

## Nonlinear absorption in ionic liquids with transition metallic atoms in the anion



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### ABSTRACT

Nonlinear absorption has been investigated by open aperture Z-scan in ionic liquids obtained by combination of 1-butyl-3-methyl-imidazolium cations with anions containing a transition metal (Co, Zn, Cu or Ni) and thiocyanate groups. The laser source was a Ti:Sapphire oscillator (80-fs pulses,  $\lambda = 810$  nm, repetition rate of 80.75 MHz). All liquids present quite low heat capacities that favor the development of strong thermal effects. Thermal effects and nonlinear absorption make them potential materials for optical limiting purposes.

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### 1. Introduction

The process of multiphoton absorption (MPA) refers to the simultaneous absorption of two or more photons by an active molecule reaching temporarily an excited state via intermediate states [1]. The possibility of change for a given molecular state is determined by the quantum mechanics selection rules that forbid determined transitions. MPA is an intensity-dependent and non parametric nonlinear effect. The absorbed energy may be dissipated, via radiative processes (fluorescence, phosphorescence) and non radiative processes (vibrational relaxation, internal conversion, intersystem crossing, energy transfer in molecular collisions...). It is undoubtedly a limiting factor in photonic nonlinear devices but it has been found very useful in other applications like frequency up-conversion lasing, data storage, microfabrication, fluorescence microscopy, optical limiting, optical reshaping or optical stabilization (see for example [1,2] and references therein). In the last two decades researchers have done a lot of effort on the survey of multiphotonic absorbing materials such as organic liquids, liquid crystals, polymers, fullerenes, organometallic compounds and biomolecules [1,3].

During the last ten years, a particular kind of salts known as ionic liquids have been the object of interest of numerous research

groups [4,5]. An ionic liquid (IL) is, by definition, any salt that melts below 100 °C. Most of them, the so-called room temperature ionic liquids, are liquids at temperatures lower than 25 °C. Typically, they are composed by a large cation (usually organic, containing nitrogen, sulfur or phosphorous and one or more alkyl chains) and an anion which can be mono or polyatomic, organic or inorganic. These emergent materials are involved in interesting applications in fields as electrochemistry, nuclear processing or renewable energies. Ionic liquids present two most valuable advantages: they are not volatile and they can be tailored. The first characteristic means that they almost do not evaporate in contrast to common organic liquids, which usually present high vapor pressures. The second characteristic means that an ionic liquid can be designed specifically for a given application by choosing an adequate combination of counterions, since the chemical and physical properties are usually determined by the cation and by the anion, respectively. Based on the available number of existing anions and cations, it has been estimated that millions of different ionic liquids could be synthesized. The technologic development around these liquids has required an enormous effort in the synthesis and in the characterization of their chemical and physical properties, needed for designing any application. Among them, optical properties have been addressed only by few researchers. Optical absorption and fluorescence have been studied in a limited set of imidazolium-based ionic liquids [6,7]; thermo-optic effect induced by different laser sources has been addressed in [8–14]. Nonlinear

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absorption has not been detected in any of the liquids characterized in these papers. Nevertheless, Sesto and coworkers have designed phosphonium based ionic liquids with cubic susceptibilities starting from those of the constituent ions [15,16]. They report the existence of nonlinear absorption in some of the liquids but they did not provide, up to our knowledge, quantitative values of neither the nonlinear absorption coefficient nor the nonlinear cross section. In this work, we study the nonlinear absorption effects in ionic liquids containing Co (L1), Ni (L2), Zn (L3) or Cu (L4) atoms in the anion and the 1-butyl-3-methyl-imidazolium cation ( $[\text{C}_4\text{C}_1\text{Im}]^+$ ).

## 2. Experimental

### 2.1. Materials

The short and long name of the ionic liquids under study are shown in Table 1. All these ILs are newly synthesized except L1, which has been bought from Iolitec. Ltd. Their molecular chemical structure are shown in Fig. 1.

