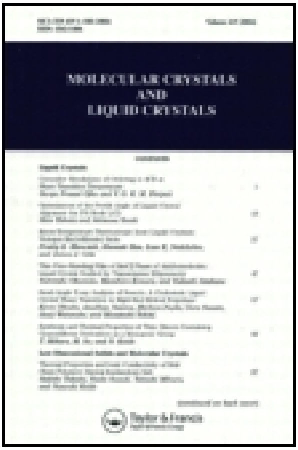

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Chlorine-Substituted Bent-Core LC-Based Sono-Gel Hybrid Materials: Synthesis and Optical Properties

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Chlorine-Substituted Bent-Core LC-Based Sono-Gel Hybrid Materials: Synthesis and Optical Properties

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We implemented the catalyst-free sonogel method to disperse and encapsulate a chlorine substituted thermotropic bent shaped liquid crystalline compound. By this means, advanced organic-inorganic hybrid materials with high optical and mechanical quality, suitable for different kind of optical applications, were obtained. Bent-core molecules have shown interesting optical properties, which have not yet been investigated in the solid-state. Therefore, we implemented the sonogel route to fabricate highly pure SiO_2 porous glassy networks which allowed the inclusion of this kind of mesogens in the colloidal sol-state. In this work, we present the preparation and optical performance of these amorphous "banana"-based hybrids via absorption and fluorescence spectroscopies, electro-optical and cubic third-harmonic generation nonlinear optical measurements.

Keywords: bent-core molecules; hybrid materials; liquid crystals; NLO; sol-gel; sonogel

1. INTRODUCTION

Optics and particularly non-linear optics have emerged in the last decades as very important research fields providing several high-tech

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applications in opto-electronics, photonic technologies, and optical data storage and processing [1–5]. During the past two decades, considerable progress has been made in understanding the factors that affect the molecular and material properties for linear and non-linear optical applications; recent investigations have demonstrated that organic materials represent a better alternative due to their fast response times, lower dielectric constants, better processability characteristics, lower production costs and enhanced NLO responses [3–6]. Under this framework, materials such as push-pull polymers, guest-host polymeric structures, organometallic complexes, ferroelectric and anti-ferroelectric liquid crystalline (LC) materials, and recently organic-inorganic SiO_2 based sol-gel hybrid composites have also been intensively investigated regarding their optical and NLO properties. The sol-gel technique has been intensively used as a standard method to confine and encapsulate diverse organic dopant species into glassy networks with high porosity on the nanometric length scale; in this way advanced organic-inorganic hybrid materials with interesting chemical and physical properties can be produced. Numerous applications have been proposed in recent years for these kinds of composites in several research fields of optics and photonics. Effects such as optical limiting (OL), photorefractivity, second and third harmonic generations (SHG, THG), nonlinear refraction, photocromicity, electro-optical switching and applications in sensing and storage devices, color displays, biomedicine and tunable solid state dye laser systems, among others have been successfully demonstrated [7–13]. It has been a difficult task however, to combine the synthesis of many of these promising organic molecules with the desired optical properties, usually expected in the solid-state at room temperature. The optimal inclusion of these molecular systems into an amorphous inorganic SiO_2 matrix to provide alternative low cost solid state optical materials has been also a challenging task of current interest. Other important aspects to be considered in the development of efficient devices suitable for optical sciences and photonics are the material malleability and the mechanical stability, requirements which are necessary in several technological implementations, for instance, in optical glasses and waveguiding systems [6–9,14]. In such applications, deposition of high quality organic thin films is essential to fill up the corresponding optical channels and circuitry, which have to remain stable for long periods of time.

From the sol-gel sciences perspective, the easy material possessing offered by the colloidal state, the low possessing temperature, the good resistance against environmental degradation, the higher thresholds for optical damage with respect to polymer matrix and recent developments on the deposition of doped sol-gel thin film layers largely satisfy the requirements mentioned above [6–9,13]. The high malleability of these materials means that they can adopt a very wide variety of shapes required for photonic purposes. Once the drying process is completed, the rigidity of the hybrid sol-gel material in the desired format can be achieved. The constituting organic compounds will contribute to a desired physical or chemical property, whereas the inorganic part of the composite increases its mechanical and thermal strength [13,15–17]. These materials can show, depending on the purity of the sol-gel precursor solvents, a very stable behavior within a wide range of temperatures. Thus, the different optical properties of the organic dopant species are preserved without decomposition of the fragile guest molecules.

