

# New developments in molecular photonics : from photoswitchable nonlinearities to nonlinear nanoplasmonics

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## ABSTRACT

We propose new strategies to increase and control molecular second-order nonlinearities, by using photoswitching processes or plasmonic resonance. First, we report on reversible switching of nonlinear optical (NLO) properties, based on the use of dipolar or octupolar metal complexes containing photochromic ligands like dithienylethene (DTE) derivatives. DTE undergo a reversible interconversion between a non-conjugated open form and a  $\pi$ -conjugated closed form. A strong relative change of the quadratic molecular nonlinearity upon visible light exposure (more than one order of magnitude) is evidenced by second harmonic generation experiments. This process is fully reversible. On another hand, we explore the quadratic NLO properties of highly NLO dyes (stilbazolium derivatives) grafted onto the surface of gold nanoparticles (NP). In spite of the fact that the plasmon resonance wavelength of gold NPs lies far from that of the second harmonic signal at 820 nm, a significant increase of the nonlinear response of this dye (when linked to a gold nanoparticle) due to surface Plasmon resonance with gold NPs is shown by Harmonic Light Scattering at 1.64  $\mu\text{m}$ . The nature of the linker has a significant influence of hyperpolarizability values, and a similar, but weaker enhancement effect, is also reported in the case of dye/NP mixtures.

**Keywords** : Nonlinear optics, metal complexes, photochromism, Plasmon resonance, gold nanoparticles, photoswitching

## 1. INTRODUCTION

The emergence of Molecular Photonics at the cross-road of physics, chemistry and device engineering is being triggered by the increasing demands in the domain of high bit rate telecommunications on one hand, and of sensor applications on the other hand. The wealth of molecular structures and the exploitation of their functional and structural flexibility open-up thoroughly renewed horizons in this domain<sup>1-4</sup>. Photonic devices containing photochromic molecules may offer valuable solutions for all-optical data storage, where both recording and reading of information are achieved by optical methods. Various physical properties can be exploited in this domain: refractive index, absorption, luminescence. In this context, photoswitching of luminescence and of NLO properties are highly promising<sup>5-7</sup>. Recently, a metal-organic molecular engineering strategy has been proposed, resulting in the synthesis of photochromic unit-containing metal complexes<sup>8</sup>. Such structures display specific advantages, especially in relation with the tuneability of their excited state energies, their strong luminescence quantum yield, and their high quadratic nonlinear response. Most studies have been based on photoswitching of luminescence so far<sup>6</sup>. These techniques are essentially based on the photo-induced modification of linear optical properties.

The expected specific interest of switching NLO properties at the molecular or material levels is related to the higher sensitivity of NLO phenomena to external perturbations, owing to the nonlinear character of the process. As an example, NLO studies have allowed to evidence a significant change of molecular quadratic nonlinearities of lanthanide derivatives when changing the nature of the rare earth central ion, whereas the linear optical properties of the same lanthanide series are strictly identical<sup>9</sup>. Here, according to the same concept, we expect that the relative change of quadratic molecular hyperpolarizabilities  $\beta$  induced by photochromic processes will be quite high (at least one order of magnitude), resulting in a very high “contrast” between both states.

Another way to increase the molecular NLO response can be based on surface plasmon resonance at the nanoscale. Noble-metal nanoparticles (NPs) have been widely investigated due to their unique size-dependent physical and chemical

properties, especially for the exaltation of optical responses<sup>10</sup>. Surface functionalisation of gold nanoparticles with various ligands resulted in the generation of nanocomposites with applications in ultrasensitive detection and imaging methods<sup>11</sup>. A number of experimental studies have been reported on the exaltation of quadratic NLO properties of molecular units by gold nanostructures<sup>12</sup>. Exaltation of second harmonic generation (SHG) from ultrathin dye layers deposited on fractal gold surfaces has been reported<sup>13</sup>. A SHG signal of individual molecules in the presence of very small gold NPs (1nm) has been evidenced in the context of biological membrane imaging<sup>14</sup>. In the present work, we will evidence a significant increase of molecular quadratic nonlinear response of NLO chromophores (stilbazolium dyes) grafted onto the surface of gold nanoparticles, in a wavelength domain far from plasmon resonance.

