

**Optical properties of hybrid organic-inorganic materials and their applications –  
Part II : Nonlinear Optics and Plasmonics**

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## 1. Hybrid materials for nonlinear optics

### 1.1 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,<sup>[1-4]</sup> 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.<sup>[5]</sup> The polarizability represents the ability of the charges in a material to be displaced 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,

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

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 ( $\beta$  and  $\gamma$ ) 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  $\mu$  is the total dipole moment,  $\mu_{(0)}$  is the permanent dipole moment,  $\alpha$  is the molecular polarizability,  $\beta$  and  $\gamma$  are the 2<sup>nd</sup> and 3<sup>rd</sup> order hyperpolarizabilities.

For large field intensities with a frequency  $\omega$ ,  $\chi^{(2)}$  is responsible for the generation of an oscillating field with double frequency  $2\omega$ . 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 microfabrication.<sup>[6]</sup> In this case there is no symmetry requirement. The non-linear absorption is proportional to the imaginary part of the third order susceptibility. In the same way the refractive index is proportional to the real part of the third order susceptibility. In this section are discussed the most recent developments in terms of hybrid materials design, properties and applications for second and third order nonlinearities.

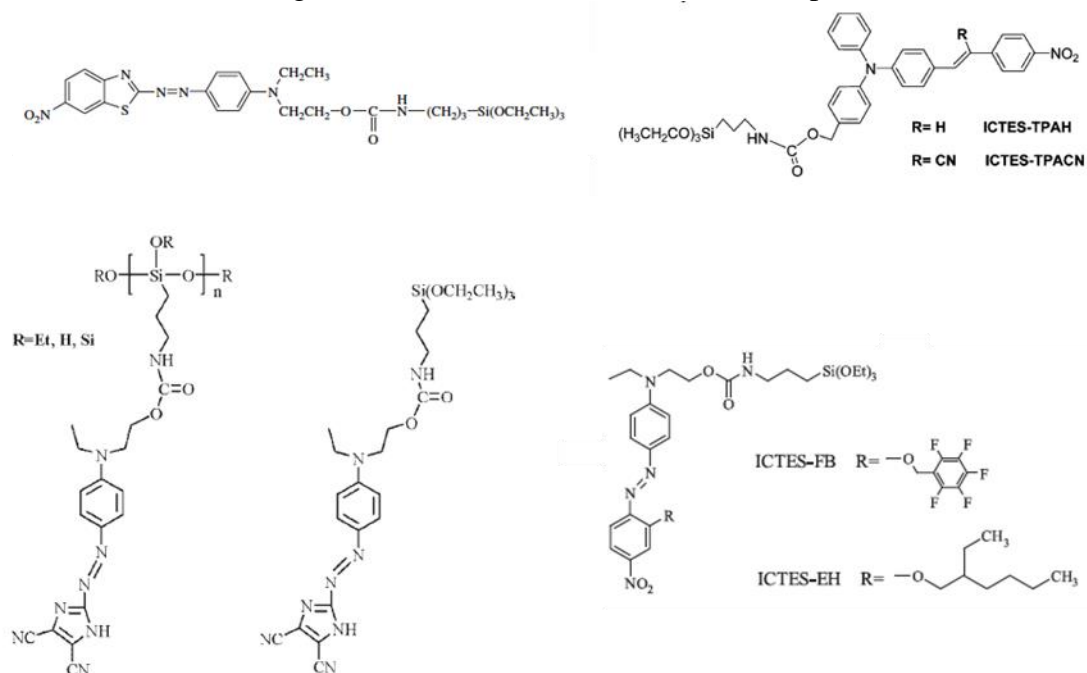
## 1.2 Second order nonlinear materials

### 1.2.1 Dyes doped inorganic matrices

The second harmonic generation of dyes doped hybrid materials, as well as for pure molecular systems, is directly 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<sup>[7-10]</sup> or optical poling.<sup>[11-13]</sup> 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.<sup>[14, 15]</sup> In the sol-gel process, typically two approaches are commonly proposed, 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,<sup>[16]</sup> 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.<sup>[17, 18]</sup> The optical response was evidently correlated to the matrix condensation level and rigidity.<sup>[19]</sup> Since then numerous work reported on the stabilization of the hybrid system and optimization of the optical and nonlinear optical responses.<sup>[14, 16-33]</sup> 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 as it was already reported.<sup>[14, 15]</sup>

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.<sup>[34-37]</sup> The grafting on sol-gel matrix can easily be achieved using silylated chromophores and numerous work reported the influence of the grafting and the matrix composition on the nonlinear optical performances. Even if large amount of important 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 Qian and co-workers investigated 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.<sup>[34, 37-48]</sup> Several types of chromophores bearing silane groups were developed (**Figure 1**). Interestingly, they were able to show that 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, which impact the temporal stability of the oriented dipole.<sup>[39, 40, 44]</sup> Such interactions were for example obtained by incorporation of aniline-silane in the matrix.<sup>[44]</sup> Moreover it was shown that the topological localization of the silane groups along the structure and the type of spacer used impacts the nonlinear optical properties.<sup>[48]</sup> This can be anticipated since it probably influences the mobility of the dyes, as well as the molecular structure and conformation (and consequently the electron transfers through the structure) as well as inter-chromophores interactions.

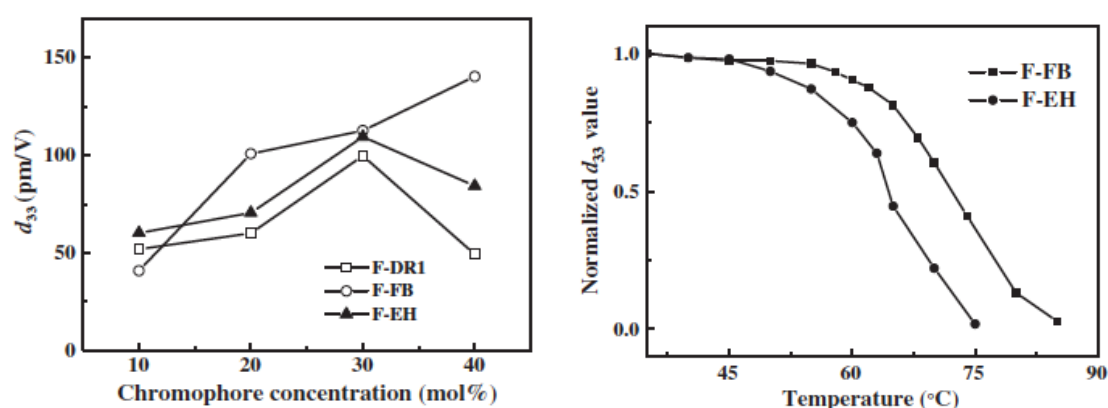


**Figure 1.** Structures of sol-gel NLO dyes, adapted with permission from ref. <sup>[40]</sup>, copyright 2007 American Chemical Society and from ref. <sup>[34, 38-48]</sup>.

Another important parameter to consider is the heating conditions during the whole process (precurving and poling). It was shown that the precurving and poling temperature considerably impacts the nonlinear optical responses due to modification of the cross-linking.<sup>[26,28,49]</sup> The precurving temperature shouldn't be too high to prevent from densification of the network. Such 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. For instance a two-dimensional alkoxy silane chromophore based on a carbazole core incorporated in a tetramethoxysilane-based matrix was compared to the well-known alkoxy silane modified DR19. A 2-dimensional system exhibited improved thermal stability compared to the one-dimensional one.<sup>[49, 50]</sup> The number of silane groups per chromophore units has also to be considered since the molecular structure can be impacted by the rigidity of the overall system. For instance chromophores with two or more silane groups were prepared for nonlinear optics and showed impact on the final properties either for second or third order nonlinearities.<sup>[51, 52]</sup> These materials generally exhibited excellent stability, in particular thermal stability. The grafting was achieved through photo-cross-linking<sup>[53]</sup> or polymerization reaction, for instance free radical polymerization in an interpenetrating methacrylate/silica hybrid matrix.<sup>[54]</sup> In this case, a chromophore bearing allyl glycidyl ether was reacted with ( $\gamma$ -methacrylpropyl)-

silsesquioxane. This strategy allowed improvement of the crosslinking, higher  $T_g$  for the final material and better stability. The poling is achieved at 200°C. The highest  $T_g$ ,  $d_{33}$  and stability are obtained for a film prepared with 15w% POSS.<sup>[54]</sup> In all cases, particular attention should be given to the structure of the dyes considering that each system (molecule structure + matrix structure) 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 2**).<sup>[47]</sup> The thermal stability was also improved using bulky fluorinated substituting groups.

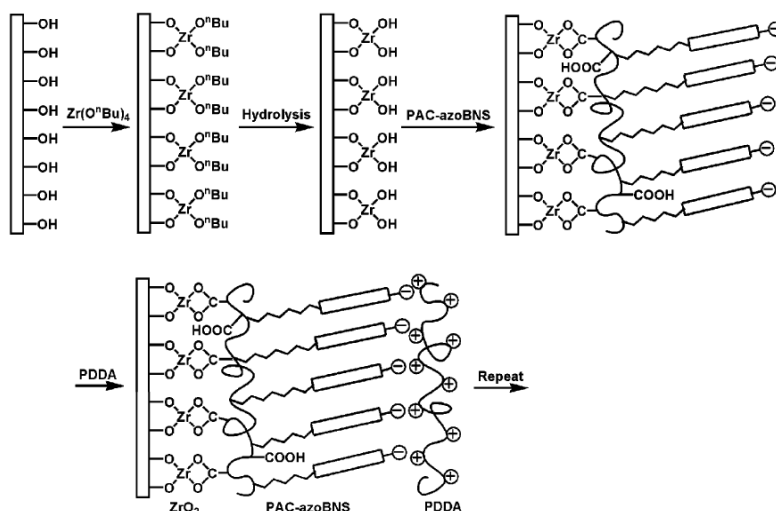
A precise control of the heating conditions seems to be crucial but needs to be optimized for each molecular structure. This has to be considered together with the crosslinking process parameters (hydrolysis-condensation conditions), which will impact the densification, orientation capacity, structure of the guest molecule and final stability, which was also shown to strongly impact NLO properties.<sup>[36, 51, 55-57]</sup>



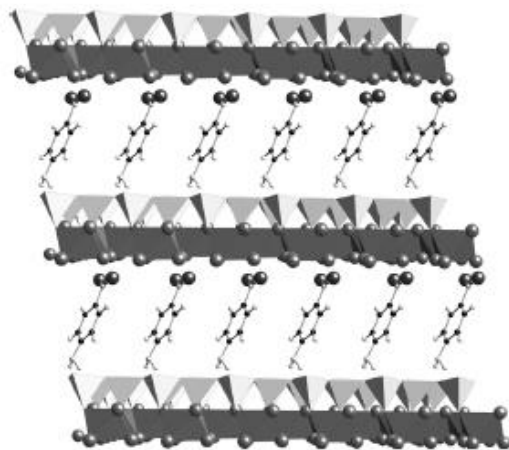
**Figure 2.** SHG and thermal stability of DR1 hybrid compared to fluorinated species (FB and EH in figure 1). Adapted with permission from reference <sup>[47]</sup>.

Besides using corona or optical poling, the orientation can also be achieved through the control of the deposition process. For instance, layer-by-Layer approach combined with the sol-gel process allows easy access to self-oriented materials.<sup>[58, 59]</sup> 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 3**).<sup>[58]</sup> Such approach can be extended to wide range of optical materials and more generally light activated systems combining for instance nanoparticles, dyes, polyoxometallates with polyelectrolytes.<sup>[60]</sup>

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.<sup>[61]</sup> Kawamata and co-workers reviewed the strategies based on incorporation in clay minerals.<sup>[62]</sup> 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 the inclusion of 4-nitroaniline into kaolinite ( $Al_2Si_2O_5(OH)_4$ ) interlayers.<sup>[63]</sup> The 4-nitroaniline spontaneously self-orientate during intercalation thanks to hydrogen bonding with the silicate nanosheets present on one side of the interlayers (**Figure 4**), thus giving rise to a SHG signal.



**Figure 3.** Self-orientation of azobenzene chromophore using a Layer-by-Layer deposition. Adapted with permission from reference <sup>[58]</sup>, copyright 2007 American Chemical Society.



**Figure 4.** Oriented intercalation of 4-nitroaniline into kaolinite interlayers by Kuroda and coworkers.<sup>[62, 63]</sup>

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 coworkers advantageously developed this approach in particular for third order nonlinearities.<sup>[64-67]</sup> 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.<sup>[67]</sup> 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 use of the wide possibilities offered by the coordination chemistry and supramolecular hybrid approaches and is developed in the next part.

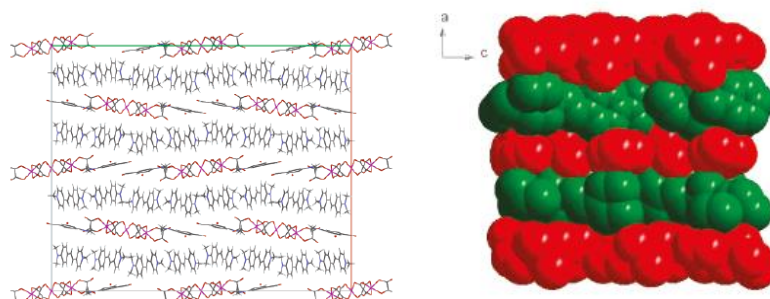
### 1.2.2 Coordination and organometallic compounds based hybrid systems

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.<sup>[68]</sup> 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 controlling the complexes organization in the crystal structure during the crystallization process.<sup>[68, 69]</sup> 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 preparation of hybrid materials for NLO applications. Metal–organic frameworks (MOFs) or Polyoxometalates (POMs) were particularly investigated for nonlinear optical applications with different proposed mechanism for the optical nonlinearities.<sup>[70, 71]</sup>

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<sup>+</sup>) which was crystallized with PW<sub>12</sub>O<sub>40</sub><sup>3-</sup> counterions.<sup>[72]</sup> 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 exhibited 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.<sup>[73, 74]</sup>

In the same way, metal polycarboxylates<sup>[69, 75-78]</sup> 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<sup>+</sup>) cationic ligands with general formula [DAMS]<sub>4</sub>[M<sub>2</sub>M'(C<sub>2</sub>O<sub>4</sub>)<sub>6</sub>].2DAMBA.2H<sub>2</sub>O (where M = Rh, Fe, Cr ; M' = Mn, Zn) giving rise to noncentrosymmetric layered structures and thus strong SHG.<sup>[77]</sup> In this case, the very large SHG is mostly explained by the important quadratic polarizability of the ligands DAMS<sup>+</sup> (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 5**). Considering 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...),<sup>[79, 80]</sup> it can certainly be expected some future development of systems for applications in nonlinear optics.



