

Hybrid organic-inorganic systems as light-harvesting antennae

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Paola Ceroni is an associate professor at the University of Bologna. In 1998 she obtained her PhD degree in Chemical Sciences at the University of Bologna, after a period in the United States (Prof. Allen J. Bard's laboratory). Her PhD thesis was awarded by the Semerano prize from the Italian Chemical Society. Current research is focused on photochemistry and electrochemistry of supramolecular systems and luminescent nanocrystals. Her research on dendrimers and nanoparticles toward photovoltaic applications has been funded by an ERC Starting Grant. She is co-author of more than 150 scientific papers in refereed international journals. h-index: 37 (ISI Web of Knowledge). She is co-author of a book entitled: "Photochemistry and Photophysics: Concepts, Research, Applications" (2014, Wiley-VCH) and the editor of three books published by Wiley and Springer. She has presented oral communications at more than 50 national and international conferences and 20 invited lectures at universities and research institutes abroad.

An antenna for light harvesting is an organized multicomponent system in which many chromophoric molecular units absorb the incident light and then channel the excitation energy to a common acceptor component.¹ Two different approaches will be discussed: (i) a multiterpyridine system coupled to a hexathiophenyl benzene core exhibiting aggregation induced phosphorescence² and (ii) a family of Silicon nanocrystals (SiNCs) functionalised by organic chromophores.³

In the first system, Mg^{2+} complexation turns on phosphorescence of the hexathiophenyl core. Metal ion coordination yields the formation of a supramolecular polymer which hinders intramolecular rotations and motions of the core chromophore, thus favoring radiative deactivation of the luminescent excited state. Upon excitation of the $[Mg(tpy)_2]^{2+}$ units of the polymeric structure, sensitization of the core phosphorescence takes place with >90% efficiency. The light-harvesting polymeric antenna can be disassembled upon fluoride ions addition, thereby switching off luminescence and offering a new tool for fluoride ion sensing.

The second approach is based on silicon nanocrystals that, in the quantum size range (2-12 nm), can be made as viable light emitters with emission wavelength that can be tuned from the near-infrared (NIR) into the visible by decreasing their size. Covalent Si-to-carbon bonding also offers the possibility of integrating inorganic and organic components

into robust structures. In the present work, the H-terminated nanocrystals were used as a platform for co-passivation with dodecene and different organic chromophores by thermal hydrosilylation. For example, we functionalised two families of SiNC of average diameter of 2.5 and 5 nm with pyrene chromophores: pyrene excitation results in a very efficient (> 95%) energy transfer to the nanocrystal core.³ To the best of our knowledge this is the first time in which highly efficient light harvesting from photoactive units to the silicon core has been demonstrated. This approach enabled us to circumvent the drawback of the low molar absorption coefficient of SiNCs. The investigated hybrid material exhibits high quantum yield (40%) also in the NIR spectral region with lifetime in the μs range.

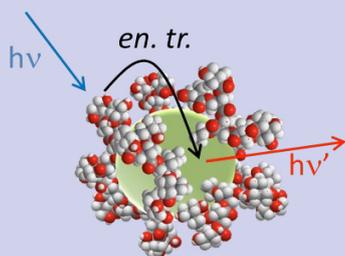


Figure 1. Schematic representation based on functionalized silicon nanocrystals.

1) *Photochemistry and Photophysics: Concepts, Research, Applications*, V. Balzani, P. Ceroni, A. Juris, Wiley-VCH, **2014**, ch. 10.

2) A. Fermi, G. Bergamini, M. Roy, M. Gingras, P. Ceroni, *J. Am. Chem. Soc.* **2014**, 136, 6395–6400.

3) See e.g., R. Mazzaro, M. Locritani, J. K. Molloy, M. Montalti, Y. Yu, B. A. Korgel, G. Bergamini, V. Morandi, P. Ceroni, *Chem. Mater.* **2015**, 27, 4390–4397.

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