Photophysical properties of metallic-phthalocyanines dispersed in sonogel optical glasses

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ABSTRACT

Phthalocyanines (Pc) based compounds having central metallic atoms of Ni were successfully embedded in mesoporous silica gels via a catalyst-free sol-gel (sonogel) process in order to fabricate optically active solid-state hybrid glasses in both bulk and thin film formats at different dopant concentrations. The organic-inorganic hybrid composites obtained at room temperature processing showed stable mechanical performance, controllable geometrical shapes, good transparency and homogeneity suitable for linear and nonlinear optical (NLO) characterizations. Hybrid samples were studied via the NLO third-harmonic generation (THG) technique. AFM studies, epi-microscopy surface evaluation, refractive-index measurements and UV-Vis spectroscopy studies were also performed in selected bulk and film samples. The morphological and spectroscopic results showed a homogeneous dispersion of the organometallic compounds within the highly pure SiO_2-sonogel network. Moreover, Brewster's angle measurements have demonstrated the feasibility of tuning the refractive index of the samples by varying the chromophore dopant concentration. Additionally, the electronic absorption spectra showed band shifts in the two characteristic bands of the organometallic compound within sonogel environment, which evidence the formation of molecular H-aggregates for the developed hybrids and the consequent modifications of their optical properties. Finally, THG measurements in hybrid film samples exhibited an important NLO activity. We conclude that the optical effects of these composites can be tuned as function of the nickel-Pc concentration and that the sonogel matrix mainly acts as an inert protective shell, giving stable mechanical and thermal properties to the guest dopant compounds.

Keywords: optical materials, phthalocyanines, hybrid composites, nonlinear optics, sol-gel.

1. INTRODUCTION

During the past two decades, organic-inorganic hybrid materials have been extensively studied and implemented to manufacture diverse linear and nonlinear optical glasses due to their good optical qualities and mechanical strength[1,2]. Among the large number of NLO molecular systems, metallic-phthalocyanines (MPc) have emerged as promising materials by virtue of their extensively two dimensional delocalized π-electron structure leading to intense excited states, relative fast NLO response times and easy material processing[3]. Optical harmonic generation, optical limiting and optical switching under resonant and nonresonant conditions have been investigated in these compounds over a wide spectrum of laser frequencies[3,4]. Through peripheral (at the ligand), axial (via the central metal) substitutions, and additional conjugation, the basic Pc structure has led to a prominent control of NLO properties. Recently, a large variety of phthalocyanines have been optically studied in organic solutions[4], obtaining good NLO responses. However for practical applications, it is essential to investigate the optical performance of phthalocyanines compounds in the solid state. A popular method to produce mesoporous hybrid NLO glasses is based on the

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incorporation of NLO active organic chromophores into chemically inert and mechanically stable inorganic SiO_2 networks via sol-gel processes[5]. In this way, the sol-gel route has been continuously and extensively used as a common technique to produce well-dispersed bulk and films samples with a variety of organic and inorganic optically-active dopant compounds. In fact, solid-state hybrid composites can be easily obtained by diverse sol-gel methodologies in order to prepare advanced materials suitable for optical applications, with special interest in the linear and nonlinear optical activity[6]. The organic compounds provide the desired optical effects, whereas the inorganic component (glassy network) increases the thermal strength and mechanical stability of the composite. In addition, the optimal inclusion of organic chromophores into an amorphous sol-gel glass can allow the manufacture of a wide variety of low-cost devices required for photonic purposes in several formats; for instance in optical wave-guiding systems[7]. Yet, only appropriate combinations of sol-gel/dopants can produce an homogeneous and stable chromophore dispersion into the glassy network[1,8], where a suitable doping control can be achieved in order to produce diverse hybrids at different doping rates and chromophore loading. Accordingly, the well-established catalyst-free (CF) sonolysis route can also produce highly inert and pure sol-gel networks which are generated via ultrasonically induced sonochemical reactions (sonogel materials)[9].

