Supplementary Data

Multifunctional Electropolymerizable Carbazole-Based Ionic Liquids

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General
Reagents and instruments:

\[ N\text{-butyl-}N\text{-methylpyrrolidinium bis((trifluoromethyl)sulfonyl)imide (BMP-TFSI)}, \]
\[ \text{tributylmethylammonium bis((trifluoromethyl)sulfonyl)imide (Bu}_3\text{MeN-TFSI)}, \]
\[ 1\text{-butyl-3-methylimidazolium hexafluorophosphate (BMIM-PF}_6\text{)} \]
\[ \text{and 1-butyl-3-methylimidazolium tetrafluoroborate (BMIM-BF}_4\text{)} \]
were prepared according to the literature procedure.\(^1\)

1-Methyl imidazole (99%) and sodium hydride (60%) dispersion in mineral oil were purchased from Sigma-Aldrich. LiTFSI (>98%) was purchased from 3M. Carbazole (95%) and 1,4-dibromobutane (>98%) were purchased from AlfaAesar. Pyridine (99.9%) and \(N,N\)-dimethyl formamide (99.8%) were purchased from ECHO chemicals. Ethyl acetate was purchased from Duksan reagents. Acetonitrile was purchased from Aencore. Dichloromethane was purchased from Seed Chem. Column chromatography was carried out on silica gel 230-400 mesh (Merck). All reagents were used as received, without further purification and solvents were distilled prior to use.

NMR spectra were acquired with Varian Mercury 400 (\(^1\)H, 400.0 MHz; \(^13\)C, 100.0 MHz). Fluorine NMR spectra were acquired with Bruker Avance III 600 MHz (\(^19\)F, 565 MHz) nuclear magnetic resonance spectrometer. Chemical shifts are reported in ppm and referenced to the corresponding residual nuclei in deuterated solvents (Merck). The mass spectra of all the compounds were recorded in Waters micromass ZQ coupled to ESCi Multi-Mode Ionization. Melting point was recorded in Fergo instrument MP-1D.

Experimental
Synthesis of 9-(4-bromobutyl)-9H-carbazole (3):

\[
\begin{array}{c}
\text{N} \\
\text{Br} \\
\text{Br} \\
1 \\
+ \\
\text{DMF, rt, 1} \text{h} \\
\text{NaH (60 %)} \\
\text{Br} \\
\text{Br} \\
2 \\
\rightarrow \\
\text{N} \\
3
\end{array}
\]

A solution of carbazole 1 (2.0 g, 11.9 mmol) in anhydrous DMF (30 mL) was added to NaH (60%) (0.7 g, 35.8 mmol) at 0 °C with stirring under \(N_2\) atmosphere. After stirring at 0 °C for 30 min, 1,4-dibromobutane 2 (18.0 g, 83.7 mmol) was added dropwise for 30 min at 0 °C and the reaction mixture was kept stirring for 1 h at ambient temperature. The reaction was monitored by TLC analysis. The reaction mass was
quenched with water and extracted with dichloromethane followed by drying over anhydrous Na$_2$SO$_4$. The organic layer was concentrated under reduced pressure and the crude compound obtained was purified by column chromatography with silica gel eluting with ethyl acetate : petroleum ether (4:96) to give product as colorless solid, yield (1.7g; 47%). M.P. 112 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.14 – 8.10 (m, 2H), 7.51 – 7.39 (m, 4H), 7.25 (ddd, $J$ = 8.0, 6.3, 1.1 Hz, 2H), 4.36 (t, $J$ = 6.9 Hz, 2H), 3.39 (t, $J$ = 6.5 Hz, 2H), 2.12 – 2.03 (m, 2H), 1.96 – 1.88 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$/ppm 140.24, 125.68, 122.86, 120.39, 118.91, 108.49, 42.13, 33.12, 30.20, 27.62.

