Molecular engineering of hybrid dye-silica fluorescent nanoparticles: influence of the dye structure on the distribution of fluorophores and consequent photoemission brightness

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SUPPORTING INFORMATION

Chart S1. Molecular structures of I3BS-NHS (a), I3MS-NHS (b) and I3NS-NHS (c)

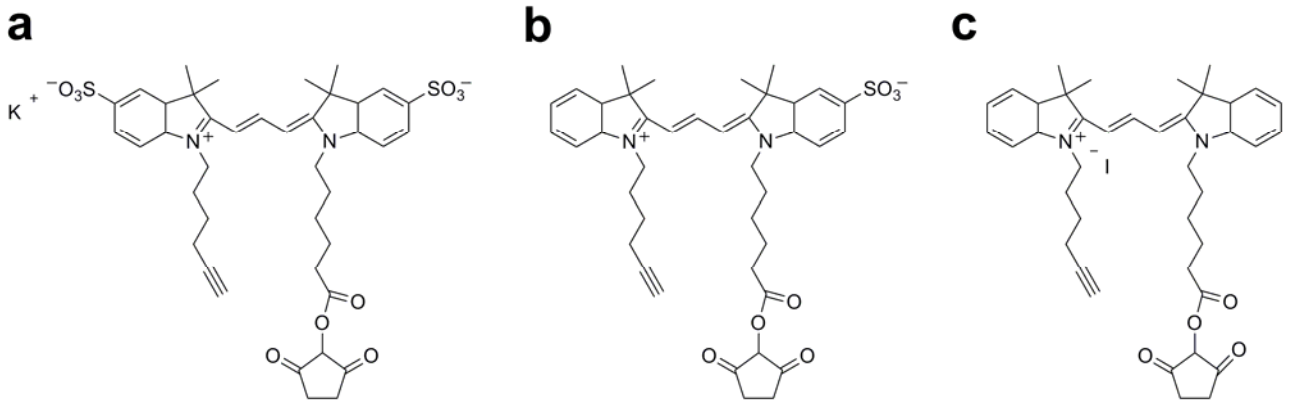

Table S1. Retention time in reverse phase HPLC analyses (as a measure of hydrophilicity/hydrophobicity) and absorption and emission quantitative features of the three cyanine-APTS derivatives

	RP-HPLC analyses	Absorption/Emission quantitative features			
Cyanine-APTS derivative	Retention Time (min) (in brackets: capacity factor)	Solvent	ε ($mol^{-1} \cdot cm^{-1}$) (in brackets: relative value)	Φ	τ^0_F
I3BS-APTS	8 (3.99)	Water	120000 (0.80)	0.025	0.20
		Cyclohexane	~	~	~
		n-hexanol	~	~	0.51
		Microemulsion	~	~	1.31
I3MS-APTS	24 (12.23)	Water	130000 (0.87)	0.037	0.35
		Cyclohexane	~	~	~
		n-hexanol	~	~	0.90
		Microemulsion	~	~	0.93
I3NS-APTS	29 (14.65)	Water	150000 (1.00)	0.05	0.42
		Cyclohexane	~	~	0.83
		n-hexanol	~	~	1.11
		Microemulsion	~	~	0.86

