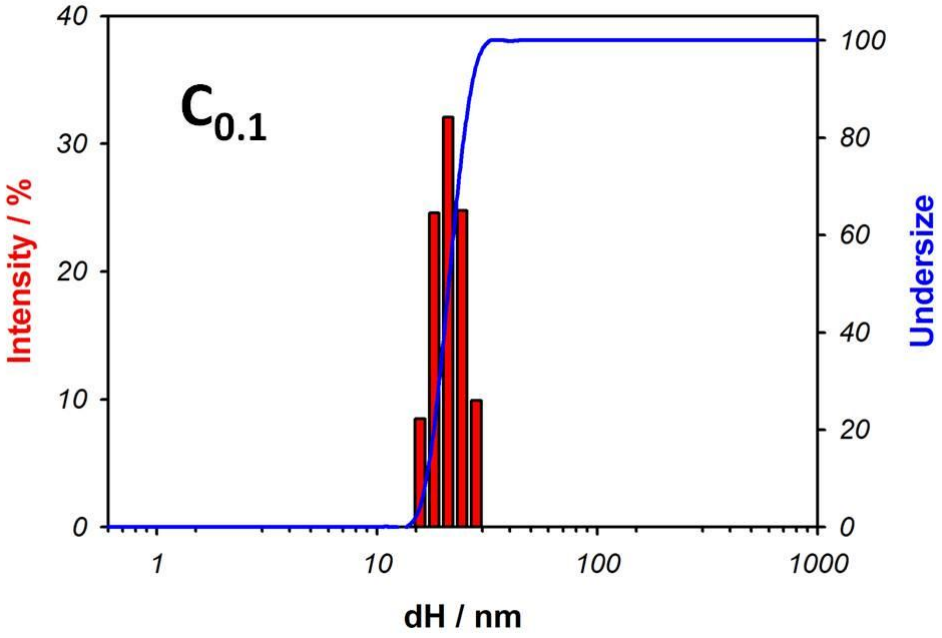


Figure S6: Intensity DLS distribution of sample $\mathbf{C_{0.1}}$ in water, 25°C. d_H = 21 nm (PdI = 0.06).

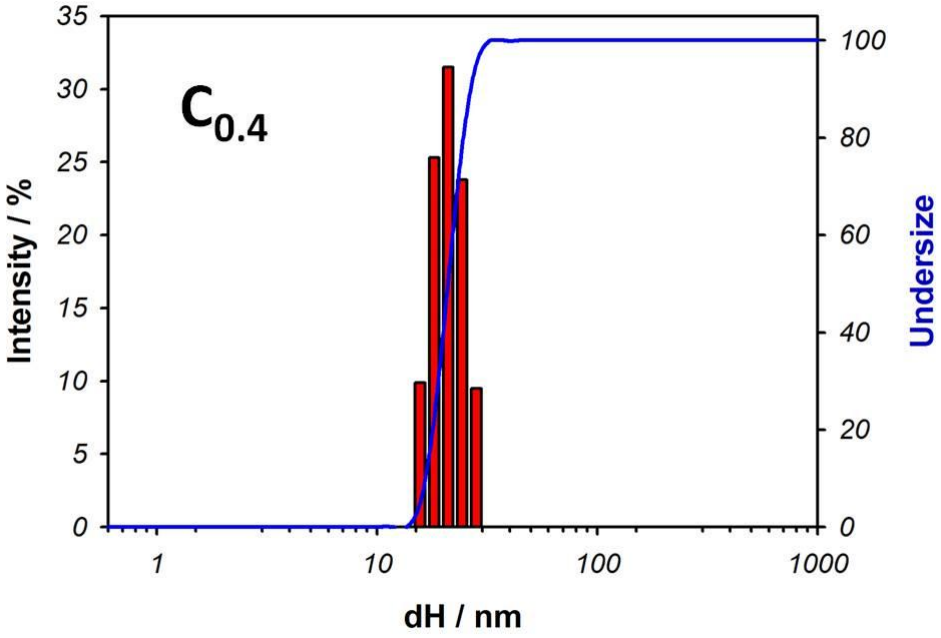


Figure S7: Intensity DLS distribution of sample **$C_{0.4}$** in water, 25°C. d_H = 21.5 nm (PdI = 0.12).

