

Optical Properties of Hybrid Organic-Inorganic Materials and their Applications

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Research on hybrid inorganic-organic materials has experienced an explosive growth since the 1980s, with the expansion of soft inorganic chemistry based processes. Indeed, mild synthetic conditions, low processing temperatures provided by “chimie douce” and the versatility of the colloidal state allow for the mixing of the organic and inorganic components at the nanometer scale in virtually any ratio to produce the so called hybrid materials. Today a high degree of control over both composition and nanostructure of these hybrids can be achieved allowing tunable structure-property relationships. This, in turn, makes it possible to tailor and fine-tune many properties (mechanical, optical, electronic, thermal, chemical...) in very broad ranges, and to design specific multifunctional systems for applications. In particular, the field of “Hybrid-Optics” has been very productive not only scientifically but also in terms of applications. Indeed, numerous optical devices based on hybrids are already in, or very close, to the market. This review describes most of the recent advances performed in this field. Emphasis will be given to luminescent, photochromic, NLO and plasmonic properties. As an outlook we show that the controlled coupling between plasmonics and luminescence is opening a land of opportunities in the field of “Hybrid-Optics”.

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1. Introduction

The field of organic-inorganic hybrid materials has been growing intensively during the past 20 years and is certainly nowadays one of the major fields of research and unambiguously one of the most exciting. The idea to combine organic and inorganic systems appears now has evidence, but considering the complexity to design association of materials that exhibit very low compatibility for each other's, it has led the chemists and physicist to imagine numerous architectures more or less easy to achieve experimentally. The rising of new characterization techniques and knowledge at the nanometer scale and even the molecular scale has been a driving force towards imagination of hybrid architectures in many major fields such as sensors, electronics, optics, lightning, medicine, catalysis, energy storage, energy conversion. Moreover, the need for always better

materials for complex devices with improved properties and multifunctional responses is a perpetual demand which often can be fulfilled by the use of hybrid materials. In particular, regarding the broad field of optical materials, ranging from lightning to energy, bioimaging, screens design, optoelectronics and many others, the design of hybrid materials has been particularly productive (Figure 1). One reason is that combining unique optical responses of organic or organometallic molecular species with either mechanical properties or optical properties of inorganic counterparts provides a unique way to elaborate highly innovating optical systems at the macro or the nanoscale. Considering the usually high sensitivity of optical responses to the environment, the interfaces between the organics and inorganics is a crucial parameter in most systems. Of course, large number of books and reviews were previously published in the different fields related to optics, both by chemists, physicists and biologists showing the large community concerned by this topic. This article aims to review the latest reported hybrid optical materials, with strong focus on the 10 last years, and trying to make an overview of the relationship between the structures and the measured properties, as well as the way to control the interfaces in the hybrids. Regarding the number of work in the field, this report cannot be exhaustive, but can give an insight in the actual state of the art in the field of hybrid materials devoted to optics and in



Figure 1. Hybrid materials and optical properties, from ancient time and art design to highly innovative functional devices. Sources of the panels are given row-wise from left to right, starting with the top: Reproduced with permission.^[529] Copyright 2012, American Chemical Society. Reproduced with permission.^[530] Copyright 2001, American Chemical Society. Reproduced with permission.^[46] Copyright 2003, Wiley-VCH. Original Source: Reproduced with permission.^[530] Copyright 2001, American Chemical Society. Second line: Left image, mid-left, and right image: Reproduced with permission.^[530] Copyright 2001, American Chemical Society. Original sources: Reproduced with permission.^[46] Copyright 2003, Wiley-VCH. Middle image: Reproduced with permission.^[531] Copyright 2006, Springer. Right image: Reproduced with permission.^[534] Copyright 1996, Elsevier. Third line: Left image reproduced with permission.^[339] Copyright 2000, Elsevier. Middle image: Reproduced with permission.^[532] Copyright 2002, Royal Society of Chemistry. Right image: reproduced with permission.^[533] Copyright 2007, National Academy of Science.

particular the relationship between the different types of structure, the organic-inorganic interfaces and the final properties of the systems.

2. Light-Emitting Hybrid Materials

2.1. Introduction to Luminescence

Luminescence is a general term that describes any non-thermal processes in which energy is emitted in the ultraviolet, visible or infrared spectral regions from an electronically excited species. Generally, the emission occurs at a higher wavelength from that at which light is absorbed (a process termed as downshifting). The term broadly includes the commonly used categories of fluorescence and phosphorescence, depending upon the electronic configuration of the excited state and the emission pathway.^[1,2] In a first order absorption process, when the photon energy of the incident radiation is lower than the energy difference between two electronic states, the photons are not absorbed and the material is transparent to such radiation energy. For higher photons energy, absorption occurs (typically in 10^{-15} s) and the valence electrons will make a transition between two electronic energy levels. The excess of energy will be dissipated through vibrational processes that occur throughout the near infrared (NIR) spectral region. **Figure 2** shows examples of radiative and non-radiative processes.



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Beatriz Julián-López (1977) received her PhD in Chemistry from Jaume I University (Castellón, Spain) in 2003 working on lanthanide-doped organic-inorganic hybrid materials. She then moved to Paris and worked in mesoporous materials for biomedical applications, under the supervision of Prof. Clément Sanchez (UPMC-CNRS-Collège de France). In 2007, she returned to Jaume I University with a “Ramón y Cajal” program, where she is currently Associate Professor. She leads the Group of Multifunctional Materials and her main interest is the rational design of luminescent hierarchically organized nanostructures, by combining soft-chemistry and self-assembling processes, for application in photonics, ceramics, catalysis and energy.



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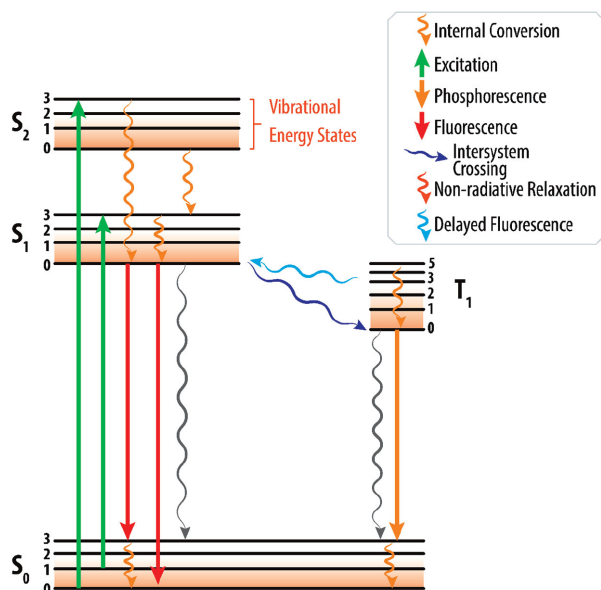


Figure 2. Jablonski diagram summarizing the typical radiative and non-radiative transitions within an electronically excited specie.

2.1.1. Non-Radiative Processes

- Internal conversion; an electron close to a ground state vibrational energy level, relaxes to the ground state via transitions between vibrational energy levels giving off the excess energy to other molecules as heat (vibrational energy). The time scale of the internal conversation and vibrational relaxation processes is 10^{-14} – 10^{-11} s.
- Intersystem crossing; the electron transition in an upper singlet (S_1) excited state to a lower energy level, such as a triplet state T_1 .
- Delayed fluorescence; after a fast intersystem crossing to T_1 and a thermally popped back into S_1 . The lifetime of S_1 increases and, in the limit, would be nearly equal to the lifetime of T_1 .^[3] Delayed fluorescence can also occur when two excited states interact and annihilate forming an emitting state, e.g., in triplet-triplet annihilation.^[4,5] Triplet-triplet annihilation is an encouraging up-conversion approach due to its low excitation power density, high quantum yield, tunable excitation/emission wavelength and strong absorption.^[6]

2.1.2. Radiative Processes

- Fluorescence; emission of a photon from S_1 to the vibrational states of the ground singlet (S_0) occurring in a time scale of 10^{-9} to 10^{-7} s.
- Phosphorescence; emission of a photon from T_1 to the vibrational states of S_0 . This process is much slower than fluorescence (10^{-3} – 10^2 s) because it involves two states of distinct multiplicity. For very long luminescence time decays (minutes and even hours), the emission is called persistent luminescence or afterglow.

Due to the non-radiative transitions, fluorescence and phosphorescence will occur at lower energy (longer wavelengths)



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than that of the absorbed photons. The energetic difference between the maximum of the emission and absorption spectra ascribed to the same electronic transition is known as Stokes-shift.^[7]

Electroluminescence results from the radiative recombination of electrons and holes injected into an inorganic, organic or organic-inorganic hybrid semiconductor material. Electroluminescence devices include light emitting diodes (LEDs), which produce light when a current is applied to a doped p-n junction of a semiconductor, and matrix-addressed displays.^[7] In the past decades, LEDs and organic light-emitting diodes (OLEDs) induced a deep revolution in the lighting industry. The first examples of the use of hybrid materials in lighting (more specifically in solid-state lighting, SSL) appeared in 2001 with layered crystalline organic-inorganic perovskites.^[8] Although the interest on these hybrid perovskites as single-phase white light emitters continue,^[9,10] the wide range of materials with potential application in SSL would include dye-bridged,^[11–17] dye-doped^[18] and quantum dots-doped^[19] siloxane-based organic-inorganic hybrids, and metal organic frameworks.^[20] Despite the interest of organic-inorganic hybrid perovskites in lighting, the most exciting application of these materials is in solar cells. Perovskite solar cells have shown remarkable progress in the last decade, with rapid increases in conversion efficiency, from 3.8% in 2009^[21] to 20% in 2015,^[22] demonstrating the potential competitiveness to traditional commercial solar cells and offering the prospective for an earth-abundant and low-energy-production solution to large-scale manufacturing of photovoltaic modules.^[23]

The potential of light-emitting hybrid materials relies on the possibility of fully exploiting the synergy between the optical features of the emitting centers and the intrinsic characteristics of the sol-gel derived hosts. Hybrid materials present several advantages for photonic and optical

applications, such as: i) versatile shaping and patterning, depending on the foreseen application; ii) optimization of composition and processing conditions, yielding excellent optical quality, high transmission, low processing temperature (<200 °C), and easy control of the refractive index by changing the relative proportion of the different precursors; and iii) photosensitivity, mechanical integrity, corrosion protection, and suitable adhesion properties.^[24–30] In general, the embedding of organic dyes, quantum dots (QDs), and trivalent lanthanide (Ln³⁺) complexes into hybrid hosts, with the corresponding formation of covalent (Class II) or non-covalent (Class I)^[31] host-guest interactions, improves the thermal stability, the mechanical resistance, and the aging and environmental stability of the guest emitting centers, relatively to what is observed for isolated centers.^[32,33] Moreover, the dispersion of these centers within the hybrid framework allows their incorporation in larger amounts, isolated from each other and protected by the hybrid host, improving the emission quantum yield and preventing the emission degradation.^[34–38]

In this section, we cover recent developments of luminescent and electroluminescent hybrid materials, with particular emphasis to specific applications, such as LEDs, random and feedback lasers, luminescent solar concentrators (LSCs), and luminescent thermometers. Examples will address organic-inorganic hybrids (essentially siloxane-based ones) embedding organic dyes, with the formation of covalent (dye-bridged hybrids) or non-covalent (dye-doped hybrids) dye-matrix interactions, QDs, inorganic nanoparticles and Ln³⁺ complexes. Hybrids with photochromic features will be discussed in Section 3, whereas hybrids for phosphors^[39] and for luminescent coatings (based on organic dyes,^[40] fluorine polymers,^[41] copper iodide clusters^[42] and on Ln³⁺ ions^[43–45]) were not reviewed in detail, being only addressed in the context of LEDs and LSCs, respectively.

General and comprehensive reviews on luminescent hybrid materials embedding organic dyes and Ln³⁺ ions were published by Carlos,^[25,28] Sanchez,^[27,46–48] Escribano,^[49] Binnemans,^[50] Zhang,^[51] and Ribeiro.^[52] Concerning electroluminescence, there is only one recent review addressing the application of dye-doped hybrids on LEDs.^[53] In view of the current trends of the subject, and balancing the literature published since these reviews, we decide to not discuss the applications of luminescent hybrid materials in integrated optics and optical telecommunications, in biomedicine, and in solar cells. While in integrated optics and optical telecommunications the review by Ferreira et al.^[26] is relatively updated, in solar cells and in biomedicine the amount of work published in the past 5 years justify independent review publications. In fact, perovskite solar cells largely dominate the current research trend of hybrid materials in photovoltaics, while in biomedicine ligand-decorated QDs and Ln³⁺-based inorganic NPs, Ln³⁺ chelates embedded within inorganic matrices and more complex core-shell and core-corona hybrid architectures have been designed as biosensing platforms for in vivo imaging, diagnostics, targeting and therapy. The subject underwent an enormous expansion during the last decade that can be tracked, for instance, in the recent reviews of Prasad et al.,^[54,55] Prodi et al.,^[56] and Bünzli.^[57]

2.2. White Light Emission and LEDs

The interest in organic-inorganic hybrids for LEDs has grown considerably during the last three decades since the seminal work of Tang and Van Slyke on dye-based OLEDs operating at low driving voltages^[58] and the first reports demonstrated the possibility of applying these materials in solid-state lasers.^[59–61]

The first examples of white LEDs (WLEDs) based in hybrids date back to the final of last century comprising dye-modified silanes incorporating hole- or electron-transporting units and light-emitting species in the orange^[62] and green^[11] spectral regions. Later on, more efficient WLEDs were reported involving silsesquioxane hybrid matrices, as, for example, that based on the phenylenevinylendiimide precursor, luminance value of 10 cd·m⁻² for voltages lower than 30 V,^[12] and that based on polyhedral oligomeric silsesquioxanes bearing in the structure a dye molecule from the cyanine family, threshold operating voltage of 4 V.^[63] An intriguing example is the fabrication of a WLEDs by coating a commercial UV LED (390 nm) with a periodic mesoporous organosilica (PMO) film doped with Rhodamine 6G (Rh6G) and synthesized by surfactant-templated sol-gel polycondensation using a 1,3,6,8-tetraphenylpyrene (TPPy)-containing organosilane precursor.^[13] The blue emission of the films, emission quantum yield of 0.70, overlaps the absorption spectra of the dye and thus efficient energy transfer occurred and the white-light is achieved by combining the blue emission of the host with the yellow light of the guest. UV pumped WLEDs have huge potential because they are easy to manufacture, the white light emission is only due to the down-converting phosphors, they exhibit a low color point variation as a function of the forward-bias currents, and they have superior temperature stability. Moreover, as the human eyes are insensitive to UV radiation, the white color is independent of the pumping LED and of the thickness of the phosphor layer.

Poly(2-hydroxyethyl methacrylate-silica) hybrids doped with organoboron dyes emitting in the blue, green and red spectral regions^[16] and dye-bridged epoxy functional oligosiloxanes emitting in the green and red spectral regions with absolute emission quantum yields of 0.85 and 0.41, respectively,^[17] were used to produce efficient multi-color light-emitting hybrids. In this latter example, WLEDs were produced using a commercial blue LED as excitation source and by controlling the dyes concentration and the ratio between the red and green emitting species (**Figure 3**). The best device has a CCT of 4810 K, a CRI of 85 and a luminous efficacy of 23.7 lm·W⁻¹, being thermally stable at 120 °C for 1200 h.^[17]

The use of organically doped layered phyllosilicate clays was introduced in the late 90's.^[64,65] Although not fabricated as WLEDs, white light-emitting soft hybrids was reported based on the supramolecular co-assembly of organoclays and ionic chromophores.^[66–68] Layered magnesium phyllo(organo)silicate was used as the inorganic counterpart, while coronene tetracarboxylate (CS), sulforhodamine G (SRG), and tetraphenylethylene derivatives (TPTS) were employed as donor-acceptor chromophores (**Figure 4**).

QDs are also used as light-emitting centers in WLEDs, although typically the host framework is a polymer (e.g., polyfluorene, PFO, or poly(phenylene vinylene)-PFO copolymers) and not an organic-inorganic hybrid.^[69,70] A recent

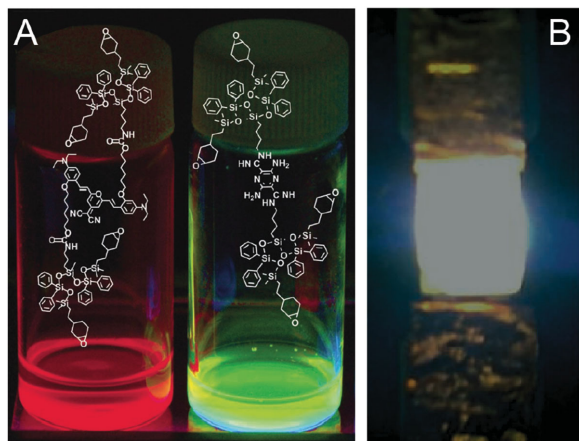


Figure 3. Photographs of A) red and green dye-bridged oligosiloxanes under UV excitation at 365 nm and B) dye-bridged nanohybrid-based white LED, CIE color coordinates of (0.348, 0.334), fabricated encapsulating a blue LED (445 nm) with a blend of red and green dyes. Reproduced with permission.^[17] Copyright 2011, Wiley-VCH.

illustrative example is the embedding of yellow-, orange- or red-emitting QDs into a polyfluorene composite (called Green B). WLEDs with luminous efficiency $>17.21 \text{ m W}^{-1}$, correlated color temperatures of 3500 and 5500 K and high-color-rendering index (CRI up to 90 at 3500 K) were fabricated.^[71] Nanocomposites of CdS QDs and silica-based carbon dots (CDs) were also proposed. A WLED was fabricated, which exhibits white light with a color coordinate of (0.27, 0.32).^[72]

Highly efficient WLEDs can be fabricated with inorganic or hybrid nanoparticles. A very intriguing example was reported by Ferreira et al. in 2014^[73] in which WLEDs were produced by combining a commercial UV-LED chip (InGaAsN, 390 nm) and boehmite (γ -AlOOH)-based organic-inorganic hybrid material as white down-converting phosphor (Figure 5A). The hybrid nanoparticles consist of few-nm thick boehmite nanoplates capped with in situ formed benzoate ligands (Figure 5B). The efficient white light emission results from a synergic energy transfer between the triplet level of the organic-phase (benzoate ligands, T_1) and the triplet state of the inorganic component (boehmite F-centers, 3P). The efficient energy transfer results from two main aspects: i) the near-resonance between the T_1 and 3P states and the ii) large spin-orbit effect that induce a high triplet radiative rate at room-temperature due to the presence of Al atoms coordinated to the benzoate groups. As a direct result of these two effects, the overall quantum yields of the boehmite hybrid nanoparticles are the highest reported so far for ultraviolet-pumped white phosphors. The WLEDs are able to emit white light with “Commission Internationale de l’Éclairage” coordinates, color-rendering index and correlated color temperature values of (0.32, 0.33), 85.5 and 6111 K, respectively; overwhelming state-of-the-art single-phase UV-pumped WLEDs phosphors. We note that an important advantage of these boehmite hybrid phosphors lies in the fact that they are made of non-toxic, abundant and low-cost materials that is desirable from an industrial and environmental viewpoint.