In this work, we report the development of bulk catalyst-free chlorine substituted bent core LC based sonogel hybrid materials and their linear, electro-optical (EO) and nonlinear optical (NLO) characterizations. Such bent-shaped (commonly called "banana" molecules) compounds have been intensively studied in recent years due to their promising technological applications in EO-switching and NLO-devices [18–23]. Until now and to the best of the authors' knowledge, no reports concerning the NLO- and switching EO-properties of bent-core LC based hybrid SiO_2 glasses have been published in the literature. Therefore, we used a chlorine substituted banana-molecule as dopant material to create solid state sonogel hybrids suitable for optical characterization, taking advantage of the novel catalyst-free (CF) sonolysis route in order to produce highly pure sol-gel samples generated via a sonochemical reaction, induced by ultrasonic (US) irradiation. This new approach has been recently developed in our research group and successfully implemented to develop several hybrid composites suitable for optical applications [24–28]. The sonogel materials obtained by this method exhibit an amorphous SiO_2-matrix with large surface areas, high purity level and nanometric porosity; which provides a favorable environment for the inclusion of interesting organic compounds with optical functions. In order to generate CF-sonogel materials, energetic pulsed ultrasonic waves, instead of acidic and basic catalysts, are applied at the TEOS/H_2O (tetraethyl-ortosilicate/three-distilled water) reactants interface to produce acoustical cavitation. After drying, the formed hybrid composites showed good physical properties suitable for several optical functions: high dopant concentrations, high micro-structural homogeneity, stable mechanical properties (monolith structure), high optical quality and high laser damage thresholds.

Although the synthesis of the first "strongly" bent-core compound can be traced back to 1929 [29–30], their smectic properties were appreciated only after their synthesis by Matsunaga *et al.* in 1993 [31–32]. Soon after, it was realized that due to closed packing requirement bent-core molecules can be polar [33–34]. This polar packing together with director tilt can give rise to chiral layer structures without chirality in the molecular level [35]. In the first few years of experimental studies six different 'banana liquid crystal' textures have been observed and labelled as B_1,. . ., B_6 according the chronological order of their observations [19,36]. Recently, two new textures have been recognized and labelled as B_7 and B_8, respectiveley [19,36–37]. Several of these phases present antiferroelectric (*AFE*) ground states, either in synclinic-*racemic* or anticlinic-*chiral domain* structures. The *AFE* arrangement can be easily switched by suitable external electric fields, to a ferroelectric (*FE*) state. In general, the bent-shape of typical alkyl or alkyloxy-based molecule, results from linking two benzylideneaniline-groups to 1,3-dihydroxy-benzene by an ester linkage. An alkyloxy/alkyl-chain is connected to each benzylidene-aniline-group [19,36–38]. On a molecular level, the structure of bent-shaped compounds show a non-centrosymmetric distribution of the conjugated π-electrons-system resulting in a permanent dipole moment along the bent direction, which is a key point for NLO-applications [18–22]. In this way, bent-core compounds seem to be ideal candidates to fabricate solid-state EO-active composites via the sonogel route.

The experimental results showed in this work, have been carried out as a first step to develop photonic organic-inorganic devices, and as a practical alternative to expensive inorganic crystals, where the use of specially designed bent-core NLO-LC-molecules plays an important role.

2. EXPERIMENTAL SECTION

2.1. Characteristics of the Chlorine Substituted Bent-Core LC-Molecules

The synthesis and characterization of the implemented chlorine substituted thermotropic bent shaped compound: 4-chlororesorcinol bis[4-(4-*n*-dodecyloxybenzoyloxy) benzoate] and homologous series, showing new nematic and monotropic phases have been recently reported by the Halle group in Germany [39–40]. In these works Weissflog *et al.* and Pelzl *et al.* showed that 4-chlororesorcinol bis[4-(4-n-dodecyloxybenzoyloxy) benzoate] forms two mesophases with unusual properties. The high temperature phase is a nematic (N)

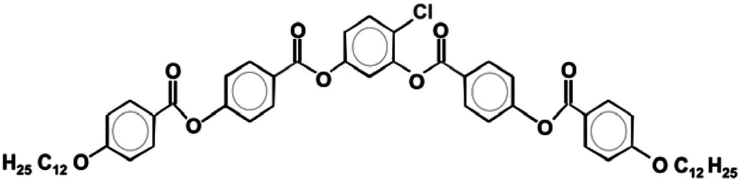


FIGURE 1 Chemical structure of the implemented chlorine substituted bent-core (12Cl) compound.

phase which spontaneously exhibits domains with opposite handedness and shows a smectic-like fan-shaped texture on application of a sufficiently high electric field. The low temperature phase is a highly viscous optically isotropic phase which forms chiral domains of opposite handedness (denominated here X-phase). X-ray investigations provided evidence that this phase possesses a periodicity with reduced long range order. Thus the usual cubic phase is ruled out. Specifically, as shown in Figure 1, we implemented compound **12Cl** [40] for the fabrication of hybrid sonogel structures, the synthesis of this compounds was achieved by the reaction of 4-chlororesorcinol with the corresponding 4-(4-n-alkyloxybenzoyloxy)benzoic acids, using dicyclohexylcarbodiimide according to the method already described for 4-chloro-1,3-phenylene bis[4-(4-n-dodecyloxybenzoyloxybenzoate] [39]. The thermal properties for compound **12Cl** are given in Table 1.