**Figure 5.** General structure showing the packing of alternate anionic organic/inorganic and cationic organic layers in the complexes [DAMS]<sub>4</sub>[M<sub>2</sub>M'(C<sub>2</sub>O<sub>4</sub>)<sub>6</sub>].2DAMBA.2H<sub>2</sub>O, along the *c*-axis (left) and *b*-axis (right). Adapted with permission from references <sup>[77, 78]</sup>, copyright 2007, 2010 American Chemical Society.

### 1.3 Third order nonlinear materials

#### 1.3.1 Dispersion of dyes in sol-gel or organic materials.

The general design of hybrid organic-inorganic materials, which exhibit third order nonlinearities, is often very similar to the materials for SHG with association of optical dyes with nonlinear activity 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 can thus focus on the interface control, concentration optimization and structure preservation of the dyes during the process. The main and almost unique application to this family of materials concerns the nonlinear absorption phenomena and the capacity of the systems to spontaneously block incident intense light radiation. It means that these materials find important use as filters to protect all type of optical sensors, sights or cameras against lasers damages. Such materials are called Optical Power Limiting (OPL) materials.<sup>[81, 82]</sup> The two main mechanisms are the Reverse Saturable Absorption (RSA) and the Two-photon Absorption (TPA) or Multi-Photon Absorption (MPA).<sup>[6, 56, 83-87]</sup> The Reverse Saturable Absorption (RSA) appears for molecular systems possessing an intersystem crossing (ISC) with a lifetime of the triplet excited state ( $T_1$ ), at least comparable or longer than the duration of the laser pulse, and an absorption coefficient of the  $T_1$  compared to that of the ground state and can thus provide an efficient limiting of pulsed laser irradiance.<sup>[88, 89]</sup>

The molecular design for third order nonlinear applications and in particular OPL (optimization of two-photon cross-section through the molecular structure optimization...), using either RSA or MPA mechanisms, has been intensively reported and optical measurements are mostly reported on molecules in solution.<sup>[6]</sup> However, the exploitation of such nonlinear phenomena in real applications requires that the optically active molecules are introduced in a solid optical host material that enables post-processing such as cutting, polishing, gluing. Solid-state materials are easily incorporated in optical devices and propose several advantages compared to liquid cells:

- Shape design for easy optical device construction.
- Higher chemical, physical and mechanical stability.
- Environment-friendly devices (no solvent).

The preparation of solid materials performing efficient nonlinear absorption appears to be the most appropriate route towards an efficient protection in any environmental conditions. One should also mention the risk that a liquid container is susceptible to break, during a laser attack or following a harsh treatment, leading to leakage of hazardous liquid material. The main drawback of solid materials is that the laser damage threshold (an important parameter to consider) is generally lower compared to liquids. This is explained by the heat diffusion mechanisms and molecules mobility, which are much higher in liquids than in solids. The liquid samples can efficiently dissipate the heat through the evaporation and formation of bubbles. The typical requirements for a material suitable for efficient optical protection using nonlinear absorption mechanisms were previously reported and discussed.<sup>[90-92]</sup> The material has to be processed preferentially as monolith for optical protection or in some cases can be used as thin films. Hybrid materials appear to be an interesting alternative to provide efficient nonlinear absorption, optical quality, processability and stability. Thus dispersion of chromophores or nanostructures in optically transparent matrices (sol-gel, polymers) such as presented for second order nonlinear materials is a consistent approach to efficient devices. The requirements for these third order nonlinear materials are (i) to preserve the molecular structure of the dyes in the final solid in order to optimize the final nonlinear properties, (ii) to control the concentration as high as possible with homogeneous dispersion preventing from

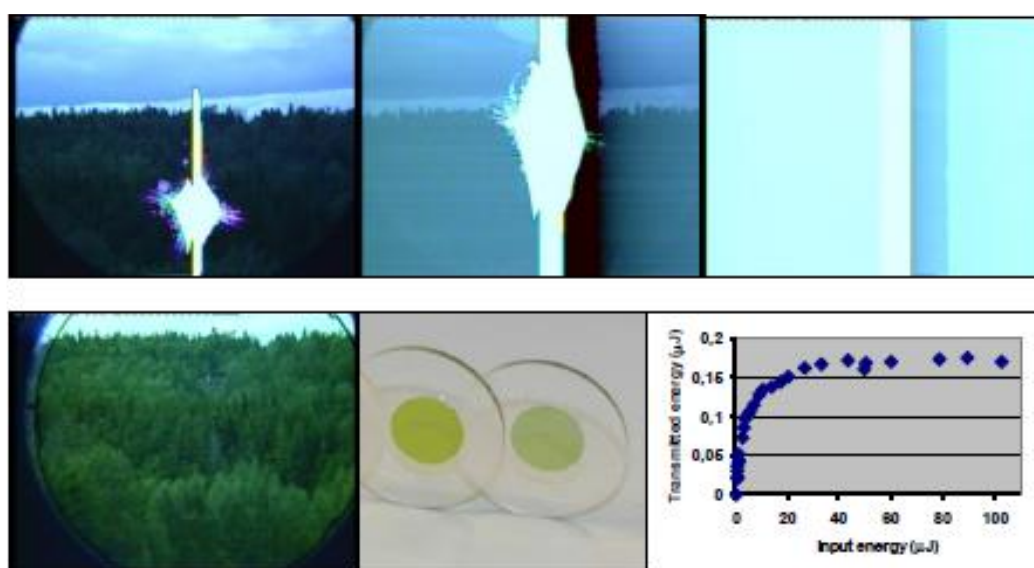
molecule-to-molecule interactions, (iii) to keep the linear transmission at maximum value, (iv) the capacity to achieve co-doping with several molecules and/or nanostructures to ensure broad band covering of the final system. It is important to note that no symmetry and orientation requirement is necessary at this stage in contrary to the second order systems. The control of organization and orientation might affect the nonlinear response but will not be discussed here due to lack of reports and only proposed as future possible implementation of on-going technologies. The ideal matrix possesses a high optical quality and a high damage threshold under the laser exposure, and a good compatibility with the chromophores. The main possible matrices are polymers or silica based materials. Polymers are interesting because they can exhibit high compatibility with the guest chromophores, 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,<sup>[93]</sup> 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 first reports on solid-state materials for nonlinear absorption applications were launched in the early 90s. The first systems were not optimized neither on the active molecular entities nor the interface with the surrounding matrices. The dispersion of metallophthalocyanine dyes with interesting RSA into SiO<sub>2</sub> sol-gel matrices was firstly reported.<sup>[24, 94]</sup> The reverse saturable absorption of the dyes was also observed in the solid materials demonstrating the capacity of the strategy. However, the spectroscopy showed that the overall systems needed optimization. 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...)<sup>[94]</sup> 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.<sup>[84, 85, 95]</sup> Although those precursor works were launching the research area, the important developments and breakthrough on materials for nonlinear absorption started from the late 90s, and several important works appeared during the past 15 years. P. Innocenzi and co-workers reported the entrapment of functionalized fullerenes in inorganic matrices for optical limiting applications.<sup>[15, 96-98]</sup> Fullerenes were selected because they present interesting RSA in the visible wavelengths.<sup>[97-100]</sup> One drawback with these systems is their poor solubility and their poor compatibility with the silica based matrix. Improved compatibility was achieved by adding silane or dendrimer pending units on the fullerenes structures.<sup>[97-99]</sup> In most of these materials the nonlinear performances of the chromophores in solution were almost totally recovered in the solid. The nonlinear response of fullerenes was similar in solution and in the solid state, exhibiting RSA mechanisms with nonlinear scattering and nonlinear refraction contributions at high fluence.<sup>[15]</sup> The main problem regarding the final application was that the clamping levels in these materials were still too high due to the low concentration of chromophores. Moreover these systems absorb strongly in the visible.

Another original strategy adopted in order to increase the concentration of nonlinear active species and try to reach the requirements was to grow nanocrystals of dyes in inorganic glasses.<sup>[64-67]</sup> Stilbene 3 nanocrystals were grown in sol-gel glasses.<sup>[101]</sup> Interestingly, the final composite materials showed strong nonlinear absorption at visible wavelengths with a three-photon absorption (two-photon absorption mechanism followed by an excited state absorption).<sup>[66]</sup> Impregnation of a previously prepared porous matrix was also used for aggregation of dyes (Naphthalocyanine for instance) into the cavities of the xerogel, which exhibited then interesting RSA response and Optical Limiting properties.<sup>[102]</sup>



Another family of dyes, based on platinum central atom and acetylides type ligands, was widely investigated with the advantage to present very low absorption in the visible wavelengths and strong nonlinear behavior with intersystem crossing (ISC) and triplet excited state absorption. The heavy atom facilitates ISC in for instance the platinum(II) square-planar complex  $\text{trans-[P(n-Bu)}_3\text{]}_2\text{Pt}[(\text{C}\equiv\text{C-p-C}_6\text{H}_4\text{-C}\equiv\text{C-p-C}_6\text{H}_5\text{)]}_2$ <sup>[83, 103, 104]</sup> This complex was reported for its extremely interesting nonlinear absorption properties in solution,<sup>[83, 103-105]</sup> and series of platinum based chromophores were prepared with improved nonlinear properties.<sup>[51, 106-115]</sup> The use of PMMA monolithic material hosting platinum acetylide derivatives was reported to be an efficient route towards OPL materials.<sup>[35, 116]</sup> The chromophores was either simply dispersed in the matrix (host-guest system) or covalently bonded to the PMMA network using methacrylate-substituted dyes. The measured linear transmissions of the PMMA materials were high, nearly 90% in the visible for wavelengths > 550 nm. Nonlinear absorption properties of the chromophores were maintained in the solid and clamping levels in the range 3-4  $\mu\text{J}$  were reached (incident intensity 115  $\mu\text{J}$ ). Interestingly the type of interaction (covalent bond or dispersion) between the chromophore and the matrix was observed to play a role on the final optical performances. The structural rigidity of the grafted dyes limited possibilities of structural changes and relaxation compared to host-guest systems, leading to a loss of OPL efficiency. Moreover, the damage threshold was impacted and decreased when using grafting processes. It is important to note that on the contrary to what was observed for second order NLO, grafting of the dyes in this case of affected negatively the NLO efficiency of the materials. Similar investigations were run in parallel on sol-gel hybrid hosting matrices.<sup>[36, 55]</sup> Functional chromophores were designed in order to improve the compatibility with the silica-based matrices and thus the optimum concentration of dyes in the inorganic phase.<sup>[36, 51]</sup> The comparison between grafted and dispersed systems was achieved. In the case of grafted systems, it was demonstrated that the hydrolysis step procedure could be used to control the way the dyes were dispersed (aggregated in the case of separate hydrolysis or homogeneously dispersed in the case of simultaneous in-situ hydrolysis). The material structure and properties could be optimized using silane functionalized dyes precursors for improving the concentration and in situ hydrolysis for homogeneous dispersion (**Figure 6**).<sup>[36]</sup> This material exhibited efficient nonlinear absorption in the visible wavelengths and was efficiently used to protect cameras from lasers.

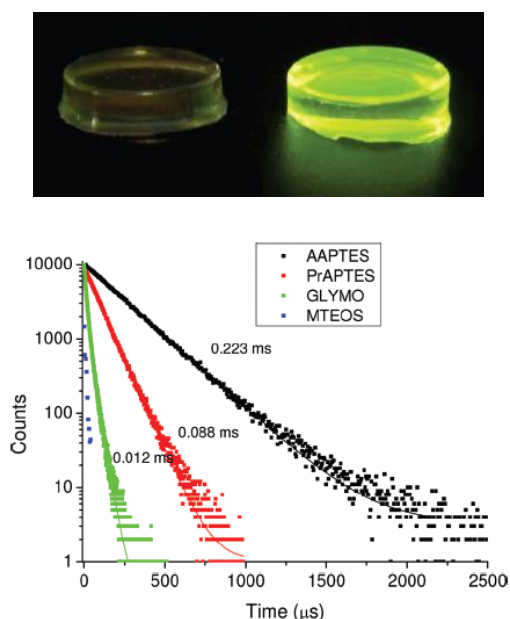


**Figure 6.** Top : visualization of the destruction of a camera under laser irradiation. Bottom: similar view from the same camera protected by highly transparent hybrid materials (left), the

filters (center) and nonlinear absorption response of the filter at 532 nm in the nanosecond regime allowing the efficient protection (right).<sup>[36]</sup>

The pH control during the process was also reported as a dramatic parameter. Many organic dyes are known to be pH sensitive. In this sense it becomes often important to have a fine control of the pH during the dyes addition to the precursors. 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 in particular for THG.<sup>[117, 118]</sup> In the case of the use of catalysts, neutralization of the sol after hydrolysis allowed easy insertion of sensitive dyes into the silica system.<sup>[36, 55, 57]</sup> In connection with the pH control, the loading capacity of the glass with the dyes (extremely important in the case of optical applications) was efficiently tuned by controlling the condensation step kinetics without need of covalent grafting (which requires often complicated chemistry on the dyes).<sup>[55, 57]</sup> A stable neutral sol was mixed with the dyes. Providing that the condensation ratio of the sol was sufficiently high to remain liquid and have only few remaining -OH groups to condense (typically in the range 70-90%), the liquid to solid transition during the condensation was efficiently achieved within a very short time (which can occur from few seconds to several minutes depending on the conditions) by adding a small amount of base (APTES). The strong advantage of the method is that the concentration of dyes can be extremely high (typically 40-50%) without any aggregation and high optical quality of the final materials. The drawback in the case of grafted systems in terms of optical response is that the structure of the inserted dyes can be affected by the strong interaction with the matrix and mechanical stresses. Thus, this approach, which allows high loading without grafting can be a real alternative for third order nonlinear optics (obviously extendable to other optical systems). It was also efficiently used recently for preparing the first materials activated in the near infrared wavelengths.<sup>[57]</sup> The study evidenced the important role of the microstructure of the matrix on the final properties. Optimization of the porosity allowed control of oxygen diffusion and thus optimization of the triplet excited states lifetime, the intersystem crossing and consequently the nonlinear absorption. The **figure 7** shows two observable consequences, on the phosphorescence emission (quenched by oxygen diffusion in pure MTEOS matrix) and the lifetime, which was strongly improved by using functional precursors reducing the microporosity of the system.

