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Supporting Information

"Inherently Chiral" Ionic-Liquid Media: Effective Chiral Electroanalysis on Achiral Electrodes

Simona Rizzo, Serena Arnaboldi, Voichita Mihali, Roberto Cirilli, Alessandra Forni, Armando Gennaro, Abdirisak Ahmed Isse, Marco Pierini, Patrizia Romana Mussini, and Francesco Sannicolò**

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SUPPORTING INFORMATION

This file includes:

1. Computational methods

DFT calculations were performed by using the computer program SPARTAN 08 (Wavefunction, Inc., Irvine, CA, USA). Ground (GS) and transition (TS) states of 3,3'-bicollidine **3** were optimized at the B3LYP/6-31G** level of theory, and afterwards submitted to single point energy calculation at the much higher M062X/6-31G** level of theory (a meta-hybrid GGA DFT functional).
The correctness of the achieved **4**-TS geometry as true saddle point was validated by checking the presence among the assessed vibrational modes of only one imaginary frequency (i 31.623 cm^{-1}), corresponding to the rotation around to the C-C rings-junction.

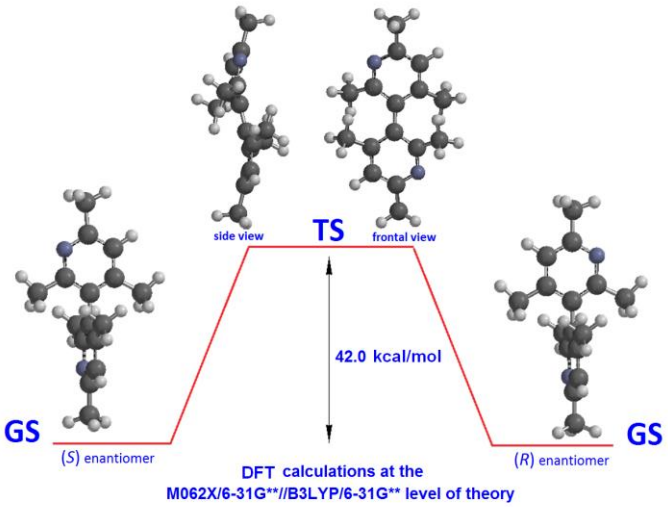


Fig. S1. The two stable enantiomers of **3** with their computed enantiomerization barrier.

2. Organic Synthesis

Specific rotations were measured by a Perkin Elmer polarimeter model 241 equipped with Na/Hg lamps. The volume of the cell was 1 cm^3 and the optical path was 10 cm. The system was set at a temperature of 20 °C. Circular dichroism spectra were measured by using a Jasco Model J-700 spectropolarimeter. The optical path and temperature were set at 0.1 mm and 25 °C, respectively. The spectra are average computed over three instrumental scans and the intensities are presented in terms of ellipticity values (mdeg). NMR spectra were recorded on Bruker AV400 and Bruker AC300 spectrometers. Chemical shifts (δ) are expressed in parts per million (ppm), and coupling constants are given in Hz. Splitting patterns are indicated as follows: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, br = broad. Reagent-grade commercially available reagents and solvents were used; dry solvents were used as purchased. Purifications by column chromatography were performed using Merck silica gel 60 (230–400 mesh for flash-chromatography and 70–230 mesh for gravimetric chromatography) and Aluminiumoxid 90 neutral. Mass spectra were recorded on VG_autospecfision instruments. Melting

points were determined on a Büchi B-540 instrument. The BT_2T_4 probe was prepared according to the known procedure.[1]

Water content was below the detection limits of the Karl Fischer method.

(±)-2,2',4,4',6,6'-Hexamethyl-3,3'-bipyridine.

A 1.6 M solution of *n*-BuLi in hexane (10.5 cm^3, 16.5 mmol) was added dropwise to a solution of 3-bromo-2,4,6-trimethylpyridine (3.0 g, 15 mmol) in dry THF (32 cm^3) cooled to −78°C, under N_2 atmosphere. The solution color turned to dark orange. The reaction mixture was stirred for 15 min, then $CuCl_2$ (3.0 g, 22.5 mmol) was rapidly added in one portion to the solution. The reaction is exothermic and temperature must be controlled between −60 and −78 °C and maintained in this range for 15 min. The reaction was quenched with H_2O and the solvent removed under reduced pressure. The residue was treated with CH_2Cl_2 (50 cm^3) and a 30% NH_3 solution (15 cm^3). The organic layer was extracted with a 30% NH_3 solution until the aqueous phase became colorless; it was then washed with brine, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by distilling off collidine, bromo- and chloro-collidines under vacuum (130 °C, 0.7 tor) to give the title compound as a white solid (mp = 97.8 - 98.8 °C, 1.02 g, 57%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.95 (s, 1H), 2.54 (s, 3H), 2.12 (s, 3H), 1.88 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.5 (s), 155.0 (s), 145.7 (s), 129.9 (s), 122.4 (s), 23.8 (s), 22.2 (s), 19.2 (s). Mass, EI-mass: calcd *m/z*: 240.16 u; found: 240 u.

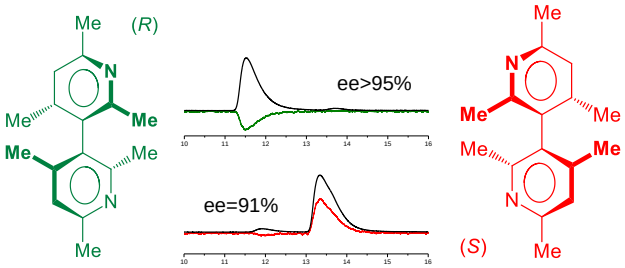
Resolution of (±)-2,2',4,4',6,6'-hexamethyl-3,3'-bipyridine with (+)-(S,S)-D- and (−)-(R,R)-L-2,3-O,O'-dibenzoyltartaric acid (+)-DBTA and (−)-DBTA).

A solution of the resolving agent (+)-DBTA (3.33 mmol) in MeOH (11.5 cm^3) was added dropwise to the hot solution of the (±)-2,2',4,4',6,6'-hexamethyl-3,3'-bipyridine (3.33 mmol) in MeOH (11 cm^3). After 24 hours at 0° C, the white precipitated salt of the (*R*)-2,2',4,4',6,6'-hexamethyl-3,3'-bipyridinium (*S,S*)-*O*,*O*-dibenzoyl hydrogen tartrate was collected by filtration (966 mg). Three additional crystallizations from MeOH gave the salt as colourless crystals (mp = 191-192°C, $[\alpha]^{20}_D$= + 75 *c*= 0.1 in MeOH). The salt was treated with a 5% NaOH solution and the free base extracted with CH_2Cl_2. The organic layer was washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure to give the (*R*)-2,2',4,4',6,6'-hexamethyl-3,3'-bipyridine (mp = 84-87°C, $[\alpha]^{20}_D$= − 8 *c*= 0.1 in EtOH) with a 95% enantiomeric purity (HPLC: CSP: Chiralpak IA-3 250 mm x 4.6 mm i.d., mobile phase: *n*-hexane-EtOH-DEA 100:0.5:0.1, flow rate: 1 cm^3/min, Detector: UV (black) and CD (green or red) at 254 nm, Temperature: 25 °C). The mother liquors of the first crystallization were concentrated to dryness to give a solid residue, which was treated with CH_2Cl_2 and a 5% NaOH solution. The organic layer was separated, washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure to give a solid residue enriched in the (*S*)-

2,2',4,4',6,6'-hexamethyl-3,3'-bipyridine enantiomer (348 mg, 1.45 mmol). A solution of (–)-DBTA (1.45 mmol) in MeOH (5 cm^3) was added dropwise to a solution of the recovered base in MeOH (5 cm^3) and the resulting solution refluxed for a few minutes. The solution was maintained at 0° C for 24 hours, then the precipitated solid was collected and crystallized three times from MeOH to give the (*S*)-2,2',4,4',6,6'-hexamethyl-3,3'-bipyridinium (*R,R*)-*O,O*-dibenzoyl hydrogen tartrate as colourless crystals suitable for X-ray diffraction analysis (mp = 191-192°C, $[\alpha]_D^{20}$= – 73 *c* = 0.1 in MeOH). The salt was treated with CH_2Cl_2 and a 5% NaOH solution and the organic layer separated, washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure to give the (*S*)-2,2',4,4',6,6'-hexamethyl-3,3'-bipyridine (mp = 82-86°C, $[\alpha]_D^{20}$= + 8 *c* = 0.1 in EtOH) with a 91% enantiomeric purity (HPLC: CSP: Chiralpak IA-3 250 mm × 4.6 mm i.d., Mobile phase: *n*-hexane/EtOH/DEA 100/0.5/0.1, Flow rate: 1 cm^3/min, Detector: UV and CD at 254 nm, Temperature: 25 °C).

