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ARTICLE

Arrangements of enantiopure and racemic ionic liquids at the liquid/air interface: the role of chirality on self-assembly and layering

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Chiral ionic liquids (CILs) have been obtained in high yield using commercial propylene oxide or natural alcohols (citronellol and nopol) as building blocks. The self-assembly ability at the interface IL/air for some couples of enantiopure and racemic CILs was explored by angle resolved XPS.

Introduction

Ionic liquids (ILs) are low-melting-point organic salts that have attracted in the last years an increasing interest as solvents or additives in numerous applications. ILs are indeed characterized by unique properties, including negligible vapor pressure at ambient conditions, good thermal stability, favorable solvation behavior and, when used as solvents, they are able to guarantee high reactivity and selectivity.[1] An enormous number of different ILs can be prepared with the possibility to fine-tune their physico-chemical properties by variations in the molecular structure of cation and/or anion and by mixing and matching different ion pairs.[2]

The coexistence of charged moieties and hydrophobic alkyl chains, generally present on cation, determines the occurrence of both electrostatic and van der Waals interactions. Moreover, depending on cation and anion structure hydrogen bonds between these species can be present. Consequently, ILs are often characterized by a high degree of self-organization:[3] in imidazolium based ILs with sufficiently long side chains (butyl or longer) the formation of apolar domains that coexist with an ionic networks characterizes both the liquid bulk[4] and the interfaces (IL/solid, IL/air, IL/other liquids).[3,5] In particular, at the IL/air interface there is pronounced layering: the outermost region of the interface is populated by the alkyl chains, whereas the bulk is characterized by a dense and tightly packed layer formed by oppositely charged ionic moieties.[6] The increase in the alkyl chain length on cation favors arrangements with the chains pointing to the gas, thus increasing the coverage of the surface with alkyl groups. On the other hand, larger anions promote a disruption of the ionic layer increasing the amount of free spaces.[6]

In this regard, ILs possessing one or more chiral centers, namely chiral ILs (CILs), can be considered a subclass of salts having special peculiarities, which have found application in analytical separation, in chiral discrimination, in asymmetric synthesis, in chiral chromatography, and as chiral solvents.[7] A significant number of CILs have been designed, synthesized and utilized recently.

Chirality is a fascinating property of molecular compounds and a powerful tool for the generation of order, directionality and, as such, of utility, in assembled nanoscale chemical devices. Chirality encoded in specific building blocks, at molecular scale, can control the nanoscale assembly of soft materials, such as gels, micelles, polymers.[8] Integration between chirality and functional aggregates is therefore a field of great current interest.[9]

Despite the intense research activity in ILs and the fact that chiral centers on cation and/or anion might determine the insurgence of a supramolecular chirality in the resulting dynamic nanostructures (both in the pure IL and in solution) investigations in this area are yet limited.[10] Actually, ILs consisting of a charged hydrophilic head group and a long hydrophobic tail possess surface properties similar to traditional surfactants and are able to give in water different kind of aggregates, such as micelles, vesicles, bilayers, etc.[11] Recently, long chain triazolium-based CILs, showing good thermal stability and surface-active behavior, have been prepared and characterized.[12] However, practically no data have been reported about the supramolecular chirality of the related self-assembled ionic systems, as well as on the comparison with the corresponding racemic salts, although these systems might be also very important for the understanding of self-assembly processes, symmetry breaking phenomena, and for the development of new materials.

Herein, we report the synthesis and characterization of new chiral long-chain ILs, using as building block the optically active propylene oxide or commercially available natural alcohols and focusing our attention in particular on aggregation behavior at the interface IL/vacuum (air).

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Experimental

General methods

Unless otherwise specified the reagents were used without any purification. (*R*)-Propylene oxide, (*S*)-(−)-β-citronellol were 99% enantiopure, whereas (1*R*)-(-)-nopol was 98% .

^{1}H NMR spectra were recorded in $CDCl_3$ or D_2O on a 200 or 300 MHz NMR spectrometer. The following abbreviations are used: s=singlet, d=doublet, dd=double doublet, t=triplet, m=multiplet, br=broad. ^{13}C NMR spectra were recorded at 75 MHz. The temperature was controlled to ±0.1 °C. ^{1}H and ^{13}C NMR chemical shifts (ppm) are referred to TMS as external standard.

Circular Dichroic (CD) spectra have been recorded on a JASCO815SE in quatz cuvettes of 1mm, 0.1 mm or demountable 0.01 mm. All spectra have been recorded at 25°C. A test at different temperature (2°C-90°C) on compound **6f** shows only a wavelength shift of 3nm and no substantial variation in intensity.

X-ray Photoelectron Spectroscopy (XPS) measurements were carried out in an ultra-high vacuum (10-9 mbar) system equipped with a VSW HAC 5000 hemispherical electron energy analyser and a non-monochromatized Mg-Kα X-ray source (1253.6 eV). The source power was 100 W (10 kVx10 mA) and the spectra were acquired in the constant-pass-energy mode at Epas = 44 eV. The recorded spectra were fitted using CasaXPS vert. 2.3.15 software employing Gauss-Lorentz curves after subtraction of a Shirley-type background. A drop of the investigated CILs were loaded onto a gold foil (dimension 1cm x 1cm), previously maintained in HNO_3 conc. The surface tension was enough to form a homogeneous and thick film of liquid as demonstrated by the absence of signals attributable to the gold substrate. The loaded sample holder was kept in the introduction chamber for at least 12 hours before the measurements, allowing the removal of volatile substances as confirmed by the pressure value achieved (2x 10^{-8} mbar), just above the instrument base pressure.