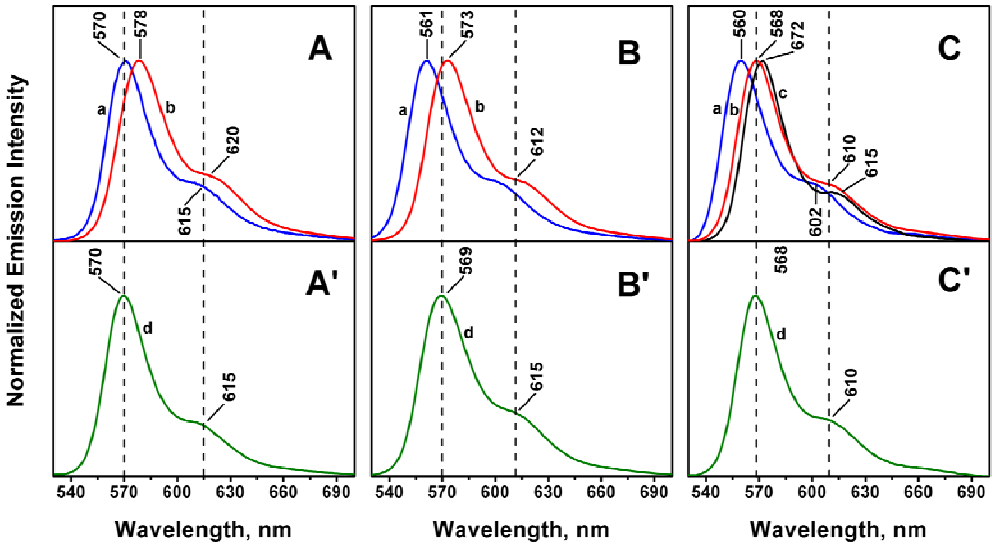

Figure S1. Emission spectra of I3BS-APTS (panel A and A') I3MS-APTS (panel B and B') and I3NS-APTS (panel C and C') in water ("a" lines, blue), *n*-hexanol ("b" lines, red), Cyclohexane ("c" lines, black) and Microemulsion ("d" lines, green)

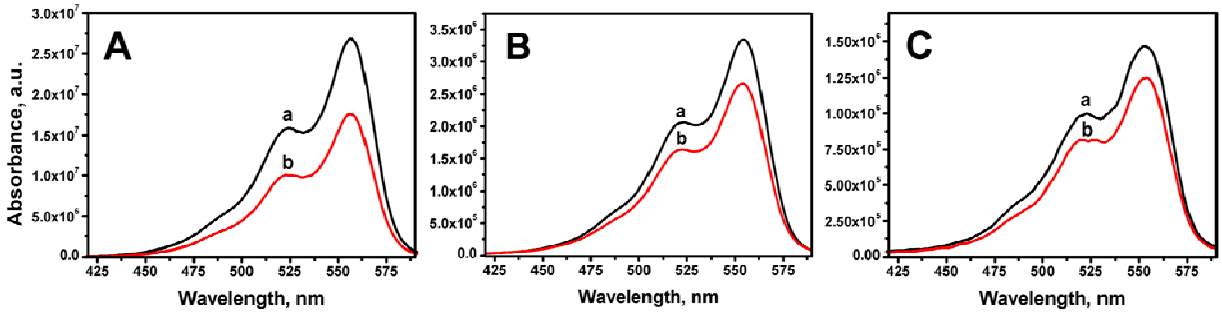

Figure S2-A. Comparison of absorption spectra of I3BS-APTS (panel A), I3MS-APTS (Panel B) and I3NS-APTS (Panel C) at the beginning (curve a, black) and after 1h of reaction (curve b, red)

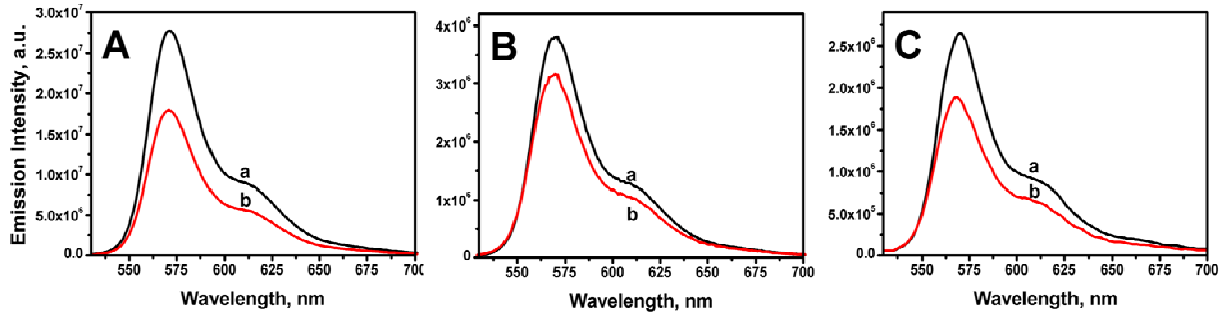

Figure S2-B. Comparison of photoemission spectra of I3BS-APTS (panel A), I3MS-APTS (Panel B) and I3NS-APTS (Panel C) at the beginning (curve a, black) and after 1h of reaction (curve b, red):

Table S2. Photoemission lifetimes of cyanine-APTS derivatives during NPs formation (in brackets population abundance, %)

