

# A new family of fluidic precursors for the self-templated synthesis of hierarchical nanoporous carbons

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## Experimental Section

### General Considerations

*N*-(2-cyanoethyl)-imidazole was purchased from Matrix Scientific. Lithium bis(trifluoromethanesulfonyl)imide and Lithium bis(perfluoroethylsulfonyl)imide were purchased from 3M. All other chemicals were purchased from Sigma-Aldrich. All chemicals were used as received without further purification. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker Avance 400, at 400MHz and 100MHz respectively. **AB Sciex QSTAR® Elite Hybrid LC/MS/MS System**, a hybrid quadrupole time of flight mass spectrometer fitted with electrospray ionization mass spectrometer was used to characterize the compounds. However in the case of **BETI** the JEOL (Peabody, MA) JMS-T100LC (AccuTOFTM) orthogonal time-of-flight (TOF) mass spectrometer was used for characterization.

### General Procedure for the Synthesis of Linked Bis-imidazolium Ionic Liquids

A 250ml round bottom flask was charged with 75ml of ethanol, 2.2 eq of *N*-(2-cyanoethyl)-imidazole and 1 eq of the appropriate bis-bromoalkane. The solution was refluxed overnight under Argon atmosphere. The solvent was removed in vacuo, and the resulting solid was triturated and washed with ethyl acetate (3 x 50ml) and ether (3 x 50ml). The solid was dissolved in deionized water and 2 eq of Lithium bis(trifluoromethanesulfonyl)imide was added. The mixture was stirred for four hours after which it was allowed to settle. The aqueous phase was decanted and the remaining ionic liquid was dissolved in ethyl acetate and washed with water until a silver nitrate test showed no residual halide in the aqueous phase. The solvent was then removed in vacuo and the resultant liquid was dried under high vacuum yielding viscous clear to pale yellow liquids.

#### 1. Ethyl Linked Bis-imidazole (TF<sub>2</sub>N)

Compound ethyl-bis-imidazolium bis(trifluoromethanesulfonyl)imide was synthesized following the described procedure using 1,2-dibromoethane. Yield: 11.9g (70 %). <sup>1</sup>H NMR (Acetone ,400MHz): δ = 9.17 (s, 2 H), 7.92 (t, J=1.7 Hz, 2 H), 7.86 (t, J=1.8 Hz, 2 H), 5.12 (s, 4 H), 4.70 (t, J=6.5 Hz, 4 H), 3.24 ppm (t, J=6.6 Hz, 4 H). <sup>13</sup>C NMR (Acetone ,101MHz): δ = 137.9, 125.6, 124.6, 124.3, 122.4, 119.3, 117.5, 116.1, 50.2, 46.4, 19.6 ppm. ESI-MS: [Cat<sup>2+</sup>-Anion]<sup>+</sup> 550.02 (+ve) ESI-MS: [Anion]<sup>-</sup> 279.91 (-ve)

#### 2. Ethyl Linked Bis-imidazole (BETI)

Compound ethyl-bis-imidazolium bis(perfluoroethylsulfonyl)imide was synthesized following the described procedure using 1,2-dibromoethane and Lithium bis(perfluoroethylsulfonyl)imide as the anion. Yield: 17.1 g (40 %). <sup>1</sup>H NMR (Acetone ,400MHz): δ = 9.26 (t, J=1.6 Hz, 2 H), 7.99 (t, J=1.9 Hz, 6 H), 7.92 (t, J=1.9 Hz, 5 H), 5.18 (s, 4 H), 4.74 (t, J=6.5 Hz, 12 H), 3.25 - 3.31 ppm (m, 4 H). <sup>13</sup>C NMR (Acetone ,101MHz): δ = 137.9, 124.5, 124.2, 123.2, 120.4, 117.6, 117.5, 115.2, 112.4, 109.5, 50.1, 46.3, 19.6 ppm. ESI-MS: [Cat]<sup>2+</sup> 270.15 (+ve) ESI-MS: [Anion]<sup>-</sup> 379.97 (-ve)