Lanthanide-bearing organic-inorganic hybrids were also proposed for WLEDs. One of the first examples reported the fabrication of WLEDs by convening near-UV LED emission

(390–420 nm) with a hybrid phosphor comprising two strontium aluminates, $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ (green emission) and $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+}$ (blue emission), and $\text{Eu}(\text{btfa})_3\text{phen}$ (red emission), where $\text{btfa}^- = 4,4,4\text{-trifluoro-1-phenyl-1,3-butanedionate}$ and phen is 1,10-phenanthroline.^[74]

In the example reported by Huang et al., a sol-gel-derived hybrid showing emission from the blue to the yellow-green in a wide range of excitation wavelengths (254–380 nm) was synthesized with poly(9,9-dihexylfluorene-*alt*-9,9-dioctylfluorene) embedded into a silica matrix (blue-emitting component) and Tb^{3+} and Eu^{3+} ions coordinated in the matrix (green- and red-emitting components, respectively).^[75]

WLEDs were also fabricated using lanthanide-bearing metal organic frameworks (MOFs) through a remarkable methodology. Eu^{3+} ions were first encapsulated into MOF-253 using a post-synthetic method. The uncoordinated bipyridyl group of MOF-253 is ideal for chelating and sensitizing the Eu^{3+} ions. The resulting MOF was further modified with tta (tta = 2-thenoyltrifluoroacetone) and functionalized with ethyl methacrylate to achieve transparent polymer-MOF hybrid materials (MOF-PEMA-3.5) through radical polymerization. Finally, the polymer-MOF hybrid is assembled on a near-UV GaN chip to fabricate near-UV WLED (Figure 6) operating at 350 mA with a CCT of 3742 K and a CRI of 87.34.^[76] Monochromatic LEDs were also fabricated based on dye-bridged hybrids^[14–17] and Ln^{3+} complexes.^[77]

2.3. Random and Feedback Lasers

Interesting applications of dye-doped organic inorganic hybrids are random and distributed feedback lasers. A random laser is an open source of stimulated emission comprising a number of phenomena related to the emission of light by spatially inhomogeneous disordered materials (not bounded by any artificial mirrors).^[78,79] Laser emission is produced by multiple scattering processes that increase the dwell time of photons inside the material allowing amplification and creating gain saturation.^[80] Random lasers were engineered to provide low spatial coherence and to generate images with superior quality than images generated with spatially coherent illumination.^[81,82] By providing intense laser illumination without the drawback of coherent artefacts (as those produced by lasers and superluminescent diodes that corrupt image formation), random lasers are well suited for full-field imaging applications, such as full-field microscopy and digital light projector systems.^[82]

With organic-inorganic hybrid materials, examples comprise ZnO nanoparticles dispersed into a polymer matrix,^[83,84] Rh6G-doped SiO_2 nanoparticles,^[78,85] Rh6G-bearing di-ureasils,^[37,80] polymer films embedded with silver nanoparticles^[86] and poly(2-hydroxyethyl methacrylate) (pHEMA) incorporating silsesquioxane nanoparticles (POSS) doped with the LDS722 and LDS730 red-emitting dyes.^[87,88]

Focusing on the example of Rh6G-bearing di-ureasils, the emission features of the ground powders were compared with those of a silica gel containing Rh6G-doped SiO_2 nanoparticles revealing a slightly larger slope efficiency and a lower threshold for laser-like emission in the later case (Figure 7).^[37,78] However, it is worth to note that these random laser performances (threshold and efficiency) in the di-ureasils have been obtained

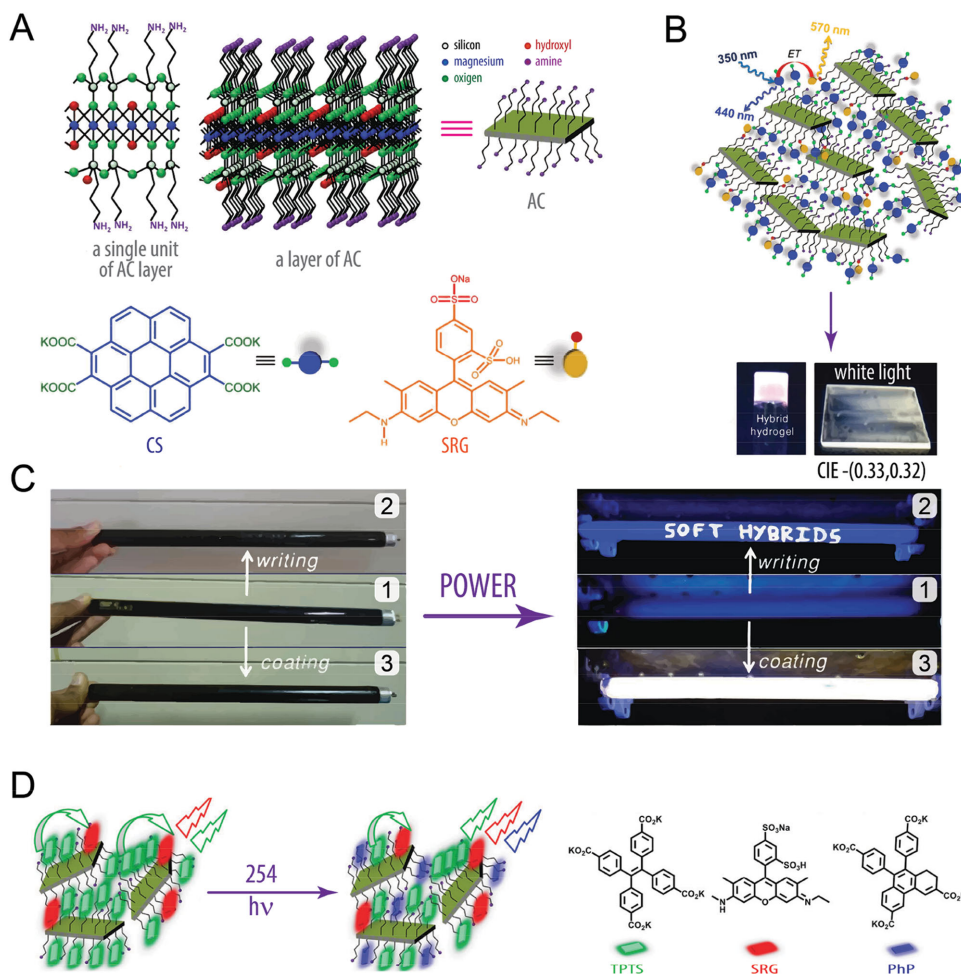


Figure 4. A) Structures and schematic representation of the organo-functionalized clay and chromophores. Reproduced with permission.^[66] Copyright 2013, Wiley-VCH B) Proposed schematic representation of the co-assembled clay-chromophore soft-hybrids and the energy-transfer process to the acceptor red-emitting SRG molecules. Photographs of the white-light-emitting hybrids in gel and film phases are shown. Reproduced with permission.^[66] Copyright 2013, Wiley-VCH C) Schematic showing the strategy for photo-modulation of the clay hybrids. Reproduced with permission.^[66] Copyright 2013, Wiley-VCH D) The hybrids were used to paint and write on commercial UV-lamps (365 nm) 1) uncoated lamp, 2) written as 'SOFT HYBRIDS' on the surface of the lamp and 3) lamp fully coated with the soft-hybrids. Hybrid-coated lamps are exposed to the UV irradiation by glowing lamps, which showed bright white light for both written letters and the fully coated lamp. Reproduced with permission.^[68] Copyright 2016, American Chemical Society.

with a Rh6G concentration four orders of magnitude lower than the one used in the silica gel which makes the di-ureasil hybrids far more attractive for applications.^[37]

Distributed feedback (DFB) laser effect was also reported with dye-doped organic-inorganic hybrid materials, comprising polymers,^[89,90] biopolymers (such as silk fibroin^[91]) and di-ureasils.^[92] DFB lasers are devices operating in longitudinal single-mode oscillation due to a grating structure existing throughout the gain medium, providing the feedback for lasing, with potential applications in medical diagnosis and communications.^[91]

2.4. Luminescent Solar Concentrators

Luminescent solar concentrators (LSCs) are cost-effective components easily integrated in photovoltaics. Despite the first reports date from 1976,^[93,94] LSCs reappeared in the last decade

as an effective approach to collect and concentrate sunlight in an economic way, enhancing solar cells' performance and promoting the integration of photovoltaics architectural elements into buildings, with unprecedented possibilities for energy harvesting in façade design, urban furnishings and wearable fabrics.^[95–100]

Conventional LSCs are optical plastic waveguides doped with phosphors (e.g., organic dyes, QDs, metal halide nanoclusters, or Ln^{3+} ions), or glass transparent (or semi-transparent) substrates coated with optically active layers embedding those phosphors. When exposed to direct and diffuse sunlight, part of the absorbing radiation is re-emitted at longer (downshifting or down-conversion) or shorter (up-conversion) wavelengths. Part of the emitted light will be lost at the surface and the rest will be trapped within the waveguide, or the substrate, and guided, through total internal reflection, to the edges, where it will be collected and converted into electricity by conventional photovoltaic cells (Figure 8A–C).

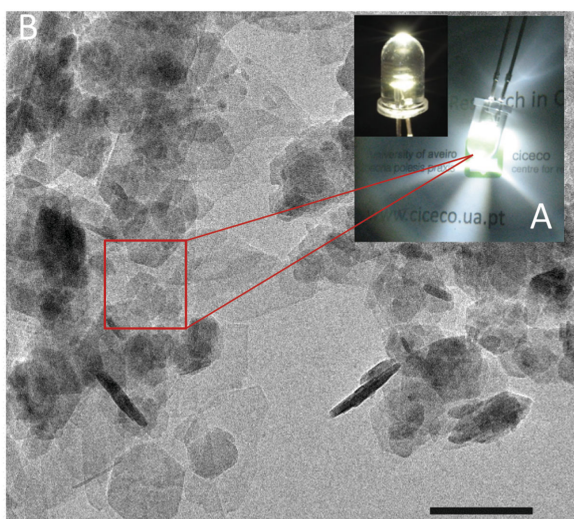


Figure 5. A) Photographs of the as-fabricated WLED using boehmite-based organic-inorganic hybrid nanoparticles operating at 3.0V. B) Representative TEM image of the boehmite hybrid nanoparticles (scale bar, 100 nm). Reproduced with permission.^[73] Copyright 2014, Nature Publishing Group.

The research in LSCs has been displayed a substantial increase over the past three decades, with the major advances of the field highlighted in several recent reviews.^[95–100] The development of LSCs faces numerous challenges, many of which related to the materials used, particularly related to the loss mechanisms that limit conversion efficiency (e.g., emission quantum yield, reabsorption losses, incomplete utilization of the solar spectrum, and escape cone losses) and long-term photostability.^[102] Various authors (even since the very beginning of the field)^[103] concluded that it is unlikely that a single (organic or inorganic) material can overcome these issues, and organic-inorganic hybrids should play a key role on the LSC design optimization.^[99,102,104] Moreover, despite the quite limited use of hybrid materials in the fabrication of LSC, their efficiency values are of the same order of magnitude as those of pure organic LSCs.^[100] Recent examples of hybrid materials used in LSCs comprise polymers doped with QDs,^[105,106] metal halide nanocluster blends^[107] and organic dyes,^[104] Eu³⁺-based bridged silsesquioxanes,^[108–110] and di- and tri-ureasils doped with organic dyes and Eu³⁺ β -diketonate complexes.^[101,111–113]

An intriguing example of lightweight and mechanically flexible high-performance waveguiding photovoltaics is the fabrication of cylindrical LSCs of plastic optical fibers (POFs) coated (bulk fibers) or filled (hollow-core fibers) with Rh6G- or Eu³⁺-doped organic-inorganic hybrids (Figure 8D–G).^[101,112] Cylindrical LSCs have a large potential compared with that of planar ones, despite the very small number of examples involving short length (10⁻² m) bulk or hollow-core POFs.^[114–116] First, the concentration factor F (that dominates the devices' performance) of a cylindrical LSC can be twice higher than that of a square-planar one of equivalent collection area and volume.^[117] Second, the cylindrical geometry allows an easier coupling with optical fibers that could transport light to a remote place for lighting or power production and renders easier photovoltaic urban integration.^[101] In the example illustrated in

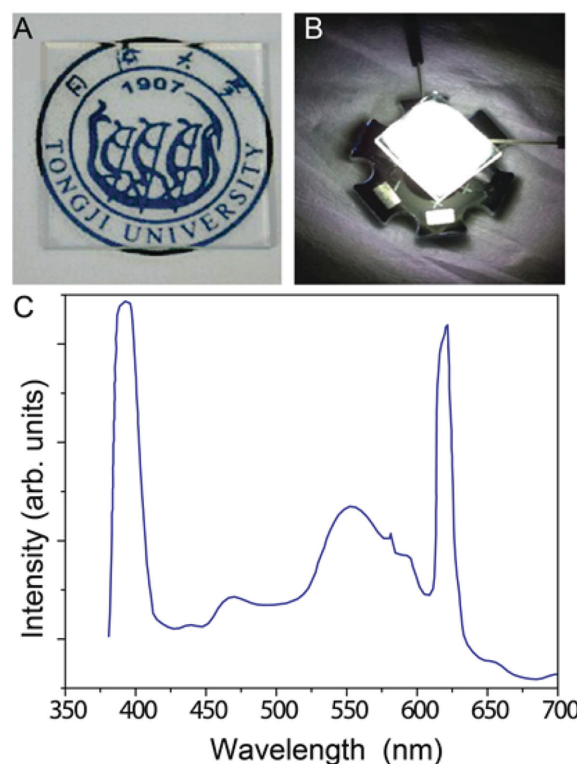


Figure 6. A) A photograph of MOF-PEMA-3.5 hybrid materials. B) The hybrids bright white light emission under excitation by a 395 nm GaN chip and C) the corresponding LED electroluminescent spectrum. Reproduced with permission.^[76] Copyright 2014, Royal Society of Chemistry.

Figure 8, a drawing optical fiber facility is used to scale up de area of the devices demonstrating the possibility of obtaining large area LSCs (length up to 2.5 m) based on bulk-coated and hollow-filled POFs with unprecedented concentration factors, up to 11.75.

2.5. Luminescent Thermometers

The already mentioned unique characteristics of organic-inorganic hybrids, in particular their capability to incarcerate luminescence organic and inorganic thermometric probes (e.g., organic dyes, QDs and Ln³⁺ ions), preventing the aggregation and the emission degradation, makes them suitable for the design of thermometric systems. Moreover, the combination of organic and inorganic counterparts can induce synergic effects resulting in an enhancement of the thermometric efficiency.^[118] Luminescent thermometry exploits the temperature dependence of the light emission features of the thermometric probes, namely emission intensity,^[119–121] peak position,^[122] and excited-states lifetime^[123,124] or risetime,^[125,126] possessing the unique advantage of high-resolution contactless measurement, even in harsh environments and under strongly electromagnetic fields.^[127–130] Although relatively recent (luminescent thermometry exploded over the past five years), the technique appears to be beneficial to many technological applications in a great variety of areas, such as microelectronics, microfluidics, bio- and nanomedicine.^[131]

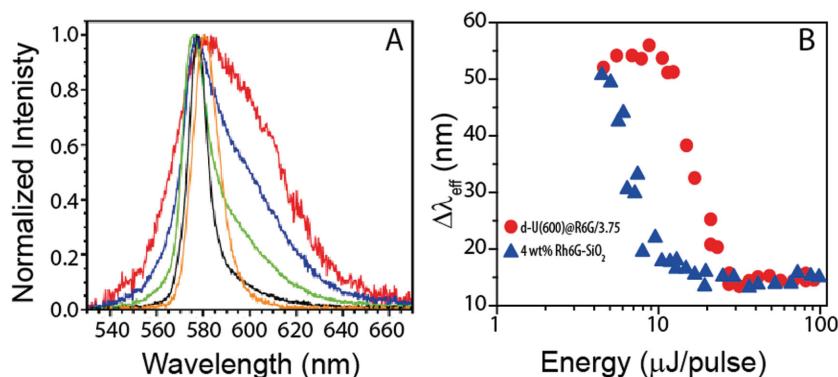


Figure 7. A) Normalized emission spectra of the ground powder of Rh6G-bearing di-ureasils obtained at 11 μJ pulse⁻¹ (red), 18 μJ pulse⁻¹ (blue), 20 μJ pulse⁻¹ (green), 24 μJ pulse⁻¹ (black), and 100 μJ pulse⁻¹ (orange). B) Spectral narrowing of the ground powders of the di-ureasil hybrid (red dots) and the bulk silica gel (blue triangles). Reproduced with permission.^[37] Copyright 2010, OSA.

Examples of luminescent thermometers based on organic-inorganic hybrids include metal-organic molecular compounds,^[132] layer double hydroxides,^[133] metal-organic frameworks,^[134] polymer nanocomposites,^[135] QDs in polymers,^[136] inorganic NPs coated with an organic (or hybrid) layer,^[137] and di-ureasil films co-doped with Eu³⁺ and Tb³⁺ β-diketonate complexes.^[119,138] These later films were used as self-referenced and efficient luminescent probes to map temperature in microelectronic circuits^[119,138,139] and optoelectronic

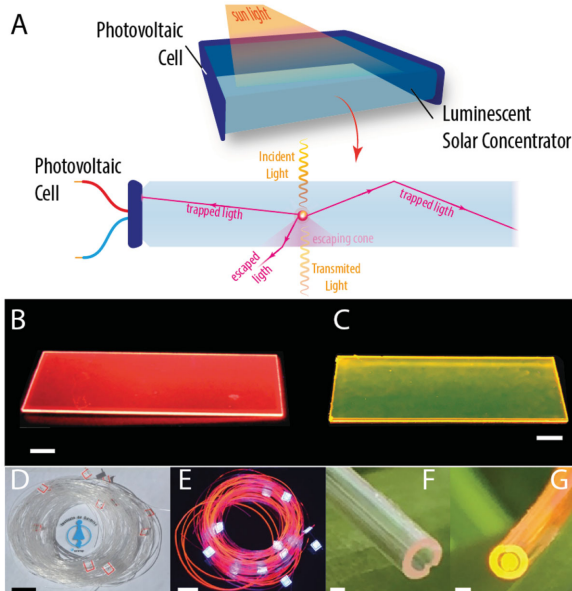


Figure 8. (A) Schematic representation of the working principle of a LSC. Photographs of two LSCs under UV irradiation (365 nm) based on (B) a di-ureasil hybrid doped with [Eu(btfa)₃(MeOH)₂]₂bpta₂, (bpta⁻ = trans-1,2-bis(4-pyridil) ethane and MeOH = methanol) and (C) a tri-ureasil hybrid doped with PTMS (phenyltrimethoxysilane) and Rh6G. Photographs of meter-length Eu-based di-ureasil LSCs under (D) daylight conditions and (E) UV irradiation (scale bars of 10⁻² m). Detailed view of the Eu- (F) and Rh6G-based (G) LSCs extremities under outdoor illumination highlighting the light concentration (scale bars of 10⁻³ m). Reproduced with permission.^[101] Copyright 2016, Royal Society of Chemistry.

devices,^[140] demonstrating an intriguing application of hybrid materials in microelectronics. The thermal gradients generated at submicrometer scale by the millions of transistors contained in integrated circuits are becoming the key limiting factor for device integration in micro- and nanoelectronics and, then, non-contact thermometric techniques with high-spatial resolution (such as luminescent thermometry) are essential for non-invasive off-chip characterization and heat management.^[141] The diureasil films incorporating [Eu(btfa)₃(MeOH)(bpeta)] and [Tb(btfa)₃(MeOH)(bpeta)] complexes allowed temperature mapping in wired-board circuits and in a Mach-Zehnder interferometer using commercial detectors and excitation sources.^[118,138,140] For instance, **Figure 9** shows temperature profiles of a FR4 printed

wiring board reconstructed from the emission spectra of the Eu³⁺/Tb³⁺-containing di-ureasil. The higher spatial resolution obtained, 0.42 μm, is 4.5 times lower than the Rayleigh limit of diffraction (1.89 μm) in the experimental conditions used, and much lower than that recorded with a state-of-the-art commercial IR thermal camera (~130 μm). As the temperature readout results of a spectroscopic measurement it is not limited by the Rayleigh criterion and, thus, the spatial resolution is only limited by the experimental setup used that produces a field-of-view averaged temperature change above the sensitivity of the detector.^[138] The measured temporal resolution is of the order of the integration time of the detectors used (5–100 ms). Although there is not a single technique able to combine sub-micrometer and sub-millisecond resolutions, up to now, the examples that have the best performance are those based on luminescent Ln³⁺-doped organic-inorganic hybrid thermometers.

3. Photochromic Hybrid Materials

3.1. Introduction to Photochromism

According to the International Union of Pure and Applied Chemistry (IUPAC)^[142] definition, *photochromism* is “a reversible transformation of a chemical specie induced in one or both directions by absorption of electromagnetic radiation between two forms, A and B, having different absorption spectra” (**Figure 10**). In most cases, the B form absorbs at longer wavelengths than A (*positive photochromism*) but the opposite case is also possible (*negative or inverse photochromism*).

This interconversion between two states is accompanied by the change of color but also change in refractive index, dielectric constant, redox potentials, solubility, viscosity, surface wettability, magnetism, luminescence, or a mechanical effect. Therefore, there is a growing list of other real or potential application areas, including ophthalmics, cosmetics, security, displays, filters, optical memories, switches, photometry, and so on.