		Reaction Time (hours)									
		0	1	2	4	6	8	10	16	20	24
I3BS	τ^0_F (ns)	1.30 (100%)	1.21 (85%)	1.19 (76%)	1.18 (73%)	1.20 (73%)	1.22 (74%)	1.22 (74%)	1.22 (57%)	1.24 (55%)	1.28 (55%)
	τ^1_F (ns)	~	1.62 (15%)	1.76 (24%)	1.79 (27%)	1.91 (27%)	2.07 (26%)	2.05 (26%)	2.05 (43%)	2.05 (45%)	2.06 (45%)
	χ^2	1.21	1.12	1.21	1.19	1.11	0.98	1.01	1.04	1.04	1.05
I3MS	τ^0_F (ns)	0.95 (97%)	0.95 (89%)	0.94 (88%)	0.95 (86%)	0.96 (82%)	0.96 (79%)	0.95 (75%)	0.95 (73%)	0.96 (74%)	0.95 (73%)
	τ^1_F (ns)	1.9 (3%)	1.94 (11%)	1.97 (12%)	2.11 (14%)	2.09 (18%)	2.10 (21%)	2.11 (25%)	2.11 (27%)	2.11 (26%)	2.10 (27%)
	χ^2	1.06	1.07	1.00	1.09	1.12	0.99	1.04	1.04	1.02	1.05
I3NS	τ^0_F (ns)	0.86 (93%)	0.86 (86%)	0.91 (80%)	0.91 (63%)	0.92 (55%)	0.91 (51%)	0.90 (44%)	0.97 (36%)	0.99 (36%)	0.99 (36%)
	τ^1_F (ns)	1.76 (7%)	1.78 (14%)	1.85 (20%)	1.92 (37%)	1.94 (45%)	1.99 (49%)	1.99 (56%)	2.03 (64%)	2.04 (64%)	2.1 (64%)
	χ^2	1.06	1.03	1.04	1.02	1.00	1.14	1.04	1.03	1.01	0.99

Table S3. Photoemission lifetimes of I3-NPs in solvents with different polarity

Cyanine-NPs	Solvent	τ^0_F	τ^1_F	χ^2
I3BS-NPs	Water	1.28 (55%)	2.07 (45%)	1.05
	Methanol	1.28 (53%)	2.07 (47%)	1.01
	Ethanol	1.28 (54%)	2.07 (46%)	1.03
I3MS-NPs	Water	0.86 (47%)	2.10 (53%)	1.09
	Methanol	0.90 (49%)	2.10 (51%)	1.08
	Ethanol	0.97 (48%)	2.10 (52%)	1.10
I3NS-NPs	Water	1.09 (35%)	2.05 (65%)	1.09
	Methanol	1.12 (38%)	2.05 (62%)	1.16
	Ethanol	1.13 (36%)	2.05 (64%)	1.12

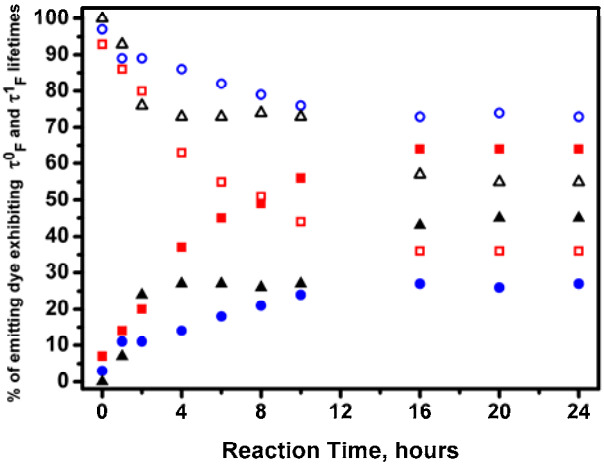

Figure S3. Evolution, along the period required for the formation of the nanoparticles, of the percentage of emitting dyes exhibiting the "shorter" lifetime (τ^0_F, open symbols) and the "longer" lifetime (τ^1_F, full symbols): I3BS-APTS (black); I3MS-APTS (blue); I3NS-APTS (red).