2.2. Preparation of Catalyst-Free Sonogels as Host Matrix for Chlorine Substituted Bent-Core LC-Molecules

The sol-gel method has been frequently used to synthesize amorphous SiO_2 based on the hydrolysis of different precursors such as TEOS, TMOS, etc., followed by condensation reactions of the hydrolyzed species. This methodology has been widely adopted as a suitable way to obtain glassy organic doped materials with good optical and mechanical quality. Both hydrolysis and condensation reactions occur

TABLE 1 Transition Temperatures (°C) and Associated Enthalpy Changes (KJ mol^{-1}) for the 12Cl Bent-Core Compound (from [40])

Compound	Phase transition (°C) and associated enthalpy change (KJ mol^{-1})						
12 Cl	Cr	98 [38.7]	X	80 [9.1]	N	95 [0.7]	ISO

normally in the presence of acidic or basic catalysts where ethanol or methanol are commonly used as standard solvents for the precursor and water reactants. Fundamental and experimental details for the sol-gel synthesis of SiO_2 can be found extensively in the literature [7–9]. On the other hand, several articles reporting emulsification of the reactive mixtures induced by ultrasonic irradiation have been published in recent years, where no solvents are used [41–42]. In this way, it is possible to obtain sonolyzed-gel materials with an elastic modulus several orders of magnitude higher than those prepared by conventional methods [43–44]. In this contribution, a novel approach for the preparation of highly pure SiO_2 sonogels is exploited. At this point, the use of both solvents and catalysts can be entirely suppressed and the hydrolyzed species are substituted by molecular radicals generated by ultrasonic irradiation, more details on the synthesis, chemistry and methodology to produce these novel materials can be found in references [24–25].

In the present report, the catalyst-free (CF)-sonogel route is implemented to obtain SiO_2 matrices with high optical quality as host materials for chlorine substituted thermotropic bent shaped LC-compounds. Following a well established procedure previously reported by our group [24–25], a precursor solution of 25 mL of tetraethyl-ortosilicate (TEOS, Fluka 99% purity) and 25 mL of three-distilled water were mixed into a glass vessel and stabilized at 1°C for 1 hour before US-irradiation. A metallic ultrasound tip (Cole-Parmer-CPX), carefully located at the TEOS/H_2O surface interface, provides an effective irradiation power density on the order of 3–4 W/cm^3 at 20 kHz. The tip of the ultrasonic-wave generator also acts as an ultrasonic-homogenizer. After 3 hours of programmed ultrasonic irradiation (on/off-intermittent sequences of 5 sec. net irradiation time: 1.5 hours), the sonicated suspension was kept in the reactor vessel at room conditions for about twenty four hours; thereafter two immiscible phases appear: the upper one, corresponding to unreacted TEOS was removed and eliminated, whereas the lower phase corresponding to a stable colloidal suspension and containing the sonicated induced hydrolyzed product (OH-TEOS) was carefully dropped into cylindrical teflon-containers at different volumes. The **12Cl** bent core LC-compounds (used as received from the Halle group) were previously dissolved in thetrahydrofuran (THF). This dopant solution (D-D) was afterwards added at different rates and ultrasonically mixed to the deposited OH-TEOS colloidal suspensions in order to start the inclusion of the guest-molecules within the CF-SiO_2 networks and the formation of bulk hybrid composites.

Concretely, in the present application, a dopant solution containing 4 mg of the **12Cl** compound and 10 mL of solvent THF was prepared. In this way a saturated solution was assured in order to fabricate several highly loaded, optically active sonogel composites. The doses ratio of the OH-TEOS versus the **12Cl** dopant-solution (OH-TEOS:D-D) was carefully prepared with a precise volumetric micropipe and deposited into the cylindrical teflon-containers (1 inch in diameter, 2 mL in volume) in order to obtain different doped optical glasses. Prepared hybrid materials were generated according to the previous methodology varying the OH-TEOS:D-D concentration ratio (in volume) as follows: 1.0:1.0, 1.5:0.5 and 1.8:0.2 mL. Undoped or pure reference (**PR**)-sonogel samples (2.0:0.0) were also prepared for reference and calibration purposes. The samples were isolated while drying with a plastic cover in order to avoid atmosphere and temperature variations, and conserved for three to four weeks at room conditions in closed recipients with a small hole in the cap in a clean-dry-dark environment. Homogeneous hybrid samples with rigid monolith shapes, adequate for optical characterization were obtained after this slow drying procedure (typical surface dimensions and thickness were in the range of 20–40 mm^2 and 0.6–2.0 mm, respectively).