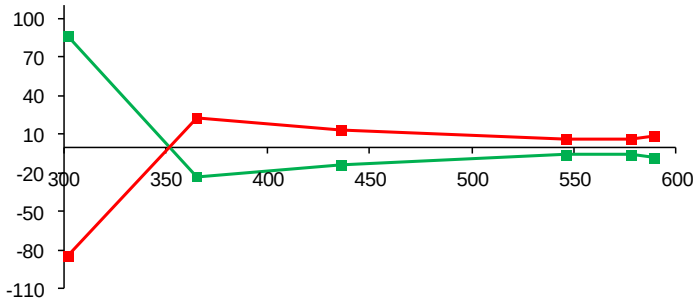
Chiroptical characterization of (*R*)-3 and (*S*)-3

HPLC purity tests



Column: Chiralpak IA-3 250 mm × 4.6 mm i.d.; Mobile phase: *n*-hexane/EtOH/DEA 100/0.5/0.1; Flow rate: 1 cm^3/min; Detector: UV (black) and CD at 254 nm (green for (*R*)-**3** and red for (*S*)-**3**); Temperature: 25 °C.

ORD curves



nm	(*S*)-(+)	(*R*)-(–)
302	–85	86
365	22	-23
436	13	-14
546	6	-6
578	6	-6
589	**+8**	**–8**

Fig. S2. Approximate ORD curves calculated by points of (*R*)-(–)-**3** (green) and (*S*)-(+)-**3** (red). (*c* = 0.1, ethanol).

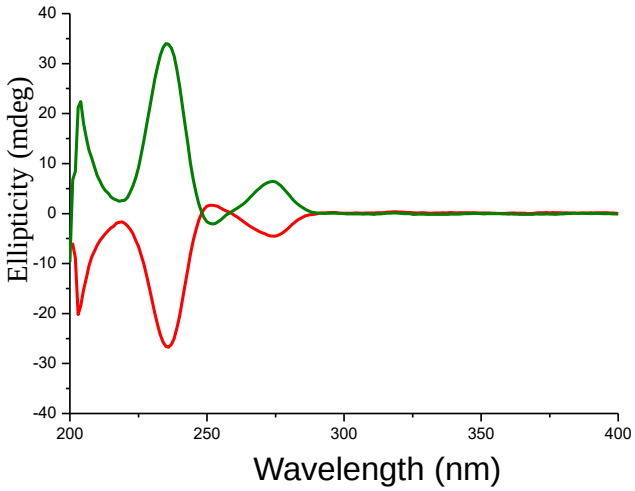
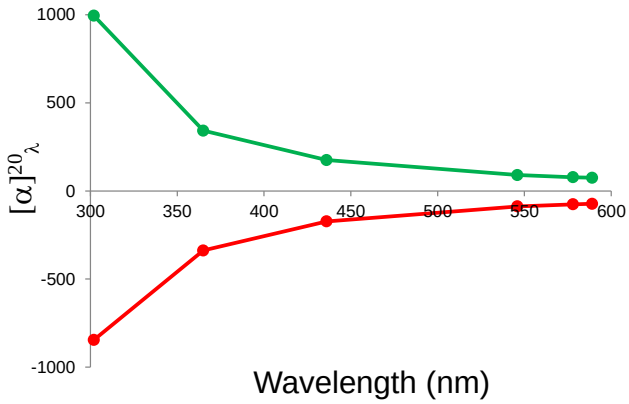


Fig. S3. CD spectra (MeOH, *c* = 0.3 mg/cm^3) of (*R*)-**3** (*S*,*S*)-*O*,*O*-dibenzoyl hydrogen tartrate (green) and (*S*)-**3** (*R*,*R*)-*O*,*O*-dibenzoyl hydrogen tartrate (red).



nm	(*S*)-(–)	(*R*)-(+)
302	845	994
365	338	342
436	173	175
546	88	90
578	76	78
589	**–73**	**+75**

Fig. S4. Approximate ORD curves calculated by points of (*R*)-**3** (*S*,*S*)-*O*,*O*-dibenzoyl hydrogen tartrate (red) and (*S*)-**3** (*R*,*R*)-*O*,*O*-dibenzoyl hydrogen tartrate (green), c = 1 mg/cm^3, MeOH.

Optimized conditions for the separation of mono- and di-alkylcollidinium salts

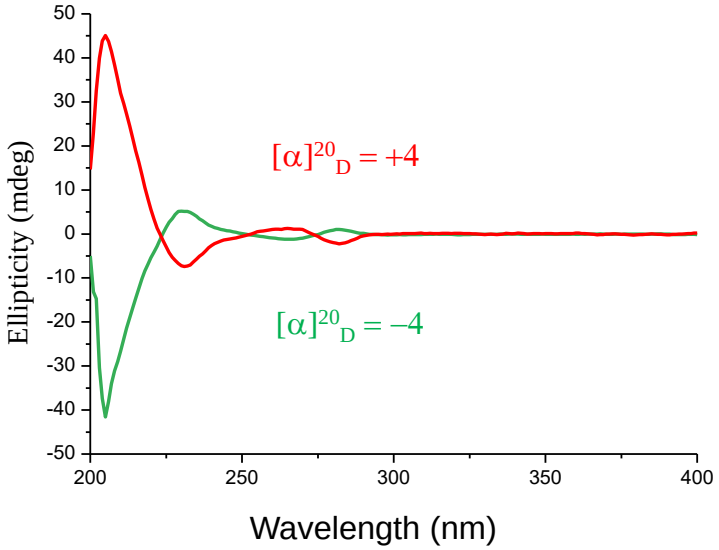
We have developed a simple very efficient separation protocol of high-purity mono- and double salts by column chromatography on neutral alumina.
Elution of the crude reaction mixture with ethyl acetate affords the recovery of the starting bicollidine **3**, if still present; then an about 5% methanol addition to the eluent effects the immediate elution of the monoalkylated product.
Final elution with higher MeOH/AcOEt ratios allows the fast recovery of the doubly alkylated compound.

