Electronic Supplementary Information

A general halide–to–anion switch for imidazolium-based ionic liquids and oligocationic systems using anion exchange resins (A⁻ form)

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Imidazolium-based systems: counteranion exchange

Method I Conventional procedures

$$M = Ag, Hg, Pb; H$$

$$H_2O$$

$$R_3 - N \stackrel{\textcircled{+}}{\longrightarrow} N_{-R_1} + MA$$

$$X^{-}$$

$$CH_2CI_2 \text{ or } Me_2CO$$

$$M = Li, Na, K; NH_4$$

$$M = Ag, Hg, Pb; H$$

$$H_2O$$

$$R_3 - N \stackrel{\textcircled{+}}{\longrightarrow} N_{-R_1}$$

Method II Via N-heterocyclic carbenes (NHC)

$$\begin{array}{c} R_{3} \xrightarrow{N \bigoplus N} R_{1} \xrightarrow{K^{+}t \cdot BuO^{-}} \left[\underset{R_{1} \xrightarrow{N} \underset{i}{\overset{}} N \underset{i}{\overset{}} N \underset{i}{\overset{}} R_{3} \xrightarrow{N \bigoplus N} R_{1} \xrightarrow{R_{1}} \right] \xrightarrow{HA} R_{3} \xrightarrow{N \bigoplus N} R_{1}$$

Method III Anion exchange resin-AER (OH form)



Scheme S1 Imidazolium-based systems: counteranion exchange [ref 4]

Method I

Method II, via *NHC*. [ref 9] and Earle MJ, Seddon KR (2001) Preparation of imidazole carbenes and the use thereof for the synthesis of ionic liquids. [World Patent WO 2001077081 A1].

Method III, anion exchange resin antecedents —AER (OH⁻ form).

- (a) Early studies, N-azolylimidazolium and N-azolylpyridinium salts. [refs 13,14]
- (b) Application to bis(imidazolium) cyclophanes. [refs 15,16]
- (c) Application to imidazolium ILs. [ref 18]

Method IV, anion exchange resin —AER (A⁻ form). [refs 1,19]

Table S1. Comparison of counteranion exchange procedures and results

Compound	Reference ^{<i>a</i>}		Our protocol
[bmim][Ph₄B]	ref 28	[bmim][Cl] \rightarrow [bmim][Ph₄B] 90% NaPh ₄ B was added to a solution of [bmim][Cl] in acetone. After 24 h the reaction mixture was filtered through a plug of Celite [®] , and the volatiles were removed under reduced pressure.	[I]→[Ph ₄ B] 65% CH ₃ OH [I]→[Ph ₄ B] 95% CH ₃ CN See Scheme 1 in text
[bmim][Ibu]	ref 27	[bmim][Cl]→[bmim][Ibu] 94% A [bmim][Cl] ethanolic solution was added slowly to a solution of NaIbu in ethanol and stirred at room temperature for 2 h. The solution was filtered on Millipore [®] and acetone was added leading to the precipitation of NaCl which was further filtered and the solvent was removed under vacuum.	[I]→[Ibu] 95% CH ₃ OH [I]→[Ibu] 100% CH ₃ CN See Scheme 1 in text [Cl]→[Ibu] 100% CH ₃ CN
[d2m2N][IBu]	ref 5	$[d_2m_2N][Br] → [d_2m_2N][Ibu] 91\%$ $[d_2m_2N][Br]$ was dissolved in distilled water by gentle heating and stirring. NaIbu was dissolved in distilled water by gentle heating and stirring. The two solutions were combined and the reaction mixture was heated and stirred for 30 min. Afterwards, the reaction mixture was cooled to room temperature, CHCl ₃ was added, and the mixture was stirred for an additional 30 min. The two phases were separated and organic phase was washed several times with cool distilled water. The solvent was removed under vacuum.	[Br]→[Ibu] 61% CH ₃ CN [Br]→[Ibu] 100% CH ₂ Cl ₂ :CH ₃ CN (7:3) See Scheme 2 in text
$PF_{6}^{-} \stackrel{N \rightarrow N}{+} N^{-}$ 1·PF ₆	ref 29	1·Cl→1·PF ₆ 89% A mixture of 1·Cl and KPF ₆ in water (15 mL) was stirred at room temperature in the dark for 4 h. The reaction mixture was then filtered and the solid product was washed with water and air dried.	$[C1] \rightarrow [PF_6] 70\%$ CH_3OH $[C1] \rightarrow [PF_6] 98\%$ $CH_3CN:CH_3OH (9:1)$ See Table S4
BF ₄ [−] N 1-BF ₄	ref 29	1·Cl→1·BF ₄ 70% A mixture of 1·Cl and NaBF ₄ in acetone was stirred at room temperature in the dark for 24 h. The reaction mixture was then filtered and the solvent was removed under reduced pressure. The solid obtained was dissolved in dichloromethane and stored at -22° C for 24 h. After filtration the solvent was removed.	[Cl]→[BF4] 78% CH ₃ OH [Cl]→[BF4] 100% CH ₃ CN:CH ₃ OH (9:1) See Table S4