2.3. Linear and Nonlinear Optical Characterization Techniques

The optical characterizations of the hybrid samples were performed according to the following methodology and equipment: **i**) ***UV-VIS Spectroscopy Measurements:*** **12Cl** molecules were dissolved in spectral quality THF solvent purchased from Aldrich. UV-VIS absorption spectra of these compounds in solution (using 1 cm quartz cells) and in the sol-gel environment were recorded within the 200–1100 nm spectral range on a double beam Shimadzu-260 UV-VIS spectrophotometer, taking air in the reference beam. **ii**) ***Photoluminescent Spectroscopic Measurements:*** Similarly, photoluminescent (PL)-spectra were obtained in the 300–900 nm spectral range with a FluoroMax-3, Jobin-Yvon-Horiba fluorimeter. The excitation wavelengths were selected according to the UV-VIS absorption spectra of the liquid or solid state hybrid samples to a convenient wavelength (near the absorption wavelength maximum). Such UV-VIS and PL-studies were initially carried out in order to verify the inclusion of **12Cl** within the SiO_2 porous network and the optical quality of the samples. **iii**) ***Laser Photo Acoustic Measurements (LPAT):*** Selected hybrid samples were irradiated with the frequency tripled beam from a commercial Q-switched Nd:YAG Laser system (Surelite I from Continuum, $\lambda_\omega = 1064\,\mathrm{nm}$, $\lambda_{3\omega} = 355\,\mathrm{nm}$, repetition rate: 10 Hz and pulse width: 7 ns). THG output pulse energies in the range of 20 μJ/pulse were used to irradiate the samples so that any structural change and/or phase transformation occurring during irradiation was monitored according to the sensitive laser photoacoustic technique (LPAT) [45–46]. Temperature dependent LPAT measurements were performed in order to investigate the thermodynamic phase transitions of the guest LC-compounds embedded into the host sonogel network, to this end, a Thermoline-21100 oven was implemented to heat the samples within the 70–110°C interval (heating rate: 1°C/min), a piezoelectric (PZT) ceramic coupled to the hybrid-sample and a digital oscilloscope were used for recording averaged signals of 200 laser shots at each temperature step. The laser beam was slightly focused on the sample with a beam spot size set to 7 mm^2. An in-situ LPAT-analysis applied to the samples allowed the determination of the **12Cl**-hibrid phase transformations. Here, the photoacoustic PA(t, E_i) function represents the interaction between the laser beam and the network of the studied material, where E_i and t represent the different energies used and the size of the temporal signal, respectively. The correlation between successive functions [PA(t, E_i), PA(t, E_{i+1})] shows the evidence of any physical change occurring within the system during laser irradiation. In the resulting correlated curves, the location of sharp peaks shows those energy intervals where major structural instabilities exist and hence, where phase transformations take place [45–46]. LPAT experiments were performed in air at atmospheric pressure of 560 Torr and at room temperature. **iv**) ***Electro-Optical Measurements:*** Selected bulk samples (thickness: 600 μm) were sandwiched between ITO substrates and sealed with a low refractive/dispersive index epoxy mixture. An amplified low frequency AC-source was used to provide square AC-waveforms (160 V pp) in order to produce optical alignment of the LC-guest materials, whereas a continuous low energy solid state laser diode operating at $\lambda = 636$ nm was implemented to measure EO-transmittance through the hybrid composites. **v**) ***NLO-THG-Measurements:*** Finally, selected samples were also studied as active media for cubic NLO-effects such as THG. The THG experimental device is schematically shown in Figure 2, where a commercial high power Q-switched Nd:YAG laser system operating at $\lambda_\omega = 1064$ nm with a repetition rate of 10 Hz and a pulse width of $\tau = 12$ ns (Continuum-Surelite II) was implemented to provide the fundamental wave. Typical pulse powers of 200 μJ were implemented in order to irradiate the film samples, with a variable intensity on the sample that ranged from 60 to 80 MW/cm^2 and controlled by neutral density filters in order to avoid laser induced damage caused by high intensities of strong focused beams. It was possible to select the

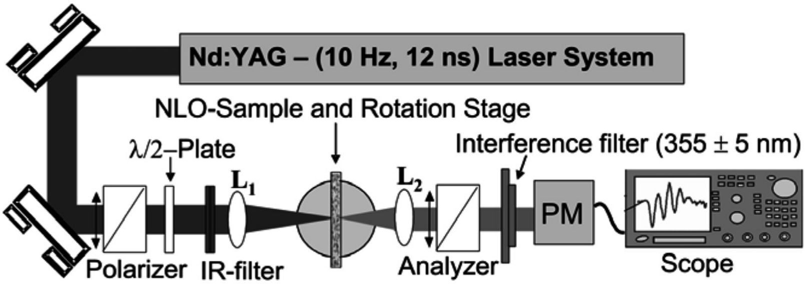


FIGURE 2 Experimental device used for NLO-THG measurements in bent-core 12Cl-based sonogel hybrid materials.

desired polarization of the fundamental beam by means of an IR-coated Glan-Taylor polarizer and a quartz-retarder ($\lambda/2$-plate, zero-order). A second polarizer was used as an analyzer, allowing the characterization of the THG-light. The third harmonic wave ($\lambda_{3\omega} = 355\,\text{nm}$) was detected by a sensitive photomultiplier tube (PMT-Hamamatsu, R-928) behind optical interference filters centered at $355 \pm 5\,\text{nm}$. The THG-device was calibrated by means of a fused silica plate ($\chi^{(3)}_{FS} = 3.11 \times 10^{-14}\,\text{esu}$, at $\lambda_{\omega} = 1064\,\text{nm}$) which is frequently used as standard NLO reference via the *Maker*-Fringes method for THG-experiments.