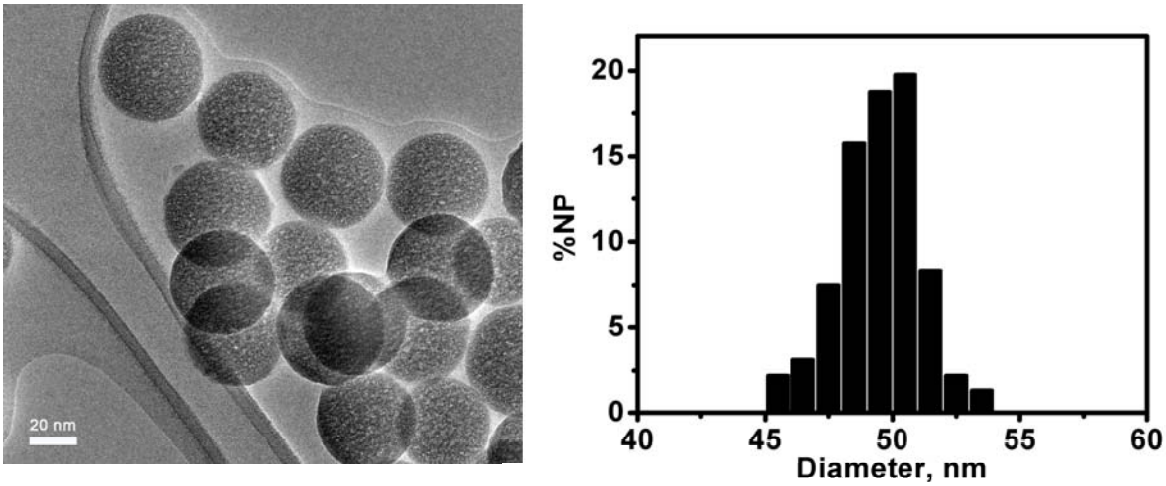

Figure S4. Representative TEM micrograph of silica NPs and correspondent histogram of their size distribution

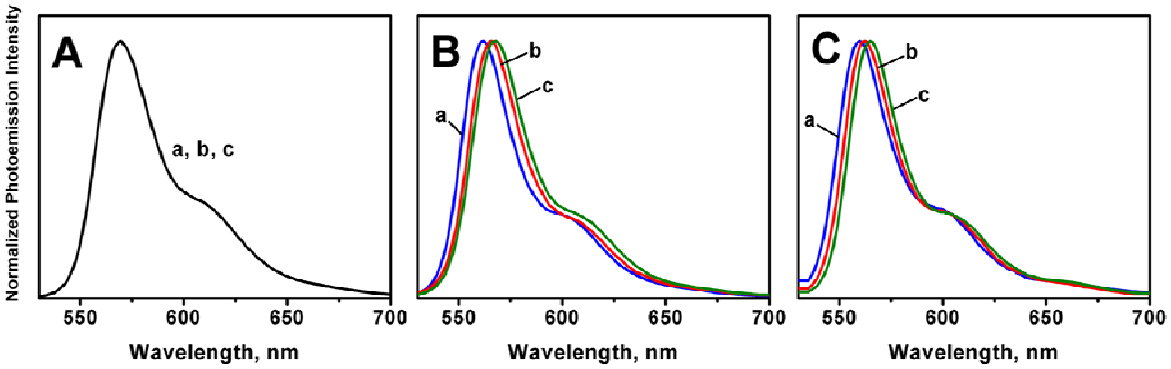

Figure S5. Photoemission (λ_{ex}= 520 nm) spectra of I3BS-NPs (panel A), I3MS-NPs (panel B) and I3NS-NPs (panel C) in water (blue, curve a), methanol (red, curve b) and ethanol (green, curve c).In the case of I3DS-NPs, all curves resulted overlapped

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I. TEOS Partition : $Si(OR)_4$ (b) $\rightleftharpoons$ $Si(OR)_4$ (m)

$Si(OR)_4$ (m) + H_2O (m) $\overset{OH^-}{\rightleftharpoons}$ $Si(OR)_3OH$ (m) + ROH (m)

$Si(OR)_4$ (b) + H2O (m) $\overset{K_p}{\rightleftharpoons}$ $Si(OR)_3OH$ (m) + ROH (m)

II. Hydrolysis : $Si(OR)_3OH$ (m) + xH_2O (m) $\xrightarrow{OH^-}$ $Si(OR)_{3-x}OH_x$ (m) + xROH (m)

x = 1,2,3

$Si(OR)_{3-x}OH_{x+1}$ (m) = "monomer" (m)

x= 0,1,2,3

III. Nucleation : n.monomer (m) ⟶ nucleus (m)

monomer (m) + monomer (m') ⟶ nucleus (m, or m')

IV. Particle Growth : monomer (m) + nucleus (m) ↘

monomer (m') + nucleus (m) ↗ growth (monomer addition)

nucleus (m) + nucleus (m') ⟶ growth (nuclei aggregation)

V. Nuclei dissolution : nucleus (m) $\xrightarrow{OH^-}$ n.monomer (m)

VI. Monomer exchange : monomer (m) $\overset{K_{ex}}{\rightleftharpoons}$ monomer (m')

VII. Monomer ionization : $Si(OH)_4$ (m) + yOH^- (m) ⟶ $SiO_yOH_{4-y}^{\ y-}$(m) + yH_2O (m)

y = 1,2

VIII. surface ionization : Si(OH) (s) $\xrightarrow{OH^-}$ SiO^- (s)

(1) **Scheme S1.**General reaction scheme of NPs formation in microemulsion (adapted from Arriagada, F.J.; Osseo-Asare, K. *Colloids Surf. A* **1999**, 154, 311)