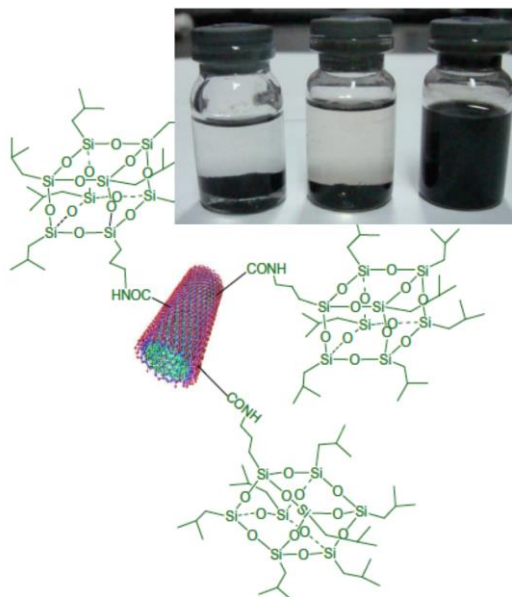
Comparison between polymer and sol-gel approach in this specific case showed few advantages for the sol-gel method. The Tg of the polymer was a limitation for use in harsh environment. The nonlinear response control appeared to be easier in the inorganic matrix. Finally the damage thresholds under intense 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.<sup>[119]</sup> Silica hosting matrix appeared to be more efficient than PMMA and the nonlinear parameters ( $n_2$ ,  $\beta$ ,  $Re[\chi^{(3)}]$ ,  $Im[\chi^{(3)}]$ ) were better in the hybrid system.



**Figure 7.** 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. Adapted with permission from reference <sup>[55]</sup>, copyright 2012 American Chemical Society.

### 1.3.2 Polysilsesquioxanes hybrids for nonlinear absorption.

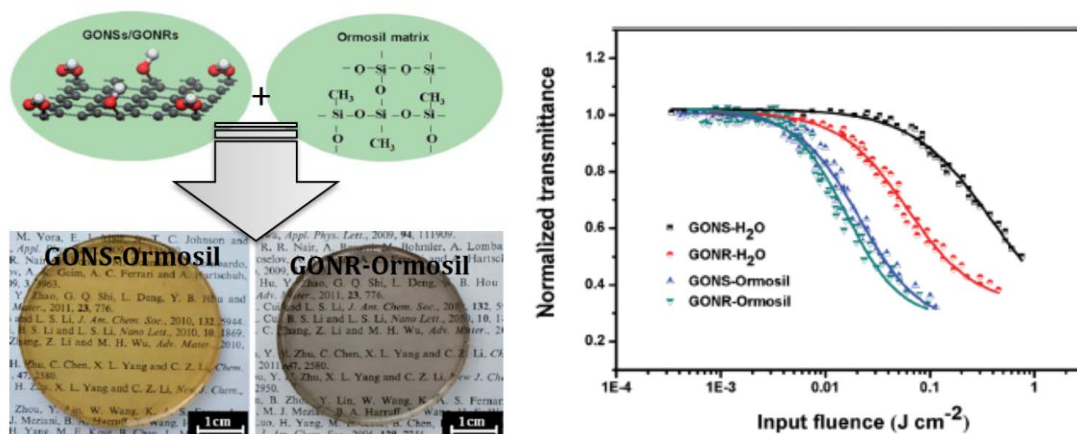
Polysilsesquioxanes (POSS) were functionalized with optically active dyes and can be considered as intermediates between the molecular level and a nanocomposite material. X. Su and co-workers reported the synthesis of POSS modified with azobenzene, acetylene or stilbene derivatives exhibiting nonlinear absorption.<sup>[120-122]</sup> 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,<sup>[123, 124]</sup> were also associated to POSS units (covalent or ionic bonding) in order to improve their solubility and optical properties (**Figure 8**).<sup>[125, 126]</sup> 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.<sup>[125, 126]</sup> 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.



**Figure 8.** 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 <sup>[125]</sup>.

### 1.3.3 Graphene based hybrid materials for nonlinear absorption.

Graphene was found to present efficient nonlinear absorption with consequently a strong potential for optical protection applications.<sup>[127-129]</sup> 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.<sup>[128]</sup> 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).<sup>[129]</sup> Also, association between dyes and graphene was successfully attempted in order to improve the nonlinear absorption properties, both experimentally and theoretically.<sup>[130, 131]</sup> 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 -COOH pending groups and iron oxide Fe<sub>3</sub>O<sub>4</sub>, enhancement of optical limiting response due to both contributions of nonlinear absorption (TPA) and nonlinear scattering was observed.<sup>[132]</sup> 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.<sup>[133, 134]</sup> They used both nanosheets (GONSs) and nanoribbons (GONRs) (**Figure 9**). The prepared materials showed high linear transmission in the visible, good thermostability and good optical limiting response attributed to both nonlinear scattering and nonlinear absorption. Similarly, Xu and coworkers reported the dispersion of GO in sol-gel matrices using modified GO for covalent grafting to the silica network.<sup>[135]</sup> 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.



**Figure 9.** The GONS-Ormosil and GONR-Ormosil hybrid materials (left) and normalized transmittance versus the input fluence (right).<sup>[133]</sup>

The NLO properties were evaluated in the solid 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. This was explained by the difference in mobility between the liquid and the solid phase. In the liquid, thermal effect under the laser beam can induce an ejection of GO out of the beam due to temperature gradient and diffusion. The consequence was a decrease in the GO concentration at the focal point followed by a decrease in nonlinear absorption efficiency. Such phenomenon could not occur in the solid preserving the local concentration in GO and thus the nonlinear efficiency. Similarly, composite materials with graphene and metal nanoparticles in sol-gel glasses was also recently proposed.<sup>[136]</sup> Hybrid composites with graphene and ZnO or CdS nanoparticles dispersed in PMMA glasses were proposed by Chen and co-workers.<sup>[137, 138]</sup> 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.

## 2. Plasmonic hybrid materials

### 2.1 Optical properties of metal nanoparticles

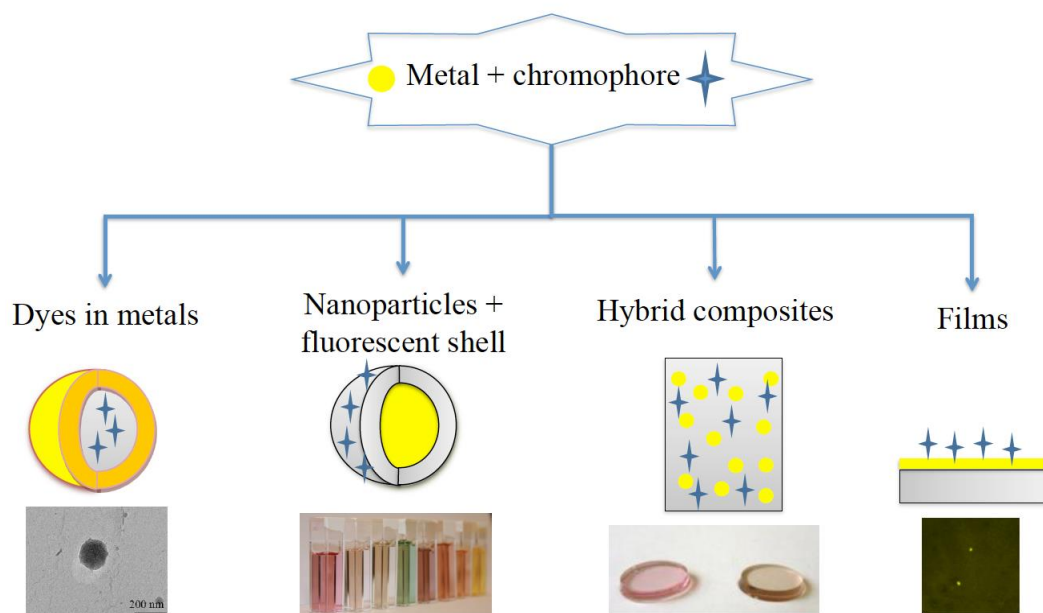
Plasmonic materials are among the most studied systems in the field of light-matter interactions and numerous articles and reviews were centered on this topic for the past decade.<sup>[139-155]</sup> Association of plasmonic nanostructure with organic entities, in particular molecules with optical properties, 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.<sup>[156-165]</sup> 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 and 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.<sup>[149, 154, 160, 163, 166-191]</sup> 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.<sup>[192]</sup> In the field of optics, these nanoobjects are extremely relevant since they provide, under light excitation, a way to strongly affect the optical responses both of the metallic nanostructures (with plasmon resonances tunable from the visible to the IR wavelengths) and of optical systems in close interaction with the metallic surfaces (such as molecular dyes or semiconductors). The control of these interactions in hybrid systems has been an important field of scientific contributions for the past ten years. The first 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 with control of metallic surface interactions with various molecular entities. 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.

## **2.2 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 for the material design, typically either on a surface, on nanoparticles, in nanoshells or associated in a composite material, depending essentially on the application mode (**Figure 9**). 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.<sup>[155, 183, 193-195]</sup> 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 nanoparticle distance and evaluating the photophysical properties in each case. The different strategies were often correlated with modeling approaches.<sup>[155]</sup> The following part reports thus on the common strategies used to combine plasmonic effect with optical responses of molecules (emission, absorption, nonlinear reponses) based essentially on the distance control between the systems.

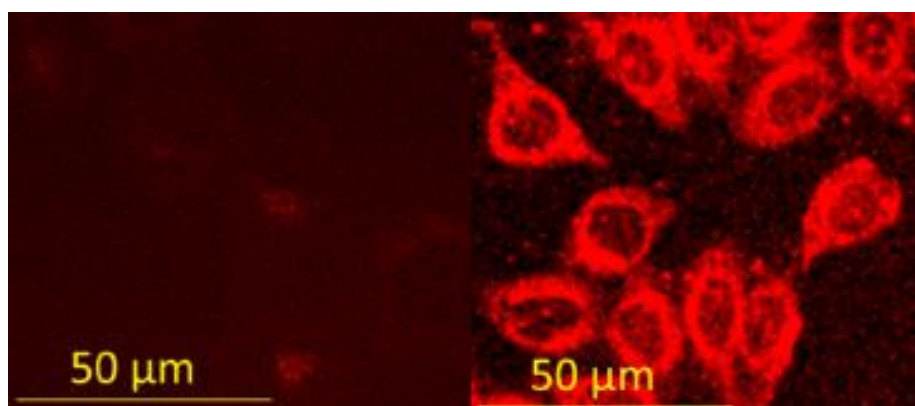


**Figure 9.** Principal strategies to control interactions between chromophores and metal nanoparticles, respectively from left to right: Incorporation of dyes into nanoshells, surface modification of nanoparticles with dyes, co-doping into solid matrix (polymer or sol-gel) and multilayered thin films. 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..).

### 2.2.1 Surface functionalization of metal nanoparticles

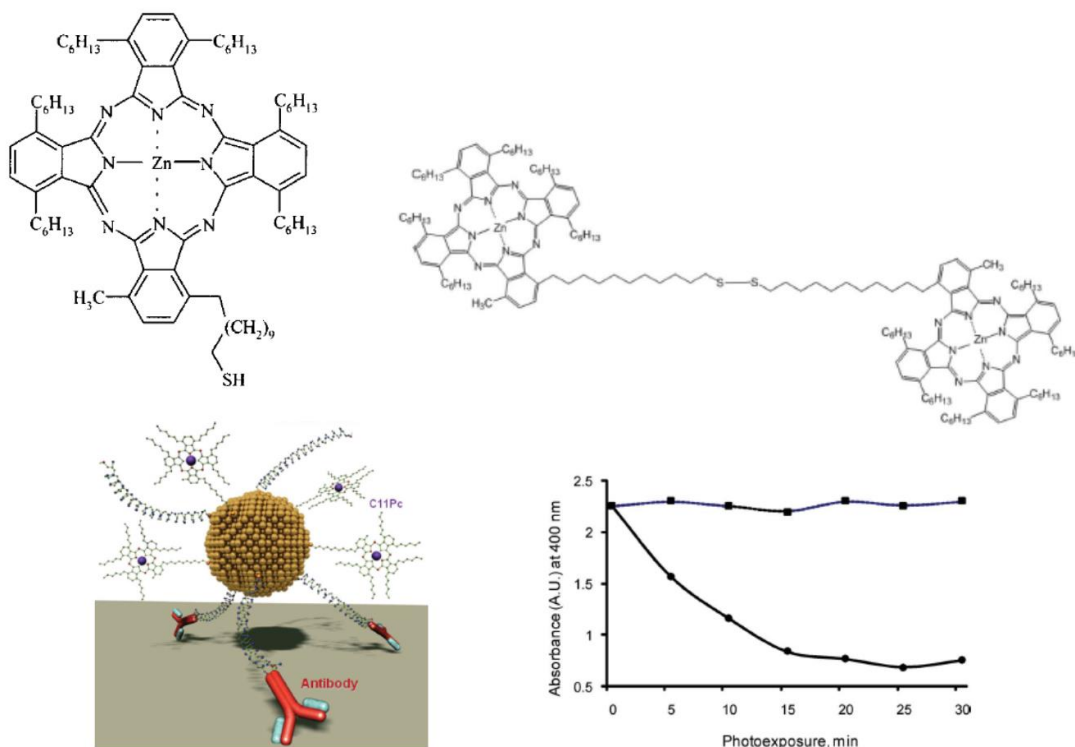
The functionalization of metallic surfaces remains the easiest way to induce interactions between the two systems since surface chemistry is well controlled on metals. Regarding the synthesis of the metallic cores, this is extremely well documented and previously reviewed. It is important to note that 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.<sup>[142, 148, 166, 196]</sup> 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 (i.e. citrate) or surfactants (i.e. CTAB) at their surface. The total or partial replacement of the stabilizing molecules can be easily achieved through ligand exchanges reactions with functional systems bearing thiol or thioctic acid pending groups.<sup>[147]</sup> 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.<sup>[147]</sup> J.-Y. Chen et al. used direct interaction between a sulfonated aluminum phtalocyanine and gold nanorods or nanocubes to enhance their fluorescence.<sup>[197]</sup> Nanorods showed limitation in the fluorescence enhancement due to the

overlap between the SPR and the emission band of the chromophore. The use of nanocubes, which combines stronger SPR than spheres and no overlapping, instead of rods, successfully lead to better enhancement in the emission. They used it for fluorescence imaging of cancer cells using two-photon excitation in the NIR (**Figure 10**).



**Figure 10.** 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). Adapted with permission from reference <sup>[197]</sup>, copyright 2014 American Chemical Society.

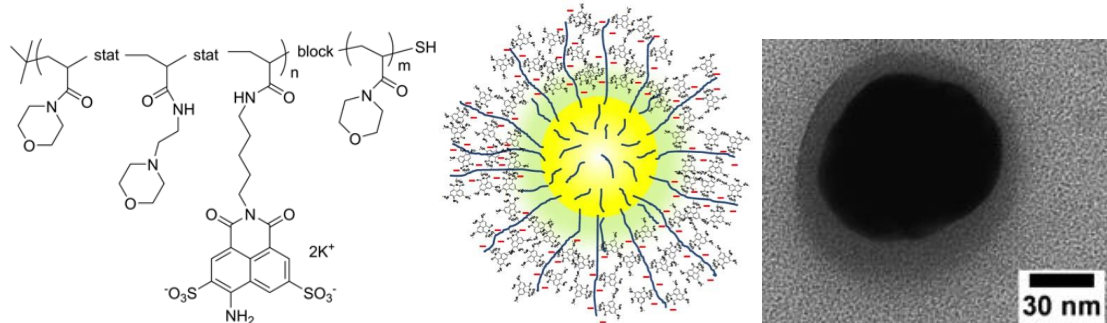
Dyes bearing thiol groups are easily attached to metal surfaces. Numerous examples can be recorded from the literature. Russel and co-workers used gold nanoparticles modified by zinc phthalocyanines and later on by antibody to achieve efficient oxygen singlet generation and photodynamic therapy of cancer cells (**Figure 11**).<sup>[198, 199]</sup> 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.





