# Promoting Spontaneous Second Harmonic Generation through Organogelation

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Ⓢ *Supporting Information*

**ABSTRACT:** An organogelator based on the Disperse Red nonlinear optical chromophore 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 preprocessing, and this SHG activity appears to be 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 second harmonic generation (SHG)-active materials for various applications in the fields of photonics,[1] optoelectronics,[2,3] or anticounterfeiting.[4] Two major requirements have to be fulfilled in order to prepare these materials. First, the corresponding molecules have to display strong hyperpolarizabilities. In this direction, hundreds of publications report the synthesis and characterizations of organic push−pull conjugated nonlinear optical chromophores (NLO-phores).[5,6] Second, 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 pretreatments (e.g., corona poling) that impede their transfer at larger scales. Therefore, it appears to be of utmost interest to develop new methodologies to process SHG-active materials, by designing derivatives with specific functions that are 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 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 during their formation or, for instance, shear stress.[18−21] Conversely, our approach consisted of 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 done on the Disperse Red unit, a benchmark SHG-active chromophore.

The straightforward synthesis of compound **1** (Scheme 1 and Supporting Information (SI)) could be done on a gram scale.

**Scheme 1. Three-Step Synthesis of Organogelator 1**
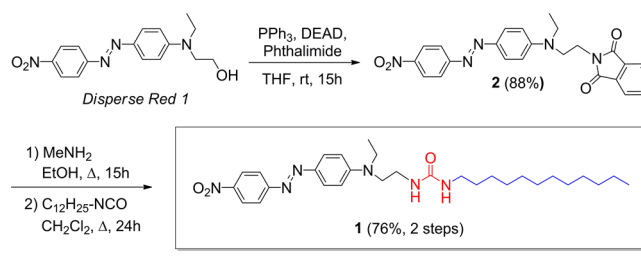


The starting Mitsunobu reaction allowed for the isolation of intermediate **2** in a single step with a 88% yield.[23] The latter was quantitatively converted into its amino analogue **3** (see SI), which afforded the target compound **1** as a deep red solid in 76% yield, through a condensation with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

The organogelating properties of compound **1** were investigated in a wide range of solvents, which differed in their dielectric constants, boiling points, and Hansen solubility parameters. Over the 17 tested solvents, nine proved to be gelled by compound **1** (Figure 1 and Table S1), with moderate critical gelation concentrations between 10 and 50 mg·mL$^{-1}$ (2 × 10$^{-2}$−10$^{-1}$ mol·L$^{-1}$).
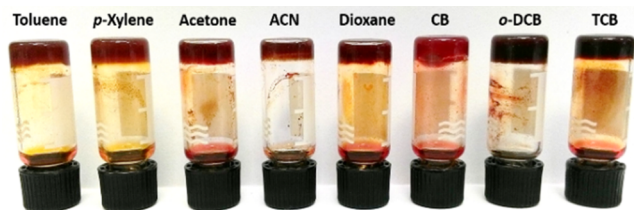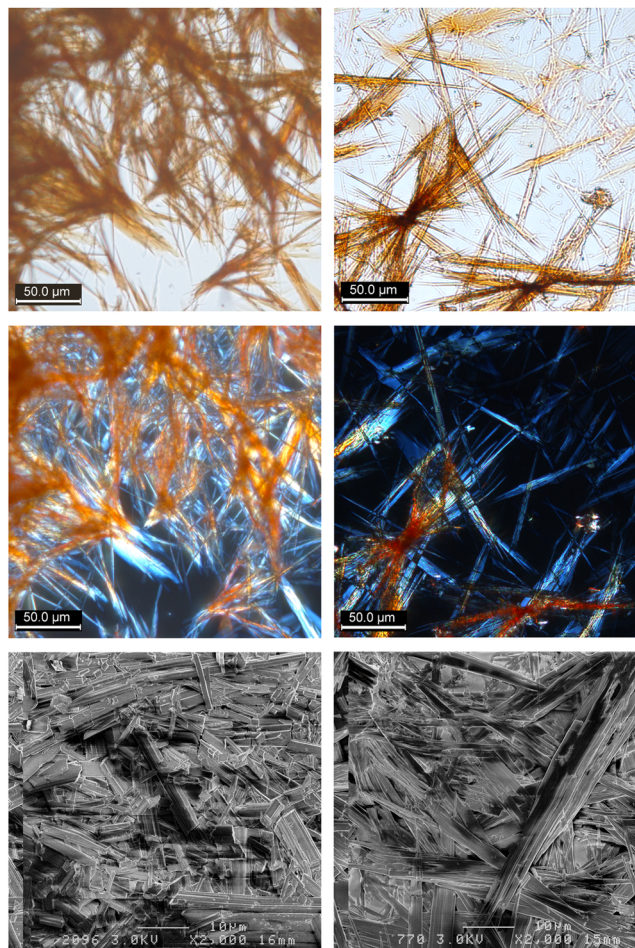
**Figure 1.** Organogels obtained from **1** in various solvents. ACN, acetonitrile; CB, chlorobenzene; o-DCB, o-dichlorobenzene; and TCB, 1,2,4-trichlorobenzene.



