Electronic Supplementary Material (ESI) for Chemical Communications.

Luminescent Micellar Nano-interfaces of Surface Active Ionic Liquid for Selective Recognition of ADP in Aqueous Medium

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Supporting Information

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Annexure S1.

Materials: Benzimidazole (>98) 1-bromobutane (>99), 1-chlorooctane, 1-chlorohexadecane, ATP (≥99), ADP (≥95), AMP (≥99), were obtained from Sigma and used without further purification. Diethyl ether, hexane, chloroform, ethyl acetate, dichloromethane, methanol, and acetone (AR Grade) has been purchased from SD fine chemicals Ltd, Mumbai, India. Millipore water having resistivity of 18Ω has been used for performing all the measurements. Procedure followed for the synthesis of SAILs and their characterization using the NMR and Mass spectrophotometer is given in annexure S2.

Methods: Surface tension measurements were performed using Data Physics DCAT II automated tensiometer employing the Wilhelmy plate method at 298.15 K. The temperature of experiment was controlled to an accuracy of ±0.1 K using the water circulating thermostat. The measurements were made in triplicate fashion and values of interfacial tension were found to be within the accuracy of ±0.1 mNm^{-1}. Systronics 308 conductivity meter having a unit cell constant was employed for measuring the specific conductance of the ionic liquid aqueous solutions at 298.15 K and temperature of each measurement was controlled using a thermostat within ±0.1 K. Uncertainty of less than 3 % was found in the triplica of measurements. Fluorescence studies were carried out at 298.15 K using Perkin Elmer LS-55 spectrophotometer in the range 295 to 550 nm by exciting the sample at a wavelength of 280 nm. Spectra were collected by sequential additions of stock solution of analyte to the fixed volume of 1.5 times cmc solutions (9 mmol L^{-1}) of SAILs at pH 7.0 in quartz cuvette of path length 1.0 cm using excitation and emission slit width of 2.5 nm. Julabo water thermostat assembly was used to control the temperature within ± 0.1 K. Dynamic light scattering (DLS) measurements were performed on Malvern's Zetasizer Nano ZS instrument equipped with a built-in temperature controller having an accuracy of ±0.1 K. Samples were analyzed in backscattering mode at a scattering angle of 173◦ in a quartz cuvette of 1 cm path length at 298.15 K. All the Samples were filtered before doing the measurements using Acrodisc syringe filters (0.45μm) to avoid interference from dust particles. Standard algorithms were used to analyze the data which is reported with an uncertainty of less than 8%. JEOL's JEM-2100 electron microscope was employed for carrying out transmission electron microscopic (TEM) measurements at a working voltage of 200 kV. On a carbon coated copper grid (300 mesh), a small drop of freshly prepared micellar solution of SAILs was placed and the residual solution was blotted off. The samples

were dried in air at room temperature for 24 hours before measurements. For carrying out cryogenic transmission electron microscopic (cryo-TEM) measurements, a drop of the aqueous solution of respective SAILs was put on a lacey TEM grid. Excess solution was blotted off. The specimens were vitrified by rapidly immerging them into liquid ethane and cooled to approximately 90 K by liquid nitrogen in a temperature controlled freezing unit (Zeiss Cryobox, Zeiss NTS GmbH, Oberkochen, Germany). During all of the sample preparation steps the temperature was monitored and kept constant in the chamber. After that, the specimen was inserted into a cryo-transfer holder (CT3500, Gatan, Mu¨nchen, Germany) and transferred to a Zeiss EM922 EF-TEM instrument. The sample was examined at temperatures around 90 K. The transmission electron microscope was operated at an acceleration voltage of 200 kV. ^{1}H, ^{13}C and ^{13}C/DEPT NMR experiments were performed in $CDCl_3$ and 10% D_2O− 90% H_2O solvents on Bruker Ascend 500 spectrometer (AVANCE III HD console) with water suppression using a 5 mm BBO (broad-band observe) double-channel probe equipped with z-gradients. Themrogravimetric analysis (TGA) for investigating the thermal stability of SAILs was performed on TGA/SDT A851 Mettler Toledo thermogravimeter analyzer under N_2 atmosphere at a heating rate of 5 $^{o}C\ min^{-1}$ in the temperature range of 25 to 600 ^{o}C. METTLER TOLEDO Differential scanning calorimeter DSC 3 instrument was employed for carrying out differential scanning calorimetry measurements which having a robust and versatile DSC sensor with 56 thermocouples. Melting point of the investigated SAILs were analyzed by scanning the samples in the temperature range of 20-120 ^{o}C at the heating rate of 2 $^{o}C\ min^{-1}$ under N_2 environment.

All the computational calculations were performed by using Jaguar program as implemented in Schrodinger suite of Programs[1]. Geometry calculations of all the stationery points were performed using Becke's three-parameter functional[2] combined with Lee, Yang, and Parr's correlation functional[3], B3LYP-D3 density functional theory with 6-31+G(d,p) basis set including the Grimme dispersion correction and solvent effects. The solvents effects were performed using Poisson-Boltzmann implicit continuum solvation model (PBF) with probe radius 1.4 and dielectric constant 80.37. Vibrational frequency calculations were also performed on the optimized geometries to confirm that the computed geometries are true equilibrium geometries. All the single point energy calculations on the optimized geometries were performed at B3LYP-D3/6-311++G(d,p) basis set including the solvents effects. The electronic properties of the optimized geometries were computed assuming that the molecules are isolated structures.

To gain clear insights and shed some light into the nature of electronic excitations time dependent density functional (TDDFT) calculations were performed for the lowest six transitions.

The electron density of the complexes have been analyzed using NCI index[4], according to which whenever a non-covalent interaction is present, there is an abrupt change in 2D plot of reduced density gradient, *s*, and the electron density, ρ in the shape of peaks. It allows to visualize and quantify the hydrogen bonding, van der Waal (vdW) interactions and repulsive forces. The hydrogen bonding and ionic interactions appear in negative sign, the vdW interactions around zero and the repulsive regions appear far toward positive regions. This NCI scheme is based on $s(\rho)$ function and is given as follows

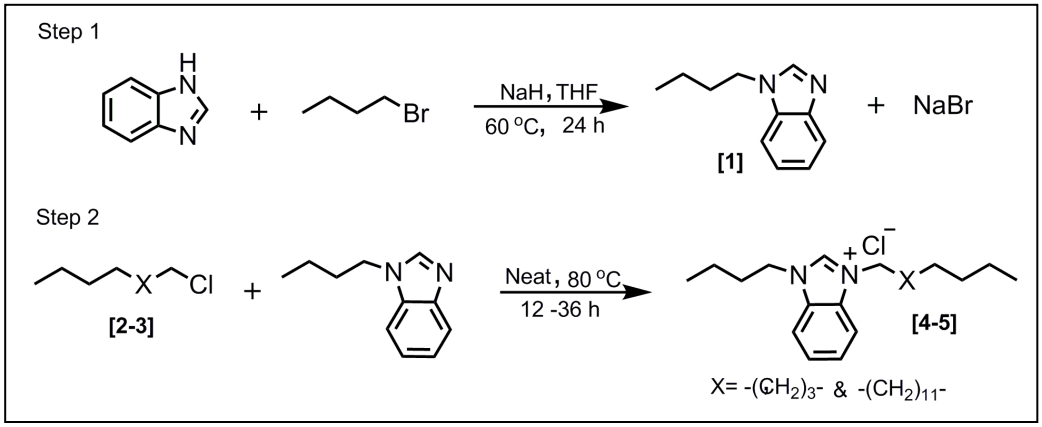
$$s(r) = \frac{1}{2(3\pi^2)^{1/3}} \frac{|\Delta\rho(r)|}{\rho(r)^{4/3}}$$

The visualization of these intermolecular bifurcation points have been shown in Figure 1.

Annexure S2.

Synthesis and characterization of the [C_4C_8bzm][Cl] and [C_4C_{16}bzm][Cl] SAILs.

The intermediate N-butylbenzimidazole and the SAILS under investigation were prepared by procedure mentioned in our previous report[5]. So the synthetic route for the synthesis of SAILs has been discussed in brief over here. The intermediate n-butylbenzimidazole (**1**; 10 mmol, 1.74 g) prepared in step 1 was allowed to react with the 1-chlorooctane (**2**, 10 mmol, 1.48g), 1-chlorohexadecane (**3**, 10 mmol, 2.66 g), at 80°C for 12-36 hours. The progress of the reaction was monitored as the disappearance of the spot corresponding to n-butylbenzimidazole on the TLC plate in 30% ethyl acetate/hexane solvent mixture.



The resulting reaction mixture was cooled to 25 °C and washed three times each with 50 mL of diethyl ether and hexane. The product obtained was cold precipitated in ethyl acetate and acetone and dried under vacuum using rotary evaporator to get pure benzimidazolium based ionic liquid surfactants (SAILSs) (**4-5**). The percentage yield of the synthesized SAILs was found to be 86.9% ([C_4C_8bzm][Cl], **4**, 2.8 g) and 89.6% ([C_4C_{16}bzm][Cl], **5**, 3.9 g). The molecular structures and purity of synthesized SAILs were confirmed by ^{1}H, ^{13}C/DEPT NMR and mass spectroscopy. Further the purity of synthesized SAILs was confirmed using Gas chromatography mass spectrometry. Thermal stability and the melting point of SAILs have been investigated using the thermogravimetric analysis (TGA) and differential scanning calorimetry. ^{1}H , ^{13}C/DEPT NMR spectra were recorded on Brüker Ascend 500 spectrometer (AVANCE III HD console) in $CDCl_3$ as solvent. Waters Q-ToF micromass equipment having ESI as the ion source was used to record high resolution mass spectra of SAILs.