Ionic Liquids Synthesis

Chiral alcohols: representative procedure

Chiral alcohols **1** were synthesized according to reported procedures with some variations that allow to avoid chromatographic purifications.[13] A solution of (R)-propylene oxide (5 g, 86.2 mmol) containing cat. copper iodide (190.45 mg, 1 mmol) in anhydrous diethyl ether was cooled to -30°C. To this solution the Grignard reagent (1 mol L-1 , solution in ether, 100 ml, 100 mmol) was added dropwise over a period of 10 min. After stirring for 2 h, the reaction was quenched with saturated aqueous NH_4Cl and extracted with Et_2O (3x20 ml). The organic phases were dried over Na_2SO_4 and after removing the solvent the crude was distilled under reduced pressure affording the pure product.

(*R*)-4-phenylbutan-2-ol (**1a**): 12.0 g (80 mmol, 93%): (±)-4-phenylbutan-2-ol (**1b**): 11.5 g (77 mmol, 90%) . ^{1}H NMR (200 MHz, $CDCl_3$, δ) 7.20 (m, 5H), 3.80 (m, 1H), 2.68 (m, 2H), 1.77(m, 2H), 1.61 (s, 1H), 1.21(d, J=6Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 142.2, 128.5, 125.9, 67.6, 40.9, 32.2, 23.7.

(R)-4,4-dimethylpentan-2-ol (**1c**): 6.92 g (56.56 mmol, 62%) 1H NMR (200 MHz, $CDCl_3$, δ) 3.95 (m, 1H), 1.37 (d, J=6Hz, 1H), 1.34 (d, J=2Hz, 1H), 1.20 (d, J=6Hz, 3H), 0.97 (t, J=1Hz, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 66.0, 53.1, 30.2, 26.1, 15.4.

Alkoxyacetic acids 2a-c: representative procedure

A solution of alcohols (50 mmol) in freshly distilled anhydrous 1,4-dioxane (30 ml) was added dropwise under nitrogen atmosphere to a suspension of NaH (60 mmol) in 1,4-dioxane (40 ml), and the mixture was stirred at rt for 2 h. Then, sodium chloroacetate (100 mmol) was added under nitrogen atmosphere and the reaction mixture was refluxed for 93 h. After cooling to rt, water was added and the mixture was concentrated under reduced pressure to remove the organic solvent. The aqueous alkaline phase was extracted with Et_2O (3x30ml) discarding the organic phase, and the aqueous phase was made acidic with HCl and extracted with Et_2O (3x30ml). The final collected organic phases were dried over anhydrous Na_2SO_4, then the solvent was removed under vacuum, obtaining the pure product.

(*R*)-2-[(4-phenylbutan-2-yl)oxy]acetic acid (**2a**): 9.93 g (47.7 mmol, 95%) transparent liquid; (±)-2-[(4-phenylbutan-2-yl)oxy]acetic acid (**2b**): 9.42 g (45.2 mmol, 91%) transparent liquid; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.24 (m, 5H), 6.79 (br s, 1H), 4.10 (d, J=7.8Hz, 2H), 3.55 (m, 1H), 2.69 (m, 2H), 1.92 (m, 1H), 1.76 (m, 1H), 1.21 (d, J=6Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, δ)174.7, 141.9, 128.5, 128.5, 126.0, 76.4, 65.6, 38.0, 31.7, 19.4.

(*R*)-2-[(4,4-dimethylpentan-2-yl)oxy]acetic acid (**2c**): 5.16 g (29.65 mmol, 59%) transparent liquid; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 6.33 (br s, 1H), 4.09 (d, J=13 Hz, 2H), 3.65 (m, 1H), 1.59 (dd, J1= 17.7Hz, J2=9Hz, 1H), 1.28 (dd, J1=17.7Hz, J2=4.5Hz, 1H), 1.18 (d, J=7.2Hz, 3H), 0.92 (s, 9H); ^{13}C NMR (75 MHz, CDCl3, δ) 173.6, 75.0, 65.2, 50.5, 30.1, 21.2.

2-Alkoxyethanols 3a-c: representative procedure

A solution of the alkoxyacetic acid (50 mmol) in anhydrous THF (15 ml) was added dropwise at 0°C to a suspension of $LiAlH_4$ (50 mmol) in anhydrous THF (60 ml) during 30 min. The reaction mixture was stirred at rt overnight (20 h) and refluxed for 6 h, then was carefully quenched with water under nitrogen atmosphere until collapse. After addition of Et_2O (30 ml), the solids were filtered off and the organic phase was dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure giving the pure product.

(*R*)-2-[(4-phenylbutan-2-yl)oxy]ethan-1-ol (**3a**): 9.3 g (47.9 mmol, 96%) yellowish liquid. (±)-2-[(4-phenylbutan-2-yl)oxy]ethan-1-ol (3b): 8.81 g (45.35 mmol, 91%) yellowish liquid. ^{1}H NMR (300 MHz, CDCl3, δ) 7.24 (m, 5H), 3.73 (m, 2H), 3.62 (m, 1H), 3.45 (m, 2H), 2.70 (m, 2H), 2.04 (br s, 1H), 1.86 (m, 1H), 1.73 (m, 1H), 1.18 (d, J=7.2Hz, 3H); ^{13}C NMR (75 MHz, CDCl3, δ) 142.3, 128.5, 125.9, 75.2, 69.4, 62.3, 38.3, 31.9, 19.7.

