Supporting information

3-Bromocarbazole (1)

To DMF (67 ml) was added carbazole (10 g, 59.80 mmol) and mixture was stirred at room temperature for 15 minutes. N-bromosuccinimide (10.6 g, 59.56 mmol) in DMF (100 ml) was added dropwise at 0°C. The mixture was allowed to warm to room temperature and stirred for two hours. White precipitates were formed after the mixture was poured into water. Precipitates were filtered and dissolved in dichloromethane. The organic layer was washed with water to remove water soluble impurities. The organic fraction was dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The resulting white solid was purified by recrystallization from ethanol to give colorless crystals (10.65 g, 72 % yield).

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.34(bs, 1H), 8.15(d, J=7.8Hz, 1H), 7.48(d, J=8.2, 1H), 7.45(m, 1H), 11.42(s, 1H).

(MS, ESI) m/z 246 (M^+)

N-Ethylhexyl-3-bromocarbazole (2)

Sodium hydride (1.3 g, 60% w/w dispersion in mineral oil, 33.9 mmol) was added slowly to a mixture of 3-carbazole (6 g, 24.2 mmol) and anhydrous DMF (50 ml). After 30 minutes 2-ethylhexyl bromide (6.04 g, 31.3 mmol) was added. The reaction was quenched with water, after stirring at room temperature for 24h and extracted with CH_2Cl_2. The organic layer was dried over anhydrous sodium sulfate. Evaporation of the solvent under vacuum resulted in a yellow residue. The residue was purified by column chromatography using 10% ethyl acetate/hexane mixture as an eluent to give pure compound as colorless viscous (8.22 g, 95 % yield).

^{1}H-NMR ($CDCl_3$, 400 MHz): δ8.20 (d, J =1.6Hz, 1H), 8.05(d, J=7.8Hz,1H), 7.52(dd, J=8.6, 1.8, 1H), 7.46(d,J=8Hz,1H), 7.40(t, 1H), 7.38 (s, 1H), 4.14(m, 1H), 2.0(m,2H), 1.78(m,2H)1.50-1.27(m,8H), 0.91(t, 3H), 0.87(t,3H)

(MS, ESI) m/z 358 (M^+)

N-Ethylhexyl-3-imidazolium carbazole (3)

A mixture of N-ethylhexyl-3-bromocarbazole (6 g, 16.7 mmol), imidazole (1.24 , 18.3 mmol), 1,10-phenanthroline(0.65 g, 3.6 mmol), CuI (0.31 g, 1.66 mmol) and K_2CO_3 (5.75 g, 0.042 mmol) in anhydrous DMF (50 ml) was stirred for 30 minutes at room temperature and then refluxed at 150°C under N_2 for 30h and cooled to room temperature. DMF was removed under high vacuum and temperature. The resulting brown solid was dissolved in water and extracted with dichloromethane. The organic extract was then dried over anhydrous Na_2SO_4. Dichloromethane was removed under high vacuum. The impure product was purified by silica gel column chromatography using ethyl acetate: hexane (1:1) to obtain the pure compound as light brown solid (5.24 g, 91 % yield).

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.11 (d, J= 7.76Hz, 1H), 8.06 (s, 1H), 7.89 (s, 1H), 7.52- 7.42 (m, 4H), 7.27 (s, 1H), 7.26 (t, 1H), 7.24 (s, 1H), 4.21 (m, 1H), 2.04 (m,4H), 1.27-1.26 (m,6H), 0.93 (t, 3H), 0.86 (t,3H)

(MS, ESI) m/z 346 (M^+)

N-Ethylhexyl-3-(3-methylimidazolium iodide) carbazole (4)

N-Ethylhexyl-3-imidazolium carbazole (1.98 g, 5.49 mmol) was dissolved in DMF in a 500ml round bottom flask. After stirring for few minutes, iodomethane (0.68 g, 10.98 mmol) was added and refluxed at 60°C for 24 h. After 24h DMF was removed under high vacuum. The crude reaction mixture was purified by silica- gel column chromatography. The column was eluted with methanol: dichloromethane (1:9). The solvent was evaporated at reduced pressure to give the required compound as white solid (2.11 g, 79 % yield).

