Promoting Spontaneous Second Harmonic Generation through Organogelation

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Supporting Information Placeholder

ABSTRACT - An organogelator based on the Disperse Red NLO-phore was synthesized according to a simple and efficient three-step procedure. The supramolecular gel organization leads to xerogels which display a spontaneous second harmonic generation (SHG) response without any need for pre-processing and this SHG activity appears stable over several months. These findings, based on an *intrinsic* structural approach are supported by favorable intermolecular supramolecular interactions, which promote a locally non-centrosymmetric NLO-active organization. This is in sharp contrast with most materials designed for SHG purposes, which generally require the use of expensive or heavy-to-handle *external* techniques for managing the dipoles alignment.

Tremendous efforts are continuously dedicated to the development of better organic and SHG active materials for various applications in the fields of photonics,[1] optoelectronics,[2,3] or anti-counterfeiting.[4] Two major requirements have to be fulfilled in order to prepare these materials. Firstly, the corresponding molecules have to display strong hyperpolarizabilities. In this direction, hundreds of publications report the synthesis and characterizations of organic push-pull conjugated NLO-phores.[5,6] Secondly, the latter have to be organized in a non-centrosymmetric fashion in order to prevent destructive interferences between second harmonic-generated photons. As a consequence, various approaches have been successfully considered in order to prepare SHG-active materials. These include the utilization of chiral compounds,[7,8] Langmuir-Blodgett films,[9] self-assembled layers,[10,11] elaborated matrices,[12] or corona poling.[13] Though efficient, these strategies require expensive conditions (*i.e.* chiral NLO-phores) or heavy-to-handle pre-treatments (*e.g.* corona poling) that impede their transfer at larger scales. Therefore, it appears of utmost interest to develop new methodologies to process SHG-active materials, by designing derivatives with specific functions able to promote the required organization for instance. The present work falls within this approach with the utilization of an organogelator. Gel-based materials have already shown their strong potential in the context of optoelectronics and photonics,[14-17] notably thanks to their high degree of organization at the supramolecular scale and their user-friendly processing. Various external methodologies have been developed in the past to promote the alignment of the micro- and nanofibers responsible for the gel state, be that through application of electric or magnetic fields along their formation or for instance shear

stress.[18-21] Conversely, our approach consisted in constraining SHG-active units in the desired non-centrosymmetric head-to-head arrangement without any additional external mediation. This could be accomplished thanks to the use of urea moieties, well-known for both their narcissistic character in supramolecular chemistry and their ability to promote gelation.[22] This proof-of-concept study was led on the Disperse Red unit, a benchmark SHG-active chromophore.

The straightforward synthesis of compound **1** (Scheme 1 and SI) could be led on the gram-scale. The starting Mitsunobu reaction allowed for the isolation of intermediate **2** in a single step with a 88% yield.[23] The latter was quantitatively converted into its amino analogue **3** (see SI), which afforded the target compound **1** as a deep red solid in a 76 % yield, through a condensation with dodecyl isocyanate.
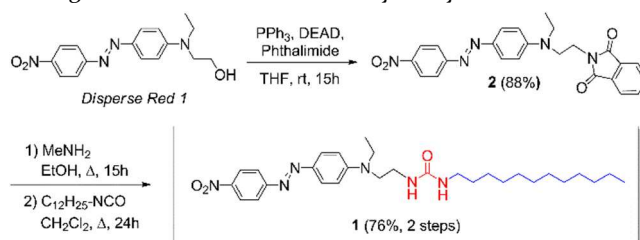
**Scheme 1.** Three-step synthesis of organogelator **1**.

The organogelating properties of compound **1** were investigated in a wide range of solvents, which differ by their dielectric constants, boiling points and Hansen solubility parameters. Over the seventeen tested solvents, nine proved to be gelled by compound **1** (Figure 1 and Table S1), with moderate critical gelation concentrations comprised between 10 and 50 mg.mL^{-1} ($2.10^{-2} – 10^{-1}$ mol.L^{-1}).
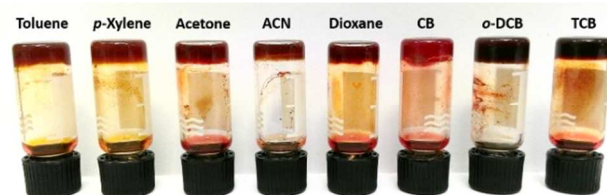
Figure 1. Organogels obtained from **1** in various solvents. ACN stands for acetonitrile, CB for chlorobenzene, *o*-DCB for *o*-dichlorobenzene and TCB for 1,2,4-trichlorobenzene.