(*R*)-2-[(4,4-dimethylpentan-2-yl)oxy]ethan-1-ol (**3c**): 6.56 g (40.96 mmol, 82%) transparent liquid. 1H NMR (300 MHz, $CDCl_3$, δ) 3.69 (m, 2H), 3.54 (m, 2H), 3.40 (m, 1H), 1.97 (s, 1H), 1.54 (dd, J1=18Hz, J2=9Hz, 1H), 1.23 (dd, J1=18Hz, J2=3Hz, 1H), 1.14 (d, J=6Hz, 3H), 0.92 (s, 9H) ; ^{13}C NMR (75 MHz, $CDCl_3$, δ) 73.8, 69.1, 62.3, 50.9, 30.2, 21.4.

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2-alkoxyethylmethanesulphonates 4e-f: representative procedure

A solution of methanesulfonyl chloride (50 mmol) in CH_2Cl_2 (20 ml) was added dropwise at 0°C to a solution of alcohol **3** (50 mmol) and Et_3N (51 mmol) in CH_2Cl_2 (25 ml) during 20 min, then the reaction mixture was stirred at rt for 24h. The reaction was quenched with saturated aqueous $NaHCO_3$ solution and was extracted with CH_2Cl_2 (3x20ml). The collected organic phases were dried over anhydrous Na_2SO_4, then the solvent was evaporated under reduced pressure giving the pure product.

(*R*)-2-[(4-phenylbutan-2-yl)oxy]ethyl methanesulfonate (**4a**): 13 g (47.76 mmol, 96%) pale yellow liquid. (±)-2-[(4-phenylbutan-2-yl)oxy]ethyl methanesulfonate (**4b**): 12.32 g (45.25 mmol, 91%) amber-colored liquid. ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.24 (m, 5H), 4.36 (t, J=5.7Hz, 2H), 3.76 (m, 1H), 3.62 (m, 1H), 3.46 (m, 1H), 3.06 (s, 3H), 2.70 (m, 2H), 1.87 (m, 1H), 1.74 (m, 1H), 1.19 (d, J=7.2Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 142.1, 128.5, 125.9, 75.5, 69.7, 66.2, 38.2, 37.7, 31.7, 19.5.

(*R*)-2-[(4,4-dimethylpentan-2-yl)oxy]ethyl methanesulfonate (**4c**): 9.95g (41.78 mmol, 84%) pale yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$, δ) 4.32 (m, 2H), 3.75 (m, 1H), 3.52 (m, 2H), 3.02 (s, 3H), 1.50 (dd, J1=17.4Hz, J2=9Hz, 1H), 1.22 (dd, J1=17.4Hz, J2=4.2Hz, 1H), 1.13 (d, J=7.2Hz, 3H), 0.91 (s, 9H); 13C NMR (75 MHz, CDCl3, δ) 74.20, 69.60, 65.82, 50.68, 37.73, 30.19, 21.23.

(*S*)-3,7-dimethyloct-6-en-1-yl methanesulfonate from (*S*)-(-)-β-Citronellol (**4d**): 11.32 g (48.3 mmol, 97%) yellow liquid. (±)-3,7-dimethyloct-6-en-1-yl methanesulfonate from (±)-β-Citronellol (**4e**): 11.0 g (48.0 mmol, 97%) yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$, δ) 5.06 (t, J=8.3 Hz, 1H), 4.25 (m, 2H), 2.98 (s, 3H), 1.97 (m, 2H), 1.67 (s, 3H), 1.68 (m, 3H), 1.59 (s, 3H). 1.33 (m, 1H), 1.19 (m, 1H), 0.92 (d, J=7.8Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 131.7, 124.3, 68.7, 37.4, 36.9, 34.0, 29.0, 25.8, 25.4, 19.2, 17.7 .

[(*1R,5S*)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl]methyl methanesulfonate (**4f**) from (*1R*)-(-)-Nopol (**3f**): 11.58 g (47.39 mmol, 95%) pale yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$, δ) 5.33 (m, 1H), 4.19 (t, J=7.5Hz, 2H), 2.97 (s, 3H), 2.39 (m, 3H), 2.21 (m, 2H), 2.07 (m, 1H), 2.02 (m, 1H), 1.25 (s, 3H), 1.12 (d, J=10,5Hz, 1H), 0.81 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 142.6, 120.0, 68.0, 45.6, 40.6, 38.1, 37.5, 36.4, 31.6, 31.4, 26.2, 21.2.

Synthesis of *N*-methylimidazolium methanesulphonates: representative procedure:
A mixture of the mesylate **4** (50 mmol) and *N*-methylimidazole (50 mmol) in CH_3CN (20 ml) was refluxed for 72h. The solvent was removed under vacuum obtaining the pure product.

(*R*)-1-methyl-3-{2-[(4-phenylbutan-2-yl)oxy]ethyl}-1H-imidazol-3-ium methanesulfonate (**5a**): 17.61 g (49.70 mmol, 99%) yellowish liquid.

(±)-1-methyl-3-{2-[(4-phenylbutan-2-yl)oxy]ethyl}-1H-imidazol-3-ium methanesulfonate (**5b**): 17.16 g (48.44 mmol, 97%) yellowish liquid. ^{1}H NMR (300 MHz, $CDCl_3$, δ) 9.40 (s, 1H), 7.37 (t, 1H, J=2.1Hz), 7.29 (t, 1H, J=2.1Hz), 7.13 (m, 5H), 4.39 (t, J=6Hz, 2H), 3.92 (s, 3H), 3.78 (m, 1H), 3.63 (m, 1H), 3.40 (m, 1H), 2.67 (s, 3H), 2.51 (m, 2H), 1.84-1,54 (m, 2H), 1.06 (d, J=7.5Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 141.9, 137.9, 128.5, 128.3, 125.9, 123.1, 122.9, 75.6, 66.4, 50.2, 39.5, 38.1, 36.4, 31.7, 19.4.

