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Nanostructured Interfaces and Surfaces
Centre of Excellence

Fluorescent hybrid dye-silica nanoparticles: role of the dye structure on the dispersion throughout the silica matrix and overall brightness

Alberto G., Caputo G., Viscardi G., Coluccia S. and Martra G.

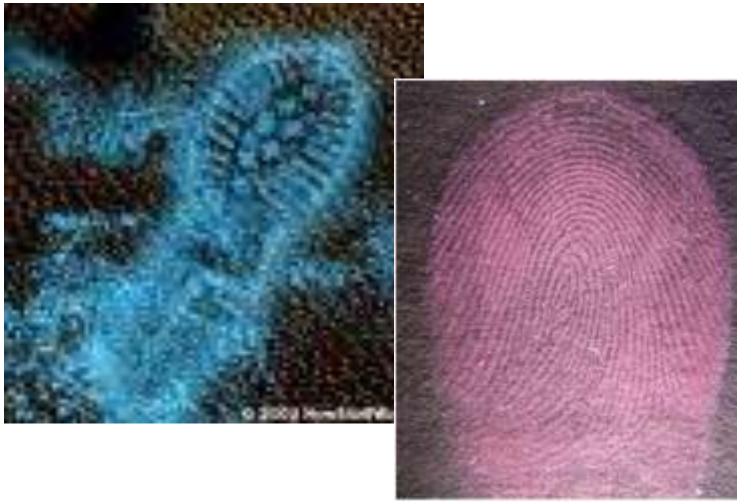
Department of Chemistry
&
“Nanostructured Interfaces and Surfaces” Centre of Excellence, University of Torino – Italy

Bukovel, August 26 - September 2, 2012

Luminescence &…

optoelectronics

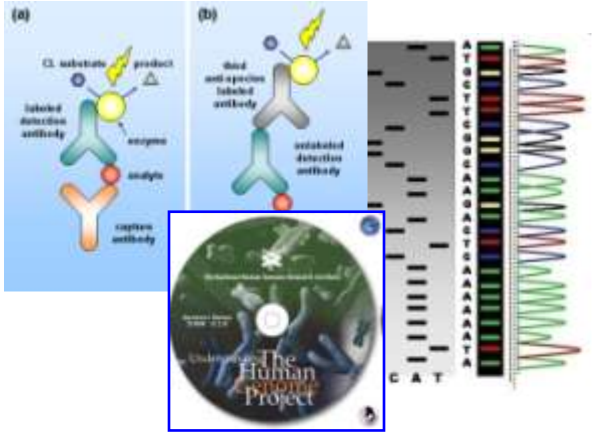
(often, elettrochemiluminescence)



niche applications: forensics

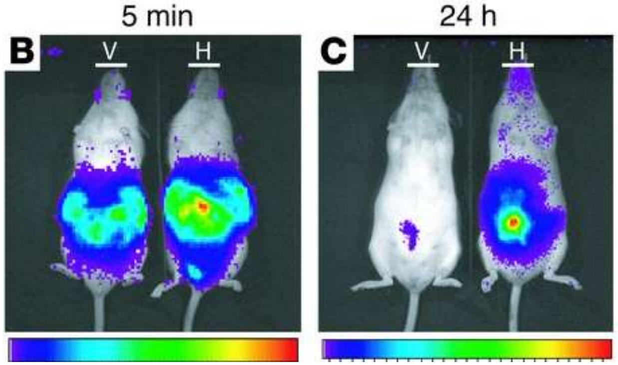
(chemi-, photoluminescence)

life science (mainly: photoluminescence)



biomolecular

in vitro



in vivo

Photoluminescence, why?

high sensitivity: C ~ 10^{-12} M

ease of excitation (light)

large amount of available photoluminescent compound

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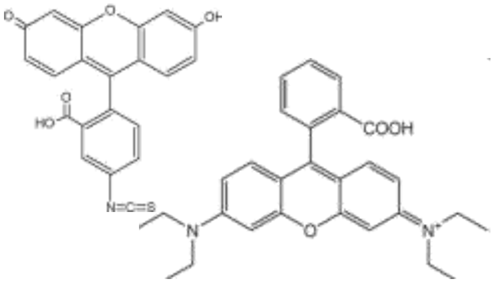
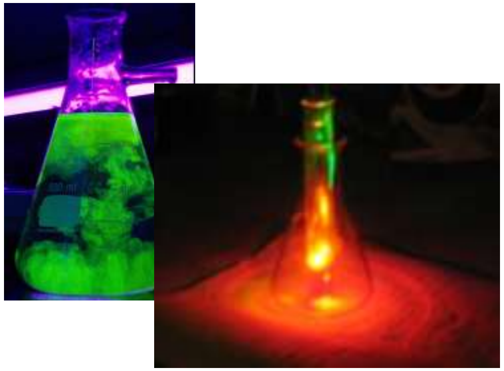
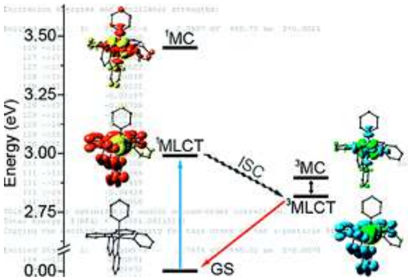
Organic fluorescent dyes





Organometallic complexes



Proteins

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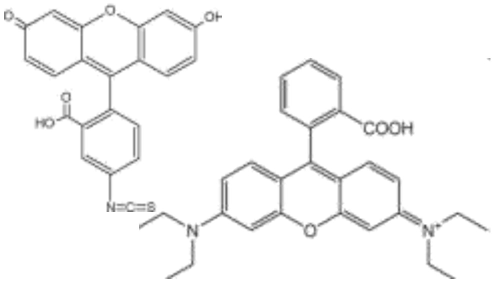

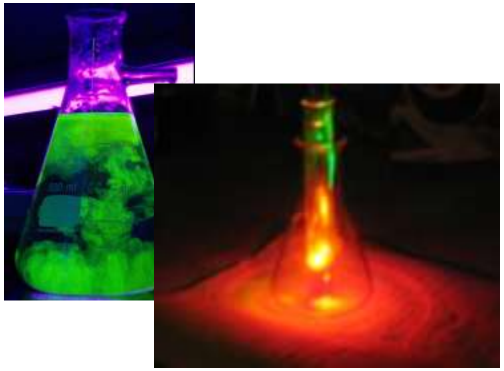

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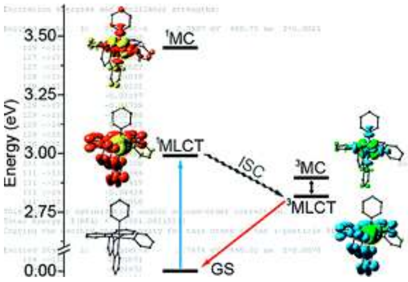
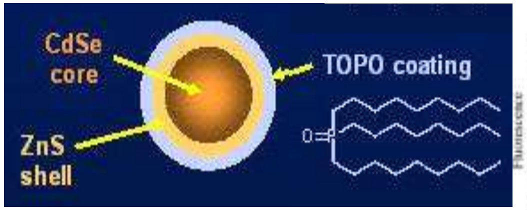
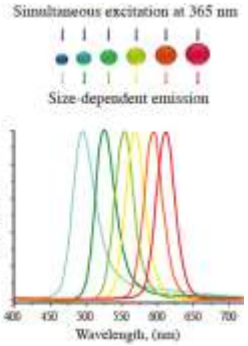


