

## Supporting Information

### ***Replacing Imidazole with Benz-Imidazole: A promising Approach to Enhance the Electrocatalytic Performance of Imidazolium based Surface Active Ionic Liquids for Greener Electrosynthesis***

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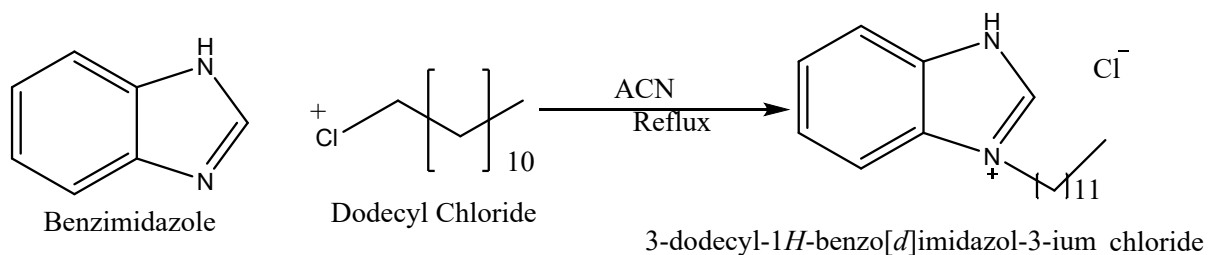
#### **1) Materials and methods:**

##### 1.1) Reagents and materials:

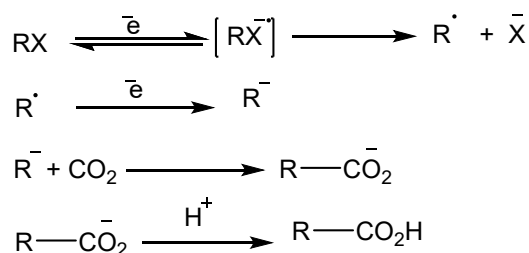
Benzimidazole (98%) and Acetonitrile was procured from TCI. 1-chlorododecane (97%), 9-Bromoanthracene (98%) and Ferrocenemethanol (97%) were purchased from sigma Aldrich. Sodium dihydrogen orthophosphate and Disodium hydrogen phosphate, both having a percentage purity of 97% were purchased from Merck. Diethyl Ether (98%) in separation procedures was purchased from Thermo Fisher Scientific. All chemicals were used as such without further purification. Triply distilled water was used for all the experiments.

##### 1.2) Synthesis of [DDBIM][Cl] SAIL:

[DDBIM][Cl] was synthesized with the help of Menshutkin reaction in which 2.9g benzimidazole and 6.09ml of 1-chlorododecane were charged into a round bottomed flask(RBF) fitted with a reflux condenser and the mixture was stirred in 25 ml of acetonitrile at 80°C in a nitrogen saturated atmosphere. After 60 hours, white solid crystals started precipitating out on bottom of RBF. The reaction mixture was stirred until all of the solid precipitated out. The decision to stop the reaction was also supported by the TLC analysis of the reaction mixture which showed no spot for reactants suggesting all the reactants have been consumed. This was followed by high vacuum rotary evaporative drying of the white product for about 5 hours ensuring the complete removal of excess reactants and solvents leaving behind fairly white hygroscopic cubic crystals of [DDBIM][Cl] as the final product. The crystals were repeatedly washed with diethyl ether and dried to yield the pure and dry [DDBIM][Cl], that was stored under inert and dry conditions in a specifically prepared desiccator. The dried samples of [DDBIM][Cl] were observed to sharply melt at 78 °C, which is well below the 100 °C limit for a salt to be considered an ionic liquid.



**Scheme S1: Menshutkin reaction for synthesis of [DDBIM][Cl]**



**Scheme S2: Mechanistic steps involved in Electrocarboxylation**

### 1.3) Instrumentation:

All the electrochemical measurements were performed at room temperature using Metrohm PGSTAT100 potentiostat/galvanostat in a 3-electrode setup. The voltammetric investigations unless mentioned otherwise were carried out under argon atmosphere. A 3 mm diameter disk shape glassy carbon electrode (GCE), properly polished over alumina powder, rinsed with water and then sonicated in ethanol for 2 minutes before each measurement was used as the working electrode. Silver wire (99.9%) and platinum (99.9%) loop were used as quasi-reference and counter electrode, respectively. Inbuilt positive feedback circuitry in the electrochemical work-station was used to evaluate and compensate for the solution resistance. The potential scale of voltammetric investigations was calibrated with respect to redox response observed for ferrocene methanol (FcMeOH) as an internal redox probe. Before their use, all the electrodes were properly cleaned following recommended procedure. The electrocatalytic performance of aqueous solutions of [DDBIM][Cl] for electrodehalogenation was monitored at various pre and post micellar concentrations and it was observed to be at its maximum for concentration at around 1mM of this SAIL. It is in this context that the detailed electrodehalogenation and Electrocarboxylation investigations were mainly carried in aqueous micellar solutions of ca. 1 mM [DDBIM][Cl]. The surface tension measurements were carried with a Kruss K11 tensiometer using ring method. For particle size measurements, Dynamic Light Scattering (DLS) investigations were carried with particle Analyser (LiteSizer 500, Anton Paar). All the spectrophotometric measurements were carried on double beam UV-Vis Shimadzu Spectrophotometer (model UV-2510). Melting points were determined on Buchi B-542 apparatus using an open capillary

method. All the NMR characterization was done on Bruker 400MHz NMR Spectrometer. Conductivity was measured on Systronics digital TDS (MK-509) conductivity meter.