*(R)-1,1'-Diethyl-2,2',4,4',6,6'-hexamethyl-[3,3'-bipyridine]-1,1'-diium iodide ((R)-**2a**) and (R)-1-ethyl-2,2',4,4',6,6'-hexamethyl-[3,3'-bipyridine]-1-ium iodide ((R)-**4a**).*

A solution of (*R*)-2,2',4,4',6,6'-hexamethyl-3,3'-bipyridine (69 mg, 0.32 mmol) and iodoethane (0.3 cm^3) in CH_3CN (4 cm^3) was heated at 80° C for two weeks. The solvent and excess iodoethane were removed under reduced pressure and the crude residue was chromatographed on a neutral alumina column (starting eluent: AcOEt; intermediate eluent: AcOEt:MeOH=10:0.5; final eluent: AcOEt:MeOH=50:3). The product eluted with the first eluent was unreacted (*R*)-2,2',4,4',6,6'-hexamethyl-3,3'-bipyridine (1.8 mg, 2.6%); the product eluted with the second eluent was the (*R*)-1-ethyl-2,2',4,4',6,6'-hexamethyl-[3,3'-bipyridine]-1-ium iodide (brownish solid, 8.0 mg, 7.0 %). ^{1}H NMR (300 MHz, CD_3OD) δ 7.84 (s, 1H), 7.04 (s, 1H), 4.90-4.80 (m, 4H), 3.06 (s, 3H), 2.60 (s, 3H), 2.56 (s, 3H), 2.16 (s, 3H), 2.14 (s, 3H), 2.00 (s, 3H), 1.58 (t, ^2J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.73 (s), 156.23 (s), 154.19 (s), 153.62 (s), 152.32 (s), 145.43 (s), 137.20 (s), 129.72 (s), 126.26 (s), 122.82 (s), 50.66 (s), 23.94 (s), 22.93 (s), 22.02 (s), 220.56 (s), 19.98 (s), 18.42 (s), 13.71 (s). ^{13}C NMR (75 MHz, CD_3OD) δ 159.81 (s), 158.02 (s), 155.77 (s), 154.01 (s), 148.59 (s), 137.73 (s), 130.86 (s), 128.76 (s), 124.66 (s), 50.61 (s), 23.62 (s), 22.32 (s), 21.54 (s), 20.78 (s), 19.82 (s), 18.28 (s), 13.90 (s). The product eluted with the third eluent was the (*R*)-1,1'-diethyl-2,2',4,4',6,6'-hexamethyl-[3,3'-bipyridine]-1,1'-diium iodide (brownish solid, $[\alpha]^{20}_D = -4$, *c* = 0.1 in MeOH, 110.0 mg, 69.3%). ^{1}H NMR (300 MHz, CD_3OD) δ 7.97 (s, 2H), 4.68 (q, ^2J = 9.0 Hz, 4H), 2.97 (s, 6H), 2.60 (s, 6H), 2.21 (s, 6H), 1.59 (t, ^2J = 6.0 Hz, 6H); ^{13}C NMR (75 MHz, CD_3OD) δ 157.91, 157.54, 154.47, 134.69, 131.55, 50.97, 21.71, 21.28, 19.22, 13.75.

*(S)-1,1'-Diethyl-2,2',4,4',6,6'-hexamethyl-[3,3'-bipyridine]-1,1'-diium iodide ((S)-**2a**) and (S)-1-ethyl-2,2',4,4',6,6'-hexamethyl-[3,3'-bipyridine]-1-ium iodide ((S)-**4a**).*

A solution of (*S*)-2,2',4,4',6,6'-hexamethyl-3,3'-bipyridine (104.5 mg, 0.44 mmol) and iodoethane (0.4 cm^3) in CH_3CN (4 cm^3) was heated at 80° C for three weeks. The solvent and excess iodoethane were removed under reduced pressure and the crude residue was chromatographed on a neutral alumina column (starting eluent: AcOEt; intermediate eluent: AcOEt:MeOH=50:2.5; final eluent: AcOEt:MeOH=50:10). The product eluted with the first eluent was unreacted (*S*)-2,2',4,4',6,6'-hexamethyl-3,3'-bipyridine (1.9 mg, 1.8%); the product eluted with the second eluent was the (*S*)-1-ethyl-2,2',4,4',6,6'-hexamethyl-[3,3'-bipyridine]-1-ium iodide (brownish solid 32.5 mg, 18.9%); the product eluted with the third eluent was the (*S*)-1,1'-diethyl-2,2',4,4',6,6'-hexamethyl-[3,3'-bipyridine]-1,1'-diium iodide (brownish solid, $[\alpha]^{20}_D = +4$, c = 0.1 in MeOH, 145.7 mg, 60.7%).



CD spectra (MeOH, *c* = 0.3 mg/cm^3) and $[\alpha]_D^{20}$ (MeOH, *c* = 1 mg/cm^3) of (*R*)-(–)-**2a** (green) and (*S*)-(+)-**2a** (red).

The anion exchange of mono- and di-alkylcollidinium salts with tetrafluoborate, hexafluophosphate and bis(trifluoromethanesulfonyl)imidate anions was performed by mixing stoichiometric amounts of the mono- or di-alkylcollidinium iodides with the corresponding silver salts in methanol or ethanol solution. The silver iodide precipitate was removed by filtration and the solvent removed under reduced pressure. The absence of iodide anion in the residue was checked by the CV electrochemical method described in the Electrochemical Section.

*(R)-1-Ethyl-2,2',4,4',6,6'-hexamethyl-[3,3'-bipyridine]-1-ium tetrafluoroborate ((R)-**4b**).*

A solution of $AgBF_4$ (2.6 mg, 0.013 mmol) in MeOH (0.2 cm^3) was dropped into a stirred solution of (*R*)-1-ethyl-2,2',4,4',6,6'-hexamethyl-[3,3'-bipyridine]-1-ium iodide (5.2 mg, 0.013 mmol) in MeOH (0.2 cm^3) and the mixture was stirred at 24° C for 48 h to complete the reaction. The silver iodide precipitate was removed by filtration and the filtrate evaporated under reduced pressure to give the title product (white solid, 2 mg, 43%). ^{1}H NMR (300 MHz, $CDCl_3$+CD_3OD) δ 7.64 (s, 1H), 7.05 (s, 1H), 4.60 (q, ^2J = 7.2 Hz, 2H), 2.86 (s, 3H), 2.53 (s, 3H), 2.43 (s, 3H), 2.09 (s, 3H), 2.08 (s, 3H), 1.89 (s, 3H), 1.49 (t, ^2J = 7.2 Hz, 3H); ^{19}F NMR (282 MHz, $CDCl_3$+CD_3OD) δ –150.41 (s); ^{13}C NMR (75 MHz, $CDCl_3$+CD_3OD) δ 158.66 (s), 156.39 (s), 154.38 (s), 153.92 (s), 152.46 (s), 146.60 (s), 136.68 (s), 129.35 (s), 126.87 (s), 123.38 (s), 48.97 (s), 23.69 (s), 22.02 (s), 20.39 (s), 19.58 (s), 19.04 (s), 17.21 (s), 13.42 (s).

*(S)-1-Ethyl-2,2',4,4',6,6'-hexamethyl-[3,3'-bipyridine]-1-ium tetrafluoroborate((S)-**4b**).*

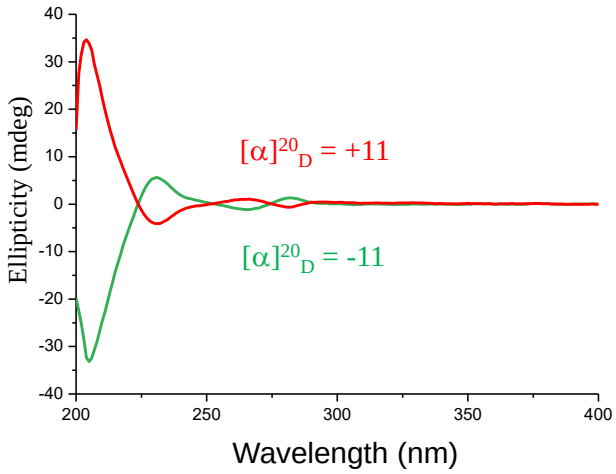
A solution of $AgBF_4$ (23.2 mg, 0.12 mmol) in MeOH (0.2 cm^3) was dropped into a stirred solution of (*S*)-1-ethyl-2,2',4,4',6,6'-hexamethyl-[3,3'-bipyridine]-1-ium iodide (47.3 mg, 0.12 mmol) in MeOH (0.2 cm^3) and the mixture was stirred at 24° C for 48 h to complete the reaction. The silver iodide precipitate was removed by filtration and the filtrate was evaporated under reduced pressure to give the title product (white solid, 26.2 mg, 62%).