## 2. SWITCHING NLO PROPERTIES USING PHOTOCHROMIC METAL COMPLEXES

### 2.1. Molecular design for NLO switching

A wide choice of noncentrosymmetric dipolar and octupolar molecules, associating electron donor and electron-acceptor conjugated moieties, have been designed and synthesized on the basis of well-established molecular engineering rules<sup>1-4</sup>. Metal complexes containing conjugated organic ligands offer interesting perspectives, not only in terms of high nonlinear hyperpolarizability values  $\beta$ , but also for their potential to perform switching of their electronic or optical properties using redox processes. For example, in ferrocene-containing molecules or ruthenium complexes, it is possible to switch their NLO response by changing the oxidation state of the metal M, from  $M^{II}$  to  $M^{III}$ , then modifying its electron-donor or electron-acceptor character<sup>15</sup>. However, the switching process must be triggered electrically, then requiring additional technological steps in the elaboration of a future device.

Another strategy for NLO switching is based on the modification of the  $\pi$ -bridge using light as a trigger. These photochromic compounds are promising candidates for the elaboration of photoswitchable NLO materials. Among these, dithienylethene (DTE) derivatives are highly attractive, due to their fast response time, good reversibility and excellent thermal stability of both isomers. These properties are required for practical applications. DTE undergoes reversible conversion between a non-conjugated open form and a  $\pi$ -conjugated closed form when irradiated in the UV and visible spectral ranges, respectively. On another hand, metal complexes containing donor-substituted styryl bipyridine conjugated ligands, used as “push-pull” NLO chromophores, have been shown to display high dipolar or octupolar hyperpolarizabilities, the central metal ion improving the acceptor character of the bipyridine moiety<sup>16</sup>. In order to achieve photoswitching of NLO properties in similar metal complexes, this organic ligand has been modified by inserting a photoswitchable DTE group, resulting in a new type of 4,4'-bis(ethenyl)-2,2'-bipyridine ligand functionalized by DTE. The corresponding zinc(II) dipolar complex can be then synthesized (Figure 1). This molecule undergoes a fully reversible interconversion between a non-conjugated colorless open form and a  $\pi$ -conjugated green closed form when irradiated at 365 and 588 nm, respectively.

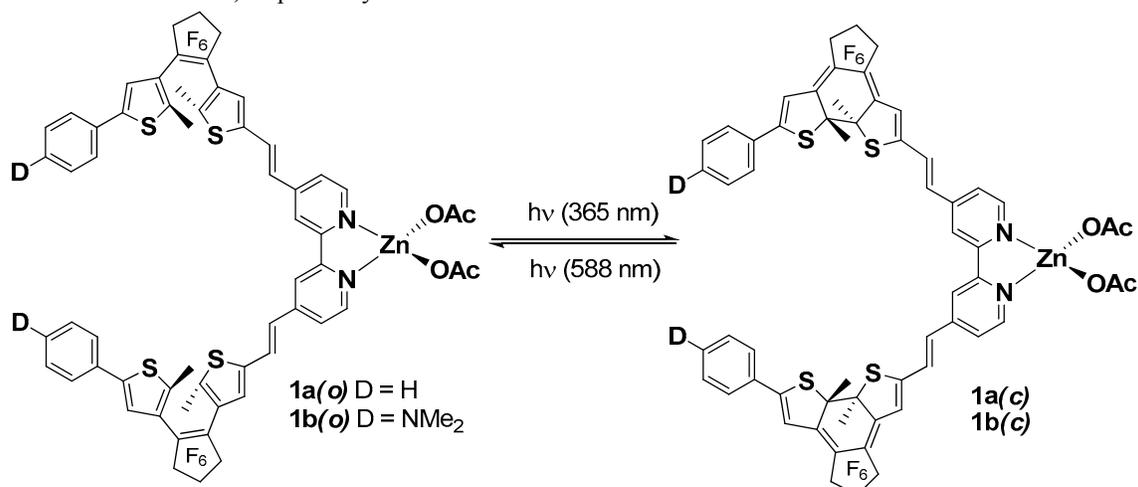


Figure 1. Structure and photoswitching mechanism of photochromic metal complexes. Two different donor groups (H and NMe<sub>2</sub>, compounds 1a and 1b, respectively) are investigated. (o) (resp. (c)) corresponds to the “open” (resp. “closed”) forms.