#### 2.1.1. Synthesis of $\text{BMIM}_4\text{Ni}(\text{SCN})_6$ (L2)

8.733 g of  $[\text{C}_4\text{C}_1\text{Im}]\text{Cl}$  (50 mmol), 13 g of KNCS (133 mmol) were dissolved in 250 ml of acetone, then 5.942 g of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (25 mmol) were added and the reaction mixture was refluxed for 5 h, after cooling the suspension was filtered off and the acetone evaporated. The residue was washed with dichloromethane filtered and concentrated. 11.326 g of  $[\text{C}_4\text{C}_1\text{Im}]_4[\text{Ni}(\text{SCN})_6]$  were isolated (93%).

#### 2.1.2. Synthesis of $\text{BMIM}_2\text{Zn}(\text{SCN})_4$ (L3)

5.220 g of  $[\text{C}_4\text{C}_1\text{Im}]\text{Cl}$  (30 mmol) and 7.995 g of KSCN (82 mmol) were dissolved in 250 mL acetone, and 2.025 g of anhydrous  $\text{ZnCl}_2$  (12.4 mmol) were added afterward and the mixture refluxed for 5 h. The reaction mixture was filtered off, the solvent evaporated and the residue washed with dichloromethane and filtered. The residue is kept overnight under vacuum. 7.900 g of  $[\text{C}_4\text{C}_1\text{Im}]_2[\text{Zn}(\text{SCN})_4]$  were isolated (93%).

#### 2.1.3. Synthesis of $\text{BMIM}_3\text{Cu}(\text{SCN})_4$ (L4)

1.048 g of  $[\text{C}_4\text{C}_1\text{Im}]\text{Cl}$  (6 mmol), 1.166 g of KNCS (12 mmol) were dissolved in 60 ml of acetone, then 0.198 g of  $\text{CuCl}_2$  (2 mmol) were added and the reaction mixture was refluxed for 5 h, after cooling the suspension was filtered off and the acetone evaporated. The residue was washed with dichloromethane filtered and concentrated. 1.364 g of  $[\text{C}_4\text{C}_1\text{Im}]_3[\text{Cu}(\text{SCN})_4]$  as a brown oil were isolated (96%).

## 2.2. Methods

### 2.2.1. NMR

NMR spectra were recorded on a Varian Mercury 300 7.04 T (300.13 MHz for  $^1\text{H}$  and 75.48 for  $^{13}\text{C}$ ).

### 2.2.2. Mass spectra

Mass spectra were recorded on a Q-TRAP (AB/MDS Sciex) with electrospray ionization.

### 2.2.3. Heat capacity

Since most of these liquids were never synthesized, we decided to perform their thermophysical characterization. Each sample was subjected to temperature ramps at  $0.25 \text{ K min}^{-1}$  in the temperature interval (280–338) K using a DSCIII calorimeter from Setaram. As a result of these experiments, heat capacity can be determined. Moreover, information about any physical or chemical process which involves heat exchange – in particular, phase transitions – can be obtained. We estimated the uncertainty of heat capacity measurements in about  $0.05 \text{ J g}^{-1} \text{ K}^{-1}$ , much higher than that usually found for other using this procedure [17,18], fact which comes from the difficult handling of these compounds.

### 2.2.4. Linear absorption

The absorption coefficient was retrieved starting from the transmittance data measured with a Perkin Elmer lambda 25 spectrometer. The absorbance range is up to 3.2. Therefore, the spectra will be distorted in spectral regions with absorbance values above this limit. The used wavelength interval is 300–1000 nm (the device allows operating from 190 to 1100 nm).

### 2.2.5. Refractive index

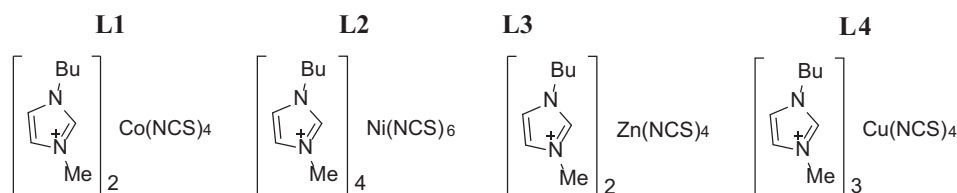
It was measured by a multiwavelength Abbe refractometer, model ATAGO DR-M2. The available interference filters allow measurement at 480 nm, 546 nm, 589 nm, 632 nm, 680 nm.