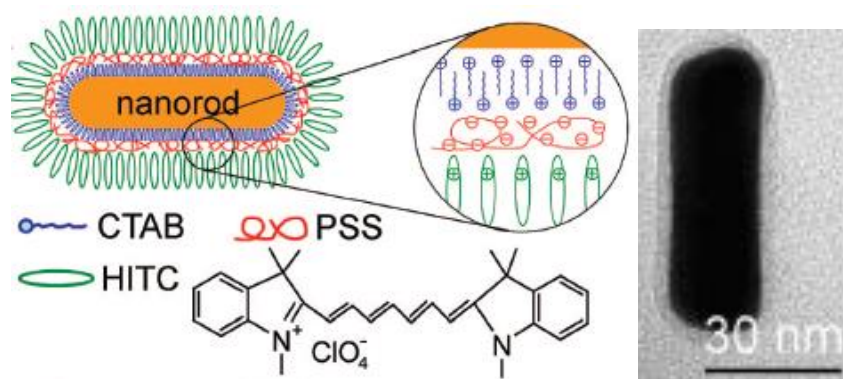
**Figure 11.** Two structures of phthalocyanine based photosensitizers (top) and preparation of the conjugate with Au-NPs (bottom left). Bottom right shows the generation of oxygen singlet evidenced by the decreasing in the absorption spectrum of the disodium 9,10-anthracenedipropionic acid (ADPA) probe (dots) versus the control sample without the photosensitizer (squares).<sup>[198, 199]</sup> Adapted from reference <sup>[198]</sup>, copyright 2002 American Chemical Society.

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 control of the distance can be achieved by using molecular spacers such as oligomers between the thiol-anchoring group and the chromophores. The synthesis of block copolymers bearing chromophores along the chains was proposed and showed efficient control over the distance by playing with the polymer structure, and the electrostatic repulsion and sterical hindrance between the chains, which contributed to the linear structuration of the polymers.<sup>[200, 201]</sup> For instance, the copolymer functionalized with Lucifer Yellow (LY) allowed preparation of luminescent gold hybrid nanostructure by playing with the polymer structural arrangement at the surface of the particle. It was shown that the size of the particle, and thus the curvature angle, impacted the surface organization and structure of the polymer going from mushroom type to extended structure (Figure 12).<sup>[200]</sup> This was confirmed by the measurements of fluorescence intensity as function of the average size of the particles. The optimized nanostructures were successfully used for cell imaging and photodynamic therapy of cancer cells using similar copolymer with a dibromobenzene derivative as photosensitizer.<sup>[200]</sup> Interestingly, it was also shown that the use of anisotropic gold core, such as nanobipyramids, allowed enhancement of the fluorescence of similar luminescent polymer while this was not observed in the case of the spherical nanoparticles.<sup>[201]</sup>



**Figure 12.** Structure of the diblock copolymer functionalized with LY dyes and hybrid gold nanoparticle bearing the luminescent polymers.<sup>[200]</sup>

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 13)<sup>[202-205]</sup> which was initially introduced to immobilize particles on surfaces<sup>[206]</sup> or for biocompatibilisation<sup>[207]</sup> to achieve bioimaging. Up to 11 layers of spacer were introduced in the structure leading to shell thicknesses in the range 1 to 20 nm.<sup>[203]</sup> The presence of the layers can easily be monitored using Zeta potential measurements.



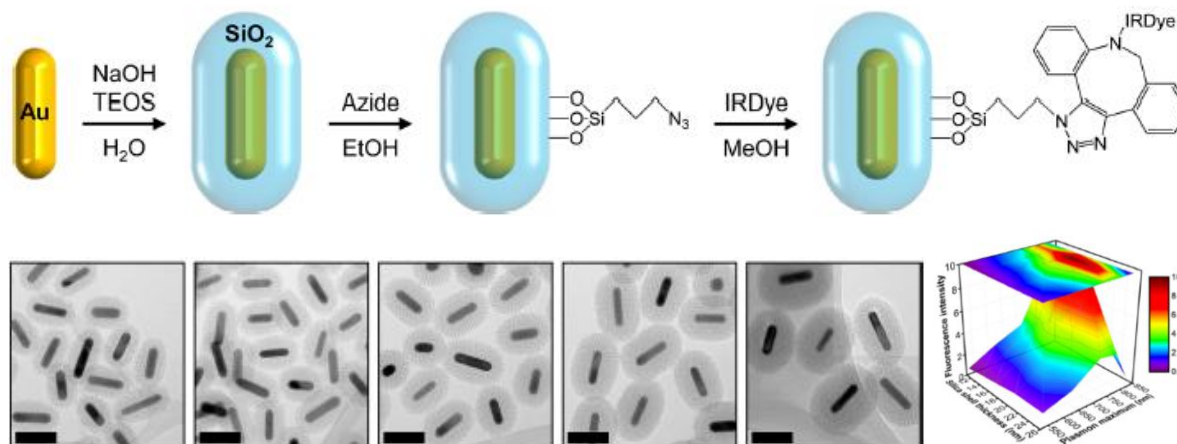
**Figure 13.** Alternate deposition of polyelectrolytes in order to control the shell thickness on gold nanorods. Adapted from reference <sup>[204]</sup>, copyright 2008 American Chemical Society. The dyes were deposited on the outer layer using electrostatic interactions.

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.<sup>[203]</sup> 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) nearby the surface with a decrease in the enhancement when going from 3 nm to 12 nm from the surface.<sup>[202]</sup>

Halas *et al.* have 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.<sup>[208]</sup> 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.<sup>[209]</sup> 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.<sup>[210]</sup> 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.<sup>[211]</sup>

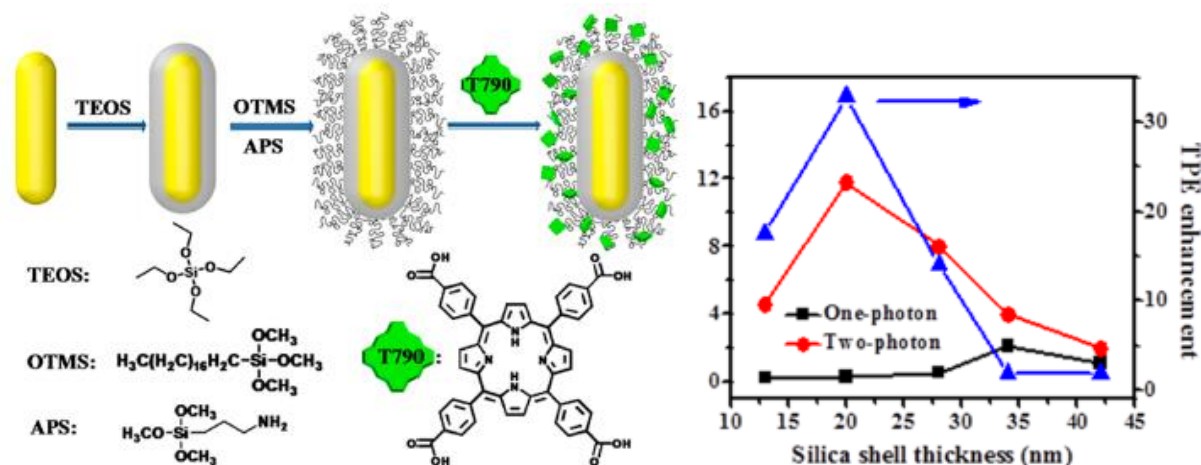
Among the most investigated strategies is the use of core shell nanostructures with metal core and silica based shell, which provides also a good possibility of spacing control between the dyes and the metallic surface.<sup>[212-222]</sup> The dye can be either directly incorporated in the silica shell during the synthesis or 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.<sup>[223]</sup> 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.<sup>[223]</sup> Murphy and coworkers showed that it was possible to have a fine-tuning of the distance and easy surface grafting using click-chemistry reactions (**Figure 14**).<sup>[215]</sup> They interestingly observed in their systems 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. Strong decrease in the lifetime was also observed when the shell was decreased.



**Figure 14.** Strategy from Murphy *et al.* using surface click chemistry on the silica layer to bind the chromophore and control the distance to the metal surface (top). Adapted from reference <sup>[215]</sup>, copyright 2014 American Chemical Society. The TEM images show the increase of silica shell thickness on one type of nanorods (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).

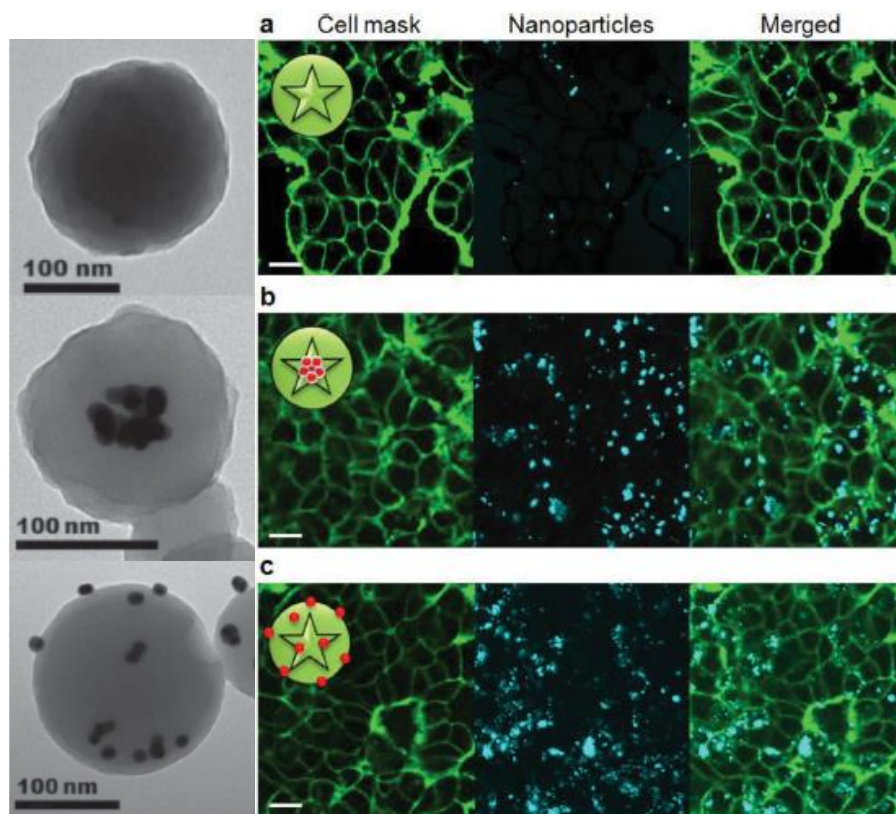
Similar strategy but with different chemical route is to ensure grafting through amide bond for instance by reacting between an amine  $\text{NH}_2$  supported on the silica and a carboxylic acid group (**Figure 15**). <sup>[213, 214]</sup> In the work from Xu *et al.*, they reported a two-photon enhancement of fluorescence maximum of 11.8 at a 20 nm distance due to the electric field amplification.



**Figure 15.** Synthesis of a photosensitizer doped silica shell on gold nanorods adapted from reference <sup>[214]</sup>, copyright 2014 American Chemical Society (left) and two-photon excitation fluorescence enhancement factors versus the silica shell thickness.

Durand and coworkers 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 16**).<sup>[222]</sup> 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@SiO<sub>2</sub> particles on which a pH sensitive dye was adsorbed exhibited enhanced sensitivity to pH sensing.<sup>[217]</sup>

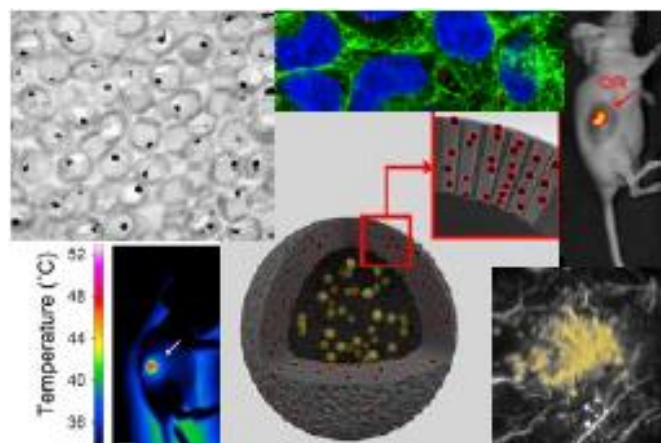


**Figure 16.** Two-photon imaging of MCF-7 cancer cells using three architectures and respective TEM images : (a) a reference two-photon photosensitizer-doped silica nanoparticle (b) introduction of a gold core in the particle and (c) attaching gold NPs at the surface of the hybrid fluorescent silica core adapted from reference <sup>[222]</sup>.

Mesoporous silica can also be used to coat metal nanoparticles. These mesoporous structures can efficiently be loaded by photosensitizers<sup>[212, 221]</sup> or up-conversion nanoparticles.<sup>[219]</sup> Such strategy was for instance efficiently used by Khlebtsov and co-workers to treat tumors in vivo using combined photodynamic and photothermal therapy.<sup>[220]</sup> This approach with porous silica shell can also be used to control diffusion of molecules in the silica membrane and achieve further efficient SERS detection.<sup>[224]</sup>

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 metal while preserving its specific optical and magnetic properties.<sup>[225]</sup> The QRs were successfully used for multimodal imaging (Fluorescence, photoacoustic), drug delivery and photothermal therapy of tumors (**Figure 17**). Hybrid materials 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.

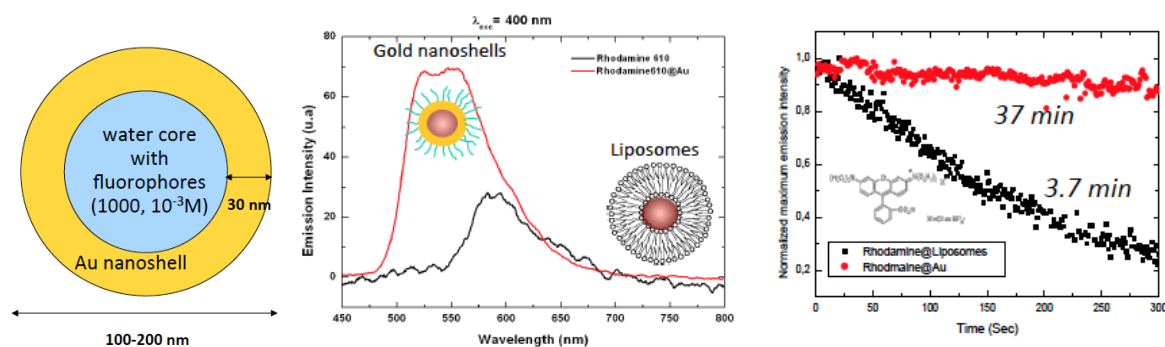


**Figure 17.** Structure of the Au@SiO<sub>2</sub> Quantum Rattles (QRs) with small AuNPs grown in the pores and their use in multimodal imaging and photothermal therapy adapted from reference [225], courtesy of the National Academy of Science.