Though no obvious correlation between the physico-chemical properties of the solvents and the obtaining of a gel phase could be highlighted (See Table S1 and Figure S1),[24] these results confirm the relevance of our strategy to design gelator **1**. The corresponding solid materials obtained after evaporation of the solvent, *i.e.* xerogels, were prepared by

depositing a piece of gel material over a glass slide and subsequent evaporation of the solvent. This simple method guarantees a lower effect of the surface on the observed microstructures and hence, on their properties. These materials were characterized by infrared absorption spectroscopy, X-ray powder diffraction analyses as well as optical and electron microscopies. The solvent of preparation does not significantly impact the IR spectrum or the diffractogram (Figures S2 and S3), which suggests that similar interactions and organizations are reached whatever the solvent under consideration. On the other hand, the recorded micrographs confirm the systematic occurrence of a dense network of intercrossed microstructures (Figure 2 and Table S2) but most importantly, this study allows for highlighting a strong solvent-structure dependency. For instance, well-defined microcrystals were observed in polar solvents displaying low boiling points (acetone, acetonitrile – Table S2) while densely packed microstructures were observed with aromatic solvents. Another important observation lies on the birefringence of these materials, which were systematically observable by polarized light optical microscopy (Table S2). This demonstrates these xerogels are anisotropic structures that display a high degree of structural organization.
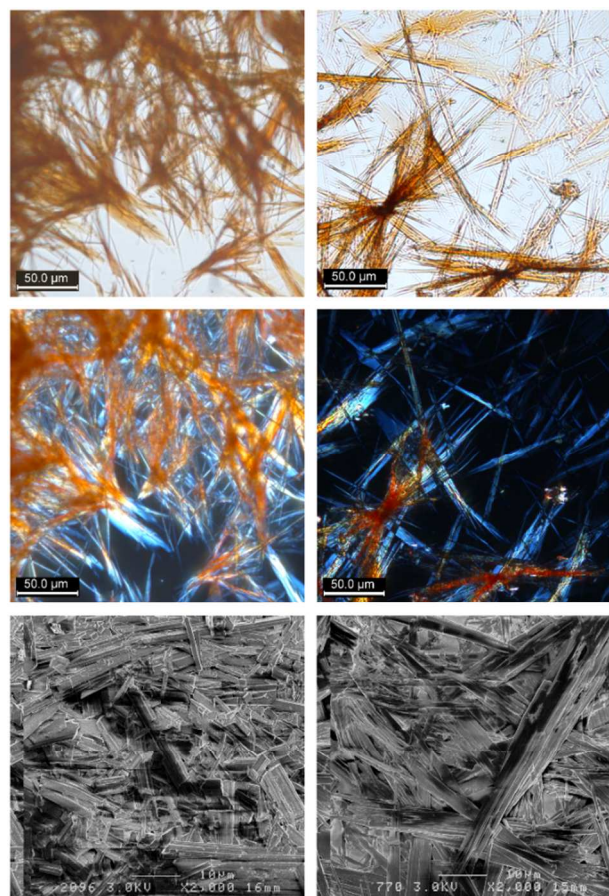
Figure 2. Optical microscopy with non-polarized (top) and polarized (middle) light as well as electron micrographs (bottom) of **1**-based xerogels prepared from dioxane (left) and octan-1-ol (right).

The same xerogels were subsequently studied by second harmonic generation microscopy employing the setup presented in Figure 3 (See also Figure S4 and its description for further details). In this setup, the objective is motionless and the sample is studied by measuring point-by-point the SHG