3. RESULTS AND DISCUSSIONS

3.1. UV-VIS and PL-Measurements

12Cl shows an intense white colour in the powder state and produces cloudy opaque monoliths in the sol-gel-phase. Figure 3 shows the comparative linear absorption spectra between two **12Cl**-doped composites (1.5:0.5 and 1.8:0.2), a PR-reference sonogel sample (2.0:0.0), an unsaturated **12Cl**-THF solution and the THF solvent. The unsaturated **12Cl**-THF solution was prepared in order to assure that the Beer–Lambert law applies for such slightly loaded (partially transparent) solution. Hence the electronic spectra and absorption properties of the **12Cl**-based solution were easily recognized and compared to these obtained from different doped sonogel glasses. In fact, very low linear absorption within the 350–1100 nm spectral range is observed for the **12Cl**-unsaturated solution, similar to that observed for the pure THF solvent. Only within the 200–350 nm range, the absorption of the **12Cl**-unsaturated solution is higher than that of the THF, differing from the solvent spectrum as it shows a main

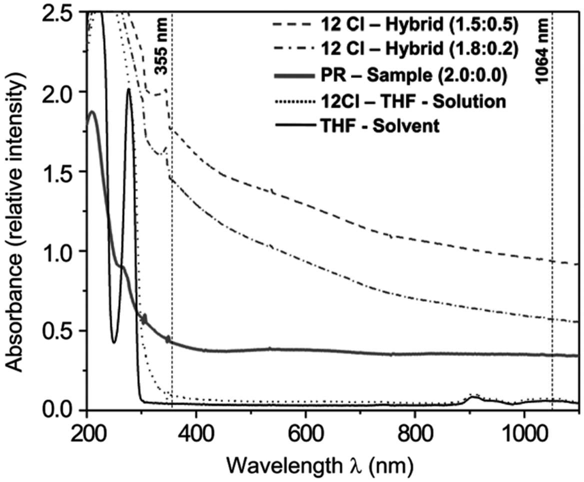


FIGURE 3 Comparative absorption spectra at room temperature of: (a) THF-solvent, (b) unsaturated THF/12Cl-solution, (c) (2.0:0.0) pure reference PR-sonogel glass and (d) slightly and heavily 12Cl doped composites (1.8:0.2 and 1.5:0.5, respectively).

absorption band around 234 nm only. This maximum decrease rapidly within the 290–380 nm interval, showing a short monotonically decreasing tail.

On the other hand, a wide high-transmission window (negligible absorption) displayed by the pure reference PR-sonogel sample within the whole VIS-NIR spectral range, demonstrates the high optical and chemical purity of the PR-sonogel network. Thus, it can be assured that the absorption bands observed for the hybrid composites are mainly due to the organic part of the composite and that the sonogel matrix does not considerably contribute to the absorption spectrum of the hybrids: for growing doping concentration, the relative absorption intensity of the hybrids increases, assuring an increment of the **12Cl** loading within the sonogel network (samples thickness: $\sim$0.7 mm). Typical features of **12Cl** in solution can be observed in the sonogel solid phase; for instance, the small 290–380 nm tail is drastically enhanced in the sonogel phase, showing strong absorption within the 400–800 nm interval, which indicate a higher conjugation degree as was explored and confirmed by means of NLO-THG experiments (see section 3.4). Last fact can be understood since in the solid state, due to the shrinking process experienced by the hybrids while dying, a larger amount of molecules may be supported, giving rise to

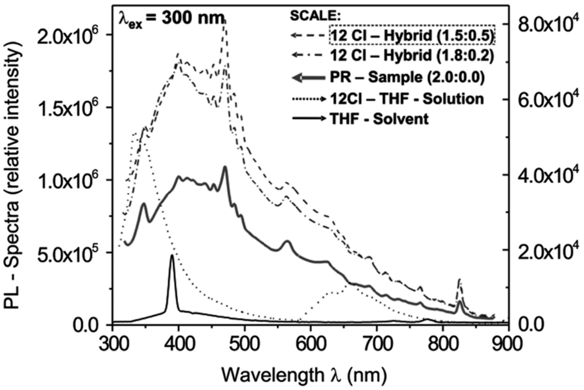


FIGURE 4 Comparative PL-spectra at room temperature obtained for: (a) THF-solvent, (b) unsaturated THF/12Cl-solution, (c) (2.0:0.0) pure reference PR-sonogel glass and (d) slightly and heavily 12Cl doped composites (1.8:0.2 and 1.5:0.5, respectively).

undesired molecular aggregation effects which are typically observed in the solid state. The appearance of this long tail in the sonogel phase may also be partially due to possible interactions between the SiO_2 network and the bent-core molecules which break the symmetry, this effect should be further investigated in future investigations. UV-absorption below 300 nm is in this case, mainly attributed to the **12Cl** molecules rather than to the SiO_2 glassy sonogel matrix. These hybrid samples, as mentioned before, were also studied under strong IR-laser irradiation in order to estimate their cubic NLO-THG properties. In this context, the available laser excitation line (at $\lambda_\omega =$ 1064 nm) and the line at the THG wavelength ($\lambda_{2\omega} = 355\,\text{nm}$) are shown in Figure 3.

