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► **To cite this version:**

Antonin Pardon, Oriane Bonhomme, Clotilde Gaillard, Pierre-François Brevet, Emmanuel Benichou.
Nonlinear Optical Signature of Nanostructural Transition in Ionic Liquids. *Journal of Molecular
Liquids*, 2021, 322, pp.114976. 10.1016/j.molliq.2020.114976 . hal-03371327

HAL Id: hal-03371327

<https://hal.science/hal-03371327v1>

Submitted on 8 Oct 2021

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1 **Nonlinear Optical Signature of Nanostructural Transition in Ionic Liquids**

2

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1 **Abstract :**

2 The homologous series of the ionic liquids 1-alkyl-3-methylimidazolium
3 bis(trifluoromethylsulfonyl)imide, $[C_nC_1im][NTf_2]$ ($n=2,4,6,8$ and 10) was studied by
4 polarization-resolved second harmonic scattering (SHS). The analysis of the polarization plots
5 clearly demonstrates that the SHS response is dominated by an octupolar contribution.
6 Orientational correlations are observed on the nanometer scale in all the investigated ionic
7 liquids, even for the shortest alkyl chain length. A radial distribution of the nonlinear optical
8 sources is evidenced. A sharp transition from short to longer range correlations occurs
9 between ionic liquids with $n=4$ and 6 , signature of the dominating role taken by the alkyl
10 chains. The SHS technique therefore provides structural observation in liquids at scales well-
11 below the diffraction limit and these findings open new interesting perspectives in the domain.

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1 **1. Introduction**

2 Ionic liquids (ILs) are a new class of solvents composed solely of ionic species. They are
3 molten salts that are liquid at relatively low temperatures. ILs have attracted a lot of interest
4 for a multitude of applications over the last 15 years as their ionic components can be chosen
5 according to specific needs, giving them unique and adjustable properties [1-5]. ILs have also
6 been identified as alternative media with lower environmental impact in electrochemical
7 applications[6,7] such as batteries and supercapacitors but also as reaction media in
8 biocatalytic processes involving proteins and enzymes[8]. The tunability of their properties is
9 the result of a wide-ranging and rich arrangement of inter- and intramolecular interactions, for
10 instance Coulombic, dipolar, π - π , solvophobic, van der Waals or hydrogen bonding,
11 established between the charged headgroups and the alkyl chains in a single pure IL [9]. The
12 complex interplay of the different molecular interactions in ILs results in the singular
13 structural organization at the nanoscale both in the bulk phase and at the interface [9-16]. The
14 bulk phase microscopic structure can be observed on different scales. The short-range local
15 order is governed by the Coulombic and Van der Waals interactions between ionic species.
16 Ab Initio and density functional theory have for example predicted the formation of ion pairs
17 [17-19]. The structuration of ILs also occurs on a larger scale. For example,
18 alkyylimidazolium-based ILs display long-range organization due to the segregation of alkyl
19 chains and the polar ionic moieties into nonpolar and polar domains, respectively. Structural
20 heterogeneities at nanometer scale has been demonstrated experimentally with small-wide
21 angle X-ray (SWAXS) [15,20-25] and neutron scattering [22,26-29]. For the 1-alkyl-3-
22 methylimidazolium bis(trifluoromethanesulfonyl)imide ILs, indicated as $[C_nC_{1im}][NTf_2]$
23 where n is the number of carbon atoms in the alkyl chain, SWAXS experiments have shown
24 that the characteristic size of the nanoscale heterogeneities varies linearly with n [23]. The
25 length of the alkyl chain affects the motion of each ion which is connected with macroscopic