In this work, we report on the development of new hybrid NLO glasses in both bulk and thin film formats containing Nickel-Pc (NiPc) molecules as dopant species within the highly pure SiO_2-based sonogel network. The morphological, linear and nonlinear optical studies were sequentially carried out on these samples: morphology studies were performed in order to evaluate the adequate dispersion and surface qualities of the hybrid samples (epimicroscopy and AFM studies); besides, optical characterizations were performed on bulk and thin film samples in order to determine important optical parameters (linear refractive indices measurement) as to explore possible interactions between the hosting SiO_2 matrix and the guest polymers (UV-Vis absorption spectroscopy analysis). NLO measurements include the test of the hybrid films as active media for cubic NLO-effects according to the THG-technique. These hybrid materials, both in thin film and bulk formats may offer important possibilities for the development of several high-tech photonic and optoelectronic prototypes.

2. EXPERIMENTAL SECTION

2.1 Implemented Metal-phthalocyanines

Fig. 1 shows the molecular structure of a Nickel(II) phthalocyanine-tetrasulfonic acid tetrasodium salt (NiPc, from Aldrich Inc.) implemented as dopant moiety within the hosting sonogel network. For this purpose, 0.90 mg of NiPc (powder) was dissolved in 4 mL of distilled water in order to obtain a sutured dopant dissolution (D-D).

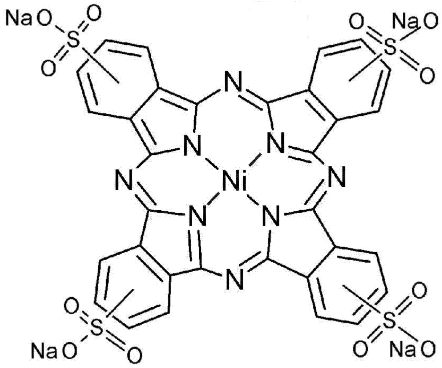

Figure 1. Chemical structure of the Ni phatlocianine implemented as dopant compound for hybrid sample preparation via the sonogel route.

2.2 Synthesis of catalyst-free sonogels as hosting networks for NiPc compounds

The catalyst-free sol-gel method consists in the synthesis of mesoporous SiO_2 networks based on the ultrasonic irradiation of the respective chemical precursors in order to obtain molecular radicals, followed by a condensation process[5]. In our particular recipe, we implemented tetraethylortosilicate (TEOS) and tri-distillated H_2O, only; fully suppressing the use any catalyst such as methanol or ethanol as the conventional sol-gel recipes usually require[5,6]. Extensive details on the chemistry and procedure to manufacture sonogel/hybrid materials can be found in the recent literature [1,8,9]. Basically this method consists of the following steps: As immiscible precursors, 25 mL of TEOS (Fluka 99% purity) and 25 mL of tri-distilled water are decanted into a glass vessel and stabilized at 1^{o}C. A stainless steel ultrasonic tip (Cole-Parmer-CPX), carefully located at the TEOS/H_2O surface interface, provides an irradiation power density of (~3.2Wcm^3 @20 kHz) and also acts as a homogenizer. After a net irradiation time of 1.5 h and 24 hrs of repose, two immiscible phases come out: the upper one, corresponding to unreacted TEOS was eliminated, whereas the more dense lower phase (sol-phase) corresponding to a stable colloidal suspension and containing the sonicated induced hydrolyzed product (OH-TEOS), is capable of producing (after drying and condensation) a highly pure SiO_2 amorphous network. In fact, in order to fabricate hybrid glasses, the chromophore doping must be performed in the liquid sol-phase; hence, the dopant solution should be previously prepared. These dopant dissolutions can be afterwards added and ultrasonically mixed with the OH-TEOS colloidal suspension in order to start the inclusion of dopants within the porosity of the forming SiO_2-glass throughout the drying course. Bulk hybrid materials were generated with a starting total volume of 2 mL (into cylindrical Teflon containers: 1 inch in diameter, 2 mL in volume) by varying the concentration ratio D-D/OH-TEOS (in volume) as follows: 2.7%, 5.3%, 8.1%, 11.1%, 14.3%, 17.7%, 21.2%, 25.0%, 29.0%, 33.3% D-D concentration, in order to obtain different doped optical glasses (bulk samples). Undoped reference sonogel samples (0.0% D-D) were also prepared for reference and calibration purposes. The samples were isolated with a plastic cover in order to avoid environment variations and conserved for 3 weeks at room conditions in a clean-dry-dark environment. After this slow and controlled drying process, a stable and homogeneous condensation produces uniform cylindrical bulk samples suitable to photophysical characterization. On the other hand, using the same D-D/OH-TEOS doping rate, thin film samples were deposited on Corning glass substrates via standard spin-coating procedures with one layer deposition at 50 rpm for 1 min. In order to avoid cluster formation, the doped OH-TEOS sol-mixture was previously filtered through 0.22 μm Teflon membrane filters before applying the spin-coating deposition process. The film sample was slowly dried at room temperature for 24 hrs. Under these conditions, mean film thicknesses of ~1.0 μm were obtained with good optical and mechanical quality (fracture-less film samples).