	ref 29	1·Cl→1·TfO 72% A mixture of 1·Cl and LiSO ₃ CF ₃ in dichloromethane was stirred at room temperature in the dark for 24 h. The reaction mixture was then filtered and the solvent was removed under reduced pressure. The solid obtained was dissolved in dichloromethane and stored at -22° C for 24 h. After filtration the solvent was removed.	[Cl]→[TfO] 93% CH ₃ OH [Cl]→[TfO] 95% CH ₃ CN:CH ₃ OH (9:1) See Table S4
$\begin{array}{c} & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & $	ref 16	3·2Cl \rightarrow 3·2PF ₆ 91% Treatment of 3·2Cl with a strongly basic anion-exchange resin (OH ⁻ form) followed by immediate collection of the eluates in aq. HPF ₆ to pH = 3.	$[C1] \rightarrow [PF_6] 63\%$ CH_3OH $[C1] \rightarrow [PF_6] 95\%$ $CH_3CN:CH_3OH (9:1)$ See Table S5

^{*a*} Corresponding reference cited in the text.

Table S2. Results of the halide exchange in imidazolium and pyridinium ionic liquids in methanolic

or acetonitrile solution.

compound		Λe	Me + N Bu [bmpy][1]		
Anion	(%) ^a	Br ⁻	(%) ^a	I (ppm) ^b	
AcO	98	<13	84 [100] ^c	<20	
BzO	100	<13	100	<20	
(S)-Lactate	100	<13	100	<20	
MeSO ₃ ⁻	92 [100] ^c	<13	100	<20	
$Bu_2PO_4^-$	100	<13	100	<20	
PF_6	91 [100] ^c	<39	100	<20	
BF_4	97	<39	98	<40	
CF ₃ SO ₃	100	<13	100	<20	
NCS	100	ND	100	ND	

NT: Not Determined ^aYield of the recovered new ion pair. Yields \geq 95 % in CH₃OH were not further investigated. ^bHalide contents after anion exchange determined by silver chromate test; 0.011 mL of AgNO₃ aqueous solution is enough to react with nearly 13 ppm (mg·L⁻¹) of bromide anion, or 20 ppm (mg·L⁻¹) of iodide anion.^cAnion exchange carried out in CH₃CN.

Table S3. Comparative results of anion exchange carried out in CH₃CN or CH₃CN:CH₂Cl₂ mixture.

compound		$() \\ N \\ (+) \\ N \\ C \\ [hmim][Cl] \\ C_6 \\ mim \\ () \\ () \\ () \\ () \\ () \\ () \\ () \\ ($			[dmim][Cl] C10mim			N → Y → y g Br Br didecyldimethyl ammonium bromide		
	CH ₃ CN	CH ₂ Cl ₂ :	CI	CH ₃ CN	CH ₂ Cl ₂ :	CI	CH ₃ CN	CH ₂ Cl ₂ :	Br [–]	
Anion	(%) ^a	CH ₃ CN (%) ^{a,b}	(ppm) c	(%) ^a	CH ₃ CN (%) ^{a,b}	(ppm) c	(%) ^a	CH ₃ CN (%) ^{a,b}	(ppm)	
Ibu [_]	90	100	<6	87	100	<6	61	100	<13	