1 physical properties [30]. However, it remains difficult to observe the existence of
2 nanostructuring for alkyl chain length shorter than butyl ($n=4$). Optical spectroscopic
3 techniques such as femtosecond optical heterodyne-detected Raman-induced Kerr-effect
4 (OHD-RIKES) spectroscopy, terahertz spectroscopy, dielectric relaxation spectroscopy
5 (DRS), low-frequency Raman and coherent anti-Stokes Raman scattering have also been used
6 to probe IL nano-structuration and their related dynamics [31-38]. Recently, the effect of the
7 structural heterogeneities on the microviscosity of ILs has been studied by time-resolved
8 fluorescence [39]. Self-assembled nanostructures have also been intensively studied by
9 molecular dynamics (MD) simulations [9,11,13,20,29,40-44]. The nonpolar domains formed
10 by the longer alkyl chains interconnect to form sponge-like nanostructures. Transition to the
11 percolation regime occurs with the butyl chain length[40] However, structural transition was
12 not directly observable from experimental measurements even if a recent MD study finely
13 analysing SWAXS data has shown it [42].

14 In the present work, the ILs nanoscale organization is revealed, even for the shortest alkyl
15 chain length. A structural transition occurring as the alkyl chain length increases is clearly and
16 directly evidenced by a nonlinear optical method, even if the information to be collected is on
17 a scale well below the diffraction limit. In addition, analysis of the results provides the chain
18 length at which this transition occurs. For that, second harmonic scattering (SHS) has been
19 used. This technique is based on the conversion of two photons at the fundamental frequency
20 ω into a single photon at the harmonic frequency 2ω . The second harmonic generation
21 process is particularly well-adapted to study interfaces [14,45,46] but is also recognized as a
22 powerful technique to probe local order in liquids [47,48]. The technique can be applied to
23 measure the second-order hyperpolarizabilities of molecular species diluted in liquid phase
24 [49,50], but also those of pure solvents such as ILs [19,51]. SHS is particularly sensitive to
25 the symmetry of the molecular species [52] and to local structures in ILs such as ion pairs[19].

1 For correlated assemblies of nonlinear sources, the point-like approximation breaks down and
2 retardation must be considered as well [53,54]. This feature has recently been used to
3 evidence long-range correlations in pure water and their progressive loss in aqueous
4 electrolytes as a function of salt concentration [48]. In this study, we apply SHS resolved in
5 polarization to probe the bulk organization of the homologous ILs series 1-alkyl-3-
6 methylimidazolium bis(trifluoromethylsulfonyl)imide $[C_nC_1im][NTf_2]$ with $n=2,4,6,8$ and 10.

7

8 **2. Materials and methods**

9 **2.1 Materials**

10 The $[C_nC_1im][NTf_2]$ ILs were purchased from Solvionic with a purity higher than 99.9%. All
11 these ILs were used as received and were stored under argon. For the SHS measurements, the
12 different ILs were poured into a quartz cell (Hellma).