2.3. Physical characterization techniques

Standard characterization techniques were applied to undoped and hybrid sonogel samples in order to determine their structural and optical properties:

i. Morphological AFM and Epi-microscopy studies: The surface morphology of the hybrid films was studied in intermittent contact mode by AFM (autoProbe CP, Park Scientific Instruments) in order to evaluate the homogeneity and thickness at the micro-scale. The composites quality was also monitored via reflection microscopy (epi-microcopy) with a digital microscope (HW10 450, TTS-Unlimited) and a CCD-camera.

ii. Refraction index measurements: The evaluation of the linear refractive index of the hybrids samples was performed with a micrometric rotation stage, a linear polarizer film and an unpolarized He-Ne laser system (@ $\lambda = 543.5$ nm) according to the well-known Brewster angle technique[10]. At Brewster's angle θ_B, the intensity of a polarized reflected laser beam becomes a minimum as only the perpendicular component (*S*-

polarization) of the incident light is reflected. From this effect, the linear refractive index can be obtained according to the following basic relation: $n_t/n_i = \tan \theta_B$, where $n_i = 1$ (air) and n_t are the refractive index of the hybrid sample.

iii. Spectral UV-Vis analysis: Linear optical absorption spectra in reference and hybrid samples were systematically obtained within the 200–1100 nm spectral range using a double beam Shimadzu UV-vis spectrophotometer, using air in the reference beam.

iv. NLO/THG characterization: The cubic NLO properties of the hybrid composites were determined via the THG-technique on single-beam transmission measurements. Details of this experimental device can be found in the literature[8]. The set-up consists of a commercial Q-switched Nd:YAG Laser system (Surelite II from Continuum, λ=1064 nm,) which provides the fundamental wave. Peak irradiances below the energy damage threshold of the hybrid composites were adjusted at the focal spot (sample position). The polarization *P* or *S* of the fundamental beam was selected by means of an IR-coated Glan-Laser polarizer and a λ/2-Quarter-retarder. A second polarizer was used as analyzer allowing the characterization of the THG-signals. The THG-waves (at $\lambda_{3\omega}$=354.6nm) were detected by a photomultiplier tube (Hamamatsu R-928) placed behind interferential optical filters (centered at 355 ±5 nm).

3. RESULTS AND DISCUSSIONS

3.1. Morphological analyses

Bulk hybrid samples present a rigid and uniform disk-like monolith shape (with diameters and thickness of ~11 and 0.7 mm, respectively) achieved under the implemented doping rates; then again, under similar doping conditions the hybrid films have also shown uniformity and good mechanical stability. The developed NiPc-based hybrids are semitransparent and exhibit an intense blue color (at high doping rates) confirming the adequate and homogeneous inclusion of the dopant chromophores within the sonogel network, see Fig 2.

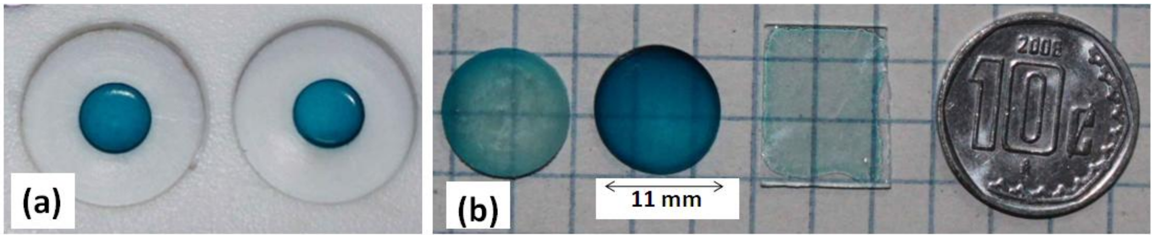

Figure 2. Set of pictures showing several manufactured NiPc/sonogel-based hybrid composites: (a) Two heavily doped composites as obtained from the Teflon containers, (b) Composites and thin film hybrid samples obtained at 2.7%, 33.3% and 33.3% D-D concentration, respectively (dimensional reference: a 10 cents Mexican coin).