**Figure 2.** Optical microscopy with nonpolarized (top) and polarized (middle) light as well as electron micrographs (bottom) of **1**-based xerogels prepared from dioxane (left) and octan-1-ol (right).

Though no obvious correlation between the physicochemical 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 subsequently evaporating 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 (IR) absorption spectroscopy and X-ray powder diffraction analyses as well as optical and electron microscopies. The solvent used in the 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 in the birefringence of these materials, which were systematically observable by polarized light optical microscopy (Table S2). This demonstrates that these xerogels are anisotropic structures that display a high degree of structural organization.

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 $\mu m^3$. 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 done 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.

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 able to generate a second harmonic without any need for pretreatment (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 co-workers 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 done 6 months after the first images were recorded and demonstrated the good stability of the SHG response over long time scales (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
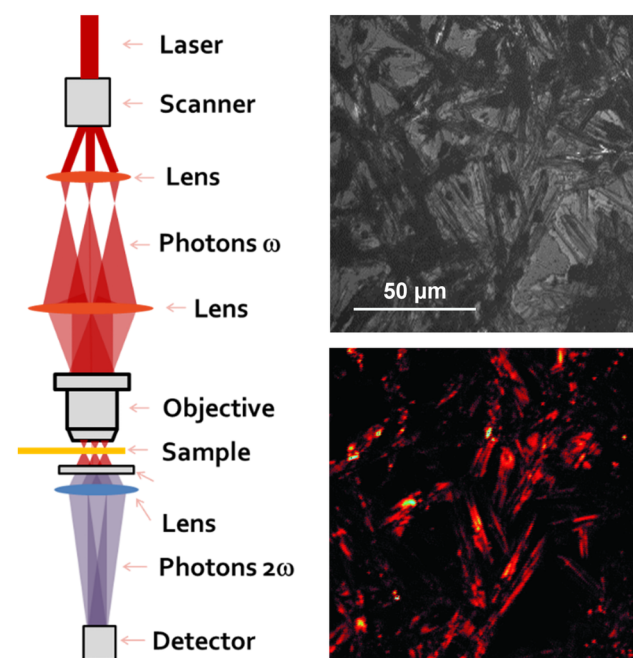
**Figure 3.** (Left) Schematic representation of a SHG microscope (for a detailed version, see Figure S4). (Right) Optical micrograph (top) and corresponding SHG image (bottom) obtained from a **1**-based xerogel prepared from octan-1-ol after a 6-month aging.

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., $\pi-\pi$ 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 done 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 done on compound **1** in deuterated chloroform (Figure S8). These showed a significant upfield shift of the signals associated with 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 $\pi-\pi$ interactions have only 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 are focused on 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

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b04554.

> Experimental details; ^{1}H and ^{13}C NMR and UV−visible spectra; additional optical, electron, and SHG micrographs; and a detailed scheme of the SHG microscope, including Tables S1−S3, Figures S1−S9, and Scheme S1 (PDF)
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> Movie S1, showing rotation of the polarization plane, allowing for turning on and off the SHG response of the microstructures under consideration (AVI)

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A.B.M. and F.A. contributed equally to the present article.

### Notes
The authors declare no competing financial interest.

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