Proteins

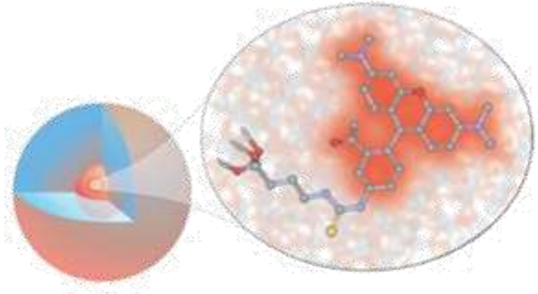
Photoluminescent nanomaterials

Quantum Dots



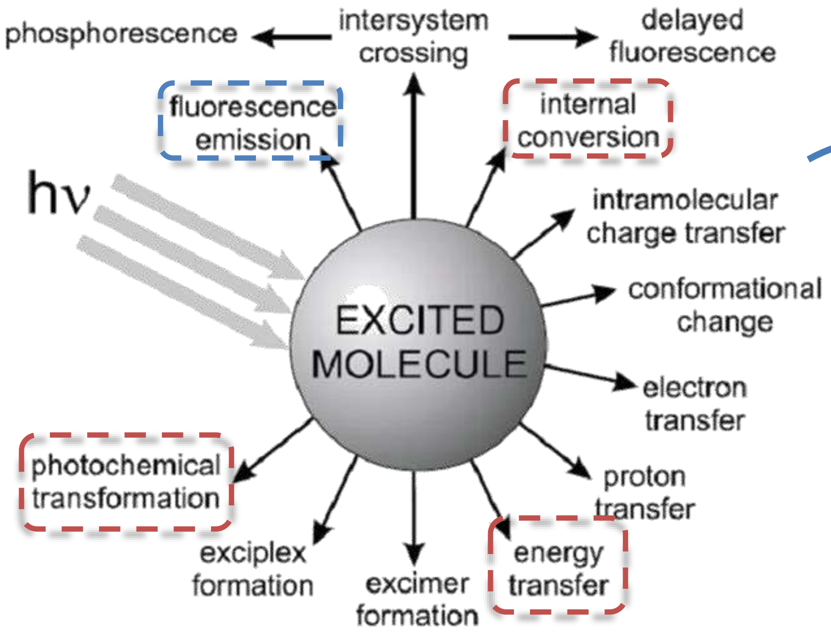


Hybrid organic dye/silica nanoparticles

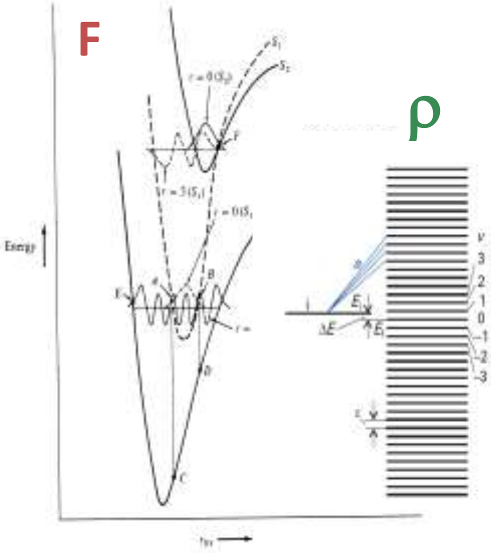


An emerging tool: Hybrid organic dye/silica nanoparticles

main competitors



quantum mechanics can help



$$k_{nr} = 2\pi\hbar^{-1}\beta^{2}\,\rho\,F$$

also the rotation levels must be taken into account

embedding of molecules decreases ρ

prevention of the interaction with O_2

Increase of molecular rigidity

Higher stability

Enhanced brightness

Influence of the particle architecture on the photophysical properties

Base-catalyzed hydrolysis and polycondensation of silica percursors and organic dyes-silane derivatives in:

a) Homogeneous solutions (Stöber method)

b) Reverse microemulsion

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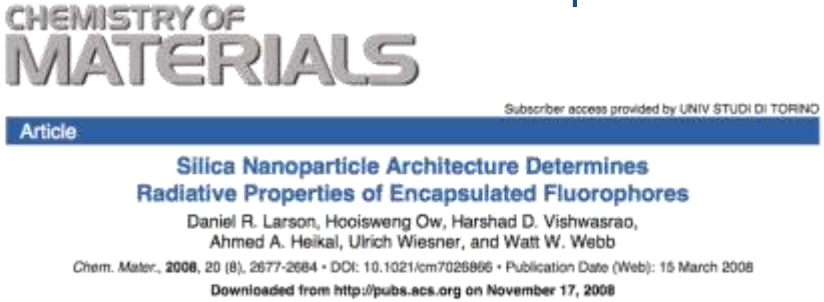

CHEMISTRY OF MATERIALS

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Article

Silica Nanoparticle Architecture Determines Radiative Properties of Encapsulated Fluorophores

Daniel R. Larson, Hooisweng Ow, Harshad D. Vishwasrao,
Ahmed A. Heikal, Ulrich Wiesner, and Watt W. Webb

Chem. Mater., **2008**, 20 (8), 2677-2684 • DOI: 10.1021/cm7026866 • Publication Date (Web): 15 March 2008

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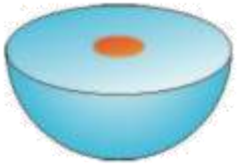
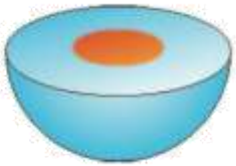
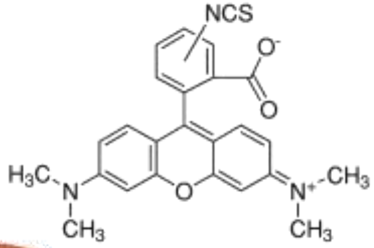
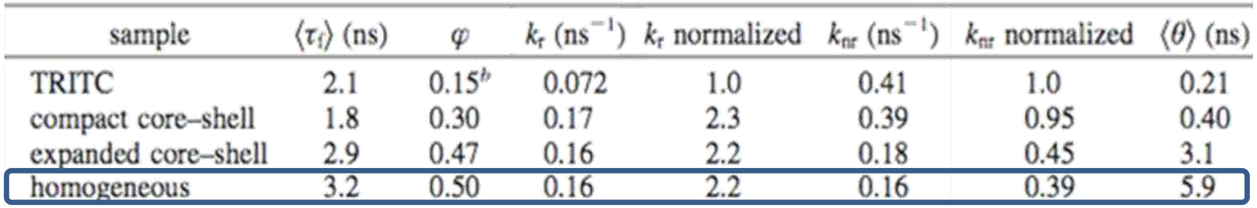






TRITC

Compact core-shell **Expanded core-shell** **Homogeneous particles**

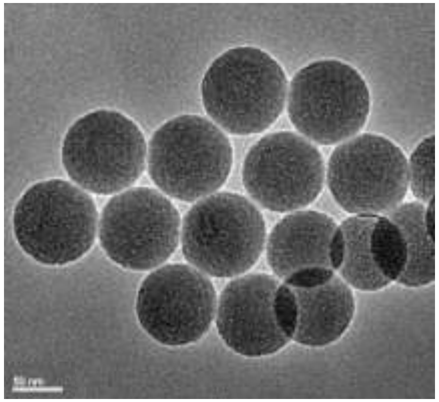


sample	$\langle\tau_f\rangle$ (ns)	φ	k_r (ns^{-1})	k_r normalized	k_{nr} (ns^{-1})	k_{nr} normalized	$\langle\theta\rangle$ (ns)
TRITC	2.1	0.15^b	0.072	1.0	0.41	1.0	0.21
compact core–shell	1.8	0.30	0.17	2.3	0.39	0.95	0.40
expanded core–shell	2.9	0.47	0.16	2.2	0.18	0.45	3.1
homogeneous	3.2	0.50	0.16	2.2	0.16	0.39	5.9

