A new class of solid state ionic conductors for application in all solid state dye sensitized solar cells

Anupam Midya, Zhibin Xie, Jia-Xiang Yang, Zhi-Kuan Chen, Daniel J-Blackwood, John Wang, Stefan Adams, Kian Ping Loh*

Electronic supplementary information

Contents

Digital image of solid state electrolyte .......................................... S1

Experimental:

Materials, characterization and synthesis ................................. S1-S5

Impedance measurement .......................................................... S6

Fig S1: Digital image of electrolyte mixture of 0.12 M SD2, 0.1 M tert-butylpyridine 0.12 M lithium bis(trifluorosulfonyl) imide (Li[(CF3SO2)2N]), and 0.012 M 1-Ethyl-3-methylimidazolium tetracyanoborate

Experimental:

Material: All reagents and chemicals were purchased from Aldrich. N, N-Dimethylformamide (DMF) was dried and distilled from CaH2. Other chemicals and reagents were used as received without further purifications.
Characterizations: The $^1$H NMR and $^{13}$C NMR spectra were recorded in solution of CDCl$_3$ or CD$_2$Cl$_2$ on a Bruker DPX (400 MHz) NMR spectrometer with tetramethylsilane (TMS) as the internal standard. Electrochemical measurements were performed using an Autolab potentiostat (model PGSTAT30) by Echorchimie. Fourier transform infrared spectrophotometry (FT-IR) was recorded on a Varian 3100 FTIR instrument and measured in KBr discs (400-4000 cm$^{-1}$). MALDI-TOF (matrix-assisted laser desorption ionization time-of-flight) analysis was performed on Bruker Autoflex II spectrometer, using dithranol as matrix. All reactions were performed under N$_2$ atmosphere unless otherwise stated.

Synthesis:

3- bromocarbazole(1):
Carbazole (15 g, 89.70 mmol) was dissolved in DMF (100 mL) in a 500 mL two necked round bottom flask. After the solution was cooled to 0 °C, N-bromosuccinimide (NBS) (15.96 g, 89.70 mmol) in DMF (150 mL) solution was added dropwise. The mixture was allowed to warm to room temperature and stirred for an additional 2 h. The mixture was then poured into water (1 L). The white precipitates was filtered, and dissolved in dichloromethane (CH$_2$Cl$_2$). The organic part was washed with water to remove water soluble impurities. Organic solvent was removed and resulting white solid was recrystallized from ethanol to give colorless crystals. Yield: 16.61 g (75%).

$^1$H NMR (CDCl$_3$, 400 MHz): δ (ppm) = 8.13 (d, J = 2.0 Hz, 2H), 8.09 (b, 1H), 7.52 (dd, J = 8.4, 2.0 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H).

N- Ethylhexyl -3- bromocarbazole (2)
To a mixture of compound 3-bromocarbazole (12 g, 48.5 mmol) and anhydrous DMF (100 mL) was added slowly NaH (2.71 g, 60% w/w dispersion in mineral oil, 67.9 mmol). After 30 min, 2-ethylhexyl bromide (12.2 g, 63 mmol) was added. The reaction was stirred at room temperature for 18 h under nitrogen. The reaction was quenched with H$_2$O and extracted with CH$_2$Cl$_2$. The organic fractions were dried under sodium sulfate and the solvent was removed under reduced pressure. The product was purified by column chromatography (10% EtOAc in hexane as eluent) to give the title compound as a colorless viscous liquid (16.68 g, 96%);
1H NMR (CD$_2$Cl$_2$, 400 MHz): δ (ppm) = 8.22 (d, J = 1.6 Hz, 1H), 8.06 (d, J = 8 Hz, 1H), 7.55 (dd, J = 8.4, 1.6 Hz, 1H), 7.50 (t, 1H), 7.44 (d, J = 8 Hz, 1H), 7.33 (d, J = 8.4 Hz, 1H), 7.24 (t, 1H), 4.16 (m, 2H), 2.05 (m, 1H), 1.43-1.21 (m, 8H), 0.92 (t, 3H), 0.86 (t, 3H).