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, subcellular 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.

### 2.2.2 Encapsulation of dyes in metals

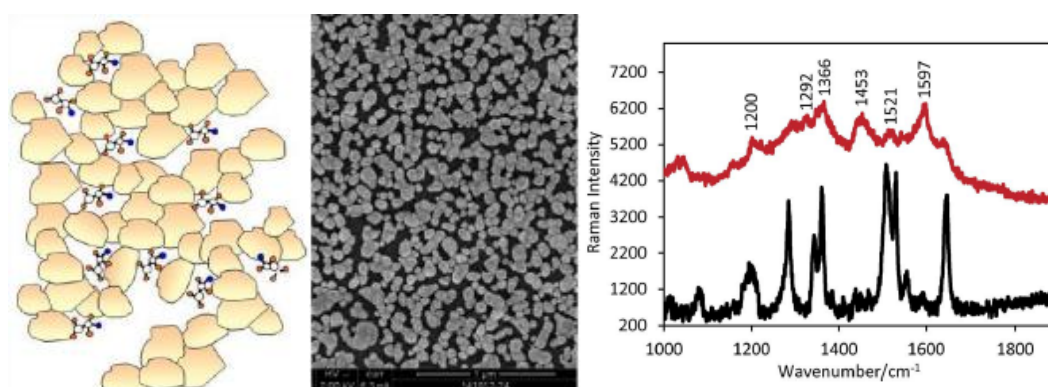
Encapsulation of dyes in the metal can be a way to achieve strong coupling between the molecules and the metallic surface and to investigate unusual interactions. Moreover this can provide a method to efficiently protect the organic chromophores against photobleaching. In this sense, the use of metallic nanoshells can be a route to built 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.<sup>[226-228]</sup> Moreover nanoshells showed important capacity to produce photothermal effect and were consequently efficiently used in photothermal therapy of cancers or in laser-tissue welding.<sup>[229-234]</sup> Thus several chemical strategies were adapted to build such nanostructures.<sup>[226, 228, 230, 235-240]</sup> Using the proposed chemical routes, it was possible to introduce organic entities inside the core of the nanoparticles and investigate the properties and in particular the optical responses in the confined media. For instance, Rhodamine 610 was included into hollow gold nanospheres (**Figure 18**).<sup>[183, 241]</sup> 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 a little brighter than the pure fluorophore.<sup>[183]</sup>



**Figure 18.** 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). Adapted from reference <sup>[183]</sup>, 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.<sup>[242]</sup> 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.<sup>[243]</sup> Nanovesicles built from self-assembly of primary gold spherical nanoparticles bearing semi-fluorinated ligands can be used to encapsulate efficiently dyes or drugs.<sup>[244]</sup> The encapsulated molecules can be released efficiently upon laser excitation and photothermal 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).<sup>[245-253]</sup> Indeed they generate the metal nanoparticles in the presence of the molecular guest and induce nano-aggregations entrapping the guests (**Figure 19**). They also developed electroless based deposition to grow hybrid films of metal aggregates entrapping molecular guests.<sup>[252]</sup> 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.<sup>[252]</sup> Such optical systems are promising hybrid materials for enhanced detection and highly sensitive sensors.

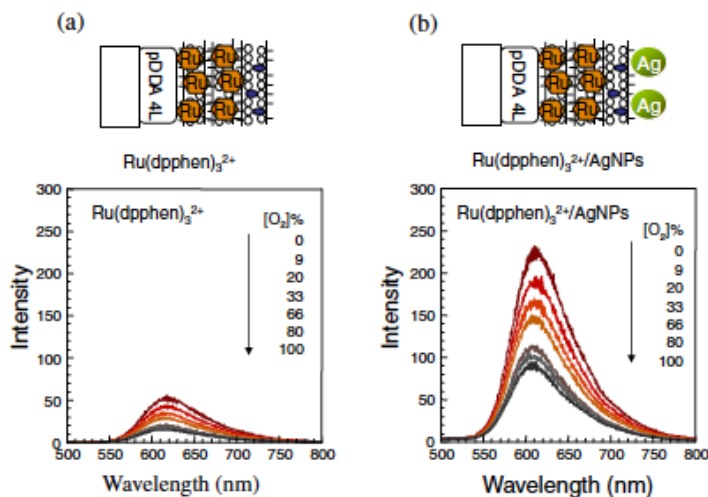


**Figure 19.** Suggested structure of molecularly doped metals from reference <sup>[253]</sup>, copyright 2014 American Chemical Society (left). SEM photo of a gold film doped with Rhodamine B (middle). Enhanced Raman spectrum of Rhodamine B in gold aggregates (red) versus the spectrum of pure Rhodamine B powder (black)(right).<sup>[252]</sup>

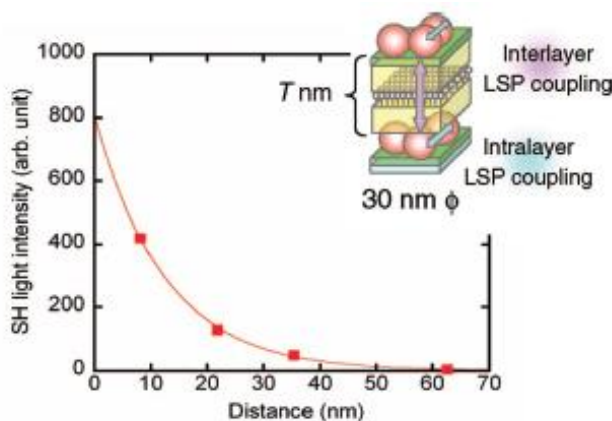
### 5.2.3 Composite materials and thin films

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<sup>[254-257]</sup>, sol-gel based matrix<sup>[258-269]</sup> or polymers.<sup>[270-273]</sup> 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 the micrometer size in resolution. In this sense the stabilization of colloidal suspension of metal nanoparticle and further dispersion in a solid matrix appear as a good alternative to controlled dispersion and also co-doping of optically active molecule and plasmonic nanostructures. For instance, recent work has strongly focused on the introduction of plasmonic nanostructures in the field of nonlinear optics to provide either direct nonlinear absorption or enhancement of nonlinear properties of chromophores. The first works were reported on the use of gold nanoparticles either precipitated in glass,<sup>[254, 255]</sup> polymers,<sup>[274, 275]</sup> or as colloidal suspension and aggregates<sup>[37, 276]</sup> and showed nonlinear absorption response essentially due to the Surface Plasmon Resonance and RSA or nonlinear scattering processes. Regarding the possibility of using hybrid 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 triplet exciton, which consequently reduces capacity to transfer to oxygen (singlet oxygen formation) and thus decreases the photooxydation and enhance the active lifetime of the polymer.<sup>[277]</sup> Similarly, core-shell Au@SiO<sub>2</sub> NPs were incorporated into the emitting layer of a LED to successfully enhance the luminous efficiency.<sup>[278]</sup> The design of thiolated silicon polymers allowed surface modification of metal nanoparticles of different shapes and efficient dispersion in sol-gel matrices.<sup>[279]</sup> Such approach was used to prepare co-doped sol-gel monoliths, which unexpectedly showed unusually long distance enhancement of nonlinear absorption processes.<sup>[280]</sup>

Multilayers systems can be an alternative to control interactions between metal NPs and luminescent polymers.<sup>[272, 281-283]</sup> M. Mitsuishi *et al.* used also hybrid polymer approach combining polymer nanosheets nanoassemblies through Langmuir-Blodgett technology and introduced metal nanoparticles layers.<sup>[281, 282]</sup> 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 (**Figure 20 and 21**). The SHG enhancement was dominated by the dipole LSP coupling (confirmed by FDTD calculations) and controlled at the nanometer scale.<sup>[281]</sup>



**Figure 20.** Hybrid polymer thin films with Ru(ddphen)<sub>3</sub><sup>2+</sup> and Ag NPs and the corresponding luminescence spectra showing the enhancement of the emission.<sup>[282]</sup>



**Figure 21.** Impact of the distance between the nanoparticles layers surrounding the SHG polymeric layer in the hybrid configuration on the second harmonic response. Adapted from reference <sup>[281]</sup>, copyright 2009 American Chemical Society.

Scattering of nanoparticles can be efficiently used to enhance the absorption of devices, in particular in the field of photovoltaics.<sup>[284]</sup> 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.<sup>[285, 286]</sup> 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.<sup>[285]</sup>

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. General conclusion and perspectives (Part I and II):

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. The review 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.

## References

- [1] W. L. L. S. I. Wawilov, *Z. Phys.* **1926**, 35, 920.
- [2] S. I. Vavilov, Ed. *Microstructure of light*, USSR Acad. Sci., Moscow, 1950.
- [3] R. W. Boyd, *Nonlinear optics 2nd edn.*, Academic San Diego, 2003.
- [4] *Springer Handbook of lasers and optics*, Springer, 2007.
- [5] T. H. Maiman, *Nature* **1960**, 187, 493.
- [6] G. S. He, L.-S. Tan, Q. Zheng, P. N. Prasad, *Chem. Rev.* **2008**, 108, 1245–1330.
- [7] P. Pantelis, J. R. Hill, G. J. Davies, in *Nonlinear Optical and Electroactive Polymers*, (Eds: P. N. Prasad, D. R. Ulrich), Plenum, New York 1988, 229.
- [8] M. A. Mortazavi, A. Knoesen, S. T. Kowel, B. G. Higgins, A. Dienes, *J. Opt. Soc. Am. B* **1989**, 6, 733.
- [9] K. D. Singer, J. E. Sohn, S. J. Lalama, *Appl. Phys. Lett.* **1986**, 49, 248.
- [10] K. D. Singer, M. G. Kuzyk, W. R. Holland, J. E. Sohn, S. J. Lalama, R. B. Comizzoli, H. E. Katz, M. L. Schilling, *Appl. Phys. Lett.* **1988**, 53, 1800.
- [11] F. Charra, F. Devaux, J. M. Nunzi, P. Raimond, *Phys. Rev. Lett.* **1992**, 68, 2440.
- [12] F. Charra, F. Kajzar, J. M. Nunzi, P. Raimond, E. Idiart, *Opt. Lett.* **1993**, 18, 941.
- [13] C. Fiorini, F. Charra, J. M. Nunzi, I. D. Samuel, J. Zyss, *Opt. Lett.* **1995**, 20, 2469.
- [14] C. Sanchez, B. Lebeau, F. Chaput, J. P. Boilot, *Adv. Mater.* **2003**, 15, 1969.
- [15] P. Innocenzi, B. Lebeau, *J. Mater. Chem.* **2005**, 15, 3821.
- [16] P. Griesmar, C. Sanchez, G. Puccetti, I. Ledoux, J. Zyss, *Molecular Engineering* **1991**, 1, 205.
- [17] B. Lebeau, C. Sanchez, S. Brasselet, J. Zyss, G. Froc, M. Dumont, *New J. Chem.* **1996**, 20, 13.
- [18] B. Lebeau, S. Brasselet, J. Zyss, C. Sanchez, *Chem. Mater.* **1997**, 9, 1012.
- [19] B. Lebeau, J. Maquet, C. Sanchez, E. Toussaere, R. Hierle, J. Zyss, *J. Mater. Chem.* **1994**, 4, 1855.
- [20] D. Avnir, D. Levy, R. Reisfeld, *J. Phys. Chem.* **1984**, 88, 5956.
- [21] D. Levy, D. Avnir, *J. Photochem. Photobiol. A* **1991**, 57, 41.
- [22] D. Levy, S. Einhorn, D. Avnir, *J. Non-Cryst. Solids* **1989**, 113, 137.
- [23] B. Schaudel, C. Guerneur, C. Sanchez, K. Nakatani, J. A. Delaire, *J. Mater. Chem.* **1997**, 7, 61.
- [24] F. Bentivegna, M. Canva, P. Georges, A. Brun, F. Chaput, L. Malier, J. P. Boilot, *Appl. Phys. Lett.* **1993**, 62, 1721.
- [25] D. Riehl, F. Chaput, Y. Levy, J. P. Boilot, F. Kajzar, P. A. Chollet, *Chem. Phys. Lett.* **1995**, 245, 36.
- [26] F. Bentivegna, M. Canva, A. Brun, F. Chaput, J. P. Boilot, *J. Appl. Phys.* **1996**, 80, 4655.
- [27] A. Dubois, M. Canva, A. Brun, F. Chaput, J. P. Boilot, *Appl. Opt.* **1996**, 35, 3193.
- [28] F. Bentivegna, M. Canva, A. Brun, F. Chaput, J. P. Boilot, *J. Sol-Gel Sci. Technol.* **1997**, 9, 33.
- [29] J. P. Boilot, J. Biteau, F. Chaput, T. Gacoin, A. Brun, B. Darracq, P. Georges, Y. Levy, *Pure Appl. Opt.* **1998**, 7, 169.
- [30] H. Goudket, M. Canva, Y. Levy, F. Chaput, J. P. Boilot, *J. Appl. Phys.* **2001**, 90, 6044.
- [31] A. C. Le Duff, M. Canva, Y. Levy, A. Brun, V. Ricci, T. Pliska, J. Meier, G. I. Stegeman, F. Chaput, J. P. Boilot, E. Toussaere, *J. Opt. Soc. Am. B* **2001**, 18, 1827.
- [32] M. Canva, G. Roger, F. Cassagne, Y. Levy, A. Brun, F. Chaput, J. P. Boilot, A. Rapaport, C. Heerdt, M. Bass, *Opt. Mater.* **2002**, 18, 391.
- [33] T. H. Nhung, M. Canva, T. T. A. Dao, F. Chaput, A. Brun, N. D. Hung, J. P. Boilot, *Appl. Opt.* **2003**, 42, 2213.