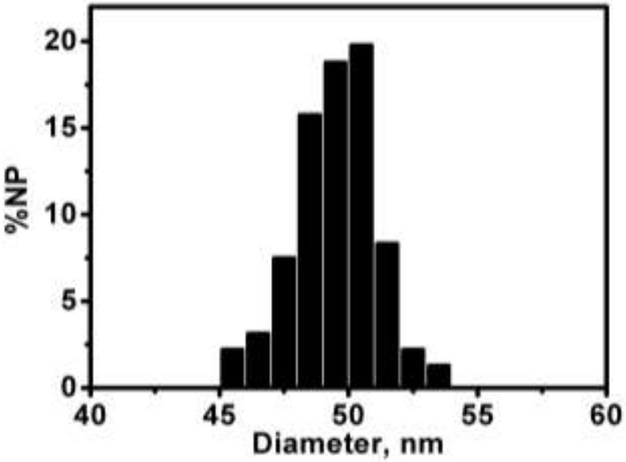
homogeneous fluorophore distribution provides best photophysical performances

This Work

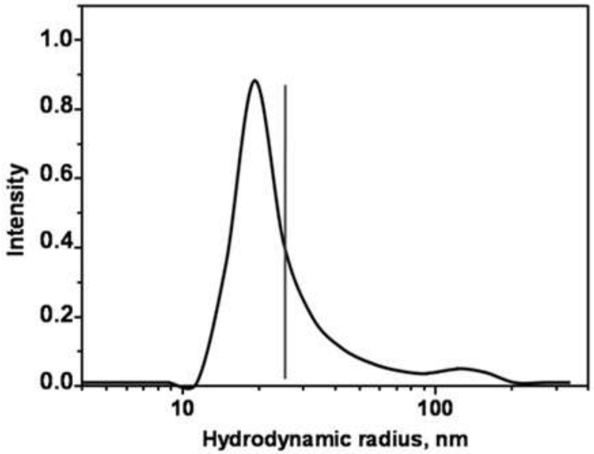
Hybrid dye-SiO_2 NPs prepared by TEOS hydrolysis and polymerization in reverse micelles in **W/O microemulsion**



homogeneus spherical morphology



size monodispersion



good dispersion in water (pH 5.5)

homogeneous behaviour in functional tests

statistical significance of quantitative evaluation

number of NPs per sample

number of Dye molecules per NP

Possibility to quantitatively evaluate the photophysical behaviour of entrapped fluorophores

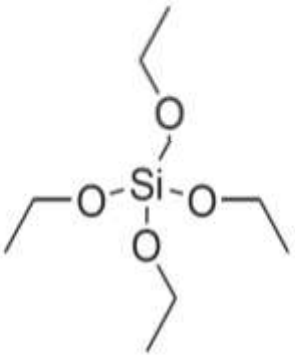
Reverse Microemulsion Technique

Key point:

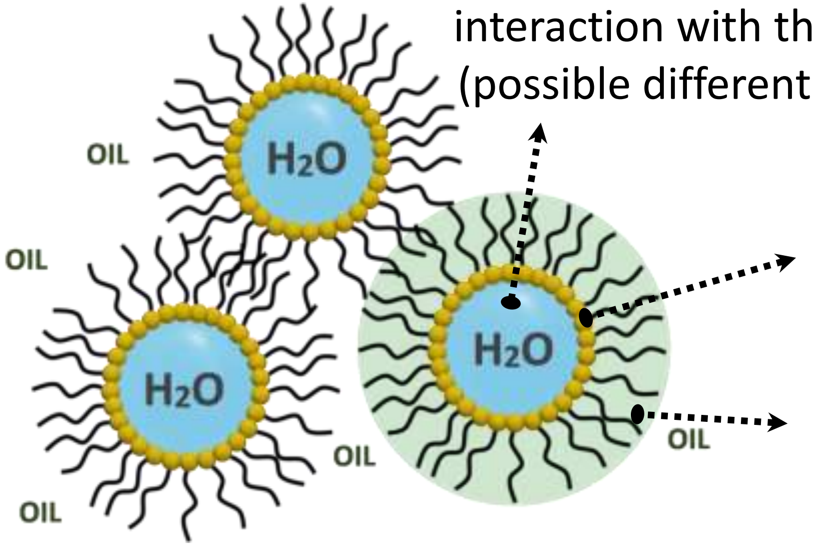
partition of reactants between oil and water, mediated by the micellar “palisade”

Reactants:

Tetraethylorthosilicate (TEOS)



Dye-silane derivative



water in the “pool”: interaction with the polar heads (possible different water states)

interface

“palisade”

surfactant:
Triton X-100, non-ionic

co-surfactant:
n-hexanol

oil:
cyclohexane

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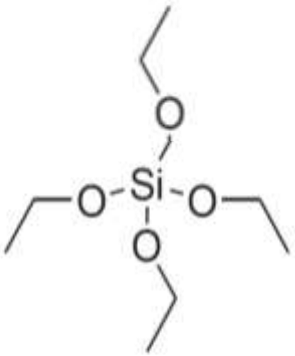

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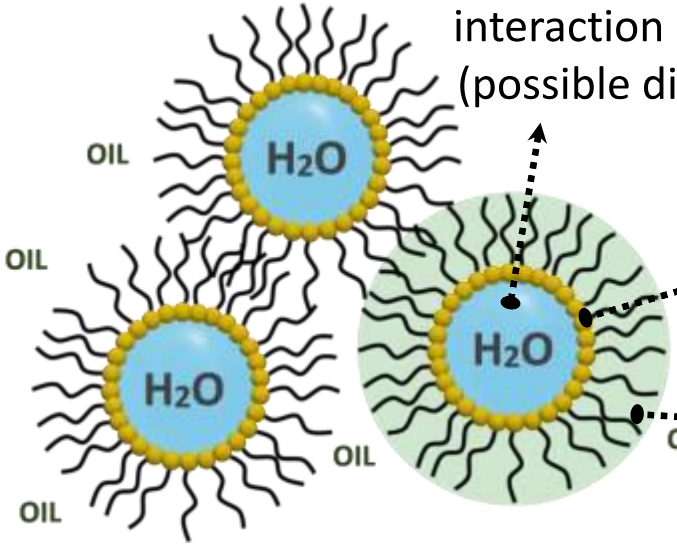

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identification of a molecular parameter that could effectively help to tailor the dispersion of the dye molecules in the final hybrid NPs

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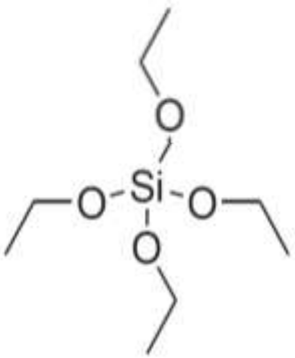