*(R)-1,1'-Diethyl-2,2',4,4',6,6'-hexamethyl-[3,3'-bipyridine]-1,1'-diium tetrafluoro borate ((R)-**2b**).*

A solution of $AgBF_4$ (34.4 mg, 0.18 mmol) in MeOH (0.4 cm^3) was dropped into a stirred solution of (*R*)-1,2'-diethyl-2,2',4,4',6,6'-hexamethyl-[3,3'-bipyridine]-1,1'-diium iodide (48.8 mg, 0.088 mmol) in MeOH (0.4 cm^3) and the mixture was stirred at 24°C for 48 h to complete the reaction. The silver iodide precipitate was removed by filtration and the filtrate evaporated under reduced pressure to give the title product (white solid, $[\alpha]^{20}_D = -11$ c = 0.1 in MeOH, 40.1 mg, 96.2%). ^{1}H NMR (300 MHz, $CDCl_3$+CD_3OD) δ 7.69 (s, 2H), 4.55 (q, ^2J = 6.9 Hz, 4H), 2.85 (s, 6H), 2.46 (s, 6H), 2.09 (s, 6H), 1.49 (t, ^2J = 6.9 Hz, 6H); ^{19}F NMR (282 MHz, $CDCl_3$+CD_3OD) δ -154.29 (s); ^{13}C NMR (75 MHz, $CDCl_3$+CD_3OD) δ 156.40 (s), 155.54(s), 153.33 (s), 133.14 (s), 130.03 (s), 49.42 (s), 20.93 (s), 20.44 (s), 17.85 (s), 13.03 (s). EI-mass: calcd *m/z*: 472 u; found: 296 u (472-2HBF_4), 281 u (100%), 267 u, 251 u, 237 u, 222 u.

*(S)-1,1'-Diethyl-2,2',4,4',6,6'-hexamethyl-[3,3'-bipyridine]-1,1'-diium tetrafluoro borate ((S)-**2b**).*

A solution of $AgBF_4$ (11.5 mg, 0.059 mmol) in MeOH (0.2 cm^3) was dropped into a solution of (*S*)-1,1'-diethyl-2,2',4,4',6,6'-hexamethyl-[3,3'-bipyridine]-1,1'-diium iodide (16.3 mg, 0.030 mmol) in MeOH (0.2 cm^3) and the mixture was stirred at 24°C for 48 h to complete the reaction. The silver iodide precipitate was removed by filtration and the filtrate was evaporated under reduced pressure to give the title product (white solid, $[\alpha]^{20}_D = +11$ c = 0.1 in MeOH, 13.5 mg, 95%).



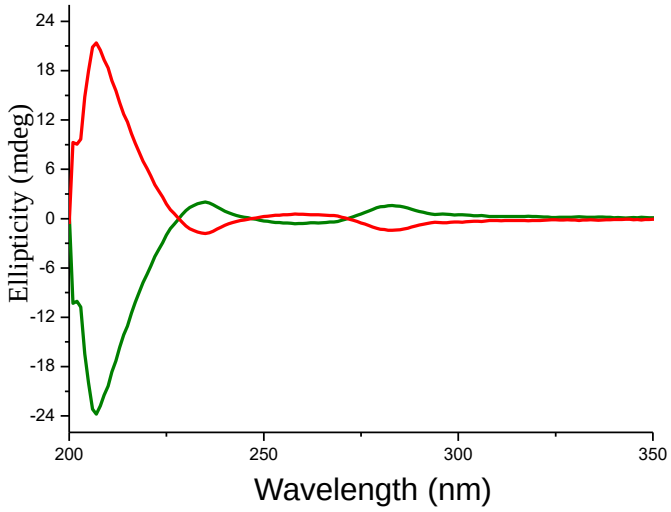
CD spectra (MeOH, *c* = 0.2 mg/cm^3) and $[\alpha]_D^{20}$ (MeOH, *c* = 1 mg/cm^3) of (*R*)-(–)-**2b** (green) and (*S*)-(+)-**2b** (red).

*(R)-1,1'-Dioctyl-2,2',4,4',6,6'-hexamethyl-[3,3'-bipyridine]-1,1'-diium iodide((R)-**2c**) and (R)-1-octyl-2,2',4,4',6,6'-hexamethyl-[3,3'-bipyridine]-1-ium iodide((R)-**4c**).*

A solution of (*R*)-2,2',4,4',6,6'-hexamethyl-3,3'-bipyridine (85.6 mg, 0.36 mmol) and octyl iodide (0.3 cm^3) in MeCN (3 cm^3) was heated at 80° C for 99 days. The solvent and excess octyl iodide were removed under reduced pressure and the crude residue chromatographed on a neutral alumina column (starting eluent: AcOEt; intermediate eluent: AcOEt:MeOH=10:0.1; final eluent: AcOEt:MeOH=4:6). The product eluted with the first eluent was the unreacted (*R*)-2,2',4,4',6,6'-hexamethyl-3,3'-bipyridine (13.1 mg, 0.05 mmol, 15.3%); the product eluted with the second eluent was the (*R*)-1-octyl-1',2,4,4',6,6'-hexamethyl-[3,3'-bipyridine]-1-ium iodide (brown waxy solid, 86.4 mg, 0.18 mmol, 50%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.05 (s, 1H), 4.81-4.61 (m, 2H), 3.05 (s, 3H), 2.59 (s, 3H), 2.58 (s, 3H), 2.18 (s, 3H), 2.14 (s, 3H), 2.05 (s, 3H), 1.82 (br quintuplet, ^2J = 8.1 Hz, 2H); 1.54 (br quint, ^2J = 7.5 Hz, 2H), 1.47-1.20 (m, 8H), 0.90 (t, ^2J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.04 (s), 156.09 (s), 154.34 (s), 153.89 (s), 152.90 (s), 146.13 (s), 137.50 (s), 129.61 (s), 126.63 (s), 123.13 (s), 55.38 (s), 31.58 (s), 29.04 (s), 28.99 (s), 28.84 (s), 26.74 (s), 24.19 (s), 23.09 (s), 22.52 (s), 22.37 (s), 20.79 (s), 20.44 (s), 18.59 (s), 13.99 (s). The product eluted with the third eluent was the (*R*)-1,2'-dioctyl-1',2,4,4',6,6'-hexamethyl-[3,3'-bipyridine]-1,1'-diium iodide (brown waxy solid, 96.6 mg, 0.134 mmol, 37%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 (s, 2H), 4.53 (br q, 4H, ^2J = 8.1 Hz), 2.96 (s, 6H), 2.68 (s, 6H), 2.23 (s, 6H), 1.82 (br quint, ^2J = 6.9 Hz, 4H); 1.54-1.12 (m, 20H), 0.83 (t, ^2J = 6.9 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.93 (s), 155.44 (s), 152.95 (s), 133.36 (s), 130.59 (s), 55.19 (s), 31.36 (s), 28.83 (s), 28.72 (s), 28.34 (s), 26.62 (s), 22.30 (s), 22.04 (s), 21.96 (s), 20.33 (s), 13.82 (s).

*(S)-1,1'-Dioctyl-2,2',4,4',6,6'-hexamethyl-[3,3'-bipyridine]-1,1'-diium iodide((S)-**2e**) and (S)-1-octyl-2,2',4,4',6,6'-hexamethyl-[3,3'-bipyridine]-1-ium iodide((S)-**4c**).*

A solution of (*S*)-2,2',4,4',6,6'-hexamethyl-3,3'-bipyridine (150.1 mg, 0.62 mmol) and octyl iodide (0.4 cm^3) in CH_3CN (3 cm^3) was heated at 80°C for about 99 days. The solvent and excess octyl iodide were removed under reduced pressure and the crude residue chromatographed on a neutral alumina column (starting eluent: AcOEt; intermediate eluent: AcOEt:MeOH=10:0.1; final eluent: AcOEt:MeOH=4:6). The product eluted with the first eluent was unreacted (*S*)-2,2',4,4',6,6'-hexamethyl-3,3'-bipyridine (20.8 mg, 0.08 mmol, 14%); the product eluted with the second eluent was the (*S*)-1-octyl-1',2,4,4',6,6'-hexamethyl-[3,3'-bipyridine]-1-ium iodide (brown waxy solid, 230.6 mg, 0.32 mmol, 51%). The product eluted with the third eluent was the (*S*)-1,2'-dioctyl-1',2,4,4',6,6'-hexamethyl-[3,3'-bipyridine]-1,1'-diium iodide (brown waxy solid, 157.7 mg, 0.219 mmol, 35%).