Synthesis of 1-(4-(9H-carbazol-9-yl)butyl)-3-methyl-1H-imidazol-3-ium bromide (4):

A solution of compound 3 (1.0 g, 3.3 mmol) in anhydrous acetonitrile (10 mL) was added to 1-methylimidazole (0.8 g, 4.9 mmol) and stirred at 50-60 °C for 12 h. The reaction was monitored by TLC. Concentrating the mixture and adding ethyl acetate to obtain the precipitates by filtration and then washing the solid with cold ethyl acetate to get product as colorless solid, yield (1.2 g; 88%). M.P. 142 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$/ppm 9.94 (s, 1H), 8.01 (d, $J$ = 7.8 Hz, 2H), 7.47 – 7.34 (m, 4H), 7.21 – 7.12 (m, 3H), 7.03 (s, 1H), 4.33 (s, 2H), 4.05 (s, 2H), 3.83 (s, 3H), 1.84 (s, 4H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$/ppm 140.00, 136.91, 125.84, 123.05, 122.58, 121.78, 120.27, 119.03, 108.79, 49.15, 42.00, 36.41, 27.65, 25.10. MS (ESI positive) (m/z): 304.22[M]+.

Synthesis of 1-(4-(9H-carbazol-9-yl)butyl)pyridin-1-ium bromide (5)
A solution of compound 3 (1.5 g, 4.9 mmol) in anhydrous acetonitrile (15 mL) was added to pyridine (0.98 g, 12.4 mmol) and stirred at 50-60 °C for 12 h. The reaction was monitored by TLC. Concentrating the mixture and adding ethyl acetate to obtain the precipitates by filtration and then washing the solid with cold ethyl acetate to get product as yellow solid, yield (1.8g; 95%). M.P. 179°C. 1H NMR (400 MHz, CD3OD) δ/ppm 8.75 (dd, J = 6.7, 1.3 Hz, 2H), 8.47 (tt, J = 7.8, 1.3 Hz, 1H), 8.09 – 8.05 (m, 2H), 7.98 – 7.91 (m, 2H), 7.52 – 7.47 (m, 2H), 7.42 (ddd, J = 8.3, 7.1, 1.2 Hz, 2H), 7.19 (ddd, J = 7.9, 7.1, 1.0 Hz, 2H), 4.48 (dt, J = 13.0, 6.7 Hz, 4H), 2.07 – 1.90 (m, 4H). 13C NMR (100 MHz, CD3OD) δ/ppm 146.75, 145.63, 141.59, 129.34, 126.87, 124.10, 121.23, 120.12, 109.94, 62.56, 42.83, 29.99, 26.40. MS (ESI positive) (m/z): 304.09[M]+.

**Synthesis of 1-(4-(9H-carbazol-9-yl)butyl)-3-methyl-1H-imidazol-3-ium bis((trifluoromethyl)sulfonyl)imide (6):**

**Compound 4 (1.1 g, 2.9 mmol) was dissolved in water (5 mL) and added with LiTFSI (0.85 g, 2.9 mmol) and stirred for 24 h at 40-50 °C to get two immiscible liquid layers. The organic layer was dissolved in dichloromethane and washed with deionized water. Afterwards, it was dried under reduced pressure to get colorless liquid, yield (1.6 g, 98%).** 1H NMR (400 MHz, CD3OD) δ/ppm 8.09 – 8.05 (m, 2H), 7.51 – 7.33 (m, 6H), 7.19 (ddd, J = 7.8, 7.0, 1.1 Hz, 2H), 4.42 (t, J = 6.3 Hz, 2H), 4.04 (t, J = 6.8 Hz, 2H), 3.78 (s, 3H), 1.95 – 1.81 (m, 4H). 13C NMR (100 MHz, CD3OD) δ/ppm 141.64, 126.84, 124.85, 124.08, 123.31, 121.19, 120.07, 109.92, 50.38, 42.84, 36.35, 28.74, 26.52. 19F NMR (565 MHz, CD3OD) δ/ppm -81.57. MS (ESI positive) (m/z): 304.09[M]+.
Synthesis of 1-(4-(9H-carbazol-9-yl)butyl)pyridin-1-i um bis((trifluoromethyl)sulfonyl)imide (7)