- [34] L. Chen, X. Jin, Y. Cui, J. Gao, G. Qian, M. Wang, *J. Sol-Gel Sci. Technol.* **2007**, *43*, 329.
- [35] R. Westlund, E. Malmström, C. Lopes, J. Öhgren, T. Rodgers, Y. Saito, S. Kawata, E. Glimsdal, M. Lindgren, *Adv. Func. Mater.* **2008**, *18*, 1939.
- [36] R. Zieba, C. Desroches, F. Chaput, M. Carlsson, B. Eliasson, C. Lopes, M. Lindgren, S. Parola, *Adv. Func. Mater.* **2009**, *19*, 235.
- [37] Y. Cui, L. Chen, M. Wang, G. Qian, *J. Phys. Chem. Solids* **2006**, *67*, 1590.
- [38] L. Chen, Y. Cui, G. Qian, M. Wang, *Dyes Pigments* **2007**, *73*, 338.
- [39] L. Chen, G. Qian, Y. Cui, X. Jin, Z. Wang, M. Wang, *J. Phys. Chem. B* **2006**, *110*, 19176.
- [40] L. Chen, G. Qian, X. Jin, Y. Cui, J. Gao, Z. Wang, M. Wang, *J. Phys. Chem. B* **2007**, *111*, 3115.
- [41] L. Chen, Q. Zhong, Y. Cui, G. Qian, M. Wang, *Dyes Pigments* **2008**, *76*, 195.
- [42] Y. Cui, L. Chen, G. Qian, M. Wang, *J. Non-Cryst. Solids* **2008**, *354*, 1211.
- [43] Y. Cui, B. Li, C. Yu, J. Yu, J. Gao, M. Yan, G. Chen, Z. Wang, G. Qian, *Thin Solid Films* **2009**, *517*, 5075.
- [44] Y. Cui, G. Qian, L. Chen, J. Gao, M. Wang, *Opt. Commun.* **2007**, *270*, 414.
- [45] Y. Cui, G. Qian, L. Chen, Z. Wang, M. Wang, *Macromol. Rapid Commun.* **2007**, *28*, 2019.
- [46] Y. Cui, G. Qian, J. Gao, L. Chen, Z. Wang, M. Wang, *J. Phys. Chem. B* **2005**, *109*, 13295.
- [47] T. Liang, Y. Cui, J. Yu, W. Lin, Y. Yang, G. Qian, *Thin Solid Films* **2013**, *544*, 407.
- [48] T. Liang, Y. Cui, J. Yu, W. Lin, Y. Yang, G. Qian, *Dyes Pigments* **2013**, *98*, 377.
- [49] P.-H. Chang, H.-C. Tsai, Y.-R. Chen, J.-Y. Chen, G.-H. Hsiue, *Langmuir* **2008**, *24*, 11921.
- [50] S. Wang, L. Zhao, J. Sun, Z. Cui, D. Zhang, *Polym. Adv. Technol.* **2011**, *22*, 759.
- [51] C. Desroches, C. Lopes, V. Kessler, S. Parola, *Dalton Trans.* **2003**, 2085.
- [52] X. Zhang, M. Li, Z. Shi, Z. Cui, *Mater. Lett.* **2011**, *65*, 1404.
- [53] S. Wang, L. Zhao, S. Yang, S. Pang, Z. Cui, *Mater. Lett.* **2009**, *63*, 292.
- [54] D. Wang, X. Chen, X. Zhang, W. Wang, Y. Liu, L. Hu, *Curr. Appl. Phys.* **2009**, *9*, S170.
- [55] D. Chateau, F. Chaput, C. Lopes, M. Lindgren, C. Brannlund, J. Öhgren, N. Djourelou, P. Nedelec, C. Desroches, B. Eliasson, T. Kindahl, F. Lerouge, C. Andraud, S. Parola, *ACS Appl. Mater. Interfaces* **2012**, *4*, 2369.
- [56] P.-A. Bouit, O. Maury, P. Feneyrou, S. Parola, F. Kajzar, C. Andraud, in *Multiphoton processes in organic materials and their applications*, (Eds: Rau I., K. F), Archives Contemporaines & Old City Publishing, Paris – Philadelphia, 2011, 275.
- [57] D. Château, Q. Bellier, F. Chaput, P. Feneyrou, G. Berginc, O. Maury, C. Andraud, S. Parola, *J. Mater. Chem. C* **2014**, *2*, 5105.
- [58] E.-H. Kang, T. Bu, P. Jin, J. Sun, Y. Yanqiang, J. Shen, *Langmuir* **2007**, *23*, 7594.
- [59] J. R. Heflin, M. T. Guzy, P. J. Neyman, K. J. Gaskins, C. Brands, Z. Wang, H. W. Gibson, R. M. Davis, K. E. Van Cott, *Langmuir* **2006**, *22*, 5723.
- [60] J. Borges, L. C. Rodrigues, R. L. Reis, J. F. Mano, *Adv. Func. Mater.* **2014**, *24*, 5624.
- [61] P. G. Lacroix, R. Clement, K. Nakatani, J. Zyss, I. Ledoux, *Science* **1994**, *263*, 658.
- [62] Y. Suzuki, Y. Tenma, Y. Nishioka, J. Kawamata, *Chem. Asian J.* **2012**, *7*, 1170.
- [63] R. Takenawa, Y. Komori, S. Hayashi, J. Kawamata, K. Kuroda, *Chem. Mater.* **2001**, *13*, 3741.
- [64] V. Monnier, N. Sanz, E. Botzung-Appert, M. Bacia, A. Ibanez, *J. Mater. Chem.* **2006**, *16*, 1401.

- [65] Nathalie Sanz, Patrice L. Baldeck, Jean-François Nicoud, Yvette Le Fur, A. Ibanez, *Solid State Sci.* **2001**, *3*, 867.
- [66] N. Sanz, A. Ibanez, Y. Morel, P. L. Baldeck, *Appl. Phys. Lett.* **2001**, *78*, 2569.
- [67] I. Wang, P. L. Baldeck, E. Botzung, N. Sanz, A. Ibanez, *Opt. Mater.* **2002**, *21*, 569.
- [68] E. Cariati, M. Pizzotti, D. Roberto, F. Tessore, R. Ugo, *Coord. Chem. Rev.* **2006**, *250*, 1210.
- [69] H. S. S. Ramakrishna Matte, A. K. Cheetham, C. N. R. Rao, *Solid State Commun.* **2009**, *149*, 908.
- [70] C. Wang, T. Zhang, W. Lin, *Chem. Rev.* **2012**, *112*, 1084.
- [71] X. Lopez, J. J. Carbo, C. Bo, J. M. Poblet, *Chem. Soc. Rev.* **2012**, *41*, 7537.
- [72] J. D. Compain, P. Mialane, A. Dolbecq, J. Marrot, A. Proust, K. Nakatani, P. Yu, F. Secheresse, *Inorg. Chem.* **2009**, *48*, 6222.
- [73] Y. Song, M. R. S. A. Janjua, S. Jamil, M. Haroon, S. Nasir, Z. Nisar, A. Zafar, N. Nawaz, A. Batool, A. Abdul, *Synth. Met.* **2014**, *198*, 277.
- [74] M. R. S. A. Janjua, C.-G. Liu, W. Guan, J. Zhuang, S. Muhammad, L.-K. Yan, Z.-M. Su, *J. Phys. Chem. A* **2009**, *113*, 3576.
- [75] X. Zhang, Y.-Y. Huang, M.-J. Zhang, J. Zhang, Y.-G. Yao, *Cryst. Growth Des.* **2012**, *12*, 3231.
- [76] F. Wang, X. Ke, J. Zhao, K. Deng, X. Leng, Z. Tian, L. Wen, D. Li, *Dalton Trans.* **2011**, *40*, 11856.
- [77] E. Cariati, R. Macchi, D. Roberto, R. Ugo, S. Galli, N. Casati, P. Macchi, A. Sironi, L. Bogani, A. Caneschi, D. Gatteschi, *J. Am. Chem. Soc.* **2007**, *129*, 9410.
- [78] E. Cariati, R. Ugo, G. Santoro, E. Tordin, L. Sorace, A. Caneschi, A. Sironi, P. Macchi, N. Casati, *Inorg. Chem.* **2010**, *49*, 10894.
- [79] Q.-L. Zhu, Q. Xu, *Chem. Soc. Rev.* **2014**, *43*, 5468.
- [80] M. Genovese, K. Lian, *Curr. Opin. Solid State Mater. Sci.* **2015**, *19*, 126.
- [81] R. C. Hollins, *Curr. Opin. Solid State Mat. Sci.* **1999**, *4*, 189.
- [82] C. W. Spangler, *J. Mater. Chem. A* **1999**, *9*, 2013.
- [83] T. J. McKay, J. A. Bolger, J. Staromlynska, J. R. Davy, *J. Chem. Phys.* **1998**, *108*, 5537.
- [84] G. S. He, J. D. Bhawalkar, C. F. Zhao, P. N. Prasad, *Appl. Phys. Lett.* **1995**, 2433.
- [85] G. S. He, R. Gvishi, P. N. Prasad, B. A. Reinhardt, *Opt. Commun.* **1995**, *117*, 133.
- [86] J. E. Ehrlich, X. L. Wu, I. Y. S. Lee, Z. Y. Hu, H. Rockel, S. R. Marder, J. W. Perry, *Opt. Lett.* **1997**, *22*, 1843.
- [87] B. A. Reinhardt, L. L. Brott, S. J. Clarson, A. G. Dillard, J. C. Bhatt, R. Kannan, L. X. Yuan, G. S. He, P. N. Prasad, *Chem. Mater.* **1998**, *10*, 1863.
- [88] C. F. Li, L. Zhang, M. Yang, H. Wang, Y. X. Wang, *Phys. Rev. A* **1994**, *49*, 1149.
- [89] J. W. Perry, K. Mansour, I. Y. S. Lee, X. L. Wu, P. V. Bedworth, C. T. Chen, D. N. S. R. Marder, P. Miles, T. Wada, M. Tian, H. Sasabe, *Science* **1996**, *273*, 1533.
- [90] M. J. Miller, A. G. Mott, B. P. Ketchel, *Proc. SPIE* **1998**, *24*, 3472.
- [91] P. A. Miles, *Appl. Opt.* **1994**, *33*, 6965.
- [92] B. L. Justus, A. L. Huston, A. J. Campillo, *Appl. Phys. Lett.* **1993**, *63*, 1483.
- [93] J. J. Doyle, J. Wang, S. M. O'Flaherty, Y. Chen, A. Slodek, T. Hegarty, L. E. Carpenter II, D. Wöhrle, M. Hanack, W. J. Blau, *J. Opt. A: Pure Appl. Opt.* **2008**, *10*, 075101.
- [94] Peter D. Fuqua, Kamjou Mansour, J. Daniel Alvarez, Seth R. Marder, Joseph W. Perry, B. S. Dunn, *Proc. SPIE, Sol-Gel Optics II* **1992**, *1758*, 499.
- [95] H. Jiang, M. DeRosa, W. Su, M. Brant, D. McLean, T. Bunning, *Proc. SPIE* **1998**, *3472*, 157.
- [96] P. Innocenzi, G. Brusatin, M. Guglielmi, R. Signorini, R. Bozio, M. Maggini, *J. Non-Cryst. Solids* **2000**, *265*, 68.

- [97] R. Signorini, M. Meneghetti, R. Bozio, M. Maggini, G. Scorrano, M. Prato, G. Brusatin, P. Innocenzi, M. Guglielmi, *Carbon* **2000**, *38*, 1653.
- [98] G. Brusatin, M. Guglielmi, P. Innocenzi, A. Martucci, G. Scarinci, *J. Electroceram.* **2000**, *4*, 151.
- [99] G. Kopitkovas, A. Chugreev, J. F. Nierengarten, Y. Rio, J. L. Rehspringer, B. Hönerlage, *Opt. Mater.* **2004**, *27*, 285.
- [100] P. Innocenzi, G. Brusatin, *Chem. Mater.* **2001**, *13*, 3126.
- [101] N. Sanz, P. L. Baldeck, A. Ibanez, *Synth. Met.* **2000**, *115*, 229.
- [102] R. T. Kuznetsova, N. S. Savenkova, G. V. Maier, S. M. Arabei, T. A. Pavich, K. N. Solov'ev, *J. Appl. Spectrosc.* **2007**, *74*, 485.
- [103] J. Staromlynska, T. J. McKay, J. A. Bolger, J. R. Davy, *J. Opt. Soc. Am. B: Opt. Phys.* **1998**, *15*, 1731.
- [104] T. M. Cooper, D. G. McLean, J. E. Rogers, *Chem. Phys. Lett.* **2001**, *349*, 31.
- [105] J. E. Rogers, T. M. Cooper, P. A. Fleitz, D. J. Glass, D. G. McLean, *J. Phys. Chem. A* **2002**, *106*, 10108.
- [106] R. Vestberg, R. Westlund, A. Eriksson, C. Lopes, M. Carlsson, B. Eliasson, E. Glimsdal, M. Lindgren, E. Malmström, *Macromolecules* **2006**, *39*, 2238.
- [107] M. Lindgren, B. Minaev, E. Glimsdal, R. Vestberg, R. Westlund, E. Malmstrom, *J. Lumin.* **2007**, *124*, 302.
- [108] E. Glimsdal, M. Carlsson, B. Eliasson, B. Minaev, M. Lindgren, *J. Phys. Chem. A* **2007**, *111*, 244.
- [109] A. T. Yeates, E. Glimsdal, A. Eriksson, R. Vestberg, E. Malmstrom, M. Lindgren, *Proc. SPIE* **2005**, *5934*, 59340N.
- [110] J. Vicente, M.-T. Chicote, M. M. Alvarez-Falcon, P. G. Jones, *Organometallics* **2005**, *24*, 2764.
- [111] C. H. Tao, N. Zhu, V. W. Yam, *Chem. Eur. J.* **2005**, *11*, 1647.
- [112] G. J. Zhou, W. Y. Wong, C. Ye, Z. Lin, *Adv. Func. Mater.* **2007**, *17*, 963.
- [113] R. Vestberg, R. Westlund, M. Carlsson, B. Eliasson, E. Glimsdal, J. Örtengren, M. Lindgren, E. Malmström, *Polym. Mater. Sci. Eng.* **2005**, *92*, 622.
- [114] G. J. Zhou, W. Y. Wong, *Chem. Soc. Rev.* **2011**, *40*, 2541.
- [115] F. Guo, W. Sun, Y. Liu, K. Schanze, *Inorg. Chem.* **2005**, *44*, 4055.
- [116] R. S. Price, G. Dubinina, G. Wicks, M. Drobizhev, A. Rebane, K. S. Schanze, *ACS Appl. Mater. Interfaces* **2015**, *7*, 10795.
- [117] O. G. Morales-Saavedra, G. Huerta, R. Ortega-Martínez, L. Fomina, *J. Non-Cryst. Solids* **2007**, *353*, 2557.
- [118] O. G. Morales-Saavedra, E. Rivera, *Polymer* **2006**, *47*, 5330.
- [119] S. Sharma, D. Mohan, S. K. Ghoshal, *Opt. Commun.* **2008**, *281*, 2923.
- [120] X. Su, H. Xu, Y. Deng, J. Li, W. Zhang, P. Wang, *Mater. Lett.* **2008**, *62*, 3818.
- [121] X. Su, S. Guang, H. Xu, J. Yang, Y. Song, *Dyes Pigments* **2010**, *87*, 69.
- [122] X. Su, S. Guang, C. Li, H. Xu, X. Liu, X. Wang, Y. Song, *Macromolecules* **2010**, *43*, 2840.
- [123] X. Sun, Y. Xiong, P. Chen, J. Lin, W. Ji, J. H. Lim, S. S. Yang, D. J. Hagan, E. W. Van Stryland, *Appl. Opt.* **2000**, *39*, 1998.
- [124] L. Vivien, D. Riehl, P. Lancon, F. Hache, E. Anglaret, *Opt. Lett.* **2001**, *26*, 223.
- [125] B. Zhang, Y. Chen, J. Wang, W. J. Blau, X. Zhuang, N. He, *Carbon* **2010**, *48*, 1738.
- [126] P. Cardiano, E. Fazio, G. Lazzara, S. Manickam, S. Milioto, F. Neri, P. G. Mineo, A. Piperno, S. Lo Schiavo, *Carbon* **2015**, *86*, 325.
- [127] G. K. Lim, Z. L. Chen, J. Clark, R. G. S. Goh, W. H. Ng, H. W. Tan, R. H. Friend, P. K. H. Ho, L. L. Chua, *Nat. Photonics* **2011**, *5*, 554.