### 2.2.6. Nonlinear absorption

The characterization of nonlinear absorption has been conducted with open aperture Z-scan technique [19]. Pulses of  $\tau_0 = 80 \text{ fs}$  (FWHM) are delivered by a Ti:Sapphire oscillator working at  $\lambda_0 = 810 \text{ nm}$  with a repetition rate of 80.75 MHz. The laser beam was focused by a positive lens to a Gaussian spot of  $17 \mu\text{m}$  of radius (at  $1/e^2$  in intensity) measured by the knife-edge method [20]. The sample, a 1 mm or a  $10 \mu\text{m}$  quartz cell filled with the IL, is moved with a motorized translation platform from a position ahead the focus toward a position behind it ( $z$  direction), with

**Table 1**  
Short names and long names of the characterized ionic liquids.

Ionic liquid	Short name	Long name
L1	$[\text{C}_4\text{C}_1\text{Im}]_2[\text{Co}(\text{SCN})_4]$	Bis(1-butyl-3-methylimidazolium) tetrathiocyanatocobaltate
L2	$[\text{C}_4\text{C}_1\text{Im}]_4[\text{Ni}(\text{SCN})_6]$	Tetra(1-butyl-3-methylimidazolium) hexathiocyanatonickelate
L3	$[\text{C}_4\text{C}_1\text{Im}]_2[\text{Zn}(\text{SCN})_4]$	Bis(1-butyl-3-methylimidazolium) tetrathiocyanatozincate
L4	$[\text{C}_4\text{C}_1\text{Im}]_3[\text{Cu}(\text{SCN})_4]$	Tris(1-butyl-3-methylimidazolium) tetrathiocyanatocuprate



**Fig. 1.** Chemical structure of the ionic liquids under study.

1 mm step. A photodiode detector measures the power transmitted by the sample as function of the relative position between the sample and the focus. All the experiments have been performed in the same conditions except for the input mean power, which varies from 0.2 W to 1.2 W to trigger the nonlinear excitation without damaging the sample.

### 3. Results and discussion

#### 3.1. NMR spectra and mass spectra (MS)

##### 3.1.1. L1

$^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$ : 8.95 (s, 1H), 7.62 (s, 1H), 7.56 (s, 1H), 4.09 (t, 2H,  $J = 7$  Hz), 3.79 (s, 3H), 1.73 (quint, 2H,  $J = 7$  Hz), 1.24 (h, 2H,  $J = 7$  Hz), 0.84 (t, 3H,  $J = 7$  Hz).

$^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ )  $\delta$ : 136.90, 124.00, 122.66, 49.14, 36.27, 31.66, 19.14, 13.50.

IR (goldengate,  $\text{cm}^{-1}$ ): 3145, 3107, 2958, 2931, 2871, 2048, 1654, 1461, 1162, 960, 831, 740, 619.

MS (electrospray, positive ion)  $m/z$  (%): 710 (40), 709 (71), (BMIM) $_3$ Co(SCN) $_4$  708 (100).

MS (electrospray, negative ion)  $m/z$  (%): BMIMCo(SCN) $_4$  430 (100), 280 (20), 235 (12).

##### 3.1.2. L2

$^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$ : 8.86 (s, 1H), 7.51 (s, 1H), 7.45 (s, 1H), 3.98 (t,  $J = 6.2, 6.2$  Hz, 2H), 0.70 (t,  $J = 7.1, 7.1$  Hz, 3H).

$^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ )  $\delta$ : 136.90, 124.00, 122.66, 49.14, 36.27, 31.65, 19.13, 13.49. IR (goldengate)  $\text{cm}^{-1}$ : 3143, 3080, 2960, 2931, 2873, 2864, 2109, 2077, 1564, 1463, 1379, 1340, 1166, 846, 648, 601.

MS (electrospray, positive ion)  $m/z$  (%): 1103 (8), 1102 (9), 1101 (13) BMIM $_5$ Ni(NCS) $_6$ , 907 (25), 906 (70), 905 (50), 904 (100)

BMIM $_4$ Ni(NCS) $_5$ , 710 (26), 709 (62), 708 (60), 707 (96) BMIM $_3$ Ni(NCS) $_4$ , 336 (65) BMIM $_2$ SC.