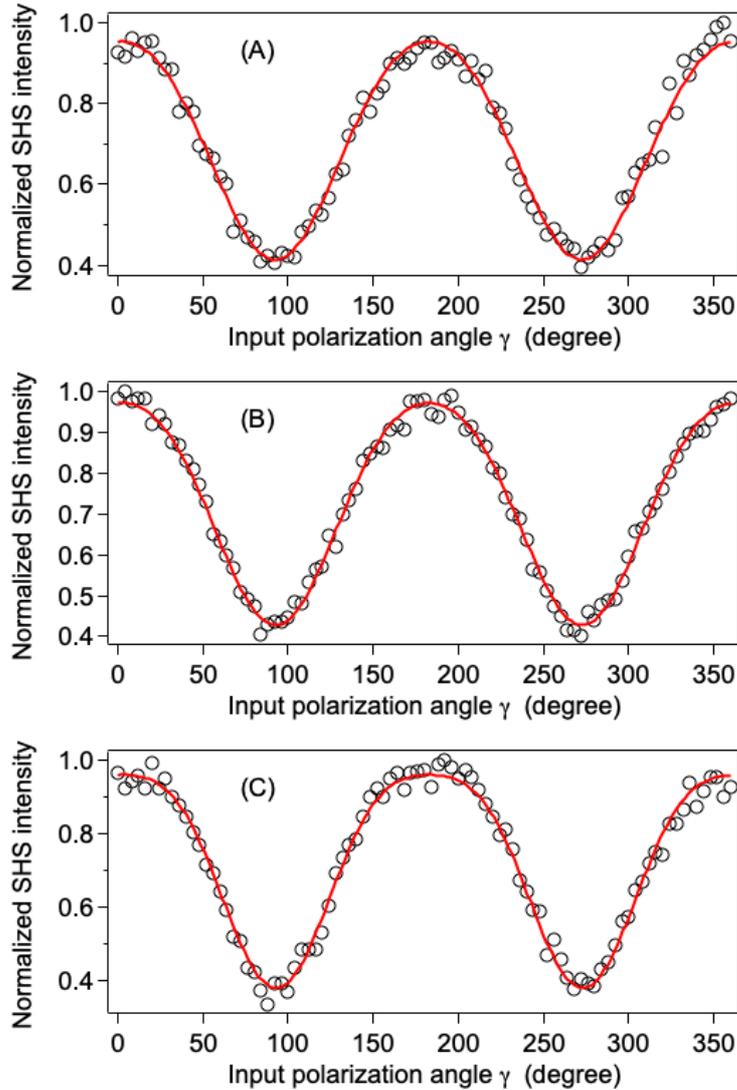
13 **2.2 Experimental set-up**

14 The experimental setup has been described in previous studies [48,54]. Briefly, a Ti:Sapphire
15 femtosecond laser is used delivering pulses at a wavelength of 800 nm, of 140 fs length, at a
16 repetition rate of 80 MHz. The beam is gently focused in the cell containing the neat ionic
17 liquid with an X10 magnification objective. The SHS intensity is collected at right angle by a
18 cooled CCD camera coupled to a spectrometer. For the polarization analysis of the SHS
19 intensity, a half-wave plate in front of the cell and an analyzer before the spectrometer are
20 installed on the setup. The polarization measurements consist in acquiring the vertically
21 polarized harmonic intensity emitted at right angle while the linear polarization of the
22 incoming beam is rotated from its vertical to horizontal orientation. The incident fundamental
23 and the scattered harmonic beams being within a horizontal plane, the horizontal polarization
24 of the light is defined from this plane.

25

1 **3. Results and discussions**

2 The polarization plots measured for $[C_2C_{1im}][NTf_2]$, $[C_4C_{1im}][NTf_2]$ and $[C_{10}C_{1im}][NTf_2]$
 3 are shown in Fig. 1. Similar plots were obtained for $[C_6C_{1im}][NTf_2]$ and $[C_8C_{1im}][NTf_2]$, see
 4 Fig. S3 in Supporting Information.



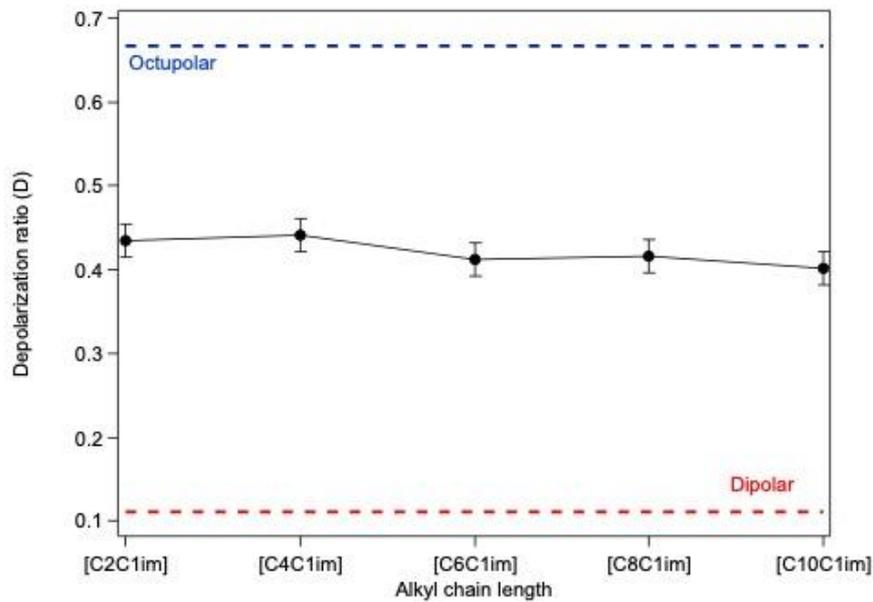
5
 6 **Fig. 1 :** Normalized vertically-polarized SHS intensity as a function of the input
 7 polarization angle γ for (A): $[C_2C_{1im}][NTf_2]$, (B): $[C_4C_{1im}][NTf_2]$ and (C):
 8 $[C_{10}C_{1im}][NTf_2]$. The red line is the plot of the function defined in Eq.4.
 9