#### 3. Butyl Linked (bis-imidazole) (TF<sub>2</sub>N)

Compound butyl-bis-imidazolium bis(trifluoromethanesulfonyl)imide was synthesized following the described procedure using 1,4-dibromobutane. Yield 10.8g (61%). <sup>1</sup>H NMR (Acetone ,400MHz): δ = 9.23 (s, 2 H), 7.93 (s, 2 H), 7.86 (s, 2 H), 4.78 (t, J=6.4 Hz, 4 H), 4.55 (br. s., 4 H), 3.29 (t, J=6.5 Hz, 4 H), 2.15 ppm (br. s., 4 H). <sup>13</sup>C NMR (Acetone ,101MHz): δ = 137.5,

125.8, 124.2, 124.0, 122.6, 119.4, 117.6, 116.2, 50.1, 46.3, 27.5, 19.9 ppm. ESI-MS: [Cat<sup>2+</sup>-Anion]<sup>+</sup> 578.05 (+ve) ESI-MS: [Anion]<sup>-</sup> 279.90 (-ve)

#### 4. Hexyl Linked Bis-imidazole (TF<sub>2</sub>N)

Compound hexyl-bis-imidazolium bis(trifluoromethanesulfonyl)imide was synthesized following the described procedure using 1,6-dibromohexane. Yield 12.6 (69%). <sup>1</sup>H NMR (Acetone, 400MHz): δ = 9.14 (s, 2 H), 7.85 (t, J=1.6 Hz, 2 H), 7.80 (t, J=1.6 Hz, 2 H), 4.72 (t, J=6.5 Hz, 4 H), 4.38 (t, J=7.3 Hz, 4 H), 3.26 (t, J=6.5 Hz, 4 H), 1.92 - 2.01 (m, 4 H), 1.44 ppm (dt, J=7.2, 3.7 Hz, 4 H). <sup>13</sup>C NMR (Acetone, 101MHz): δ = 137.2, 128.2, 125.6, 124.0, 123.7, 122.4, 119.3, 117.5, 116.1, 50.6, 46.1, 30.3, 26.0, 19.7 ppm. ESI-MS: [Cat<sup>2+</sup>-Anion]<sup>+</sup> 606.05 (+ve) ESI-MS: [Anion]<sup>-</sup> 279.93 (-ve)

#### 5. Nonyl Linked Bis-imidazole (TF<sub>2</sub>N)

Compound nonyl-bis-imidazolium bis(trifluoromethanesulfonyl)imide was synthesized following the described procedure using 1,9-dibromononane. Yield 11.4g (60%). <sup>1</sup>H NMR (Acetone, 400MHz): δ = 9.21 (s, 2 H), 7.88 (t, J=1.7 Hz, 2 H), 7.85 (t, J=1.7 Hz, 2 H), 4.76 (t, J=6.5 Hz, 4 H), 4.40 (t, J=7.3 Hz, 4 H), 3.28 (t, J=6.5 Hz, 4 H), 1.90 - 2.02 (m, 4 H), 1.25 - 1.43 ppm (m, 10 H). <sup>13</sup>C NMR (Acetone, 101MHz): δ = 137.3, 128.4, 125.8, 124.1, 123.7, 122.6, 119.4, 117.5, 116.2, 50.8, 46.2, 30.7, 29.8, 29.5, 26.7, 19.8 ppm. ESI-MS: [Cat<sup>2+</sup>-Anion]<sup>+</sup> 648.17 (+ve) ESI-MS: [Anion]<sup>-</sup> 279.92 (-ve)