There are many types of organic and inorganic chemical species exhibiting photochromism. Among organic compounds, spiropyrans (SP) and spirooxazines, fulgides, diarylethenes,

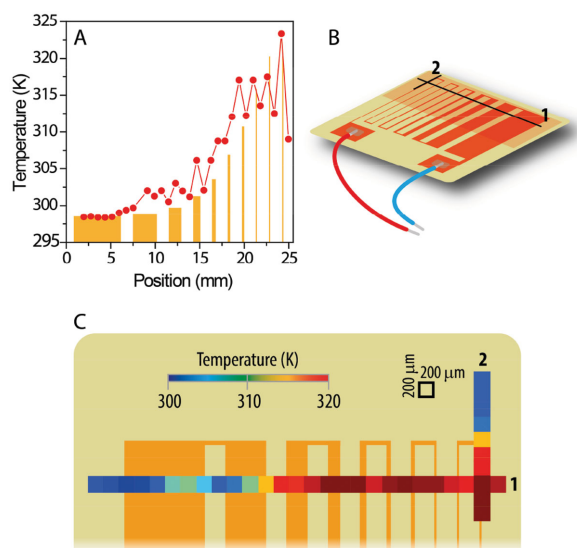


Figure 9. (A) Temperature profile obtained with a $\text{Eu}^{3+}/\text{Tb}^{3+}$ co-doped di-ureasil film of the FR-4 wire-board depicted in (B). The emission of the film (excited at 365 nm) is collected with a 200 μm core diameter fiber along the direction denoted by 1 using a scanning step of 200 μm . The temperature uncertainty is 0.5 K. The orange shadowed areas correspond to the distinct copper tracks. (C) Pseudo-color temperature maps reconstructed from the emission of the di-ureasil along the two perpendicular directions denoted by 1 and 2 of the FR4 printed wiring board.

dithienylethene, azo compounds, polycyclic aromatic compounds, quinones or viologens are the most studied families. Their photochromism involves pericyclic reactions, cis-trans (E/Z) isomerizations, intramolecular hydrogen/group transfers, dissociation processes and electron transfers. Inorganic photochromic compounds are much limited in number, i. e. silver halides, WO_3 , MoO_3 , oxides of group IVB and VB metals (TiO_2 , V_2O_5 , Nb_2O_5 ...), polyoxometalates, zinc sulfide, alkali metal azides, sodalite, and Prussian blue analogs. The origin of the color change usually relies on their ability to change stoichiometry and to create electron/hole pairs by interaction with their environment. Thus, the photochromic properties show a critical dependence on the surrounding medium, which is often hard to predict and systematize. For more information about photochromism fundamentals, several books can be consulted.^[143–146]

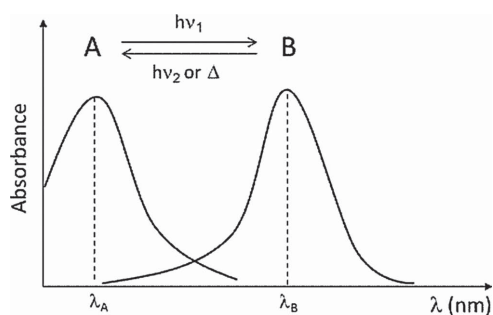


Figure 10. Reversible photochromism. Reproduced with permission.^[142] Copyright 2001, De Gruyter.

The adequate design of hybrid photochromic materials allows: (i) to improve photophysical and photochemical properties (especially via molecular modification in organic chromophores), (ii) to offer easy-to-shape materials for a real commercial deployment (via integration of the active species into functional matrices) and (iii) to explore new photoresponsive multicomponent systems. Excellent reviews have been written by J. Yao,^[147] G. C. Guo^[148] and D. Levy.^[149,150] However, despite the huge amount of academic studies, important technical issues must be resolved for real industrial applications, such as:

1. The material must develop a strong color rapidly upon UV-vis irradiation.
2. The fade rate back to the colorless state must be controllable.
3. The response must be constant through many coloration cycles.

The choice of the system and the specific requirements depend on the targeted application. In sunglasses or protective coatings, for instance, the consumer needs robust systems with an immediate reaction to a change of external conditions. Also, a change from white (or colorless) to grey or even black is preferred, especially for large-volume displays (display panels, front and rear windows, and mirrors for cars and trucks...). For other applications, multicolored systems can be desirable. Indeed, most of the photochromic compounds do changes between two or more different colors, and that is useful for sensors or markers. For memories, data storage or switches, for instance, a good contrast between the two states is probably the most valuable property. In the following sections, a brief overview of the most recent progress in this area is presented.

3.2. Organic Photochromism in Hybrids

The micro-/nano-structuring of photochromic molecules into organic-inorganic hybrid materials (classical sol-gel glasses, polymers, nanoparticles, etc...) via weak (*Class I* hybrid)^[31] or strong (*Class II* hybrid) chemical interactions^[151–165] is the main approach to achieve robust and functional photochromic-based devices that could be easily handled and integrated in solid materials. Many photochromic organic molecules have been entrapped in ORMOSIL (Organically Modified Silanes) hybrid matrices.^[144,166] A huge work was done on this area in the late 90's and early 2000's with the "boom" of *Soft Chemistry*.^[167] In this hybrid materials, the active molecules can be stored preserving or improving their photochemical and photophysical properties. The main advantages of silane matrices over pure organic polymers (PMMA, PAA...) are the higher thermal stability and the possibility of chemical modification that can be of interest for a particular application (including specific functional groups or changing properties like refractive index, the hydrophilic/phobic character, etc.). This approach is also more convenient than obtaining photochromic single crystals^[168–170] since few of them preserve their properties in the solid state^[171] and their shaping is really difficult. In the last years, extended literature can still be found on photochromic dyes randomly embedded (covalently bonded or just doped) into amorphous

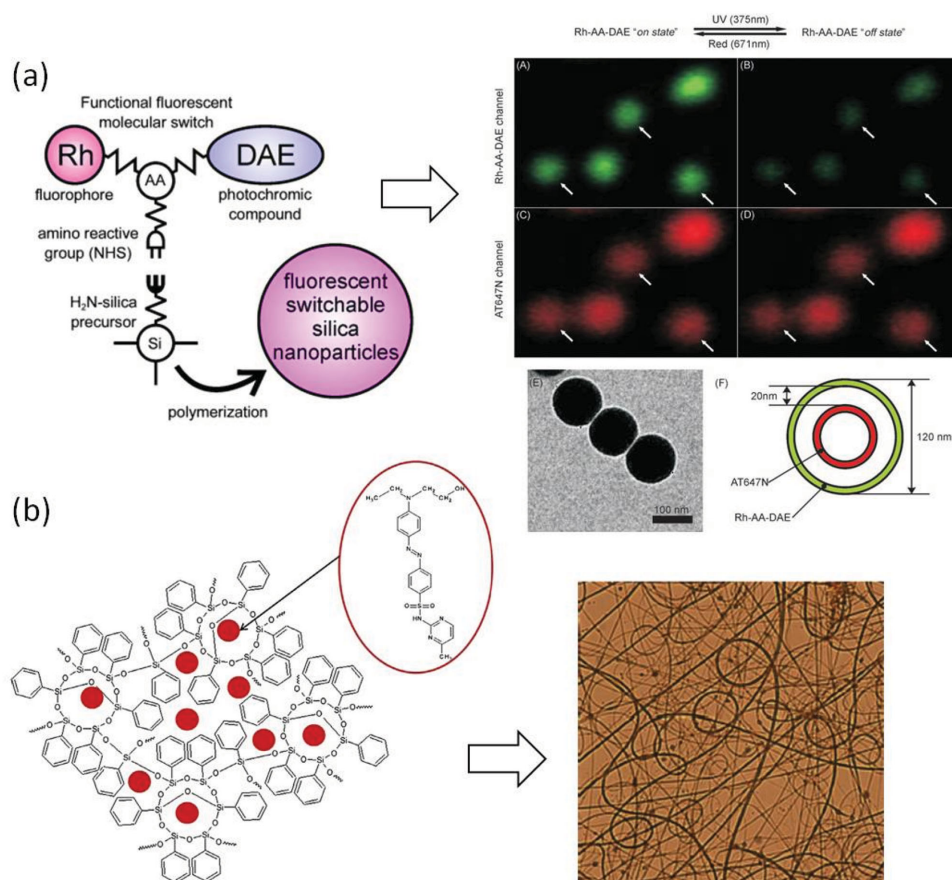


Figure 11. (Top) Chemical structure of the fluorescent molecular switch Rh-AA-DAE and the photochromic reaction responsible for the fluorescence modulation. The fluorophore moiety is excited with green light: red light is emitted in the on state, while resonant energy transfer prevents this emission in the off state. Confocal images of fluorescent NPs (120 nm) doubly stained with Rh-AA-DAE and AT647N, recorded in two channels. The lower panel shows a TEM image of the particles (E) and a scheme with the distribution of the dyes inside each particle (F). Reproduced with permission.^[172] Copyright 2008, Wiley-VCH. (Bottom) The guest-host system containing photoactive dye of SMERe incorporated into triethoxyphenylsilane matrix. SEM pictures showing the fibrous structure of the hybrid materials. Reproduced with permission.^[174] Copyright 2014, Elsevier.

hybrid silica derivatives (nanoparticles,^[172] films,^[173] fibers,^[174] and also in layered materials.^[175] The most recent articles, combine the photochromic activity and other functionalities to get smart multifunctional systems. For instance, J. Fölling^[172] designed a highly efficient fluorescent molecular switch (FMS) for fluorescence microscopy by coupling a fluorescent dye with a photochromic diarylethene on silica nanoparticles (Figure 11(a)). Other works are devoted to develop new procedures of shaping and conformation, such as the fibers shown in Figure 11(b).

An interesting idea to facilitate photochromic transformations is to include the organic dye into mesostructured materials with inorganic and organic domains separated at the nanometric scale. G.D. Stucky^[176] reported a block-copolymer/silica nanocomposite used as host for two photochromic dyes, a spirooxazine and a spiroxan, where the dyes are incorporated predominantly within the hydrophobic occlusions. The materials exhibit direct photochromism with faster response times, being at that time in the range of the best values reported so far for solid-state composites. These silica/block-copolymers can also be processed in any desired shape, including fibers, thin films, monoliths, waveguide structures, and optical coatings.

Similar systems based on spiroxan doped PMMA-silica have been reported, in which the presence of PMMA reduces the polar character of the matrix, facilitates the solubility of the dyes, modify the stability of particular isomers, and increases the chemical durability of the hybrid (Figure 12).^[177] The organic-inorganic interface can be tuned to favor the dye-matrix compatibility, thus increasing the content of photochromic species, and afford more stable systems with higher photochromic conversions. That was the main goal of F. Ribot et al. work regarding spirooxazine-doped tin-based nano-building blocks (NBBs) embedded in PEG copolymers.^[178]

Other publications addressed this dye-matrix interaction to fully exploit the properties and tuneability of the systems. Thus, R. A. Evans et al.^[179] reveal that the intramolecular interactions of flexible PDMS (poly dimethylsiloxane) oligomers with spirooxazine 1 (Figure 13) make possible faster chemical processes (thermal fade parameters $T_{1/2}$ and $T_{3/4}$ reduced by 75% and 94%), greatly increasing the dye switching speed in a rigid hybrid system such as PDMS ophthalmic lenses. Both coloration and fade behavior indicate that the dye is in a highly mobile, near solution-like environment within the rigid matrix. This is a quite surprising result because bonding dyes

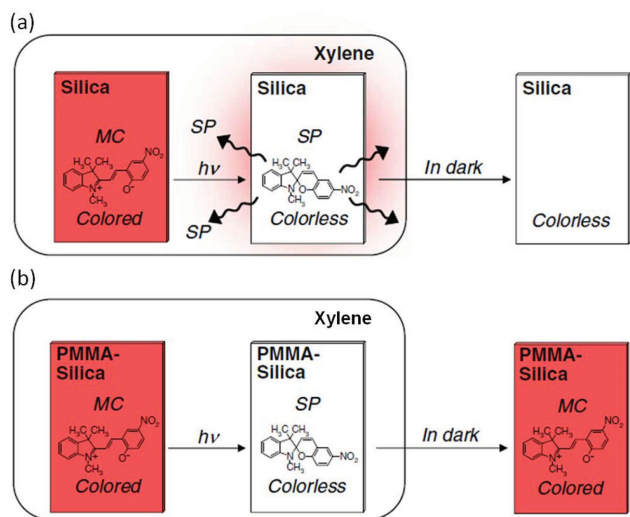


Figure 12. Schematic illustration on the changes in the state of spirooxazine molecules during soaking in xylene for pure silica (a) and PMMA-silica (b) systems under visible light and in the dark. Reproduced with permission.^[177] Copyright 2011, Elsevier.

to polymers usually slows down the switching process.^[180] In this case, the low T_g oligomer provides a favorable environment near/around the dye, allowing a greater molecular mobility for the photochromic reaction, which can find utility in data recording or optical switching. The rigid environment of a dye within the matrix can be beneficial, for instance, to avoid a non-desired photochromic transformation. This fact is detailed in amine-alcohol-silicate hybrid materials doped with naphthopyran,^[181] where the isomerization of one specific colored isomer (which is a space demanding reaction) is hindered, and films present fast and fully reversible coloration/transparent cycles upon irradiation/dark (Figure 14).

A dye-matrix *template effect* can also be exploited to get periodically organized nanostructures. This effect is used in hybrids including viologens (1,1'-disubstituted-4,4'-bipyridinium, V^{2+} cations) to afford stable separated charge state systems that find applications in electrochromic displays, molecular electronics, solar energy conversion, etc. N. Mercier published an excellent review showing peculiar interactions between viologen dications and anions of hybrid structures.^[182] One pioneer result was found in $(MV)[MX_{5-x}X'_x]$ ($M = Bi^{III}, Sb^{III}; X = Cl, Br, I;$

Spirooxazines

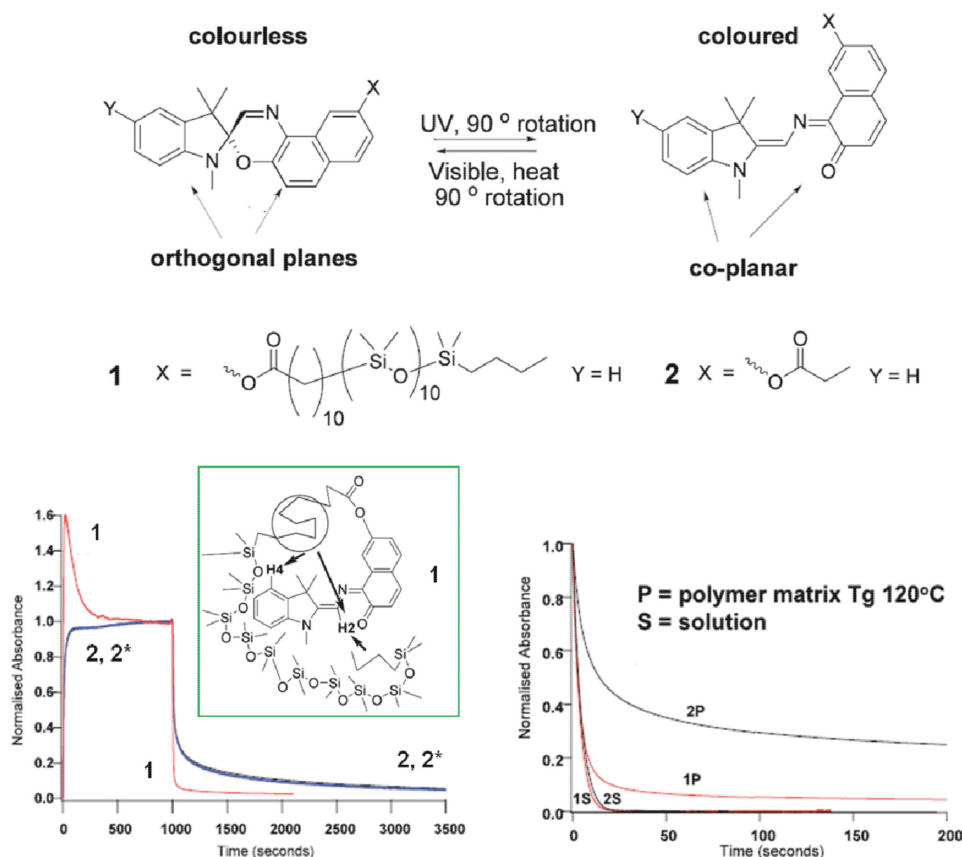


Figure 13. Top: Structural changes of spirooxazine during photochromic switching. Bottom left: Positive effect of conjugating a spirooxazine (compound 2) with a short PDMS chain (compound 1) on coloration and decoloration speeds. The covalent bonding between dye and silane oligomer is crucial for increasing the transformation speed (where 2* is the spirooxazine with PDMS oligomers added to the matrix, without chemical bonding). The intramolecular interaction of PDMS units with dye is shown in a green square. Bottom right: The solution-like fade performance of compound 1 in the rigid silane matrix (curve 1P) as compared to 1 and 2 in toluene solution (curves 1S and 2S) and compound 2 in the identical rigid silane matrix (curve 2P). Reproduced with permission.^[179] Copyright 2005, Nature Publishing Group.

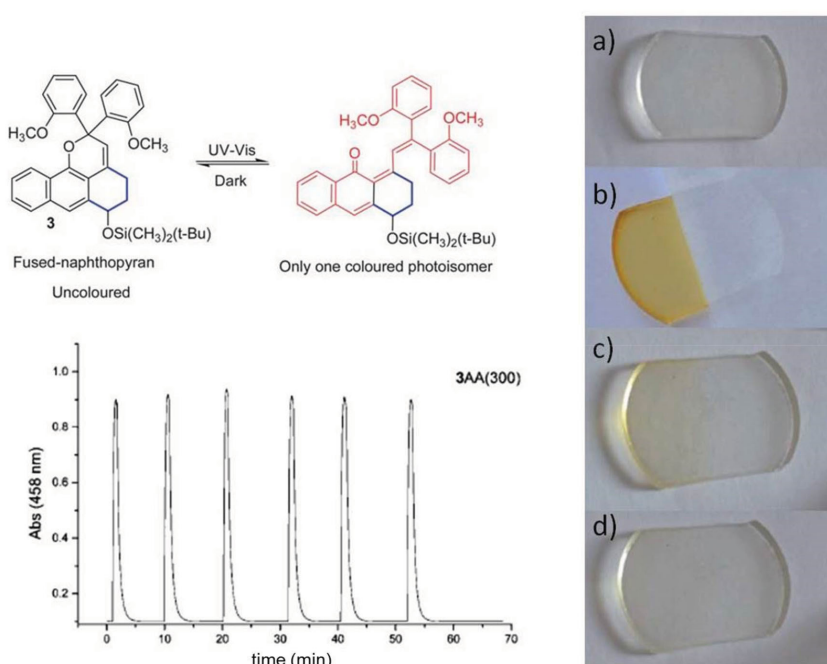


Figure 14. Photochromic equilibrium for the fused-naphtho[1,2-*b*]pyran. UV-Vis irradiation/dark cycles of gels doped with naphthopyran 3 measured at 458 nm. Samples 3AA(300) in the dark (a), exposure of half of the sample to sunlight for 1 min (b), sample after 60s in the dark (c) and after 120s in the dark (d). Reproduced with permission.^[181] Copyright 2013, Royal Society of Chemistry.

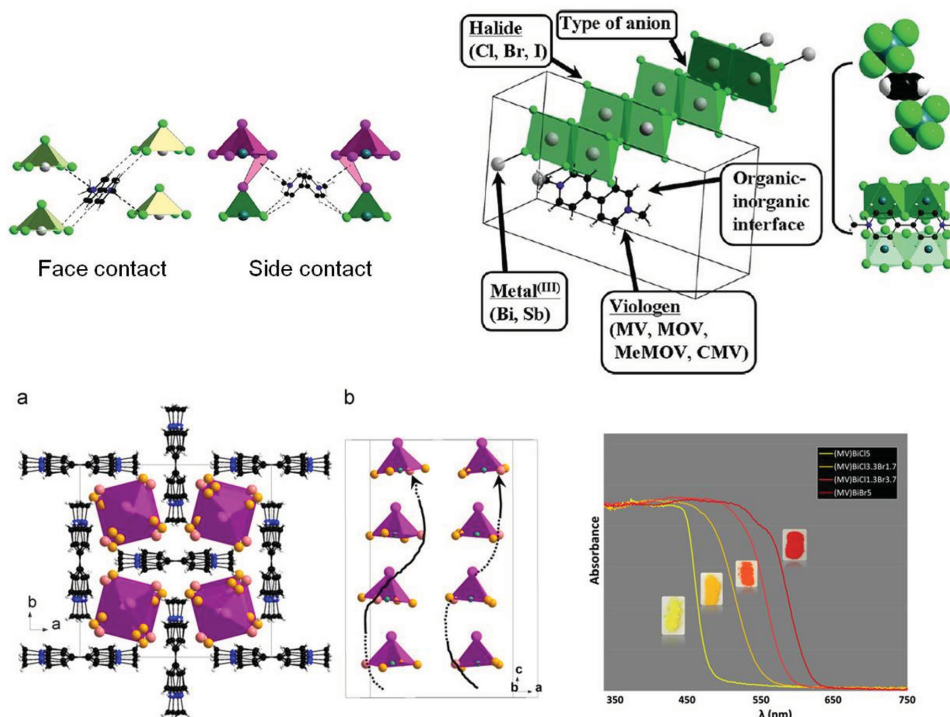


Figure 15. *Top:* (Left) Interactions at the organic-inorganic interface between one methylviologen cation and two anionic chains showing face and side contacts. (Right) Part of the structure of $(MV)[Bi_2Cl_8]$ showing one methylviologen entity and the inorganic network (left) and interactions between the organic cation and two inorganic anions (right: side view in space-filling representation and viewed along the direction perpendicular to the viologen plane), and the different parameters that can influence the photoinduced charge-transfer process in viologen halometalate salts. Reproduced with permission.^[182] Copyright 2013, Wiley-VCH. *Bottom:* Structure of $(MV)[SbBr_{3.8}]_{1.2}$ viewed along the chain axis showing the tetragonal arrangement (a), and *syn* coupling of two neighboring chains which displays opposite chiralities (b). UV-Vis spectra and pictures of $(MV)[Bi_2Cl_{5-x}Br_x]$ ($x = 0, 3.7, 5$) hybrids. Reproduced with permission.^[183] Copyright 2012, Elsevier.