According to epi-microscopy images of pure and highly doped (33% D-D) sonogel monoliths (see Fig. 3(a) and (b), respectively), the samples show relatively small inhomogeneities (with largest flaw diameters of ~7 μm, only) that may be produced by irregular local evaporation and shirking process occurring in different regions of the sample's surface; nevertheless, still good optical quality and uniformity can be achieved in order to perform optimal optical characterizations. In fact, in NLO-measurements, due to the small laser spot dimension (~60 μm in diameter) implemented during THG-experiments, these tiny material inhomogeneities can be considered as negligible in the sense that the obtained optical signals rather represent an averaged output response of the light-matter interactions.

Correspondingly, AFM micrographs confirm again the correct inclusion of the NiPc chromophores within the SiO_2-matrix, see Fig. 3(a') and (b'). Here, AFM-images show a drastic decrease of the average surface roughness of about 150% from the pure reference sample (Fig. 3(a')) to the hybrid thin film at 33% D-D (Fig.

3(b')). This remarkably roughness decrease can be attributable to the efficient chromophore loading within the sonogel mesoporosity, forming soft NiPc-based clusters that could cover and fill some material irregularities overall the glass structure.

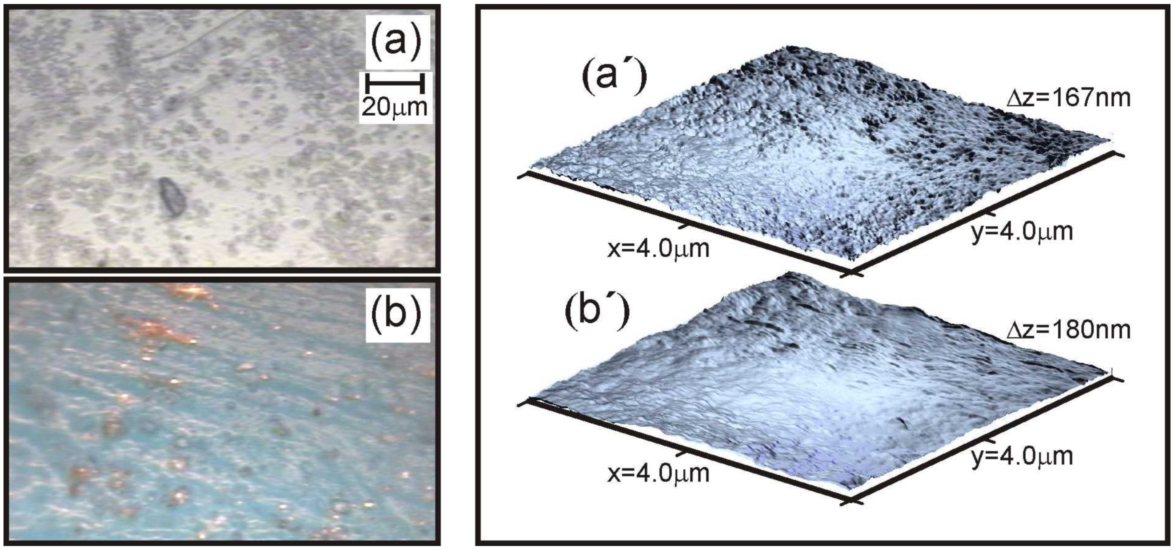

Figure 3. Representative morphological images of the manufactured hybrid systems: Epi-microscopy texture pictures of (a) a pure 0.0% D-D sonogel reference, and (b) a heavily 33.3% D-D doped NiPc/sonogel hybrid glass showing small 1D-microscopic tracks originated from regular in-wards radial shrinking of the sample within the Teflon mold. Note the typical blue color of the doped glass characteristic of the embedded NiPc compound. AFM images (in false-colors) confirms the variation in the surface topology (as a roughness decrease in the doped sample) between (a´) a pure sonogel reference; and (b´) a heavily 33.3% doped NiPc/sonogel hybrid composite.