^{1}H NMR and mass spectroscopy data for synthesized ILSs:

[C_4C_8bzm][Cl]: ^{1}H NMR (500 MHz, $CDCl_3$, δ-ppm) 0.859 (t, 3H, dodecyl terminal-C*H*$_3$), 0.994 (t, 3H, N−CH_2−CH_2−CH_2−C*H*$_3$), 1.243 (br s, 14H, (-C*H*$_2$-)$_7$), 1.347 (br m, 2H, N^+−CH_2−CH_2−CH_2−C*H*$_2$−), 1.429 (br m, 2H,−N^+−CH_2−CH_2−C*H*$_2$−CH_2−), 1.455 (m, 2H,−N−CH_2−CH_2−C*H*$_2$−CH_3), 2.041 (m, 2H,−N−CH_2−C*H*$_2$−CH_2−CH_3), 2.065 (m, 2H,−N^+−CH_2−C*H*$_2$−CH_2−CH_2−), 4.639 (m, 2H,−N−C*H*$_2$−CH_2−CH_2−CH_3), 4.655 (m, 2H,−N^+−C*H*$_2$−CH_2−CH_2−CH_2−), 7.649 (m, 1H, −N−C=C*H*−CH=CH−CH=C−N^+−), 7.667 (m, 1H, −N−C=CH−C*H*=CH−CH=C−N^+−), 7.702 (m, 1H, −N−C=CH−CH=C*H*−CH=C−N^+−), 7.722 (m, 1H, −N−C=CH−CH=CH−C*H*=C−N^+−), 11.638 (s, 1H, −N−C*H*−N^+−).

^{13}C NMR ($CDCl_3$) δ ppm: 13.53 (-N−CH_2−CH_2−CH_2−*C*H_3), 14.04 (−CH_2−CH2−CH_2−*C*H_3), 19.85 (-N−CH_2−CH_2−*C*H_2−CH_3), 22.56 (−CH_2−*C*H2−*C*H_2−CH_3), 26.56 (-N^+−CH_2−CH_2−*C*H_2−CH_2−), 29.00−29.57 (chain (-*C*H_2-)$_3$), 31.42 (−CH_2−*C*H2−CH_2−CH_3), 31.66 (-N−CH_2−*C*H_2−CH_2−CH_3), 47.46 (-N−*C*H_2−CH_2−CH_2−*C*H_3), 47.72 (-N^+−*C*H_2−CH_2−CH_2−), 113.09 (-N−C=*C*H−CH=CH−*C*H=C−N^+−), 126.97 (-N−C=CH−*C*H=*C*H−CH=C−N^+−), 131.38 (-N−*C*=CH−CH=CH−CH=*C*−N^+−), 143.64 (−N−*C*H−N^+−).

^{13}C/DEPT NMR ($CDCl_3$) δ ppm: 13.53 (+ve,−N−CH_2−CH_2−CH_2−*C*H_3), 14.04 (+ve,−CH2−CH_2−*C*H_3), 19.85 (-ve, −N−CH_2−CH_2−*C*H_2−CH_3), 22.56 (-ve, −CH2−*C*H_2−CH_3), 26.56 (-ve, −N^+−CH_2−CH_2−*C*H_2−CH_2−), 29.00−29.57 (-ve, chain (-C*H*$_2$-)$_3$), 31.42 (-ve, −*C*H2−CH_2−CH_3), 31.66 (-ve,−N−CH_2−*C*H_2−CH_2−CH_3), 47.46 (-ve, -N−*C*H_2−CH_2−CH_2−CH_3), 47.72 (–ve, –N^+−*C*H_2−CH_2−CH_2−CH_3), 113.05 (+ve,−N−C=*C*H−CH=CH−*C*H=C−N^+−), 126.97 (+ve, −N−C=CH−*C*H=*C*H−CH=C−N^+−), 143.64 (+ve, −N−*C*H−N^+−). ESI-HRMS positive ions m/z (for $C_{19}H_{31}N_2^+$): 287.2441, 288.2485.

[C_4C_{16}bzm][Cl]: ^{1}H NMR (500 MHz, $CDCl_3$, δ-ppm) 0.877 (t, 3H, dodecyl terminal-C*H*$_3$), 0.996 (t, 3H, N−CH_2−CH_2−CH_2−C*H*$_3$), 1.235 (br s, 14H, (-C*H*$_2$-)$_7$), 1.346 (br m, 2H, N^+−CH_2−CH_2−CH_2−C*H*$_2$−), 1.419 (br m, 2H,−N^+−CH_2−CH_2−C*H*$_2$−CH_2−), 1.459 (m, 2H,−N−CH_2−CH_2−C*H*$_2$−CH_3), 2.035 (m, 2H,−N−CH_2−C*H*$_2$−CH_2−CH_3), 2.055 (m, 2H,−N^+−CH_2−C*H*$_2$−CH_2−CH_2−), 4.636 (m, 2H,−N−C*H*$_2$−CH_2−CH_2−CH_3), 4.656 (m, 2H,−N^+−C*H*$_2$−CH_2−CH_2−CH_2−), 7.646 (m, 1H, −N−C=C*H*−CH=CH−CH=C−N^+−), 7.665 (m, 1H, −N−C=CH−C*H*=CH−CH=C−N^+−), 7.697(m, 1H, −N−C=CH−CH=C*H*−CH=C−N^+−), 7.713 (m, 1H, −N−C=CH−CH=CH−C*H*=C−N^+−), 11.667 (s, 1H, −N−C*H*−N^+−).

^{13}C NMR ($CDCl_3$) δ ppm: 13.53 (-N−CH_2−CH_2−CH_2−*C*H_3), 14.12 (−CH2−CH_2−*C*H_3), 19.85 (−N−CH_2−CH_2−*C*H_2−CH_3), 22.69 (−CH2−*C*H_2−CH_3), 26.57 (−N^+−CH_2−CH_2−*C*H_2−CH_2−), 29.06−29.69 (chain (−C*H*$_2$−)$_{11}$), 31.42 (−*C*H2−CH_2−CH_3), 31.92 (-N−CH_2−*C*H_2−CH_2−CH_3), 47.45 (-N−*C*H_2−CH_2−CH_2−*C*H_3), 47.72 (−N^+−*C*H_2−CH_2−CH_2−), 113.07 (−N−C=*C*H−CH=CH−*C*H=C−N^+−), 126.96 (−N−C=CH−*C*H=*C*H−CH=C−N^+−), 131.38 (−N−*C*=CH−CH=CH−CH=*C*−N^+−), 143.67 (−N−*C*H−N^+−).

^{13}C/DEPT NMR ($CDCl_3$) δ ppm: 13.53 (+ve,−N−CH_2−CH_2−CH_2−*C*H_3), 14.12 (+ve,−CH2−CH_2−*C*H_3), 19.85 (-ve, −N−CH_2−CH_2−*C*H_2−CH_3), 22.69 (-ve, −CH2−*C*H_2−CH_3), 26.57 (-ve, −N^+−CH_2−CH_2−*C*H_2−CH_2−), 29.06−29.69 (-ve, chain (−C*H*$_2$−)$_{11}$), 31.42 (-ve, −*C*H2−CH_2−CH_3), 31.92 (-ve,−N−CH_2−*C*H_2−CH_2−CH_3), 47.45 (-ve, -N−*C*H_2−CH_2−CH_2−CH_3), 47.72 (–ve, –N^+−*C*H_2−CH_2−CH_2−), 113.07 (+ve,−N−C=*C*H−CH=CH−*C*H=C−N^+−), 126.96 (+ve, −N−C=CH−*C*H=*C*H−CH=C−N^+−), 143.73 (+ve, −N−*C*H−N^+−). ESI-HRMS positive ions m/z (for $C_{23}H_{39}N_2^+$): 399.7677, 400. 7567. 401.7636

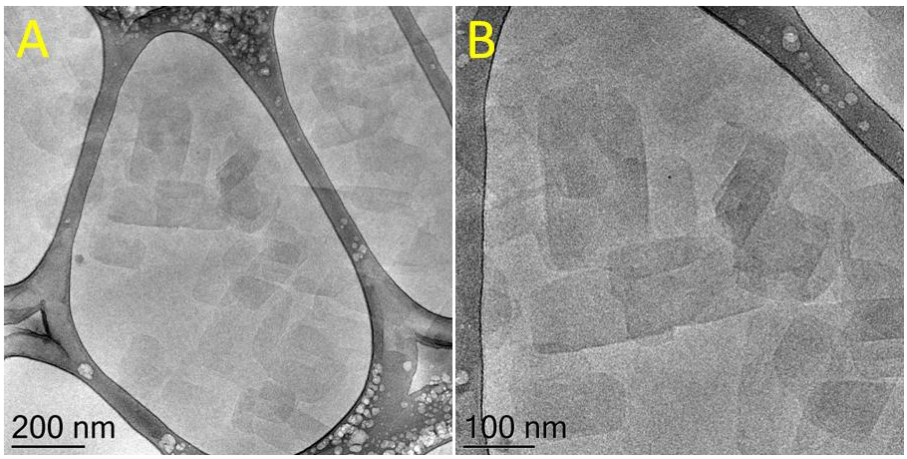


Fig. S1 (A-B): Thin nano sheets formed in the aqueous solutions of [C_4C_{16}bzm][Cl] at concentration above cac.