$x = 0-5$) compounds that exhibited ferroelectric properties thanks to the electron-donor interaction of a methylviologen dication with polar MX_5 chains of trans-connected octahedra (Figure 15).^[183]

Asymmetric viologen ligands can be also coordinated to Zn(II) centers through a *template effect*, leading to the first example of bulk electron-transfer photochromic compound with intrinsic second-order nonlinear optical (NLO) photoswitching properties.^[184] The electron transfer is possible thanks to the synergetic interaction between the ligand and a metal center with acentric coordination geometry (Figure 16).

The use of light as an external trigger to switch the second-order NLO activity has been increasingly addressed for nondestructive data storage or opto-optical switching in the emerging field of photonic devices.^[185] Regarding this field, M. Schulze et al.^[186] propose the anchoring of photochromic fulgimide molecules into a self-assembly monolayer (SAM) on a Si(111) surface. The use of silicon, one of the most relevant materials for semiconductor devices, as a substrate for SAM formation and the further anchoring

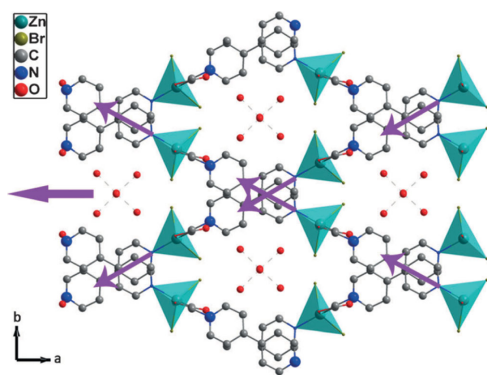


Figure 16. Molecular packing in a crystal of $[\text{ZnBr}_2(\mu\text{-CEbpy})\cdot 3\text{H}_2\text{O}]$ view along the c -axis. The violet arrows indicate the whole remnant polarity. Reproduced with permission.^[184] Copyright 2014, Wiley-VCH.

and aligning of molecular switches paves the way for an efficient switching of the NLO response with higher contrast (**Figure 17**).

Periodically organized systems have demonstrated to enhance the photochemical processes over amorphous photoresponsive materials. Thus, the covalent grafting of organic molecules (flavilium, spiroyrans, etc.) in different types of mesoporous matrices (MCM-41, SBA-15, polymers, and so on) has also been investigated. The ordered nanostructure and the strong dye-matrix bonding enhance their photostability and avoid leaching of the dyes. To mention some of the most interesting achievements, S. Gago^[187] prepared a solid state pH-dependent photochromic material with fast kinetics in color change thanks to the highly ordered hexagonal arrays of channels in mesoporous silica. More

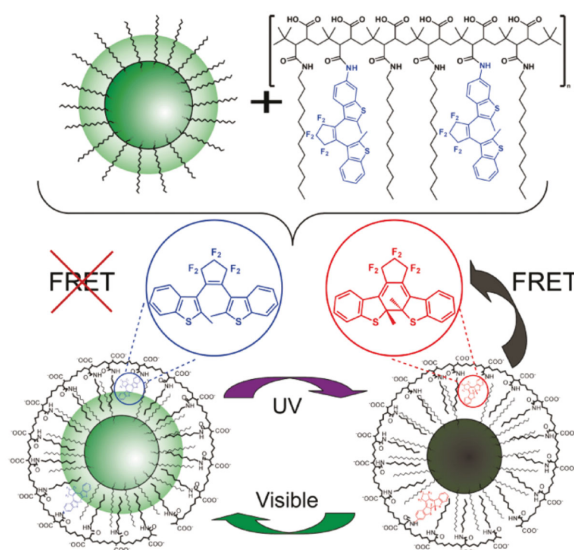


Figure 18. Photoswitching QDs coated with an amphiphilic photochromic polymer. The fluorescence of the psQD is toggled with FRET by modulating the absorbance of the photochromic polymer with UV and visible light. Reproduced with permission.^[199] Copyright 2011, American Chemical Society.

sophisticated designs, such as core-shell or hollow spheres^[188] have also great interest. An example can be the smart nanocapsules reported by J. Allouche^[189] that are made of a dense silica core with mesoporous photochromic (SP) silica shell in a dual templating sol-gel method. A different strategy is explored by J. Hernando and D. Ruiz-Molina^[190] in which photochromic molecules are encapsulated into liquid-filled polyamide capsules to achieve high switching speeds in solid materials.

Regarding non-silica systems, N. Andersson^[191] synthesized ordered honeycomb porous films made of a spiroyrans functional PAA polymers that shows a rapid and intense color changes upon irradiation with UV and vis light. An attractive point is that these nanostructures can also entrap metal ions (Pt, Pd,...) or nanoparticles that shift the absorption and the chromic response, acting as reversible metal ion sensors.^[192] Complex architectures can be designed to make possible energy transfers between photochromic dyes and other luminescent species such as Quantum Dots,^[193] up-converting nanocrystals^[194–196] or plasmonic metal nanoparticles.^[197,198] One nice example is the decoration of CdSe/ZnS QDs with an amphiphilic photochromic polymer coating.^[199] The core-shell architecture permits the accommodation of hydrophobic acceptor dyes in a close proximity to the QD donor, thereby providing an effective FRET probe in a small (~ 7 nm diameter) water-soluble package (**Figure 18**) that opens up numerous applications in biological and live cell studies.

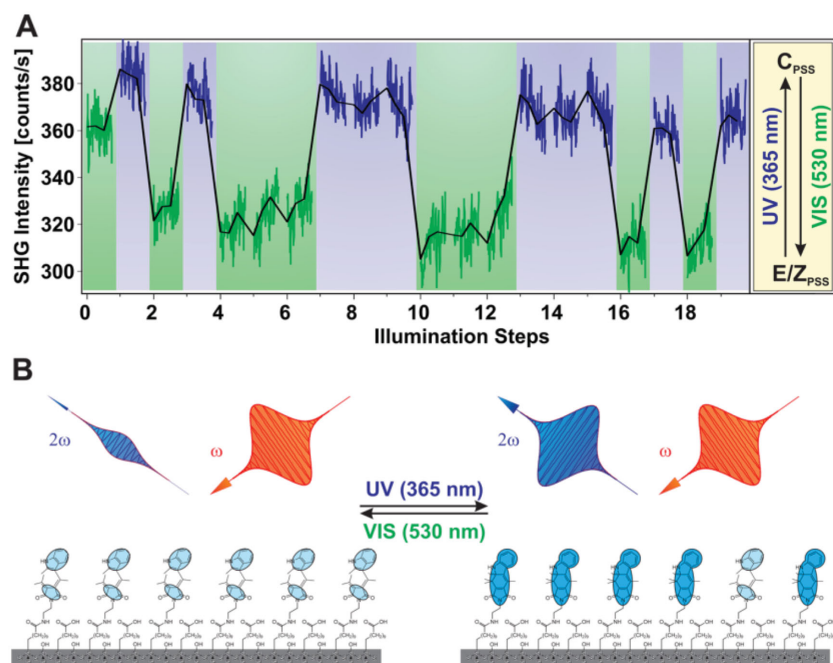


Figure 17. (A) Changes in the second harmonic generation (SHG) signal amplitude as a function of illumination with different wavelengths (365 and 530 nm), demonstrating the light-induced reversible changes in the NLO interfacial response due to the ring-opening/closure reaction. (B) Scheme of the reversible photoinduced switching probed with SHG. Reproduced with permission.^[185] Copyright 2006, American Chemical Society

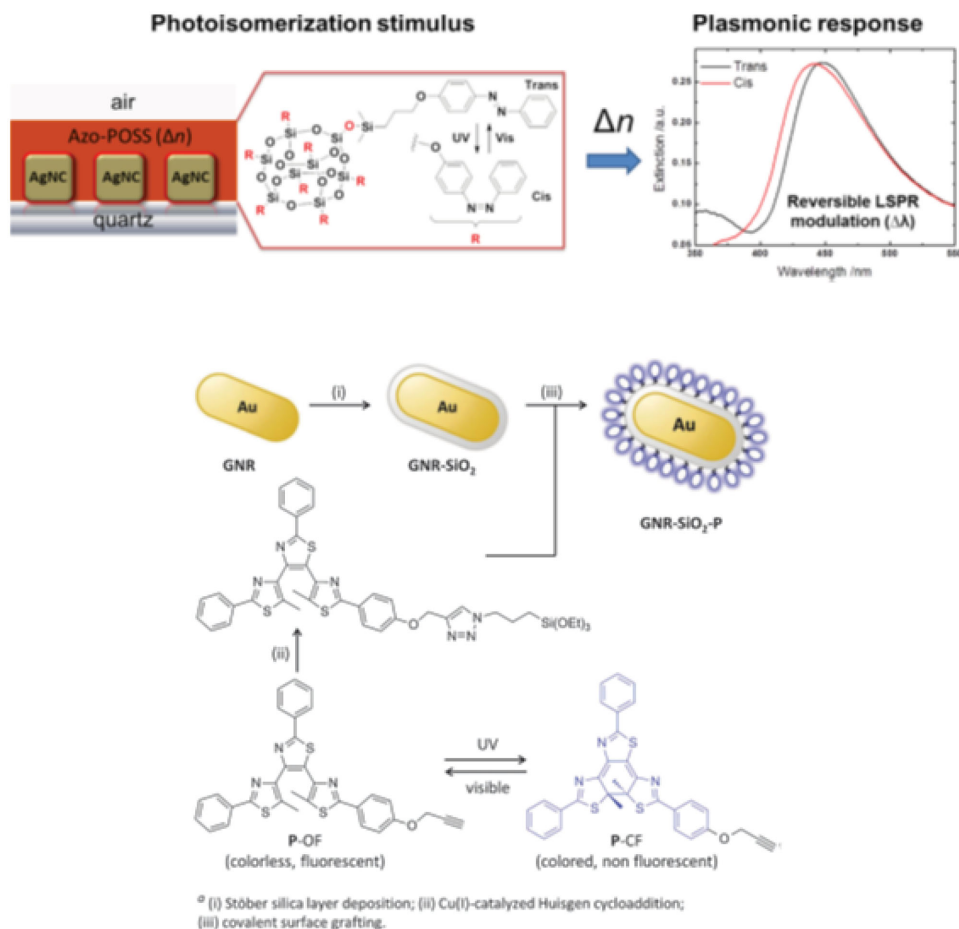


Figure 19. Top: Branched Azo-POSS conjugates as a variable-refractive-index matrix for plasmonic nanoparticles. Reproduced with permission.^[200] Copyright 2015, American Chemical Society. Bottom: Synthesis of the silica-coated gold nanorods with surface grafted photochromic and fluorescent derivatives. Reproduced with permission.^[204] Copyright 2014, Royal Society of Chemistry.

Hybrid nanomaterials combining organic photochromes with plasmonic nanoparticles have also gained considerable interest in the fields of data storage, photovoltaics, biosensing, etc.^[200,201] The mutual interplay between organic molecules and metal properties can be used to finely tune the photochrome reactivity as well as the energy of the localized surface plasmon resonance (LSPR) of the metallic nanoparticles. In some cases, the light-induced photochromic process results in significant changes in other properties like refractive index, with interest for optical switching and filtering. Most of the studies reported so far deal with grafted diarylethene^[202] and spiropyrane^[203] derivatives, characterized by an initial colorless state and a colored photoreacted state that causes an energy shift of the LSPR band in a privileged manner. P. A. Ledin^[200] reports the fabrication of silver nanocubes coated with photochromic azosilsesquioxane hybrid derivatives and deposited onto quartz substrates (Figure 19 top). The photochromic transformation induces variations in the refractive-index medium and a reversible tuning of the plasmonic modes of noble-metal nanostructures. Also, gold nanorods can be coated with silica and functionalized with grafted fluorescent and photochromic derivatives (Figure 19 bottom).^[204] Spectroscopic investigations demonstrated that cross-coupled interactions between

plasmonic, photochromic, and fluorescence properties play a major role in such nanosystems, depending on the thickness of the silica spacer, leading to multi-signal photoswitchability.

Multicolored systems have been developed by embedding two or more active species in matrices. These materials can be used in multifrequency photochromic recording, multi-color displays, inks, barcodes, and other applications, and are able to benefit from the control offered by a single material with several interconverted states. One example is reported by N. Branda,^[205] where three dithienylethene (DTE) derivatives providing the three primary colors are covalently linked to norbornene-based water-soluble monomers. Thus, a new family of multiaddressable photoresponsive copolymers is prepared by ring-opening metathesis polymerization (ROMP). Since DTE compounds exhibit fast response times, good thermal stability of both isomers (colorless ring-open and colored ring-closed), high fatigue resistance and their structures can be easily modified, they are some of the most promising candidates for use in devices. For instance, a three-component hybrid system (CP4, Figure 20) has been successfully tested as multicolor barcode. Readers with interest on DTE-including materials and their application in memories, switches, and actuators can consult the review of M. Irie et al.^[206]

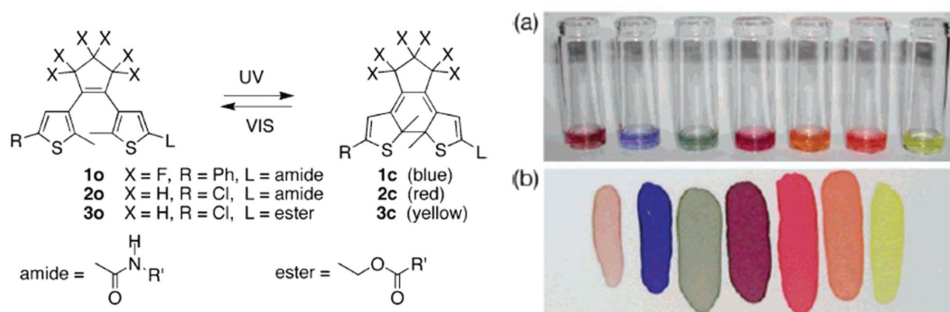


Figure 20. DTE derivatives whose ring-closed isomers exhibit primary colors. (a) Colors mixing of DTE homopolymers P1–P3 after THF solutions are irradiated with 313-nm light. The solutions contain (from left to right) [P1 + P2 + P3], [P1], [P1 + P3], [P1 + P2], [P2], [P2 + P3], and [P3]. (b) Samples of homo- and copolymers (from left to right) CP4, P1, CP2, CP1, P2, CP3, and P3 painted onto a silica plate followed by irradiation with 313 nm light. Reproduced with permission.^[205] Copyright 2005, American Chemical Society.

Multicolor photochromism can also be provided by supramolecular coordination polymers accommodating guest water molecules and anions (perchlorates, halides, pseudo-halides...^[207] The soft metal organic hybrid material interacts with the environment, leading to a solvent- and anion-controlled photochromism via different charge transfers with the electron-accepting bipyridinium moieties.

Multicolor systems combining photochromic dyes with graphene have recently been published. S. Sharker developed a stimuli-responsive material based on graphene oxide coupled with a polymer conjugated with spiropyran dye and hydrophobic boron dipyrromethane dye, for application in triggered target multicolor bioimaging.^[208] The different color of the functionalized graphene oxide is induced by both irradiation with UV light and by changing the pH from acidic to neutral. The stability, biocompatibility, and quenching efficacy of this nanocomposite open a different perspective for cell imaging in different independent colors, sequentially and simultaneously. Despite the efforts of the scientists on developing multicolor photochromic systems, most of them are based on polymers,^[39] single crystals^[207] or organogels^[209,210] containing organic moieties (no organic-inorganic hybrids), and they still present strong limitations for a real implementation in commercial devices.

3.3. Inorganic and Organometallic Photochromism in Hybrids

A brief review of photochromic hybrids of metal halides, cyanides and chalcogenides, polyoxometalates, and metal–organic complexes was reported in 2010.^[148] Some hybrid systems including these inorganic photochromes have already been fabricated. However, despite all the efforts of scientists, their use in technical applications such as erasable optical storage media, large-area displays, chemical sensors, control of radiation intensity or self-developing photography is still incipient due to the necessity of improving the variety of colors and the kinetics of coloration and fading.

The photochromic activity of silver halides lays on its dissociation into colloidal silver upon UV radiation. Its use in ophthalmic lenses is well-known since the sixties, but the development of new materials with a wider palette of colors, faster

bleaching kinetics, lower density, etc. is still a subject of extensive investigation. Numerous papers reporting smart photochromic properties of Ag^[211–215] species deposited onto TiO₂ substrates have appeared in the last years. Interesting properties are developed in titanate nanotubes loaded with AgCl or Ag NPs.^[216] For AgCl–titanate nanotubes (TNTs), the photochromic behavior consists on the red coloration on the material after irradiation by red light due to the photoreduction of silver halide to Ag nanoparticles. In the case of Ag NPs loaded TNTs, the materials exhibit multicolor photochromism corresponding to that of incident light associated to particle-plasmon-assisted electron transfer from Ag nanoparticles to TiO₂. This example reveals how important is to control the active species involved in the photo- and electro-optical processes.

One interesting advance in terms of industrial application is reported by F. Tricot^[214] in 2015 who prepared a flexible Ag:TiO₂ photochromic material using ink-jet and flexography printing processes compatible with industrial scale production (Figure 21). For that, a titanium precursor solution is printed on a plastic substrate thanks to adaptation of printing processes. After incorporating silver, the coating shows a reversible photochromic behavior with a good contrast between the colored and bleached state. This breakthrough technology offers a new means to store updatable data and to secure products in smart cards or goods packaging areas.

Cu NPs exhibiting unique photochromic properties onto TiO₂ substrates have also appeared. The redox process of copper, Cu²⁺, Cu⁺ and Cu⁰, associated to photochromism can be controlled by varying the light source and exposure time. For instance, D. M. Tobaldi^[217] reports Cu–TiO₂ hybrid nanoparticles with tunable, rapid and sensitive photochromism under both UVA and visible-light exposure. The material is 2 nm Cu NPs decorating the surface of ~10 nm TiO₂ NPs. Under UVA, Cu²⁺ is completely reduced to Cu⁰ in few minutes, and under visible-light, Cu²⁺ reduces only to Cu⁺ and in a lesser extent.

Regarding photochromic WO₃ and MoO₃ materials, significant advances have been made in the past decades, such as the response to visible light, and the improved photochromism by proton donors.^[218,219] However, organic-inorganic hybrid derivatives could solve other critical questions: (i) to improve reversibility; (ii) to fabricate systems exhibiting a wide variety of colors; and (iii) to enhance the sensitivity of the photochromic effect

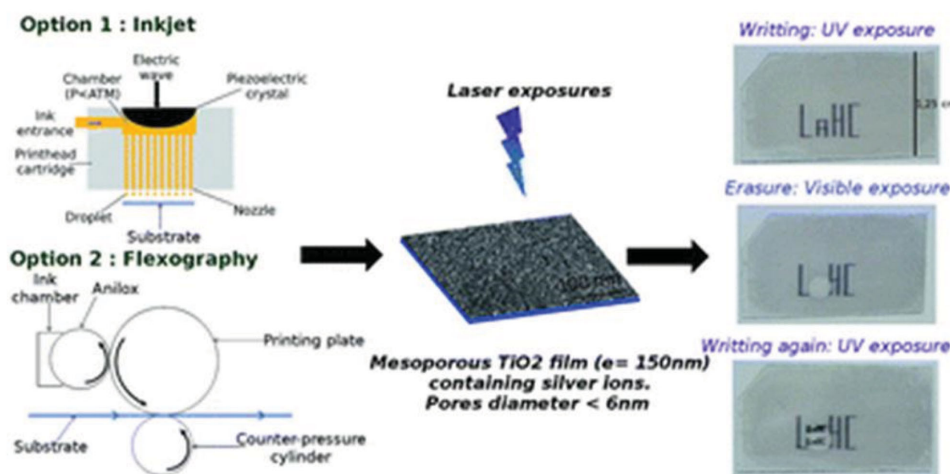


Figure 21. Principle of inkjet and flexography process (left), description of the Ag:TiO₂ material (center) and pictures of UV exposure inscription and visible exposure erasing on a film coated by flexography (right). Reproduced with permission.^[214] Copyright 2015, Royal Society of Chemistry.

in the near-ultraviolet range. Some groups have investigated the intercalation of organic molecules such as diaminoalkane, phenethylamine, pyridine and poly(ethylene glycol) in the inter-layer space of both structures, WO₃ and MoO₃.^[220–223] A nice example is the preparation of tungsten oxide layers intercalated with acetic acid and hexamethylenetetramine (HMT) molecules with a 3D flowerlike morphology.^[224] The most important result of the work is the good reversibility (as high as 98.4%, which is much higher than conventional WO₃ materials) and the good coloration response expanded to the visible-light region, which is a critical challenge for practical applications using solar energy and other visible laser sources. A second approach is to develop anisotropic organic–inorganic nano-hybrids,^[225] in which the 1D organization of MoO_x nanoclusters enhances the photochromic sensitivity, and tunable components endow them with tailored performance.