(*R*)-3-{2-[(4,4-dimethylpentan-2-yl)oxy]ethyl}-1-methyl-1H-imidazol-3-ium methanesulfonate (**5c**): 15.99 g (49.94 mmol, 99%) yellow solid; mp: 76°C. ^{1}H NMR (300 MHz, $CDCl_3$, δ) 9.65 (br s, 1H), 7.41 (t, J=1.8 Hz, 1H), 7.37 (t, J=1.8Hz, 1H), 4.39 (dt, J1=7.8Hz, J2=4.2Hz, 2H), 3.95 (s, 3H), 3.76 (m, 1H), 3.59 (m, 1H), 3.43 (m, 1H), 2.69 (s, 3H), 1.39 (dd, , J1=17.4Hz, J2=8.7Hz, 1H), 1.14 (dd, J1=17.4Hz, J2=4.2Hz, 1H), 1.00 (d, J=7.2Hz, 3H), 0.76 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 138.0, 123.1, 122.9, 74.0, 65.9, 50.6, 50.3, 39.7, 36.3, 30.0, 21.1.

(*S*)-3-(3,7-dimethyloct-6-en-1-yl)-1-methyl-1H-imidazol-3-ium methanesulfonate (**5d**): 15.65 g (49.47 mmol, 99%) yellowish liquid. (±)-3-(3,7-dimethyloct-6-en-1-yl)-1-methyl-1H-imidazol-3-ium methanesulfonate (**5e**): 15 g (49.47 mmol, 99%) yellowish liquid. ^{1}H NMR (300 MHz, $CDCl_3$, δ) 9.31(s, 1H), 7.52 (t, J=2.4 Hz, 1H), 7.33 (t, J=2.4 Hz, 1H), 5.01 (t, J=8.4Hz,1H), 4.23 (dt, J1=7.5Hz, J2=2.4Hz, 2H), 4.01 (s, 3H), 2.72 (s, 3H), 1.93 (m, 4H), 1.63 (s, 3H), 1.55 (s, 3H), 1.38 (m, 2H), 1.19 (m, 1H), 0.93 (d, J=7.8Hz, 3H); ^{13}C NMR (75 MHz, CDCl3, δ) 137.9, 131.7, 124.0, 123.7, 121.7, 48.1, 39.7, 37.3, 36.6, 36.3, 29.8, 25.7, 25.2, 18.9, 17.7.

3-{[(*1R,5S*)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2yl] methyl}-1-methyl-1H-imidazol-3-ium methanesulfonate (**5f**): 16.02 g (49.11 mmol, 98%) white solid; mp: 113-118°C. ^{1}H NMR (300 MHz, D_2O, δ) 7.44 (d, J=2.1Hz,1H), 7.38 (d, J=2.1Hz, 1H), 5.28 (br s, 1H), 4.22 (t, J=8.1Hz, 2H), 3.85 (s, 3H), 2.77 (s, 3H), 2.53 (t, J=9Hz, 2H), 2.36 (m, 1H), 2.14 (br s, 2H), 2.04 (m, 2H), 1.23 (s, 3H), 0.915 (d, J=10.2Hz, 1H), 0.69 (s, 3H); ^{13}C NMR (75 MHz, D2O, δ) 142.6, 122.9, 121.8, 120.1, 46.9, 44.0, 39.7, 38.0, 36.8, 35.7, 35.1, 30.7, 30.4, 25.0, 19.8.

Metathesis reactions. Representative procedure:
An aqueous solution of $LiTf_2N$ (50 mmol) was added to an aqueous solution of IL **5** (50 mmol) and the mixture was stirred at rt for 24 h. The insoluble oily material was separated adding CH_2Cl_2 and the organic layer was washed with water and brine and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure to give the expected product.

(*R*)-1-methyl-3-{2-[(4-phenylbutan-2-yl)oxy]ethyl}-1H-imidazol-3-ium bis[(trifluoromethyl)sulfonyl]imide (**6a**): 26.6 g (49.3 mmol, 99%). (±)-1-methyl-3-{2-[(4-phenylbutan-2-yl)oxy]ethyl}-1H-imidazol-iumbis[(trifluoromethyl)sulfonyl]imide (**6b**): 25.2 g (49 mmol, 99%) pale yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$, δ) 8.62 (s, 1H), 7.34 (t, J=2.1Hz, 1H), 7.28-7.07 (m, 6H), 4.27 (t, J=5.7Hz, 2H), 3.94 (s, 3H), 3.76 (m, 1H), 3.61 (m, 1H), 3.40 (m, 1H), 2.55 (m, 2H), 1.87-1.56 (m, 2H), 1.09 (d, J=7.5Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 142.0, 136.4, 128.5, 128.4, 126.8, 126.0, 123.4, 122.4, 117.3, 113.4, 75.8, 65.9, 50.5, 38.0, 36.3, 31.7, 19.2.

(*S*)-3-(3,7-dimethyloct-6-en-1-yl)-1-methyl-1H-imidazol-3-ium bis[(trifluoromethyl)sulfonyl]imide (**6d**): 16 g (49.5 mmol, 99%) pale yellowish liquid. (±)-3-(3,7-dimethyloct-6-en-1-yl)-1-methyl-1H-

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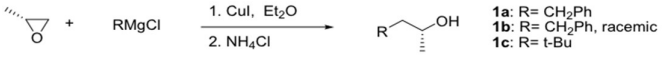
imidazol-3-ium bis[(trifluoromethyl)sulfonyl]imide (**6e**): 15 g (46.5 mmol, 93%) pale yellowish liquid. ^{1}H NMR (300 MHz, $CDCl_3$, δ) 8.71 (s, 1H), 7.32 (t, J=2.1Hz, 1H), 7.29 (t, J=2.1Hz, 1H), 5.04 (t, J=8.4Hz,1H), 4.16 (m, 2H), 3.91 (s, 3H), 2.07-1.11 (m, 7H), 1.65 (s, 3H), 1.57 (s, 3H), 0.93 (d, J=7.5Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 137.9, 131.7, 124.0, 123.7, 121.7, 48.1, 39.7, 37.3, 36.6, 36.3, 29.8, 25.7, 25.2, 18.9, 17.7.