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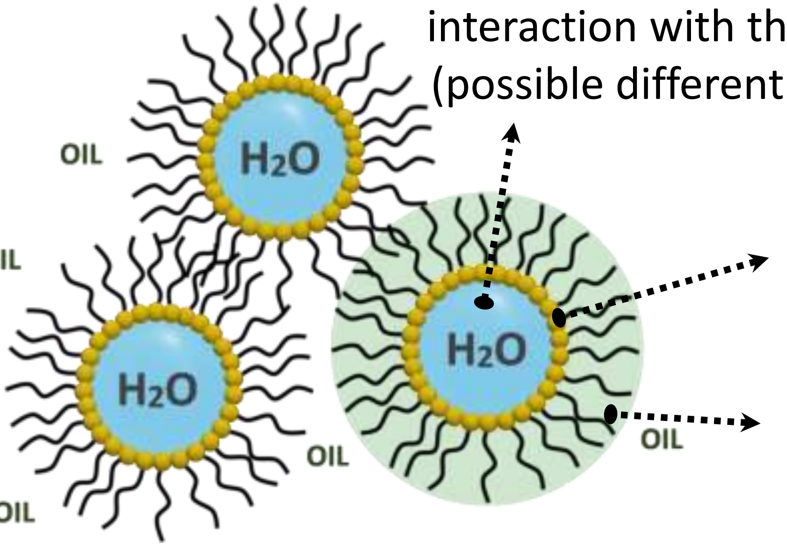

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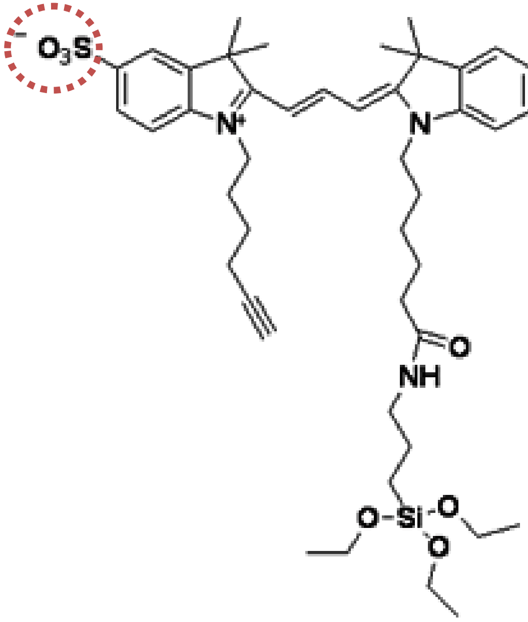
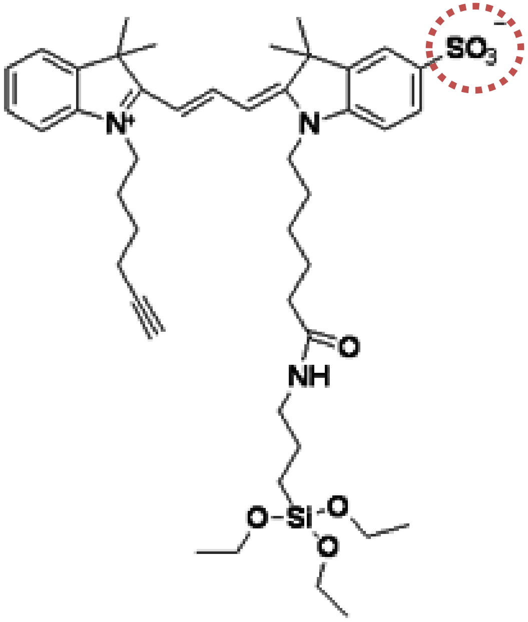
Molecular parameter selected:

relative hydrophobicity of TEOS and Dyes

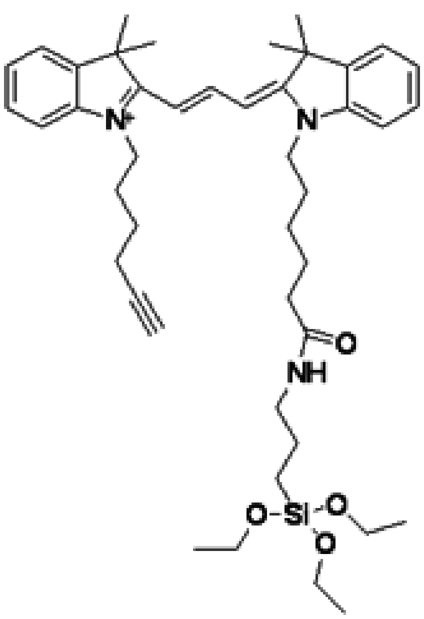
Fluorescent Dyes: Cyanines



I3BS-APTS



I3MS-APTS



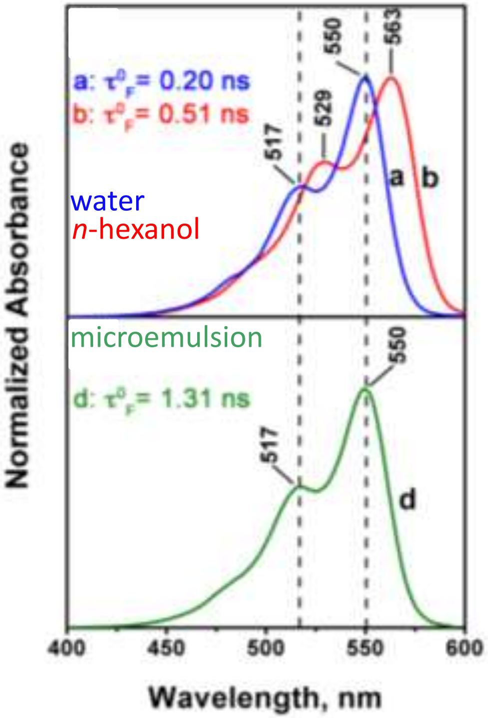
I3NS-APTS

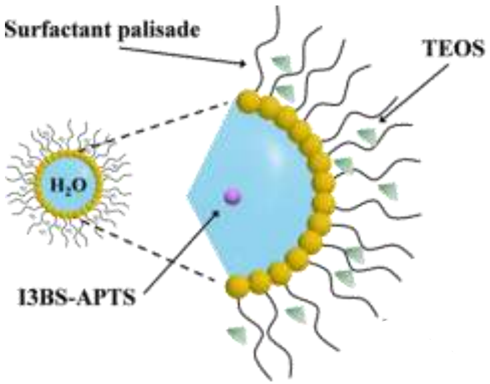
Hydrophobicity

Expected different partition between oil/reverse micelle palisade/water pool

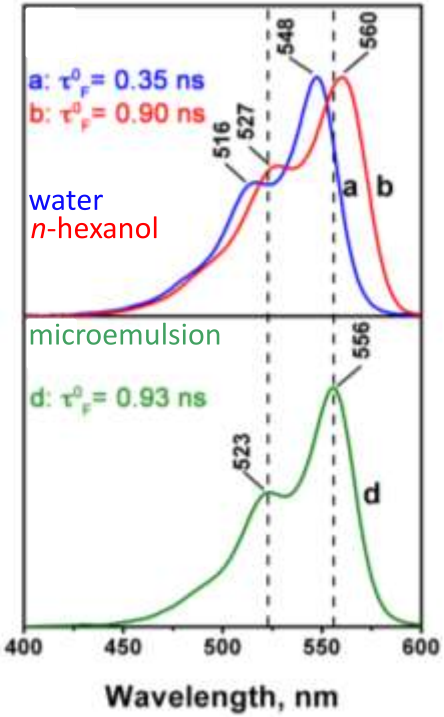
Cyanines at the starting-line

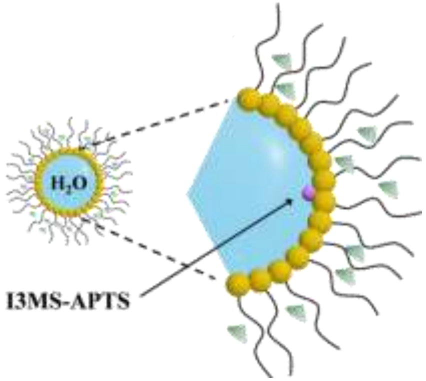
I3BS-APTS



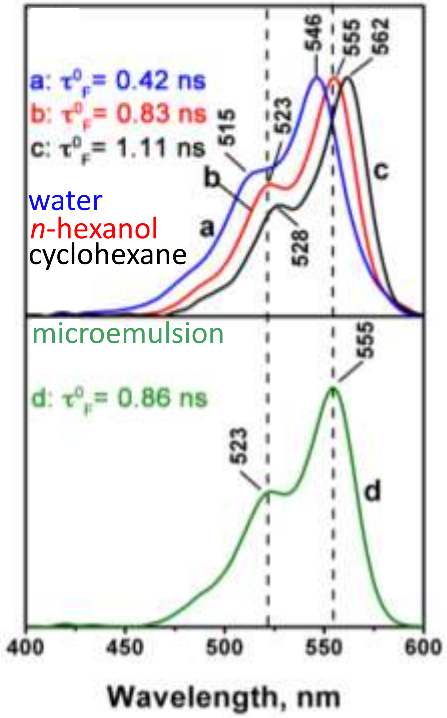


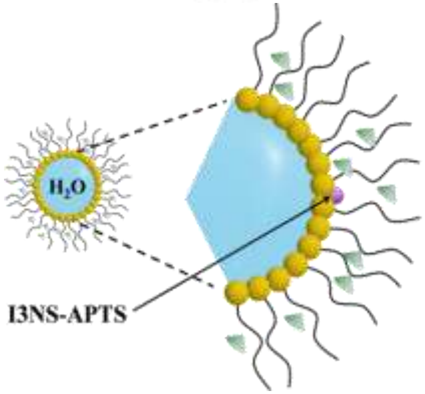
I3MS-APTS





I3NS-APTS





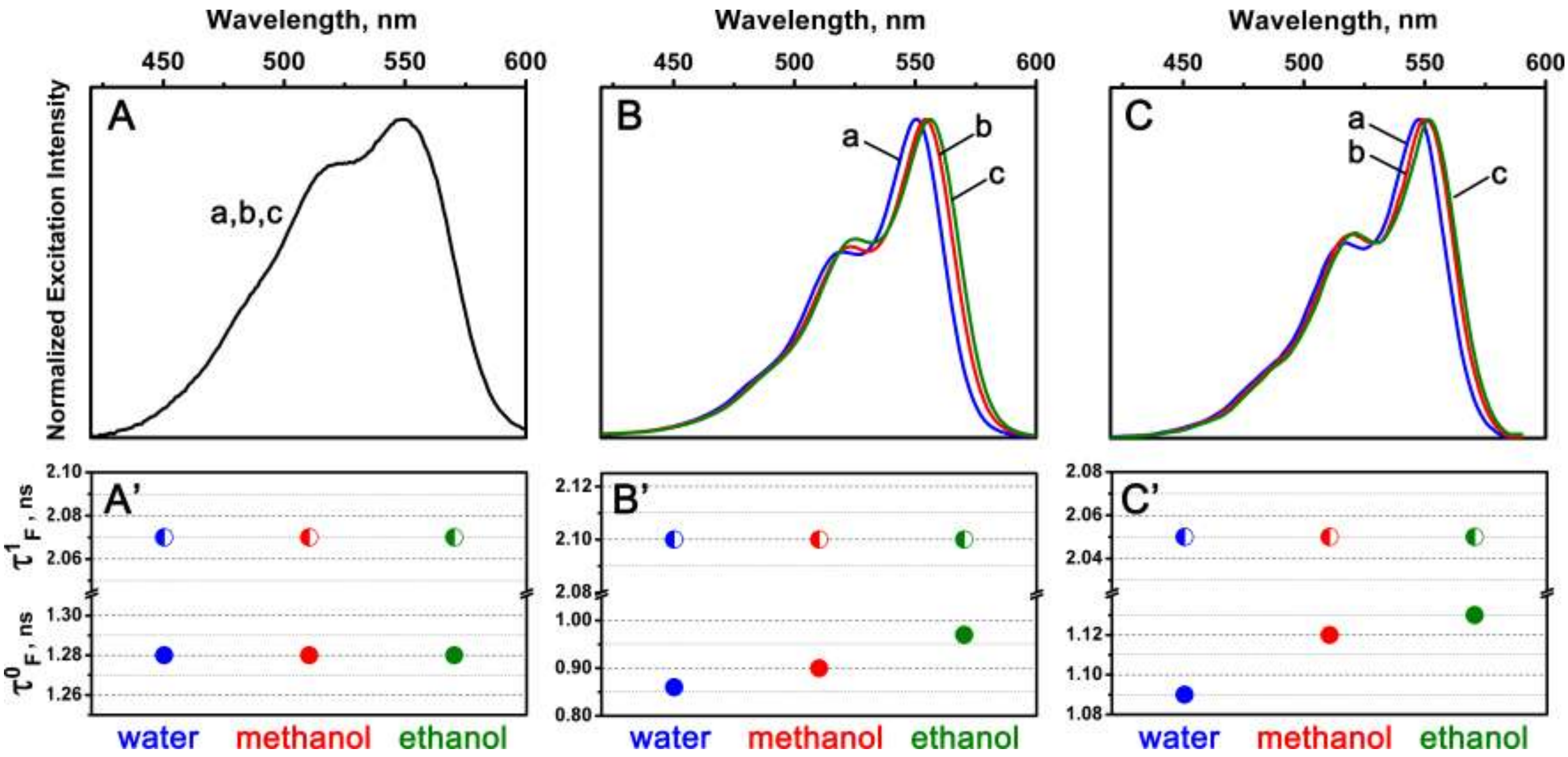
different location of Cy with respect the oil/water interface depending on their hydrophobicity

Cyanines location in the final materials

I3BS-NPs

I3MS-NPs

I3NS-NPs



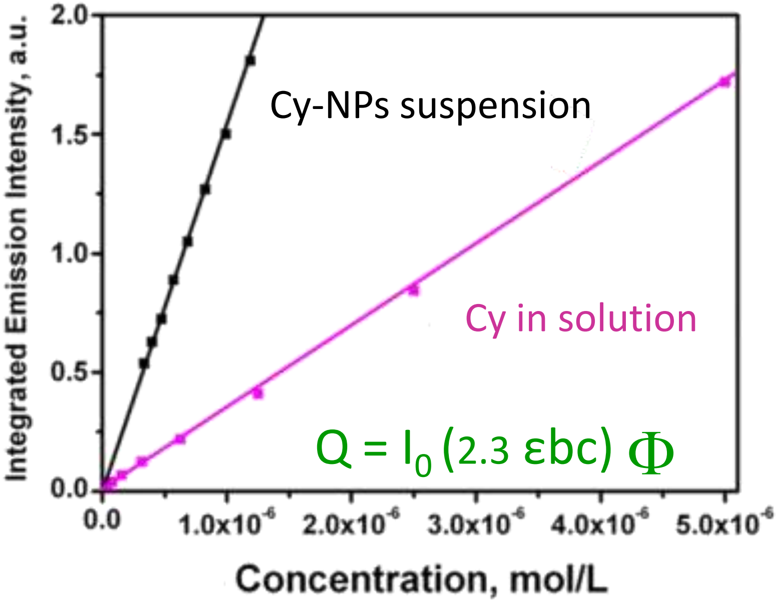
Complete inclusion of I3BS-APTS molecules within the NPs

Presence of some I3MS-APTS molecules on the surface

Presence of some I3NS-APTS molecules on the surface

Methodological Aspect: quantitative treatment of photoluminescent intensity and lifetime data