- [128] Z. B. Liu, Y. Wang, X. L. Zhang, Y. F. Xu, Y. S. Chen, J. G. Tian, *Appl Phys Lett* **2009**, *94*.
- [129] J. Wang, Y. Hernandez, M. Lotya, J. N. Coleman, W. J. Blau, *Adv. Mater.* **2009**, *21*, 2430.
- [130] L. Zhang, L.-Y. Zou, J.-F. Guo, A.-M. Ren, D. Wang, J.-K. Feng, *New J. Chem.* **2014**, *38*, 5391.
- [131] W. Song, C. He, W. Zhang, Y. Gao, Y. Yang, Y. Wu, Z. Chen, X. Li, Y. Dong, *Carbon* **2014**, *77*, 1020.
- [132] X.-L. Zhang, X. Zhao, Z.-B. Liu, S. Shi, W.-Y. Zhou, J.-G. Tian, Y.-F. Xu, Y.-S. Chen, *J. Opt.* **2011**, *13*, 075202.
- [133] X. Zheng, M. Feng, H. Zhan, *J. Mater. Chem. C* **2013**, *1*, 6759.
- [134] X. Zheng, M. Feng, Z. Li, Y. Song, H. Zhan, *J. Mater. Chem. C* **2014**, *2*, 4121.
- [135] L. Tao, B. Zhou, G. Bai, Y. Wang, S. F. Yu, S. P. Lau, Y. H. Tsang, J. Yao, D. Xu, *J. Phys. Chem. C* **2013**, *117*, 23108.
- [136] C. Zheng, Y. Zheng, W. Chen, L. Wei, *Opt. Laser Technol.* **2015**, *68*, 52.
- [137] Q. Ouyang, Z. Xu, Z. Lei, H. Dong, H. Yu, L. Qi, C. Li, Y. Chen, *Carbon* **2014**, *67*, 214.
- [138] Q. Ouyang, H. Yu, Z. Xu, Y. Zhang, C. Li, L. Qi, Y. Chen, *Appl. Phys. Lett.* **2013**, *102*, 031912.
- [139] D. J. de Aberasturi, A. B. Serrano-Montes, L. M. Liz-Marzan, *Adv. Opt. Mater.* **2015**, *3*, 602.
- [140] J. R. Lakowicz, *Plasmonics* **2006**, *1*, 5.
- [141] A. Lauchner, A. E. Schlather, A. Manjavacas, Y. Cui, M. J. McClain, G. J. Stec, F. J. G. de Abajo, P. Nordlander, N. J. Halas, *Nano Lett.* **2015**, *15*, 6208.
- [142] Y. B. Zheng, B. Kiraly, P. S. Weiss, T. J. Huang, *Nanomedicine* **2012**, *7*, 751.
- [143] A. Guerrero-Martinez, M. Grzelczak, L. M. Liz-Marzan, *ACS Nano* **2012**, *6*, 3655.
- [144] L. M. Liz-Marzan, *J. Phys. Chem. Lett.* **2013**, *4*, 1197.
- [145] M. Kauranen, A. V. Zayats, *Nat. Photonics* **2012**, *6*, 737.
- [146] E. C. Dreaden, A. M. Alkilany, X. H. Huang, C. J. Murphy, M. A. El-Sayed, *Chem. Soc. Rev.* **2012**, *41*, 2740.
- [147] M. C. Daniel, D. Astruc, *Chem. Rev.* **2004**, *104*, 293.
- [148] P. X. Zhao, N. Li, D. Astruc, *Coord. Chem. Rev.* **2013**, *257*, 638.
- [149] P. K. Jain, X. H. Huang, I. H. El-Sayed, M. A. El-Sayed, *Acc. Chem. Res.* **2008**, *41*, 1578.
- [150] S. W. Zeng, D. Baillargeat, H. P. Ho, K. T. Yong, *Chem. Soc. Rev.* **2014**, *43*, 3426.
- [151] D. A. Giljohann, D. S. Seferos, W. L. Daniel, M. D. Massich, P. C. Patel, C. A. Mirkin, *Angew. Chem. Int. Ed.* **2010**, *49*, 3280.
- [152] M. Bauch, K. Toma, M. Toma, Q. Zhang, J. Dostalek, *Plasmonics* **2013**, *9*, 781.
- [153] J. A. Webb, R. Bardhan, *Nanoscale* **2014**, *6*, 2502.
- [154] T. K. Sau, A. L. Rogach, F. Jackel, T. A. Klar, J. Feldmann, *Adv. Mater.* **2010**, *22*, 1805.
- [155] J. R. Lakowicz, K. Ray, M. Chowdhury, H. Szmecinski, Y. Fu, J. Zhang, K. Nowaczyk, *Analyst* **2008**, *133*, 1308.
- [156] U. Kriebig, M. Vollmer, Eds., *Optical Properties of Metal Clusters*, Springer-Verlag, Berlin Heidelberg, Germany 1995.
- [157] C. F. Bohren, D. R. Huffman, Eds., *Absorption and Scattering of Light by Small Particles*, Wiley-Interscience, New York 1983.
- [158] A. Henglein, *Chem. Rev.* **1989**, *89*, 1861.
- [159] U. Kriebig, L. Genzel, *Surf. Sci.* **1985**, *156*, 678.
- [160] S. Link, M. A. El-Sayed, *J. Phys. Chem. B* **1999**, *103*, 4212.

- [161] S. Link, Z. L. Wang, M. A. El-Sayed, *J. Phys. Chem. B* **1999**, *103*, 3529.
- [162] E. Hutter, J. H. Fendler, *Adv. Mater.* **2004**, *16*, 1685.
- [163] S. Eustis, M. A. El-Sayed, *Chem. Soc. Rev.* **2006**, *35*, 209.
- [164] N. Liu, M. Hentschel, T. Weiss, A. P. Alivisatos, H. Giessen, *Science* **2011**, *332*, 1407.
- [165] J. M. Luther, P. K. Jain, T. Ewers, A. P. Alivisatos, *Nat. Mater.* **2011**, *10*, 361.
- [166] P. K. Jain, K. S. Lee, I. H. El-Sayed, M. A. El-Sayed, *J. Phys. Chem. B* **2006**, *110*, 7238.
- [167] S. Link, M. B. Mohamed, M. A. El-Sayed, *J. Phys. Chem. B* **1999**, *103*, 3073.
- [168] M. Grzelczak, J. Perez-Juste, P. Mulvaney, L. M. Liz-Marzan, *Chem. Soc. Rev.* **2008**, *37*, 1783.
- [169] D. Chateau, A. Liotta, F. Vadcard, J. R. Navarro, F. Chaput, J. Lerme, F. Lerouge, S. Parola, *Nanoscale* **2015**, *7*, 1934.
- [170] Y. Yin, C. Erdonmez, S. Aloni, A. P. Alivisatos, *J. Am. Chem. Soc.* **2006**, *128*, 12671.
- [171] G. S. Metraux, Y. C. Cao, R. C. Jin, C. A. Mirkin, *Nano Lett.* **2003**, *3*, 519.
- [172] L. J. Sherry, R. C. Jin, C. A. Mirkin, G. C. Schatz, R. P. Van Duyne, *Nano Lett.* **2006**, *6*, 2060.
- [173] J. E. Millstone, S. J. Hurst, G. S. Metraux, J. I. Cutler, C. A. Mirkin, *Small* **2009**, *5*, 646.
- [174] J. Zhang, S. Z. Li, J. S. Wu, G. C. Schatz, C. A. Mirkin, *Angew. Chem. Int. Ed.* **2009**, *48*, 7787.
- [175] J. A. Zhang, M. R. Langille, M. L. Personick, K. Zhang, S. Y. Li, C. A. Mirkin, *J. Am. Chem. Soc.* **2010**, *132*, 14012.
- [176] M. L. Personick, M. R. Langille, J. Zhang, C. A. Mirkin, *Nano Lett.* **2011**, *11*, 3394.
- [177] M. R. Langille, M. L. Personick, J. Zhang, C. A. Mirkin, *J. Am. Chem. Soc.* **2012**, *134*, 14542.
- [178] E. Ringe, J. Zhang, M. R. Langille, C. A. Mirkin, L. D. Marks, R. P. Van Duyne, *Nanotechnology* **2012**, *23*.
- [179] M. L. Personick, M. R. Langille, J. S. Wu, C. A. Mirkin, *J. Am. Chem. Soc.* **2013**, *135*, 3800.
- [180] M. L. Personick, M. R. Langille, J. Zhang, J. S. Wu, S. Y. Li, C. A. Mirkin, *Small* **2013**, *9*, 1947.
- [181] J. D. Padmos, M. L. Personick, Q. Tang, P. N. Duchesne, D. E. Jiang, C. A. Mirkin, P. Zhang, *Nat. Commun.* **2015**, *6*.
- [182] F. Lux, F. Lerouge, J. Bosson, G. Lemercier, C. Andraud, G. Vitrant, P. L. Baldeck, F. Chassagneux, S. Parola, *Nanotechnology* **2009**, *20*, 355603.
- [183] S. Zaiba, F. Lerouge, A. M. Gabudean, M. Focsan, J. Lerme, T. Gallavardin, O. Maury, C. Andraud, S. Parola, P. L. Baldeck, *Nano Lett.* **2011**, *11*, 2043.
- [184] J. R. Navarro, D. Manchon, F. Lerouge, N. P. Blanchard, S. Marotte, Y. Leverrier, J. Marvel, F. Chaput, G. Micouin, A. M. Gabudean, A. Mosset, E. Cottancin, P. L. Baldeck, K. Kamada, S. Parola, *Nanotechnology* **2012**, *23*, 465602.
- [185] J. R. Navarro, D. Manchon, F. Lerouge, E. Cottancin, J. Lerme, C. Bonnet, F. Chaput, A. Mosset, M. Pellarin, S. Parola, *Nanotechnology* **2012**, *23*, 145707.
- [186] C. J. Johnson, E. Dujardin, S. A. Davis, C. J. Murphy, S. Mann, *J. Mater. Chem.* **2002**, *12*, 1765.
- [187] B. D. Busbee, S. O. Obare, C. J. Murphy, *Adv. Mater.* **2003**, *15*, 414.
- [188] C. J. Orendorff, T. K. Sau, C. J. Murphy, *Small* **2006**, *2*, 636.
- [189] C. J. Murphy, L. B. Thompson, D. J. Chernak, J. A. Yang, S. T. Sivapalan, S. P. Boulos, J. Y. Huang, A. M. Alkilany, P. N. Sisco, *Curr. Opin. Colloid Interface Sci.* **2011**, *16*, 128.
- [190] S. E. Lohse, C. J. Murphy, *Chem. Mater.* **2013**, *25*, 1250.

- [191] M. Grzelczak, A. Sánchez-Iglesias, B. Rodríguez-González, R. Alvarez-Puebla, J. Pérez-Juste, L. M. Liz-Marzán, *Adv. Func. Mater.* **2008**, *18*, 3780.
- [192] C. Goldmann, R. Lazzari, X. Paquez, C. Boissiere, F. Ribot, C. Sanchez, C. Chaneac, D. Portehault, *ACS Nano* **2015**, *9*, 7572.
- [193] M. Thomas, J.-J. Greffet, R. Carminati, J. R. Arias-Gonzalez, *Appl. Phys. Lett.* **2004**, *85*, 3863.
- [194] F. Tam, G. P. Goodrich, B. R. Johnson, N. J. Halas, *Nano Lett.* **2007**, *7*, 496.
- [195] X. Meng, R. R. Grote, J. I. Dadap, N. C. Panoiu, R. M. Osgood, *Opt. Express* **2014**, *22*, 22018.
- [196] S. Lal, S. Link, N. J. Halas, *Nat. Photonics* **2007**, *1*, 641.
- [197] Y. K. Xu, S. Hwang, S. Kim, J. Y. Chen, *ACS Appl. Mater. Interfaces* **2014**, *6*, 5619.
- [198] D. C. Hone, P. I. Walker, R. Evans-Gowing, S. FitzGerald, A. Beeby, I. Chambrier, M. J. Cook, D. A. Russell, *Langmuir* **2002**, *18*, 2985.
- [199] T. Stuchinskaya, M. Moreno, M. J. Cook, D. R. Edwards, D. A. Russell, *Photochem. Photobiol. Sci.* **2011**, *10*, 822.
- [200] J. R. Navarro, F. Lerouge, C. Cepraga, G. Micouin, A. Favier, D. Chateau, M. T. Charreyre, P. H. Lanoe, C. Monnereau, F. Chaput, S. Marotte, Y. Leverrier, J. Marvel, K. Kamada, C. Andraud, P. L. Baldeck, S. Parola, *Biomaterials* **2013**, *34*, 8344.
- [201] J. R. Navarro, F. Lerouge, G. Micouin, C. Cepraga, A. Favier, M. T. Charreyre, N. P. Blanchard, J. Lerme, F. Chaput, M. Focsan, K. Kamada, P. L. Baldeck, S. Parola, *Nanoscale* **2014**, *6*, 5138.
- [202] S. T. Sivapalan, J. H. Vella, T. K. Yang, M. J. Dalton, R. N. Swiger, J. E. Haley, T. M. Cooper, A. M. Urbas, L. S. Tan, C. J. Murphy, *Langmuir* **2012**, *28*, 9147.
- [203] J. R. Navarro, A. Liotta, A. C. Faure, F. Lerouge, F. Chaput, G. Micouin, P. L. Baldeck, S. Parola, *Langmuir* **2013**, *29*, 10915.
- [204] W. Ni, Z. Yang, H. Chen, L. Li, J. Wang, *J. Am. Chem. Soc.* **2008**, *130*, 6692.
- [205] G. Schneider, G. Decher, N. Nerambourg, R. Praho, M. H. Werts, M. Blanchard-Desce, *Nano Lett.* **2006**, *6*, 530.
- [206] A. Gole, C. J. Murphy, *Chem. Mater.* **2005**, *17*, 1325.
- [207] H. Ding, K.-T. Yong, I. Roy, H. E. Pudavar, W. C. Law, E. J. Bergey, P. N. Prasad, *J. Phys. Chem. C* **2007**, *111*, 2552.
- [208] R. Bardhan, N. K. Grady, J. R. Cole, A. Joshi, N. J. Halas, *ACS Nano* **2009**, *3*, 744.
- [209] X. Gu, Y. Wu, L. Zhang, Y. Liu, Y. Li, Y. Yan, D. Wu, *Nanoscale* **2014**, *6*, 8681.
- [210] P. Yuan, R. Ma, Z. Guan, N. Gao, Q. H. Xu, *ACS Appl. Mater. Interfaces* **2014**, *6*, 13149.
- [211] S. Shimron, A. Ceconello, C. H. Lu, I. Willner, *Nano Lett.* **2013**, *13*, 3791.
- [212] Z. Jiang, B. Dong, B. Chen, J. Wang, L. Xu, S. Zhang, H. Song, *Small* **2013**, *9*, 604.
- [213] P. Huang, J. Lin, S. Wang, Z. Zhou, Z. Li, Z. Wang, C. Zhang, X. Yue, G. Niu, M. Yang, D. Cui, X. Chen, *Biomaterials* **2013**, *34*, 4643.
- [214] T. Zhao, K. Yu, L. Li, T. Zhang, Z. Guan, N. Gao, P. Yuan, S. Li, S. Q. Yao, Q. H. Xu, G. Q. Xu, *ACS Appl. Mater. Interfaces* **2014**, *6*, 2700.
- [215] N. S. Abadeer, M. R. Brennan, W. L. Wilson, C. J. Murphy, *ACS Nano* **2014**, *8*, 8392.
- [216] X. Ke, D. Wang, C. Chen, A. Yang, Y. Han, L. Ren, D. Li, H. Wang, *Nanoscale Res. Lett.* **2014**, *9*, 2492.
- [217] Z. Bai, R. Chen, P. Si, Y. Huang, H. Sun, D. H. Kim, *ACS Appl. Mater. Interfaces* **2013**, *5*, 5856.
- [218] Y. Pang, Z. Rong, J. Wang, R. Xiao, S. Wang, *Biosens. Bioelectron.* **2015**, *66*, 527.
- [219] N. Niu, F. He, P. Ma, S. Gai, G. Yang, F. Qu, Y. Wang, J. Xu, P. Yang, *ACS Appl. Mater. Interfaces* **2014**, *6*, 3250.