Similarly, PL-spectra (not normalized) show higher emission activity for the doped samples although no special features of the bent-core compound can be identified in the solid state (see Fig. 4). In fact, **12Cl** compound shows a considerably weaker PL-activity as compared to the sonogel matrix (PR-sample). In this case, the stronger PL-emission of the sonogel network, which exhibit typical features of SiO_2 glassy materials, overshadows the weak emissions of the guest molecular systems.

3.2. LPAT Measurements

According to DSC measurements (see Table 1), three important phase transitions occur in pristine **12Cl** compounds, namely the isotropic

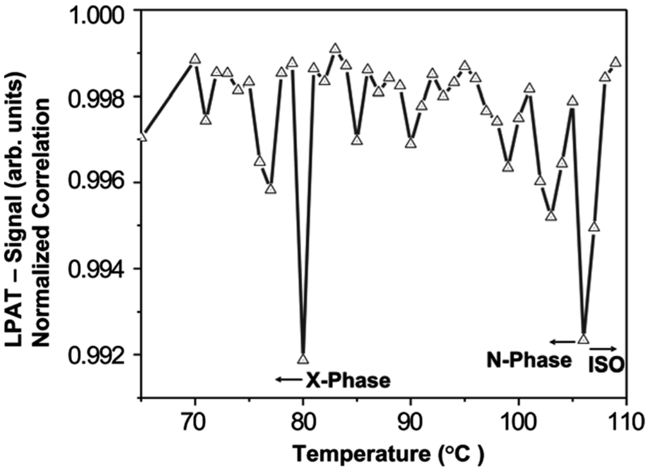


FIGURE 5 Temperature phase transition for 12Cl bent-core LC-based sonogel hybrids resolved by the laser photoacoustic technique (LPAT).

(ISO), Nematic (N) and X-phase transitions. Figure 5 shows a sensitive LPAT-measurement performed in a 1.5:0.5-**12Cl** composite in order to investigate the thermodynamic behavior of the confined bent-core molecular systems. In fact all three mesophases were properly identified within the solid state confinement: the cold X-phase transition was precisely observed at 80°C, in full agreement to the previously reported value; however, the high temperature N-phase, and correspondingly, the ISO-phase transition of compound **12Cl** within the SiO_2 amorphous confinement was drastically shifted to a higher temperature (~106°C). Beyond this temperature, the doped sample starts its degradation process induced by combustion of the LC-mesogen. Last result confirms the fact that an effective mechanical and thermal shelter can be created by the SiO_2 matrix, protecting the organic dopant from thermal damage and allowing an enhancement on the thermal operational range.

3.3. EO-Measurements

EO-measurements were achieved in slightly doped 1.8:0.2-hybrid bulk samples and with the thinnest available thickness (600 μm). Such measurements, as shown in Figure 6, were performed at high applied voltages with square AC-waveforms within the hybrid Nematic phase at 90°C. In fact, only low frequency AC-fields in the range of 160 V pp and 0.6–10 Hz were able to produced EO-switching of the confined

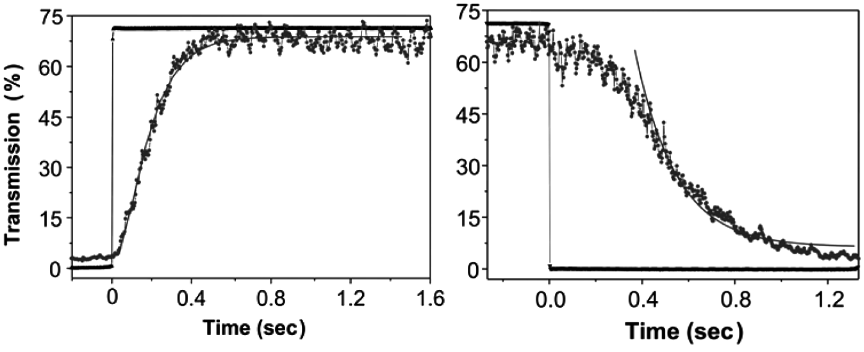


FIGURE 6 (a) Switching ON and (b) OFF states for 12Cl bent-core LC-based sonogel hybrids in the Nematic phase (1.8:0.2-hybrid Sample, thickness: 600 μm, square AC-field: 160 V pp at 0.6 Hz, T = 90°C).