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 10.29 (s, 1H), 8.44 (d, J=1.92Hz, 1H),8.21 (d, J= 7.8Hz, 1H), 7.73- 7.69 (m, 2H), 7.59-7.43 (m, 3H), 7.41 (d, J= 8Hz, 1H), 7.37 (t, 1H), 4.22 (s, 3H), 2.06 (m,2H), 1.98 (m, 4H), 1.28-1.22 (m,6H), 0.89-0.82 (m, 6H).

(MS, ESI) m/z 360 (M^+)

Carbazoleimidazolium trifluoromethanesulfonate [CI][OTf] (5)

Compound **4** (0.5 g, 1 mmol) was anion exchanged with sodium trifluoromethanesulfonate (0.19 g, 1.3 mmol) in a biphasic solution where CII was dissolve in DCM while a saturated solution of NaOTf was prepared in water. The biphasic solution of DCM and water was stirred for 3-4 days, the lower layer of DCM was separated from water and washed with water several times to remove the by-product (sodium salt of iodide) which was highly soluble in water. DCM was evaporated under high vacuum and freeze-dried to remove small amounts of water. The product was obtained as yellow solid (0.48 g, 93 % yield).

^{1}H-NMR ($CDCl_3$, 400 MHz): Carbazoleimidazolium cation: δ 9.72 (s, 1H), 8.57 (d, J=2.16 Hz, 1H), 8.19 (d, J= 7.6Hz, 1H), 7.95- 7.77 (m, 2H),7.65 (m, 1H), 7.29 (t, 1H), 4.35 (s, 3H), 3.96 (m, 2H), 1.99 (m, 4H), 1.31-1.16 (m,6H), 0.84-0.76 (m, 6H);

^{19}F-NMR: ($CDCl_3$, 250 MHz) Trifluoromethanesulfonate: δ -79.22.

(MS, ESI^+) m/z 360, (MS, ESI^-) m/z 149

Carbazoleimidazolium bis(trifluoromethylsulfonyl)imide [CI][NTf_2] (6)

Compound **4** (0.1 g, 0.21 mmol) was anion exchanged with $LiNTf_2$ (0.07 g, 0.24 mmol) followed the same procedure as described in **5.** The product was obtained as yellow viscous solid (0.1g, 76 % yield).

^{1}H-NMR ($CDCl_3$, 400 MHz): Carbazoleimidazolium cation δ 9.90 (s, 1H), 8.34 (d, J=1.96Hz, 1H),8.19 (d, J= 7.8Hz, 1H), 7.62-7.56 (m, 2H), 7.54-7.52 (m, 3H), 7.47 (d, J= 8.28 Hz, 1H), 7.32 (t, 1H), 4.22 (s, 3H), 2.34 (m,2H), 1.40 (m, 4H), 1.28-1.26 (m, 6H), 0.95-0.85 (m, 6H).

(MS, ESI^+) m/z 360, (MS, ESI^-) m/z 280

^{19}F-NMR: ($CDCl_3$, 250 MHz): bis(trifluoromethylsulfonyl)imide: δ -78.78

Carbazoleimidazolium bis(pentafluoroethylsulfonyl)imide - [CI] [BETI] (7)

Compound **4** (0.1 g, 0.21 mmol) was anion exchanged with LiBETI (0.096 g, 0.24 mmol) followed the same procedure as described in **5.** The product was obtained as yellow solid (0.15 g, 98 % yield). MP: if solid (check).

^{1}H-NMR ($CDCl_3$, 400 MHz): Carbazoleimidazolium cation: δ 10.39 (s, 1H), 8.37 (d, J=2Hz, 1H),8.18 (d, J= 7.48Hz, 1H), 7.58-7.42 (m, 2H),7.40 (d, J=8Hz, 1H), 7.38 (t, 1H), 4.16 (s, 3H), 4.05 (m, 2H), 1.97 (m, 4H), 1.36-1.25 (m,6H), 0.90-0.85 (m, 6H);

^{19}F-NMR: ($CDCl_3$, 250 MHz): δ -117.64, -79.33.

(MS, ESI) m/z 360 (M^+), (MS, ESI^-) m/z 380

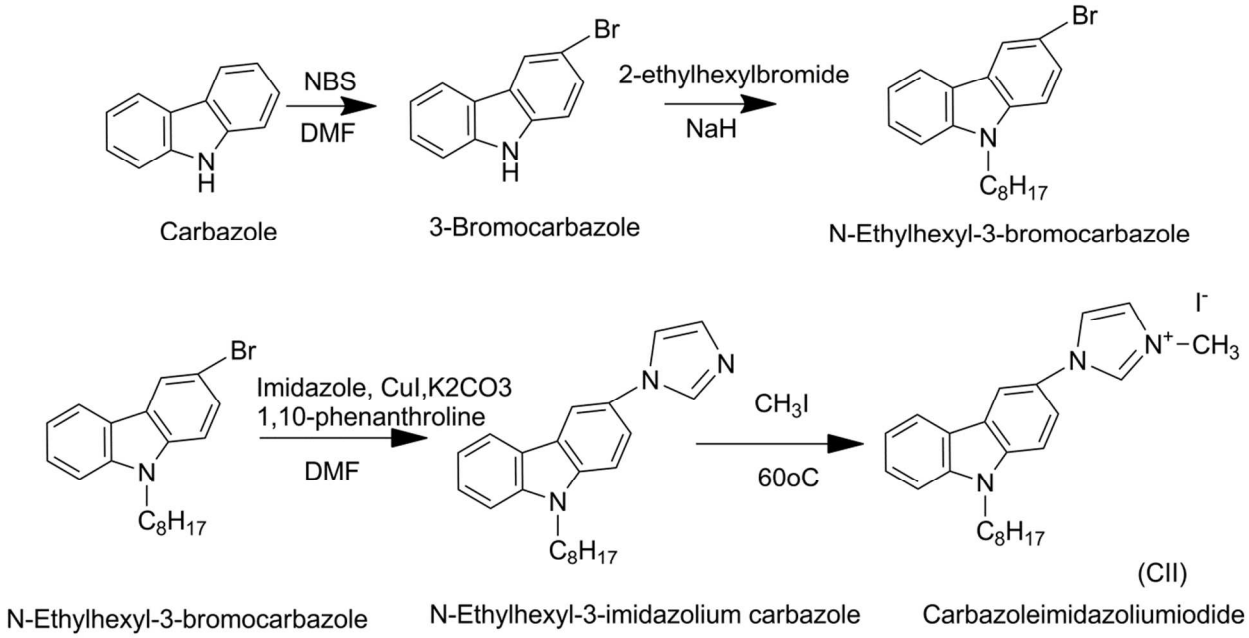

Fig. S1. Synthesis Scheme

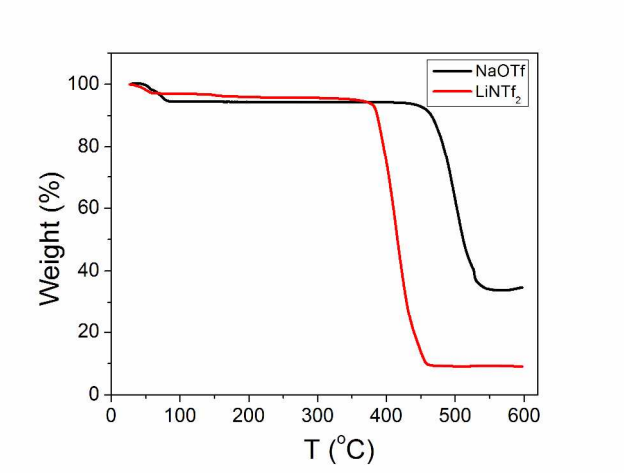

Fig. S2 Thermogravimetric analysis for NaOTf and $LiNTf_2$

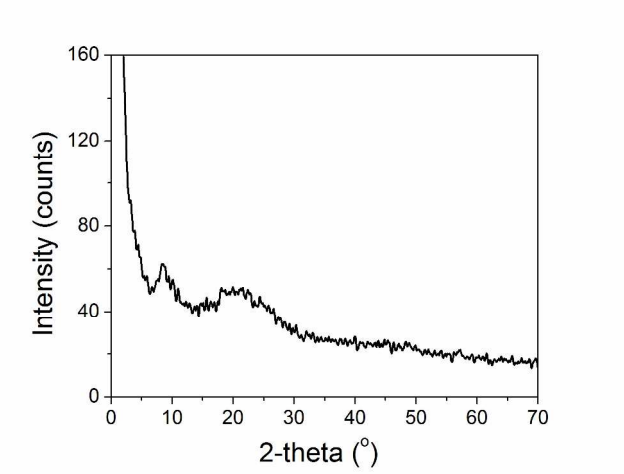

Fig. S3 XRD for [CI][NTf_2]

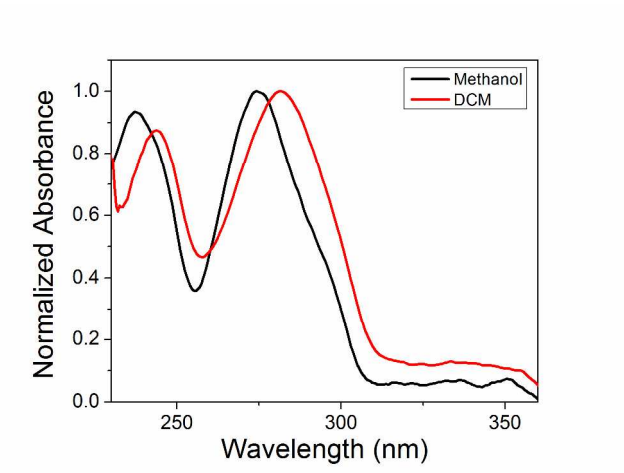

Fig. S4 Normalized absorption spectra of [CI][NTf_2] in methanol and DCM

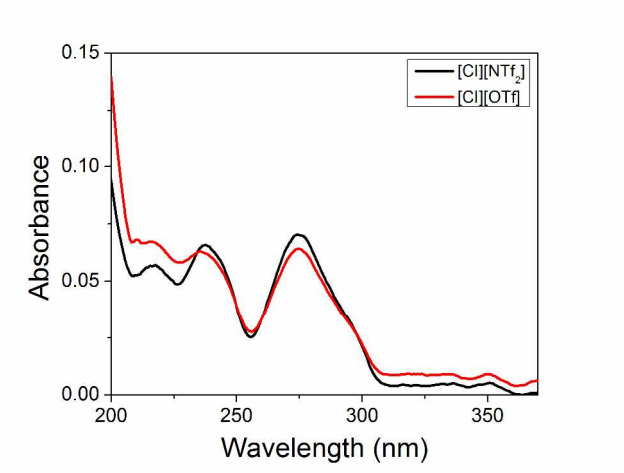

Fig. S5 Absorption spectra of [CI][OTf] and [CI][NTf_2] in methanol

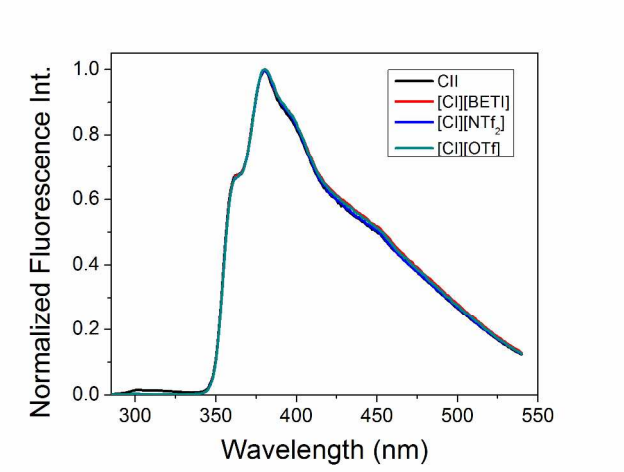

Fig. S6 Fluorescence emission spectra of CII, [CI][OTF], [CI][NTf_2] and [CI][BETI] in methanol

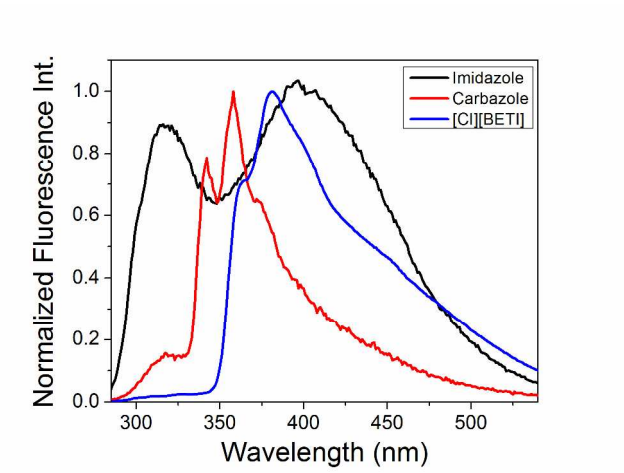

Fig. S7 Fluorescence emission spectra of imidazole, carbazole and [CI][BETI] in methanol, λ_{ex} 275 nm