- [220] G. Terentyuk, E. Panfilova, V. Khanadeev, D. Chumakov, E. Genina, A. Bashkatov, V. Tuchin, A. Bucharskaya, G. Maslyakova, N. Khlebtsov, B. Khlebtsov, *Nano Res.* **2014**, *7*, 325.
- [221] Y. Li, T. Wen, R. Zhao, X. Liu, T. Ji, H. Wang, X. Shi, J. Shi, J. Wei, Y. Zhao, X. Wu, G. Nie, *ACS Nano* **2014**, *8*, 11529.
- [222] J. Croissant, M. Maynadier, O. Mongin, V. Hugues, M. Blanchard-Desce, A. Chaix, X. Cattoen, M. W. C. Man, A. Gallud, M. Gary-Bobo, M. Garcia, L. Raehm, J. O. Durand, *Small* **2015**, *11*, 295.
- [223] M. A. Noginov, G. Zhu, A. M. Belgrave, R. Bakker, V. M. Shalaev, E. E. Narimanov, S. Stout, E. Herz, T. Suteewong, U. Wiesner, *Nature* **2009**, *460*, 1110.
- [224] A. J. H. Maryuri Roca, *J. Am. Chem. Soc.* **2008**, *130*, 14273.
- [225] M. Hembury, C. Chiappini, S. Bertazzo, T. L. Kalber, G. L. Drisko, O. Ogunlade, S. Walker-Samuel, K. S. Krishna, C. Jumeaux, P. Beard, C. S. Kumar, A. E. Porter, M. F. Lythgoe, C. Boissiere, C. Sanchez, M. M. Stevens, *PNAS* **2015**, *112*, 1959.
- [226] R. D. A. S.J. Oldenburg, S.L. Westcott, N.J. Halas, *Chem. Phys. Lett.* **1998**, 288, 243.
- [227] S. J. Oldenburg, J. B. Jackson, S. L. Westcott, N. J. Halas, *Appl. Phys. Lett.* **1999**, *75*, 2897.
- [228] L.-J. W. Han-Pu Liang, Chun-Li Bai, Li Jiang, *J. Phys. Chem. B* **2005**, *109*, 7795.
- [229] M. H. L. Andre M. Gobin, Naomi J. Halas, William D. James, Rebekah A. Drezek, Jennifer L. West, *Nano Lett.* **2007**, *7*, 1929.
- [230] R. Bardhan, W. Chen, C. Perez-Torres, M. Bartels, R. M. Huschka, L. L. Zhao, E. Morosan, R. G. Pautler, A. Joshi, N. J. Halas, *Adv. Func. Mater.* **2009**, *19*, 3901.
- [231] A. M. Gobin, D. P. O'Neal, D. M. Watkins, N. J. Halas, R. A. Drezek, J. L. West, *Lasers Surg. Med.* **2005**, *37*, 123.
- [232] S. Lal, S. E. Clare, N. J. Halas, *Acc. Chem. Res.* **2008**, *41*, 1842.
- [233] D. P. O'Neal, L. R. Hirsch, N. J. Halas, J. D. Payne, J. L. West, *Cancer Lett.* **2004**, *209*, 171.
- [234] R. J. Bernardi, A. R. Lowery, P. A. Thompson, S. M. Blaney, J. L. West, *J. Neurooncol.* **2008**, *86*, 165.
- [235] S. L. Westcott, S. J. Oldenburg, T. R. Lee, N. J. Halas, *Langmuir* **1998**, *14*, 5396.
- [236] X. Li, Y. Li, C. Yang, Y. Li, *Langmuir* **2004**, *20*, 3734.
- [237] W. Shi, Y. Sahoo, M. T. Swihart, P. N. Prasad, *Langmuir* **2005**, *21*, 1610.
- [238] B. T. M. Yugang Sun, Younan Xia, *Nano Lett.* **2002**, *2*, 481.
- [239] M. Yang, X. Yang, L. Huai, *Appl. Phys. A* **2008**, *92*, 367.
- [240] Y. Jin, X. Gao, *J. Am. Chem. Soc.* **2009**, *131*, 17774.
- [241] A.-M. Gabudean, F. Lerouge, T. Gallavardin, M. Iosin, S. Zaiba, O. Maury, P. L. Baldeck, C. Andraud, S. Parola, *Opt. Mater.* **2011**, *33*, 1377.
- [242] A. De Luca, R. Dhama, A. R. Rashed, C. Coutant, S. Ravaine, P. Barois, M. Infusino, G. Strangi, *Appl. Phys. Lett.* **2014**, *104*, 103103.
- [243] P. Zhang, Y. Guo, *J. Am. Chem. Soc.* **2009**, *131*, 3808.
- [244] K. Niikura, N. Iyo, Y. Matsuo, H. Mitomo, K. Ijro, *ACS Appl. Mater. Interfaces* **2013**, *5*, 3900.
- [245] H. Behar-Levy, D. Avnir, *Chem. Mater.* **2002**, *14*, 1736.
- [246] I. Yosef, D. Avnir, *Chem. Mater.* **2006**, *18*, 5890.
- [247] I. Yosef, R. Abu-Reziq, D. Avnir, *J. Am. Chem. Soc.* **2008**, *130*, 11880.
- [248] R. Ben-Knaz, D. Avnir, *Biomaterials* **2009**, *30*, 1263.
- [249] Y. Ben-Efraim, D. Avnir, *J. Mater. Chem.* **2012**, *22*, 17595.
- [250] Y. Aouat, G. Marom, D. Avnir, V. Gelman, G. E. Shter, G. S. Grader, *J. Phys. Chem. C* **2013**, *117*, 22325.
- [251] Y. Aouat, Y. Azan, G. Marom, D. Avnir, *Sci. Adv. Mater.* **2013**, *5*, 598.

- [252] H. Naor, D. Avnir, *J. Mater. Chem. C* **2014**, *2*, 7768.
- [253] D. Avnir, *Acc. Chem. Res.* **2014**, *47*, 579.
- [254] S. Qu, Y. Gao, X. Jiang, H. Zeng, Y. Song, J. Qiu, C. Zhu, K. Hirao, *Opt. Commun.* **2003**, *224*, 321.
- [255] S. L. Qu, C. J. Zhao, X. W. Jiang, G. Y. Fang, Y. C. Gao, H. D. Zeng, Y. L. Song, J. R. Qui, C. S. Zhu, K. Hirao, *Chem. Phys. Lett.* **2003**, *368*, 352.
- [256] B. F. Mangelson, M. R. Jones, D. J. Park, C. M. Shade, G. C. Schatz, C. A. Mirkin, *Chem. Mater.* **2014**, *26*, 3818.
- [257] D. Wang, Z. H. Zhou, H. Yang, K. B. Shen, Y. Huang, S. Shen, *J. Mater. Chem.* **2012**, *22*, 16306.
- [258] S. Besson, T. Gacoin, C. Ricolleau, J. P. Boilot, *Chem. Commun.* **2003**, 360.
- [259] T. Gacoin, S. Besson, J. P. Boilot, *J. Phys. Condens. Matter* **2006**, *18*, S85.
- [260] P.-W. Wu, W. Cheng, I. B. Martini, B. Dunn, B. J. Schwartz, E. Yablonovitch, *Adv. Mater.* **2000**, *12*, 1438.
- [261] Y. Battie, N. Destouches, L. Bois, F. Chassagneux, N. Moncoffre, N. Toulhoat, D. Jamon, Y. Ouerdane, S. Parola, A. Boukenter, *J. Nanopart. Res.* **2009**, *12*, 1073.
- [262] L. Bois, F. Bessueille, F. Chassagneux, Y. Battie, N. Destouches, C. Hubert, A. Boukenter, S. Parola, *Colloids Surf., A* **2008**, *325*, 86.
- [263] L. Bois, F. Chassagneux, Y. Battie, F. Bessueille, L. Mollet, S. Parola, N. Destouches, N. Toulhoat, N. Moncoffre, *Langmuir* **2010**, *26*, 1199.
- [264] L. Bois, F. Chassagneux, C. Desroches, Y. Battie, N. Destouches, N. Gilon, S. Parola, O. Stephan, *Langmuir* **2010**, *26*, 8729.
- [265] L. Bois, F. Chassagneux, S. Parola, F. Bessueille, Y. Battie, N. Destouches, A. Boukenter, N. Moncoffre, N. Toulhoat, *J. Solid State Chem.* **2009**, *182*, 1700.
- [266] S. De, G. De, *J. Phys. Chem. C* **2008**, *112*, 10378.
- [267] M. C. Ferrara, L. Mirengi, A. Mevoli, L. Tapfer, *Nanotechnology* **2008**, *19*, 365706.
- [268] S. Pal, G. De, *Phys. Chem. Chem. Phys.* **2008**, *10*, 4062.
- [269] E. D. Martinez, C. Boissiere, D. Grosso, C. Sanchez, H. Troiani, G. J. A. A. Soler-Illia, *J. Phys. Chem. C* **2014**, *118*, 13137.
- [270] F. Formanek, N. Takeyasu, T. Tanaka, K. Chiyoda, A. Ishikawa, S. Kawata, *Opt. Express* **2006**, *14*, 800.
- [271] K. Kaneko, H.-B. Sun, X.-M. Duan, S. Kawata, *Appl. Phys. Lett.* **2003**, *83*, 1426.
- [272] N. Kalfagiannis, P. G. Karagiannidis, C. Pitsalidis, N. Hastas, N. T. Panagiotopoulos, P. Patsalas, S. Logothetidis, *Thin Solid Films* **2014**, *560*, 27.
- [273] F. Stellacci, C. A. Bauer, T. Meyer-Friedrichsen, W. Wenseleers, V. Alain, S. M. Kuebler, S. J. K. Pond, Y. Zhang, S. R. Marder, J. W. Perry, *Adv. Mater.* **2002**, *14*, 194.
- [274] S. Porel, N. Venkatram, D. N. Rao, T. P. Radhakrishnan, *J. Appl. Phys.* **2007**, *102*.
- [275] S. Porel, N. Venkatram, D. N. Rao, T. P. Radhakrishnan, *J. Nanosci. Nanotechnol.* **2007**, *7*, 1887.
- [276] W. Sun, Q. Dai, J. G. Worden, Q. Huo, *J. Phys. Chem. B* **2005**, *109*, 20854.
- [277] G. D. Hale, J. B. Jackson, O. E. Shmakova, T. R. Lee, N. J. Halas, *Appl. Phys. Lett.* **2001**, *78*, 1502.
- [278] J. Peng, X. Xu, Y. Tian, J. Wang, F. Tang, L. Li, *Appl. Phys. Lett.* **2014**, *105*, 173301.
- [279] H. Lundén, A. Liotta, D. Chateau, F. Lerouge, F. Chaput, S. Parola, C. Brännlund, Z. Ghadyani, M. Kildemo, M. Lindgren, C. Lopes, *J. Mater. Chem. C* **2015**, *3*, 1026.
- [280] D. Chateau, A. Liotta, H. Lundén, F. Lerouge, F. Chaput, D. Krein, T. Cooper, C. Lopes, A. A. G. El-Amay, M. Lindgren, S. Parola, *Adv. Funct. Mater.* **2016**, DOI 10.1002/adfm.201601646.
- [281] M. Ishifuji, M. Mitsuishi, T. Miyashita, *J. Am. Chem. Soc.* **2009**, *131*, 4418.
- [282] M. Mitsuishi, M. Ishifuji, H. Endo, H. Tanaka, T. Miyashita, *Polym. J.* **2007**, *39*, 411.

- [283] W. Zhang, Y. Chen, L. Gan, J. Qing, X. Zhou, Y. Huang, Y. Yang, Y. Zhang, J. Ou, X. Chen, M. Qiu Zhang, *J. Phys. Chem. Solids* **2014**, *75*, 1340.
- [284] V. E. Ferry, J. N. Munday, H. A. Atwater, *Adv. Mater.* **2010**, *22*, 4794.
- [285] J.-L. Wu, F.-C. Chen, Y.-S. Hsiao, F.-C. Chien, P. Chen, C.-H. Kuo, M. H. Huang, C.-S. Hsu, *ACS Nano* **2011**, *5*, 959.
- [286] S. D. Standridge, G. C. Schatz, J. T. Hupp, *J. Am. Chem. Soc.* **2009**, *131*, 8407.