#### 6. Xylyl Linked Bis-Imidazole (TF<sub>2</sub>N)

Compound xylyl-bis-imidazolium bis(trifluoromethanesulfonyl)imide was synthesized following the described procedure using α,α'-Dibromo-*p*-xylene. Yield 13.7g (72%). <sup>1</sup>H NMR (Acetone, 400MHz): δ = 9.34 (s, 2 H), 7.93 (s, 2 H), 7.86 (s, 2 H), 7.60 (s, 4 H), 5.70 (s, 4 H), 4.80 (t, J=6.5 Hz, 4 H), 3.30 ppm (t, J=6.5 Hz, 4 H). <sup>13</sup>C NMR (Acetone, 101MHz): δ = 136.8, 135.1, 129.4, 124.8, 123.3, 121.7, 118.5, 116.7, 115.3, 52.6, 45.5, 18.9 ppm. ESI-MS: [Cat<sup>2+</sup>-Anion]<sup>+</sup> 626.13 (+ve) ESI-MS: [Anion]<sup>-</sup> 279.91 (-ve)

### Characterization

Nitrogen adsorption isotherms were measured at -196°C using TriStar 3000 volumetric adsorption analyzer manufactured by Micromeritics Instrument Corp. (Norcross, GA), and Autosorb 1C from Quantachrome Instruments (Boynton Beach, FL). Before adsorption measurements the finely ground carbon powders were degassed in flowing nitrogen from one to two hours at 200°C.

X-ray photoelectron spectroscopy (XPS) data were collected using a PHI 3056 spectrometer with an Al anode source operated at 15 kV and an applied power of 350 W. Graphite and dry graphene samples were manually pressed between two pieces of Indium foil instead of a carbon tape as support to avoid any contributions to the carbon and oxygen signals from the tape. The piece of Indium foil with the sample on it was then mounted to the sample holder and energy shifts were corrected relative to C1s a 284.8 eV (J. F. Moulder et al., Perkin-Elmer Corp., Ed. J. Chastain, 1992). An inert gold cup was used to hold a sample of the IL used in these experiments. High resolution data (for least squares fitting of the peaks) was collected at a pass energy of 5.85 eV with 0.05 eV step sizes and a minimum of 100 scans to improve the signal to noise ratio; lower resolution survey scans (atomic concentration data) were collected at a pass energy of 93.5 eV with 0.5 eV step sizes and a minimum of 25 scans. Data were analyzed using the PHI MultiPak suite of programs and standard sensitivity factors for each element.

For TEM characterization, carbon powders were dispersed in ethanol using ultrasonic bath. The final suspensions were transferred to lacy carbon coated 200-mesh copper TEM grids and dried in ambient air prior to electron microscopy analysis. Specimens were then characterized using a Hitachi HD-2000 operating in STEM mode using a secondary electron (SE) and/or bright-field STEM detector operating at 200 kV.

For the capacitive energy storage measurements, a slurry of the carbon samples, carbon black (~13 wt%) and ~13 wt% of polyvinylidene fluoride (PVDF) [5wt % in N-methylpyrrolidone (NMP)] was cast onto nickel foam electrode and dried in an oven at 80°C overnight. Electrodes (10 mm<sup>2</sup> covered area) were soaked in 6M aqueous KOH solution for at least 2h. Cyclic voltammetry (CV) was performed on the Gamry G300 potentiostat with a potential range of -0.2 to -1.0 V. The gravimetric capacitance was calculated from the CV curve following the formula:

$$C_g = \frac{\int_{\epsilon_1}^{\epsilon_2} i(\epsilon) d\epsilon}{2(\epsilon_2 - \epsilon_1) m v} \quad (1)$$

Where  $C_g$  is the specific capacitance of individual sample.  $\varepsilon_1$  and  $\varepsilon_2$  are the cutoff potentials in cyclic voltammetry,  $i(\varepsilon)$  is the instantaneous current,  $\int_{\varepsilon_1}^{\varepsilon_2} i(\varepsilon) d\varepsilon$  is the total voltammetric charge obtained by integration of positive and negative sweep in cyclic voltammograms,  $(\varepsilon_2 - \varepsilon_1)$  is the potential window width,  $m$  is the mass of the sample in the electrode, and  $\nu$  is the scan rate.