TEM Experiments:

A Philips CM 100 transmission electron microscope operating at 80 kV was used. For TEM investigations a standard 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 suspension diluted with water (1:50). The size distributions were obtained analyzing different images with blocks of several hundred of nanoparticles. The obtained histograms were fitted according to a Gaussian distribution to obtaining the average diameter for the silica nanoparticles core.

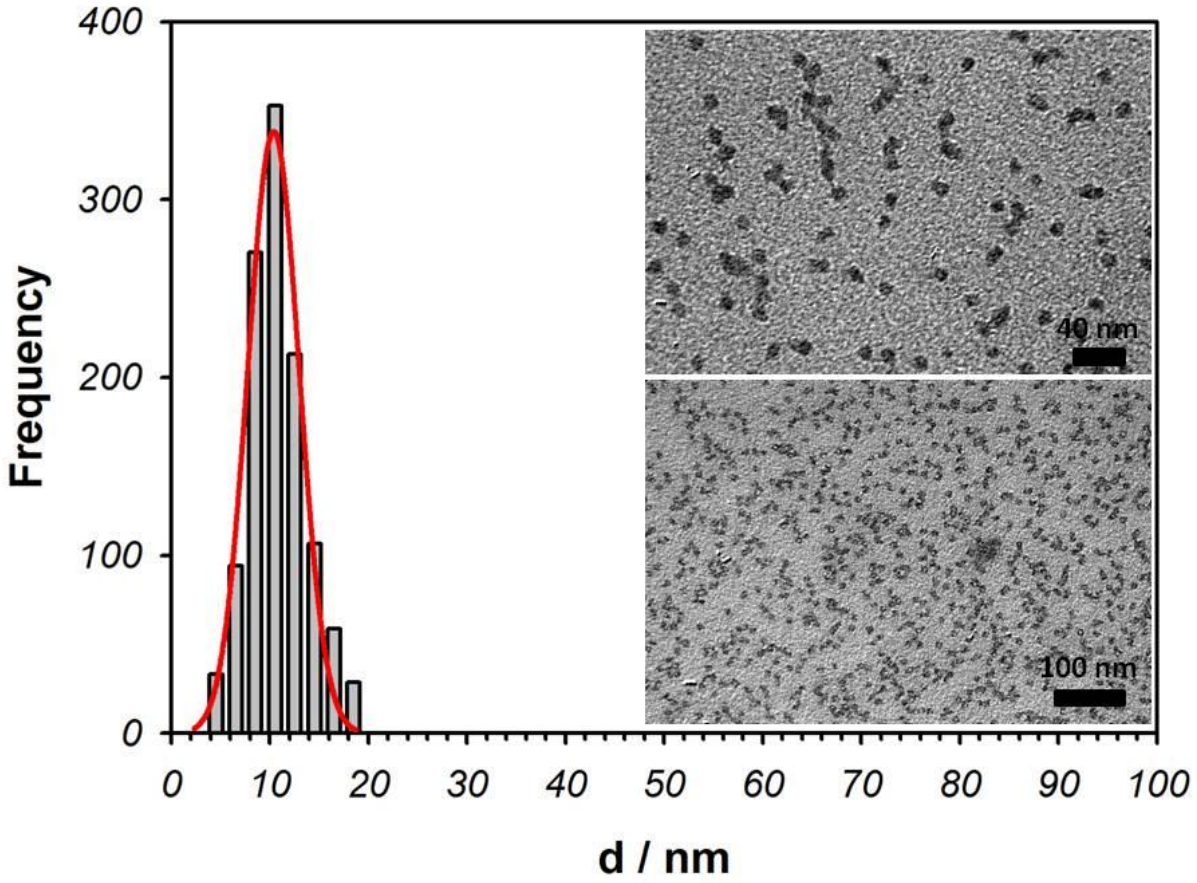


Figure S8: representative TEM images of PluS NPs and silica core diameter distribution, for all the NPs samples: d_{core} = (11 ± 3) nm.