Photochromic WO₃ and MoO₃ shaped as thin films,^[226–228] nanorods,^[229] nanowires^[229] or nanoflakes^[230] were reported in the last decade, but very few are devoted to real organic–inorganic hybrids. In those reports, organic molecules (EDTA,^[229] citric acid,^[231] etc.) are used to prevent the uncontrolled precipitation of the inorganic oxides and also act as directing agents, giving to tunable morphologies. Only one paper^[232] reports tungsten oxide included in a fluoro-polymer matrix but yield a modest photochromic response. The photochromic properties of these oxides can be modified by interaction with species such as CdS NPs,^[233] Ag^[234]/Cu^[227] species, TiO₂,^[235,236] silica,^[237] or cellulose.^[238] These nanocomposite materials are not strictly hybrid organic–inorganic materials, so these issues are out of the scope of this manuscript.

Photochromic polyoxometalates (POMs) are by far the most studied systems in the last years. A complete report about photochromism in composites and hybrid materials based on polyoxometalates was reported in 2006.^[147] POMs are organically modified inorganic metal–oxygen cluster anions (i.e., polyoxomolybdates and polyoxotungstates), and they are promising candidates for photochromic applications due to their highly versatile and tunable structural, chemical, and redox properties. POMs, upon UV or VIS radiation, are able to accept electrons

and/or protons from organic donor counter-cations in a reversibly exchange without decomposing or undergoing changes to its structural arrangement, to become mixed valence colored species (*heteropolyblues* or *heteropolybrowns*). In these complex structures, the organic moieties play an important role in the optical processes since purely inorganic POMs have no reversible photochromism and the color change is not attractive. In general, the photo-generated colors of these hybrids depend on the chemical composition and topology of the POMs, while the coloration and fading kinetics are related to the nature of the organic cations and their interactions at the organic–inorganic interface. We can cite a stimulating work in which photochromic organic–inorganic materials are constructed via the coupling of liquid-crystalline nonionic surfactants and polyoxometalates (POMs).^[239] The chemical interaction of the complex nanostructures with organic molecules from the environment (solvent, air, etc.) has a clear effect in the photochromic response, providing new sensors and smart catalysts. An interesting work has been reported in 2009,^[240] metal–organic frameworks constructed from titanium–oxo clusters and dicarboxylate linkers, exhibit a reversible photochromic behavior induced by alcohol adsorption. The combination of POMs with organic dyes to enhance the activity or to provide new multichromic hybrid organic–inorganic supramolecular assemblies has also been explored. For instance, spiropyran molecules, with high photochromic performance, have been recently integrated in POM structures via covalent bonds^[241–243] and non-covalent interactions^[244,245] with different performances. The systematic study of Hakouk et al.^[242] is especially interesting since they analyze the photochromic behavior taking into account several physical parameters (SP structural characteristics, SP/POM and SP/solvent solid-state interactions, molar volume, etc.). The study reveals that the coloration of the materials before UV exposure is governed by a low-energy intermolecular charge-transfer (CT) transition between SP donor and POM acceptor (see **Figure 22**). The CT transition energy can be tailored by tuning the intrinsic ligand-to-metal charge-transfer (LMCT) of the POM unit, which allows drastic improvement of the photo-coloration contrasts.

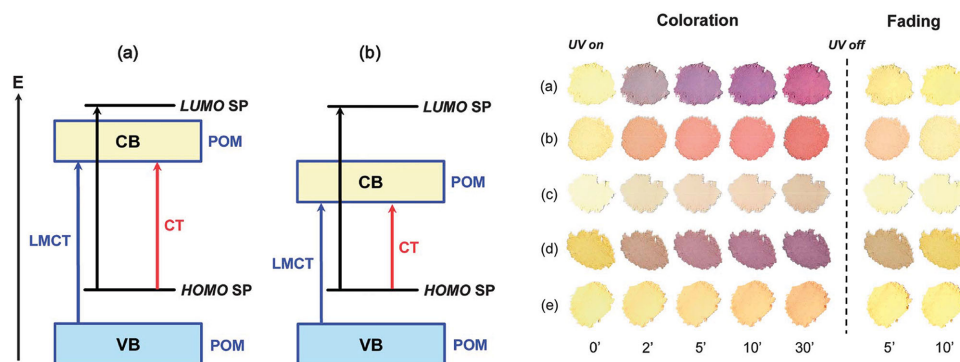


Figure 22. Schematic energetic diagrams displaying the three absorption phenomena predictable in SP-POM self-assembled structures when the POM unit is assembled with a POM unit having (a) a high-energy LMCT transition and (b) a low-energy LMCT transition. Photographs of powders of (a) $\text{SP}_4\text{Mo}_8\cdot\text{CH}_3\text{CN}$, (b) $\text{SP}_4\text{Mo}_8\cdot\text{DMSO}$, (c) $\text{SP}_4\text{Mo}_8\cdot\text{DMF}$, (d) SP_3Mo_8 , and (e) SP_2AlMo_6 at different time during the coloration process under UV irradiation (365 nm – 6 W), and the fading process under ambient light at room temperature. All panels reproduced with permission.^[242] Copyright 2014, Royal Society of Chemistry.

Furthermore, most of these systems exhibit electrochromism (Figure 23). Also cucurbituril-POMs dyads^[246] exhibit reversible photochromic properties as well as excellent photocatalytic activities toward the degradation of methyl orange (MO) and rhodamine-B (RB) under visible light irradiation. Interconversion pathways and chemical factors affecting the stabilization of the different species are highlighted and discussed in hybrids based on DABCO,^[247] piperazine and molybdate.^[248]

Some exotic systems such as 3D iodoplumbate open-framework material exhibited interesting wavelength-dependent photochromic properties.^[249]

However, to apply them in useful devices, the challenge is to encapsulate or integrate POMs into organic, polymeric or inorganic matrices or substrates to find new materials with adequate optical, mechanical, and chemical properties and applications such as catalysis, energy storage or biomedicine.^[250] The first attempt to process photoactive porous POMs as thin films with high optical quality have already been done.^[251] The work presents a simple route for the preparation of colloids of a flexible porous iron carboxylate (MIL-89) with tailored sorption properties that can be extended to other polyoxometallates and metal-organic frameworks.

Mesoporous bulk silicas have been used as supports for the immobilization of photochromic POMs by co-condensation

and direct post-grafting, both based on covalent bonding and by impregnation.^[245,252,253] Photochromic POMs have also been introduced in bulk silica matrices by sol-gel to produce POM/silica hybrid films.^[254,255] Other works explore non-covalent interactions between the photochromic species and the matrix, such as the lanthano phosphomolybdates anions immobilized through electrostatic forces onto positively charged silica nanoparticles.^[256] Ormosils like tri-ureasils have also been used to embed POMs providing transparent, flexible and rubbery photochromic materials.^[245,257]

4. Hybrid Materials for Nonlinear Optics

4.1. Introduction to Nonlinear Optics

Nonlinear optics phenomena appear when light meets nonlinear media giving rise to a nonlinear response of the dielectric polarization versus the incident electric field. Even if the phenomena has been observed before the discovery of lasers,^[258–261] it occurs essentially at high light intensity. Thus, the strong development of nonlinear optics is directly related to the development of lasers in the 60's.^[262] The polarizability represents the ability of the charges in a material to be displaced

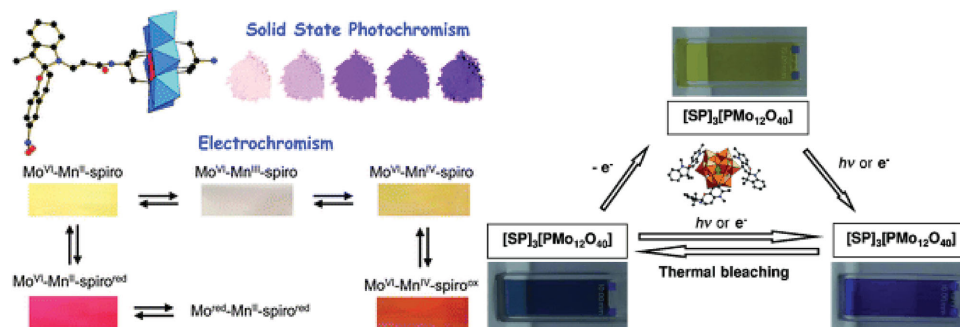


Figure 23. Structures of dual photochromic/electrochromic compounds based on spiropyran and polyoxometallates with “covalent bonding” (left) (Reproduced with permission.^[241] Copyright 2012, Royal Society of Chemistry.) and “electrostatic interaction” (right, Reproduced with permission.^[244] Copyright 2010, Wiley-VCH.).

by an electric field, E . When the electric field is lower than the internal fields, the overall macroscopic polarization P can be expressed as a function of the electrical susceptibility,

$$\chi : P = P_0 + \chi^{(1)}E \quad (1)$$

In Equation (1), P_0 is the permanent polarization; P is the total macroscopic polarization; $\chi^{(1)}$ is the linear susceptibility of the first order and $\chi^{(1)}E$ is the term for the induced linear polarization. However, when increasing the intensity of the light such as in the case of lasers, the induced polarization is not linear anymore. It can be expressed as in Equation (2):

$$P = P_0 + \chi^{(1)}E + \chi^{(2)}E^2 + \chi^{(3)}E^3 + \dots \quad (2)$$

In Equation (2), P is the total induced macroscopic polarization, $\chi^{(1)}$ is the linear polarizability, $\chi^{(2)}$ and $\chi^{(3)}$ are the nonlinear susceptibility tensors which correspond respectively to the hyperpolarizabilities for the quadratic and cubic terms (β and γ) at the molecular level.

The response to an external field E for the induced molecule is shown by Equation (3):

$$\mu = \mu_0 + \alpha E + \beta E^2 + \gamma E^3 + \dots \quad (3)$$

where μ is the total dipole moment, μ_0 is the permanent dipole moment, α is the molecular polarizability, β and γ are the 2nd and 3rd order hyperpolarizabilities. For large field intensities with a frequency ω , $\chi^{(2)}$ is responsible for the generation of an oscillating field with double frequency 2ω . It can be used for instance for optical storage, electrooptical modulation, optical switchers, wavelength conversion. This phenomenon is only observed in molecules or materials possessing a noncentrosymmetrical structure, which represents a specific requirement in the design of materials. The $\chi^{(3)}$ is the term which generates the nonlinear absorption activity or multiphoton absorption (MPA). It can be used for instance in optical limiting systems (laser protection), two-photon imaging, 3D data storage and micro-fabrication.^[263] In this case there is no symmetry requirement. In this section are discussed the most recent developments in terms of hybrid materials design, properties and applications for second and third order nonlinearities.

4.2. Second Order Nonlinear Materials

4.2.1. Dye-Doped Inorganic Matrices

The second harmonic generation of dyes doped hybrid materials, as well as for pure molecular systems, is dependent on the orientation of the molecular dipoles. Most common matrices for dyes dispersion are polymers or inorganic sol-gel networks since they do not require harsh treatment for their final stabilization. In all cases, the poling process, which induces the overall noncentrosymmetry, and the final material structure stability, which prevents from molecular relaxation and loss of noncentrosymmetry are critical. The orientation can be achieved through for instance common corona poling^[264–267]

or optical poling.^[268–270] Previous reviews emphasized the potential strong impact of the interface between the dyes and the matrix on the NLO response and the stability of the material.^[46,271] In the sol-gel process, two approaches are commonly proposed, either simple dispersion with low energy coupling (Class I) or covalent bonding with strong coupling (Class II), the latest being often mentioned as the most stable one. Since the very precursor works in the early 90's when was demonstrated the efficient doping and orientation of dyes in inorganic matrices,^[272] large number of reports explored the capacity of sol-gel matrices to stabilize the orientation of chromophores. Large second order optical nonlinearities were observed using covalent grafting of the dyes to the silica backbone.^[163,165] The optical response was evidently correlated to the matrix condensation level and rigidity.^[164] and since then numerous work reported on the stabilization of the hybrid system and optimization of the optical and nonlinear optical responses.^[46,151,153–159,161,163–166,272–276] It is now well established that the strong binding of the molecular guest to the hosting matrix induces an improvement of the stability of the final nonlinear optical material in particular after the orientation process.^[46,271]

Comparison between polymer matrices (often polymethylmethacrylate PMMA) and sol-gel matrices evaluated for both second and third order nonlinearities are often in favor of the siloxane chains that usually show a higher stability combined with good optical properties.^[277–280] Numerous work reported the influence of the grafting and the matrix composition on the nonlinear optical performances. Even if large amount of work were reported since the early 90's, there is still a tendency to improve the properties and evaluate the process parameters and the impact on the NLO, without real breakthrough in terms of SHG values. For instance the thermal behavior and possibility to enhance the second harmonic generation and improve the stability of the optical properties by using covalent grafting to the matrix were investigated.^[277,280–291] Several types of chromophores bearing silane groups were proposed (Figure 24). Thermal stability of the nonlinear optical properties were improved by combining covalent bonding of the dyes and hydrogen bonding or by playing with the sterical hindrance.^[282,283,287] Such interactions were for example obtained by incorporation of aniline-silane in the matrix.^[287] Moreover it was shown that the topological localization of the silane groups along the structure and the type of spacer used impacts the NLO properties.^[291]

It was shown that the precuring and poling temperature impacts the nonlinear optical responses due to modification of the cross-linking.^[155,156,292] An excessive cross-linking would decrease the mobility of the dyes and consequently lower the poling efficiency. This depends also in the rotational capacity of the dyes. A 2-dimensional system showed improved thermal stability compared to the one-dimensional one.^[292,293] Chromophores with two or more silane groups were prepared with relative impact on the final properties.^[294,295] The grafting was achieved through photo-cross-linking^[296] or polymerization reaction, for instance free radical polymerization in an interpenetrating methacrylate/silica hybrid matrix.^[297] In this case, a chromophore bearing allyl glycidyl ether was reacted with (γ -methacrylpropyl)-silsesquioxane. This strategy allowed improvement of the crosslinking, higher T_g for the final

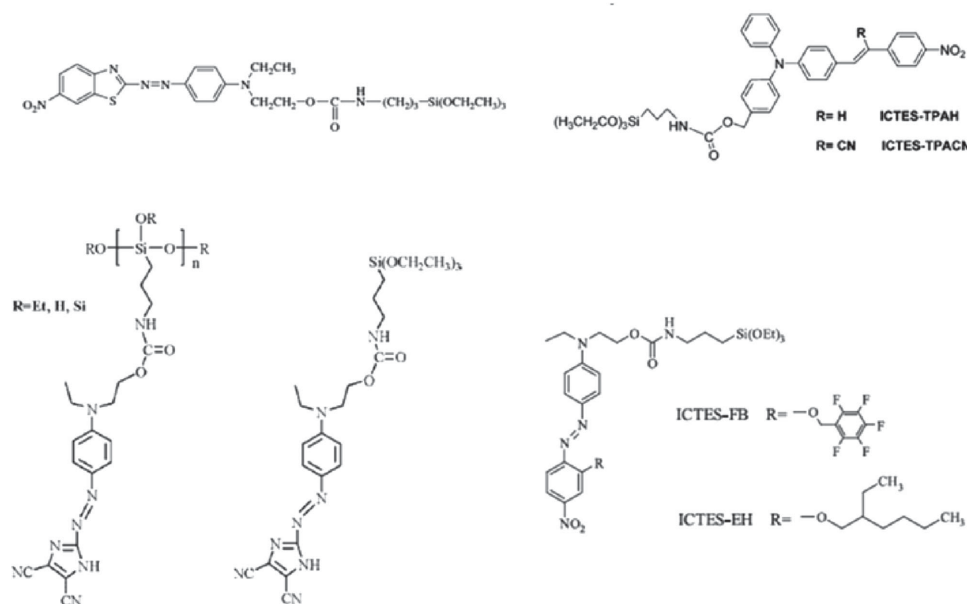


Figure 24. Structures of sol-gel NLO dyes. Reproduced with permission.^[283] Copyright 2007, American Chemical Society. Modified using several sources.^[277,281–291]

material and better stability. In all cases, particular attention should be given to the structure of the dyes considering that each system is different. For instance it was shown that the use of fluorinated groups on dyes induced a better nonlinear optical activity than the basic chromophore (DR1 in this example, **Figure 25**).^[290] The thermal stability was also improved using bulky fluorinated substituting groups.

A precise control of the heating conditions seems to be crucial but needs to be optimized for each molecular structure. This has to be considered together with the crosslinking process parameters (hydrolysis-condensation conditions), which will impact the densification, orientation capacity, structure of the guest molecule and final stability, which was also shown to strongly impact NLO properties.^[279,294,298–300]

Besides using corona or optical poling, the orientation can also be achieved through the control of the deposition process. Layer-by-Layer approach combined with the sol-gel process allows easy access to self-oriented materials.^[301,302] In this case

the orientation can be induced by the strong repulsive forces between the negatively charged ZrO_2 and the sulfonate groups of the chromophore (**Figure 26**).^[301] Such method can be extended to wide range of optical materials and more generally light activated systems combining for instance nanoparticles, dyes, polyoxometallates with polyelectrolytes.^[303]

Another way of controlling the orientation is to intercalate the chromophore in the interlayer space of layered inorganic materials. This strategy was used in the early 90's by P. G. Lacroix et al. who managed to intercalate stilbazolium dyes with spontaneous poling into manganese based inorganic layered material (MPS_3) rising to efficient second-harmonic generation combined with permanent magnetization below 40 Kelvin due to the presence of Mn^{2+} ions.^[304] Kawamata and co-workers reviewed the strategies based on incorporation in clay minerals.^[305] Using this approach, very regular orientation of the dyes can be obtained and thus enhancement of the optical nonlinearities. For instance, Kuroda et al. reported

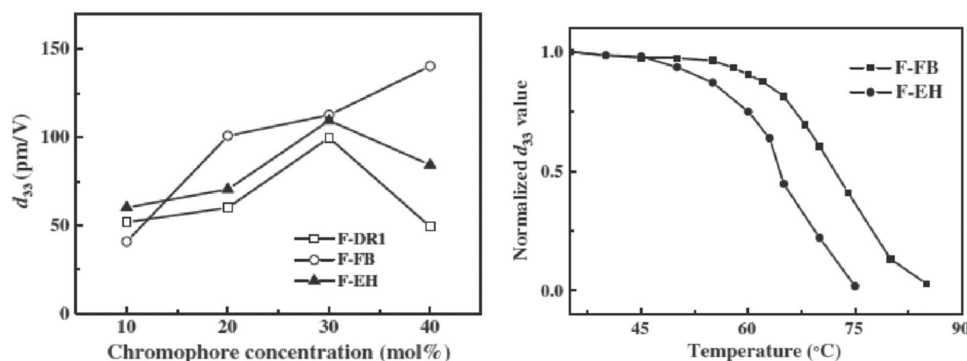


Figure 25. SHG and thermal stability of DR1 hybrid compared to fluorinated species (FB and EH in Figure 41). Reproduced with permission.^[290] Copyright 2013, Elsevier.

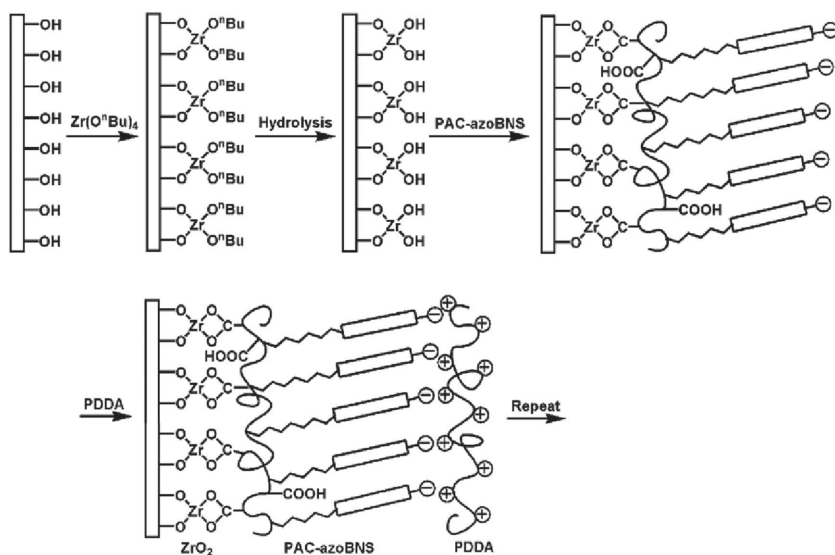


Figure 26. Self-orientation of azobenzene chromophore using a Layer-by-Layer deposition. Reproduced with permission.^[301] Copyright 2007, American Chemical Society.

the inclusion of 4-nitroaniline into kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) interlayers.^[306] The 4-nitroaniline spontaneously self-orientate during intercalation thanks to hydrogen bonding with the silicate nanosheets present on one side of the interlayers (Figure 27), thus giving rise to a SHG signal.