10 All these plots exhibit a similar two-peak pattern. The intensity at the input vertical
 11 polarization angle ($\gamma = 0^\circ$) corresponds to the linearly polarized harmonic scattered light in
 12 the vertical-vertical geometry, namely I_{VV} intensity. The intensity at the input horizontal
 13 polarization angle ($\gamma = 90^\circ$) is labelled I_{HV} . These two intensities can be written as a function

1 of the hyperpolarizability tensor elements β_{IJK} expressed in the laboratory frame. I_{VV} is thus
 2 proportional to $\langle\beta_{XXX}^2\rangle$ and I_{HV} to $\langle\beta_{XXY}^2\rangle$ where the X axis corresponds to the vertical
 3 polarization of the fundamental light in the laboratory frame whereas the Y-direction
 4 corresponds to the horizontal polarization. The brackets stand for an orientational average
 5 owing to the isotropy of the liquid phase. The depolarization ratio D can be directly
 6 determined from the I_{VV} and I_{HV} SHS intensities and is thus linked to the hyperpolarizability
 7 elements as follows [19,55]

$$8 \quad D = \frac{I_{HV}}{I_{VV}} = \frac{\langle\beta_{XXY}^2\rangle}{\langle\beta_{XXX}^2\rangle} \quad (1)$$

9 The experimentally determined depolarization ratios D do not depend on the chain length
 10 within experimental errors. These ratios are reported in Fig. 2. D is approximately constant
 11 and equal to (0.42 ± 0.03) . This value is in agreement with previous works on
 12 $[C_2C_{1im}][NTf_2]$ and $[C_4C_{1im}][NTf_2]$ but extended here to longer chain lengths [19].



13
 14 **Fig. 2:** Depolarization ratio as a function of the alkyl chain length. The values of the
 15 depolarization ratio for pure dipolar and pure octupolar systems are reported as
 16 red and blue dashed lines respectively.
 17

18 For low-symmetry structures in liquid phase, it is generally more convenient to use the
 19 irreducible spherical representations of the hyperpolarizability β tensor. This permits the use

1 of the mixed spherical-Cartesian formalism to discuss SHS measurements in terms of
 2 multipolar components [56]. Using this formalism allows the β tensor, a symmetric rank-3
 3 tensor, to be decomposed as the irreducible sum of a dipolar ($J = 1$) and an octupolar ($J = 3$)
 4 tensorial β_J component. The depolarization ratio varies between the value of a pure octupole-
 5 like structure ($D=2/3$) and that of a pure dipolar-like structure ($D=1/9$). In the case of the
 6 present ILs, the depolarization ratios all have an intermediate value as shown in Fig. 2.