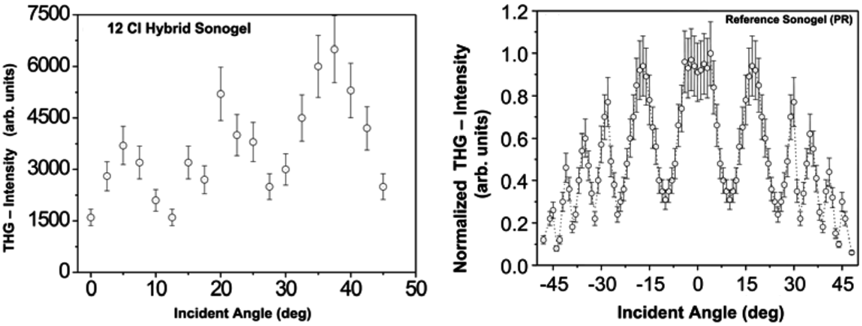
LC-guest molecules (Figs. 6a–b). Since the nanometric confinement of the LC-molecules (nano-droplets) within the porous SiO_2 network impose strong conditions for optical alignment (no EO-switching was observed for highly doped 1.5:0.5-hybrids), and the implemented laser source at $\lambda = 636$ nm is considerable absorbed by the LC-composite, the transmission of the probe-beam in the ON-switching states is limited to about 70% (for OFF switching states, strong scattering effects produce minimal transmittance of about 3% only). In fact gel dispersed liquid crystal (GDLCs) materials exhibit, in general, high voltage thresholds for EO-switching and slow response times [47–50]. As can be seen from Figure 6b, a very long time is required for the confined compounds to achieve a relaxed state, thus EO-switching is only possible for very low frequencies. Nevertheless, LC-based sonogel composites showing EO-effects at room temperatures can still be considered as good candidates for some applications where fast switching times are not essentially required, for instance in “intelligent-windows” (opaque-translucent-transparent devices) and visualisation screens with high reliability.

Although no ideal experimental conditions were implemented in such EO-measurements, we believe that the present result plays an important role in the development of such LC-based sol-gel applications, and that the deposition of film layers with thickness of few microns, will improve the EO-properties of these materials in order to increase its applicative possibilities [47–51].

3.4. NLO-THG Measurements

The amorphous solid state sonogel hybrid composites were also studied as active media for cubic $\chi^{(3)}$-nonlinear optical effects such as THG, from where the complex value of the non-degenerated $\chi^{(3)}(-3\omega;\ \omega,\ \omega,\ \omega)$ coefficient was evaluated. An advantage of the THG technique is that the THG response accounts only for the ultra-fast electronic response, so that vibrational, orientational, and thermal effects, which may contribute to the overall nonlinear optical response of the material, are excluded. Here we report the cubic NLO-properties of the developed hybrid structures. Since the amorphous sol-gel phase exhibits an isotropic and centro-symmetric-like network arrangement, no crystalline and symmetry conditions are required for the observation of cubic $\chi^{(3)}$ NLO-effects [1,3–6]. On the other hand, experimental single beam techniques based on THG give direct access to the cubic $\chi^{(3)}$ nonlinear optical coefficient, which is completely determined by the ultra-fast electronic response. Thus, vibrational, orientational, and thermal effects, which may contribute to the overall non-linear response of the material, are excluded. For these reasons, we implemented the THG-technique in order to evaluate the complex value of the non-degenerate $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ cubic nonlinear coefficient, which can additionally be related to the degenerate $\chi^{(3)}(-\omega;\omega,-\omega,\omega)$ component in order to give a good estimate of the intensity dependent refractive index (IDRI or n_2): $\mathrm{Re}[\chi^{(3)}(-\omega;\omega,-\omega,\omega)]$.

In Figure 7a, we report a typical THG Maker-fringe pattern experiment of the 0.60 mm thick 1.5:0.5 **12Cl** doped composite (resonant



(a) (b)

FIGURE 7 Angle dependent THG-measurements at room temperature performed in: (a) a 1.5:0.5–12Cl solid state hybrid sample (not normalized THG intensity), and (b) a 2.0:0.0–PR sonogel (normalized THG intensity).

configuration: $\lambda_{\omega} = 1064\,\text{nm}$, $\lambda_{3\omega} \sim 355\,\text{nm}$, THG intensity not normalized) in the room temperature Cr-phase, whereas in Figure 7b the Maker-fringe pattern of an undoped (2.0:0.0) PR-reference glassy sample is shown (normalized THG intensity). The Maker-fringe signals of the hybrid systems are compared to the fine fringe pattern produced by the **PR**-sample and the standard reference. Intensity in Figure 7b is normalized independently to a maximum value. In case of Figure 7a however, due to the huge THG-signals measured for the hybrid composites, the implementation of neutral density filters during THG-experiments was necessary, thus the amplitude of the THG-signals has been re-scaled to the real values. Estimated experimental error bars have been included in these graphs.