## 2.2. NLO characterization : experimental details

The synthesis of photochromic metal complexes has been described in detail elsewhere<sup>8</sup>. The molecular second-order nonlinearities of these neutral, dipolar complexes are measured using the electric-field induced second harmonic generation (EFISH) technique<sup>17</sup>. This method provides a direct measure of the scalar product of the permanent dipole moment ( $\mu$ ) with the dipolar component  $\beta_{vec}$  of the hyperpolarizability  $\beta$  tensor. An amplified nanosecond Nd<sup>3+</sup>:YAG laser at 1.06  $\mu\text{m}$  and 10 Hz repetition rate pumps a hydrogen Raman cell so as to obtain a larger wavelength (1.907  $\mu\text{m}$ ) for which both the fundamental and harmonic frequencies lie far away from the resonance of the investigated molecules. A Schott RG 1000 filter is used to filter out any remaining visible light from the laser flash lamp. Suitable neutral density filters are used to control the power of the incident beam and a half wave plate and polarizer are used to set the incident polarisation along the direction of the applied electric field. In addition, a band pass filter is mounted on the front of the photomultiplier used for detection, to remove any remaining radiation at the fundamental wavelength. A high voltage (8 kV), synchronized with the 1.907  $\mu\text{m}$  laser pulse, is applied across the EFISH cell containing the solution. The EFISH cell consists of a stainless steel container with two quartz optical windows, which are fixed to form a wedge shaped cavity within the cell. The inter-electrode distance is 2 mm, giving a static electric field around 25  $\text{kVcm}^{-1}$ . The cell is mounted on an electrically isolated translation stage. The whole cell is then translated horizontally relative to the incident beam to produce a periodic second harmonic generation signal (Maker fringes). Each measurement is referenced separately to the Maker fringes of the pure reference solvent used to dissolve the chromophores. A home-made computer program is used to calculate the interfringe distance and the fringe amplitude. These data are then used to calculate the  $\mu\beta_{vec}$  value of the chromophore.

The zero-frequency hyperpolarisability ( $\mu\beta_{vec0}$ ) value is inferred from the experimental  $\mu\beta_{vec}(\lambda)$  value using a two level dispersion model<sup>17</sup>:

$$\beta_{vec0} = \left(1 - \left(\frac{\lambda_0}{\lambda}\right)^2\right) \left(1 - \left(\frac{2\lambda_0}{\lambda}\right)^2\right) \beta(\lambda)$$

where  $\lambda_0$  is the maximum absorption wavelength of the molecule in solution, and  $\lambda$  the fundamental laser wavelength (here 1.9  $\mu\text{m}$ ).

## 2.3. Results and discussion

The strong modification of the optical properties of NLO metal complexes is clearly visible from the absorption spectra (Figure 2) of compound 1b in dichloromethane. A wide and intense absorption band appears in the case of the “closed” form. The solution containing the photochromic molecule becomes dark, then justifying the use of a relatively “long” fundamental wavelength (1.9  $\mu\text{m}$ ) for EFISH measurements, in order to avoid the absorption of the second harmonic signal.

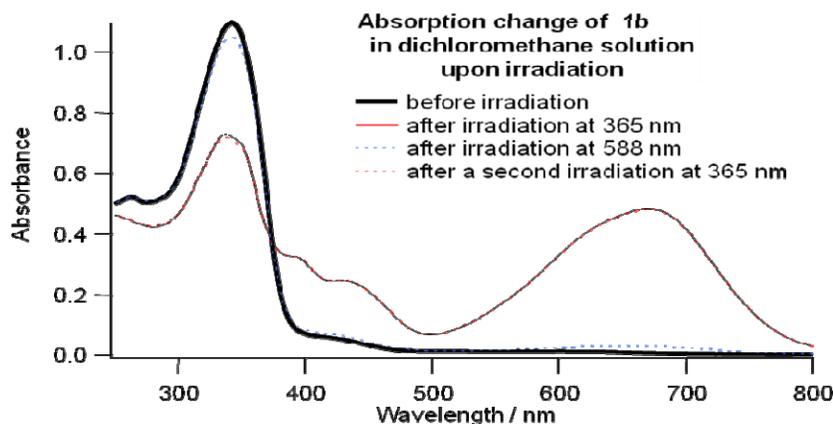


Figure 2 : Absorption spectra of 1b for the open (before irradiation) and closed (after irradiation) forms. Dotted lines : spectra corresponding to the second photochromic cycle