Photoluminescence intensity of equimolar Cy solution/Cy-NPs suspensions

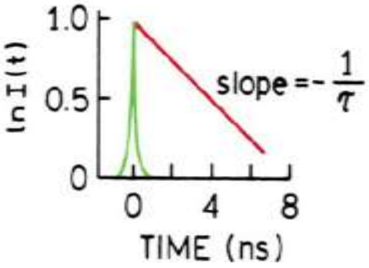


A) Photoluminescence intensity, n. NPs/mL and n. Cy/NP allow to determine the

average gain in Φ

per Cy molecule entrapped in a NP

averaged on ALL Cy molecules in a NP (both fluorescent and not-fluorescent)



τ^0_F (ns)	1.09 (35%)
τ^1_F (ns)	2.05 (65%)
χ^2	1.09

B) fluorescence lifetime $(\tau \propto \Phi)$:

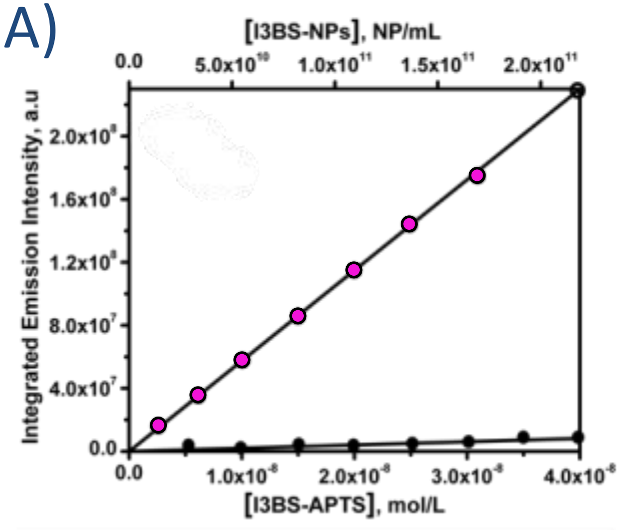
-signal ONLY due to fluorescent Cy

- gain in τ (Φ) dependent on the Cy environment

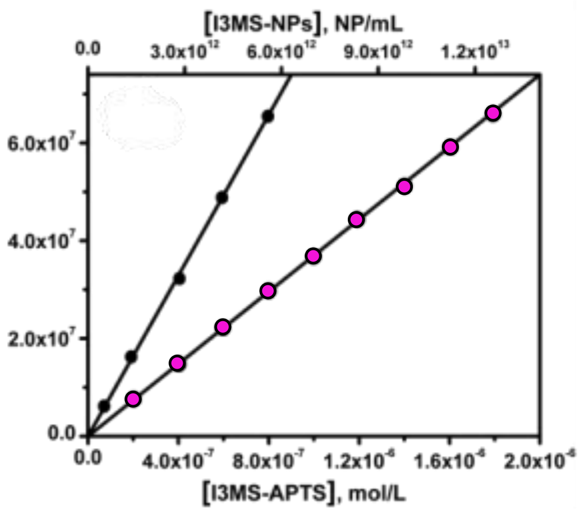
number and relative extent of “families” of fluorescent Cy

quantitative treatment of photoluminescent intensity and lifetime data

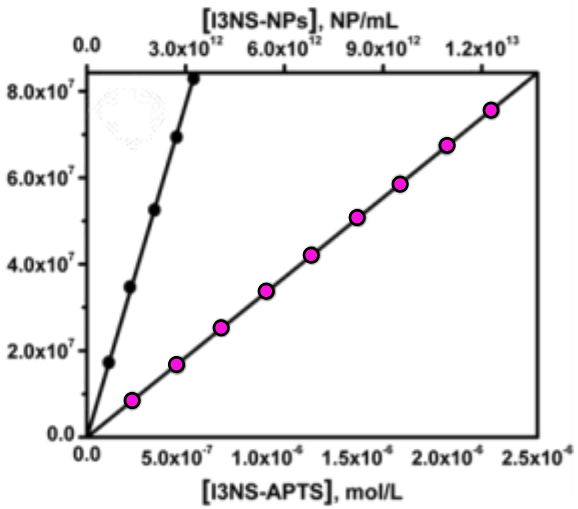
A)



Φ_{NPs} / Φ_{Cy} : 0.04



Φ_{NPs} / Φ_{Cy} : 2.7



Φ_{NPs} / Φ_{Cy} : 4.3

quantitative treatment of photoluminescent intensity and lifetime data

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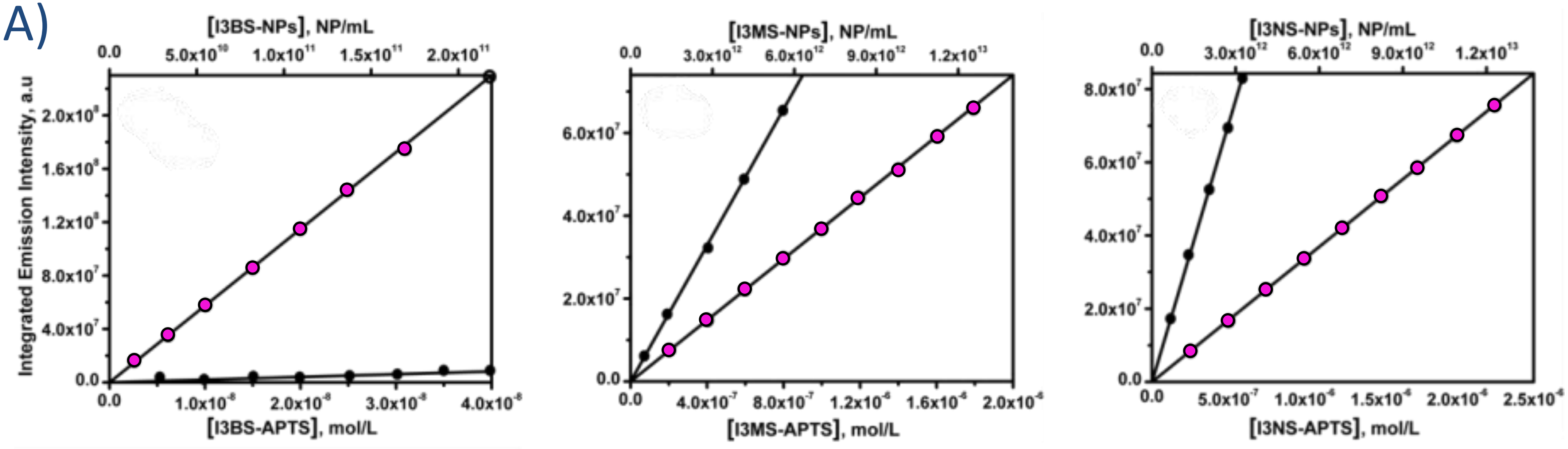

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B)

Relative Φ expected gain: $\Sigma\, x_i(\tau_i NP/\tau_i Mol)$

(averaged on EMITTING Cy)

	I3DS-APTS	I3DS-NPs
τ^0_F	0.20 (100%)	1.28 (55%)
τ^1_F	---	2.06 (45%)
χ^2	1.02	1.03

5.7

	I3MS-APTS	I3MS-NPs
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	I3NS-APTS	I3NS-NPs
τ^0_F	0.42 (100%)	1.09 (35%)
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χ^2	1.2	1.09