MS (MALDI-TOF, m/z): Calcd for C$_{20}$H$_{24}$Br$_3$N, 357.109; found, 356.985.

9-(2-ethylhexyl)-3-(1H-imidazol-1-yl)-9H-carbazole (3)

A mixture of N-ethylhexyl-3-bromocarbazole (11.20 g, 31.2 mmol), imidazole (2.33 g, 34.3 mmol), CuI (0.59 g, 3.12 mmol), 1,10-phenanthroline (1.23 g, 6.8 mmol), and K$_2$CO$_3$ (10.80 g, 78.15 mmol) were suspended in 60 mL of anhydrous DMF in round bottom flask equipped with magnetic stir bar and reflux condenser. The reaction container was then evacuated three times and backfilled with N$_2$. The reaction mixture was stirred for 30 min at room temperature and then refluxed at 150 °C with vigorous stirring under N$_2$ protection for 30 h and cooled to ambient temperature. DMF solvent was removed under high vacuum and temperature. The residue brown mixture was extracted with dichloromethane (50 mL × 4), and the organic extracts were combined, dried over Na$_2$SO$_4$, and purified by silica gel column chromatography (1:1 ethylacetate / hexanes ) to obtain the titled compounds as light brown solid (10.35 g, 95%).

1H NMR (CD$_2$Cl$_2$, 400 MHz): δ (ppm) = 8.13 (d, J = 8.4 Hz, 1H), 8.11 (s, 1H), 7.91 (s, 1H), 7.52-7.47 (m, 4H), 7.40 (s, 1H), 7.29-7.25 (t, 1H), 7.19 (s, 1H), 4.23 (m, 2H), 2.12-2.08 (m, 1H), 1.45-1.23 (m, 8H), 0.94 (t, 3H), 0.87 (t, 3H).

MS (MALDI-TOF, m/z): Calcd for C$_{23}$H$_{27}$N$_3$, 345.220; found, 345.256.

SD2

A mixture of 3 (2 g, 5.79 mmol) and iodomethane (0.72 mL, 11.58 mmol) was placed in a sealed reaction vessel (0.2-2 mL) with a magnetic stir bar inside the sample holder of the microwave reactor. The reaction mixture was heated up to 60 °C at 10 W and then hold at this temperature for 15 min. The reaction mixture was cooled down to room temperature in the microwave system. The crude reaction mixture was purified by silica-gel column chromatography. The titled compound solid SD2 was eluted with methanol and dichloromethane solvent mixture (1:10). The solvent was removed at reduced pressure to give the title compound as a white solid (Yield: 1.83 g, 65%). mp 184-190°C.
$^1$H NMR (CD$_2$Cl$_2$, 400 MHz): $\delta$ (ppm) = 10.42 (s, 1H), 8.54 (d, J = 2 Hz, 1H), 8.24 (d, J = 8 Hz, 1H), 7.78 (dd, J = 8.4, 2 Hz, 1H), 7.71 (s, 1H), 7.57-7.53 (m, 2H), 7.48 (d, J = 8.4 Hz, 1H), 7.29 (t, 1H), 4.22-4.18 (m, 5H), 2.06 (m, 1H), 1.42-1.23 (m, 8H), 0.91 (t, 3H), 0.86 (t, 3H)

$^{13}$C NMR (CD$_2$Cl$_2$, 100 MHz): $\delta$ (ppm) = 141.89, 141.01, 135.94, 127.09, 126.25, 123.82, 123.42, 121.99, 121.38, 121.11, 119.81, 119.26, 114.51, 110.32, 109.73, 47.73, 39.39, 37.23, 30.95, 28.74, 24.36, 22.96, 13.68, 10.61.

MS (MALDI-TOF, m/z): Calcd for C$_{24}$H$_{30}$N$_3$\(^+\) (M-I), 360.244; found, 359.382.

**SD3**

SD3 was synthesized from 3 and iodoheaxane as the same procedure for the synthesis of SD2 with 60% in yield.