Finally the use of crystals of dyes grown in an inorganic composite layer can be an alternative to the dispersion of molecular entities in sol-gel matrices. A. Ibanez and co-workers advantageously developed this approach in particular for third order nonlinearities.^[307–310] However, the poling process is reported to be hard to achieve due to the ionic conductivity at high temperature and also disorientation during the cooling down.^[310] On the other hand, the use of noncentrosymmetric crystal organization can be a way to achieve strong SHG at the molecular level. This has been recently developed through the possibilities offered by the coordination chemistry and supramolecular hybrid approaches.

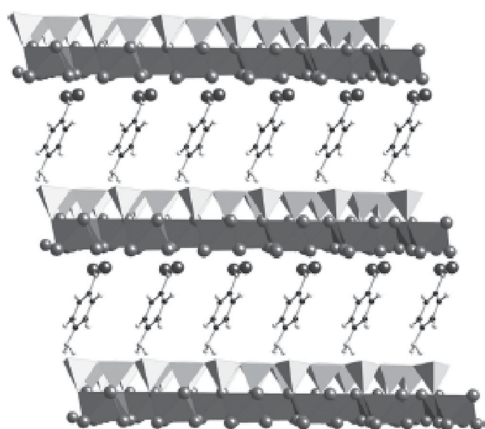


Figure 27. Oriented intercalation of 4-nitroaniline into kaolinite interlayers by Kuroda and co-workers. Reproduced with permission.^[305,306] Copyright 2012, Wiley-VCH. Copyright 2001, American Chemical Society.

4.2.2. Coordination and Organometallic compounds Based Hybrid Systems

Coordination chemistry offers a large range of possible molecular and supramolecular architectures by association of metallic centers and organic ligands. The introduction of metal centers has shown interesting impact on the NLO response of coordinating organic dyes in a push-pull configuration.^[311] The charge transfer is usually less efficient when introducing a metallic center between the push and pull systems. In the case of 3D self-assembled materials, typically crystalline materials, the noncentrosymmetry can be achieved by the organization in the crystal structure during the crystallization process.^[311,312] High organization and thus SHG response can be expected in such molecular arrangement. During the past decade, numerous works were devoted to the use of such molecular

based self-assembly in crystals for NLO applications. Metal-organic frameworks (MOFs) or Polyoxometalates (POMs) were particularly investigated with different mechanism for the optical nonlinearities.^[313,314]

Crystallization in noncentrosymmetric space groups being hard to achieve, a possible way of controlling the noncentrosymmetry during the crystallization process is to use chiral ligands. For instance, A. Dolbecq and co-workers used a chiral stilbazolium cation (CHIDAMS^+) which was crystallized with $\text{PW}_{12}\text{O}_{40}^{3-}$ counterions.^[315] In this system a charge transfer between the electron donor organic part and the acceptor inorganic counterpart, the POMs, was observed. The presence of 3 independent organic molecules on one POM prevents the formation of head-to-tail dimeric units, which would reduce the noncentrosymmetry and thus the NLO activity. This complex shows high SHG response, which was evaluated to be 30 times higher than the one measured in KDP crystal. Theoretical investigation on charge transfer and NLO response of Lindqvist type POMs (hexamolybdate/molybdate anions) functionalized with side chains organic ligands showed that the charge transfer from molybdate central core to the ligands has a central role in the enhancement of the SHG and significant values of second-order polarizability can be obtained in such configuration.^[316,317]

In the same way, metal polycarboxylates^[312,318–321] based crystals have shown promising potentialities in terms of second harmonic generation. E. Cariati and co-workers reported several complexes using *trans*-4-(4-dimethylaminostyryl)-1-methylpyridinium (DAMS^+) cationic ligands with general formula $[\text{DAMS}]_4[\text{M}_2\text{M}'(\text{C}_2\text{O}_4)_6] \cdot 2\text{DAMBA} \cdot 2\text{H}_2\text{O}$ (where $\text{M} = \text{Rh}, \text{Fe}, \text{Cr}$; $\text{M}' = \text{Mn}, \text{Zn}$) giving rise to noncentrosymmetric layered structures and thus strong SHG.^[320] In this case, the very large SHG is mostly explained by the important quadratic polarizability of the ligands DAMS^+ (much more important than the SHG from the metal-to-ligand charge transfers contribution) combined with their self-organization in a layered structure with an optimized J-type aggregate configuration (Figure 28). Considering

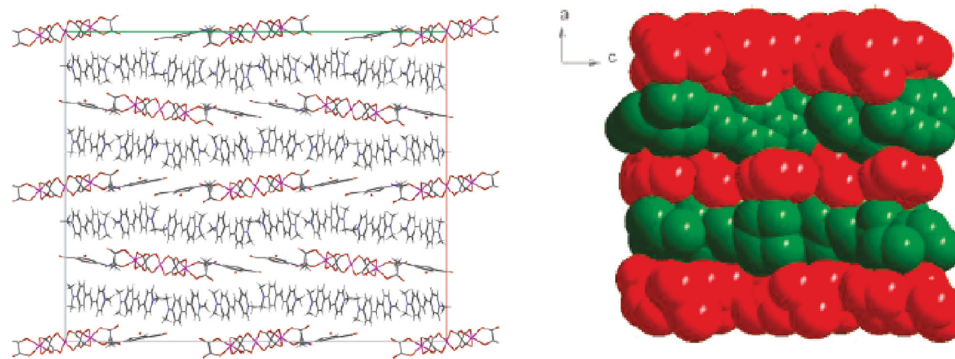


Figure 28. General structure showing the packing of alternate anionic organic/inorganic and cationic organic layers in the complexes $[\text{DAMS}]_4[\text{M}_2\text{M}'(\text{C}_2\text{O}_4)_6]\cdot 2\text{DAMBA}\cdot 2\text{H}_2\text{O}$, along the c -axis (left) and b -axis (right). Left panel reproduced with permission.^[320] Copyright 2007, American Chemical Society. Right panel reproduced with permission.^[321] Copyright 2010, American Chemical Society.

their high potential in terms of SHG and since such molecular self-assembled crystalline materials can easily be incorporated in composite materials (inclusion in polymers or sol-gel matrices, Layer-by-Layer assembly on surfaces...),^[322,323] it can certainly be expected some future developments for applications in nonlinear optics.

4.3. Third Order Nonlinear Materials

4.3.1. Dispersion of Dyes in Sol-gel or Organic Materials

The general design of hybrid materials exhibiting third order nonlinearities is often very similar to the materials for SHG, with association of NLO dyes with to inorganic or hybrid matrices. However one important difference is the symmetry rules. In the case of THG, no symmetry rule is required. The preparation of the materials focuses on the interface control, concentration optimization and structure preservation of the dyes during the process. The main application for these materials concerns the nonlinear absorption phenomena and the capacity of the systems to block intense light radiation. These materials act as filters to protect optical sensors, sights or cameras against lasers damages (Optical Power Limiting (OPL) materials).^[324,325] The two main mechanisms are the Reverse Saturable Absorption (RSA) and the Two-photon Absorption (TPA) or Multi-Photon Absorption (MPA).^[263,299,326–332]

The molecular design for third order nonlinear applications has been intensively studied and optical measurements are mostly reported on molecules in solution.^[263] However, exploitation of such nonlinear phenomena in real applications requires that the dyes are introduced in a solid host material that enables post-processing such as cutting or polishing. The typical requirements for such material were previously detailed.^[333–335] The dispersion of dyes or nanostructures in optically transparent matrices such as presented for SHG materials is a consistent approach to efficient devices. It is important to note that no symmetry and orientation requirement is necessary at this stage in contrary to the second order systems. The ideal matrix possesses a high optical quality and a high damage threshold under the laser exposure, and a good compatibility with the chromophores. Polymers are interesting because

they can exhibit high compatibility with the dyes, good optical quality, and are easy to prepare. Inorganic materials, such as silica based systems used in optical glasses, are also promising candidates because of high optical quality and high damage thresholds. Even if few articles report the use of thin films,^[336] the preparation of monolithic materials represents the best potential approach since they can be designed and shaped conveniently to be adapted to the final OPL set-up. Moreover, such 3D monolithic materials present higher loading capacity in chromophores than films and a better focusing efficiency of the beam.

The dispersion of metallophthalocyanine dyes with interesting RSA into SiO_2 sol-gel matrices was firstly reported.^[157,337] The RSA of the dyes was also observed in the solid materials demonstrating the capacity of the strategy. The presence of dimers showed that the dyes were not totally homogeneously dispersed, and protonated species which showed that the process should be adapted to the dyes sensitivity (Control of pH...)^[337] The final nonlinear properties are comparable to the one in buffer solution. In the same period investigations on the use of polymeric matrices were reported.^[327,328,338] Several important works appeared then during the past 15 years. P. Innocenzi and co-workers reported the entrapment of functionalized fullerenes in inorganic matrices for optical limiting.^[271,339–341] Fullerenes present RSA in the visible wavelengths.^[340–343] One drawback is their poor solubility and poor compatibility with the silica based matrix. Improved compatibility was achieved by adding silane or dendrimer units on the fullerenes structures.^[340–342] The nonlinear response of fullerenes was similar in solution and in the materials, showing RSA with nonlinear scattering and nonlinear refraction contributions at high fluence.^[271] An original strategy adopted in order to increase the concentration of nonlinear active species was to grow nanocrystals of dyes in inorganic glasses.^[307–310] Stilbene 3 nanocrystals were grown in sol-gel glasses.^[344] The final composite materials showed strong nonlinear absorption at visible wavelengths.^[309] Impregnation of a porous matrix was also used for aggregation of dyes (Naphthalocyanine) into the cavities of xerogel, which exhibited interesting RSA response.^[345]

A family of platinum dyes with low absorption in the visible and strong nonlinear behavior was investigated. For instance the platinum(II) square-planar complex

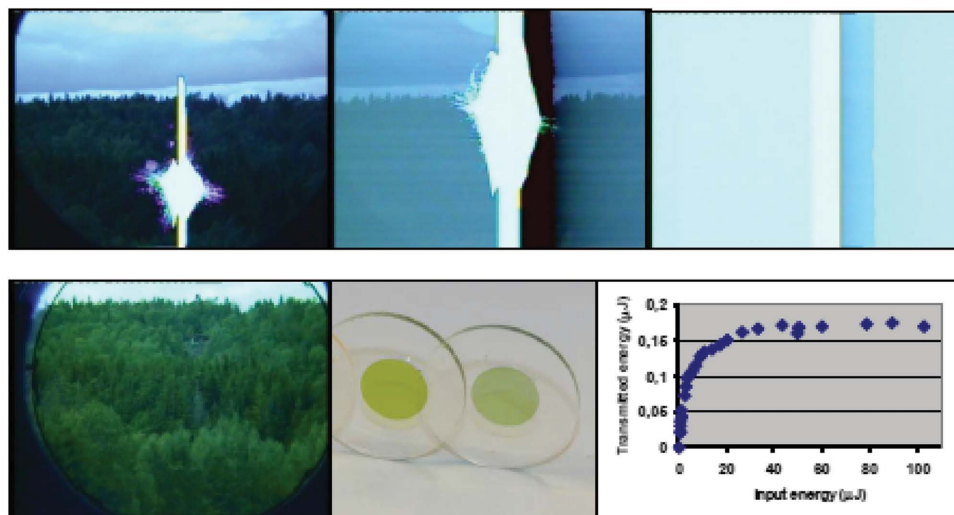


Figure 29. Top: visualization of the destruction of a camera under laser irradiation. Bottom: similar view from the same camera protected by highly transparent hybrid materials (left), the filters (center) and nonlinear absorption response of the filter at 532 nm in the nanosecond regime allowing the efficient protection (right). Reproduced with permission.^[279] Copyright 2009, Wiley-VCH.

trans-[P(n-Bu)₃]₂Pt[(C≡C-p-C₆H₄-C≡C-p-C₆H₅)₂]^[326,346,347] was reported for efficient nonlinear absorption in solution,^[326,346–348] and series of derivatives were prepared with improved properties.^[294,349–358] The use of PMMA monoliths hosting platinum derivatives was an efficient route towards OPL materials.^[278,359] The measured linear transmissions were nearly 90% in the visible and NLO properties were maintained in the solid. The structural rigidity in the case of grafted dyes limited possibilities of relaxation compared to host-guest systems, leading to a loss of efficiency. Moreover, the damage threshold was impacted and decreased with grafting processes. On the contrary to what was observed for second order NLO, grafting of the dyes affected here negatively the NLO efficiency. Similar investigations were run on sol-gel hosting matrices.^[279,298] Functional dyes were designed in order to improve their concentration in the inorganic phase.^[279,294] The material expressed efficient nonlinear absorption in the visible wavelengths and protection capabilities (**Figure 29**).^[279]

Many organic dyes are known to be pH sensitive and it is often important to control the pH during the dyes addition. The use of sonogel was mentioned by Morales-Saavedra et al. as an alternative to avoid the use of acidic or basic catalyst and thus preserve the integrity of the dyes.^[360,361] In the case of the use of catalysts, neutralization of the sol after hydrolysis allowed insertion of sensitive dyes into the silica system.^[279,298,300] In connection with the pH control, the loading capacity of the glass with the dyes was efficiently tuned by controlling the condensation step kinetics, without need of covalent grafting.^[298,300] The optimization of the porosity allowed also optimization of the nonlinear absorption. The **Figure 30** shows the phosphorescence emission and the lifetime, strongly improved by using functional precursors reducing the microporosity of the system.

Comparison between polymer and sol-gel approach in this specific case showed few advantages for the sol-gel method. The T_g of the polymer was a limitation for use in harsh environment. The nonlinear response control appeared to be easier

in the inorganic matrix. Finally the damage thresholds under intense laser irradiation are often higher in inorganic than organic systems. Comparison between PMMA and sol-gel silica doped with Rhodamine 6G gave the same conclusions.^[362] Silica hosting matrix appeared to be more efficient than PMMA and the nonlinear parameters (n_2 , β , $Re[\chi^{(3)}]$, $Im[\chi^{(3)}]$) were better in the hybrid system.

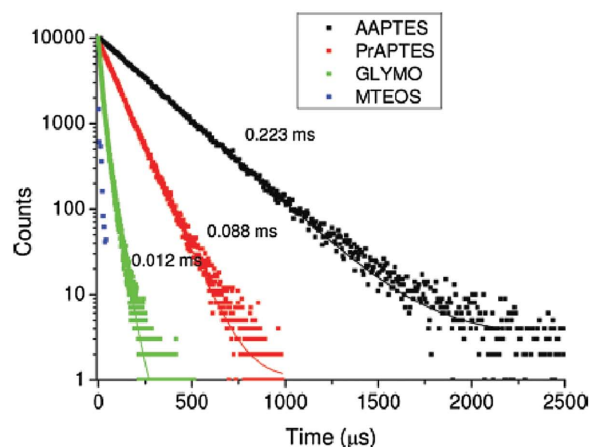
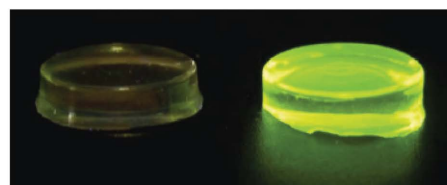


Figure 30. Impact of the porosity on the optical properties of platinum acetylides doped hybrid silica xerogels. Top: Irradiation under UV of hybrid materials prepared with MTEOS (left) and MTEOS/GLYMO (right) precursors. Down: Lifetime changes versus the matrix composition. Reproduced with permission.^[298] Copyright 2012, American Chemical Society.

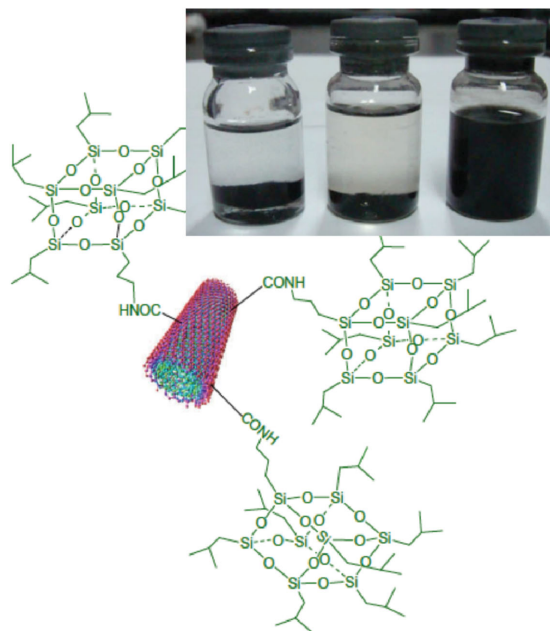


Figure 31. POSS functionalized multiwall Carbon Nanotubes and photo showing the suspension stability improvement of the MWCNTs/POSS (right) compared to MWCNTs (left) and MWCNTs-COOH (middle) adapted from reference. Reproduced with permission.^[368] Copyright 2010, Elsevier.

4.3.2. Polysilsesquioxanes Hybrids for Nonlinear Absorption

Polysilsesquioxanes (POSS) were functionalized with optically active dyes and can be considered as intermediates between the molecular level and a nanocomposite material. X. Su and co-workers reported the synthesis of POSS modified with azobenzene, acetylene or stilbene derivatives exhibiting nonlinear absorption.^[363–365] These systems exhibited large $\chi^{(3)}$ susceptibility and efficient reverse saturable absorption with enhanced thermal stability. They were processed as thin films. Carbon nanotubes, well known for their optical limiting response due to nonlinear scattering of in situ formed microbubbles,^[366,367] were also associated to POSS units (covalent or ionic bonding) in order to improve their solubility and optical

properties (Figure 31).^[368,369] The prepared nanocomposites with multiwall carbon nanotubes (MWCNTs) and POSS showed much better stability in suspension and a better processability. These hybrids exhibited efficient optical limiting performances for nanosecond pulses at 532 nm, attributed to the nonlinear scattering thermally induced.^[368,369] It also revealed a good photostability under the laser irradiation. However, even if the hybrid composites materials based on Polysilsesquioxane bricks appeared to improve noticeably the nonlinear optical responses and stabilities, the processability in films or monoliths and their optical characterizations have not been reported so far.

4.3.3. Graphene Based Hybrid Materials for Nonlinear Absorption

Graphene was found to present efficient nonlinear absorption with consequently a strong potential for optical protection applications.^[370–372] Graphene oxide (GO) suspensions in DMF exhibited both two-photon absorption in picosecond regime and Excited State Absorption in nanosecond regime and differed from the nonlinear absorption mechanisms observed in carbon nanotubes based essentially on nonlinear scattering.^[371] The graphene dispersion in DMA showed important nonlinear scattering in nanosecond regime, due to the formation of solvent bubbles, and broadband optical limiting (532 and 1064 nm).^[372] Also, association between dyes and graphene was successfully attempted in order to improve the nonlinear absorption properties, both experimentally and theoretically.^[373,374] Consequently, numerous works recently reported the potential use of graphene-based materials for nonlinear absorption. In the case of hybrid nanomaterials based on the association between graphene oxide bearing $-\text{COOH}$ pending groups and iron oxide Fe_3O_4 , enhancement of optical limiting response due to both contributions of nonlinear absorption (TPA) and nonlinear scattering was observed.^[375] Bulk materials were prepared by dispersion or co-dispersion of graphene derivatives in either organic or inorganic matrices. Zhan and co-workers reported the efficient synthesis of graphene embedded in sol-gel Ormosil glasses.^[376,377] They used both nanosheets (GONSs) and nanoribbons (GONRs) (Figure 32). The prepared materials showed high linear transmission in the visible, good thermostability and good optical limiting response attributed to both nonlinear

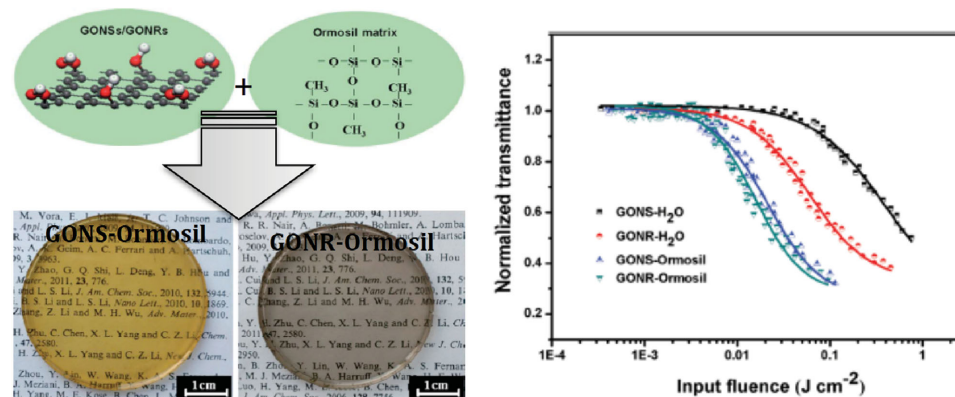


Figure 32. The GONS-Ormosil and GONR-Ormosil hybrid materials (left) and normalized transmittance versus the input fluence (right). Reproduced with permission.^[376] Copyright 2014, Royal Society of Chemistry.

scattering and nonlinear absorption. Similarly, Xu and co-workers reported the dispersion of GO in sol-gel matrices using modified GO for covalent grafting to the silica network.^[378] The GO-COOH was modified using 3-aminopropyltriethoxysilane (APTES) providing -CO-NH- bond between the COOH and the amino group of APTES. The GO-APTES was then co-hydrolyzed and co-condensed with the silicon precursors (TEOS). The functionalization of GO with APTES and covalent bonding to the silica network allowed better dispersion and homogeneity of the prepared sol-gel materials while GO tend to aggregate when simply dispersed in the matrix.