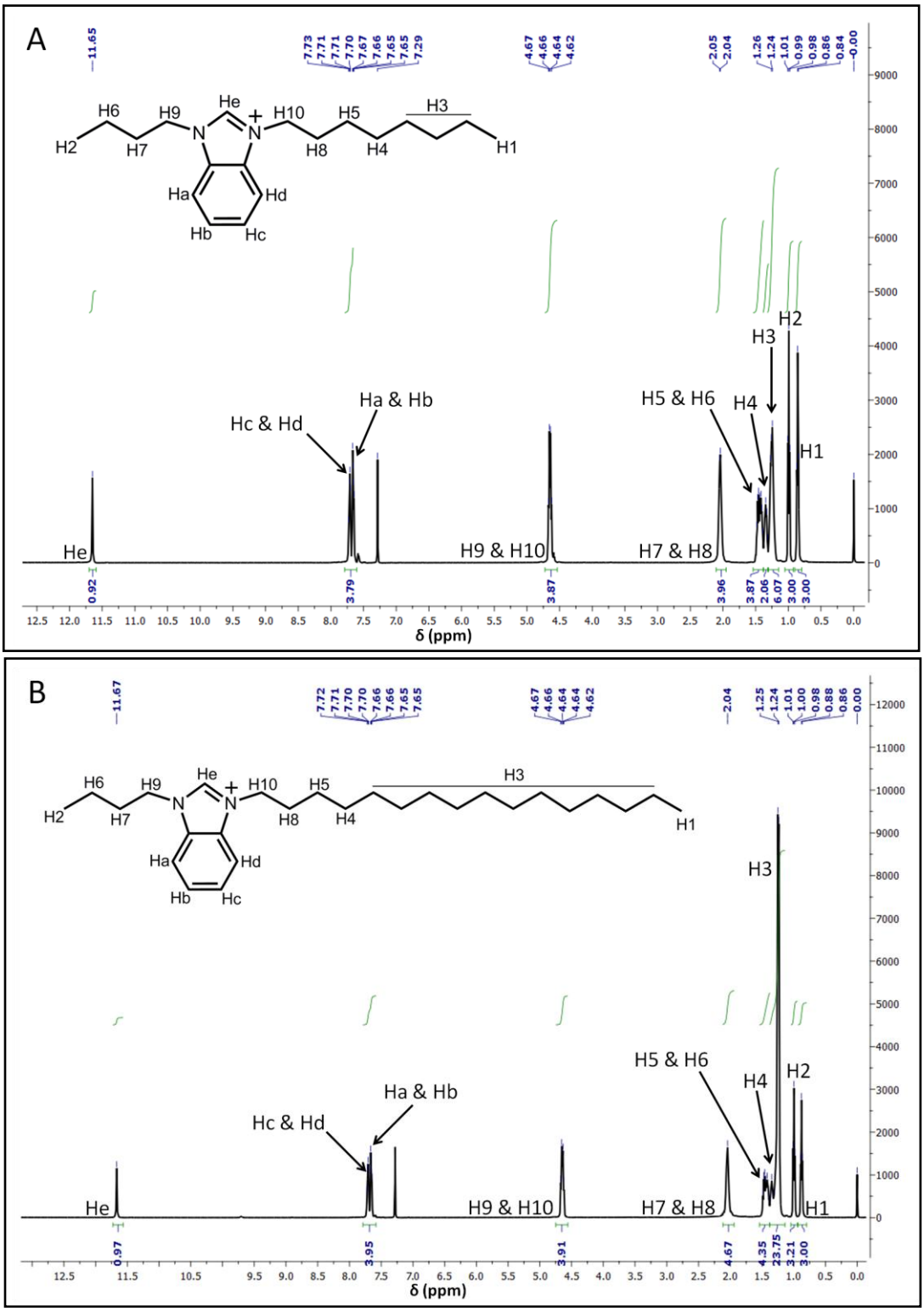


Fig. S2(A-B): Labelled ^{1}H NMR spectra of the two SAILs (A) [C_4C_8bzm][Cl] and (B) [C_4C_{16}bzm][Cl] along with their molecular structures.

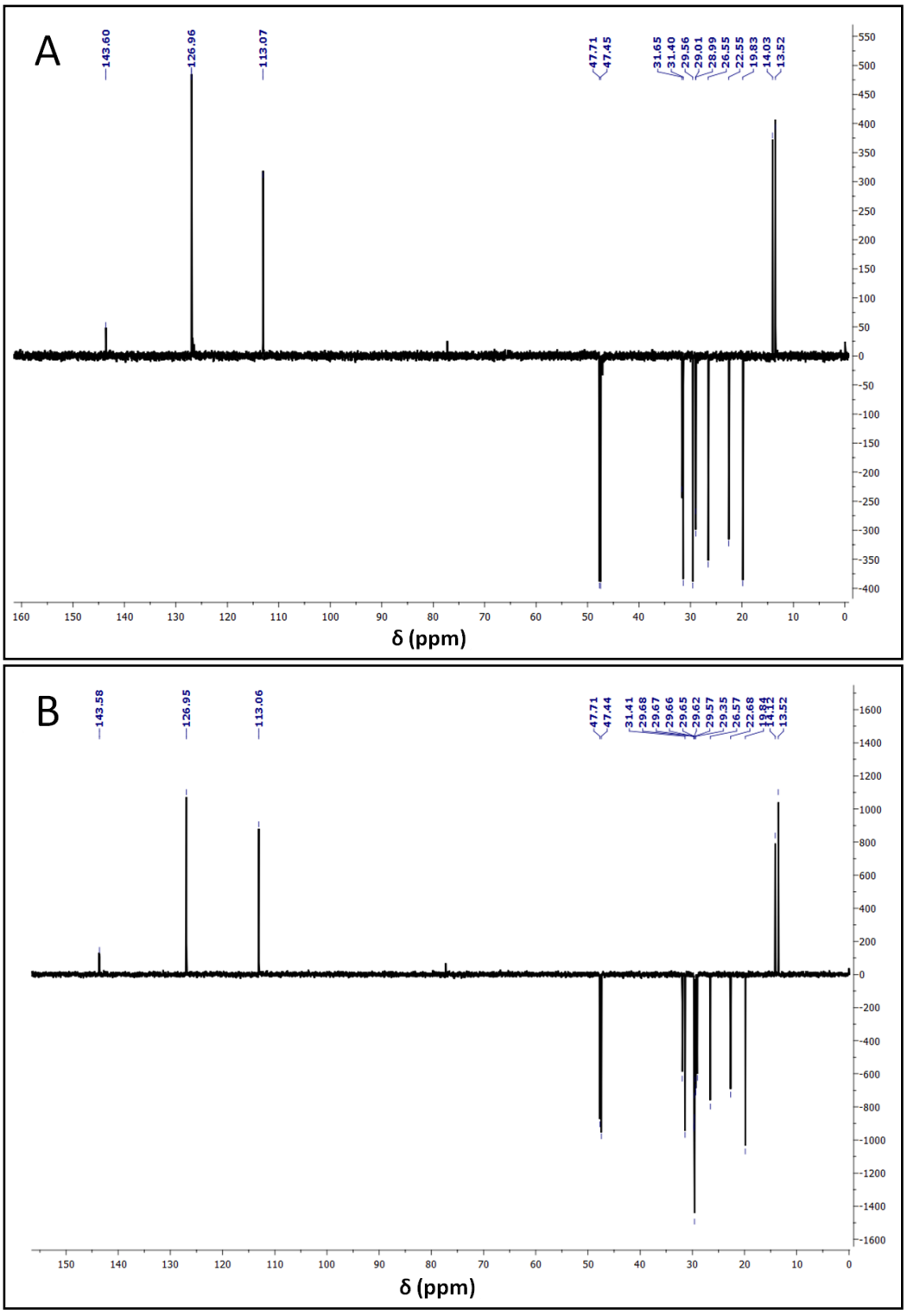


Fig. S3 (A-B): ^{13}C/DEPT NMR spectra of the two SAILs (A) [C_4C_8bzm][Cl] and (B) [C_4C_{16}bzm][Cl].

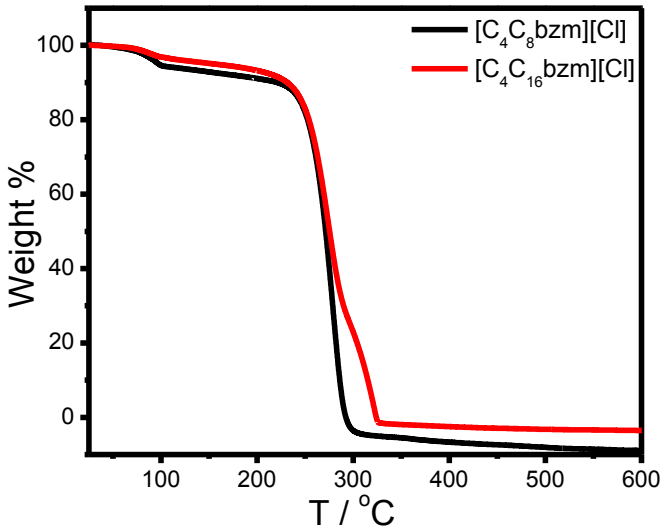


Fig. S4: Thermogravimetric analysis curves for the SAILs under investigation.