3-{[(*1R,5S*)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2yl] methyl}-1-methyl-1H-imidazol-3-ium bis[(trifluoromethyl) sulfonyl]imide (**6f**): 24.73 g (48.4 mmol, 97%) pale yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$, δ) 8.71 (br s, 1H), 7.30 (t, J=2.1Hz 1H), 7.28 (t, J=2.1Hz, 1H), 5.31 (m, 1H), 4.19 (t, J=9Hz, 2H), 3.92 (s, 3H), 2.52 (t, J=9Hz, 2H), 2.40 (m, 1H), 2.19 (br s, 2H), 2.06 (m, 2H), 1.27 (s, 3H), 1.00 (d, J=10.5Hz, 1 H), 0.76 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 142.3, 136.2, 127,6, 123.7, 122.4, 122.4, 121.1, 112.3, 48.2, 45.1, 40.6, 38.1, 37.1, 36.4, 31.7, 31.4, 26.1, 21.0.

Results and discussion

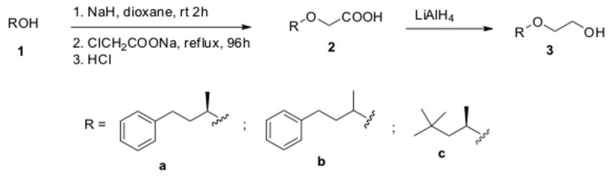
To obtain ILs possessing a bulky non-polar chiral architecture capable to give rise to stereochemically dependent hydrophobic interactions or, in the case of CILs containing aromatic groups, π−π interactions, chiral secondary alcohols were synthesized starting from propylene oxides. In particular, the enantiopure commercial (R)-propylene oxide (or the corresponding racemic epoxide) was reacted with a Grignard reagent in the presence of a catalytic amount of CuI, affording the desired secondary alcohol in 60-90% yield (Scheme 1).



Scheme 1

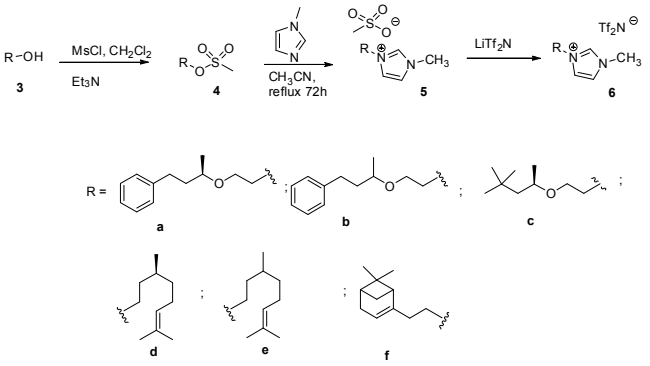
Furthermore, to favor the self-organization of the chiral hydrophobic chains of the final planned imidazolium salts, we decided to lengthen the synthesized secondary alcohols introducing a proper spacer (a C2 tether). The tether was introduced as described in Scheme 2. The chiral alcohols **1** were treated with sodium hydride and the resulting sodium alkoxides were reacted with sodium chloroacetate, affording the alkoxyacetic derivatives **2** in good-excellent yields. The $LiAlH_4$ reduction of the carboxylic group gave alcohols **3** in excellent yields. Longer spacers were avoided to prevent an excessive conformational freedom. The applied synthetic strategy was supported by the possibility to easily convert the primary hydroxyl groups into the corresponding mesylates (**4**), which, in turn, can be displaced by the nucleophilic nitrogen of the imidazole ring.

Finally, two chiral natural alcohols ((*R*)-nopol and (*S*)-citronellol) and racemic citronellol were used to prepare imidazolium based CILs: in this case, however, being the chiral centre sufficiently distant from the hydroxyl group, alcohols were directly converted to the corresponding mesylates.



Scheme 2

From alcohols **3**, CILs were prepared in three steps (Scheme 3). The reaction of the alcohols with methanesulphonyl chloride afforded the corresponding mesylates, in very high yields, which could be quantitatively transformed into the corresponding salts **5** by reaction with *N*-methylimidazole. To obtain information about the eventual role of anion on the assembly properties of CILs, ILs **5a-b** and **5d-f** were transformed into the corresponding bis[(trifluoromethyl)sulfonyl]imide based ILs **6**, by anion exchange.



Scheme 3

It is noteworthy that with the exception of **5c** and **5f** all the other salts were uncolored or pale yellow liquids at room temperature. The presence of an ethereal group on the side alkyl chain appears able to give moderately or low viscous liquids also in the presence of a phenyl ring.

Chiroptical Properties

A preliminary CD investigation was conducted initially on the less viscous bis[(trifluoromethyl)sulfonyl]imide based CILs **6a**, **6d** and **6f** and, to obtain information on the role anion, on CIL **5d**. The neat samples have been measured in quartz cuvettes at 25°C. Results are reported in Figure 1 and the asymmetry factor g values at CD band maximum are given in Table 1.