^aYield of the recovered new ion pair. ^bCH₃CN:CH₂Cl₂ (3:7). ^cHalide contents after anion exchange determined by silver chromate test; 0.011 mL of AgNO₃ aqueous solution is enough to react with nearly 6 ppm (mg·L⁻¹) of chloride anion, or 13 ppm (mg·L⁻¹) of bromide anion.

 Table S4. Comparative results of (anthrylmethyl)imidazolium salt 1·Cl anion exchange.

	CH ₃ OH (%) ^a	CH ₃ CN:CH ₃ OH (%) ^{a,b}
1·CI		
PF ₆	70	98
BF_4	78	100
$CF_3SO_3^-$	93	95

^a Yield of the recovered new ion pair. ^bCH₃CN:CH₃OH (9:1).

Table S5. Results of the halide exchange in bis(imidazolium) salts 2·Cl, 3·2Cl and 4·Br in

methanol, acetonitrile or solvent mixtures.

compound		2CI Z Z Bu CI	Z		n-C ₁₀ H ₂₁ n-C ₁₀ H ₂₁ (+) (+) (+) (+) (+) (+) (+) (+)		
	(%) ^a	Cl ⁻	(%) ^a	Cl	(%) ^a	Br	
Anion		(ppm) ^b		(ppm) ^b		(ppm) ^b	
AcO ⁻	70	<6	95	<6	100 ^d	<13	
	[100] ^c						
BzO	100	<6	100	<6	NT		
(S)-Lactate	100	<6	100	<6	NT		
MeSO ₃ ⁻	42	<6	100	<6	100 ^d	<13	
	[100] ^c						
$Bu_2PO_4^-$	96	<6	100	<6	98 ^d	<13	
PF_6^-	32	<6	63	<6	97 ^d	<13	
	[95] ^c		[95] ^c				
BF_4	91	<6	100	<6	NT		
	[100] ^c						
CF ₃ SO ₃	100	<6	100	<6	NT		
NCS	95	nd	95	nd	NT		

^aYield of the recovered new ion pair. Yields \geq 95% in CH₃OH were not further investigated. ^bHalide contents after anion exchange determined by silver chromate test; 0.011 mL of AgNO₃ aqueous solution is enough to react with nearly 6 ppm (mg·L⁻¹) of chloride anion, or 13 ppm (mg·L⁻¹) of bromide anion ^cAnion exchange carried out in CH₃CN:CH₃OH (9:1) mixture solution. ^dAnion exchange carried out in CH₃CN.



Figure S1 Application of the AER (A⁻ form) method in organic solvents. In CH₃OH or CH₃CN:CH₃OH [9:1]: (anthrylmethyl)imidazolium salt **1**·Cl was transformed to **1**·PF₆⁻, **1**·BF₄⁻ and **1**·CF₃SO₃⁻; chloride exchange for a variety of anions from bis(imidazolium)-based anion receptors **2**·2Cl and **3**·2Cl to **2**·2A and **3**·2A, respectively. In CH₃CN: calix[4]arene **4**·2Br to **4**·2A.

Supplementary Material (ESI) for Chemical Communications This journal is (c) The Royal Society of Chemistry 2011 EXPERIMENTAL PROCEDURES

General Information

¹H NMR spectra were recorded on a Varian Gemini 300 (300 MHz for ¹H and 75.4 MHz for ¹³C) and Mercury 400 (400 MHz for ¹H and 100.6 MHz for ¹³C) spectrometers at 298 K. ¹H and ¹³C chemical shifts were referenced with TMS as an internal reference. Mass spectrometric analyses were performed on a LC/MSD-TOF (2006) mass spectrometer with a pumping system HPLC Agilent 1100 from Agilent Technologies at Serveis Científico-Tècnics of Universitat de Barcelona under the following experimental conditions: • Solvent: H₂O:CH₃CN (1:1, v/v) • Gas temperature: 300 °C • Capillary voltage: 4 KV (positive) and 3.5 KV (negative) • Fragmentor: 75/175 V • Spray gas: N₂ pressure = 15 psi • Drying gas: N₂ flow: 7.0 L·min⁻¹ • Flow rate: 200 μ L·min⁻¹.