4.2

quantitative treatment of photoluminescent intensity and lifetime data

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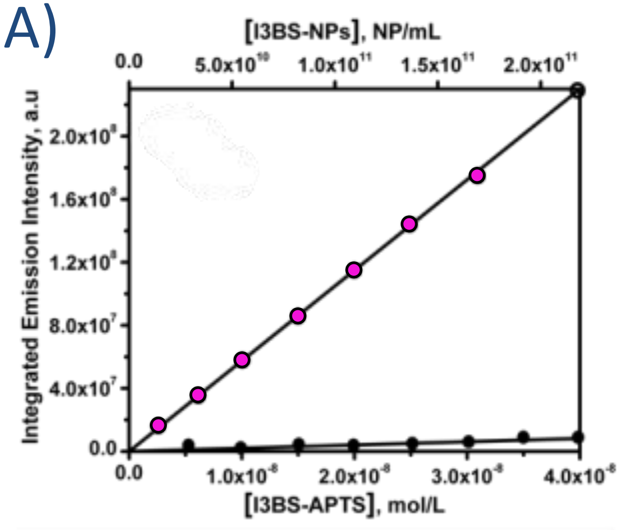

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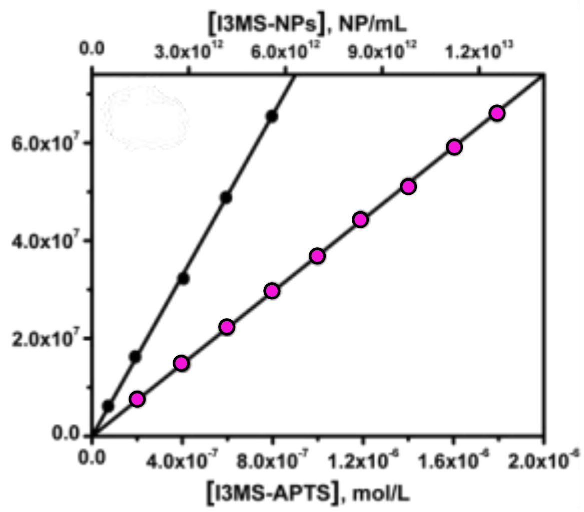

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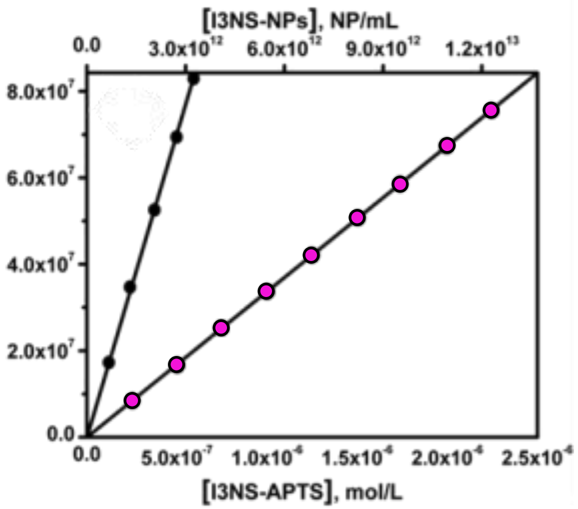

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4.2

% emitting Cy

0.5

63

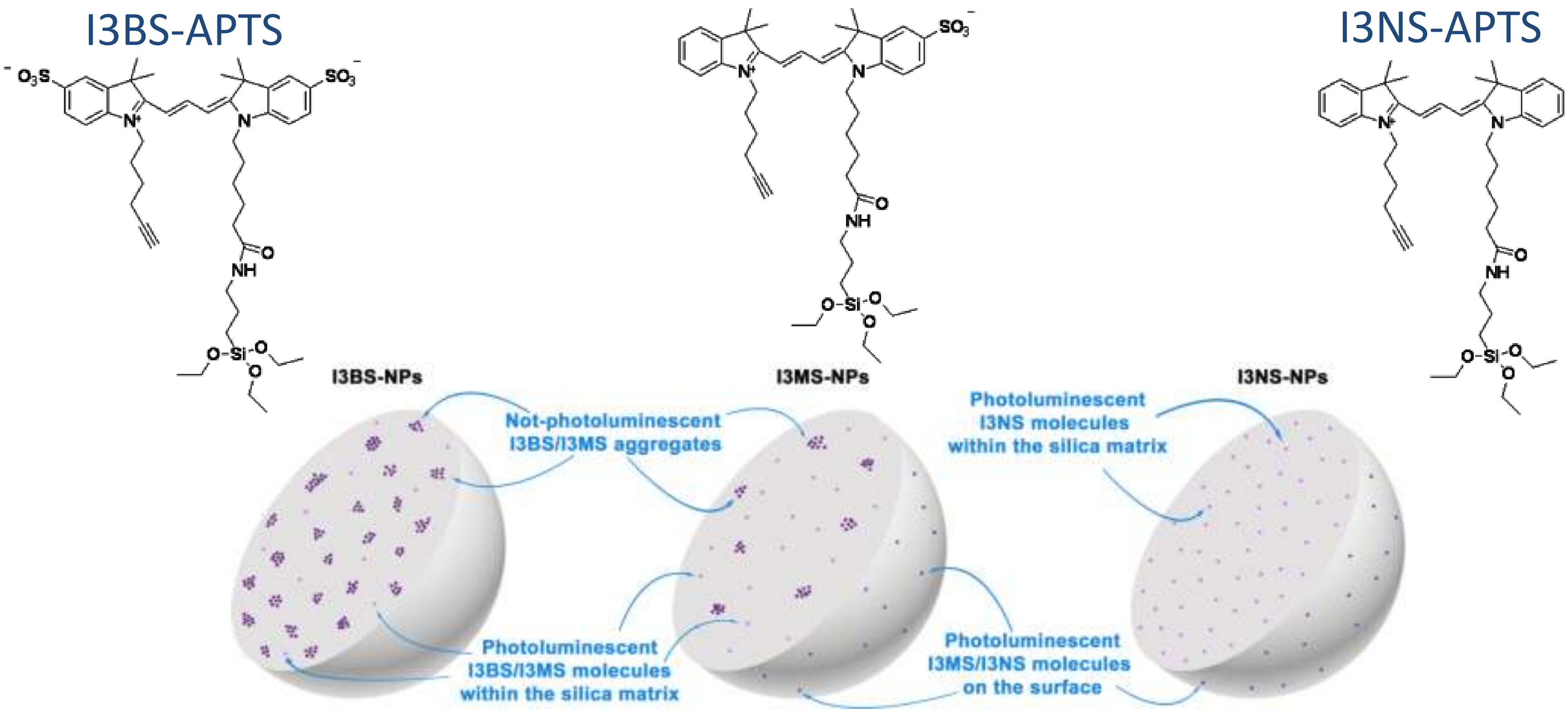
97

Photoluminescence performances of dyes in NPs *vs* dye in solution

I3BS-APTS

I3MS-APTS

I3NS-APTS



Cyanines per NP		
110	86	110
Average Photoemission Gain per Cy		
0.04	2.7	4.3
Overall Brightness Enhancement per NP		
4.4	232	481

Conclusions

The control of molecular parameters can actually result in a virtuous design of the photophysical behaviour of highly homogeneous hybrid dye-silica NP: “wise” optimization of the use of organic fluorophores

The interplay between steady state and time resolved photoluminescence actually represents an unique tool to monitor and understand the “molecular story” leading to the final materials

For further details you can refer to G.Alberto et al. *Chem. Mater*. 2012, 24, 2792-2801

Perspectives

Possibility to increase the number of dye molecules per NP keeping the optimized dye distribution, location and photoluminecence intensity

Possibility to consider other photoluminescent molecules with higher Φ

Possibility to consider other photoluminescent molecules emitting in the Red-NIR boundary region