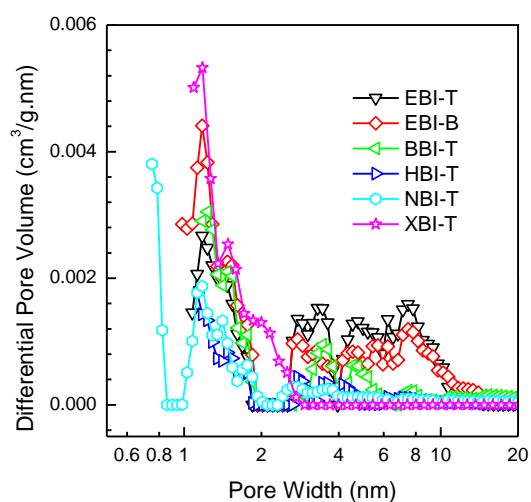
**Table S 1** - Calculated parameters from the nitrogen adsorption analysis at  $-196^\circ\text{C}$  for carbons obtained after carbonization of various ionic liquids at  $850^\circ\text{C}$ .

Sample	$V_{SP}$ [cm <sup>3</sup> /g] [a]	$S_{BET}$ [m <sup>2</sup> /g] [b]	$V_{mi}^t$ [cm <sup>3</sup> /g] [c]	$S_{mi}^t$ [m <sup>2</sup> /g] [d]	W [nm] [e]	GC [F/g] [f]
EthylBisImidazolium-[Tf <sub>2</sub> N] <sub>2</sub> (EBI-T)	1.00	854	0.12	269	1.2 (7.5)	131
EthylBisImidazolium-[BETI] <sub>2</sub> (EBI-B)	1.28	1277	0.34	757	1.2 (7.5)	154
ButylBisImidazolium-[Tf <sub>2</sub> N] <sub>2</sub> (BBI-T)	0.52*	870	0.33	716	1.2	-
HexylBisImidazolium-[Tf <sub>2</sub> N] <sub>2</sub> (HBI-T)	0.33*	643	0.28	601	1.1	104
NonylBisImidazolium-[Tf <sub>2</sub> N] <sub>2</sub> (NBI-T)	0.34*	588	0.24	520	0.75	112
XylylBisImidazolium-[Tf <sub>2</sub> N] <sub>2</sub> (XBI-T)	0.33	706	0.32	686	1.2	-
EBI-T/10CB	0.61	386	0.04	99	15.2	-
EBI-T/25CB	0.60	196	0.01	34	16.9	-

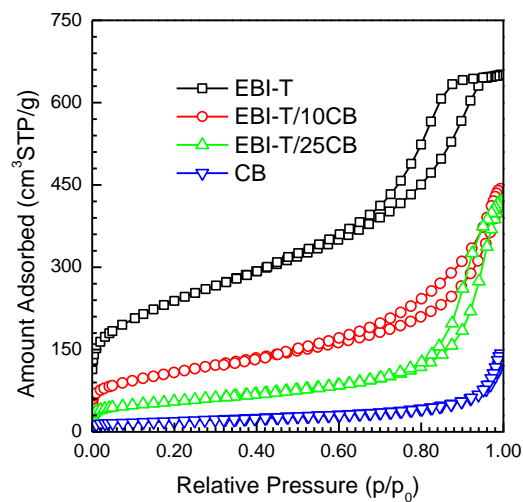
[a] single point pore volume from adsorption isotherms at  $p/p_0 \sim 0.98$  ( $p/p_0 \sim 0.92$ ) [b] specific surface area calculated using the BET equation in the relative pressure range of 0.05-0.20 [c] micropore volume and [d] micropore surface area calculated in the t-plot range of 0.5-0.7nm film thickness using the Carbon Black STSA equation [e] pore width from the maximum of the pore size distribution calculated by a NLDFT method for carbons with slit-pore geometry. Values in parenthesis indicate largest mesopore widths [f] gravimetric capacitance calculated from cyclic voltammograms using 5mV/s as scan rate.