The pH was measured with benchmeter pH1100 (Eutech Instrumments), using Hamilton Flushtrode pH electrode for hydroalcoholic solutions.

Chemical Information

Commercially available products: ion exchanger resin Amberlyst A-26 (Aldrich, OH⁻ form), glacial acetic acid, benzoic acid, (*S*)-lactic acid (85% solution in water), methanesulfonic acid, dibutylphosphoric acid, hexafluorophosphoric acid solution (65%, gravimetric in water), tetrafuoroboric àcid (50 % in water), Ibuprofen, ammonium acetate, ammonium chloride, ammonium hexafluorophosphate, ammonium thiocyanate, ammonium trifluoromethanesulfonate, ammonium tetrafluoroborate, ammonium tetraphenylborate, 1-bromodecane, [bmim][Cl], [hmim][Cl], [dmim][Cl] and [d₂m₂N][Br]. All solvents were reagent grade and methanol was distilled prior to use. *Compounds prepared according with the literature:* **[bm₂im][Br]**,[†] **[bmpy][I]**,[‡] **1·Cl**,²⁹ **2·2Cl**,³⁰ **3·2Cl**,¹⁶ and 5,17-bis-(imidazol-1-yl)-25,26,27,28tetrapropoxycalix[4]arene.¹⁶

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- ³⁰ K. Sato, Y. Sadamitsu, S. Arai, T. Shimada, H. Inoue and T. Yamagishi, *Heterocycles*, 2005, 66, 119.
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5,17-bis-(3-decyl-1-imidazolium)-25,26,27,28-tetrapropoxycalix[4]arene dibromide 4·2Br

A solution of 5,17-bis-(imidazol-1-yl)-25,26,27,28-tetrapropoxycalix[4]arene (0.300 g, 0.413 mmol) in 1bromodecane (5 ml) was heated to reflux for 16h, under an argon atmosphere. A light brown solid was collected by filtration and washed with several portions of diethyl ether (3 x 10 mL), obtaining compound **4·2Br** (0.402 g, 83%). m.p. = 268-270 °C. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 9.28 (s, 2H, Im), 8.20 (s, 2H, Im), 7.27 (d, 4H, H_{10,12,22,24}), 7.16 (t, 2H, H_{11,23}), 6.68 (s, 2H, Im), 6.53 (s, 4H, H_{4,6,16,18}), 4.49-4.54 (m, 8H, H_{ax} and N-C<u>H</u>₂-), 4.05 (t, 4H, O-C<u>H</u>₂), 3.70 (t, 4H, O-C<u>H</u>₂), 3.25 (d, 4H, H_{eq}), 1.87-1.99 (m, 8H), 1.74 (m, 4H), 1.21 (m, 28H), 1.12 (t, 6 H), 0.86 (t, 6 H), 0.91 (t, 6 H). ¹³C-NMR (100.6 MHz, CDCl₃) δ : 156.9, 137.1, 135.4, 134.0, 129.9, 128.9, 124.8, 124.1, 120.0, 118.9, 77.7, 76.9, 50.4, 31.9, 31.1, 30.7, 29.5, 29.3, 29.2, 26.3, 23.5, 23.0, 22.8, 14.2, 10.8 and 9.9.

Loading the AER (resin (OH⁻ form) with acids or ammonium salts.