response of the material thanks to a computer-controlled X-Y platform. The device also includes an eyepiece to position the sample and check that no degradation occurs upon irradiation. The voxel, that is the volume in which the irradiation intensity is powerful enough to promote SHG, is estimated to be about 74 μm^3. This important assessment indicates the local non centrosymmetry of the material is probed at the microscale. In order to avoid a "false positive", control experiments were first led on films prepared from solutions of reference compound **4** (*N,N*-diethyl-4-(4-nitrophenylazo)aniline) (Scheme S1) or Disperse Red 1 itself in various solvents. Whatever the conditions, we were unable to detect any second harmonic signal in the latter cases.
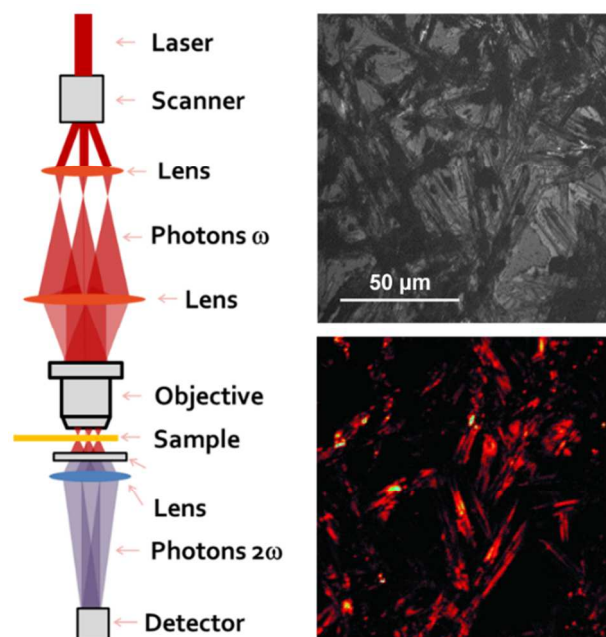
Figure 3. *Left:* Schematic representation of a SHG microscope (for a detailed version, see Figure S4). *Right:* Optical micrograph (top) and corresponding SHG image (bottom) obtained from a **1**-based xerogel prepared from octan-1-ol after a five-month ageing.

The SHG micrographs of the xerogels prepared from gelator **1** and different solvents are presented in Table S3. These prove to display a SHG response in all cases and match the corresponding optical images. Since SHG is a polarization-dependent phenomenon and since all the microstructures are not oriented along the same axis, all the objects cannot be SHG active simultaneously. However, the rotation of the polarization plane allows for turning on and off the SHG response of the microstructures under consideration (Movie S1). These results constitute a first experimental evidence that organogelator **1**, though achiral, is capable to generate a second harmonic without any need for pre-treatment (*e.g.* corona poling, shear-induced orientation,...). Interestingly, depending on the solvent of preparation, the SHG response varies, which appears reasonable since very different microstructures are obtained. De Greef, Meijer and coworkers have recently showed how crucial the choice of the solvent is to control the self-assembly process and hence, the associated properties.[25] However, to the best of our knowledge, such an influence has never been reported so far in the context of SHG-active materials. Attempts to quantify the SHG response depending on the solvent of preparation were also

performed through the Maker fringes experiment. However, the samples proved to be highly scattering, which impeded quantitative measurements.

SHG microscopy experiments were also led 6 months after the first images were recorded and demonstrated the good stability of the SHG response over long timescales (Figure 3; the SHG image recorded with the same sample right after the evaporation of the solvent is available in Table S3. The SHG-active xerogels prepared from acetonitrile and acetone were also aged and studied 6 months later (see Figure S5)). Such a behavior is in sharp contrast with the classic case of dyes dispersed in a polymeric matrix and processed by corona poling.[26] Indeed, after few weeks, the latter materials usually do not display SHG activity anymore because of relaxation processes occurring within the material and leading to the undesired centrosymmetric head-to-tail arrangement. In light of the structure of gelator **1**, we believe the different possible supramolecular interactions, *i.e.* π–π stacking, hydrogen bonds and dispersion forces, lock gelating molecules in the desired head-to-head arrangement. This hypothesis was further confirmed through X-ray diffraction analyses led on monocrystals of compound **5** (see SI for synthetic details and characterizations), which is functionalized by an octyl chain instead of the dodecyl one to promote crystallization (see Figures S6 and S7).[27] The corresponding X-ray crystal structure demonstrates the occurrence of a hydrogen bonding network between urea functions and more importantly, a phase segregation between chromophoric units on one hand and alkyl chains on the other hand. In order to get insight on the role of the different supramolecular forces, concentration-dependent NMR analyses were led on compound **1** in deuterated chloroform (Figure S8). These showed a significant upfield shift of the signals associated to urea protons (from 4.49 and 4.30 ppm at 20 mM to 4.40 and 4.21 ppm at 0.35 mM) and a small and progressive downfield shift of the aromatic signals upon decreasing the concentration. Such observations underline the prominent role of urea functions in the aggregation process and suggest π–π interactions only have a minor contribution.