3.2. UV-Vis Spectroscopic Measurements

Fig. 4 shows the comparative and representative absorption spectra of the 33.3%-, 25%-, 14%-, 2.7% D-D doped composites, a 0.0% D-D reference sample, and a low concentration NiPc/H_2O-based solution. The spectrum of the NiPc/H_2O-based solution presents a near-ultraviolet absorption band, identified in the literature as the S-band[3,4]. Then, a transparent region within the 400-544 nm range takes place; after this region, the main absorption band (centered at 621 nm) and defined in literature as the Q-band, appear[3,4]; thereafter a long 740-930 nm transparent region become evident. Finally, a small absorption band centered at 973 nm and identify as the first IR-absorption band characteristic of water, can be identified[11,12]. On the other hand, in congruence with spectral studies of SiO_2, the pure sonogel reference exhibits low absorption from the near UV to the near IR region. This wide transparent window guarantees the easy detection of the dopant loading within the hybrid structures. In fact, solid-state composites also manifest the characteristic S- and Q-bands and, in accordance with the Beer's law, it is evident that as the dopant loading increase within the hybrid samples, the intensity of these bands in the respective absorption spectra, also increase. It is worth noting that for heavily doped composites (33% D-D) a spectral blue-shift of ~14 nm in the main absorption band can be detected. This band-shift can be explained by the formation of H-aggregates due to a dense encapsulation of NiPc clusters within the sonogel network. Finally, none of the hybrid samples exhibit the water absorption band, which is indicative of an optimal drying course of the glassy hybrid samples.

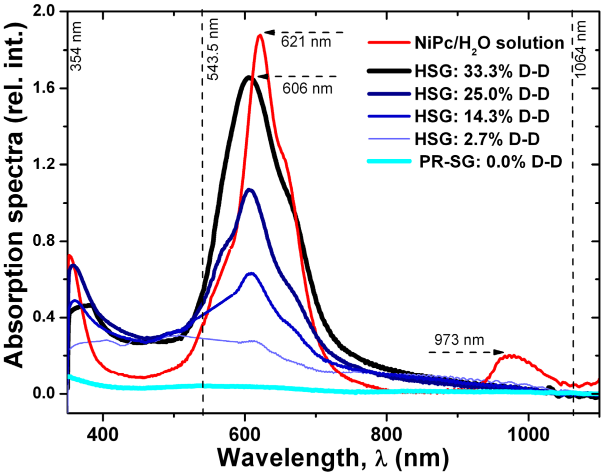

Figure 4. Comparative UV-Vis absorption spectra of the NiPc/H_2O solution, the pure-reference sonogel (PR-SG) matrix and the hybrid sonogel (HSG) composites doped at different D-D ratios.

3.3. Linear refractive index measurements

Since all the hybrid composites and film samples have adequate reflective surfaces, the Brewster angle condition is relatively easy to be found in order to perform refractive index measurements. Fig. 5 shows the average (over 10 measurements) refractive index n-values as function of the dye concentration (in D-D percentage). In the bulk phase, the pure sonogel sample presents a lower $n = 1.3$ value compared to common (more dense) optical glasses; this can be due to the larger content of air within the highly porous structure of the sonogel glass. The incorporation of the organic dopants increases the n-values to a limit defined by the $n_{lim} = 1.46$ of the pristine dopant chromophore (in powder), which is calculated via the fitting curve in the experimental data. This low n-value of the NiPc-compound is in agreement with the literature[13, 14]. On the other hand, due to a lower packing density, the refraction index of film samples is reduced. Indeed, the refractive index of a film generally present lower n-values than those reported for the respective bulk materials[15]. This is corroborated in our results concerning the n-values of the developed hybrid films when compared to their respective bulk composites. However, refractive index in the hybrid layers also increases as the dopant content augments. As this is a preliminary characterization study of these kinds of MPc/sonogel-based hybrid composites, in a future work a more detailed refractive index study will be presented (including a broad spectral range).