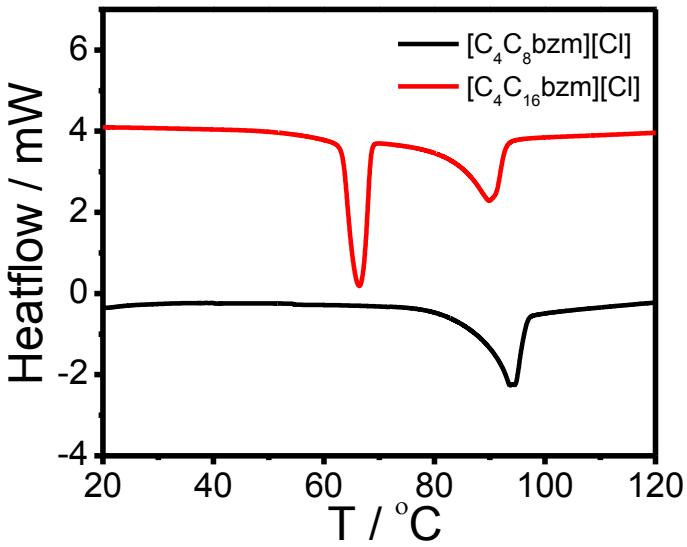


Fig. S5: Differential Scanning Calorimetry profiles of the SAILs under investigation.

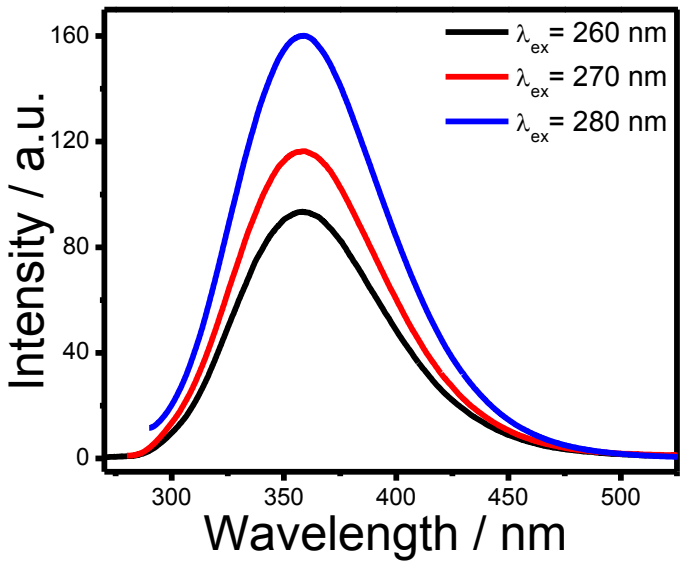


Fig. S6: Emission Spectra of aqueous solutions of $[C_4C_8bzm][Cl]$ at different excitation wavelengths.

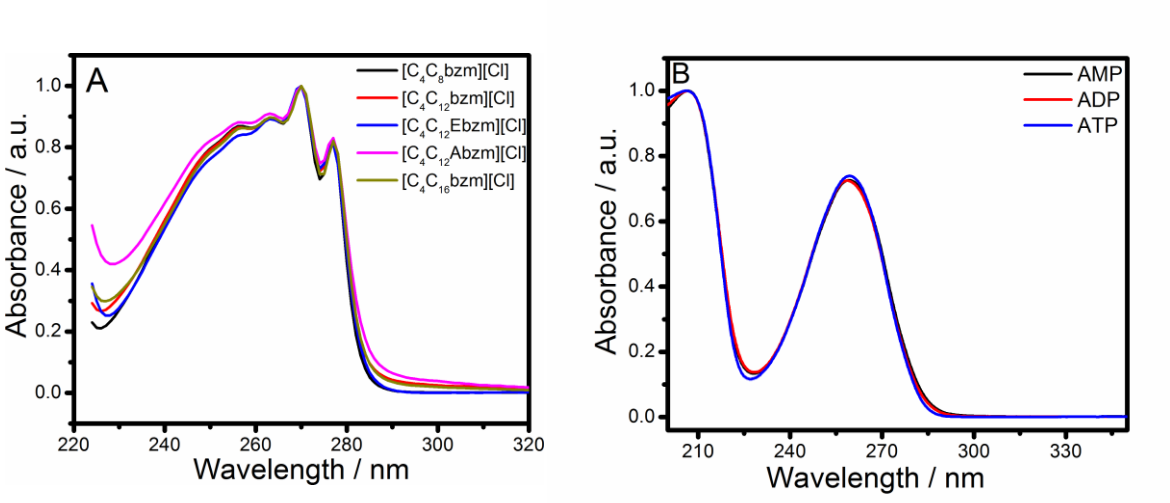


Fig. S7 (A-B): Absorption spectra of the aqueous solutions of (A) SAILs and (B) nucleotides under investigation at 298.15 K

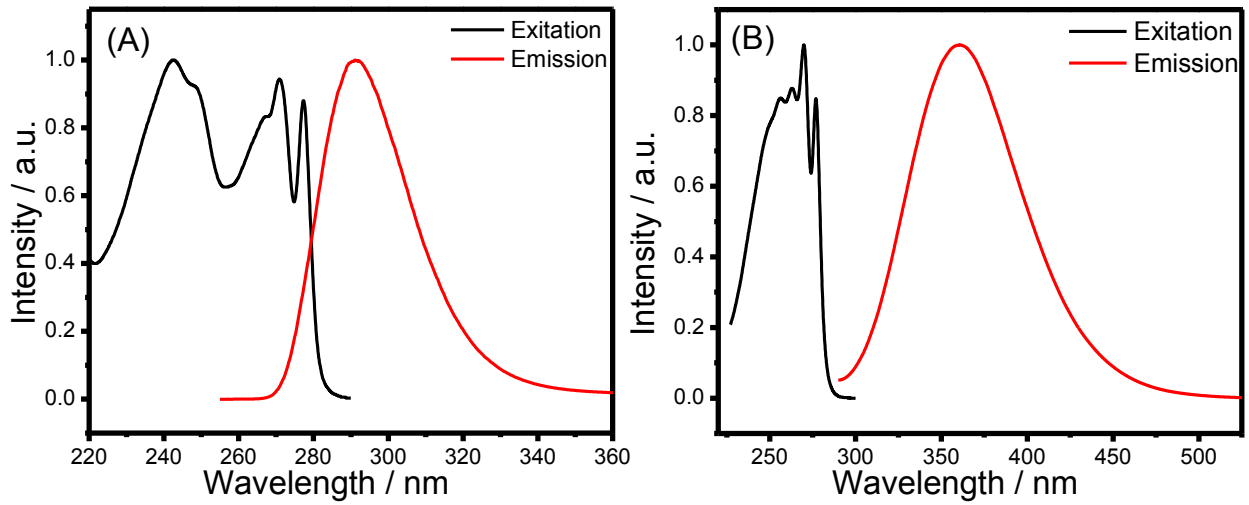


Fig. S8 (A-B): Excitation and emission spectra of the aqueous solutions of (A) benzimidazole and (B) $[C_4C_8bzm][Cl]$ at 298.15 K

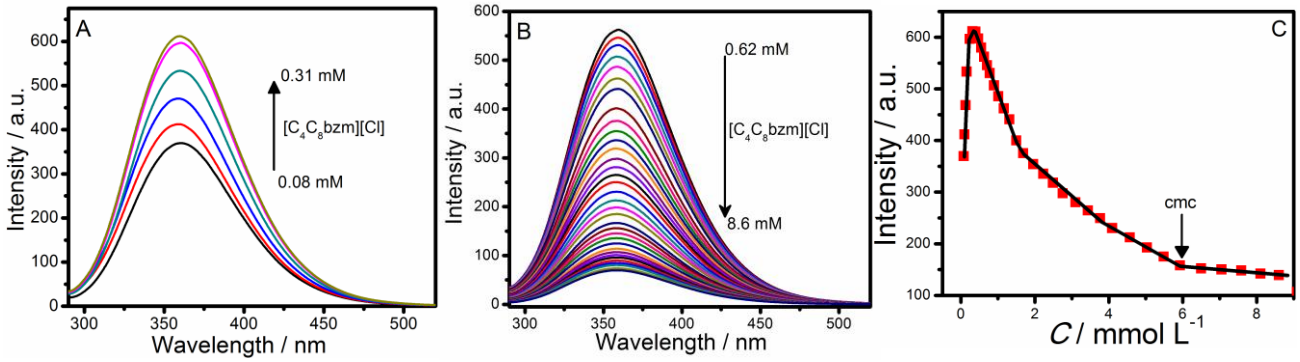


Fig. S9 (A-C): (A) Initial enhancement of fluorescence intensity in aqueous solution with increase in concentration; (B) Quenching of the fluorescence intensity in aqueous solutions with further increase in concentration and (C) variation in the fluorescence intensity of $[C_4C_8bzm][Cl]$ with concentration at 298.15 K.