MS (electrospray, negative ion)  $m/z$  (%): 825 (1.5), 824 (0.5), 823 (1), BMIM $_3$ Ni(NCS) $_6$  628 (7), 627 (3), 626 (11), BMIM $_2$ Ni(NCS) $_4$  431 (32), 429 (49), BMIMNi(NCS) $_4$  234 (59), 232 (100) Ni(SCN) $_3$ .

##### 3.1.3. L3

$^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$ : 9.03 (s, 1H Im-H2), 7.68 (t, 1H,  $J = 1.7$  Hz), 7.62 (t, 1H,  $J = 1.73$  Hz), 4.16 (t, 2H,  $J = 7.23$  Hz), 3.85 (s, 3H, N-Me), 1.85–1.73 (m, 2H), 1.30 (h, 2H,  $J = 7.5$  Hz), 0.90 (t, 3H,  $J = 7.34$  Hz).

$^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ )  $\delta$ : 137.20, 135.33, 124.31, 122.99, 49.48, 36.49, 31.99, 19.46, 13.77. IR (goldengate)  $\text{cm}^{-1}$ : 3143, 2958, 2933, 2831, 2063, 1566, 1461, 1162, 744, 648.

MS (electrospray, positive ion)  $m/z$  (%): 717 (20), 715(26), 713 (24) BMIM $_3$ Zn(SCN) $_4$ , 336 (10) BMIM $_2$ SCN, 293 (50), 291 (21), 186 (100).

MS (electrospray, negative ion)  $m/z$  (%): 439 (4), 437 (5), 435 (8), BMIMZn(SCN) $_4$  242 (47), 240 (70), 238 (100) Zn(SCN) $_3$ .

##### 3.1.4. L4

$^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$ : 9.07 (s, 1H), 7.73 (t,  $J = 1.5$  Hz, 1H), 7.67 (t,  $J = 1.5, 1\text{H}$ ), 4.15 (t,  $J = 7.2, 7.2$  Hz, 2H), 3.84 (s, 3H), 1.74 (p,  $J = 7.5, 7.5, 7.3, 7.3$  Hz, 2H), 1.24 (h,  $J = 7.3, 7.3, 7.2, 7.2, 7.2$  Hz, 2H), 0.87 (t,  $J = 7.3$  Hz, 3H).

$^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )  $\delta$ : 136.88, 124.03, 122.68, 49.01, 36.22, 31.80, 19.24, 13.72. IR (goldengate,  $\text{cm}^{-1}$ ): 3140, 3095, 2959, 2050, 1750, 1643, 1165, 751, 620.

MS (electrospray, positive ion)  $m/z$  (%): 853 (0.5), 852 (0.5), 851 (2) BMIM $_4$ Cu(SCN) $_4$ , 656 (1), 655 (1), 654 (2) BMIM $_3$ Cu(SCN) $_4$ , 336 (100) BMIM $_2$ SCN.

MS (electrospray, negative ion)  $m/z$  (%): 181 (76), 179 (100), Cu(SCN) $_2$ , 255 (45) BMIM(SCN) $_2$ .