Maximum absorption wavelengths  $\lambda_0$  and  $\mu\beta_{\text{vec}0}$  values are given in Table 1. The  $\mu\beta_0$  values for the open forms are small, according to the fact that the  $\pi$ -conjugation between the two thiophene rings of the DTE fragment, and therefore between the donor and acceptor groups of the ligand, is broken. After the conversion to the closed form in the photostationary state, the NLO activity dramatically increases, jumping from 160 to  $1800 \times 10^{-48}$  esu for **1b**. This huge enhancement of  $\mu\beta_{\text{vec}0}$ , by a factor of 11, is clearly related to the wide delocalization of the  $\pi$ -electron system in the closed forms and confirms the high sensitivity of the NLO response to ON/OFF photo-induced switching processes. This is to our knowledge the first example of metal-containing photochromic ligands allowing an efficient switching of the nonlinear optical properties.

	$\lambda_{\text{abs}}(\epsilon)^a$ <b>open form</b>	$\lambda_{\text{abs}}(\epsilon)^a$ <b>closed form</b>	$\mu\beta_{\text{vec}}^b$ <b>open form</b>	$\mu\beta_{\text{vec}}^b$ <b>closed form</b>	$\mu\beta_{\text{vec}0}^c$ <b>open form</b>	$\mu\beta_{\text{vec}0}^c$ <b>closed form</b>
<b>1a</b>	357 (55000)	629 (32000)	90±20	2000±100	75	1000
<b>1b</b>	346 (76000)	683 (34560)	200±50	4200±200	170	1800

<sup>a</sup> nm (M<sup>-1</sup> cm<sup>-1</sup>). <sup>b</sup> 10<sup>-48</sup> esu. <sup>c</sup> 10<sup>-30</sup> esu

Table 1 : Maximum absorption wavelength  $\lambda_{\text{abs}}$  and quadratic nonlinear optical response  $\mu\beta_{\text{vec}}$  (resp.  $\mu\beta_{\text{vec}0}$ ) at 1.9  $\mu\text{m}$  (resp. at zero-frequency) for the photochromic 1a and 1b zinc complexes.

### 3. EXALTATION OF MOLECULAR NONLINEARITIES USING GOLD NANOPARTICLES

#### 3.1. Elaboration of gold nanoparticles functionalized with NLO molecules

Surface Plasmon resonance may strongly enhance the optical response, including NLO properties, of organic molecules located on the surface of a noble metal. Among the various organic structures currently used for NLO applications, 4-dimethylamino-*N*-methyl-4-stilbazolium tosylate (DAST) **1** is one of the most studied molecules. Due to its high activity, this organic salt has already been used for high-sensitive electric field sensors and Terahertz (THz) wave generation<sup>18</sup>. The cationic part of this salt will be used in the present work to investigate the influence of gold NP's on its NLO response.

Monodisperse gold NPs were synthesized in dichloromethane by reduction of AuCl<sub>4</sub><sup>-</sup> with sodium borohydride, in the presence of stabilizing agents (dodecylamine). Then thiol-functionalized gold nanoparticles **Au-3** and **Au-4** were obtained through exchange reaction of the stabilizing agent with the corresponding ligands previously dissolved in N,N-dimethylformamide (DMF)<sup>19-20</sup>. In the third set of Au<sup>0</sup>-NPs (**Au-1**), Au<sup>0</sup> surface was first capped with thiophenol. Structures of **Au-1** –**Au-4** are displayed on Figure 3.