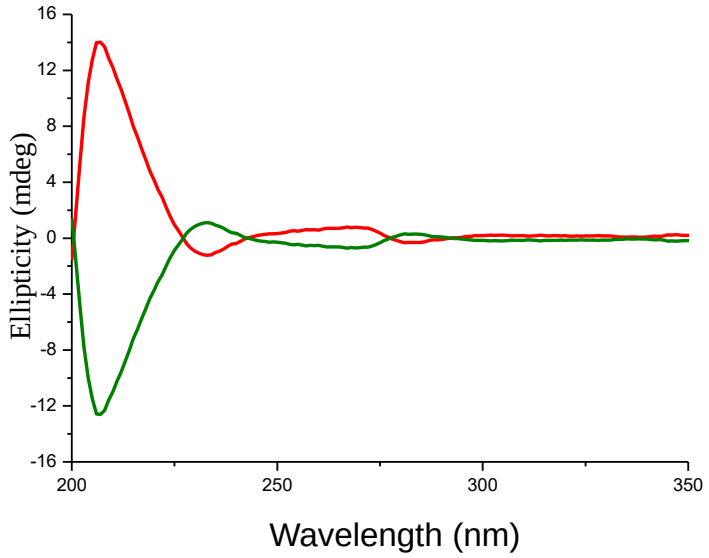
CD spectra (MeOH, *c* = 0.2 mg/cm^3) of (*R*)-**2c** (green) and (*S*)-**2c** (red).

*(R)-1,1'-Dioctyl-2,2',4,4',6,6'-hexamethyl-3,3'-bipyridine-1,1'-diium bis(trifluoro methanesulfonyl)imidate ((R)-**2d**).*

A solution of $AgN(SO_2CF_3)_2$ (5.9 mg, 0.015 mmol) in EtOH (0.3 cm^3) was dropped into a stirred solution of (*R*)-1,1'-dioctyl-2,2',4,4',6,6'-hexamethyl-3,3'-bipyridine-1,1'-diium iodide (5.5 mg, 0.008 mmol) in EtOH (0.2 cm^3) and the mixture was stirred at 24° C for 48 h to complete the reaction. The silver iodide precipitate was removed by filtration and the filtrate was evaporated under reduced pressure to give the title product (brown liquid, 2.6 mg, 0.002 mmol, 33%). ^{1}H-NMR ($CDCl_3$+CD_3OD) δ 7.72 (s, 2H), 4.45 (br t, ^2J = 8.1 Hz, 4H), 2.91 (s, 6H), 2.51 (s, 6H), 2.16 (s, 6H), 1.85 (br s, 4H), 1.52-1.25 (br m, 20H), 0.88 (br t, ^2J = 6.6 Hz, 6H); ^{19}F NMR (282 MHz, $CDCl_3$+CD_3OD) δ -79.8 (s); ^{13}C NMR (75 MHz, $CDCl_3$+CD_3OD); δ 156.61 (s), 155.75 (s), 152.97 (s), 133.28 (s), 130.57 (s), 119.6 (q, ^2J(C,F) = 319.5 Hz), 54.17 (s), 31.51 (s), 28.93 (s), 28.71 (s), 28.26 (s), 26.60 (s), 22.44 (s), 21.27 (s), 20.61 (s), 18.05 (s), 13.91 (s).

*(S)-1,1'-Dioctyl-2,2',4,4',6,6'-hexamethyl-3,3'-bipyridine-1,1'-diiumbis(trifluoro methane sulfonyl)imidate((S)-**2d**).*

A solution of $AgN(SO_2CF_3)_2$ (4.7 mg, 0.012 mmol) in EtOH (0.2 cm^3) was dropped into a stirred solution of (*S*)-1,1'-dioctyl-2,2',4,4',6,6'-hexamethyl-3,3'-bipyridine-1,1'-diium iodide (4.4 mg, 0.006 mmol) in EtOH (0.2 cm^3) and the mixture was stirred at 24°C for 48 h to complete the reaction. The silver iodide precipitate was removed by filtration and the filtrate was evaporated under reduced pressure to give the title product (brown liquid, 3.3 mg, 0.003 mmol, 53%).



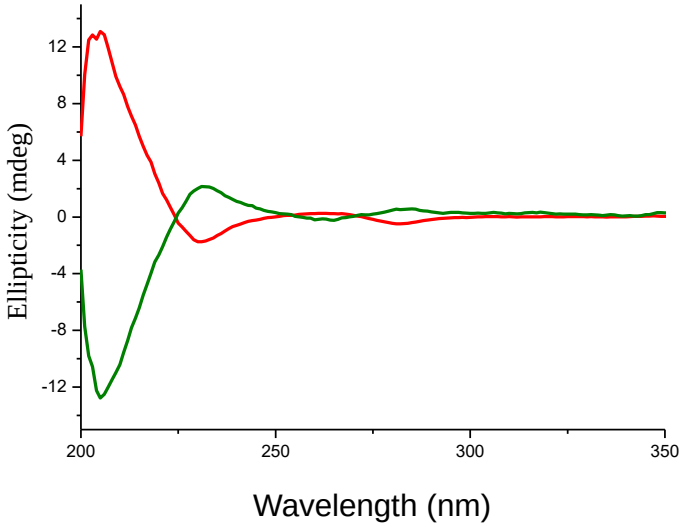
CD spectra (MeOH, *c* = 0.2 mg/cm^3) of (*R*)-**2d** (green) and (*S*)-**2d** (red).

*(R)-1-Octyl-1'-methyl-2,2',4,4',6,6'-hexamethyl-[3,3'-bipyridine]-1,1'-diium iodide ((R)-**2e**).*

(*R*)-1-Octyl-2,2',4,4',6,6'-hexamethyl-[3,3'-bipyridine]-1-ium iodide (10.8 mg, 0.22 mmol), was dissolved in methyl iodide (0.2 cm^3). The reaction mixture was stirred at 24° C for 12 days. The methyl iodide was removed under reduced pressure and the crude residue was washed with hexane to give the title product (brown solid, $[\alpha]^{20}_D = -14$, *c* = 0.1 in MeOH, 8.2 mg, 58.6%). ^{1}H NMR (300 MHz, CD_3OD) δ 8.00 (s, 2H), 4. 61 (br t, ^2J = 8.4 Hz, 2H), 4.22 (s, 3H), 3.00 (s, 3H), 2.95 (s, 3H), 2.62 (s, 3H), 2.57 (s, 3H), 2.25 (s, 6H), 1.98 (br quint, ^2J = 7.8 Hz, 2H), 1.65-1.24 (m, 10H), 0.93 (t, ^2J = 6.0 Hz, 3H); APT NMR (75 MHz, CD_3OD) δ 158.10 (s), 157.66 (s), 157.53 (s), 155.45 (s), 154.59 (s), 134.69 (s), 134.00 (s), 131.39 (s), 130.57 (s), 55.22 (s), 42.16 (s), 32.90 (s), 30.31 (s), 30.13 (s), 29.29 (s), 27.69 (s), 23.68 (s), 22.35 (s), 21.66 (s), 21.15 (s), 20.98 (s), 19.70 (s), 19.18 (s), 14.40 (s).