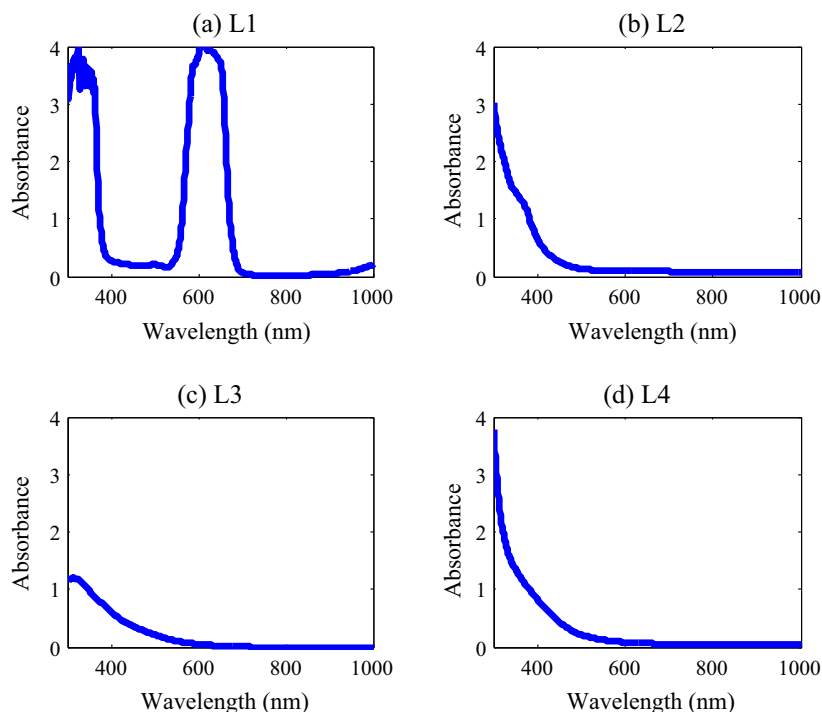


Fig. 2. Linear absorbance of the ionic liquids under study. Cell thickness is 10  $\mu\text{m}$  except in (c) that is 1 mm. The spectra are distorted at the wavelength intervals where absorbance is higher than 3.2.

**Table 2**  
Heat capacity per unit mass for the studied ionic liquids,  $c_p$  ( $J g^{-1} K^{-1}$ ).

T (K)	L1	L2	L3	L4
283.15	1.52	1.35	1.53	1.67
298.15	1.56	1.48	1.57	1.69
313.15	1.61	1.92 <sup>a</sup>	1.61	1.70
333.15	1.63	1.97 <sup>a</sup>	1.64	1.70

<sup>a</sup> Supercooled liquid.

### 3.2. Heat capacity

We found that all ionic liquids present quite low values, (see Table 2), which makes them quite sensitive to heating and, particularly, to that induced by laser pulsed radiation, as it is shown below.  $[C_4C_1IM]_4[Ni(SCN)_6]$  presents a solid–solid and solid–liquid transition at 315 and 335 K, with transition enthalpies of 4 and 45  $J g^{-1}$ , respectively. This liquid phase presents a quite high supercooling capability, fact that made possible the measurements in liquid state below the melting point (see Table 2).

### 3.3. Linear absorption and refractive index

The absorbance spectrum of each ionic liquid from 290 to 1000 nm is shown in Fig. 2. The pathlength of the cells,  $L$ , was 10  $\mu m$  except in the case of L3 that was 1 mm. All liquids present negligible linear absorbance at the excitation wavelength, 810 nm. L1 has an absorption band between 500 and 700 nm that is responsible of its blue coloration. This liquid may act as a bandpass filter selecting wavelengths at the 400–500 nm interval.

We have also estimated the refractive index values for L1 ( $n_0 \sim 1.59$ ) and L3 ( $n_0 \sim 1.55$ ) at 680 nm by Abbe refractometry. The high absorbance in bands of visible region prevented an accurate measurement of the linear refractive index with the available devices. L2 refractive index could not be determined by these means because, although it is a metaestable material that remains liquid when it is cooled from 50 °C to room temperature, a thin film solidifies faster at room temperature. The films present birefringent domains that may be seen with an optical microscopy as it is shown in Fig. 3a. Fig. 3b shows an image of the same area taken with a polarizing microscope.

### 3.4. Nonlinear absorption

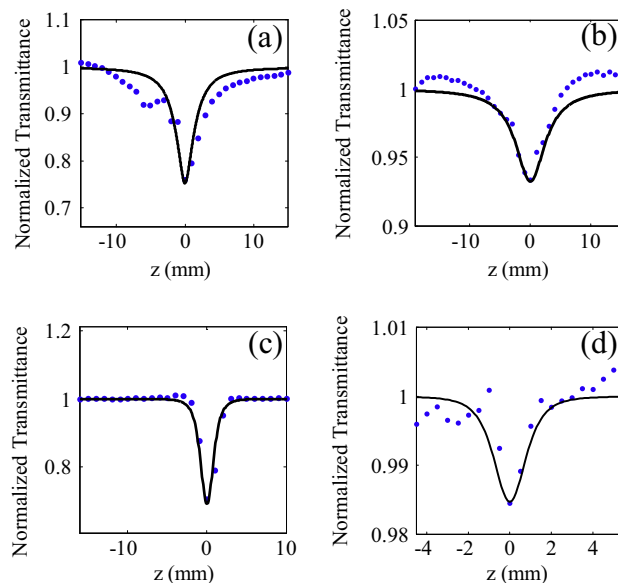
We have determined, for each ionic liquid, the minimum irradiance levels ( $I_{min}$ ) needed for detecting nonlinear absorption in the conditions of the experiments. We have also determined the irradiance level that damages the sample or induces the generation

**Table 3**  
Two ( $\beta_{2PA}$ ) and three photon ( $\beta_{3PA}$ ) absorption coefficients and minimum ( $I_{min}$ ) and maximum ( $I_{max}$ ) irradiances used in the nonlinear absorption characterization of each ionic liquid.