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Table 1. Asymmetry factor g values for CILs.

	λ (nm)	g factor	cell pathlength (mm)
6f	338	5×10^{-3}	0.2
6d	287	1×10^{-4}	1
5d	293	1×10^{-4}	0.1
6a	263	3.6×10^{-5}	~≈0.01

The comparison of the CD spectra of ILs **5d** and **6d** seems to suggest a negligible effect of the anion on the Cotton effect, despite of the fact that the interactions of the two anions (mesylate and bis[(trifluoromethyl)sulfonyl]imide) with the imidazolium cation should be significantly different.

Finally, it is noteworthy that only the presence of a bulky chiral group, dimethylbicyclo[3.1.1]hept-2-en-2yl, in **6f** originates a quite intense CD band. Moreover, for this CIL the CD signal (considering the g factor, which can be evaluated without explicit knowledge of concentration) is the same for the neat sample and acetonitrile solutions.

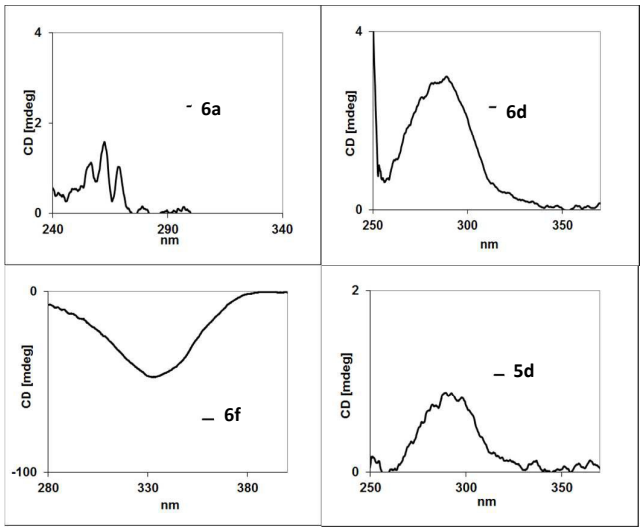

Fig 1. CD spectra on neat ILs, for g values and pathlengths see Table 1

Surface Properties

In order to verify if the outermost regions of the IL/air interface, which are often primarily populated in imidazolium salts by the cation alkyl chains, are affected by the presence of a chiral center, the structure of CILs **5a** and **5d** at the liquid/vacuum interface was investigated by means of angle resolved-XPS (AR-XPS). Furthermore, since enantiopure compounds and racemic mixtures can be characterized by different interaction ability and consequently by a distinct self-assembly behavior, measurements were carried out also on the corresponding racemic mixtures, ILs **5b** and **5e**. Experiments were always carried out by changing the sample orientation with respect to the electron analyzer in order to change the thickness of the probe depth. The spectra were recorded at different angles from normal (0° or 90° take off) to grazing (75°, 15° take off) emission angle.

Figure 2 displays the O s1 XPS spectra collected at normal and grazing angle for **5a** and **5b**. In accordance with literature data [14] the spectra were fitted by means of two components attributable to the oxygen atoms of methansulfonate anion (BE 532.2 eV) and of the ethereal group on imidazolium cation, R-O-R (BE 530.7 eV). At normal emission angle, racemic mixture (**5b**) is characterized by a nearly stoichiometric composition (3 : 1, ratio between the two components) (Figure 2A). Vice versa, in the spectrum of the enantiopure IL **5a** the stoichiometry is not satisfied: an enrichment in the cation component can be envisaged (atomic ratio is close to 1:1) (Figure 2C). In both samples, the decrease in the probing depth leads to an enhancement of the peak attributable to the methansulfonate anion (Figure 2B and 2D). This effect is more pronounced in the enantiopure liquid **5a** with respect to the racemic mixture, as shown by Figure 2.

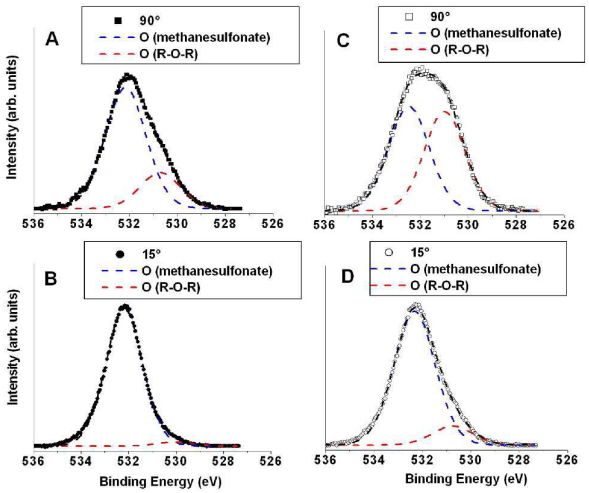

Fig 2. O 1s Xps spectra collected at normal (90° take off angle) and grazing angle (15°) on 5b (A, B) and 5a (C, D) sample**.**

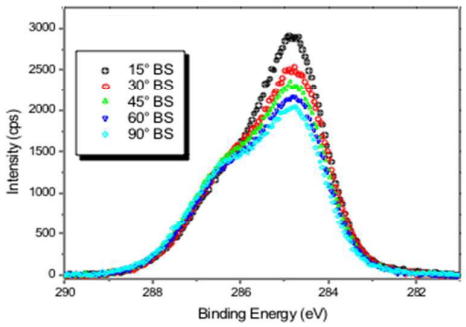

Fig 3. Normalized C 1s spectra as function of take-off angle for **5a** sample.