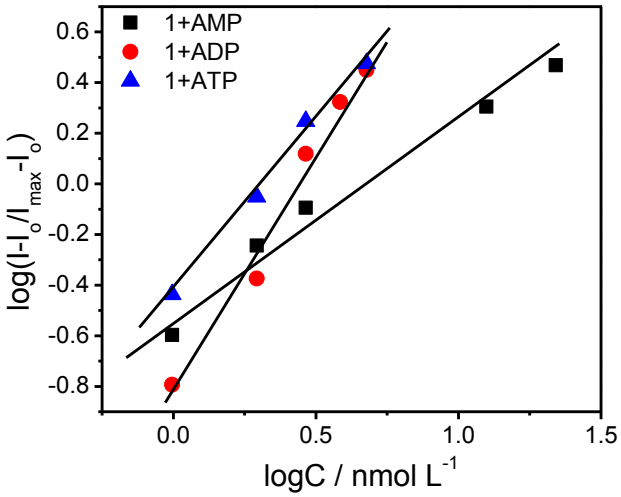


Fig. S10: Hills plots analysis of fluorescence intensity change of **1** in the presence of AMP, ADP and ATP.

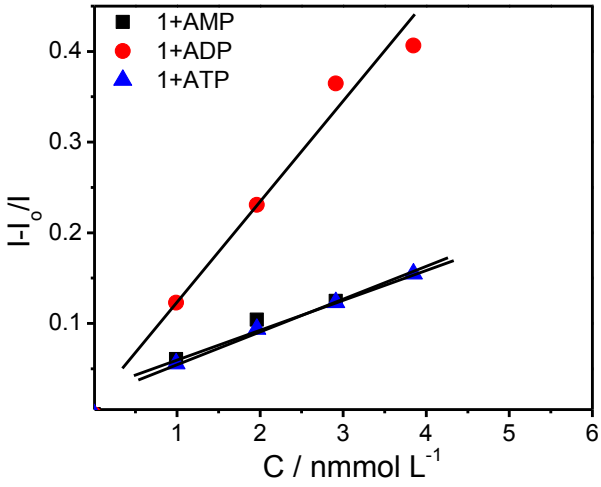
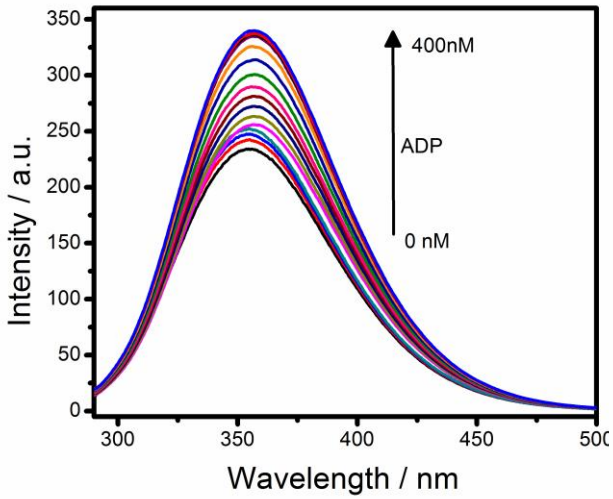


Fig. S11: Ratio of fluorescence intensity change to the intensity at particular concentration of **1** as function of concentration of AMP, ADP and ATP for detection limit calculations.



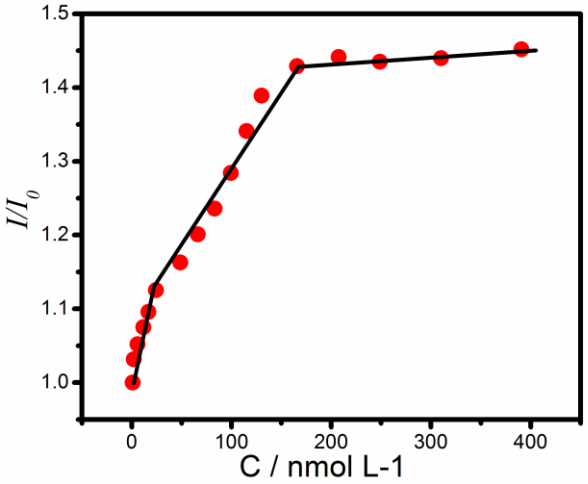


Fig. S12 (A-B): (A) Enhancement in fluorescence intensity and (B) variation in I/I_o values for aqueous solution of $[C_4C_8bzm][Cl]$ with increase in concentration of ADP in the presence of ATP and AMP at 298.15 K.

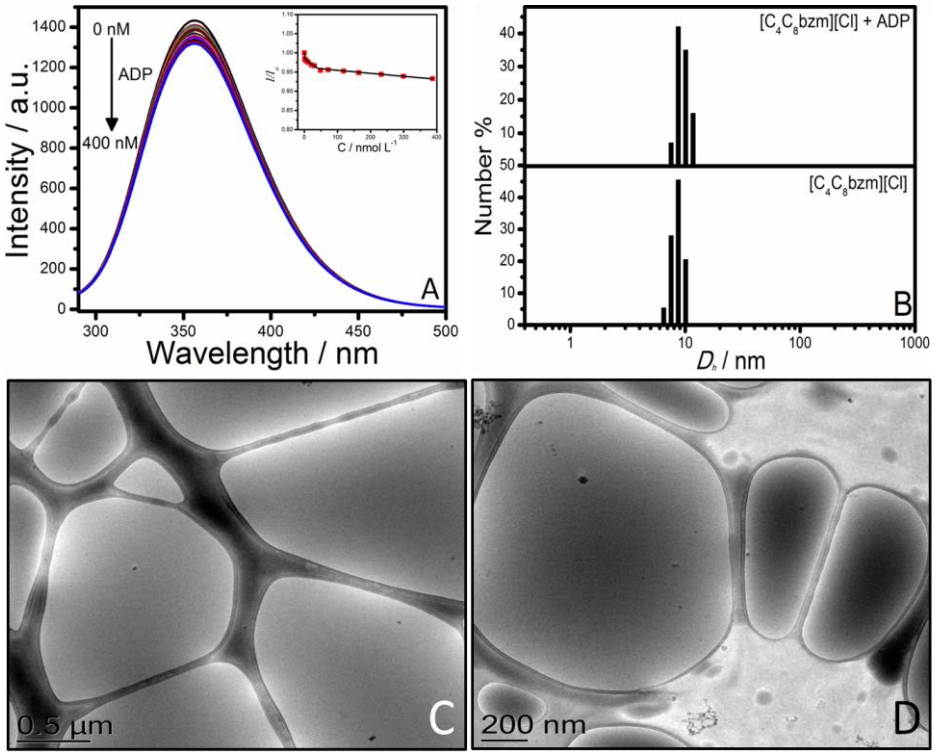


Fig. S13(A-D): (A) Minimal fluorescence quenching of $[C_4C_8bzm][Cl]$ in monomer concentration region; (B) Number weighed size profile and (C-D) Cryo TEM images of $[C_4C_8bzm][Cl]$ without and with ADP respectively.

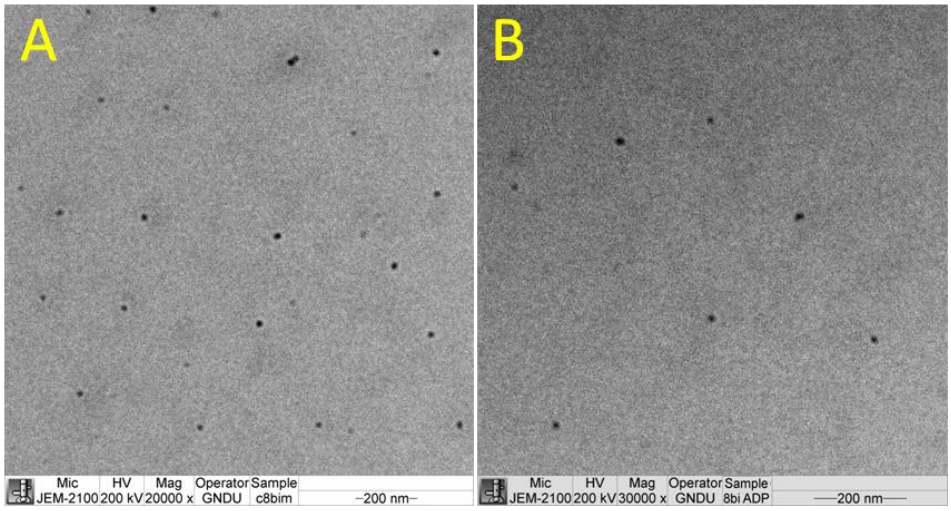


Fig. S14(A-B): TEM images of $[C_4C_{16}bzm][Cl]$ without (A) and (B) with ADP.

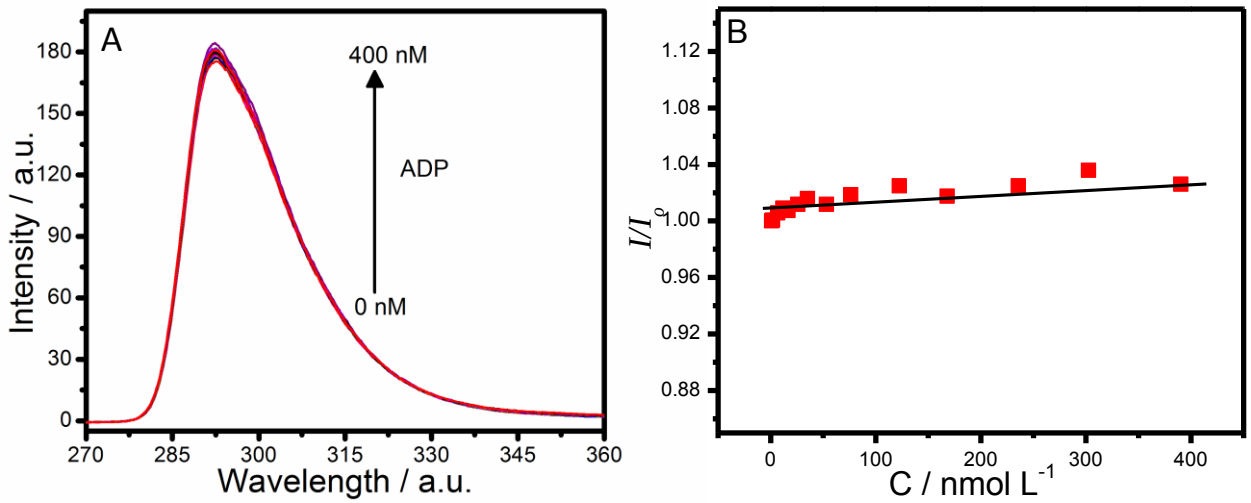


Fig. S15 (A-B): (A) Minimal increase in fluorescence intensity and (B) Variation in I/I_o values of aqueous solution of benzimidazole with addition of ADP at 298.15 K.

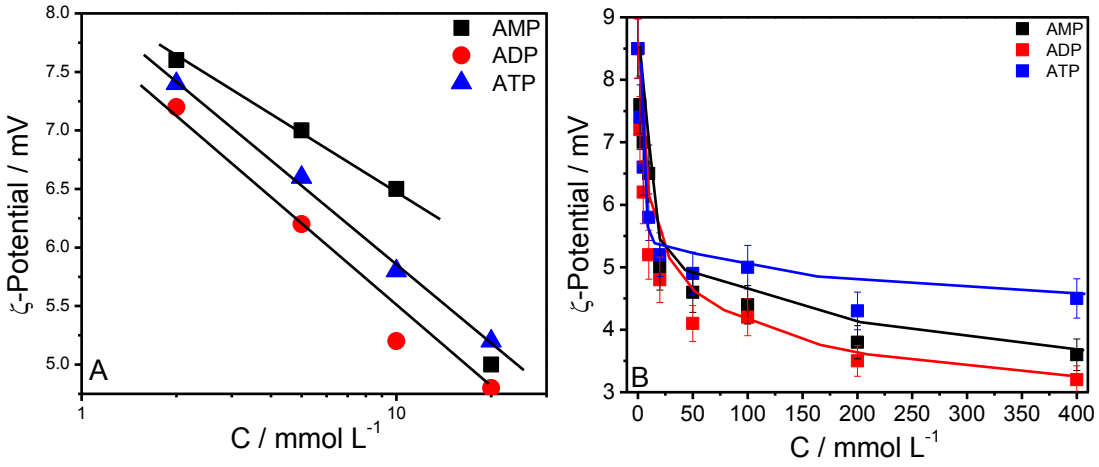


Fig. S16 (A-B): Change in the Zeta potential values of **1** in **(A)** lower concentration range of ADP and (B) over the whole titration concentration range of ADP at 298.15 K

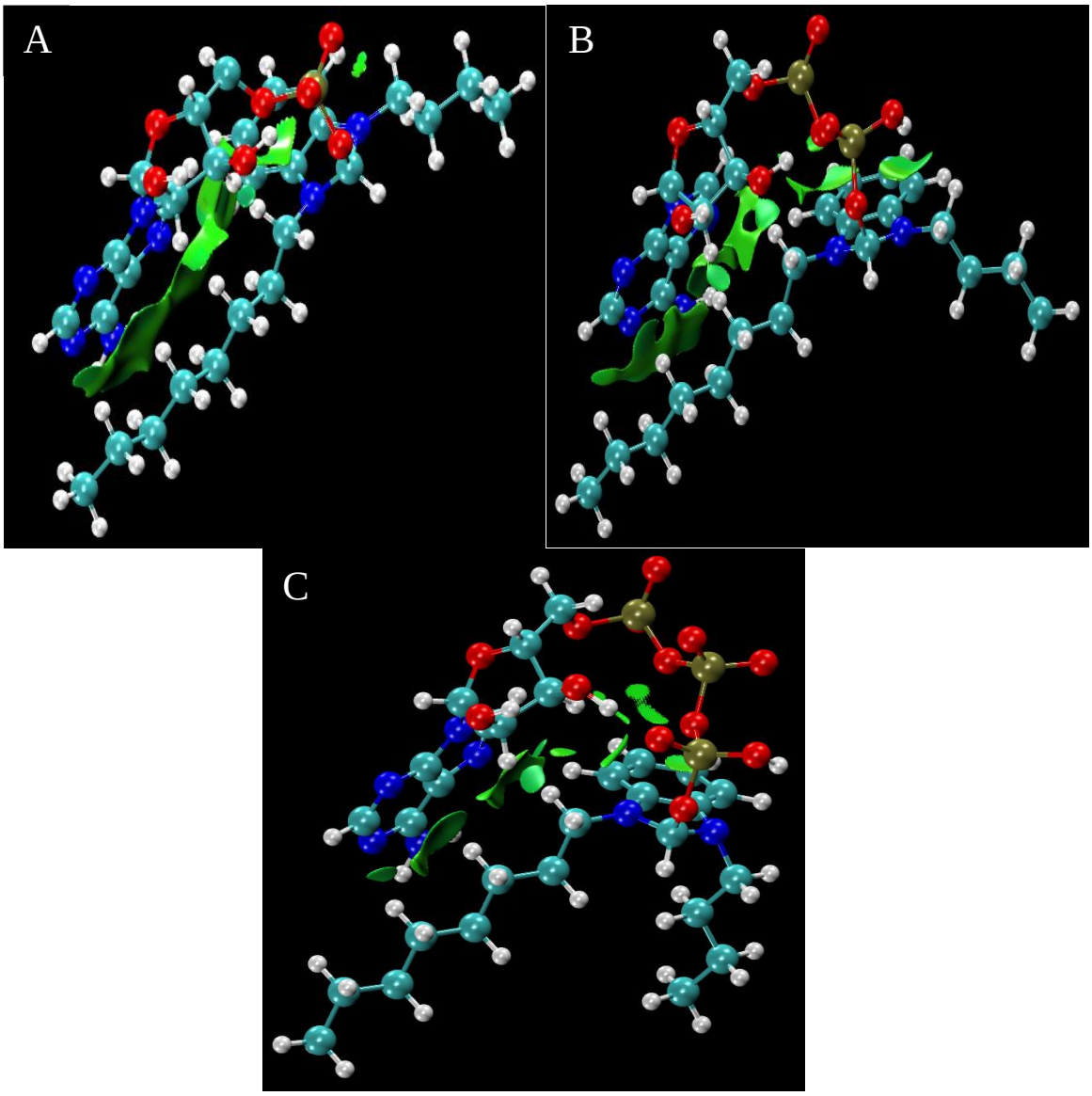


Figure S17 (A-C): Gradient isosurfaces (*S*=0.5) for the complexes of $[C_4C_8bzm][Cl]$ with (A) AMP; (B) ADP and (C) ATP.

Annexure S3: The optimized geometries of the complexes as well as monomer units compute at B3LYP-D3/6-31+G(d,p) level of theory.

ATPcomplex

P	-4.24310	4.58481	0.00804
C	-5.82106	4.91411	-2.06316
O	-4.54261	4.41837	-1.61615
C	-6.82193	3.79606	-2.41045
O	-6.86897	3.60625	-3.85314
C	-6.50215	2.39471	-1.86432
O	-6.89862	2.17400	-0.52965
C	-7.27207	1.49265	-2.83760
O	-8.66501	1.48449	-2.53352
C	-7.09509	2.24328	-4.17883
N	-5.34114	-0.88898	-7.96554
O	-5.46605	4.06663	0.76657
C	-6.53859	-0.80838	-7.36155
O	-3.77201	5.98644	0.31624
N	-6.92469	-0.01408	-6.34973
O	-3.09011	3.45267	0.23924
C	-5.92832	0.80766	-5.96510
C	-4.63481	0.84608	-6.50407
C	-4.33988	-0.07926	-7.53699
N	-3.12446	-0.18313	-8.11287
N	-3.87969	1.83581	-5.89775
C	-4.69307	2.37562	-5.01602
N	-5.94575	1.79050	-4.98923
H	-4.45243	3.20949	-4.37412
H	-5.64788	5.52133	-2.95720
H	-7.82349	4.09129	-2.07355
H	-5.43120	2.21124	-1.99376
H	-6.40284	2.83752	0.02765
H	-6.87098	0.47139	-2.88420
H	-8.74792	1.45236	-1.56227
H	-7.98890	2.12915	-4.80279
H	-7.29943	-1.48313	-7.75001
H	-2.33429	0.34664	-7.76366
H	-2.94810	-0.92620	-8.78274
H	-6.26894	5.55962	-1.30218
C	-0.61039	5.99235	-2.63195
C	-0.72595	6.01044	-4.03558
C	-1.02651	4.84859	-1.96489
C	-1.24055	4.91543	-4.72738
C	-1.64802	3.75167	-4.04555
C	-1.52728	3.73187	-2.66396
H	-0.21702	6.84748	-2.09058
H	-0.40744	6.89440	-4.58135
H	-1.32539	4.94760	-5.81014
H	-2.03277	2.90316	-4.59778
N	-1.03926	4.53169	-0.61156

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N         -1.78702        2.72406       -1.71914
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C         -2.23374        0.50611       -2.87614
H         -3.02715        1.22868       -1.00251
H         -3.63243        2.07388       -2.41367
C         -3.39063       -0.47582       -3.11319
H         -1.89224        0.90317       -3.83783
H         -1.37594        0.00152       -2.41427
C         -3.15792       -1.53426       -4.19678
H         -4.27812        0.10494       -3.40194
H         -3.65233       -0.96884       -2.16633
C         -4.42791       -2.36015       -4.44299
H         -2.32403       -2.19293       -3.91751
H         -2.86294       -1.03495       -5.12941
C         -4.35033       -3.33713       -5.62038
H         -5.25984       -1.66638       -4.62776
H         -4.69240       -2.90693       -3.52628
C         -5.68830       -4.04229       -5.88008
H         -3.56580       -4.08619       -5.44216
H         -4.05779       -2.78759       -6.52408
C         -5.68843       -4.89076       -7.15413
H         -6.48001       -3.28466       -5.95296
H         -5.94657       -4.66583       -5.01341
H         -4.91573       -5.66735       -7.11598
H         -5.48946       -4.26563       -8.03230
H         -6.65293       -5.38684       -7.30773
C         -0.41470        5.31031        0.44258
C          1.11645        5.20113        0.38763
H         -0.79875        4.95007        1.40213
H         -0.73761        6.35475        0.35126
C          1.83472        6.07448        1.42015
H          1.39966        4.14900        0.52528
H          1.45005        5.47916       -0.62062
C          3.36034        5.95843        1.31868
H          1.50903        5.79244        2.42978
H          1.53346        7.12182        1.28265
H          3.71157        6.26385        0.32567
H          3.86388        6.58859        2.05962
H          3.68772        4.92355        1.47972
H         -1.25512        2.65491        0.33370

ADPcomplex
P         -4.84244        6.20330       -2.51522
P         -3.80998        4.96062        0.01849
C         -7.25140        5.01252       -2.17201
O         -6.12376        5.28702       -3.02430
C         -7.59429        3.53682       -2.15298
O         -7.90963        3.04379       -3.49147
C         -6.48185        2.60199       -1.64948
O         -6.43482        2.47059       -0.24314
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C	-6.83874	1.27276	-2.32315
O	-7.87524	0.59045	-1.61199
C	-7.38842	1.73666	-3.69290
N	-4.95638	-0.93315	-7.43470
O	-5.34067	7.33194	-1.62680
O	-3.04744	6.14475	0.57315
C	-6.12591	-1.15359	-6.79943
O	-4.06978	6.51386	-3.77672
O	-5.18243	4.65408	0.63268
N	-6.72393	-0.39600	-5.86640
O	-3.98646	5.09727	-1.62157
O	-2.98021	3.56271	0.14949
C	-6.04586	0.74383	-5.63753
C	-4.85062	1.13120	-6.27004
C	-4.26482	0.20222	-7.17006
N	-3.05839	0.38950	-7.78048
N	-4.44876	2.37779	-5.81873
C	-5.35623	2.71635	-4.91841
N	-6.33942	1.75890	-4.73968
H	-5.38789	3.64958	-4.37061
H	-8.10458	5.59188	-2.54124
H	-8.48772	3.41363	-1.52425
H	-5.51770	2.95931	-2.02635
H	-5.96814	3.27779	0.12499
H	-5.97516	0.61351	-2.44229
H	-7.81027	0.80581	-0.66289
H	-8.17425	1.06925	-4.06067
H	-6.64197	-2.07275	-7.06939
H	-2.42514	1.09454	-7.41533
H	-2.60899	-0.42345	-8.19703
H	-7.05002	5.32111	-1.14190
C	0.20522	5.70418	-2.20194
C	0.13229	6.03128	-3.57185
C	-0.54267	4.62238	-1.75973
C	-0.65854	5.28729	-4.44991
C	-1.40329	4.18088	-3.99724
C	-1.31998	3.85790	-2.65250
H	0.81380	6.28825	-1.51897
H	0.69934	6.87968	-3.94406
H	-0.71454	5.57050	-5.49741
H	-2.03362	3.61488	-4.67549
N	-0.63760	4.01309	-0.51059
C	-1.68973	3.06888	-0.53124
N	-1.85743	2.79487	-1.91878
C	-2.88902	1.89801	-2.41322
C	-2.34573	0.58870	-3.00925
H	-3.56268	1.68079	-1.57903
H	-3.48026	2.42824	-3.16302
C	-3.46832	-0.43231	-3.22896
H	-1.86638	0.80869	-3.97292
H	-1.57898	0.17305	-2.34394
C	-3.08687	-1.64277	-4.08936

H	-4.31144	0.06827	-3.71986
H	-3.83814	-0.77241	-2.25057
C	-4.21142	-2.68584	-4.16261
H	-2.16345	-2.10335	-3.70827
H	-2.85276	-1.29132	-5.10656
C	-3.99532	-3.77107	-5.22181
H	-5.15690	-2.17278	-4.38140
H	-4.33694	-3.15227	-3.17353
C	-5.11604	-4.82100	-5.25287
H	-3.02684	-4.26526	-5.05704
H	-3.92932	-3.28837	-6.20991
C	-4.98315	-5.81274	-6.41081
H	-6.08562	-4.30949	-5.32783
H	-5.13192	-5.36411	-4.29676
H	-4.02733	-6.34811	-6.36073
H	-5.02185	-5.29327	-7.37826
H	-5.79040	-6.55750	-6.39871
C	0.01259	4.48345	0.70320
C	1.46231	3.97589	0.76431
H	-0.56671	4.13104	1.56296
H	-0.02068	5.58171	0.72929
C	2.26320	4.50272	1.96353
H	1.44517	2.87694	0.78085
H	1.97323	4.26505	-0.16534
C	3.70970	3.98008	1.96945
H	1.75638	4.21499	2.89644
H	2.27173	5.60107	1.94457
H	4.24221	4.28425	1.05848
H	4.27684	4.35960	2.83232
H	3.72880	2.88571	2.00918
H	-1.52217	2.17705	0.07677

ATPcomplex

P	-5.51039	7.27963	-2.70851
P	-4.71127	6.44524	0.08813
P	-4.05006	3.90048	1.41759
C	-7.55893	5.58792	-2.80688
O	-6.30836	5.98373	-3.38660
C	-7.72254	4.08198	-2.78206
O	-7.61718	3.51656	-4.11275
C	-6.72520	3.29718	-1.91884
O	-7.16956	3.30150	-0.58058
C	-6.83644	1.88160	-2.55334
O	-7.94736	1.20352	-1.97762
C	-7.14726	2.17876	-4.03883
N	-4.23696	-0.98171	-6.94653
O	-6.50514	8.23003	-2.07994
O	-3.82785	7.53277	0.65812
O	-5.42186	3.23143	1.39155

C	-5.39085	-1.17916	-6.28693
O	-4.56763	7.77837	-3.77572
O	-6.12578	6.30794	0.59483
O	-3.59774	4.51391	2.72337
N	-6.09782	-0.31383	-5.54722
O	-4.63361	6.49580	-1.55810
O	-3.91184	4.97440	0.19306
O	-2.98677	2.70873	0.99411
C	-5.52931	0.90732	-5.54712
C	-4.35264	1.27698	-6.21429
C	-3.66835	0.24923	-6.91436
N	-2.49867	0.43647	-7.56316
N	-4.09080	2.62632	-6.02850
C	-5.06951	3.04928	-5.24973
N	-5.96941	2.05670	-4.91652
H	-5.20937	4.06304	-4.89760
H	-8.37994	6.03789	-3.38000
H	-8.72862	3.87423	-2.38808
H	-5.71462	3.71120	-2.01985
H	-6.40512	3.32145	0.06692
H	-5.92789	1.27969	-2.45475
H	-8.02535	1.57944	-1.07535
H	-7.89581	1.47428	-4.42032
H	-5.79991	-2.18534	-6.35985
H	-1.96830	1.28972	-7.43361
H	-2.00537	-0.37536	-7.92247
H	-7.64112	5.93064	-1.76937
C	-0.27111	5.34603	-1.71331
C	-0.47843	5.78909	-3.03335
C	-1.00737	4.26316	-1.26154
C	-1.39477	5.13951	-3.86157
C	-2.13798	4.03995	-3.40266
C	-1.94652	3.62751	-2.08934
H	0.46455	5.82516	-1.07307
H	0.09099	6.63380	-3.41096
H	-1.53563	5.47802	-4.88468
H	-2.81030	3.51460	-4.06840
N	-0.92019	3.56008	-0.02333
C	-1.97816	2.55284	-0.04055
N	-2.51587	2.58201	-1.37406
H	-1.58545	1.56392	0.21791
C	-3.22709	1.45666	-1.94919
C	-2.32416	0.34217	-2.51415
H	-3.89426	1.05151	-1.17963
H	-3.86801	1.84151	-2.74885
C	-3.13963	-0.83624	-3.06451
H	-1.68612	0.76604	-3.30055
H	-1.65240	-0.01380	-1.72174
C	-2.28891	-1.99840	-3.60078
H	-3.80031	-0.48018	-3.86565
H	-3.80074	-1.21370	-2.27172
C	-3.13984	-3.19344	-4.05344

H	-1.58659	-2.32628	-2.82118
H	-1.67462	-1.64646	-4.44188
C	-2.33201	-4.39888	-4.55145
H	-3.81800	-2.86698	-4.85105
H	-3.78012	-3.51375	-3.21905
C	-3.22128	-5.57499	-4.98012
H	-1.64401	-4.73379	-3.76154
H	-1.69928	-4.09408	-5.39782
C	-2.42935	-6.79764	-5.45690
H	-3.89967	-5.24287	-5.77791
H	-3.86603	-5.86302	-4.13835
H	-1.76700	-7.17195	-4.66696
H	-1.80308	-6.55192	-6.32307
H	-3.09468	-7.61786	-5.74945
C	0.43001	3.01985	0.27759
C	0.97485	2.04777	-0.78505
H	0.38888	2.53451	1.25870
H	1.10742	3.87390	0.37738
C	2.43131	1.63561	-0.54078
H	0.34847	1.14671	-0.82289
H	0.89438	2.52277	-1.77008
C	2.95536	0.67379	-1.61452
H	2.52290	1.16814	0.44859
H	3.06307	2.53369	-0.51436
H	2.89901	1.12724	-2.61133
H	3.99930	0.39553	-1.43352
H	2.36314	-0.24891	-1.64148

AMP

C	0.77422	-1.44928	1.30322
O	2.14812	-1.26441	1.42452
C	2.80773	-1.69828	0.20478
C	1.90628	-2.82016	-0.32046
O	2.15385	-4.02581	0.39364
C	0.51089	-2.25687	0.00182
O	-0.44893	-3.28583	0.16247
C	2.94756	-0.56169	-0.81379
O	3.37931	0.60595	-0.15353
P	3.43824	2.00890	-1.10957
O	3.81550	3.10737	-0.15765
O	4.13023	1.65333	-2.39271
O	1.80115	2.15432	-1.46056
N	0.08539	-0.14864	1.25394
C	0.61437	1.12582	1.35144
N	-0.30274	2.06930	1.24197
C	-1.48660	1.37961	1.05722
C	-1.26281	-0.00233	1.05629
N	-2.18726	-0.96447	0.86268
C	-3.40640	-0.44413	0.66714
N	-3.76479	0.84901	0.64215

C	-2.81365	1.78737	0.83168
N	-3.17354	3.10072	0.81901
H	0.39036	-1.99475	2.17392
H	3.78624	-2.06758	0.51823
H	0.20499	-1.56904	-0.79447
H	2.03789	-2.97801	-1.39996
H	1.68292	1.26967	1.44724
H	-4.20927	-1.15782	0.50065
H	-1.28449	-2.83524	0.39807
H	1.30825	-4.49558	0.45771
H	1.98659	-0.37170	-1.31657
H	3.66198	-0.86934	-1.59178
H	-4.08025	3.33113	0.44195
H	-2.43726	3.78873	0.75599
H	1.39915	2.69747	-0.76720

ADP

P	45.21175	3.97469	39.61044
O	45.24415	5.38103	40.18861
O	43.78578	3.72594	38.82392
O	46.34425	3.45513	38.76782
P	43.70235	2.67375	41.87406
O	42.50149	3.32801	41.19349
O	43.66133	1.27105	42.40452
O	45.01964	2.89868	40.92213
O	44.08431	3.62934	43.21800
C	44.16804	5.03511	43.03327
C	42.79544	5.70007	43.16950
O	42.12713	5.29902	44.41712
C	42.89265	7.22039	43.30310
O	41.62837	7.82860	43.03397
C	43.25447	7.36693	44.79215
O	42.84830	8.62083	45.33217
C	42.50705	6.15973	45.42659
N	43.38229	5.46777	46.40401
C	43.92653	4.19648	46.34403
N	44.68044	3.91562	47.39595
C	44.63561	5.06035	48.16640
C	45.25613	5.43426	49.36860
N	46.03874	4.56200	50.07795
N	45.06367	6.67771	49.85500
C	44.28032	7.52045	49.15825
N	43.63503	7.29644	48.00763
C	43.84173	6.04237	47.55549
H	43.08522	3.67998	39.52184
H	44.85419	5.40121	43.81278
H	44.59347	5.30349	42.05328
H	42.14978	5.36563	42.35742
H	43.66762	7.63099	42.64363
H	41.58400	8.62984	43.57582

H	44.33559	7.23830	44.91821
H	43.00419	8.56925	46.29279
H	41.63081	6.50697	45.98963
H	43.75826	3.56621	45.47408
H	46.66420	4.96960	50.75707
H	46.35882	3.74186	49.58154
H	44.16561	8.51432	49.58483

ATP

P	6.55990	22.41637	11.43106
P	3.55993	22.58324	12.39525
P	1.57234	20.83219	10.86439
C	5.29812	21.15501	9.30153
O	6.49493	21.59130	9.94298
C	5.02379	19.67117	9.48221
O	6.02806	18.87328	8.75019
C	5.06214	19.15836	10.92657
O	4.12169	18.10163	11.14221
C	6.47389	18.56257	11.08488
O	6.49332	17.43777	11.95533
C	6.85352	18.16784	9.63521
N	11.47907	16.34396	8.04248
O	7.38121	23.65515	11.17862
O	3.67415	21.36220	13.30717
O	2.16721	19.74632	11.98704
C	10.30319	15.72147	8.28134
O	6.98179	21.39267	12.45647
O	3.09093	23.90412	12.93159
O	1.85641	20.26568	9.48931
N	9.14719	16.24421	8.68797
O	4.97964	22.85446	11.58291
O	2.64821	22.10797	11.09007
O	0.17833	21.26157	11.25281
C	9.22023	17.57615	8.86738
C	10.36942	18.35882	8.63645
C	11.51601	17.67781	8.21484
N	12.69433	18.35273	7.93756
N	10.12725	19.68886	8.91189
C	8.86226	19.70956	9.30403
N	8.26768	18.46053	9.30178
H	8.28206	20.58431	9.59153
H	5.41936	21.34725	8.22583
H	4.04396	19.45375	9.04888
H	4.90639	19.95405	11.65835
H	3.28133	18.55990	11.40718
H	7.13360	19.34010	11.48011
H	5.54682	17.20423	12.03136
H	6.75248	17.08502	9.50255
H	2.71689	20.27067	12.66422
H	10.31029	14.64422	8.12267

H	12.74828	19.27454	8.35276
H	13.52787	17.78720	8.01996
H	4.42412	21.70756	9.65391

IONICLIQUID

C	-8.90248	-0.83864	-0.98960
C	-7.78003	-0.76051	0.05054
H	-8.73611	-1.66699	-1.68851
H	-8.96133	0.08524	-1.57736
H	-9.87683	-0.99411	-0.51486
C	-6.39729	-0.54069	-0.57570
H	-7.76402	-1.68506	0.64462
H	-7.98925	0.05472	0.75719
C	-5.26828	-0.46513	0.45869
H	-6.41114	0.38613	-1.16805
H	-6.18719	-1.35485	-1.28480
C	-3.88604	-0.24106	-0.16623
H	-5.25353	-1.39347	1.04825
H	-5.48056	0.34684	1.16943
C	-2.76275	-0.17154	0.87583
H	-3.89679	0.68982	-0.75134
H	-3.67167	-1.05107	-0.87798
C	-1.38113	0.05829	0.24969
H	-2.74992	-1.10360	1.45865
H	-2.97868	0.63655	1.58928
C	-0.28759	0.11534	1.31968
H	-1.38198	0.99334	-0.32378
H	-1.14882	-0.74748	-0.45842
N	1.05098	0.37306	0.75477
C	1.51722	1.59883	0.27370
C	2.82002	1.37154	-0.20058
C	3.59604	2.39800	-0.74546
C	3.00905	3.65792	-0.79441
C	1.69963	3.88746	-0.31749
C	0.92714	2.86529	0.22512
H	-0.22795	-0.82636	1.87212
H	-0.48379	0.90903	2.04666
N	3.09218	0.01625	0.00619
C	2.01451	-0.53797	0.57461
C	4.36940	-0.64419	-0.33963
C	4.40340	-2.13570	-0.01853
H	5.15643	-0.11465	0.20713
H	4.53058	-0.47692	-1.40941
H	4.22948	-2.29201	1.05443
H	3.60367	-2.65381	-0.56428
C	5.75710	-2.75535	-0.40100
C	5.81621	-4.25465	-0.09100
H	1.92606	-1.57489	0.85691
H	1.28569	4.88839	-0.37644
H	-0.07792	3.04397	0.58957
H	4.60188	2.22493	-1.10965

H	3.57118	4.48783	-1.20886
H	5.94099	-2.59142	-1.47055
H	6.55842	-2.23469	0.13894
H	5.66508	-4.44552	0.97736
H	6.78836	-4.67169	-0.36839
H	5.04758	-4.80487	-0.64507

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