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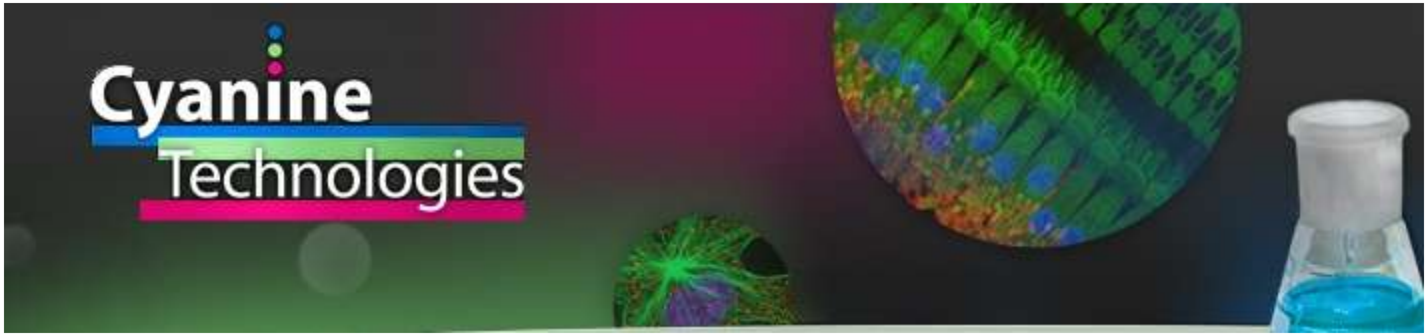
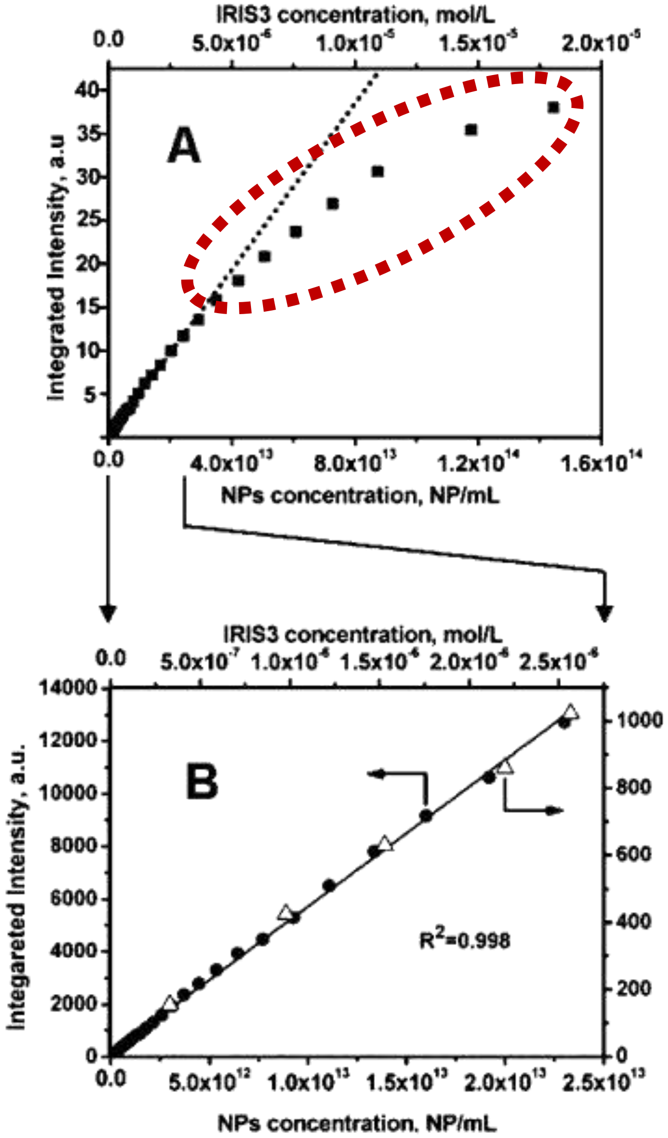


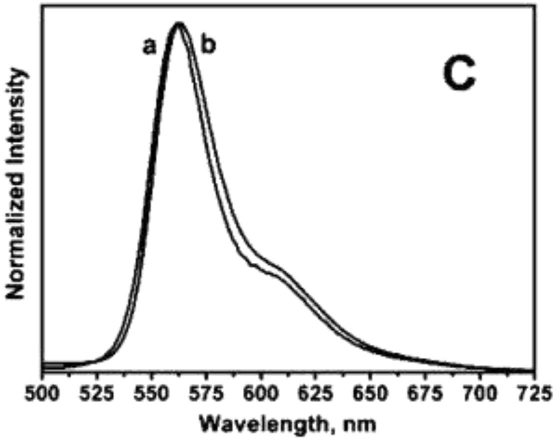
Photophysical performances of hybrid dyes/silica NP

Intensity: pay attention to interparticles effects!



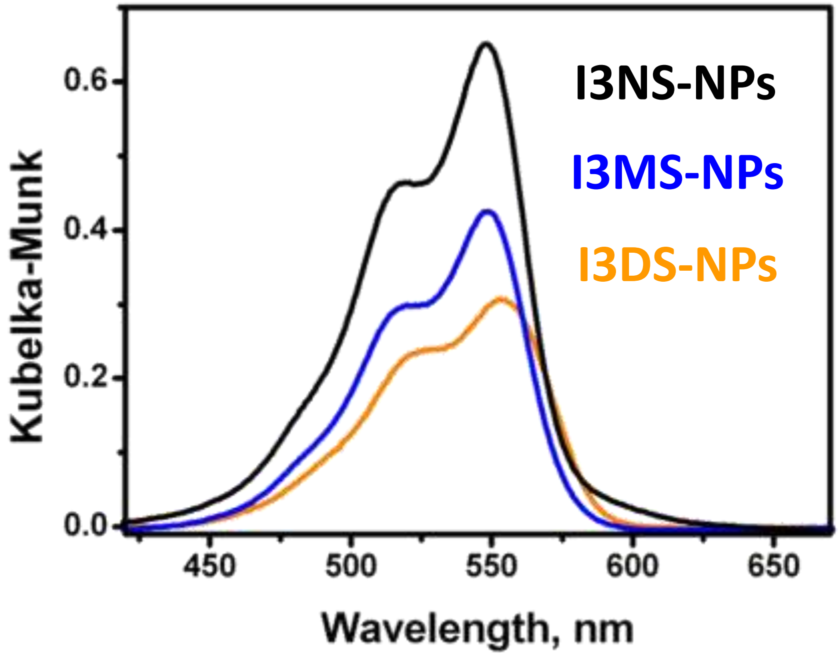
from diluted to concentrated suspensions

- light scattering
- inner filter effects
- self-absoprtion



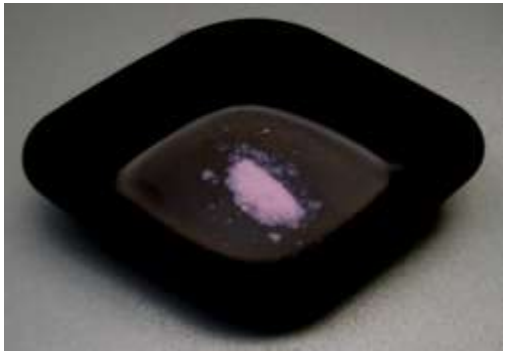
Where are the missing, not photoluminecent cyanines ?

Trace: space



I3DS-NPs

I3MS-NPs



I3NS-NPs

prevalence of diffusion towards adsorption