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Fitting the C 1s peak is much more complicated with respect to the O 1s due to the larger number of overlapping components contributing the XPS spectra of carbon. Therefore, the unambiguous assignment of all the different components was not reliable. Nevertheless, the peaks can be regarded as the sum of at least two different groups of peaks. One, at lower binding energy values (284.8 eV), attributable to the carbons of the aliphatic chain (and, probably, of the phenyl ring) and the another one, located at higher energy (286.3 eV), attributable to the carbon of the imidazolium ring and methansulfonate anion. In accordance with previous studies,[15] the contribution at lower B.E. value is dominant in the spectra collected at grazing angle (thinner probing depth) (see Figure 3). This observation undoubtedly shows that the contribution of aliphatic carbons increases in the uppermost portion of the liquid; *i.e.* these groups are pointing away from the bulk liquid. This trend characterizes both the enantiopure CIL **5a** and the corresponding racemic mixture **5b**. However, side chain carbons seem to contribute more extensively to the surface composition in the case of the racemic mixture, as evidenced by the diagram reported in Figure 4.

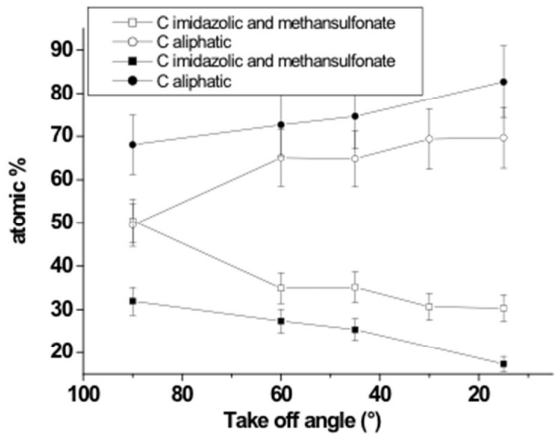

Fig 4. Contributes to the C 1s peak by aliphatic and imidazolium carbons as function of take-off angle for **5b** (full symbols) and **5a** (empty symbols) sample.

A different preferential orientation of the side chains with respect to the liquid surface, attributable to the chiral center and consequently to the different packing ability of the racemic mixture and enantiopure CIL, could determine the observed differences in the XPS spectra of **5a** and **5b.** A cartoon-like representation of the preferred orientations of these two ILs at the air-liquid interface, accentuating the principal differences between racemic and enantiopure IL, is reported in Figure 5.

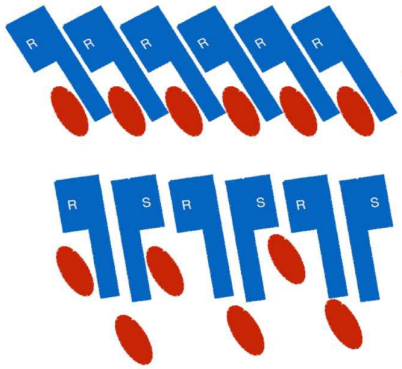

Fig 5. Cartoon-like representation of the preferred orientations of **5a** and **5b** at the air-liquid interface

It is noteworthy that substitution of the aromatic ring on the side alkyl chain of cation with a double bond, ILs **5d** and **5e**, induces some interesting phenomena at the liquid/vacuum interface can be evidenced. As observed for **5a** and **5b**, the outermost portion of these liquids results enriched in the aliphatic components, *i.e.* cation alkyl side chains. However, both for **5d** and **5e** the surface enrichment is much less marked (see Figure 6). Furthermore, there are no evident differences between the racemic and enantiopure IL. These data suggest less "structured" surfaces in the case of **5d**/**5e** with respect to **5a**/**5b**.

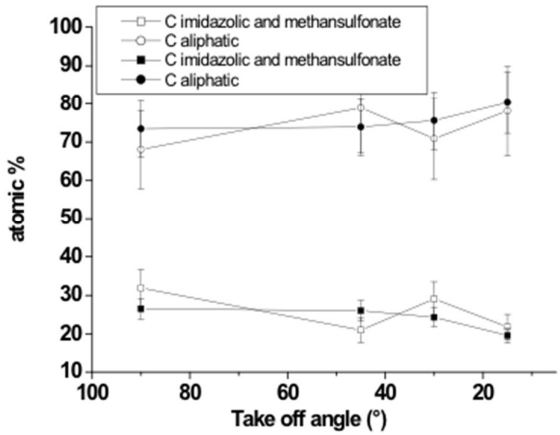

Fig 6. Contribute to the 1s peak of aliphatic and imidazolic carbon as function of take off angle for **5e** (full symbols) and **5d** (empty symbols) sample.

Interesting information have been obtained also substituting the methansulfonate anion of **5d** and **5e** with bis[(trifluoromethyl)sulfonyl]imide. The XPS spectra of **6d** and **6e** show dramatic differences in the region characteristic of C 1s. Along the large and complex shaped peak due to the superimposing of several contributes of carbons in different chemical environments, at very high energy a lonely peak attributable to the $-CF_3$ group of

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bis[(trifluoromethyl)sulfonyl]imide anion appears in the spectrum (Figure 7).

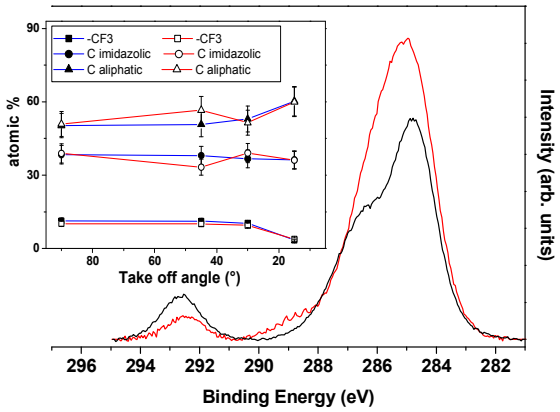

Fig 7. XPS (C1s) spectra for **6d** at normal emission (black curve) and grazing angle (red curve). The inset displays the relative contributes for **6d** (full symbols) and **6e** (empty symbols).