A glass column (1 cm diameter) packed with 2.5 g (\sim 3 cm³) of commercially wet strongly basic anion exchange Amberlyst A-26 (OH⁻ form) was washed with water, and the column bed was equilibrated progressively with water-solvent mixtures until reaching the selected solvent media used afterwards for anion loading (\sim 25 mL of each solvent mixture). A 1% acid or ammonium salt solution in the appropriate solvent was passed slowly through the resin until the eluates had the same pH value as the original selected acid solution, and then the resin was washed generously with solvent until constant pH. The process was carried out at room temperature, using gravity as the driving force.

Anion exchange.

A solution of the imidazolium salt (50-60 mM) in 10 mL of the selected solvent was passed slowly through a column packed with $\sim 3 \text{ cm}^3$ of Amberlyst A-26 (A⁻ form), and then washed with 25 mL of solvent. The combined eluates were evaporated, and the residue obtained was dried in a vacuum oven at 60 °C with P₂O₅ and KOH pellets.

It should be pointed out that Clare et al. have demonstrated that the use of alumina and silica columns can leave a low level of residual particulate contamination in ILs.^{§,9} Consequently, nano-particulates may also be an issue when using strongly basic anion exchange resins (A⁻ form) but the analysis of possible particulate contamination was out of the scope of the present study.

Silver chromate test

The amount of halide contents was determined by a silver chromate test following a similar protocol to that described by Sheldon and co-workers.²⁴ An aqueous solution (5 mL) of potassium chromate (5 % p/v in Milli-Q water, 0.257 M) was added to the sample (5-10 mg). To 1 mL of the resulting dark yellow solution was added a silver nitrate aqueous solution (0.24 % p/v in Milli-Q water, 0.014 M). A persistent red suspension of silver chromate would be observed if the sample was free of halide. The minimum measurable amount of silver nitrate aqueous solution was 0.011 mL; consequently, the detection limit is approx. 6 ppm for Cl⁻, 13 ppm for Br⁻ or 20 ppm for I⁻. The halide content was determined at least twice for each sample.

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Table S6. ¹H NMR chemical shift values of 1-butyl-3-methylimidazolium salts

[bmim][A] in CDCl₃ (300 MHz) at 298 K.^a



Anion	H-2	H-4	H-5	Bu	Me	A
BzO	11.54	7.09	7.09	4.29; 1.84; 1.33; 0.92	4.08	8.10; 7.33
Ph_4B^-	4.52	5.95	5.77	3.13; 1.32; 1.12; 0.89	2.73	7.52; 6.92; 6.78
Ph_4B^{-b}	8.29	7.33	7.29 ^c	4.09; 1.79; 1.33; 0.94	3.78	7.29; 6.99; 6.84
Ph_4B^{-d}	9.06	7.74	7.68	4.14; 1.75; 1.27; 0.90	2.07	7.18; 6.93; 6.79
Ibu	9.86	7.10	7.02	4.02; 1.66; 1.24; 0.87	3.71	7.26; 6.95; 3.53;
						2.35; 1.75; 1.39; 0.82

^aSolution concentrations are 0.02 M. ^bIn CD₃CN.^cIncluded in the Ph signal. ^dIn DMSO-d₆.

Table S7.	¹ H NMR chemical shift values of 1-butyl-2,3-dimethylimidazolium salts
[bm ₂ im][A] in CDCl ₃ (300 MHz) at 298 K. ^a



Anion	H-4	H-5	Me-	Me-3	Bu	A ⁻
			2			
AcO	7.58	7.36	2.59	3.82	4.06; 1.67; 1.26; 0.86	1.72
BzO	7.54	7.27	2.50	3.71	3.90; 1.58; 1.23; 0.85	7.97; 7.27
(S)-Lactate	7.49	7.26	2.70	3.92	4.12; 1.79; 1.40; 0.98	3.87; 1.30
MeSO ₃ ⁻	7.47	7.27	2.69	3.94	4.14; 1.80; 1.38; 0.98	2.74
$Bu_2PO_4^{-}$	7.55	7.27	2.68	3.92	4.13; 1.76; 1.37; 0.96	3.77; 1.56; 1.37; 0.89
PF_6	7.46	7.30	2.70	3.90	4.11; 1.79; 1.40; 0.96	
BF_4	7.40	7.27	2.68	3.88	4.10; 1.79; 1.40; 0.97	
CF ₃ SO ₃ ⁻	7.32	7.22	2.66	3.86	4.09; 1.80; 1.40; 0.97	
NCS ⁻	7.43	7.32	2.77	3.96	4.17; 1.83; 1.43; 0.98	

 Table S8.
 ¹H NMR chemical shift values of 1-butyl-4-methylpyridinium salts

[bmpy][A] in CDCl₃ (300 MHz) at 298 K.