As a first estimation of the cubic NLO-properties of these hybrid composites, considering samples under strong resonant (absorption) conditions, the determination of $\chi^{(3)}$ may be approximated by the following Eq. (52):

$$\chi^{(3)-Hybrid} \propto \chi^{(3)-reference}\left(\frac{2l_c^{reference}}{\pi}\frac{\alpha/2}{1-e^{-\alpha/2}}\right)\left(\frac{I_{3\omega}^{Hybrid}}{I_{3\omega}^{reference}}\right)^{1/2}, \tag{1}$$

where α is the absorption coefficient of the hybrid sample and $l_c^{reference}$, represents the coherence length of the reference material ($\sim 4\,\mu\text{m}$). $\chi^{(3)-Hybrid}$ and $\chi^{(3)-reference}$ are, respectively, the values of the cubic nonlinear coefficients of the doped samples and the fused silica plate, while $I_{3\omega}^{Hybrid}$ and $I_{3\omega}^{reference}$ are the peak intensities of the Maker-fringe patterns of both the hybrid sample and the reference plate. In this way, the $\chi^{(3)}$ value of a new material relative to the value of the reference standard can be obtained; hence a calibrated result with a high degree of accuracy can be reported.

Assuming that the doping agents are homogeneously dispersed within the SiO_2 sonogel matrix, and since no quadratic SHG signals were measured in our amorphous samples for the corresponding mesogenic Cr-phase, only cubic $\chi^{(3)}$ resonant enhancements are permitted in such amorphous systems, therefore the THG-process is completely dominated by three-photon resonances $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ and no cascading effects were considered [4–5,53]. From the Maker-fringe experiments, the cubic NLO coefficient for the 1.5:0.5-hybrid sample was evaluated according to Eq. (1) to: $\chi^{(3)}_{-12Cl(1.5:0.5)} \approx 1.5 \times 10^{-11}$ esu. This $\chi^{(3)}$-coefficient was the highest among the studied doped samples and is considerably larger than those measured for the pure reference sonogel (**PR**) and the reference standard (fused silica: **FS**): $\chi^{(3)}_{PR} = 3.0 \times 10^{-13}$ esu and $\chi^{(3)}_{FS} = 3.11 \times 10^{-14}$ esu. All $\chi^{(3)}$-values were measured at room temperature at phase matching-conditions; these measurements reveal an increment for the THG-signal with increasing **12Cl** loading, being the 1.5:0.5-sample the most doped hybrid available, showing highest THG conversion.

From Figures 7a–b, it is clear that the THG-signal obtained from the 1.5:0.5-hybrid composite do not show a sharp oscillating behavior when comparing to that obtained from the **PR**-sample. Besides, the THG-responses produced by the hybrid composite are considerably stronger than those observed for the **PR**-sample. The lack of sharp oscillations for the hybrid systems is due to the resonant conditions occurring in our experiments using the available laser source, where the generated THG free waves at $\lambda_{3\omega} = 355\,\text{nm}$ are highly absorbed by the huge amount of NLO-chromophores embedded into the SiO_2 network (see Fig. 3); hence, the THG-intensity will no accurately follow the typical phase-matching dependent oscillations with the medium thickness, according to the Maker-fringe experiments. For the **PR**-sample, absorption and scattering effects are negligible and thus a fine fringe pattern can be easily recognized.

4. CONCLUSIONS

The highly pure SiO_2 sol-gel materials created by ultrasonic action behave as an appropriate host for bent-core LC-compounds. Large surface areas of up to $650\,\text{m}^2\,\text{g}^{-1}$ at room temperature and stable mechanical behavior up to 1000°C of the obtained sonogels [24–25], create an excellent environment for the confinement of dopant species. A newly synthesized chlorine-substituted (**12Cl**) bent-core liquid crystalline mesogen has been successfully introduced within the amorphous SiO_2 network. The resulting amorphous hybrid composites exhibit good mechanical and thermal properties, and large THG-signals in the bulk. Large cubic NLO values were obtained according to the THG-technique and the Maker-fringes method. In these experiments, the highest $\chi^{(3)}$-value, three orders of magnitude larger than that of the reference glass, was obtained for the highly doped hybrid composite ($\chi^{(3)}_{-12Cl(1.5:0.5)} \approx 1.5 \times 10^{-11}\,\text{esu}$). The photoacoustic technique has enabled us to accurately determine different phase transitions of the hybrid materials, in order to identify interesting thermodynamic states, to be optically studied.

Finally, although strong scattering effects produced by the amorphous hybrid materials, EO-swithching was obtained in the N-phase for slightly doped samples at low frequency AC-fields.

Further studies on the NLO properties of the **12Cl** based hybrids should be performed within the Cr-, N- and X-phases, according to the SHG, THG and Z-Scan techniques in order to provide a full optical description of these hybrid systems and explore its potentials in photonic applications. Besides, other interesting LC-materials exhibiting Nematic phases at room temperature should be tested as candidates for EO-switching within the sonogel phase in film layers, which will potentially increase its applicative possibilities. Such experiments are currently under development and will be presented elsewhere.

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