*(S)-1-Octyl-1'-methyl-2,2',4,4',6,6'-hexamethyl-[3,3'-bipyridine]-1,1'-diium iodide ((S)-**2e**).*

(*S*)-1-Octyl-2,2',4,4',6,6'-hexamethyl-[3,3'-bipyridine]-1-ium iodide (100.2 mg, 0.21 mmol), was dissolved in methyl iodide (0.5 cm^3). The reaction mixture was stirred at 24°C for 20 days. Methyl iodide was removed under reduced pressure and the crude residue was washed with hexane to give the title product (brown solid, $[\alpha]^{20}_D$ = +14 *c* = 0.1 in MeOH, 115.6 mg, 88.6%).



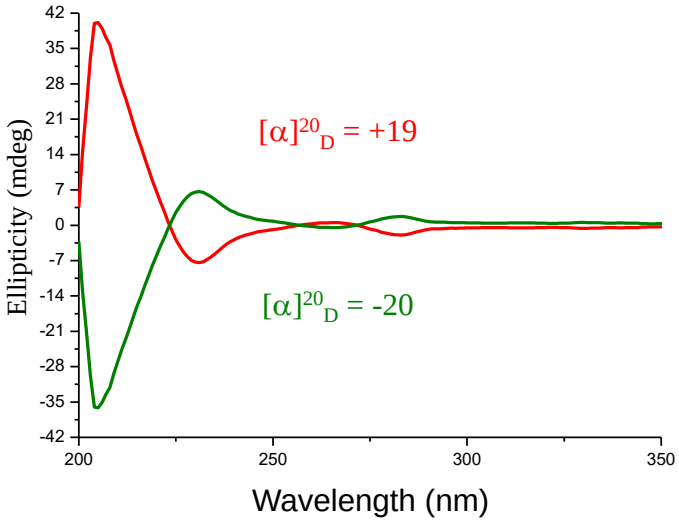
CD spectra (MeOH, *c* = 0.2 mg/cm^3) of (*R*)-**2e** (green) and (*S*)-**2e** (red).

*(R)-1-Octyl-1'-methyl-2,2',4,4',6,6'-hexamethyl-[3,3'-bipyridine]-1,1'-diium bis(trifluoro methanesulfonyl)imidate ((R)-**2f**).*

A solution of $AgN(SO_2CF_3)_2$ (5.6 mg, 0.015 mmol) in EtOH (0.2 cm^3) was dropped into a stirred solution of (*R*)-1-octyl-1'-methyl-2,2',4,4',6,6'-hexamethyl-[3,3'-bipyridine]-1,1'-diium iodide (4.5 mg, 0.007 mmol) in EtOH (0.5 cm^3). The reaction mixture was stirred at 24 °C for 72 h. The silver iodide was removed by filtration and the filtrate was evaporated under reduced pressure to give the title product (brown liquid, $[\alpha]^{20}_D$ = – 20, *c* = 0.1 in MeOH, 2.3 mg, 0.003 mmol, 20%). ^{1}H NMR (300 MHz, $CDCl_3$+CD_3OD) δ 7.58 (s, 1H), δ 7.586 (s, 1H), 4. 24 (br t, ^2J = 9.9 Hz, 2H), 3.90 (s, 3H), 2.70 (s, 3H), 2.65 (s, 3H), 2.26 (s, 3H), 2.21 (s, 3H), 1.94 (s, 6H), 1.66 (br quint, ^2J = 7.8 Hz, 2H), 1.30 (br quint, ^2J = 7.5 Hz, 2H), 1.24-1.00 (m, 8H), 0.66 (t, ^2J = 6.3 Hz, 3H); ^{19}F NMR (282 MHz, $CDCl_3$+CD_3OD) δ -75.9 (s); ^{13}C NMR (75 MHz, $CDCl_3$+CD_3OD) δ 158.39 (s), 157.13 (s), 156.74 (s), 156.35 (s), 154.43 (s), 153.57 (s), 133.85 (s), 133.02 (s), 130.84 (s), 129.97 (s), 120.12 (q, ^2J(C,F) = 318.9 Hz), 54.50 (s), 41.32 (s), 32.01 (s), 29.42 (s), 29.20 (s), 28.70 (s), 27.00 (s), 22.86 (s), 22.06 (s), 21.41 (s), 20.72 (s), 18.89 (s), 18.22 (s), 14.13 (s).

*(S)-1-Octyl-1'-methyl-2,2',4,4',6,6'-hexamethyl-[3,3'-bipyridine]-1,1'-diium bis(trifluoro methanesulfonyl)imidate ((S)-**2f**).*

A solution of $AgN(SO_2CF_3)_2$ (33.2 mg, 0.086 mmol) in EtOH (0.2 cm^3) was dropped into a stirred solution of (*S*)-1-octyl-1'-methyl-2,2',4,4',6,6'-hexamethyl-[3,3'-bipyridine]-1,1'-diium iodide (26.6 mg, 0.043 mmol) in EtOH (2 cm^3). The reaction mixture was stirred at 24 °C for 72 h. The silver iodide was removed by filtration and the filtrate was evaporated under reduced pressure to give the title product (brown liquid, $[\alpha]^{20}_D = +19$, *c* = 0.1 in MeOH, 34.2 mg, 0.042 mmol, 98%).



CD spectra (MeOH, *c* = 0.3 mg/cm^3) and $[\alpha]_D^{20}$ (MeOH, *c* = 1 mg/cm^3) of (*R*)-(–)-**2f** (green) and (*S*)-(+)-**2f** (red).

3. Water content determination in ICILs 2d and 2f and in commercial ILs $(BMIM)PF_6$, $(BIMIM)BF_4$ and CILs (*S*)-2-aminopropionate and L-lactate

Water content in commercially available ILs $(BMIM)PF_6$, $(BIMIM)BF_4$ and CILs 1-ethyl-3-methylimidazolium (*S*)-2-aminopropionate and L-lactate (Sigma Aldrich) was determined by Karl Fischer amperometric titration, on 200 mg samples, following the classical procedure in line with GMP rules. Titrator: KF Titrando, Metrohm, Herisau, Switzerland.
Water content was found to be below the protocol detection limit in all samples.

Water presence in ICILs **2d** and **2f** was checked by evaluating the weight loss in TGA experiments, from 35 to 600 °C, at 10 °C/min, under nitrogen (50 cm^3/min). Instrumentation: TGA 2, Mettler Toledo, Greifensee, Switzerland. No loss was observed in temperature scans from 35 to 300 °C in both cases (Fig. S5 and S6). Strong weight loss, related to the typical dealkylation of quaternary ammonium salts at high temperature, double in these cases, starts at about 310 °C.

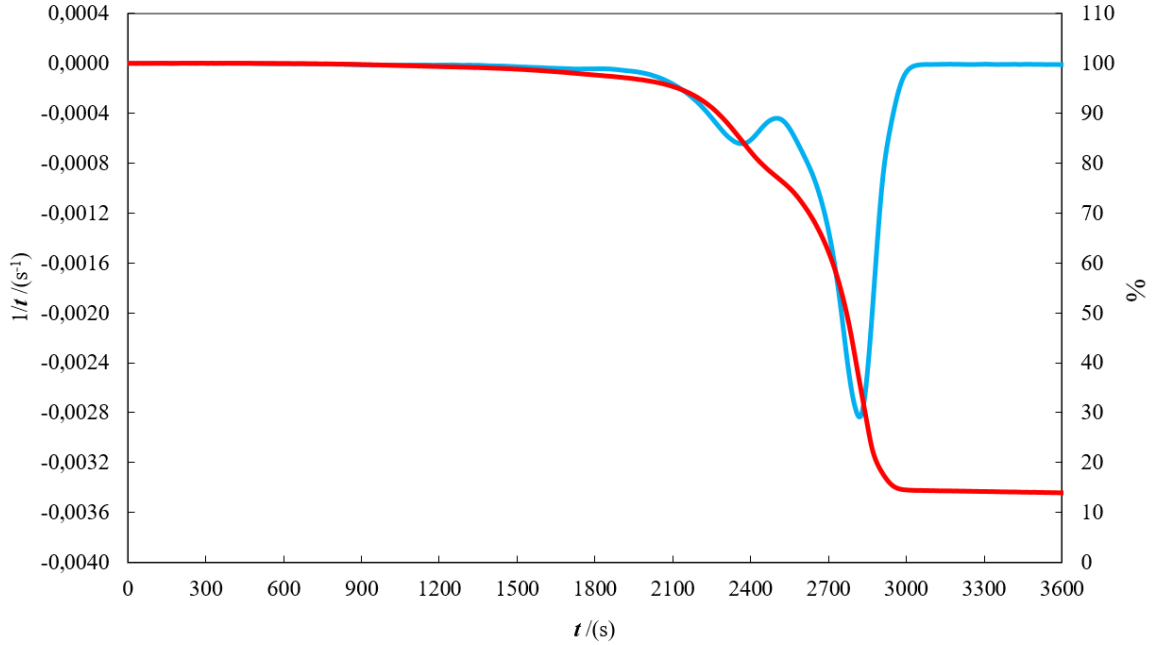


Fig. S5. TGA profile (red) and its derivative (blue) of ICIL **2d**.