The NLO properties were evaluated and attributed to TPA process since no bubble can be formed in solid environment to the contrary of suspensions in solvents. The performances were improved in the solid compared to the solution. Similarly, composite materials with graphene and metal nanoparticles in sol-gel glasses was also recently proposed.^[379] Hybrid composites with graphene and ZnO or CdS nanoparticles dispersed in PMMA glasses were proposed by Chen and co-workers.^[380,381] They showed that the interfacial charge transfer between ZnO and graphene induced enhanced nonlinear absorption and nonlinear scattering properties. Graphene based hybrid materials appear clearly as extremely promising composites for THG applications both in nanosecond and picosecond regimes. Combination of graphene with other type of dyes or nanostructures in hybrid composites could provide an important breakthrough in the field of THG materials in the near future.

Hybrid sol-gel monolithic materials appear to be versatile systems allowing easy dispersion of chromophores or nanostructures with relatively high concentrations and good stability in particular under laser irradiation. The growing knowledge regarding the relationships between the process, the microstructure, the dyes localizations and the optical properties open a wide access to highly improved new optical materials with third order nonlinearities. Hybrid materials exhibiting synergetic effects between the guest systems (molecules and nanostructures) will certainly bring strong improvements in the optical responses and important innovations in the field of nonlinear optical devices.

5. Plasmonic Hybrid Materials

5.1. Optical Properties of Metal Nanoparticles

Plasmonic materials are among the most studied systems in the field of light-matter interactions and numerous articles and reviews were centered on this topic for the past decade.^[382–398] Association of plasmonic nanostructure with organic entities, in particular molecules with optical properties, has been intensively investigated for several purposes, such as stabilization of the metal nanostructures or metal-to-dyes interactions. Indeed, the specific optical response of such metallic nanostructure gives rise to unexpected interactions with optically active molecules. The methods for controlling these interactions in hybrid systems are reviewed in this part as well as the impact on the optical responses with respect to theoretical predictions.

When nanoparticles, which possess sufficient free carriers concentration in their structure (typically noble metals or

semiconductors), are excited by an incoming light source with wavelengths much larger than their size they express specific optical response due to collective oscillation of the free-electrons in their structure.^[399–408] This phenomenon is commonly called Localized Surface Plasmon Resonance (LSPR) and can be experimentally easily observed as a modification of the absorption spectra. It provides also a large electromagnetic field enhancement at the metallic surface vicinity and local thermal effects and in some cases important scattering of light. Gold and silver based nanostructures were the most reported due to their easy accessibility in terms of synthesis, structure versatility, and stability. The absorption bands relative to the LSPRs are essentially dependent on the metal, the particles size and shape, the potential collaborative effects between particles and the refractive index of the surrounding media.^[392,397,403,406,409–434] D. Portehault and co-workers demonstrated recently the impact of the ligand (aromatic thiolates)-to-gold particle charge transfer on the plasmon resonance position using an original approach by spectroscopic ellipsometry.^[435]

In the field of optics, these nanoobjects provide, under light excitation, a way to strongly affect the optical responses of optical systems in close interaction with the metallic surfaces (such as dyes or semiconductors). The control of these interactions in hybrid systems has been an important field of scientific contributions for the past ten years. Important reports concerned the enhancement of sensitivity for molecular detection using Raman spectroscopy. Large amount of work were then launched related to Surface Enhanced Raman Spectroscopy (SERS) in the field of sensing and detection. Such plasmon-molecules or plasmon-particles interactions opened then a broad field of research related to enhancement of luminescence and absorption properties as well as nonlinear optical properties for applications in medical imaging, photodynamic therapy, lightning, LEDs, solar cells, sensors, photocatalysis.

5.2. Hybrids with Dyes and Plasmonic Nanostructures : Luminescence and Nonlinear Optical Properties

Interactions between a dye and a metallic surface can be achieved and controlled through different architectural approaches, typically either on a surface, on nanoparticles, in nanoshells or associated in a composite material, depending essentially on the application mode (Figure 33). In all cases the impact of the interaction on the properties strongly depends on the molecule-to-surface distance but also on the dipoles respective orientations. Theoretical reports have shown that the chromophore optical response can be strongly affected by the presence of the local enhanced electromagnetic field (provided by either single particle or dimers, aggregates...), in particular the emission, depending on the distance, dipoles orientations and spectral overlaps between the LSPR band and the emission band.^[398,426,436–438] Experimentally, the control of the dipole orientation remains extremely complicated and poorly documented while large amount of work was published on different ways of controlling the dyes to metal distance. The different strategies were often correlated with modeling approaches.^[398]

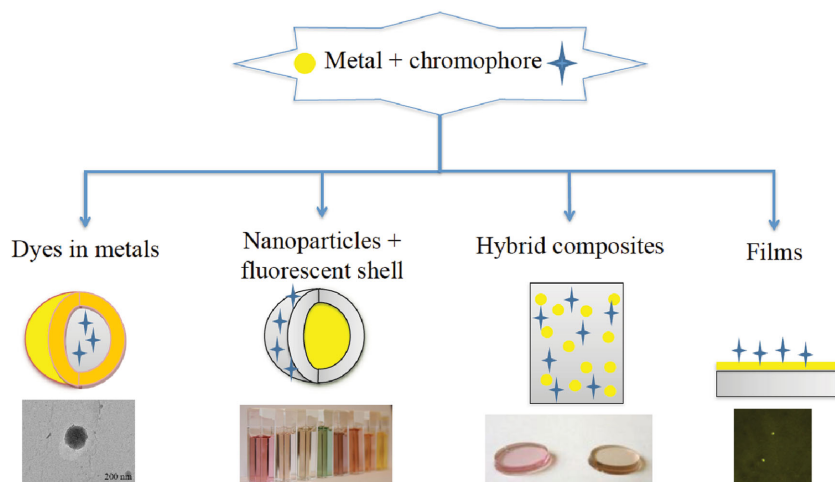


Figure 33. Principal strategies to control interactions between chromophores and metal nanoparticles, respectively from left to right: Incorporation of dyes into nanoshells, surface modification of nanoparticles with dyes, co-doping into solid matrix (polymer or sol-gel) and multilayered thin films. The two first approaches on colloidal systems are often proposed for biomedical imaging or therapy (injectable nanoplatforms) and the composites/films for optical devices design (optical filters, photovoltaic, sensors...).

5.2.1. Surface Functionalization of Metallic Nanoparticles

The chemistry and growth mechanisms of metallic nanostructures, especially silver and gold, are nowadays well mastered. This allows a fine control over the size and morphologies (spheres, rods, cubes, stars, bipyramids...) and thus a precise tuning of the SPR band from the visible to the NIR.^[385,391,409,439] The surface state of the native nanostructures is depending on the synthesis route, and the particles are usually stabilized through the presence of an organic ligand or surfactants at their surface. The total or partial replacement of the stabilizing molecules can be achieved through ligand exchanges reactions with functional systems bearing thiol or thioic acid pending groups.^[390] These groups possess a strong affinity for the metal surface and ensure efficient binding. The use of electrostatic interactions (i.e., with polyelectrolytes) can also be a way for surface modification.^[390] J.-Y. Chen et al. used direct interaction between a sulfonated aluminum phthalocyanine and gold nanorods or nanocubes to enhance their fluorescence.^[440] They used it for fluorescence imaging of cancer cells using two-photon excitation in the NIR (**Figure 34**).

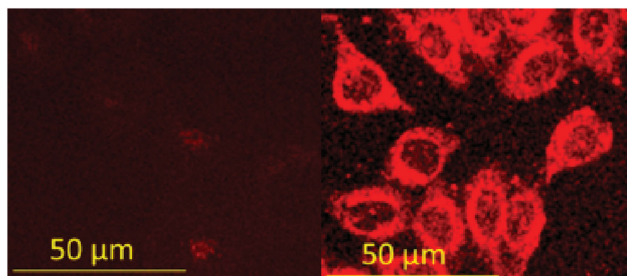


Figure 34. Two-photon fluorescence imaging of cancer cell lines using pure aluminum phthalocyanine (left) and aluminum phthalocyanine combined with gold nanocubes (right) (Exc. 800 nm/fs laser). Reproduced with permission.^[440] Copyright 2014, American Chemical Society.

Dyes bearing thiol groups are easily attached to metal surfaces. Numerous examples can be recorded from the literature. Russel and co-workers used gold nanoparticles modified by zinc phthalocyanines and later on by antibody to achieve efficient oxygen singlet generation and photodynamic therapy of cancer cells (**Figure 35**).^[441,442] In this case, the distance between the dyes and the surface is mostly determined by the C11 chain between the molecule core and the thiol groups or the disulfides.

Since the chromophore to particle distance is a crucial parameter in the control of the charge or energy transfers between the two systems, several spacing strategies were investigated. The synthesis of block copolymers bearing chromophores along the chains showed efficient control over the distance by playing with the polymer structure.^[443,444] The copolymer functionalized with Lucifer Yellow (LY) allowed preparation of luminescent gold hybrid nanostructure (**Figure 36**).^[443] The optimized nanostructures were successfully used for cell imaging and photodynamic therapy of cancer cells.^[443] Interestingly, it was also shown that the use of anisotropic gold core, such as nanobipyramids, allowed enhancement of the fluorescence while this was not observed in the case of the spherical nanoparticles.^[444]

The distances of interactions can be also tuned by using charged spacers such as polyelectrolytes for surface modifications of nanoparticles through Layer-by-Layer self-assembly stabilized by electrostatic interactions (**Figure 37**).^[445-448] which was initially introduced to immobilize particles on surfaces^[449] or for biocompatibilisation.^[450] Up to 11 layers of spacer were introduced in the structure leading to shell thicknesses in the range 1 to 20 nm.^[446]

In the case of nanostars coated with polyelectrolytes, it was shown that the fluorescence emission of the dyes could be recovered with a distance of about 10 nm.^[446] However in this case no enhancement could be observed on the emission. Interestingly, C. J. Murphy and co-workers showed that the use of nanorods with similar strategy allowed an enhancement of the two photon absorption cross section of an organic chromophore (AF348-3A) with a decrease in the enhancement when going from 3 nm to 12 nm from the surface.^[445]

Halas et al. used human serum albumin as spacer of about 8 nm between NIR fluorophores (IR800) and gold nanoshells or nanorods, attached to the surface through electrostatic interactions.^[451] They were able to observe large increases in the quantum yield compared to isolated chromophores. Nanoshells appeared to be more efficient for emission enhancement (40-fold enhancement, 86% QY) and this is mostly attributed to their important scattering cross section at the emission wavelength of the chromophores compared to nanorods. The use of DNA is also an interesting alternative to control optical responses of hybrid nanosystems. For instance thiol-terminated DNA can easily bind the metal surface and DNA hybridization can thus be used for fluorescence enhancement.^[452]

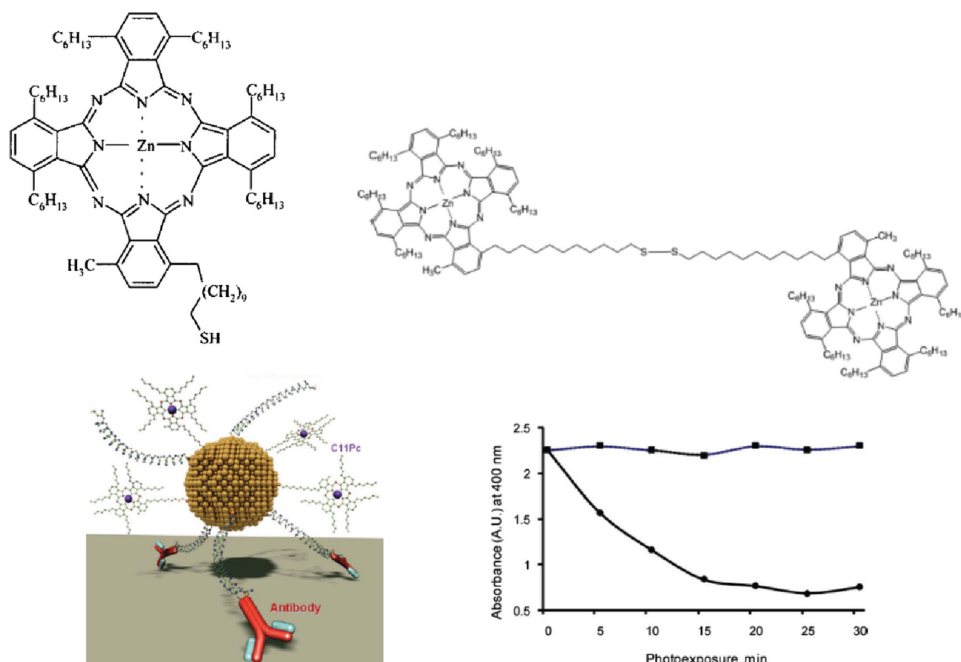


Figure 35. Two structures of phthalocyanine based photosensitizers (top) and preparation of the conjugate with Au-NPs (bottom left). Bottom right shows the generation of oxygen singlet evidenced by the decreasing in the absorption spectrum of the disodium 9,10-anthracenedipropionic acid (ADPA) probe (dots) versus the control sample without the photosensitizer (squares). Top left reproduced with permission.^[441] Copyright 2002, American Chemical Society. Top right and bottom are reproduced with permission.^[442] Copyright 2011, Royal Society of Chemistry.

Thiol modified DNA was also used to control plasmon coupling between Au nanoparticles aggregates and the induced two-photon luminescence from the metal, which could be enhanced by a factor 265 in the best case (2 nm distance for 41 nm aggregates) and used for DNA sequences detection.^[453] Willner and co-workers used DNA tweezers modified with a 10 nm Au NP and a fluorophore (Cy3) to build switchable closure and opening with controlled fluorescence enhancement or quenching depending on the state.^[454]

Among the most investigated strategies is the use of core shell nanostructures with metal core and silica based shell, which provides also a good possibility of spacing control between the dyes and the metallic surface.^[455–465] The dye can be either directly incorporated in the silica shell during the synthesis of post-grafted at the surface of the silica. M. A. Noginov used this configuration to generate core-shell structure functionalized at the surface by Oregon green 488 fluorophore encapsulated in the outer silica shell.^[466] This structure, with

a spherical gold core of 14 nm in diameter and a silica shell of 15 nm thickness, allowed the demonstration of a spaser-based nanolaser in the visible range.^[466] Murphy and co-workers showed that it was possible to have a fine-tuning of the distance and easy surface grafting using click-chemistry reactions (**Figure 38**).^[458] They observed enhancement of fluorescence of an IR dye (800CW DBCO) with hotspots (10-fold enhancement) in the range 14–22 nm thicknesses for the silica shell and SPR maxima at 750–800 nm, overlapping the emission spectrum of the dye. The main mechanism was strong coupling between the dye and the metal, and almost no contribution of the scattering effects was detected.

Similar strategy but with different chemical route is to ensure grafting through amide bond for instance by reacting between an amine NH_2 supported on the silica and a carboxylic acid group (**Figure 39**).^[456,457] In the work from Xu et al., they reported a two-photon enhancement of fluorescence maximum of 11.8 at a 20 nm distance due to the electric field

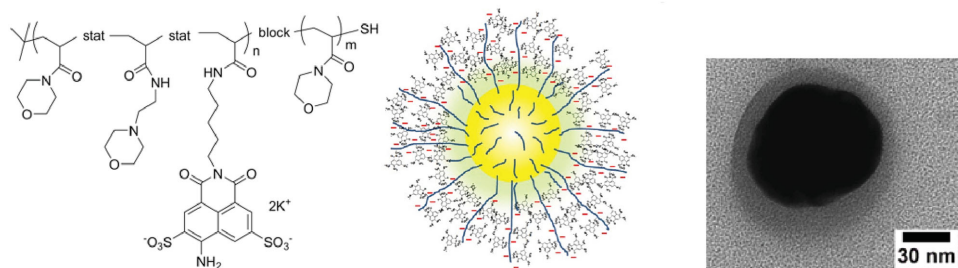


Figure 36. Structure of the diblock copolymer functionalized with LY dyes and hybrid gold nanoparticle bearing the luminescent polymers. Reproduced with permission.^[443] Copyright 2013, Elsevier.

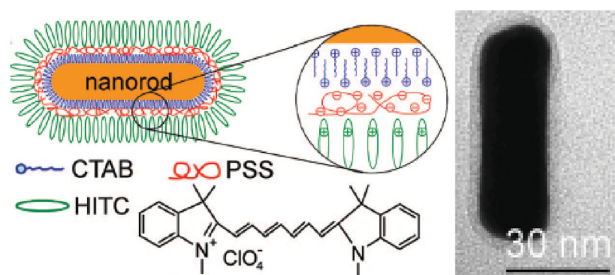


Figure 37. Alternate deposition of polyelectrolytes in order to control the shell thickness on gold nanorods. Reproduced with permission.^[447] Copyright 2008, American Chemical Society. The dyes were deposited on the outer layer using electrostatic interactions.

amplification. Durand and co-workers introduced grafted chromophores directly in the silica nanoparticles and either incorporated Au NPs in the core or grafting them at the surface of the fluorescent silica (Figure 40).^[465] Comparison between the different systems showed that the introduction of the Au NPs provided strong enhancement of the emission in both configurations and these hybrid particles could efficiently be

internalized in cells and used for two-photon imaging with a much better efficiency than without the Au NPs. Fluorescent pH sensors can also be achieved through similar approach. For instance Ag@SiO₂ particles on which a pH sensitive dye was adsorbed exhibited enhanced sensitivity to pH sensing.^[460]

Mesoporous silica can also be used to coat metal nanoparticles. These mesoporous structures can efficiently be loaded by photosensitizers^[455,464] or up-conversion nanoparticles.^[462] Such strategy was for instance used by Khlebtsov and co-workers to treat tumors using combined photodynamic and photothermal therapy.^[463] Porous silica shell can also be used to control diffusion of molecules in the silica membrane and achieve efficient SERS detection.^[467]

Regarding the perspectives on innovative metal-based nanostructures, researchers have started to investigate smaller size metal nanoparticles such as gold quantum dots (AuQDs). Such systems show interesting absorption/emission properties in the NIR corresponding to the commonly reported biological window. The main drawback of such small AuQDs remains their cytotoxicity. It was recently demonstrated that incorporation of such AuQDs into hollow mesoporous silica nanoparticles (Quantum rattles QRs) is an alternative to stabilize the

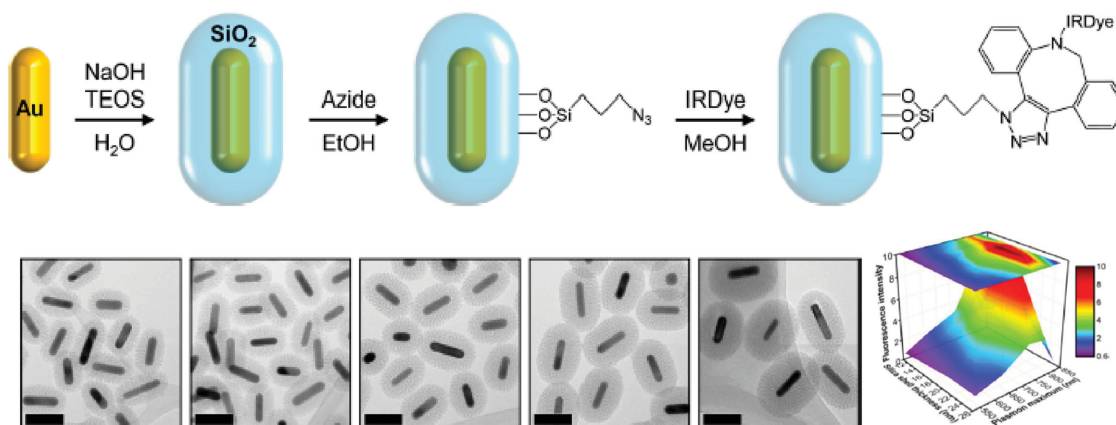


Figure 38. Strategy from Murphy et al. using click chemistry on silica to bind the dyes and control the distance to the metal surface (top). Reproduced with permission.^[458] Copyright 2014, American Chemical Society. The TEM show the increase of silica shell thickness (bottom left). The 3D two-tier contour of emission intensity versus both the shell thickness and SPR band shows the hotspot fluorescence in the best configuration (bottom right).