In summary, an achiral compound derived from the benchmark SHG-active Disperse Red 1 unit has been synthesized in an efficient and simple three-step procedure. Thanks to its well-suited functionalization, gels were obtained in very different solvents, affording microstructures with miscellaneous shapes and spectroscopic properties. Most importantly, our strategy, which involves an intermediate gel state for the preparation of SHG-active materials, proved to be relevant since the studied xerogels systematically showed stable SHG responses over several months. To our knowledge, this is the first example of spontaneous second harmonic generation produced thanks to an achiral gelator. Presently, our efforts consist in studying alternative organogelators, which also display spontaneous second harmonic generation in order to get additional insights over the scope of this supramolecular approach in the construction of well-defined nanostructures.

ASSOCIATED CONTENT

Supporting Information

Experimental details, ${}^1H$, ${}^{13}C$ NMR and UV-visible spectra, additional optical, electron and SHG micrographs as well as a detailed and commented scheme of the SHG microscope.

This material is available free of charge via the Internet at http://pubs.acs.org."

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Author Contributions

A. Belén Marco and Fatima Aparicio made equal contributions to the present article.

Notes

The authors declare no competing financial interests.

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(27) Despite numerous attempts, single crystals of compound **1** could not be obtained. This is the reason why reference compound **5** was synthesized by reacting amine **3** with octylisocyanate (see SI). The corresponding X-ray crystal structure was deposited on the Cambridge Database (CCDC 1486984).

Spontaneous Second Harmonic Generation from Gels
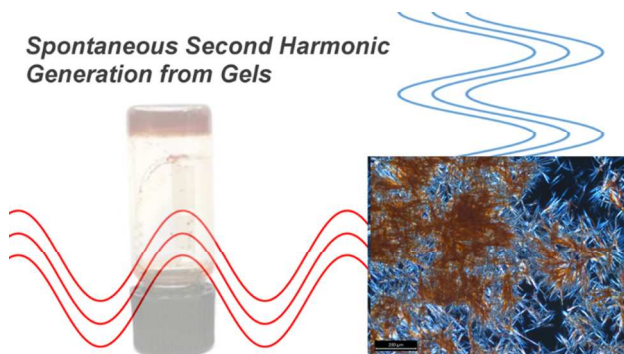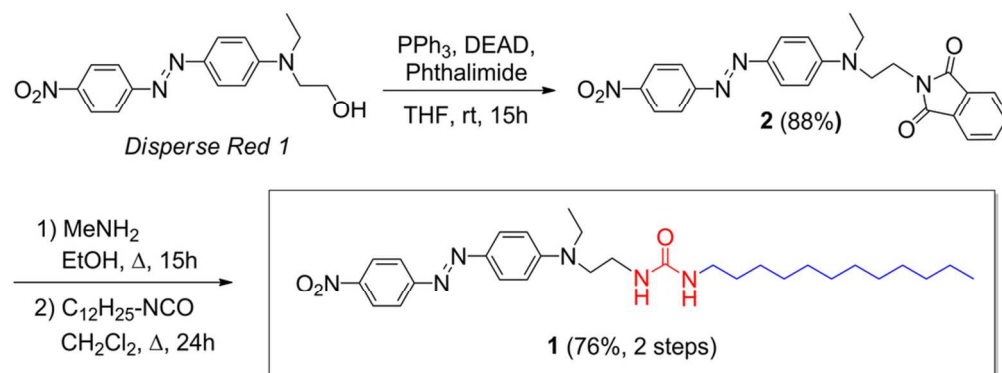
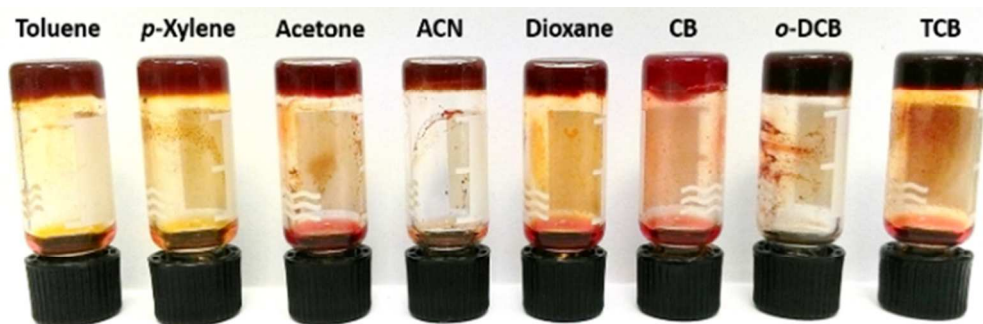Scheme 1. Three-step synthesis of organogelator 1.
90x33mm (300 x 300 DPI)