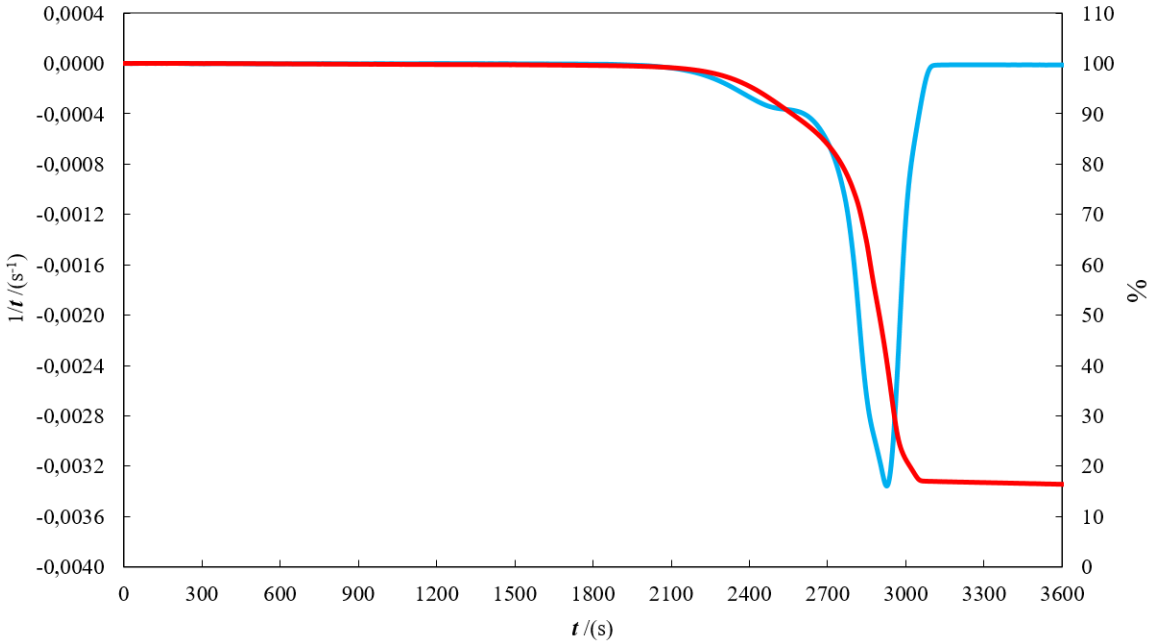


Fig. S6. TGA profile (red) and derivative (blue) of ICIL **2f**.

4. Electrochemistry

The new compounds were characterized by cyclic voltammetry, CV, in a wide scan range, using an Autolab PGSTAT potentiostat (Eco-Chemie, Utrecht, The Netherlands), run by a PC with the GPES software provided by the same manufacturer. The substrate working solutions (3 cm^3) were 5×10^{-4} M in acetonitrile (Sigma-Aldrich, analytical grade on molecular sieves) with 0.1 M tetraethylammonium tetrafluoroborate (TEA)BF_4, (Aldrich, electrochemical grade) as supporting electrolyte, recrystallized from EtOH; they were deaerated by N_2 purging before each experiment, the cell being equipped with a presaturator to grant constant working volume. The working electrodes were glassy carbon (GC) disks embedded in glass (0.031 cm^2, Metrohm). The optimised finishing procedure for the disk electrodes consisted in surface polishing with a diamond powder of 1 μm diameter (Aldrich) on a wet DP-Nap cloth (Struers). The counter electrode was a platinum disk. The reference electrode was an aqueous saturated calomel electrode (SCE) operating in a double bridge, filled with the working medium, to avoid water and KCl leakage into the working solution. The ohmic potential drop was compensated by the positive feedback technique.

The absence of iodide anion in the BF_4^- and PF_6^- bicollidinium salts was verified by the usual simple CV method.

The enantioselectivity tests were carried out with the same instrumentation, but working on SPEs provided by Metrohm/Dropsens (DRP-220 AT-ND) having gold working and counter electrodes, and a silver pseudo reference electrode. Each test was performed on a drop of ionic liquid medium+chiral probe solution. The ionic liquid medium was achiral (BMIM)PF_6 or (BIMIM)BF_4 (Aldrich ≥98.5%), used as such or in the presence of a small quantity of one of the newly synthesized inherently chiral additives (bicollidine **3**, ICILs **2d** and **2f**, inherently chiral salts **2b** and **4b**, all of them of course, as enantiopure antipodes). The chiral probes were either enantiopure FcA (Aldrich, purified by flash chromatography) at 0.002-0.004 M concentration, or enantiopure BT_2T_4,[1] or L- and D-DOPA methyl esters, prepared from L- and D-DOPA (Aldrich) by a literature protocol.[2]

The absence of iodide anion, which has a characteristic voltammetric signal at ~ + 0.64 V *vs* SCE, in the mono- and di-alkylcollidinium tetrafluoborates, hexafluophosphates and bistrifylimidates was checked by cyclic votammetry on SPEs, performing few redox cycles in a solution containing the corresponding achiral ionic liquid and the additive in the same quantity used during the enantiorecognition tests.

4a. CV pattern of 3

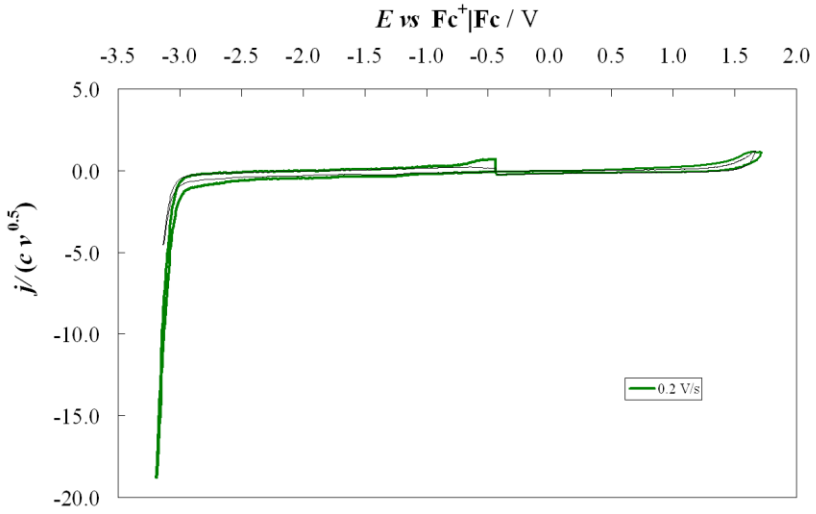


Fig. S7. Normalized CV pattern of **3** at 0.2 V/s, on GC electrode, in CH_3CN + 0.1 M $(TEA)BF_4$.