Anion	H-	H-	Me	Bu	A
	2,6	3,5			
AcO	9.35	7.82	2.62	4.82; 1.96; 1.35; 0.94	1.96
BzO	8.94	7.70	2.47	4.67; 1.82; 1.25; 0.83	8.00; 7.31
(S)-Lactate	9.05	7.81	2.57	4.65; 1.88; 1.35; 0.87	3.89; 1.26
MeSO ₃ ⁻	9.09	7.83	2.57	4.65; 1.91; 1.32; 0.87	2.68
Bu ₂ PO ₄	9.36	7.83	2.53	4.72; 1.89; 1.30; 0.83	3.78; 1.50; 1.30; 0.83
PF_6^-	8.60	7.80	2.66	4.54; 1.95; 1.39; 0.95	
BF_4	8.73	7.82	2.66	4.60; 1.95; 1.39; 0.95	
CF ₃ SO ₃ ⁻	8.80	7.82	2.65	4.60; 1.94; 1.38; 0.94	
NCS	8.94	7.91	2.70	4.77; 2.03; 1.44; 0.99	

 Table S9.
 ¹H NMR chemical shift values of imidazolium

salts [hmim][A] and [dmim][A], and quaternary ammonium

salt [d₂m₂N][A] in CDCl₃ (300 MHz) at 298 K.





Cation	Anion	H-2	H-4	H-5	C_nH_{n+1}	Me	A
[hmim]	[Cl ⁻]	10.80	7.44	7.31	4.30; 1.89; 1.30; 0.86	4.11	_
	[Ibu [_]]	9.72	7.08	7.01	4.05; 1.74; 1.26; 0.86	3.75	7.28; 7.01; 3.54;
							2.37; 1.78; 1.41; 0.86
[dmim]	[Cl]	10.82	7.38	7.27	4.32; 1.89; 1.27; 0.86	4.12	_
	[Ibu [_]]	10.58	7.01	6.99	4.11; 1.78; 1.25; 0.87	3.81	7.31; 6.98; 3.60;
							2.39; 1.79; 1.46; 0.87
$[d_2m_2N]$	[Br]				3.51; 1.65; 1.30; 0.88	3.41	_
	[Ibu [_]]				3.10; 1.52; 1.26; 0.88	3.01	7.30; 7.00; 3.57;
							2.39; 1.81; 1.42; 0.88

 Table S10. ¹H NMR chemical shift values of 1-[(9-antryl)methyl]-3

methylimidazolium salts 1·A in CD₃CN (300 MHz) at 298 K.



Anion	H-2	H-4	H-5	Antryl	-CH ₂ -	Me	A
Cl	8.73	7.38	7.30	8.77; 8.36; 8.18; 7.63	6.42	3.70	
PF_6^-	8.13	7.35	7.28	8.72; 8.24; 8.15; 7.62	6.26	3.65	
BF_4^-	8.16	7.33	7.29	8.71; 8.23; 8.14; 7.61	6.27	3.66	
TfO ⁻	8.09	7.40	7.29	8.79; 8.26; 8.20; 7.64	6.31	3.65	
BPh ₄ ⁻	8.10	7.36	7.30	8.79; 8.25; 8.20; 7.64	6.29	3.62	7.28; 6.99; 6.84
BPh4 ^{-b}	8.80	7.18	7.18	8.85; 8.8.45; 8.22; 7.68	6.47	3.72	7.18; 6.92; 6.78

^aSolution concentrations are 0.02 M. ^bIn DMSO-d₆

Table S11.	H NMR chemical shift values of 9,10-bis[(3-butyl-1-
imidazolio)n	hethyl]anthracene 2·2A in CDCl ₃ (300 MHz) at 298 K.