Ionic liquid	$I_{min}$ (GW/cm <sup>2</sup> )	$I_{max}$ (GW/cm <sup>2</sup> )	$\beta_{2PA}$ (cm/GW)	$\beta_{3PA}$ (cm <sup>3</sup> /GW <sup>2</sup> )
L1	67	210 <sup>a</sup>	11 ± 5	
L2	24	37 <sup>a</sup>	21 ± 5	
L3	110	210 <sup>b</sup>		(1.4 ± 0.5) 10 <sup>-3</sup>
L4	170	>210 <sup>b</sup>		(1.9 ± 0.5) 10 <sup>-4</sup>

<sup>a</sup> Damage threshold.

<sup>b</sup> Light emission.

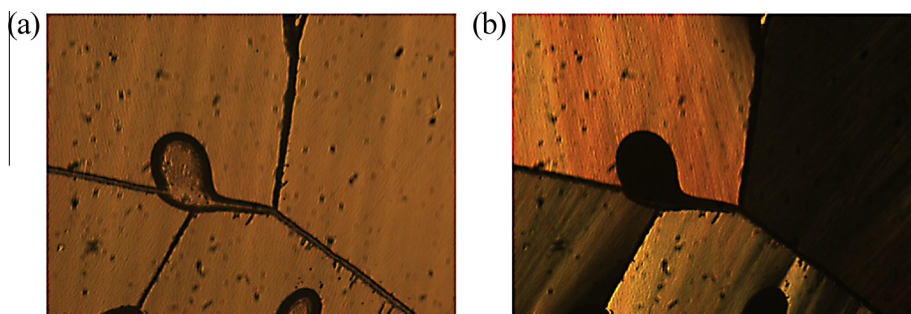


**Fig. 4.** Z-scan curves of the ionic liquids: (a) L1, (b) L2, (c) L3 and (d) L4.

of light vibrating at new frequencies (naked eye detection). We identify it with the notation  $I_{max}$ . The two values are shown in Table 3 for each ionic liquid.

All ILs present strong thermal effects at very low mean powers compared with those previously characterized in [8–14], as expected due to their low heat capacity. They are stronger in Ni and weaker in Zn.

The Z-scan curves (see Fig. 4) reveal the presence of nonlinear absorption in all ILs but the origin differs from one material to another. The Z-scan curve of L1 and L2 are compatible with a two photon absorption effect whereas the corresponding to L3 and L4 suggest a three photon absorption effect [3].



**Fig. 3.** Image of a region of a thin film of L<sub>2</sub> taken with an optical microscope (a) and between crossed polarizers (b). (Area: 400 × 300  $\mu m^2$ .)



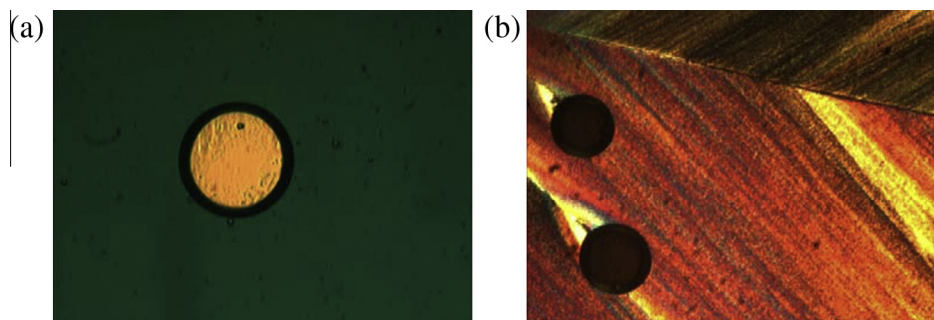


Fig. 5. (a) Hole created in L1 after irradiation (b) photodarkening in L2 after irradiation observed between crossed polarizers. (Area:  $400 \times 300 \mu\text{m}^2$ .)

Dots in Fig. 4a–d correspond to the experimental data. The continuous lines represent the fit of the pure two or three photon absorption model to the experimental data.

The transmittance model for two photon absorption is [3]:

$$T(z) = \sum_{m=0}^{\infty} \left[ (-q_0(z, 0))^m / (m+1)^{3/2} \right] \quad (1)$$

where  $q_0$  and  $L_{\text{eff}}$  are:

$$q_0(z, t) = \beta_{2PA} I_0(t) L_{\text{eff}} / (1 + z^2/z_0^2) \quad (2)$$

$$L_{\text{eff}} = (1 - e^{-\alpha_0 L}) / \alpha_0 \quad (3)$$

The transmittance in a process of three photon absorption is [3]:

$$T(z) = \sum_{m=1}^{\infty} (-1)^{m-1} p_0^{2m-2} / [(2m-1)! \sqrt{2m-1}] \quad (4)$$

being

$$p_0(z, t) = \sqrt{2\beta_{3PA} I_f^2(z, t) L_{\text{eff}}^{3PA}} \quad (5)$$

$$L_{\text{eff}}^{3PA} = (1 - e^{-2\alpha_0 L}) / 2\alpha_0 \quad (6)$$

$$I_f(z, t) = I_0(t) / (1 + z^2/z_0^2) \quad (7)$$

being  $\beta_{iPA}$  ( $i = 2, 3$ ) the pure two or three photon absorption coefficient,  $\alpha_0$  the linear absorption coefficient at 810 nm,  $L$  the sample length,  $I_0$  the on-axis irradiance of the input pulse at the focus and  $z_0$  the Rayleigh distance.

The values of the two and three photon absorption coefficients are listed in Table 3.

Regarding L2, we have not detected any anisotropic behavior with the implemented Z-scan set-up. Maybe the laser induces strong thermal effects causing a solid–liquid transition that breaks the microscopic local order.

The behavior of the ionic liquids is rather different for irradiances higher than  $I_{\text{max}}$ . In L1, L3 and L4, it is observed visible light emission. Since the frequency of the emitted light is higher than that of the pump, the origin may be attributed to multiphoton induced fluorescence. In L1 the high powers cause, besides visible light emission, transparent holes as the one shown in Fig. 5a. The size of the holes depends on the irradiation time and the fluence. They may disappear with time once the irradiance is off or may keep stables if they are large enough. A different behavior has been observed in the ionic liquid containing Ni that suffers strong thermal absorption due to the laser heating that causes irreversible darkening of the IL for powers higher than  $37 \text{ GW/cm}^2$  (see Fig. 5b). The photosensitivity of this ionic liquid makes it a potential material for photolithography.

Finally, it is worth to note that the ionic liquids are saved at room temperature and they remain stable during months. In the heat capacity experiments, they were heated up to 345 K; no

decomposition signs were observed in the thermograms, although several heating cycles were applied to the samples. Moreover, the measured optical properties are also a proof of their stability against time; these measurements were done in time periods about several weeks and no important differences were observed for the same sample, a fact that can be ascribed to their good thermal and chemical stability.

#### 4. Conclusions and future work

Nonlinear absorption has been detected in four ionic liquids containing metallic atoms, three of them being newly synthesized. The absorption coefficients have been characterized in all of them by the open aperture Z-scan technique at 810 nm. In those ILs containing Co and Ni, the theoretical model of two photon absorption [3] matches well to the experimental data, whereas the behavior observed in ILs with Cu and Zn is compatible with three photon absorption. It is worth to note that we have made experiments also for the ionic liquid  $[\text{C}_4\text{C}_1\text{Im}]_3[\text{Fe}(\text{SCN})_6]$  which presents strong linear absorption at the excitation wavelength, demonstrating also a strong nonlinear behavior that could not be characterized. After some irradiation time, the ionic liquid ( $10 \mu\text{m}$  of path length) absorbs all the input light, and at a later time it scatters light of a shorter wavelength. The mechanism underlying the nonlinear absorption is not identified yet and complementary research must be done to clarify this behavior. A possible origin may be excited state absorption and the emission of light may be attributed to induced fluorescence or phosphorescence. Work in this direction is on.

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