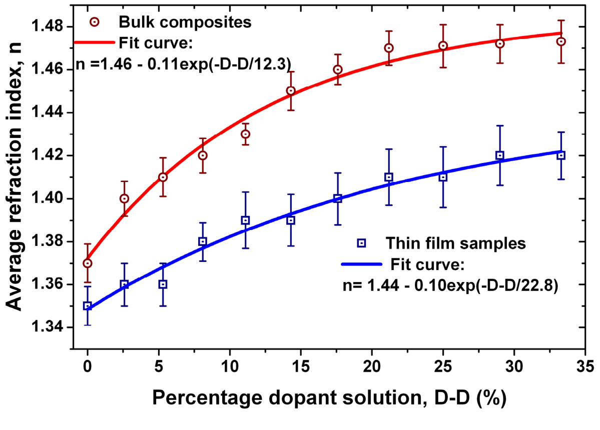

Figure 5. Average refractive index n-values of the bulk hybrid (circles) and thin films (squares) composites obtained at different doping rates (fitting curves and experimental error-bars are also presented).

3.4. THG analysis

Since the manufactured sonogel hybrid materials are isotropic in nature, they do not present second order NLO effects; nevertheless, these systems can perform well for cubic NLO-phenomena such as THG; this effect allows the conversion of the fundamental laser wave from $\lambda_{\omega} = 1064$ to $\lambda_{3\omega} = 354$ nm in a three photon absorption-emission process. Indeed, Fig. 6 shows the non-resonant THG-signal intensities obtained from selected high-quality bulk and film hybrid sample and the respective reference/undoped materials. Experiments were carried out under same experimental conditions. In fact, at a S_{in}-P_{out} excitation-detection experimental polarization configuration, the THG-emission of the hybrid samples was practically negligible, as expected according to the material isotropic nature. By contrast, at a P_{in}-P_{out} polarization geometry, significant THG-signals can be detected, in the same order of magnitude as that obtained for a quartz NLO-reference crystal. The pure/undoped sonogel reference sample does not exhibit significant THG-activity at the implemented laser power regime, indicating that the NLO-activity is fully due to the chromophore contribution with a significant increase with the dopant concentration.

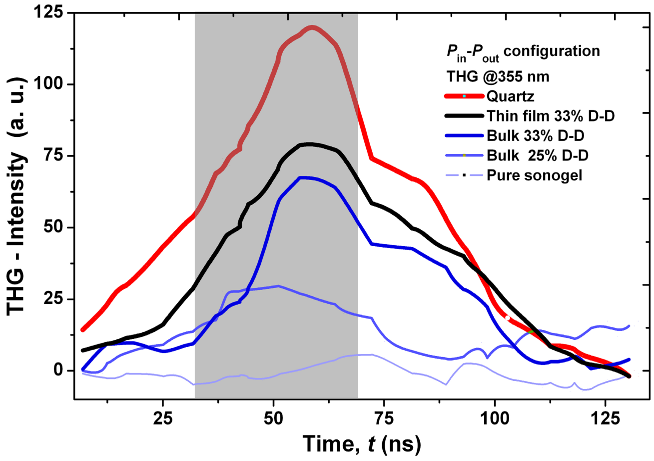

Figure 6. Comparative THG-measurement of the hybrid sonogel (HSG) composites doped at different MPc rates, a heavily doped hybrid film, a pure-reference sonogel matrix and a quartz reference crystal (NLO-calibration reference).