7 The anisotropy parameter $\rho = |\beta_{J=3}|/|\beta_{J=1}|$ compares the relative contributions of the
 8 octupolar and dipolar components to the hyperpolarizability tensor β . This parameter is
 9 related to the depolarization ratio through [19]:

$$10 \quad D = \frac{1 + \frac{12}{7}\rho^2}{9\left(1 + \frac{2}{7}\rho^2\right)} \quad (2)$$

11 The anisotropy parameter can be deduced from equation Eq.(2), permitting to determine the
 12 relative contributions of the octupolar components to the hyperpolarizability tensor with:

$$13 \quad \phi(\beta_{J=3}) = \rho/(1 + \rho) \quad (3)$$

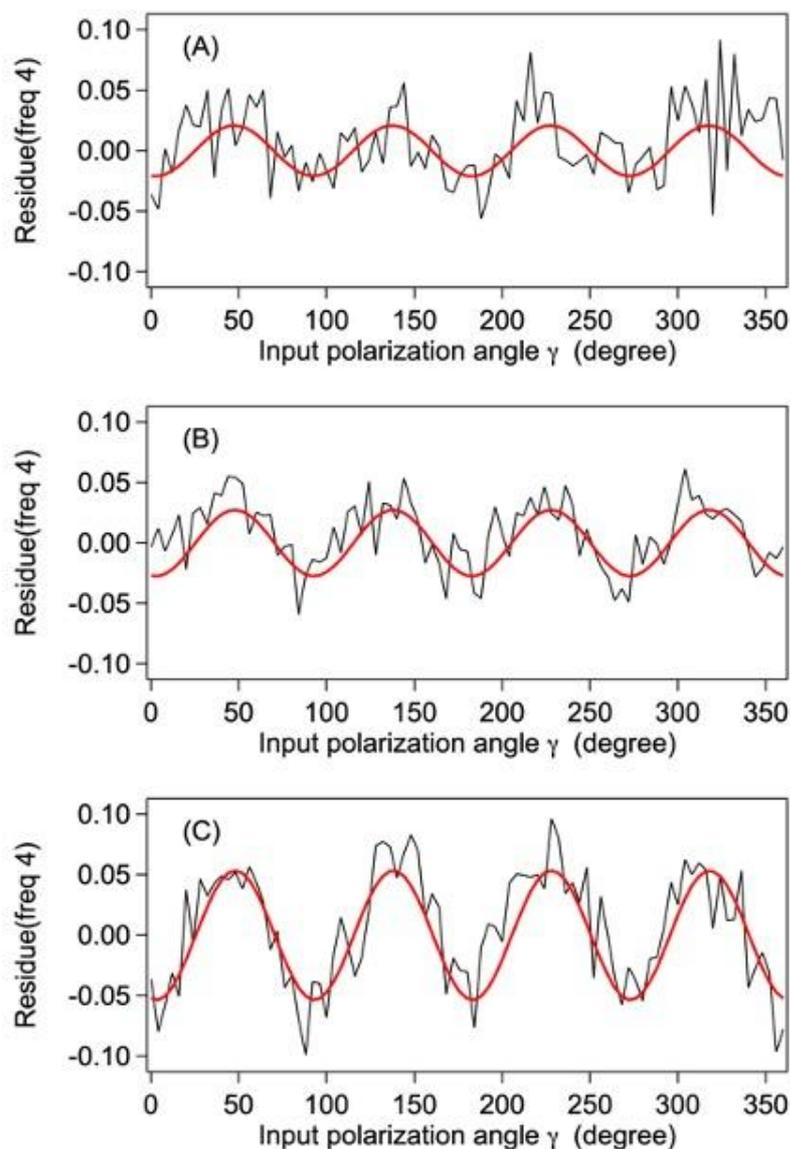
14 The $\phi(\beta_{J=3})$ contribution for the different ILs is equal to (0.68 ± 0.02) indicating that the
 15 SHS response is dominated by an octupolar contribution. This result is in very good
 16 agreement with Rodriguez *et al.* who interpreted with DFT calculations the octupolar
 17 character of the hyperpolarizability from the local microscopic structures involving at least a
 18 double ion pair [19]. In our measurements, the constant value of $\phi(\beta_{J=3})$ indicates that the
 19 symmetry is unaffected by the alkyl chain length.

20

21 To obtain information on the long-range liquid structuration from the polarization plots of Fig.
 22 1, these data were analysed as a Fourier series[48]:

$$23 \quad I_{SHS}(\gamma) = i_0 + i_2 \cos(2\gamma) + i_4 \cos(4\gamma) \quad (4)$$

1 where i_0 , i_2 and i_4 are the amplitudes of the constant, the harmonic 2γ and the harmonic 4γ
2 terms. In Eq.(4), the parameters i_0 and i_2 are related to the local microscopic structure, i.e. the
3 first hyperpolarizability and i_4 to the long-range correlations[48] In the case of randomly
4 oriented species, SHS is a purely incoherent phenomenon and the amplitude i_4 vanishes [48].
5 On the contrary, when molecular orientations are correlated, the scattered photons have well-
6 defined phase relationship and i_4 differs from 0.
7 From the polarization plots of Fig. 1, the constant intensity i_0 and the intensity i_2 at frequency
8 2γ were subtracted in order to only exhibit the residue at frequency 4γ . The corresponding
9 residue plots at frequency 4γ are provided in Fig. 3. The data for $[C_6C_{1im}][NTf_2]$ and
10 $[C_8C_{1im}][NTf_2]$ are given in Supporting Information, see Fig. S3, and are very similar to
11 those of $[C_{10}C_{1im}][NTf_2]$.
12

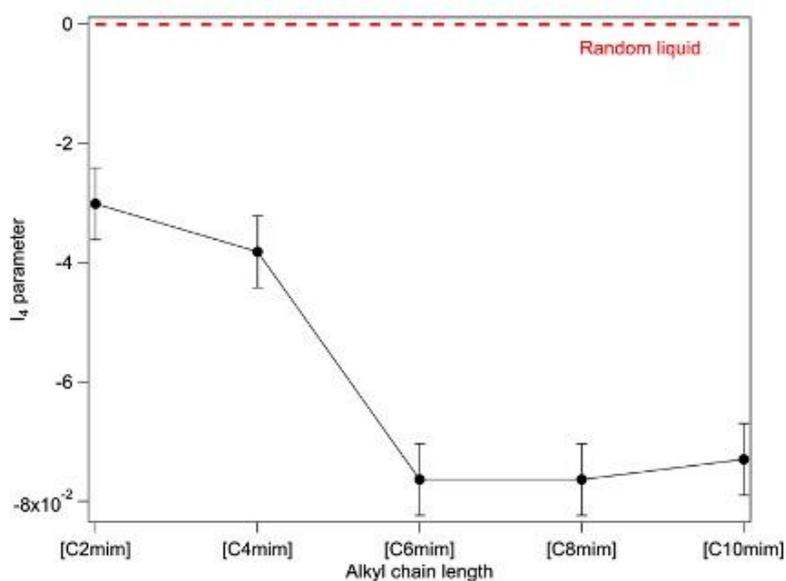


1
2 **Fig. 3:** Residue at the harmonic 4γ of the polarization resolved SH intensity for (A):
3 $[C_2C_{1im}][NTf_2]$, (B): $[C_4C_{1im}][NTf_2]$ and (C): $[C_{10}C_{1im}][NTf_2]$. The red lines are
4 the plots of $i_4 \cos(4\gamma)$.
5

6 All these plots show a clear oscillation at frequency 4γ indicating that i_4 has a non-vanishing
7 value. It is therefore concluded that orientational correlations are present in the bulk phase of
8 these ILs, even for the shortest alkyl chains. Moreover, it is clear on Fig. 3 that the residue at
9 the harmonic 4γ is not constant with the alkyl chain length.

10 To study the increase of the i_4 amplitude, we introduced a normalized parameter defined by
11 $I_4 = i_4/i_0$. The 4γ -frequency amplitude can be either positive or negative. This change of

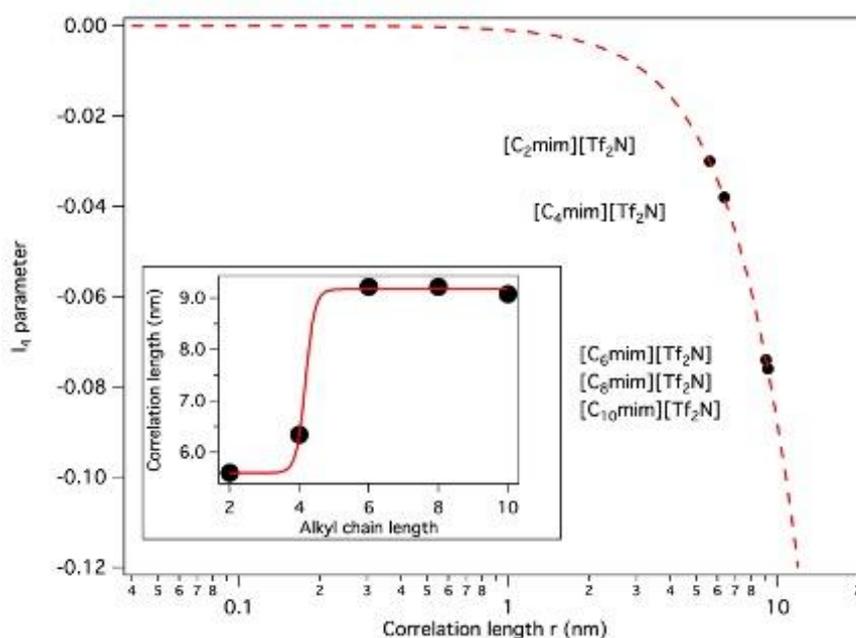
1 sign is linked to the spatial orientational structuration. Indeed, this parameter is positive,
 2 $I_4 \approx 3 \times 10^{-2}$ in the case of pure water whereas it decreases to $I_4 \approx -1 \times 10^{-2}$ at salt
 3 concentration close to 1M [48], evidencing a change of the interactions that drive the
 4 orientational correlation. In the case of $[C_n C_1 \text{im}][\text{NTf}_2]$ ILs, Fig. 4 shows that the sign of
 5 parameter I_4 does not change with n . This parameter is always negative and decreases
 6 significantly with n with an abrupt transition between two regimes between $n=4$ and 6. For
 7 the short alkyl chains, its value is $I_4 \approx -3 \times 10^{-2}$ whereas for the long alkyl chains its value
 8 reaches $I_4 \approx -7 \times 10^{-2}$. The transition occurring between $n=4$ and $n=6$ may also be the
 9 reinforcement of the alkyl chain steric potential with subsequent saturation effect at largest
 10 chain lengths $n=10$.



11
 12 **Fig. 4:** Experimental I_4 parameter as a function of the alkyl chain length.

13
 14 In order to interpret the evolution of this parameter I_4 with the alkyl chain length, we use the
 15 analytical model recently developed for polarization-resolved SHS intensity to describe the
 16 orientational organization of water [48] (details can be found in Supporting Information). In
 17 the case of $[C_n C_1 \text{im}][\text{NTf}_2]$ ILs, it can be assumed that the main contribution to the SHS
 18 intensity is provided by the imidazolium cation, stemming from the aromatic heterocycle. The
 19 relative values of the hyperpolarizability tensor elements at the microscopic scale are obtained

1 through the value of the depolarization ratio previously defined. Then, the resulting
 2 hyperpolarizability at a mesoscopic scale is calculated by summing all the microscopic
 3 hyperpolarizabilities within a defined volume, accounting for the different orientations and
 4 correlation length r . In this work, we assumed a radial distribution of the different nonlinear
 5 sources where all these sources point towards a unique centre. This choice is motivated by the
 6 fact that this distribution corresponds to a micelle-like geometry which is justified for
 7 amphiphilic systems such as imidazolium salts [57]. In addition, this choice is also motivated
 8 by the fact that this distribution gives a negative I_4 compared to other distributions such as the
 9 azimuthal or polar distributions, as expected from experiments. Finally, to account for the ILs
 10 isotropy, global orientational averaging is performed. The resulting I_4 parameter as a function
 11 of the distance r is reported in Fig. 5.