Anion	H-2	H-4	H-5	Ar	-CH ₂ -	Bu	A
AcO ^{-a}	10.04	7.71	7.64	8.74; 7.99	6.78	4.37; 2.00; 1.50; 1.14	1.94
BzO ^{-b}	c	7.63	7.52	8.52; 7.93	6.58	4.10; 1.75; 1.26; 0.89	7.77; 7.34
(S)-Lactate	10.26	7.07	7.07	8.13; 7.46	6.44	4.07; 1.70; 1.20; 0.83	3.87; 1.25
MeSO ₃ ⁻	9.15	7.74	7.13	7.88; 7.33	6.28	4.03; 1.62; 1.14; 0.76	2.44
Bu ₂ PO ₄	10.20	7.33	7.15	8.03; 7.35	6.44	4.06; 1.69; 1.18; 0.83	3.72; 1.51; 1.31; 0.83
PF_6^-	9.29	8.27	7.04	7.79; 7.30	6.38	4.03; 1.60; 1.14; 0.78	
BF_4	9.03	8.38	7.08	7.79; 7.24	6.36	4.01; 1.58; 1.12; 0.76	
$CF_3SO_3^{-a}$	c	8.40	8.40	7.74; 7.37	6.40	4.02; 1.71; 1.23; 0.85	
NCS	8.70	8.18	7.22	7.89; 7.41	6.33	4.01; 1.65; 1.20; 0.80	

^aIn CD₃CN. ^bIn CD₃OD. ^cSignal not observed.

 Table S12.
 ¹H NMR chemical shift values of bis(imidazolium)

heterophane **3·2A** in DMSO-d₆ (300 MHz) at 298 K.

Anion	H-2	H-4,5	-CH ₂ -	Ph	A
AcO ⁻	10.77	7.82	5.42	7.81; 7.59; 7.40	1.68
BzO	10.70	7.80	5.43	7.80; 7.59; 7.40	7.93; 7.28
(S)-Lactate	9.91	7.79	5.42	7.79; 7.58; 7.49	3.50; 1.35
MeSO ₃	9.34	7.81	5.43	7.81; 7.59; 7.48	2.31
Bu ₂ PO ₄	10.49	7.77	5.41	7.73; 7.59; 7.42	3.63; 1.44; 1.29; 0.83
PF_6	8.20	7.75	5.39	7.75; 7.54; 7.38	
BF_4	9.68	7.82	5.43	7.59; 7.49; 7.33	
CF ₃ SO ₃	9.23	7.82	5.43	7.57; 7.51; 6.93	
NCS	9.23	7.82	5.43	7.82; 7.56; 6.94	

 Table S13.
 ¹H NMR chemical shift values of

bis(imidazolium)calixarene 4·2A in CDCl₃ (300 MHz) at 298 K.^a



Anion	H ₂	H ₄	H ₅	H ₁₀ ,	H ₁₁ ,	H4'	N-CH ₂ -	Ha	He	A ⁻
Br	9.28	8.20	6.68	7.27	7.16	6.53	4.51	4.52	3.25	
AcO	9.87	7.71	7.05	7.25	7.05	6.46	4.20	4.48	3.25	1.95
MeSO ₃	9.07	7.70	6.83	7.26	7.06	6.47	4.31	4.50	3.25	2.80
Bu ₂ PO ₄	9.74	8.00	6.90	7.27	7.07	6.43	4.27	4.47	3.25	3.86; 1.60; 1.38; 0.86
PF_6^{-b}	8.72	6.61	6.59	7.45	6.51	7.14	4.17	4.54	3.31	
PF_6^{-c}	9.79	8.26	8.01	6.36	6.36	7.59	4.23	4.43	3.30	

^aSolution concentrations are 0.02 M. ^bIn CD₃CN. ^cIn DMSO-d₆.