4. CONCLUSIONS

In this work, the successful preparation, morphological and optical characterizations of optically active NiPc/sonogel-based hybrid structures have been reported. Both bulk and film hybrid samples have presented excellent mechanical characteristics making these composites suitable for photophysical characterizations and NLO-photonic device applications. The sonogel route allowed us to perform the tuning of the optical properties of these composites by varying the NiPc-dopant concentration. Indeed, the feasibility of adjusting the linear refractive index values at different dopant concentrations was clearly evidenced in this report for the developed hybrid structures. Moreover, it has been also shown that the hybrid monoliths exhibit larger *n*-values than those obtained from the film samples. On the other hand, in spite of some superficial micro flaws observed in the bulk hybrid samples, the morphological analyses performed at different length-scales have demonstrated, in general, an appropriate dispersion of the NiPc-dyes into the mesoporous sonogel network and good sample homogeneity. From the optical point of view, the obtained UV-Vis absorption spectra have also evidenced the absolute evaporation of water and solvent residuals within the obtained hybrids and the easy identification of the absorptive electronic bands of the guest NiPc-moieties; these two characteristics reveal the high purity level achieved via the sonogel route. Finally, the relatively high NLO/THG-emissions observed in these kinds of hybrid systems represent a first step in the development of functional NiPc-based hybrid sonogel systems. We should remark that the sample quality and low-cost manufacturing process implemented to fabricate these optically active hybrid glasses is very promising for the development of NLO sonogel-based optoelectronic devices. In a future work, the cubic NLO-properties (via Z-Scan measurements) and the luminescent and electro-luminescent activity of these materials will be presented as an extension of the present report.

Acknowledgments

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REFERENCES

[1] Torres-Zúñiga, V., Morales-Saavedra, O.G., Rivera, E., Castañeda-Guzmán, R., Bañuelos, J.G., and Ortega-Martínez, R., "Preparation and photophysical properties of monomeric liquid-crystalline azo-dyes embedded in bulk and film SiO2-sonogel glasses," J. of Sol-Gel Sci. and Tech. 56 (1), 7-18 (2010).

[2] Chen, C.-C., Lin, D.-J., Don, T.-M., Huang, F.-H., and Cheng, L.-P., "Preparation of organic-inorganic nano-composites for antireflection coatings," J. of Non-Crystalline Sol. 354 (32), 3828-3835 (2008).

[3] De La Torre, G., Claessens, C.G.,and Torres, T. "Phthalocyanines: Old dyes, new materials. Putting color in nanotechnology," Chem. Comm (20), 2000-2015 (2007).

[4] Claessens, C. G., Blau, W.J., Cook, M., Hanack, M., Nolte, R.J.M., Torres, T., and Wöhrle, D., "Phthalocyanines and Phthalocyanine Analogues: The Quest for Applicable Optical Properties," Monatsh. Chem., 132, 3-11. (2001).

[5] Wen, J., and Wilkes, G.L., "Organic/inorganic hybrid network materials by the sol-gel approach"Chem Mat. 8 (8), pp. 1667-1681 (1996).

[6] Dunn, B., and Zink, J.I., "Optical properties of sol-gel glasses doped with organic molecules" J. Mat. Chem. 1 (6), 903-913 (1991).

[7] Almeida, R.M., and Marques, A.C. "The potential of ion exchange in sol-gel derived photonic materials and structures," Mat. Sci. and Eng. B. 149 (2), 118-122 (2008)

[8] Morales-Saavedra, O.G., and Rivera, E., "Linear and nonlinear optical properties of trans- and cis-poly(1-ethynylpyrene) based sonogel hybrid materials" Polymer 47 (15), 5330-5337 (2006)

[9] Ocotlán-Flores, J., and Saniger, J. M., "Catalyst-free SiO2 sonogels," J. of Sol-Gel Sci. and Tech, 39 (3) 235-240 (2006)

[10] Mian, S.M., Hamad, A.Y., and Wicksted, J.P., "Refractive index measurements using a CCD" Opt. and Photonics News 7 (5), 12-13 (1996)

[11] Gody, R.M. [Atmosferic radiation: I Theorical Basis]. Clarendon, Oxford, pp- 436 (1964)

[12] Howare, J.N. Burch, D.L., and Williams, D., "Infrared transmission through synthetic atmospheres," Geophys. Res. Papers No 40 244p (1955).

[13] Yakuphanoglu, F., Durmuş, M., Okutan, M., Köysal, O., and Ahsen, V. "The refractive index dispersion and the optical constants of liquid crystal metal-free and nickel(II) phthalocyanines" Physica B 373 (2),. 262-266 (2006).

[14] El-Nahass, M.M., Farag, A.M., Abd El-Rahman, K.F., and Darwish, A.A.A. "Dispersion studies and electronic transitions in nickel phthalocyanine thin films," Opt. and Laser Tech. 37 (7), 513-523 (2005).

[15] Pulker, H. K., "Characterization of optical thin films", Appl. Opt, 18 1969-1977 (1979).