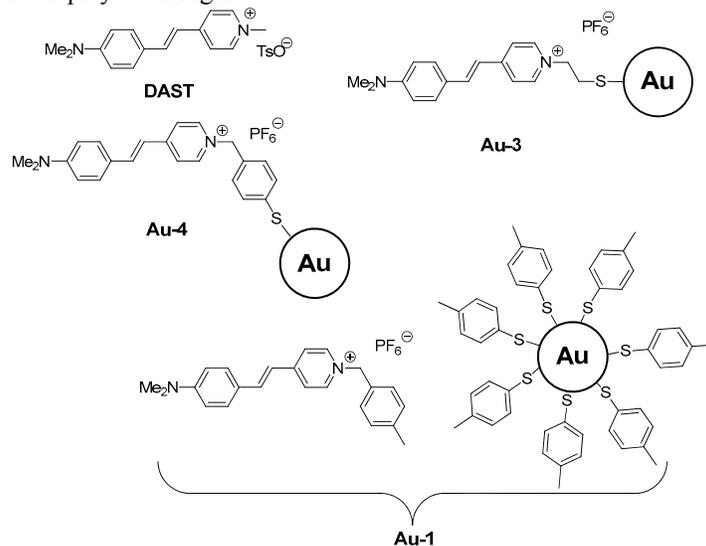


Figure 3 : Structures of **Au-3** and **Au-4** functionalized gold NPs (top), and composition of the **Au-1** sample (bottom).

TEM images of all samples show no specific aggregation phenomena. The average core diameter of these gold NPs is  $4 \pm 1$  nm.

### 3.2. Characterization of molecular NLO responses in the presence of gold NPs : Harmonic Light Scattering

In the present work, hyperpolarizability ( $\beta$ ) measurements have been made using the Harmonic Light Scattering (HLS)<sup>21</sup> technique at  $\lambda = 1.64 \mu\text{m}$  as the fundamental wavelength. EFISH is not suitable here, as the NLO organic molecules are ionic, then preventing the application of a high electric field to the solution. As the harmonic wavelength at 820 nm lies far from 2-photon resonance, any contribution from 2-photon fluorescence to HLS signal becomes negligible. The 1.64  $\mu\text{m}$  fundamental beam is emitted by an optical parametric oscillator (OPO) from GWU (VersaScan/170) pumped at 355 nm by a frequency-tripled Nd<sup>3+</sup>:YAG nanosecond laser (SAGA from Thales Laser) at a 10 Hz repetition rate. The typical energy per pulse at 1640 nm is 7 mJ. The intensity of the incoming fundamental beam is varied using a half-wave plate rotated between two crossed polarizers. HLS photons at 820 nm are focused onto a photomultiplier using two collecting lenses. The detected signal is then sampled and averaged using a Boxcar and processed by a computer. A low intensity reference beam is extracted from the main beam at a 45° incidence angle by a glass plate and focused onto a highly nonlinear NPP (*N*-4-nitrophenyl-prolinol) powder used as a frequency doubler. The variation of the second harmonic intensity scattered from the solution is recorded on the computer as a function of the reference second harmonic signal provided by the NPP powder. The expected behavior is a linear one. The reference solution is a concentrated ( $1.15 \cdot 10^{-2}$  mol L<sup>-1</sup>) solution of Ethyl Violet (EtV). Its octupolar  $\beta$  value is  $230 \cdot 10^{-30}$  esu at 1.64  $\mu\text{m}$ . Then  $\beta$  values of DAST derivative are inferred from the slopes of the resulting lines, as compared to those of the EtV solution.

### 3.3. Linear absorption spectra of DAST derivatives – Influence of gold NP's

Electronic absorption spectra of DAST derivatives and their gold NP derivatives are presented in Figure 4. Spectra of “free” DAST derivatives show an intense band, centered at 485 nm in the visible region, corresponding to the  $\pi(-\text{NMe}_2) \rightarrow \pi^*(\text{pyridinium})$  intramolecular charge transfer (ICT) excitation from the  $-\text{NMe}_2$  electron donors groups to the pyridinium acceptor moiety. The absorption spectra of the DAST derivative attached to gold NPs are made of two main absorption bands, the first one around 461 nm (resp. 474 nm) for **Au-3** (resp. **Au-4**), and the second one, with a similar intensity compared to the first band, around 541 nm (resp. 533 nm) for **Au-3** (resp. for **Au-4**). Clearly the first band corresponds to the ICT band of the pure chromophore, the second one to the surface plasmon band (SPB) of Au-NPs. A slight hypsochromic shift for the ICT band of DAST and a bathochromic shift of the SPB (for non-functionalized gold NPs) are observed after covalent linkage of the chromophores to Au-NPs. For the DAST derivative/NPs mixture, **Au-1**, the ICT band is apparently not shifted, but more intense, due to the overlap with the SPB of gold nanoparticles. This result is consistent with a physical mixing of a chromophore with NPs, the overall observed spectrum corresponding to the simple addition of the ICT band of the chromophore and the SPB band of the gold particles. For **Au-3** and **Au-4**, only chromophores grafted onto the Au<sup>0</sup> surface are detected and the ICT band is nearly as intense as the SPB band.