4b. CV Pattern of bicollidinium salt 2d

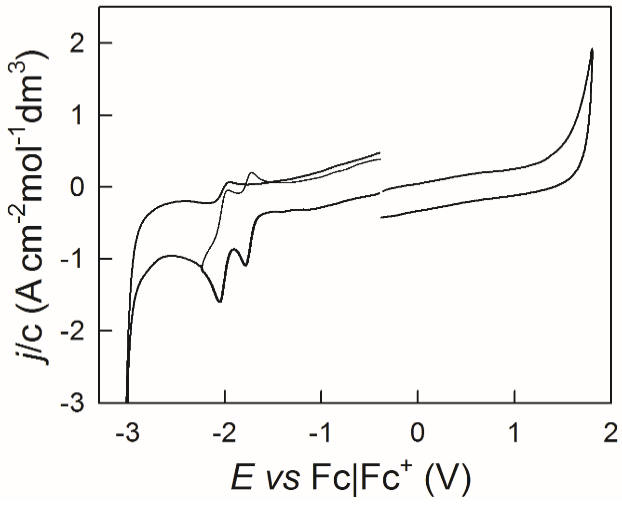


Figure S8. CV pattern of bicollidinium salt (ICIL) **2d** on GC at 0.2 V s^{-1} in CH_3CN + 0.1 M $TBAPF_6$.

4c. Enantiodiscrimination CV test of FcA antipodes in enantiopure 1-ethyl-3-methylimidazolium (*S*)-2-aminopropionate medium

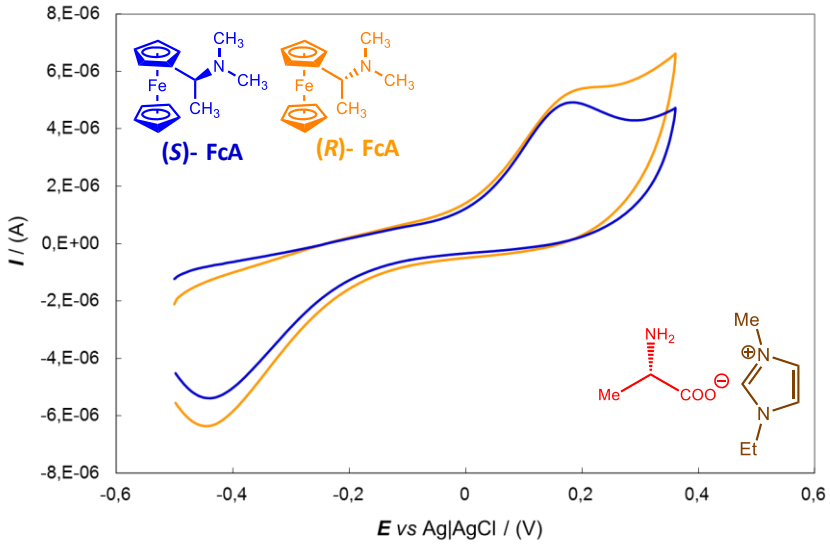


Fig. S9. Enantiodiscrimination CV tests on (*R*) and (*S*) antipodes of chiral probe FcA (blue and orange lines, respectively), on SPE supports with Au working electrodes, in enantiopure 1-ethyl-3-methylimidazolium (*S*)-2-aminopropionate medium (*c* = 0.02 M).

5. UV-Vis patterns of collidine, 3,3'-bicollidine and quaternary salts

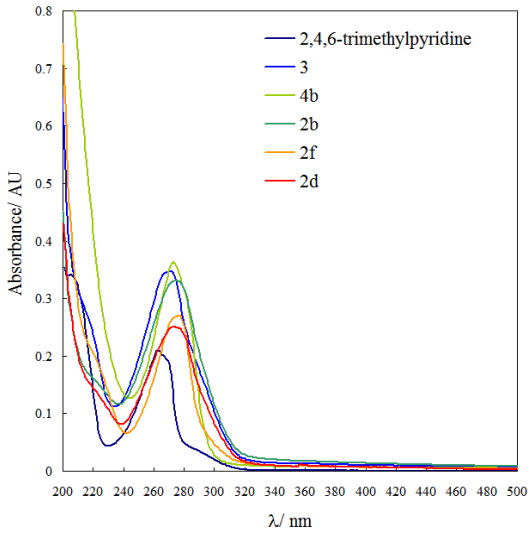


Fig. S10. UV-Vis patterns of collidine and 3,3'-bicollidine **3** together with salts **4b**, **2b**, **2f** and **2d** in CH_3CN (concentration: $6.2 \cdot 10^{-5}$).

UV-Vis spectra of salts **4b**, **2b**, **2d** and **2f** display one sharp peak at wavelengths slightly red shifted with respect to parent scaffold **3** (Fig. S8). This implies a slight narrowing of the HOMO LUMO gap in the salts, which could originate from higher communication between the two rings.

6. Crystallographic data for (*S*)-2,2',4,4',6,6'-hexamethyl-3,3'-bipyridinium (*R*,*R*)-*O*,*O*-dibenzoyl hydrogen tartrate

The intensity data were collected on a Bruker Smart Apex CCD area detector using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Data reduction was made using SAINT programs; absorption corrections based on multiscan were obtained by SADABS.[3] The structures were solved by SHELXS-97 [4] and refined on F^2 by full-matrix least-squares using SHELXL-97.[4] All the non-hydrogen atoms were refined anisotropically, hydrogen atoms were included as 'riding' and not refined, except for the carboxylic hydrogen atoms bonded to heteroatoms (H1, H3 and H6), for which the coordinates have been refined (a DFIX restraint on the O–H3 distance has been required). The isotropic thermal parameters of H atoms were fixed at 1.2 (1.5 for methyl groups) times the equivalent thermal parameter of the atoms to which they are bonded. Crystal data and results of the refinement: colorless plate 0.48×0.25×0.10 mm, Mr = 598.63, monoclinic, space group $P2_1$, a = 7.7287(6) Å, b = 16.7425(12) Å, c = 12.6606(9) Å, β = 103.0602(12)°, V = 1595.9(2) $Å^3$, Z = 2, T = 296(2) K, μ = 0.089 mm^{-1}. 27004 measured reflections, 3868 independent reflections, 3215 reflections with $I > 2\sigma(I)$, $3.30 < 2\theta < 55.46°$, Rint = 0.0291. Refinement on 3215 reflections, 412 parameters, 2 restraints. Final R = 0.0512, wR = 0.1291 for data with $F^2 > 2\sigma$ (F^2), S = 1.055, $(\Delta/\sigma)_{max}$ = 0.002, $\Delta\rho_{max}$ = 0.519, $\Delta\rho_{min}$ = –0.387 $eÅ^{-3}$. CCDC 1458698 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Among the two acidic protons of DBTA, it was found that one (H3) is not transferred to **3**, while the other, H6, is statistically transferred to the nitrogen atom N1 of **3** with 50% probability. Two strong hydrogen bonds are present in the structure. One, O6–H6···O3 (H···O, 1.73 Å; O–H···O, 167°) connects molecules of tartaric acid forming infinite chains. The other, N1–H1···O5 (H···O, 1.90 Å; N–H···O, 161°) connects tartaric acid with **3**. Owing to the statistical disorder affecting H6 and H1, the two hydrogen bonds are mutually exclusive.

7. Supporting Information references

[1] F. Sannicolò, S. Rizzo, T. Benincori, W. Kutner, K. Noworyta, J.B. Sobczak, V. Bonometti, L. Falciola, P.R. Mussini, M. Pierini, *Electrochim. Acta* **2010**, *55*, 8352.

[2] S. Park, H. Oh, M. Kang, H. Cho, J.B. Prasad, J. Won, K. Lee, *Bioorg. Med. Chem.* **2007**, *15*, 3938.

[3] Bruker, SMART, SAINT and SADABS (Bruker AXS Inc., Madison, Wisconsin, USA, **1997**).

[4] G. M. Sheldrick, *Acta Cryst*. **2008**, *A64*, 112.

8. Acknowledgements

The research on inherently chiral molecular materials is also being developed in the context of the SmartMatLab project (Regione Lombardia/Fondazione Cariplo/Università di Milano/ISTM CNR).