$^1$H NMR (CD$_2$Cl$_2$, 400 MHz): $\delta$ (ppm) = 10.47 (s, 1H), 8.61 (d, J = 2 Hz, 1H), 8.27 (d, J = 7.6 Hz, 1H), 7.81-7.78 (m, 2H), 7.57-7.51 (m, 3H), 7.47 (d, J = 8 Hz, 1H), 7.27 (t, 1H), 4.50 (m, 2H), 4.17(m, 2H), 2.06-1.97 (m, 3H), 1.44-1.22 (m, 14H), 0.92-0.87 (m, 9H).

$^{13}$C NMR (CD$_2$Cl$_2$, 100 MHz) $\delta$ (ppm) = 141.87, 140.97, 135.23, 127.05, 126.31, 123.43, 122.57, 122.06, 121.39, 121.22, 119.77, 119.09, 114.45, 110.25, 109.69, 50.48, 47.73, 39.39, 31.09, 30.95, 30.19, 28.74, 25.85, 24.36, 22.95, 22.38, 13.67, 13.65, 10.60.

MS (MALDI-TOF, m/z): Calcd for C$_{25}$H$_{40}$N$_3$\(^+\) (M-I), 430.322; found, 429.423.

**SD1**

The compound SD3 (2.22 g) was dissolved in acetone (25 mL) and NaSCN (2 equiv) was added to the solution. The mixture was allowed to stir at room temperature for 48 h. The resulting suspension was filtered, and the filtrate was subjected to a vacuum to remove volatile solvents. The residue was dissolved in dichloromethane and again filtered. The procedure was repeated to remove all dissolved salt. Final filtrate was dried using anhydrous sodium sulfate and concentrated in rotary evaporator. SD1 was obtained as a white solid (99% yield).
FTIR (KBr pellet): 2041.88 cm\(^{-1}\) (SCN);

\(^1\)H NMR (CD\(_2\)Cl\(_2\), 400 MHz): \(\delta\) (ppm) = 9.89 (s, 1H), 8.45 (d, J = 2 Hz, 1H), 8.23 (d, J = 8 Hz, 1H), 7.76 (s, 1H), 7.71 (dd, J = 8, 2 Hz, 1H), 7.56-7.51 (m, 3H), 7.46 (d, J = 8.4 Hz, 1H), 7.27 (t, 1H), 4.44 (t, 2H), 4.15 (m, 2H), 2.06-1.96 (m, 4H), 1.42-1.22 (m, 14H), 0.92-0.84 (m, 9H).

\(^{13}\)C NMR (CD\(_2\)Cl\(_2\), 100 MHz) \(\delta\) (ppm) = 141.88, 141.02, 135.28, 127.06, 126.30, 123.46, 122.59, 122.03, 121.77, 121.08, 119.80, 119.21, 114.33, 110.36, 109.70, 50.70, 47.70, 39.39, 31.08, 30.95, 30.18, 28.74, 25.93, 24.36, 22.96, 22.37, 13.67, 13.65, 10.60.

MS (MALDI-TOF, m/z): Calcd for C\(_{29}\)H\(_{40}\)N\(_3\)\(^+\) (M-SCN), 430.322; found, 430.156.
Measurement of triiodide diffusion coefficients of SD1-SD3 electrolytes:

Electrochemical impedance spectroscopy (EIS) measurements were performed using an Ecochemie Autolab (PGSTAT 302N and FRA2). The cell configuration is Pt/SD x electrolyte/Pt. The EIS measurements in dark were conducted in the frequency range of $10^5$ - $10^1$ Hz and an ac amplitude of 10mV.

![Impedance Spectrum](image)

**Fig S2:** A typical impedance spectrum for Pt/SD2 electrolyte/Pt. (a) Black squares are original data and red line is the fitting based on the equivalent circuit shown in (b)

The diffusion coefficient was calculated based on the following equation from the references R1 and R2.

$$D_a = \frac{L^2}{\omega}$$

The L is the thickness between the two Pt electrodes (12.5µm) and $\omega$ (0.7 for SD2) is the fitting value for W1 element.

References:
