Biophysical analysis of triazolium-based protic ionic liquid incorporated bile salt media

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SUPPORTING INFORMATION

Table S1. List of Abbreviations

1	RTILs	Room Temperature Ionic Liquids
2	1-but3HTTFA	1-butyl-1,2,4-triazolium trifluoroacetate
3	1-pent3HTTFA	1-pentyl-1,2,4-triazolium trifluoroacetate
4	1-hex3HTTFA	1-hexyl-1,2,4-triazolium trifluoroacetate
5	1-hept3HTTFA	1-heptyl-1,2,4-triazolium trifluoroacetate
6	Bile salts	BSs
7	NaC	Sodium Cholate

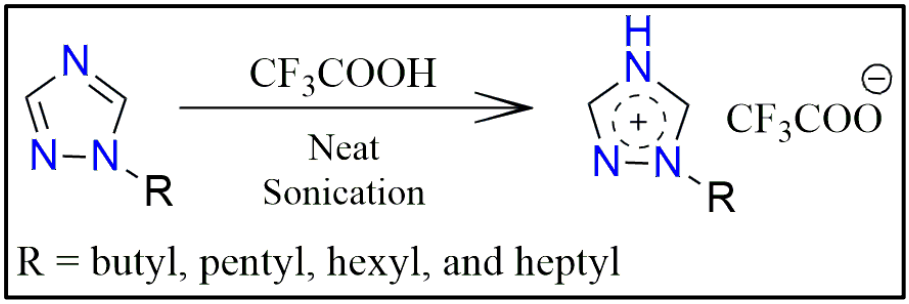
8	NaDC	Sodium Deoxycholate
9	AN	Anthracene
10	DLS	Dynamic Light Scattering
11	PDI	Polydispersity Index
12	DMSO	Dimethyl Sulfoxide
13	TFA	Trifluoroacetic Acid
14	THF	Tetrahydrofuran
15	Nm	Nanometer
16	a.u.	Arbitrary unit
17	M	Molar
18	Mm	Millimol
19	FE-SEM	Field Emission Scanning Electron Microscopy
20	EDS	Energy Dispersive Spectroscopy

Table S2. Purity of Chemicals

Sl.No.	Chemical	Source	Purity
1	1,2,4-triazole	AVRA, India	98%
2	Tetrahydrofuran	AVRA, India	99%
3	1,8-Diazabicyclo[5.4.0]undec-7-ene	AVRA, India	97%
4	1-bromopentane	AVRA, India	98%
5	1-bromohexane	AVRA, India	98%
6	1-bromoheptane	AVRA, India	98%

7	1-bromooctane	AVRA, India	98%
8	Trifluoroacetic acid	AVRA, India	98%
9	Sodium deoxycholate	SRL	Pure
10	Sodium cholate	SRL	Pure
11	Anthracene	Sigma Aldrich	Scintillation grade
12	Dimethyl sulfoxide	SRL	Spectroscopic grade

Synthesis of RTILs



Scheme S1. Synthesis of 1-alkyl-1,2,4-triazolium trifluoroacetate

NMR details of 1-alkyl-1,2,4-triazolium RTILs

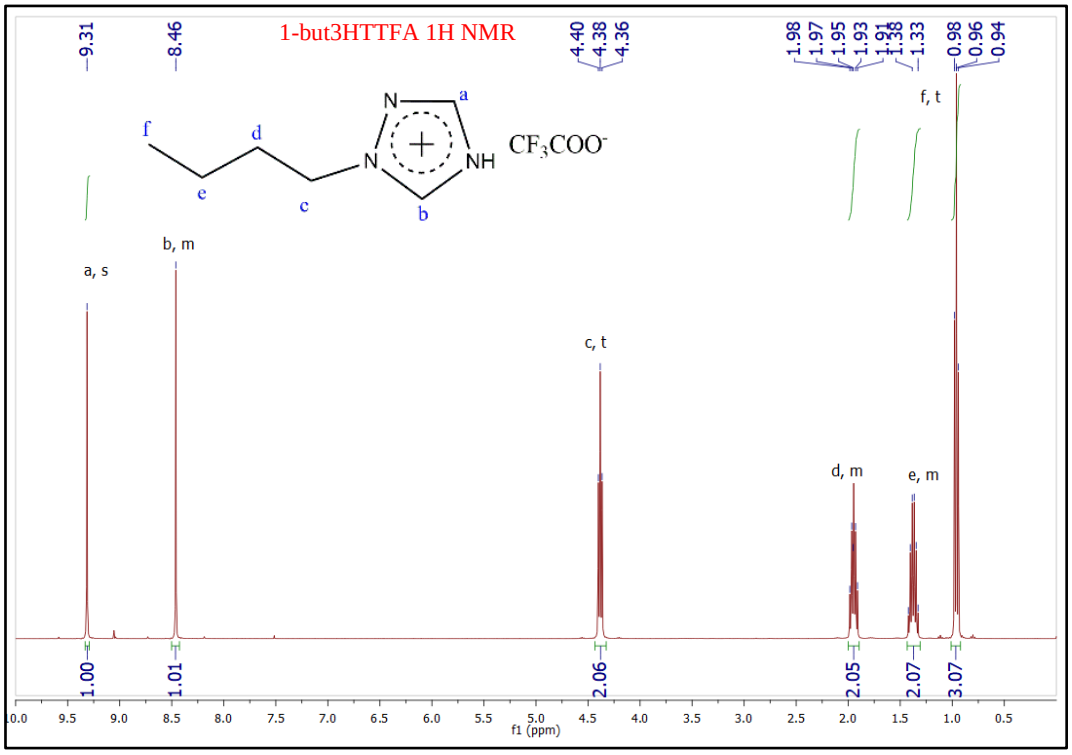


Fig. S1 1-but3HTTFA-^{1}H NMR

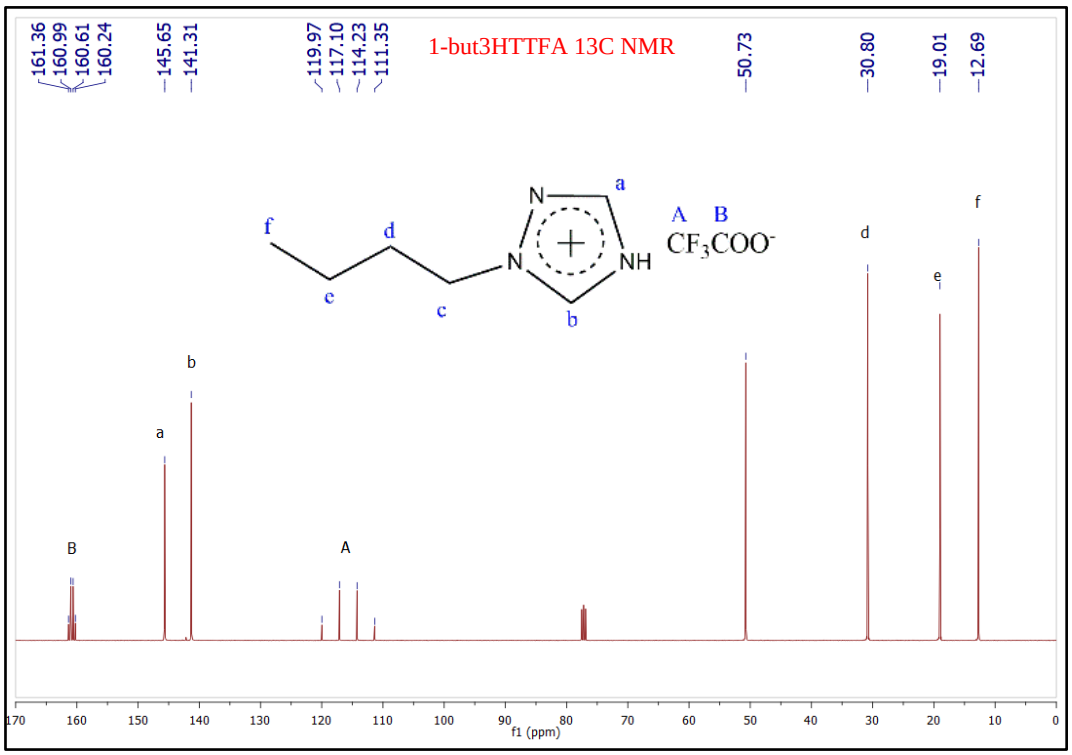


Fig. S2 1-but3HTTFA - ^{13}C NMR

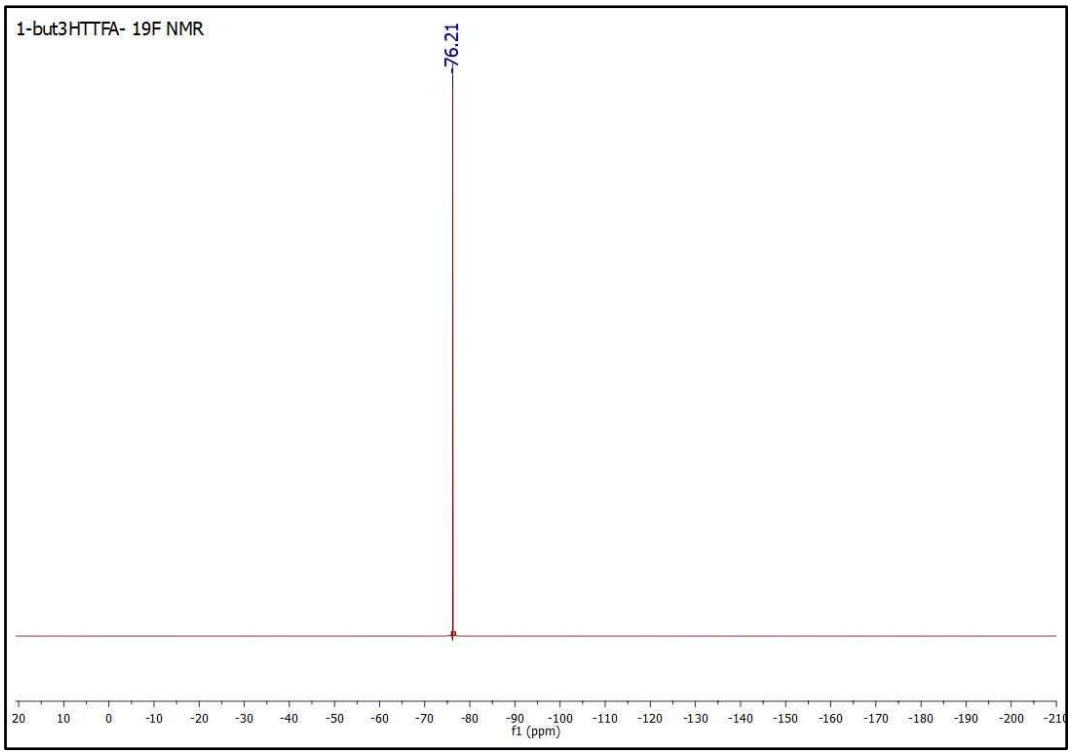


Fig. S3 1-but3HTTFA-^{19}F NMR

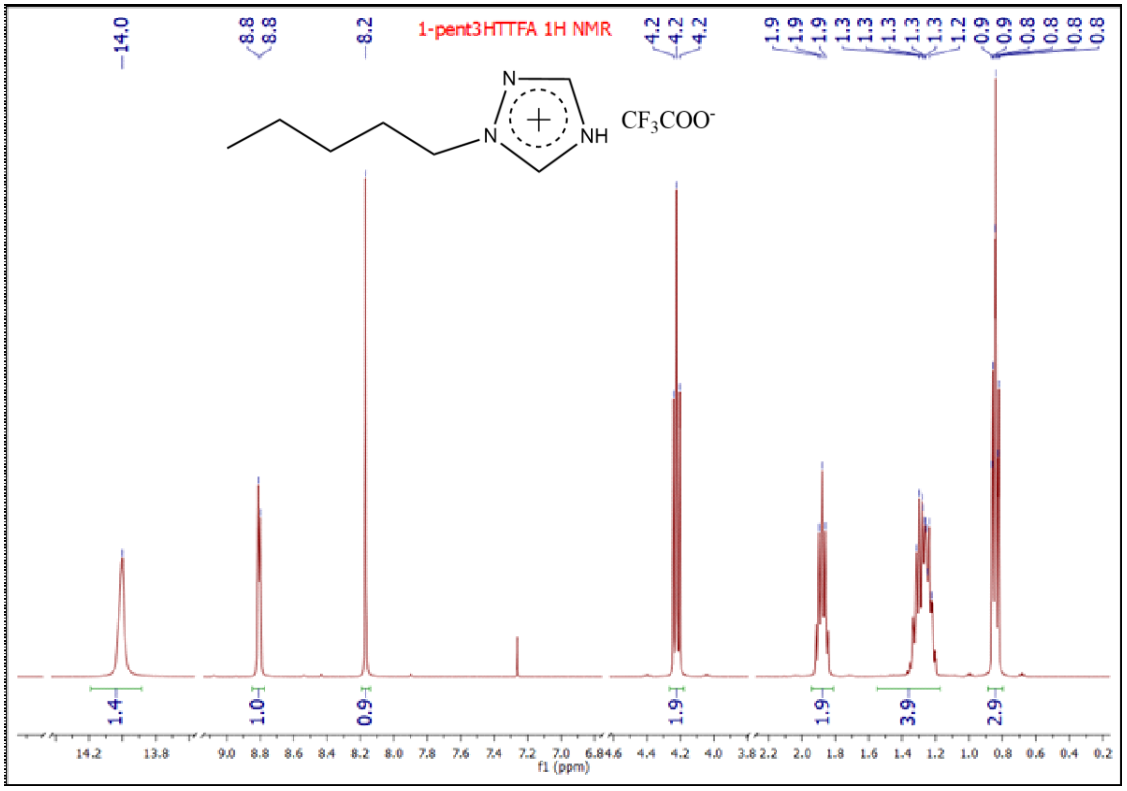


Fig. S4 1-pent3HTTFA-^{1}H NMR

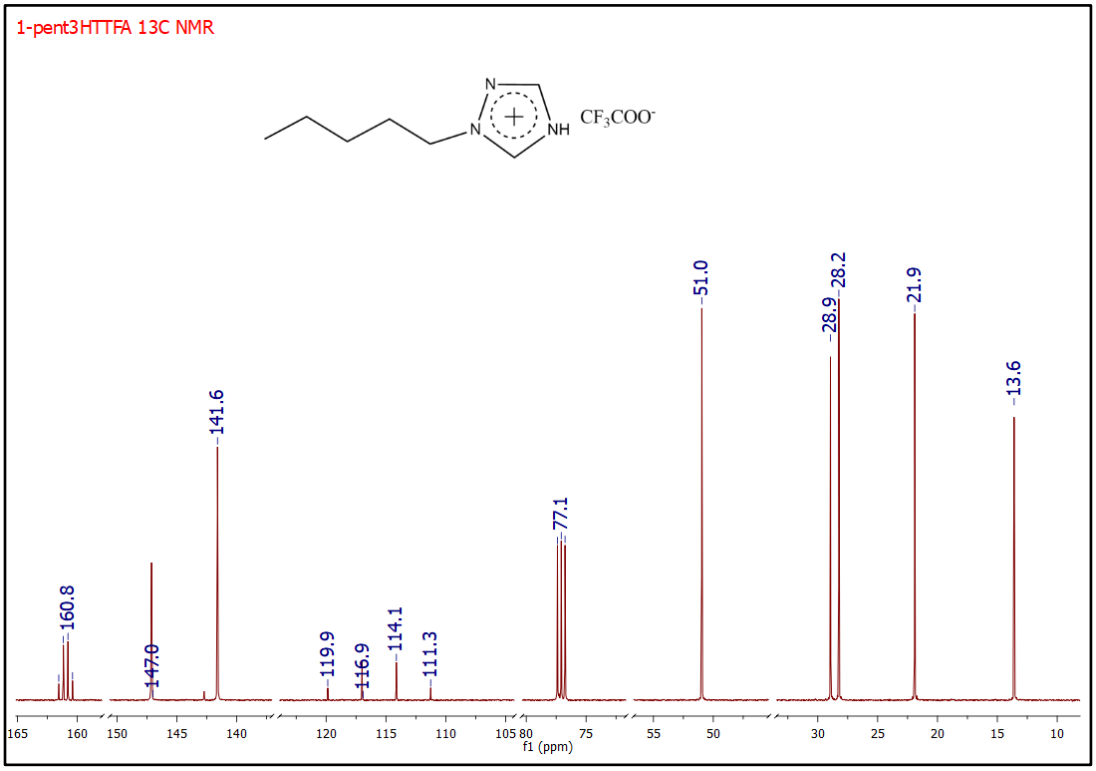


Fig. S5 1-pent3HTTFA-^{13}C NMR

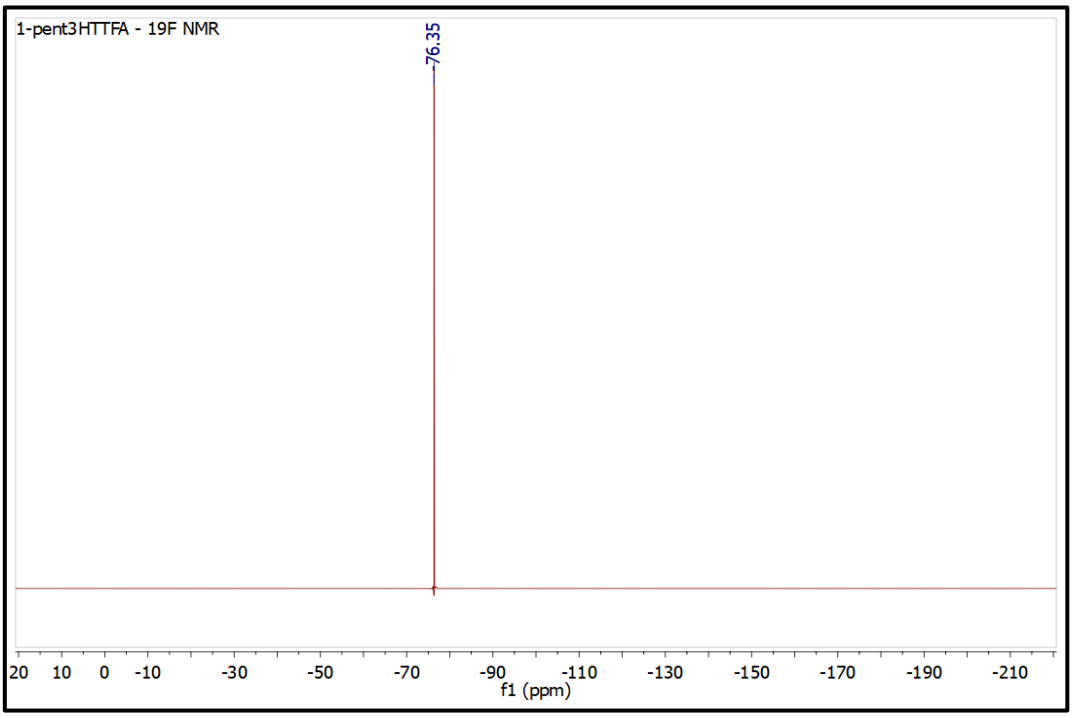


Fig. S6 1-pent3HTTFA-^{19}F NMR

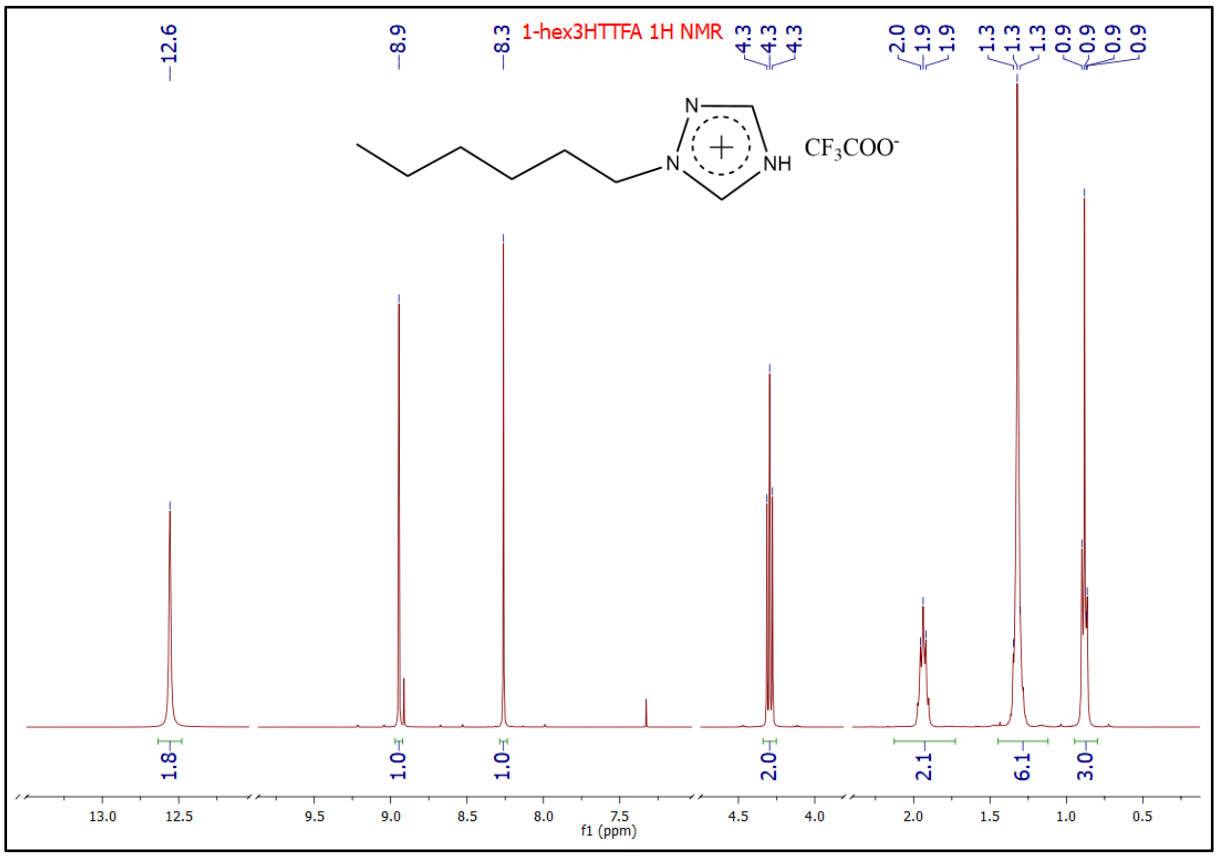


Fig. S7 1-hex3HTTFA-^{1}H NMR

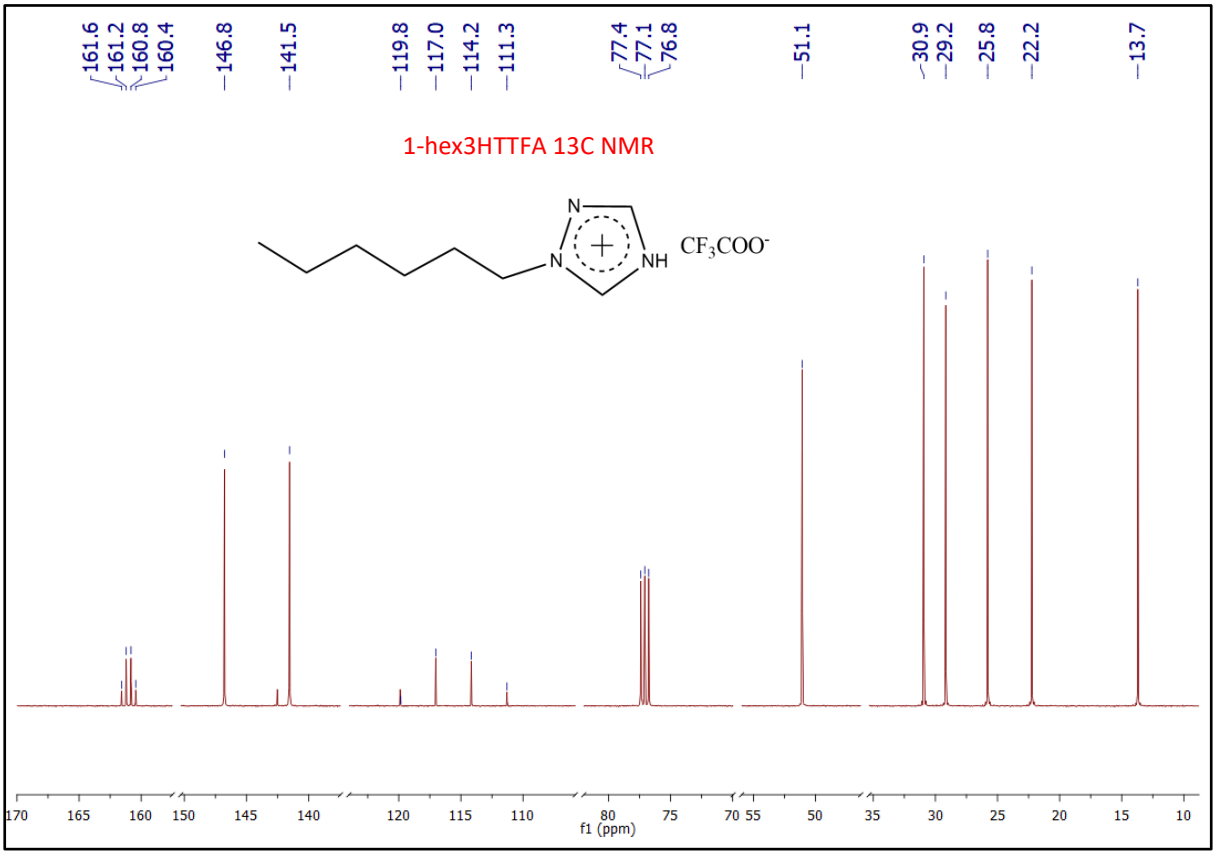


Fig. S8 1-hex3HTTFA-^{13}C NMR

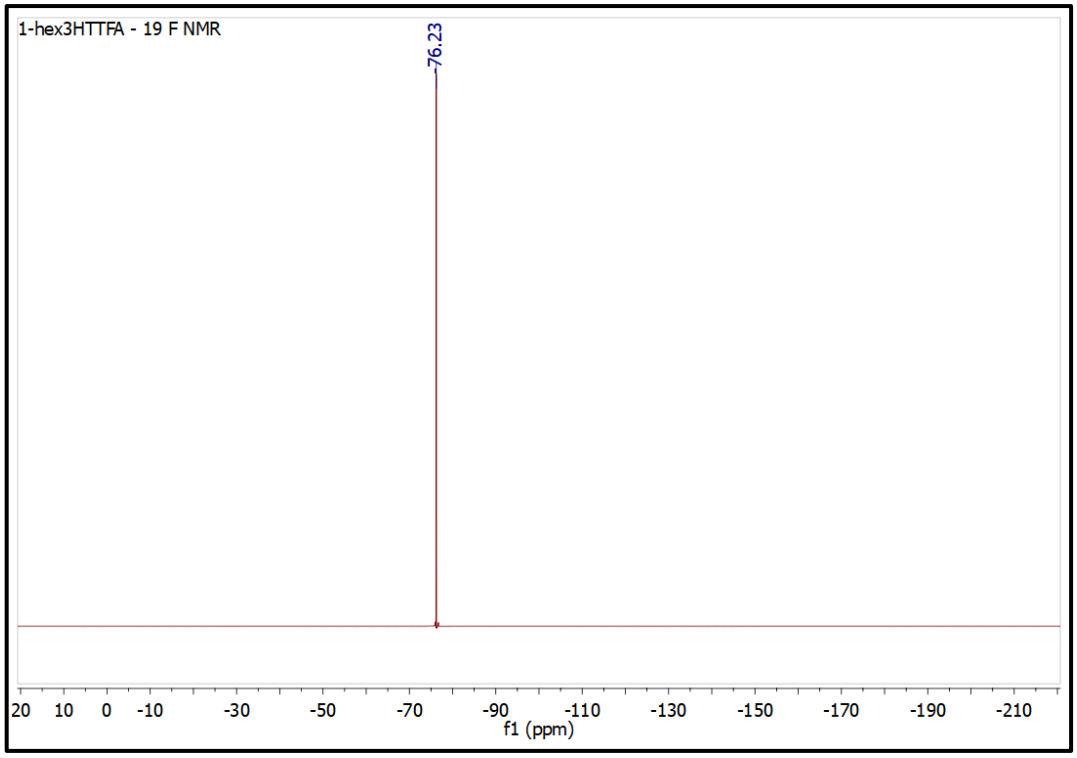


Fig. S9 1-hex3HTTFA-^{19}F NMR

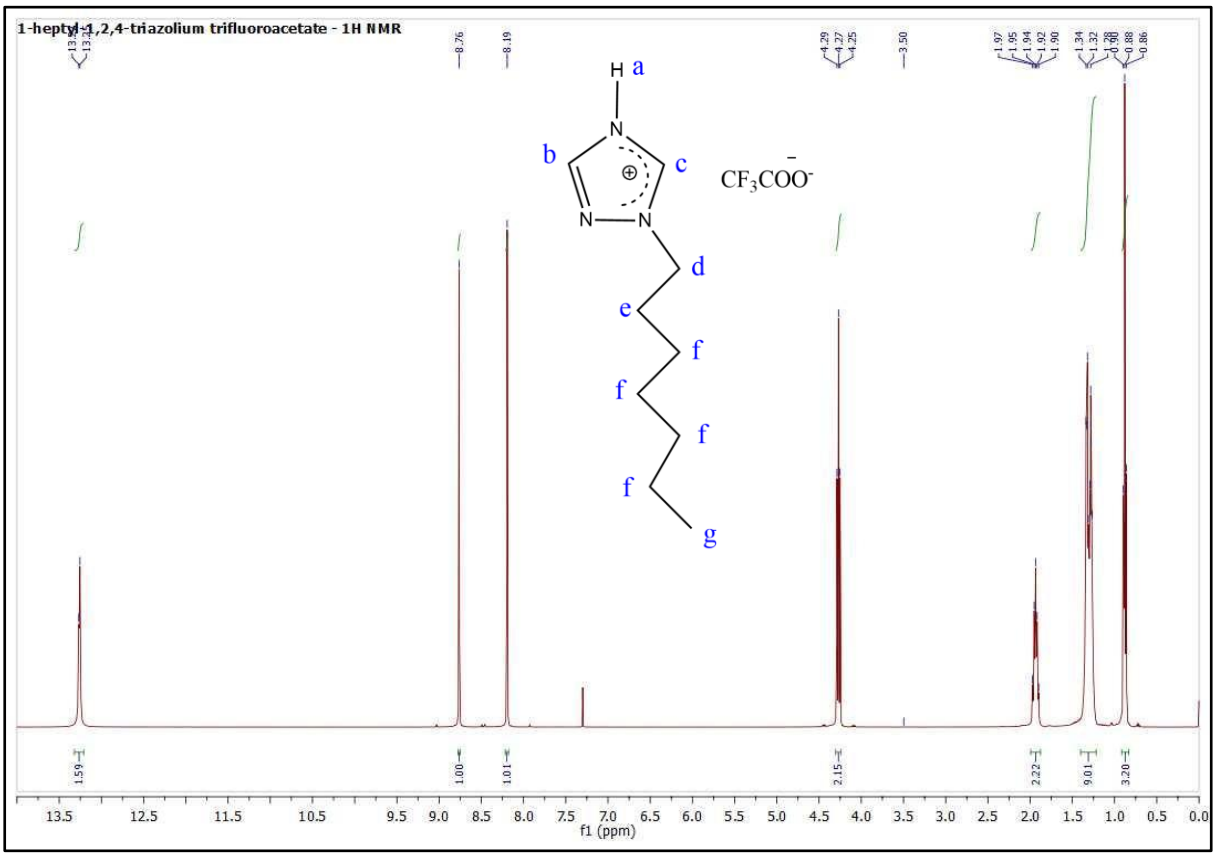


Fig. S10 1-hept3HTTFA-^{1}H NMR

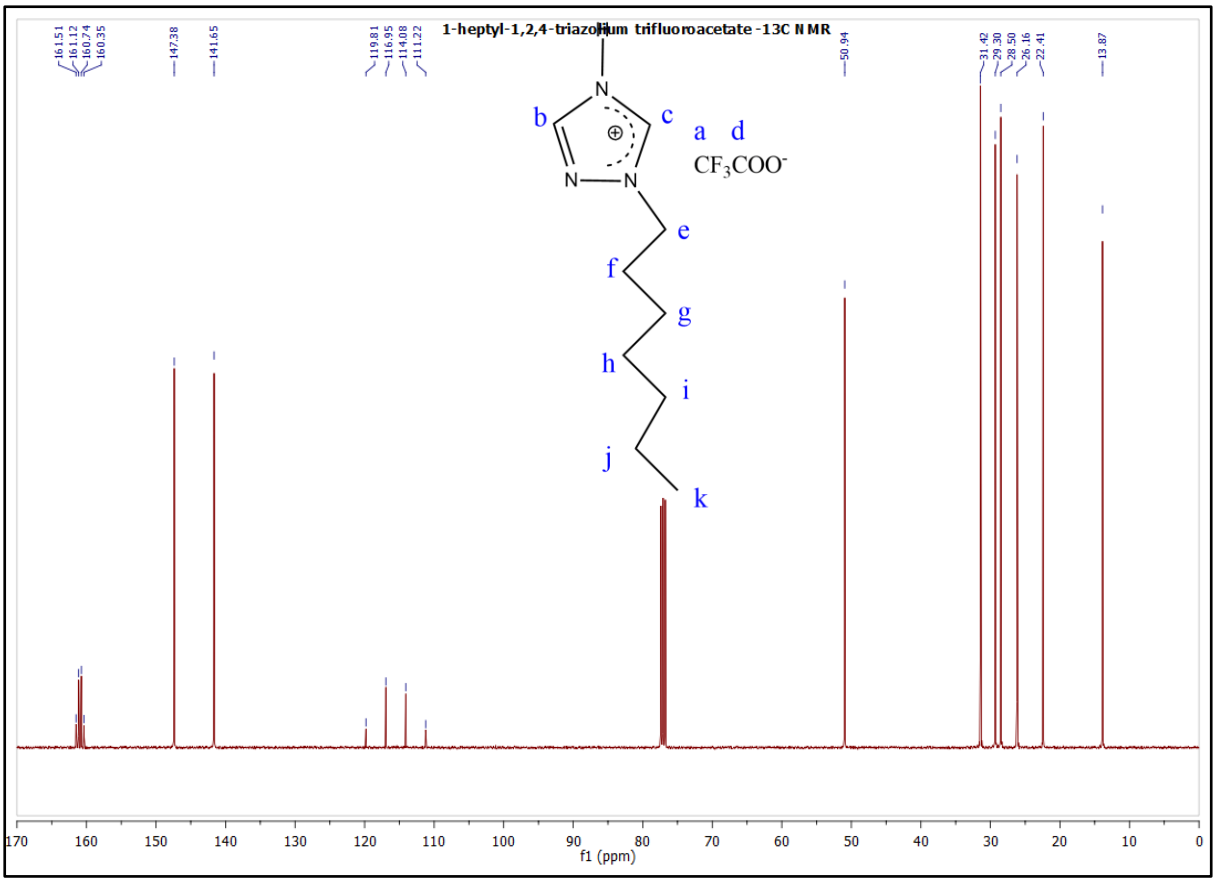


Fig. S11 1-hept3HTTFA-^{13}C NMR

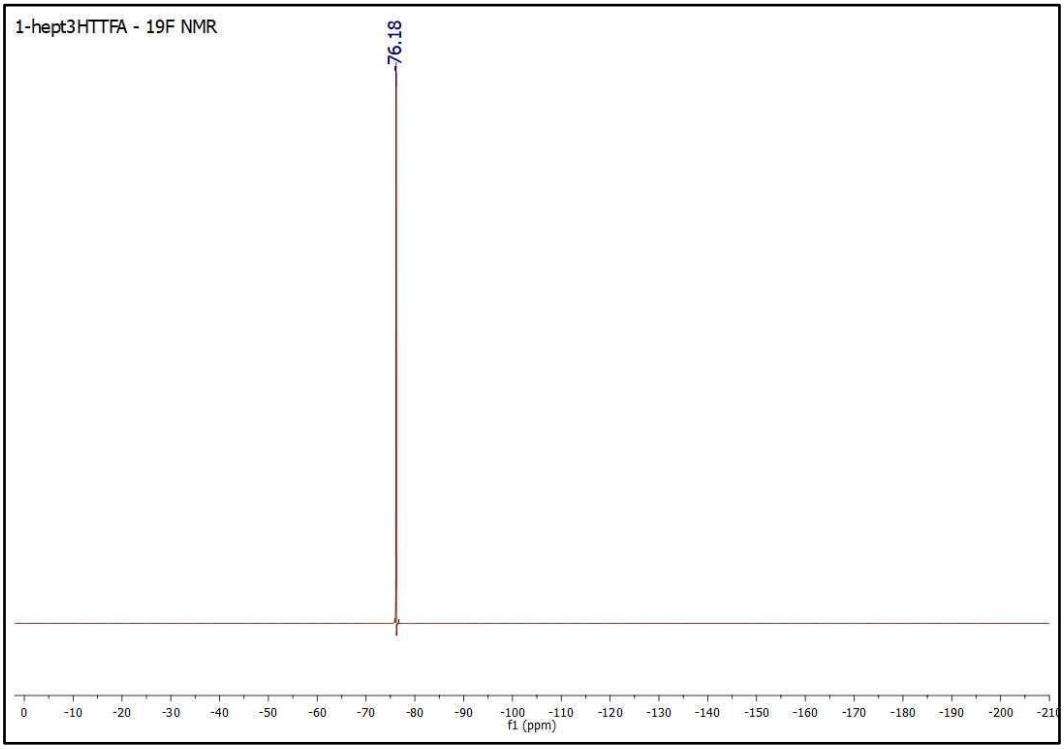


Fig. S12 1-hept3HTTFA-^{19}F NMR

Spectral data

1-butyl-1,2,4-triazolium trifluoroacetate (1-but3HTTFA)

Colourless liquid; (yield 98%). ^{1}H-NMR ($CDCl_3$, 400 MHz): 9.31 (s, 1H, 3CH), 8.46 (s, 1H, 5CH), 4.38 (t, 2H, *C*H_2-CH_2-CH_2-CH_3), 1.97 (m, 2H, CH_2-*C*H_2-CH_2-CH_3), 1.37 (m, 2H, CH_2-CH_2-*C*H_2-CH_3), 0.96 (t, 3H, CH_2-CH_2-CH_2-*C*H_3). ^{13}C NMR ($CDCl_3$, 100 MHz): 160.8 (*C*F_3COO^-), 145.6 (C-3), 141.31 (C-5), 115.61(CF_3*C*OO^-), 50.73 (*C*H_2-CH_2-CH_2-CH_3), 30.80 (CH_2-*C*H_2-CH_2-CH_3), 19.01 (CH_2-CH_2-*C*H_2-CH_3), 12.69 (CH_2-CH_2-CH_2-*C*H_3). ^{19}F NMR ($CDCl_3$, 400 MHz): -76.21 (C*F*$_3COO^-$).

1-pentyl-1,2,4-triazolium trifluoroacetate (1-pent3HTTFA)

Colourless liquid; (yield 98%). ^{1}H-NMR ($CDCl_3$, 400 MHz): 14 (s, 1H NH), 8.8 (s, 1H, 3CH), 8.2 (s, 1H, 5CH), 4.2 (t, 2H, C*H*$_2$-CH_2-CH_2-CH_2-CH_3), 1.9 (m, 2H, CH_2-C*H*$_2$-CH_2-CH_2-CH_3), 1.3 (m, 4H, CH_2-CH_2-C*H*$_2$-*CH*$_2$-CH_3), 0.96 (t, 3H, CH_2-CH_2-CH_2-CH_2-C*H*$_3$) .^{13}C NMR ($CDCl_3$, 100 MHz): 160.8 (*C*F_3COO^-), 147 (C-3), 141.6 (C-5), 115.5(CF_3*C*OO^-), 51 (*C*H_2-CH_2-CH_2- CH_2-CH_3), 28.9 (CH_2-*C*H_2-CH_2- CH_2-CH_3), 28.2 (CH_2-CH_2-*C*H_2-CH_2-CH_3), 21.9 (CH_2-CH_2-CH_2-*C*H_2-CH_3), 13.6 (CH_2-CH_2- CH_2-CH_2-*C*H_3). ^{19}F NMR ($CDCl_3$, 400 MHz): -76.35 (C*F*$_3COO^-$).

1-hexyl-1,2,4-triazolium trifluoroacetate (1-hex3HTTFA)

Colourless liquid; (yield 98%). ^{1}H-NMR ($CDCl_3$, 400 MHz): 12.6 (s, 1H NH), 8.9 (s, 1H, 3CH), 8.3 (s, 1H, 5CH), 4.3 (t, 2H, C*H*$_2$-CH_2-CH_2-CH_2-CH_2-CH_3), 1.9 (m, 2H, CH_2-C*H*$_2$-CH_2-CH_2-CH_2-CH_3), 1.3 (m, 6H, CH_2-CH_2-C*H*$_2$-C*H*$_2$-*CH*$_2$-CH_3), 0.9 (t, 3H, CH_2-CH_2-CH_2-CH_2-CH_2-C*H*$_3$) .^{13}C NMR ($CDCl_3$, 100 MHz): 160.8 (*C*F_3COO^-), 146.8 (C-3), 141.5 (C-5), 115.6 (CF_3*C*OO^-), 51.1 (*C*H_2-CH_2-CH_2-CH_2-CH_2-CH_3), 30.9 (CH_2-*C*H_2- CH_2-CH_2- CH_2-CH_3), 28.9 (CH_2-CH_2-*C*H_2-CH_2-CH_2-CH_3), 25.8 (CH_2-CH_2-CH_2-*C*H_2-CH_2-CH_3), 22.2 (CH_2-CH_2-CH_2-CH_2-*C*H_2-CH_3), 13.7 (CH_2-CH_2-CH_2-CH_2-CH_2-*C*H_3). ^{19}F NMR ($CDCl_3$, 400 MHz): -76.23 (C*F*$_3COO^-$).

1-heptyl-1,2,4-triazolium trifluoroacetate (1-hept3HTTFA)

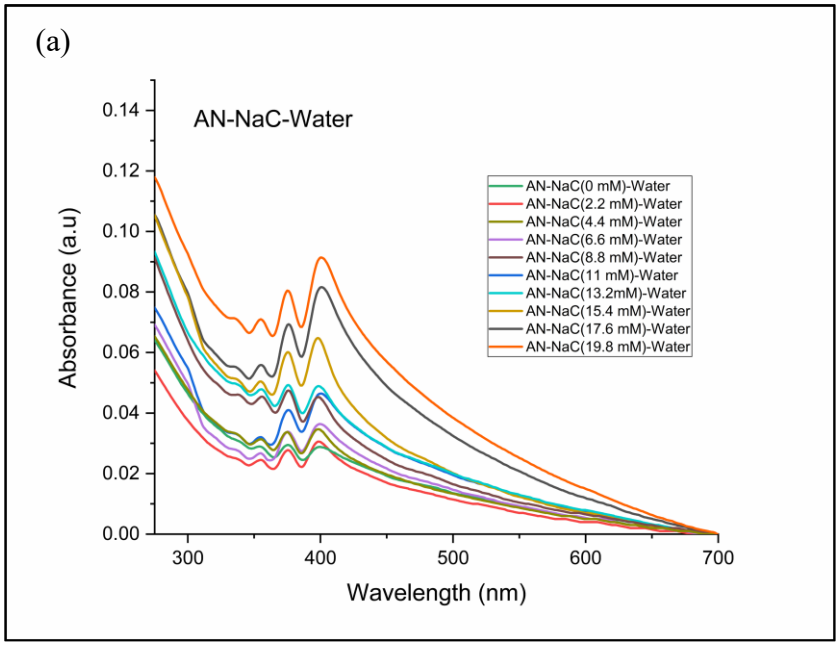
Slightly yellow liquid; (yield 97%). ^{1}H-NMR ($CDCl_3$, 400 MHz): 13.25 (s, 1H NH), 8.76 (s, 1H, 3CH), 8.19 (s, 1H, 5CH), 4.27 (t, 2H, C*H*$_2$-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3), 1.94 (m, 2H, CH_2-C*H*$_2$-CH_2-CH_2-CH_2-CH_2-CH_3), 1.32 (m, 8H, CH_2-CH_2-C*H*$_2$-C*H*$_2$-C*H*$_2$-*CH*$_2$-CH_3), 0.88 (t, 3H, CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-C*H*$_3$) .^{13}C NMR ($CDCl_3$, 100 MHz): 160.93 (*C*F_3COO^-),

147.38 (C-3), 141.65 (C-5), 115.51 (CF_3COO^-), 50.94 (CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3), 31.42 (CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3), 29.30 (CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3), 28.50 (CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3), 26.16 (CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3), 22.41 (CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3), 13.87 (CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3). ^{19}F NMR ($CDCl_3$, 400 MHz): -76.18 (CF_3COO^-).

Table S3. Specific ^{1}H, ^{13}C and ^{19}F NMR ppm values of 1-alkyl-1,2,4-triazolium RTILs

Sl. No	Compounds	NH (ppm)	3-CH (ppm)	5-CH (ppm)	3-C (ppm)	5-C (ppm)	[a]C (ppm)	[b]C (ppm)	F (ppm)
1	1-but3HTTFA		9.31	8.46	145.6	141.3	160.8	115.6	-76.21
2	1-pent3HTTFA	14	8.8	8.2	147.0	141.6	160.8	115.5	-76.35
3	1-hex3HTTFA	12.6	8.9	8.3	146.8	141.5	161	115.5	-76.23
4	1-hept3HTTFA	15.9	8.76	8.19	147.38	141.65	160.93	115.51	-76.18

Absorption Studies



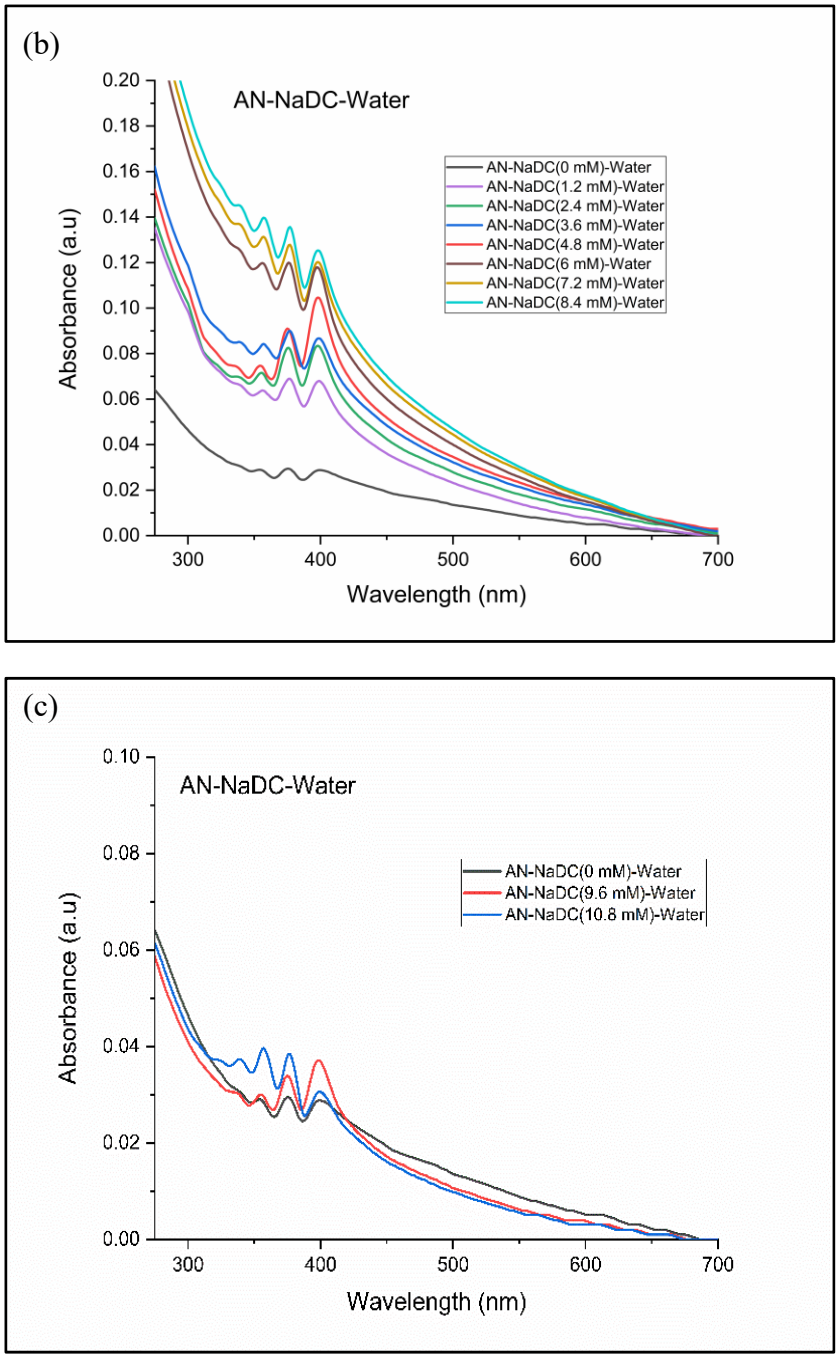


Fig. S13 Absorption spectra of AN in (a) NaC media (2.2 mM – 19.8 mM) (b) NaDC (1.2 mM – 8.4 mM) (c) higher concentration of NaDC media (9.6 mM – 10.8 mM)

Electrical Conductivities Studies

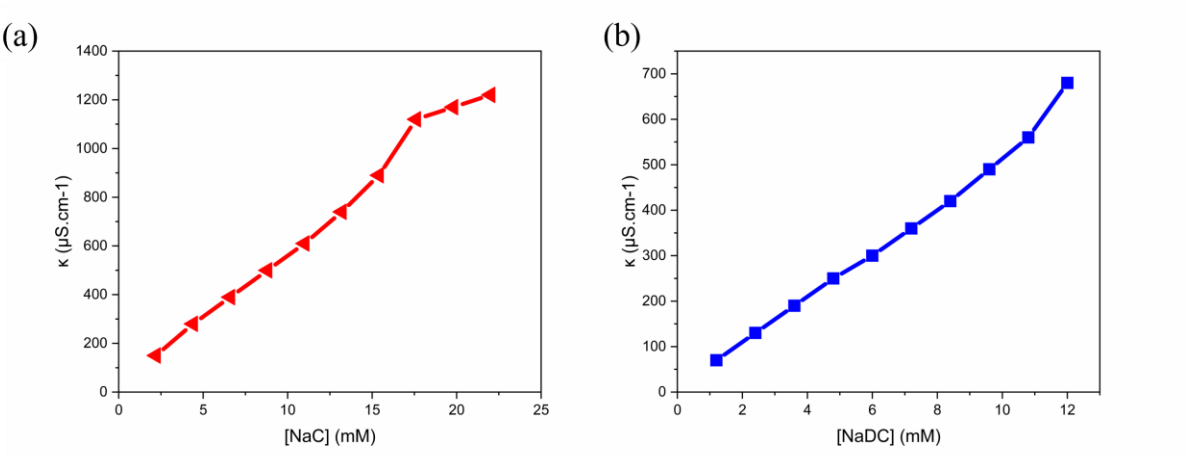


Fig S14. Representative plots of κ versus concentration of (a) NaC and (b) NaDC in pure water

Association of anthracene and RTILs – Fluorescence studies

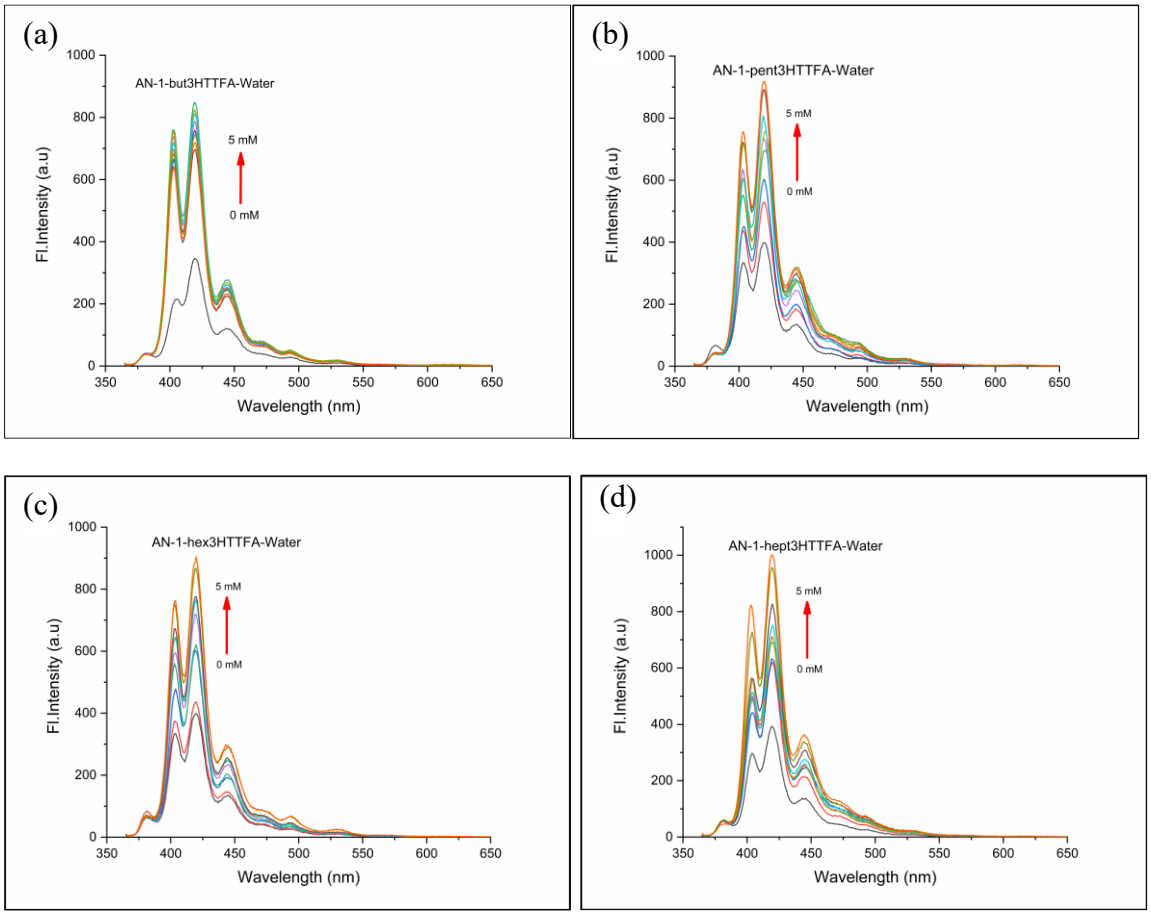


Fig. S15 Fluorescence emission spectra of AN in different concentrations of RTILs (λ_{ex} = 355 nm) (a) 1-but3HTTFA, (b) 1-pent3HTTFA, (c) 1-hex3HTTFA, (d) 1-hept3HTTFA

Effect of 1-but3HTTFA on bile salt dimers - Fluorescence Studies

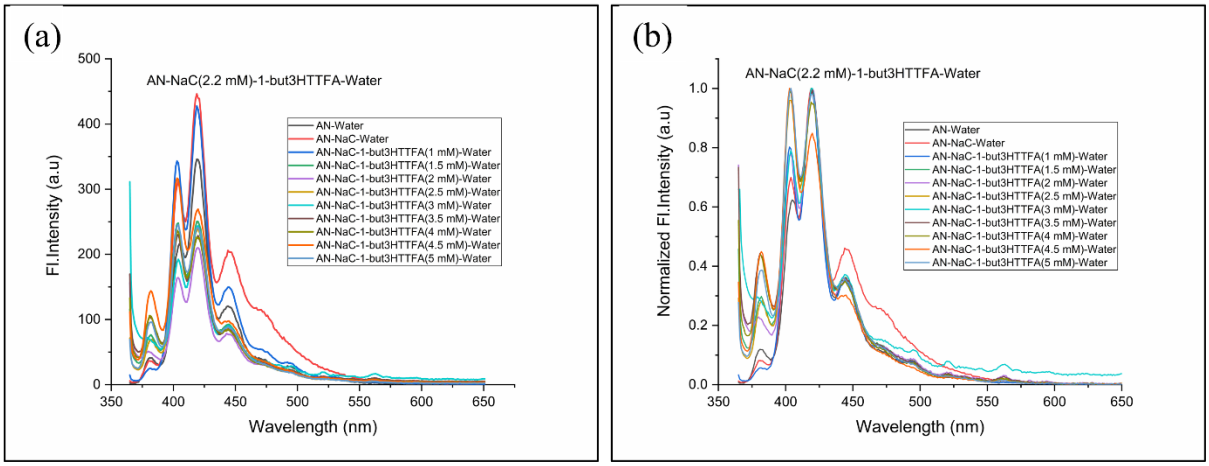


Fig. 16 (a) Fluorescence emission spectra (b) Normalized fluorescence spectra of AN in the presence of [NaC] = 2.2 mM with varying concentrations of 1-but3HTTFA (λ_{ex} = 355 nm)

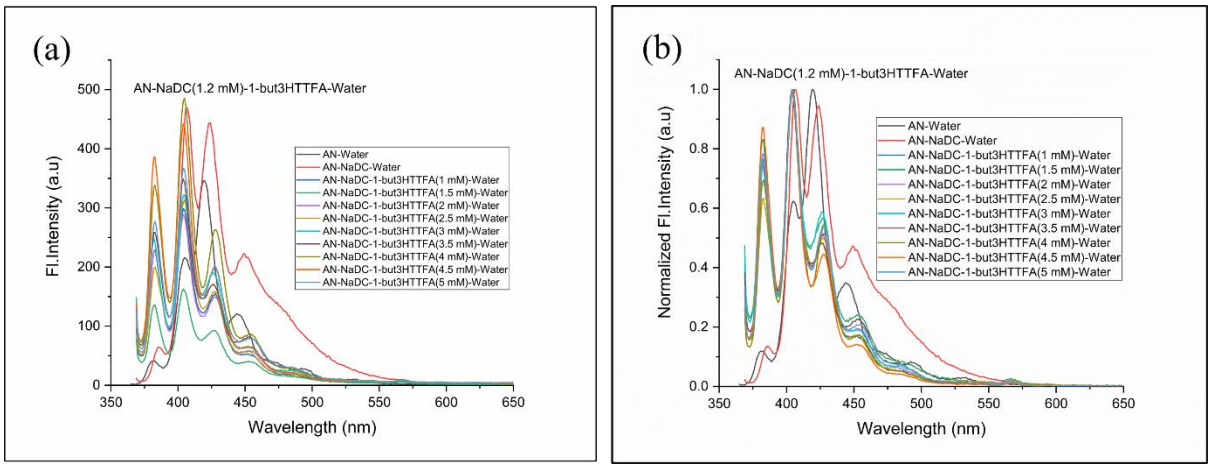


Fig. 17 (a) Fluorescence emission spectra (b) Normalized fluorescence spectra of AN in the presence of [NaDC] = 1.2 mM with varying concentration of 1-but3HTTFA (λ_{ex} = 359 nm)

Effect of ionic liquid on aggregation of bile salt micelles - Fluorescence Studies

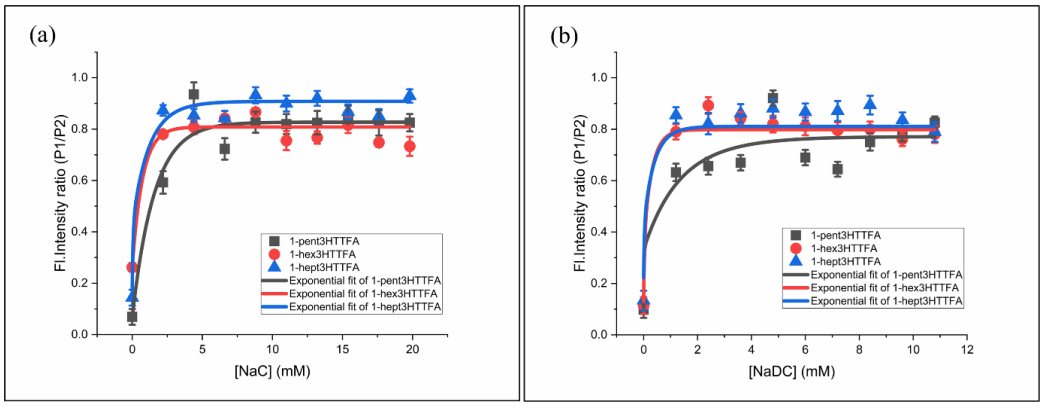


Fig. S18 Plot of variation of fluorescence intensity ratio (P1/P2) of AN different concentration of BSs and RTILs (5 mM) (a) NaC (2.2 mM – 19.8 mM), λ_{ex}= 355 nm (b) NaDC (1.2 mM – 10.8 mM), λ_{ex}= 359 nm

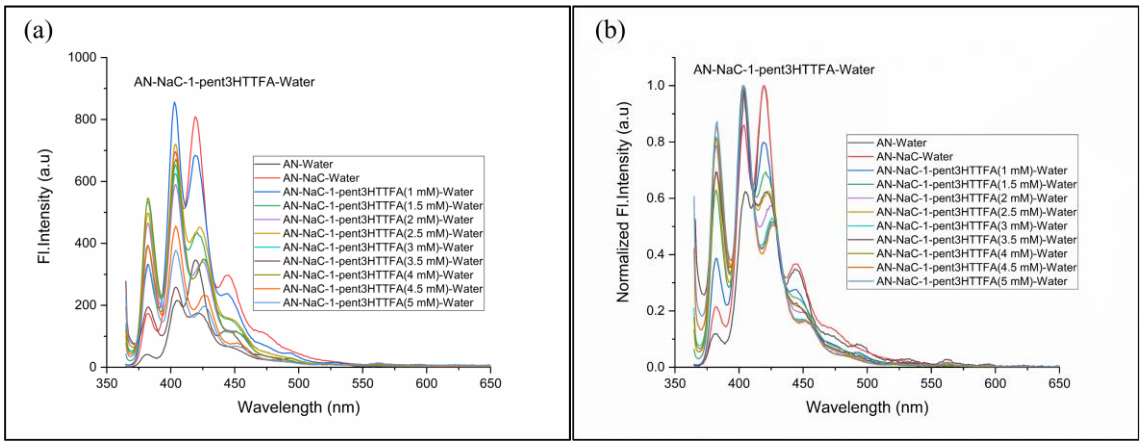


Fig. S19 Fluorescence emission and normalized fluorescence emission spectra of AN in the presence of [NaC] = 19.8 mM with varying concentrations of RTIL (1-5 mM), λ_{ex}= 355 nm (a) and (b) 1-pent3HTTFA

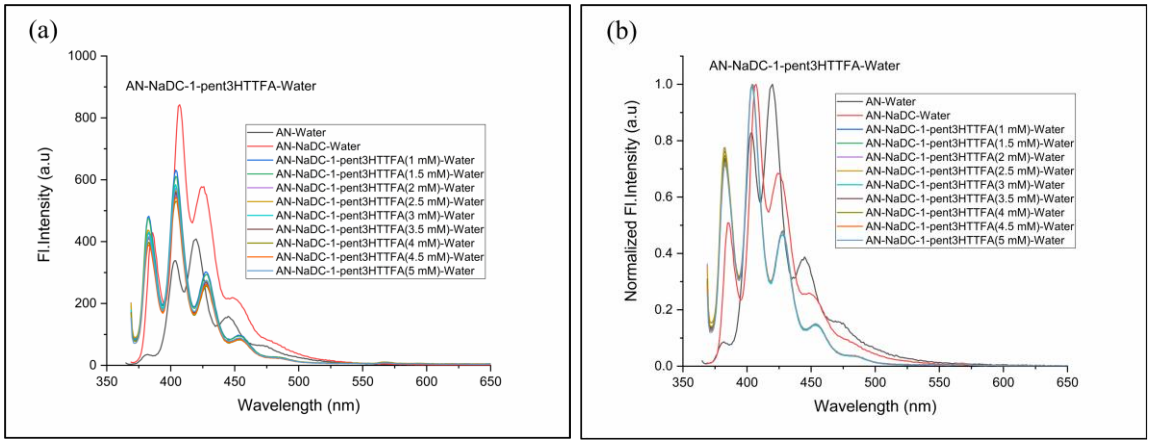


Fig. S20 Fluorescence emission and normalized fluorescence emission spectra of AN in the presence of [NaDC] = 10.8 mM with varying concentrations of RTIL (1-5 mM), λ_{ex}= 359 nm (a) and (b) 1-pent3HTTFA