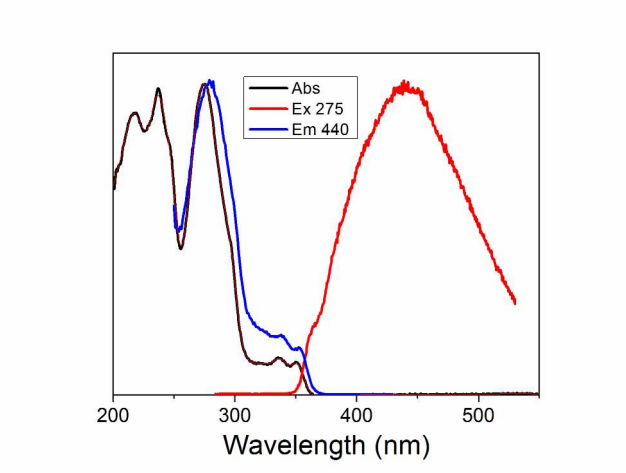

Fig. S8 Absorption, fluorescence emission of [Cl][BETI] in DCM, λ_{ex} 275 nm

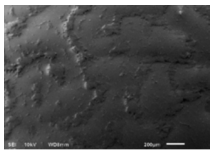

Fig. S9 SEM image of [Cl][BETI] film deposited on quartz

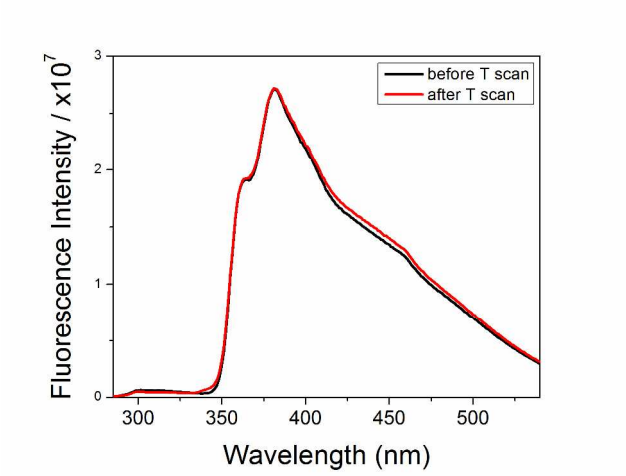

Fig. S10 Fluorescence emission spectra of [Cl][BETI] before and after temperature scan

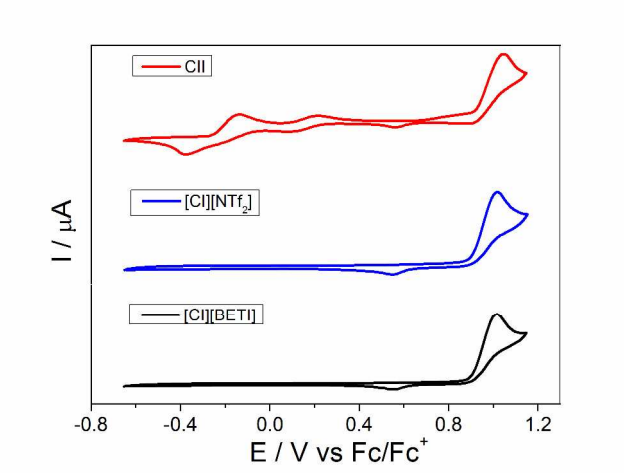

Fig. S11 Cyclic voltammograms for CII, [CI][NTf_2] and [CI][BETI] in DCM at 0.1Vs^{-1}

Table S1. Life time measurements of GUMBOS in methanol

GUMBOS	τ_1/ns	α_1	τ_2/ns	α_2	τ_3/ns	α_3	τ_{avg}/ ns	χ^2_{red}
[CI][OTf]	0.133	0.481	1.640	0.029	4.823	0.490	2.480	1.008
[CI][NTf_2]	0.131	0.510	1.607	0.026	4.853	0.464	2.361	1.018
[CI][BETI]	0.094	0.626	1.485	0.020	4.832	0.354	1.799	1.018

Full reference 27

(27) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Wallingford CT, 2009.