12
 13 **Fig. 5:** Calculated I_4 parameter as a function of the correlation length. The experimental
 14 values of this parameter for the different ILs are reported in the plot. Inset:
 15 Extracted correlation length with the alkyl chain length (the line is a guide to the
 16 eye).
 17

18 This figure exhibits a rapid decrease of I_4 with longer correlation lengths. With this model, the
 19 decrease of the I_4 parameter observed in Fig. 4 is associated to an increase of the correlation

1 length r . This correlation length is in turn plotted for the different ILs as a function of the
2 alkyl chain length, see inset of Fig. 5. An abrupt transition is clearly shown. For shorter alkyl
3 chains, a correlation length between 5 to 6 nm is deduced, signature of a non-random
4 organization at the molecular level in these ILs. For $n \geq 6$, the correlation length is larger,
5 constant and equal to about 9 nm. In comparison, SWAXS experiments reported in the
6 literature have shown that the characteristic size of nanoscale heterogeneity varies linearly
7 with the alkyl chain length n , in the range 1.5 – 2.5 nm [25]. This was deduced from the peak
8 centered around $2\text{-}3 \text{ nm}^{-1}$ in the SWAXS data for the longer alkyl chain length ($n \geq 6$). For
9 shorter alkyl chain length, the emergence of this peak being hidden by the tail of a second
10 peak centered around $8\text{-}9 \text{ nm}^{-1}$, the linear trend was only extrapolated. It was then deduced
11 that a nanoscale segregation of alkyl chains into nonpolar domains, and of the polar ionic
12 moieties into polar domains. Such segregation seems to begin for $n \geq 3$ or 4. MD
13 calculations have also shown the existence of such segregation. Recently, MD has been used
14 to finely analyze SWAXS experiments showing that the structural transition occurs for $n \geq 5$,
15 from which a percolation regime appears [40]. More precisely, it has been demonstrated that
16 for the smaller alkyl chain lengths ($n=2$ and 4), the nonpolar aggregates form elongated
17 clusters that become more oblate around $n=5$ and start to percolate for the longer alkyl chain
18 length. The linear trend reported in SWAXS experiments is not observed in the present SHS
19 data. Moreover, the correlation lengths deduced from the SHS data cannot be directly
20 associated with the dimensions observed in SWAXS experiments. Nevertheless, the transition
21 observed in the correlation length from 5 to 9 nm occurs in the same chain length as the
22 appearance of the percolation regime.

23

24 **4. Conclusion**

1 In summary, SHS measurements were performed on the 1- Alkyl-3-
2 MethylimidazoliumBis(trifluoromethylsulfonyl)imide IL homologous series $[C_nC_{1im}][NTf_2]$
3 ILs with $n=2,4,6,8$ and 10. Polarization-resolved analysis of the SHS intensity reveals the
4 dominant octupolar nature of the molecular SH response of ILs at all alky chain lengths.
5 Orientational correlations at the nanometer scale are also extracted from the polarization-
6 resolved SHS intensities. These correlations are interpreted as stemming from the radial
7 distribution of the alkyl chains, even for the ILs with the shortest alkyl chains. An abrupt
8 transition to longer correlation distances is observed from the hexyl chain onwards, revealing
9 a clear structural transition. The SHS technique therefore provides a direct observation of
10 structural transition in liquids at scales well-below the diffraction limit and these findings
11 open new interesting perspectives in the future.

12

13 **Acknowledgements**

14 The authors thank the financial support of the French National Agency for Research under
15 project PROFILE (ANR-17-CE29-0009). The financial support from the Research Federation
16 André Marie Ampère (FRAMA) is also acknowledged.

17

18

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