Compound 5 (1.0 g, 2.6 mmol) was dissolved in water (5 mL) and added with LiTFSI (0.75 g, 2.6 mmol) and stirred for 24 h at 40-50 °C to get two immiscible liquid layers. The organic layer was dissolved in dichloromethane and washed with deionized water. Afterwards, it was dried under reduced pressure to get colorless liquid, yield (1.47 g 96%). $^1$H NMR (400 MHz, CD$_3$OD) $\delta$/ppm 8.66 (dd, $J$ = 6.7, 1.3 Hz, 2H), 8.43 (tt, $J$ = 7.8, 1.3 Hz, 1H), 8.08 – 8.03 (m, 2H), 7.94 – 7.87 (m, 2H), 7.50 – 7.37 (m, 4H), 7.18 (ddd, $J$ = 7.9, 7.0, 1.1 Hz, 2H), 4.43 (td, $J$ = 6.7, 3.6 Hz, 4H), 2.05 – 1.90 (m, 4H). $^{13}$C NMR (100 MHz, DC$_3$OD) $\delta$/ppm 146.71, 145.51, 141.56, 129.31, 126.89, 124.07, 121.21, 120.12, 109.92, 62.57, 42.77, 29.91, 26.33. $^{19}$F NMR (565 MHz, CD$_3$OD) $\delta$/ppm -81.57. MS (ESI positive) (m/z): 301.11[M]$^+$. 
$^1$H NMR, $^{13}$C NMR spectra for compounds 3, 4, 5, 6 and 7. $^{19}$F NMR spectra for compounds 6 & 7:
Fig. S1 $^1$H and $^{13}$C NMR spectra of compounds 3, 4, 5, 6 and 7. $^{19}$F NMR spectra of compounds 6 and 7. The presence of TFSI anion was confirmed.
EDX spectra

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Fig. S2 SEM images and EDX analysis of electropolymerized compound 6 (a,b,c,d) and electropolymerized compound 7 (e,f,g,h) prepared from (a,e) BMP-TFSI, (b,f) Bu₃MeN-TFSI, (c,g) BMIm-BF₄, and (d,h) BMIm-PF₆. Electropolymerization was achieved using continuous cyclic voltammetry with 20 scan cycles under a scan rate of 50 mV∙s⁻¹.
Dependence of oxidation peak on concentration of uric acid

Fig. S3 CVs of uric acid with concentrations of 0, 0.1, 0.5, 1.0, and 1.5 mM in PBS (pH 7.0) recorded at electrodes shown in Figs. 1a and b respectively. Scan rate: 50 mV·s⁻¹. Insets show the dependence of anodic peak current on the concentration of uric acid.

Voltammetric behavior of uric acid at poly(IL)-coated ITO

Fig. S4 CVs of uric acid (1 mM) in PBS (pH 7.0) recorded at the relevant electrodes shown in Fig. 1 (c, d, g and h) respectively. Scan rate: 50 mV·s⁻¹.
Comparison of voltammetric behavior of ferricyanide at various electrodes

**Fig. S5** CVs of 5 mM K$_3$[Fe(CN)$_6$] in PBS (pH 7.0) recorded at the relevant electrodes. The contents in the parentheses indicate the ILs used as the electrolytes for electropolymerization. The same approach shown in **Fig. 1** was used for the electropolymerization but 10 cycles of potential scan was used as the parameter for the formation of polycarbazole.

Spectroscopic behavior of polycarbazole-coated ITO

**Fig. S6** Absorption spectra of polycarbazole-coated ITO electrodes recorded in a self-made spectroelectrochemical cell containing (a) 0.1 M NaCl and (b) 0.1 M NaClO$_4$ during a cyclic voltammetric study. Spectra were acquired at the oxidative (1.2 V) and the reductive (0.2 V) states, respectively, of polycarbazole that was prepared using the same approach shown in **Fig. 1** from BMI$_3$-PF$_6$ containing 50 mM carbazole (10 cycles of potential scan were performed to form polycarbazole).
Voltammetric behavior of compounds 6 and 7 in conventional solvent

Fig. S7 CVs of (a) compound 6 (50 mM), and (b) compound 7 (50 mM) recorded at ITO electrode in acetonitrile containing 0.1 M LiTFSI under the scan rate of 50 mV⋅s\(^{-1}\) for 20 cycles. Insets show the absorption spectra of the gel-like oligomer/polymer spread upon ITO electrodes. The gel-like oligomer/polymer were prepared via bulk electrolysis and extraction with water and ethyl acetate.

Reference