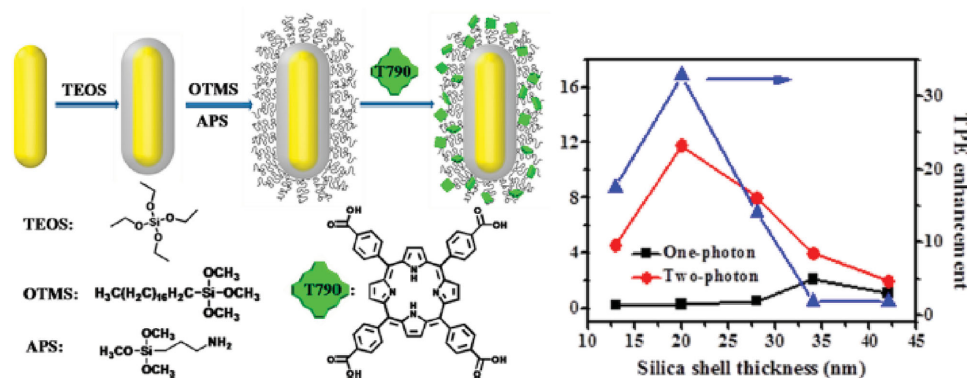


Figure 39. Synthesis of a photosensitizer doped silica shell on gold nanorods (left) and two-photon excitation fluorescence enhancement factors versus the silica shell thickness (right). Reproduced with permission.^[457] Copyright 2014, American Chemical Society.

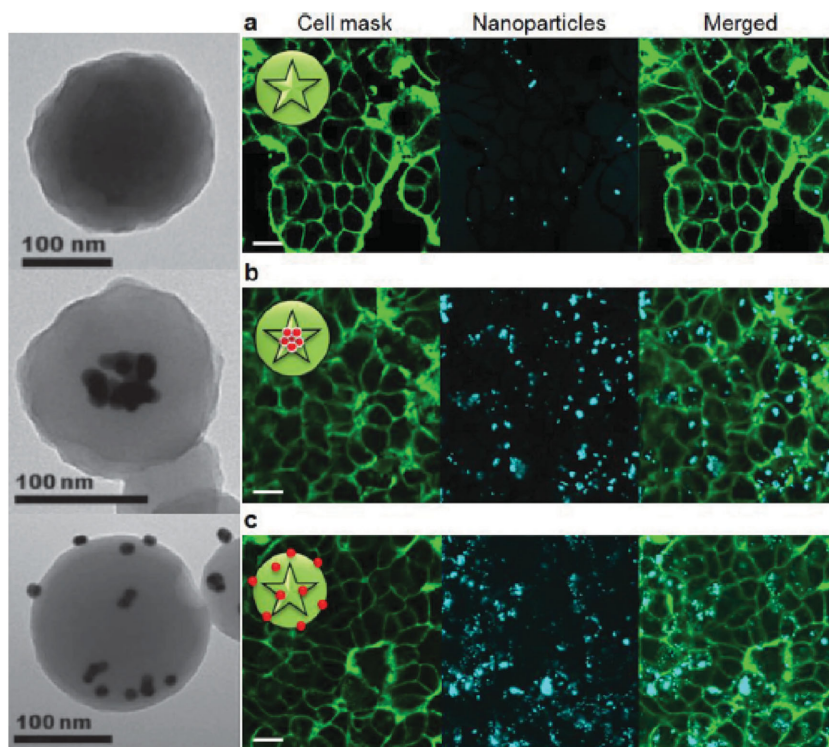


Figure 40. Two-photon imaging of MCF-7 cancer cells using three architectures and respective TEM images: (a) a reference two-photon photosensitizer-doped silica nanoparticle (b) introduction of a gold core in the particle and (c) attaching gold NPs at the surface of the hybrid fluorescent silica core. Reproduced with permission.^[465] Copyright 2015, Wiley-VCH.

metal while preserving its specific optical and magnetic properties.^[468] The QRs were successfully used for multimodal imaging (Fluorescence, photoacoustic), drug delivery and photothermal therapy of tumors (**Figure 41**). Hybrid materials

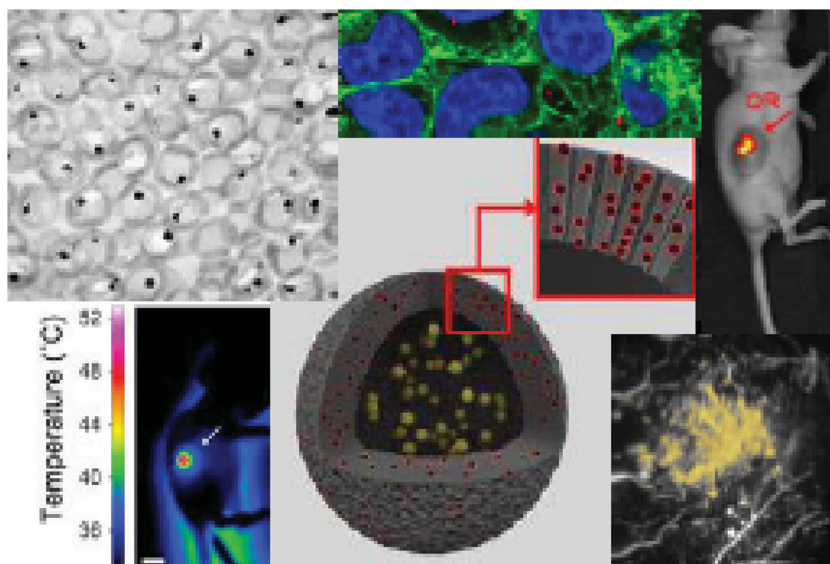


Figure 41. Structure of the Au@SiO₂ Quantum Rattles (QRs) with small AuNPs grown in the pores and their use in multimodal imaging and photothermal therapy. Reproduced with permission.^[468]

using specific responses of stabilized small metal NPs, which have not been fully explored yet, represent certainly a wide range of possible future innovations routes in the fields of nanomedicine or catalysis.

Consequently, the use of hybrid fluorescent metal nanoparticles in different configurations showed several important advantages for applications in particular in biomedical fields. These strategies usually allow high chromophore loading capacity, good stability, enhanced cellular uptake efficiency, enhanced fluorescence and enhanced photodynamic therapy using the SPR effects, sub-cellular characterization through possible combined fluorescence imaging (fluorescence of dyes and of metal nanoparticles), photoacoustic, scattering of metal (dark field imaging) and photo-theranostic by using photoinduced therapies (photothermal, photodynamic). Moreover the enhance permeability and retention (EPR) effect can be used to better accumulate the hybrid particles in tumoral tissues and opens important perspective in terms of targeting.

5.2.2. Encapsulation of Dyes in Metals

Encapsulation of dyes in the metal can be a way to achieve strong coupling between the molecules and the metallic surface and to investigate unusual interactions. Moreover this can provide a method to efficiently protect the organic chromophores against photobleaching. In this sense, the use of metallic nanoshells can be a route to build core-shell structures entrapping dyes in the core. Both core-shell structures and hollow nanospheres were reported in the literature since they were supposed to exhibit specific optical resonances in particular in the NIR.^[469–471] Moreover nanoshells showed important capacity to produce photothermal effect and were consequently efficiently used in photothermal therapy of cancers or in laser-tissue welding.^[472–477] Several strategies were adapted to build such nanostructures.^[469,471,473,478–483] It was possible to introduce organic entities inside the core of the nanoparticles and investigate the optical responses in the confined media. For instance, Rhodamine 610 was included into hollow gold nanospheres (**Figure 42**).^[426,484] Interestingly this confinement showed a strong decrease in the emission lifetime from 1.7 ns in water to less than 150 ps in the shell together with a strong improvement of the photostability of the dyes (an order of magnitude). The object appeared also brighter than the pure fluorophore.^[426]

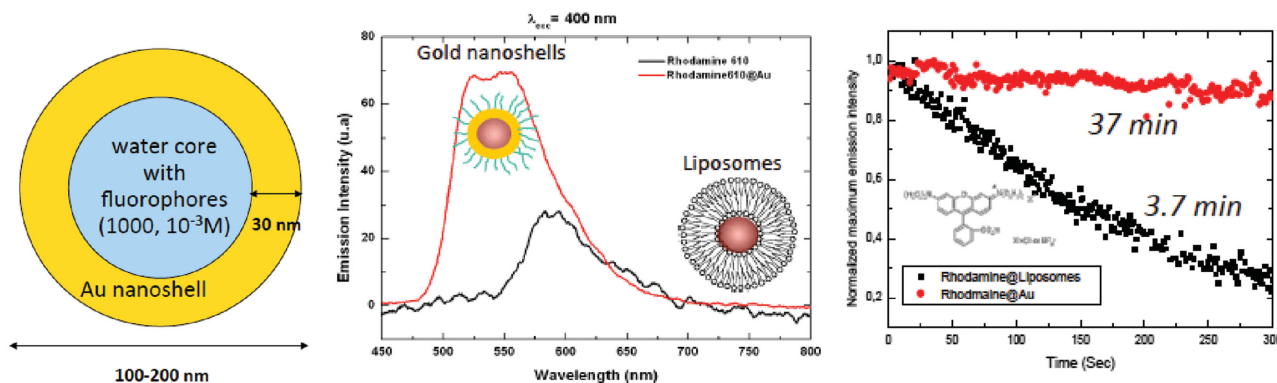


Figure 42. Structure of hybrid luminescent gold nanoshell (left), emission spectrum of the hybrid nanoshell and liposome of with same concentration of fluorophore in the core (middle), fluorescence photoresistance of the hybrid and the free fluorophore (right). Reproduced with permission.^[426] Copyright 2011, American Chemical Society.

Recently, strong exciton-plasmon coupling was evidenced in a Rhodamine doped silica core surrounded by gold shell in a very similar configuration.^[485] Silica doped core combined with gold shell was also used to achieve SERS inside the nanoshells exhibiting a giant enhancement due to the cavity effect which concentrate the electromagnetic radiation.^[486] Nanovesicles built from self-assembly of primary gold spherical nanoparticles bearing semi-fluorinated ligands can be used to encapsulate efficiently dyes or drugs.^[487] The encapsulated molecules can then be released efficiently upon laser excitation and photo-thermal conversion of the laser electromagnetic energy.

D. Avnir and co-workers have introduced original ways to entrap molecular dyes into different metals (Ag, Au, Cu, Fe).^[152,488–495] Indeed they generate the metal nanoparticles in the presence of the molecular guest and induce nano-aggregations entrapping the guests (**Figure 43**). They also developed electroless based deposition to grow hybrid films of metal aggregates entrapping molecular guests.^[494] Such structure can lead to rather homogeneous hybrid films with very interesting properties such as enhanced Raman response. They also interestingly showed that they were able to recover part of the emission of the Rhodamine.^[494] Such optical systems are promising hybrid materials for enhanced detection and highly sensitive sensors.

5.2.3. Composite Materials and Thin Films

Preparation of solid shapeable materials is extremely important on the way to the design of efficient devices. Regarding optical systems, most of the materials are processed as thin films or bulk monoliths. In both case, the use of plasmonic nanostructures has been investigated in different configurations, either introduced directly in the matrix as composite material or deposited on a surface. In the case of composite materials, basically two approaches can be found, either in situ synthesis of metal nanostructures in the matrix using chemical, thermal or photoinduced reductions; or incorporation of nanoparticles colloidal dispersions during the matrix preparation. The matrix can typically be inorganic,^[496–499] sol-gel based matrix^[215,500–510] or polymers.^[511–514] Regarding the in situ growth, the main drawbacks are the limitations in terms of control of the shape of the particles, which are often spherical or wire-type structures and the homogeneity in size and dispersion. The control of the growth using laser and in particular two-photon induced fabrication is limited to micrometer size in resolution. In this sense the stabilization of colloidal suspension of metal nanoparticle and further dispersion in a solid appear as a good alternative to dispersion and also co-doping of optically active molecule and plasmonic particles. For instance, recent work has focused

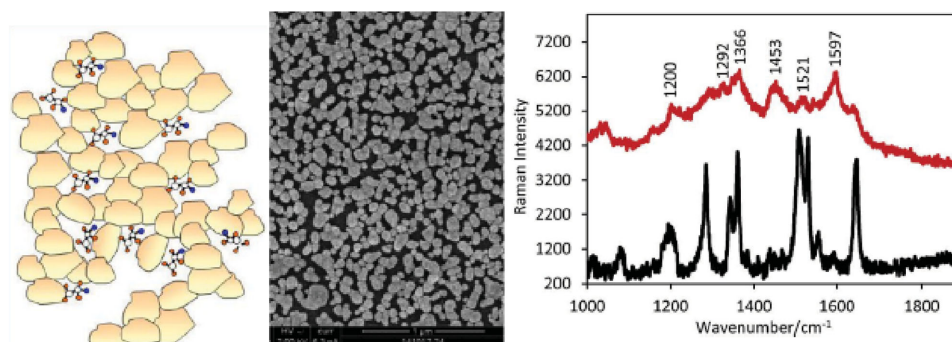


Figure 43. Suggested structure of molecularly doped metals (left). Reproduced with permission.^[495] Copyright 2014, American Chemical Society. SEM photo of a gold film doped with Rhodamine B (middle). Enhanced Raman spectrum of Rhodamine B in gold aggregates (red) versus the spectrum of pure Rhodamine B powder (black) (right). Reproduced with permission.^[494] Copyright 2014, Royal Society of Chemistry.

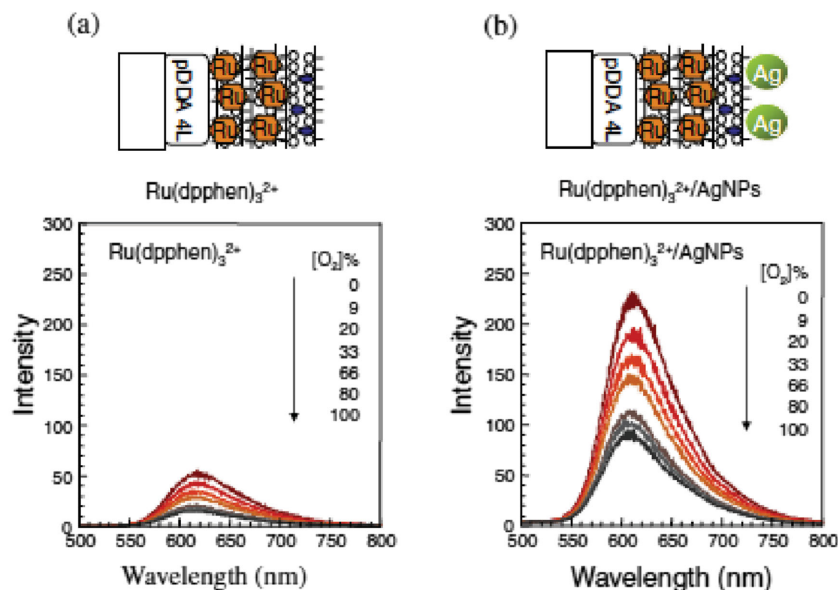


Figure 44. Hybrid polymer thin films with $\text{Ru}(\text{dpphen})_3^{2+}$ and Ag NPs and the corresponding luminescence spectra showing the enhancement of the emission. Reproduced with permission.^[523] Copyright 2015, Elsevier.

on the introduction of plasmonic nanostructures in the field of nonlinear optics to provide either direct nonlinear effects or enhance the nonlinear properties of dyes. The first works were reported on the use of gold nanoparticles either precipitated in glass,^[496,497] polymers,^[515,516] or as colloidal suspension and aggregates^[280,517] and showed nonlinear absorption response essentially due to the Surface Plasmon Resonance and RSA or nonlinear scattering processes. Regarding the possibility of using systems doped with metal nanoparticles for enhancement of optical responses, composites using luminescent polymers with dispersion of metal were mostly investigated hitherto. For instance, N. J. Halas and co-workers reported the use of core-shell silica-gold nanoparticles incorporated to semiconducting luminescent polymers to induce a quenching of the polymer

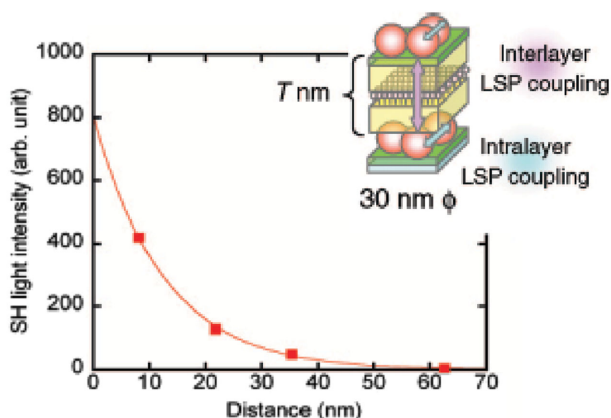


Figure 45. Impact of the distance between the nanoparticles layers surrounding the SHG polymeric layer in the hybrid configuration on the second harmonic response. Reproduced with permission.^[522] Copyright 2009, American Chemical Society.

triplet exciton, which consequently reduces capacity to transfer to oxygen (singlet oxygen formation) and thus decreases the photooxidation and enhances the active lifetime of the polymer.^[518] Similarly, core-shell $\text{Au}@\text{SiO}_2$ NPs were incorporated into the emitting layer of a LED to successfully enhance the luminous efficiency.^[519] The design of thiolated silicon polymers allowed surface modification of metal nanoparticles of different shapes and efficient dispersion in sol-gel matrices.^[520] Such approach was used to prepare co-doped sol-gel monoliths, which unexpectedly showed unusually long distance enhancement of nonlinear absorption processes.^[521]

Multilayers systems can be an alternative to control interactions between metal NPs and luminescent polymers.^[513,522–524] M. Mitsuishi et al. used also hybrid polymer approach combining polymer nanosheets nanoassemblies through Langmuir-Blodgett technology and introduced metal nanoparticles layers.^[522,523] The polymer layer part included chromophores (for luminescence or NLO), and the distance to the nanoparticles

deposited on the films or between two films was controlled by the length and the thickness of the polymers. They were able to demonstrate SHG and luminescence enhancement on free-standing ultrathin films (Figures 44 and 45). The SHG enhancement was dominated by the dipole LSP coupling (confirmed by FDTD calculations) and controlled at the nanometer scale.^[522]

Scattering of nanoparticles can be efficiently used to enhance the absorption of devices, in particular in the field of photovoltaics.^[525] Future applications of polymer-metal NPs interaction in solar cells are thus extremely promising, and can for instance be used to increase drastically the light absorption of the organic photovoltaic device through the local field enhancement.^[526,527] Indeed, in the work from J.-L. Wu et al. the gold nanoparticles scattering effect increased the optical path in the layer improving the absorption. Moreover, the rate of generation of the excitons was improved by the presence of the LSPR, which reduced the recombinations and thus the exciton loss.^[526]

All the reported systems tend to show that the control of optical properties of chromophore using plasmonic interactions is not trivial and each case is specific in the interpretation of the optical response. The optimization of the hybrid structures needs to take in consideration a multiparameter approach and in particular the molecular absorption/emission mechanisms. In particular, recent results tend to show that interesting innovations might be to come in the future, with for instance short or long distances effects, which were not at all considered experimentally at that point.

6. Conclusion and Perspectives

The field of hybrid materials with optical properties is growing intensively nowadays with breakthrough related to the fields

of imaging, sensing, protection, therapy, energy and many others. This interest is mostly based on the fact that light is a natural source for energy (photovoltaics, lasers), is a critical environmental issue (lightning) which have become crucial for humanity. Moreover optical systems are often related to human eyes (color changes, protection, cameras...), which make them of high concern for the human being. The strong interest of researchers for the development of devices activated by light, generating light or modulating the optical signal is thus a logical consequence, and is boosted by the technological developments and implementation of the scientific knowledge. This review, extracted from two full book chapters,^[528] shows clearly the high level of control reached by the scientists in the architectural achievements of the hybrid systems, in particular in the mastering of the interactions between the organic entities and their inorganic counterparts. This induce consequently a precise tuning of the optical responses of the materials, an increased efficiency and the possibility to integrate them in final operating devices such as Light Emitting Diodes (LEDs) for screens or lightning, photovoltaics for energy conversion, optical filters in cameras or optical detections for biological entities. Even more interesting for the future, the use of interactive optically active organic and inorganic systems remains to be fully explored, and for instance the controlled coupling between plasmonics and luminescence, intensively investigated, is opening a land of opportunities in the field of optical systems.

Finally, hybrid materials are not only a domain of interface for chemists (Organic, inorganic, analytic) but it has become a strong node of fruitful interactions for very different communities such as chemists, physicists, physicians, radiologists, biochemists, theoreticians, computer scientists, textile developers, and many more in particular when related to optics. Important breakthrough should be expected in terms of developments at these crucial interfaces in the future years.

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