Figure 1. Organogels obtained from 1 in various solvents. ACN stands for acetonitrile, CB for chlorobenzene, o-DCB for o-dichlorobenzene and TCB for 1,2,4-trichlorobenzene.
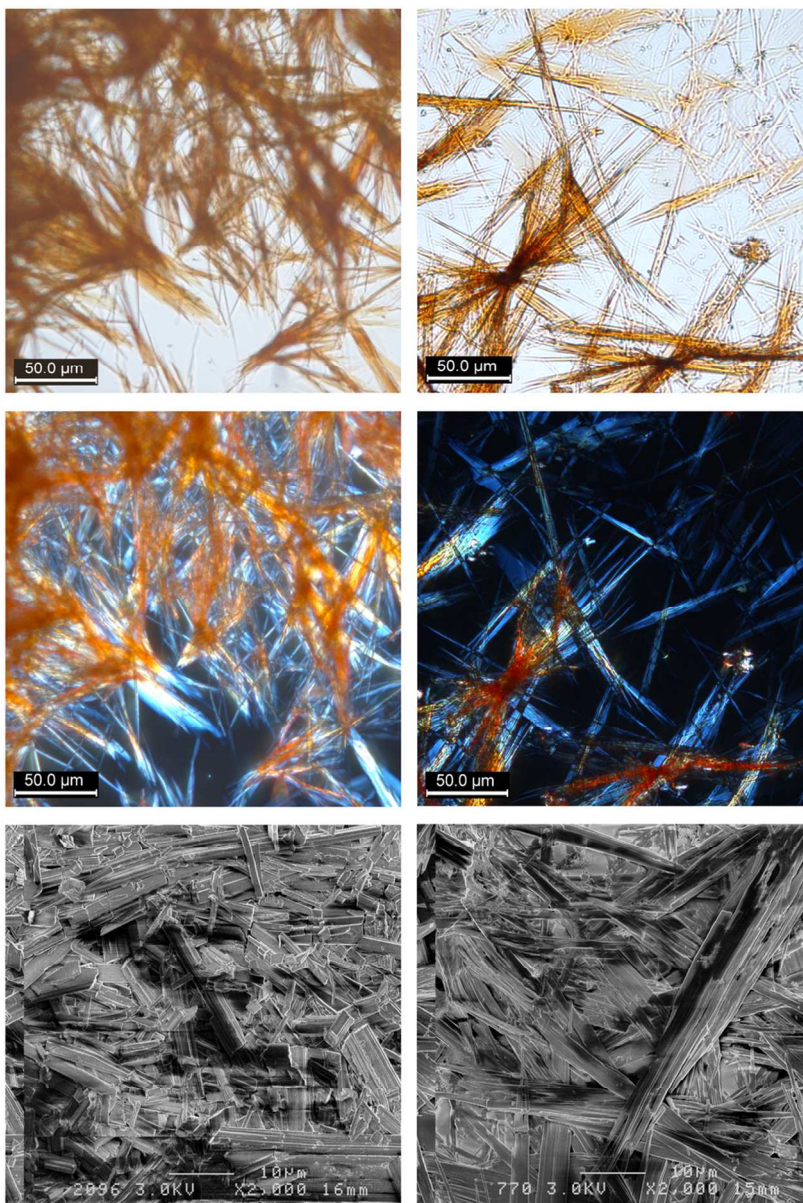85x28mm (300 x 300 DPI)