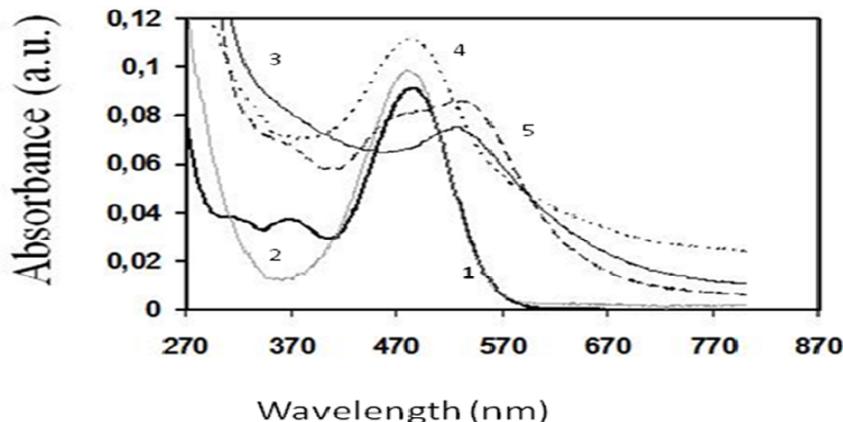


Figure 4 : Absorption spectra of free DAST derivatives (curves 1, thick line, and curve 2, thin grey line), and of a DAST derivative grafted on gold NPs according to **Au-3** (curve 3, thin black line), **Au-4** (curve 5, dashed line), and **Au-1** (curve 4, dotted line) structures.

### 3.4. NLO properties of DAST derivatives grafted of gold NPs : evidence of plasmonic enhancement

We have compared the NLO response of the **Au-3** and **Au-4** composites with a simple mixture of chromophore and gold NPs without covalent linkers or electrostatic interactions (sample **Au-1**). Results are displayed on Table 2.

Samples	$\lambda_{\text{max}}$ [nm]	$\beta(\times 10^{-30}\text{ues})$
<b>DAST derivative for Au 3</b>	483	<b>790</b>
<b>DAST derivative for Au 4</b>	483	<b>840</b>
<b>Au-3</b>	541	<b>1800</b>
	461	
<b>Au-4</b>	533	<b>2380</b>
	474	
<b>Au-1</b>	526	<b>1580</b>
	482	
<b>Au-PhSH</b>	526	<b>260</b>

**Table 2** : Maximum absorption wavelength  $\lambda_{\text{max}}$  and hyperpolarizability values per ligand unit for **Au-1 –Au-4**.

In spite of the fact that the plasmon resonance wavelength of gold NPs lies far from that of the second harmonic signal at 820 nm, we evidenced a clear exaltation factor of the hyperpolarizability of stilbazolium derivatives (up to 3 for **Au-4**) when they are grafted to a gold nanoparticle. The nature of the linker has a significant influence of  $\beta$  values, the phenyl group favorizing the interaction of the chromophore with the gold NP. A weaker, however detectable magnification is also observed for a simple mixture of stilbazolium ligand and NPs functionalized with thiophenol (**Au-PhSH**).

Further studies will focus on the influence of the NP shape on the NLO response, e.g. by using rod-like gold particles. A spectroscopic approach using the tuneability offered by the OPO source should permit a systematic study of the impact of plasmon resonance on the NLO response of the ligands. Reaching high exaltation factors might allow for the detection of the SHG emission from single objects involving a weak number of NLO molecules, with interesting perspectives in imaging applications.

## 4. CONCLUSION

We have evidenced two efficient ways to improve and to control quadratic molecular nonlinearities. By attaching photochromic ligands to metal ions, we have been able to increase static molecular NLO responses by one order of magnitude, in-keeping an excellent photochemical stability and a high reversibility of the photochromic process. On another hand, we have evidenced a significant enhancement of the molecular hyperpolarizability of DAST derivatives when grafted to gold nanoparticles, even in a non-resonant regime. This work confirms the interest of hybrid organic-inorganic structures from nonlinear optics and opens interesting perspectives for applications in the domain of optical storage and bio-imaging.

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