Also in this case, by reducing the take-off angle (*i.e.* decreasing the thickness of the investigated samples) the contribution of aliphatic carbons increases. The intensity ratio between the two components (aliphatic/imidazolium carbons) constantly increases from 1.3 at 90° (normal incidence) to about 1.7 at 15° (grazing angle). Very little differences, within the experimental error, were observed between the enantiopure IL (**6d**) and the racemic mixture (**6e**, inset of Figure 7). At the same time, the relative area of the peak attributable to $-CF_3$ carbon decreases in both the samples on going from 90 to 15°.

Contrarily to the case of **5a** and **5b**, where we observed an increase of the component related to the anion as the probing depth decreased, in this case the component related to the anion ($-CF_3$ of bis[(trifluoromethyl)sulfonyl]imide) appears depleted in the outermost portion of the surface. Actually, two main processes can account for this experimental behavior: (a) shadowing effects played by fluorine atoms that are positioned pointing towards vacuum, (b) a real depletion of bis[(trifluoromethyl)sulfonyl]imide anion at the surface. In order to shed some light about these possibilities we analyzed the N 1s peaks. This region of the spectrum presents two well separated peaks (see Figure 8). In accordance with the literature data these peaks can be easily assigned to the nitrogen atoms in the imidazolium ring (B.E. 401.7 eV) and in bis[(trifluoromethyl)sulfonyl]imide anion (399.1 eV).[16] Since the sensitivity factor is the same, the atomic ratio between these chemical species can be straightforwardly obtained by the direct comparison of the peaks area values. At normal emission, the area ratios resulted nearly identical for the two liquids (2.03:1 for **6d** and 2.00:1 for **6e**, respectively) and very close to the expected stoichiometric value, 2:1. Reducing the sampling depth, this ratio slightly changed toward higher values (2.06:1 for **6d** and 2.08:1 for **6e**, respectively).

Therefore, it is possible to state that regardless the enantiomeric purity of the liquid at the very top layer there is a slightly depletion in bis[(trifluoromethyl)sulfonyl]imide anion.

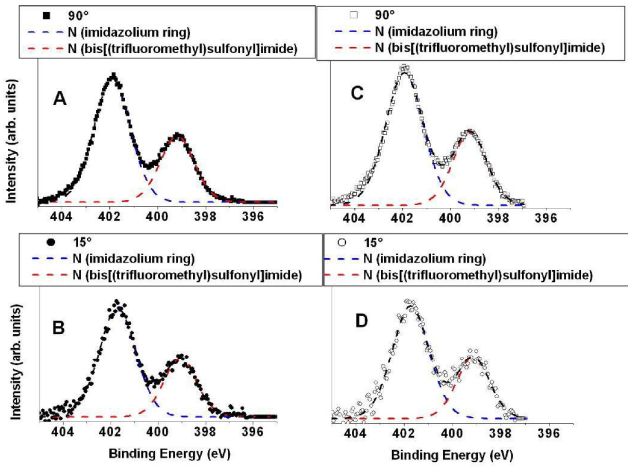

Fig 8. N 1s Xps spectra collected at normal (90° take off angle) and grazing angle (15°) recorded on **6d** (A, B) and **6e** (C, D) sample.

Conclusions

Chiral ionic liquids have been obtained in high yield using as building block commercial propylene oxide and natural alcohols. The self-assembly at the interface IL/vacuum, investigated for some couples of enantiopure and racemic CILs, show that the presence of a chiral centre on the cation side chain and the enantiomeric purity of the related imidazolium based CILs can affect the orientation and layering of the liquid components in the outmost regions of the interface. This ability depends primarily by the structural features of the side chain. The presence of a phenyl ring, probably able to give π–π interactions, appears fundamental to have significantly different IL/vacuum (air) surfaces going from racemic and enantiopure ILs. This feature, associated with the optical purity of some of the investigated ILs, might be useful when the surface of ILs is used for synthetic processes, for example for polymerization reactions. Air/ionic liquid interface properties of achiral ILs containing metal salts have been used[17] for the one-pot fabrication of large-area polymeric film through oxypolymerization processes: the structural surface features of racemic or enantiopure ILs might affect polymer uniformity and thickness. On the other hand, the different assembly of racemic and enantiopure ILs surely affects also the dynamic nanostructures characterizing the pure ionic liquid bulk, as well as the different kind of aggregates (micelles, vesicles and so on) formed by ILs in an immiscible solvent. These features might exert an important role in metal nanoparticles and/or other (nano)material synthesis.

Acknowledgements

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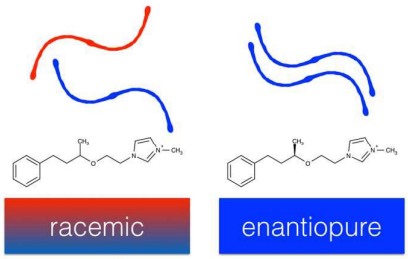
Graphical Abstract

Arrangements of enantiopure and racemic ionic liquids at the liquid/air interface: the role of chirality on self-assembly and layering

S. Caporali, C. Chiappe, T. Ghilardi, A. Iuliano, G. Longhi, P. Margari and C. S. Pomelli

This paper reports on the self-assembly ability at the interface IL/air for some couples of enantiopure and racemic chiral ILs



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