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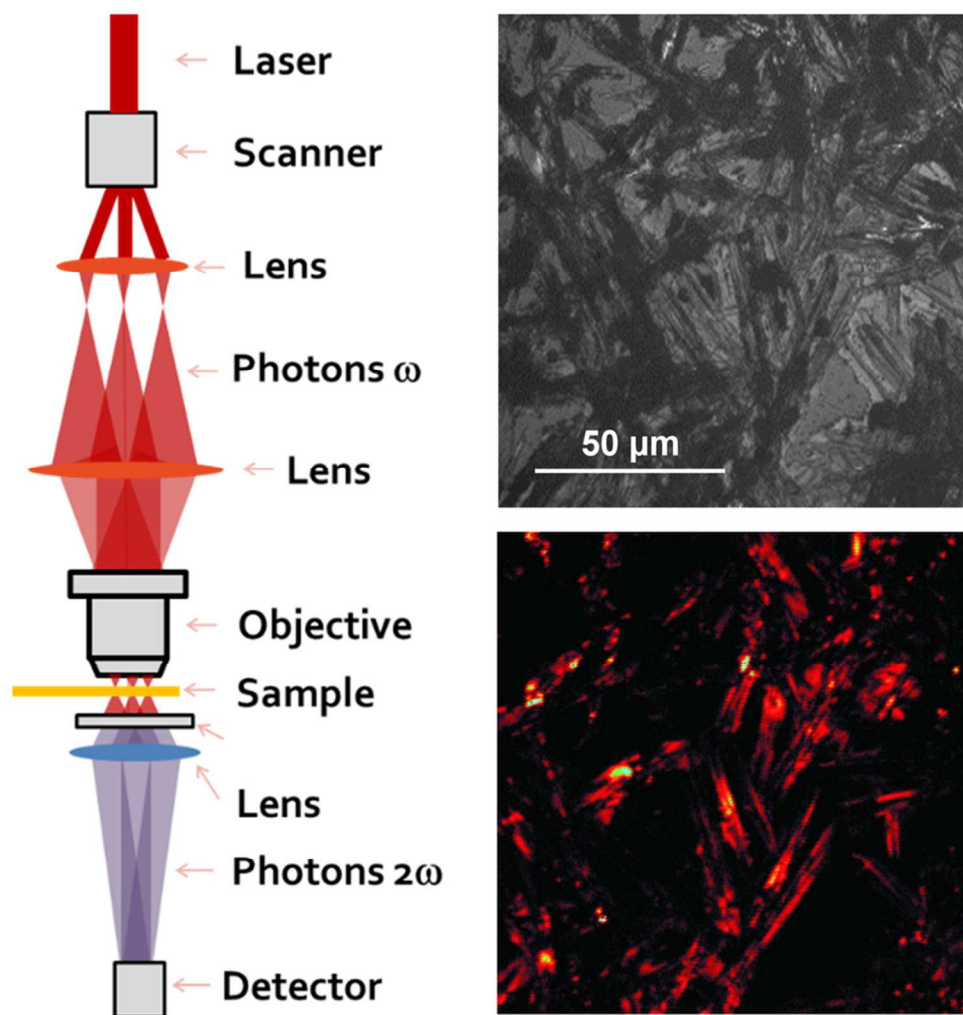45
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Figure 2. Optical microscopy with non-polarized (top) and polarized (middle) light as well as electron micrographs (bottom) of 1-based xerogels prepared from dioxane (left) and octan-1-ol (right).
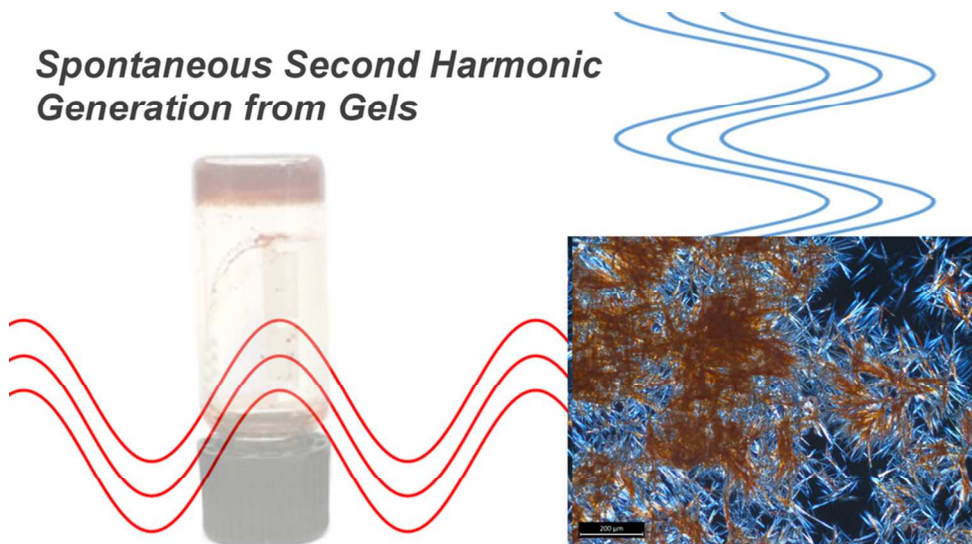85x125mm (300 x 300 DPI)

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Figure 3. Left: Schematic representation of a SHG microscope (for a detailed version, see Figure S4). Right: Optical micrograph (top) and corresponding SHG image (bottom) obtained from a 1-based xerogel prepared from octan-1-ol after a five-month ageing.
85x91mm (300 x 300 DPI)

Spontaneous Second Harmonic Generation from Gels

TOC image
85x47mm (300 x 300 DPI)