**Table S 2** - XPS data for materials obtained from carbonization at 850°C of the bi-imidazolium ionic liquids, bis-phenyl-imidazolium, and carbon black nanocomposites.

Sample	C-C	C-N, C=O	C-O	CO <sub>3</sub>	C-F	CN(H)C	C-N-C	NO <sub>x</sub>	N*	C=O	C-O	S-O	SO <sub>x</sub>	F1	F2	C-N-O-S-F (at.%)
EBI-T	284.72	286.20	288.52	290.80	293.13	398.15	400.68	403.26	405.68	530.85	532.77	535.58	538.48	688.12	693.31	82.8-6.7-4.1-0.7-5.6
	55.2	24.6	9.5	7.0	3.7	33.2	51.3	9.9	5.7	25.1	42.9	18.6	13.4	8.4	91.1	
EBI-B	284.77	286.21	288.41	290.62	292.92	398.23	400.76	403.26	405.56	530.85	533.03	536.46				84.8-7.3-7.2-0.7-0
	55.9	24.8	9.5	6.5	3.4	29.8	56.2	9.0	5.0	20.8	75.2	4.0				
BBI-T	284.76	286.23	288.55	290.81	293.13	398.16	400.75	403.26	405.95	530.83	532.84	535.58				86.5-6.8-4.3-1.0-1.4
	57.0	24.2	9.3	6.5	3.0	29.5	52.0	10.6	7.9	27.5	40.8	31.8				
HBI-T	284.79	286.20	288.51	290.72	292.89	398.22	400.82	403.26	405.69	530.92	533.08	535.58	538.26	688.99	692.93	86.9-6.6-3.8-0.8-2.0
	56.0	25.2	9.2	6.3	3.2	29.4	54.5	9.1	7.0	25.9	45.4	18.7	10.1	40.8	59.2	
NBI-T	284.74	286.26	288.57	290.83	293.11	398.19	400.74	403.26	404.73	530.99	533.07	536.17		688.64	691.94	85.5-5.7-5.4-0.8-2.3
	58.5	23.3	9.2	6.1	2.9	29.1	56.1	10.0	4.9	38.3	44.6	17.1		38.1	61.9	
XBI-T	284.75	286.28	288.52	290.66	292.86	398.25	400.66	403.26	405.91	530.82	533.02	535.38				79.6-6.5-10.5-2.4-1.1
	61.3	22.5	8.2	5.5	2.5	34.1	50.4	9.6	5.9	12.8	79.3	8.0				
EBI-T/10CB	284.81	286.23	288.56	290.78	293.05	398.28	400.93	403.26	405.32	531.02	532.77	536.83				88.9-7.1-2.8-0.4-0.8
	54.9	25.5	9.5	6.9	3.1	29.2	55.5	6.8	8.5	28.6	62.2	9.2				
EBI-T/25CB	284.81	286.27	288.69	290.95	293.19	398.63	401.14	403.26	405.32	531.06	532.76	535.58				94.8-2.6-1.6-0.3-0.7
	61.3	21.5	7.4	6.7	3.1	34.1	50.3	9.8	5.8	15.3	77.5	7.2				



(A)



(B)

**Figure S 1** – Calculated PSDs for pores up to 20nm from N<sub>2</sub> -196 °C isotherms (A). Nitrogen -196 °C sorption isotherms for the EBI-T and EBI-T carbon black nanocomposites prepared by the “brick and mortar” method. Increasing ratios of CB particles added to the TSILs induces formation of carbons with increasingly larger pores (see shifts in capillary condensation steps to higher  $p/p_0$ ), and lower specific surface areas, due to thinning of carbon film connecting the CB particles.