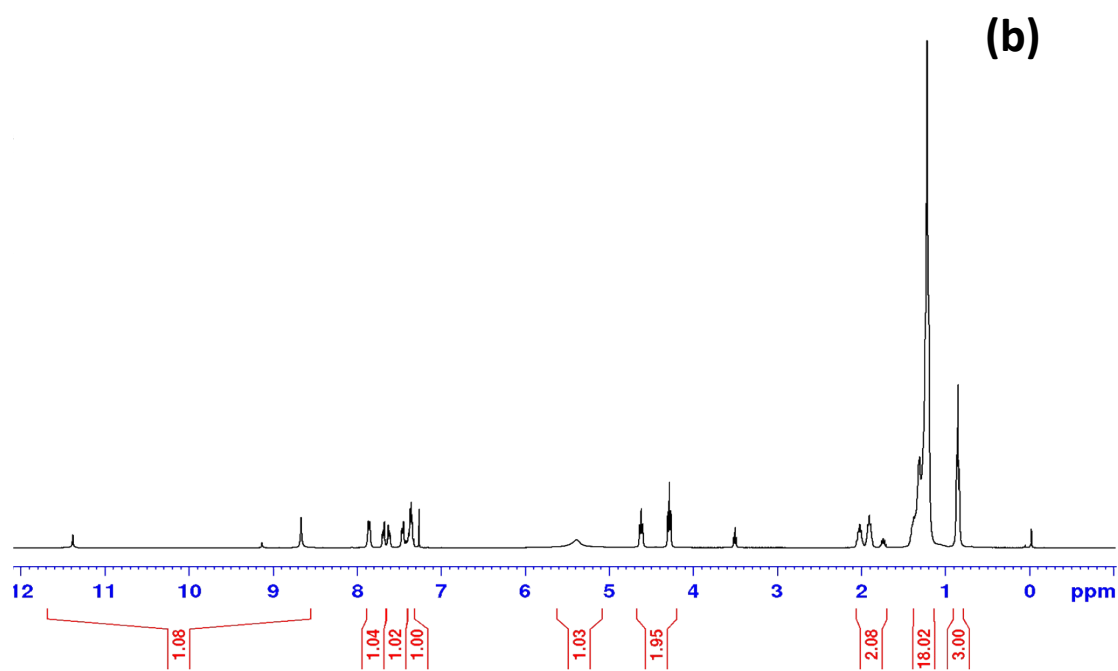
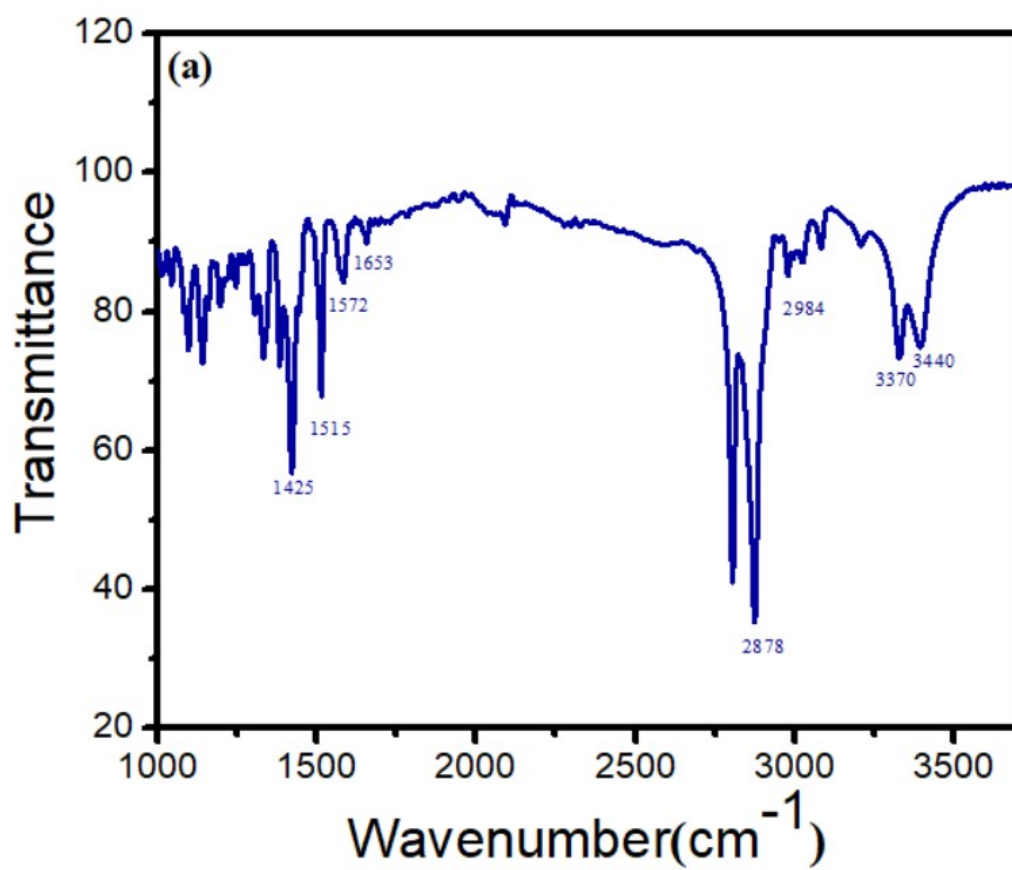
#### 1.4) Physicochemical Characterization of [DDBIM][Cl]:

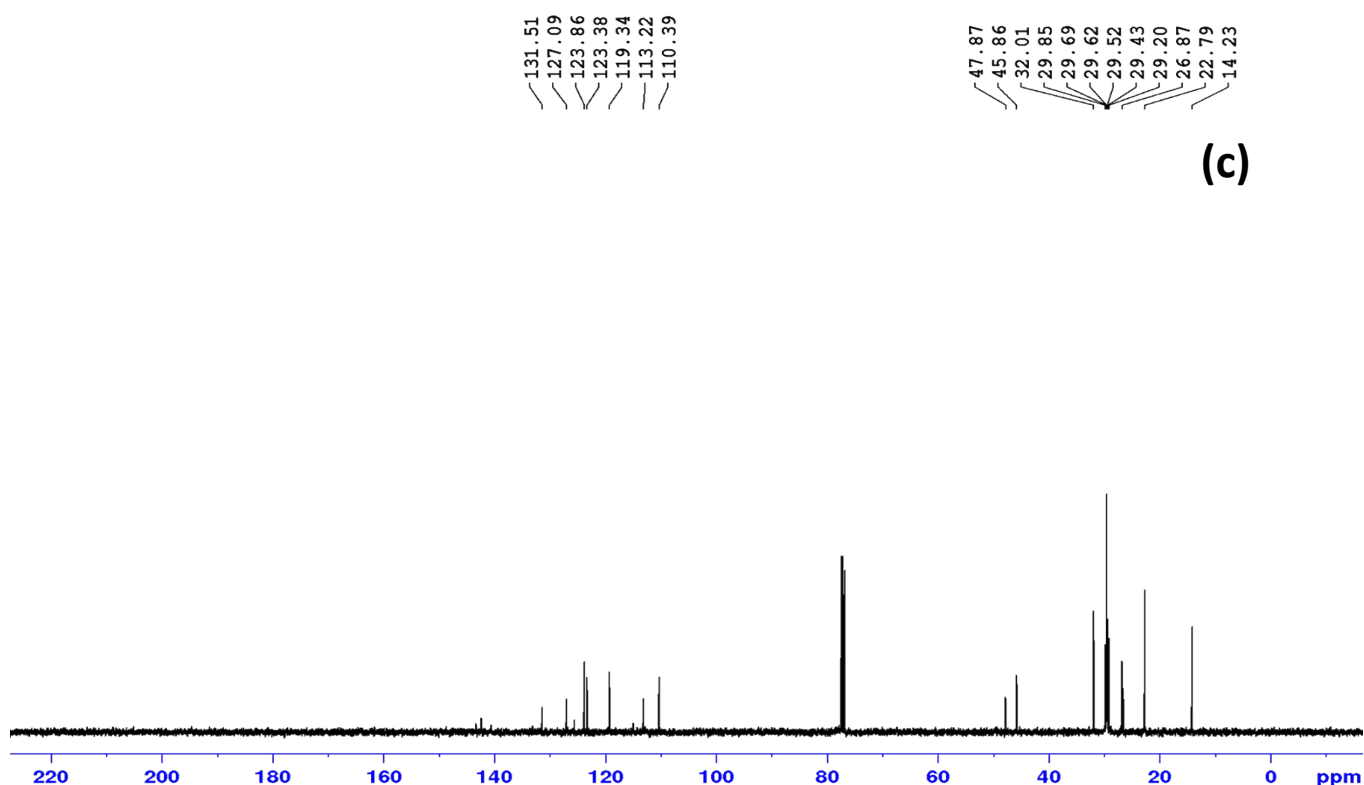
While the sharpness of the melting point established the purity, the chemical identity of the final product was established through spectroscopic investigations. Figure S1(a), depicts a sample FTIR spectrum recorded over the freshly synthesized sample of [DDBIM][Cl]. The peaks at 3440, 3370 and 2984  $\text{cm}^{-1}$  noted in the FTIR spectrum, correspond to the C-H stretch of n-dodecyl hydrogens and the peak at 1699  $\text{cm}^{-1}$  corresponds to the C=N stretch. The band at 2878  $\text{cm}^{-1}$  corresponds to the NH stretch and the bands at 1653, 1515 and 1425  $\text{cm}^{-1}$  can be attributed to C=C vibrations of benzimidazolium ring skeleton of this ionic liquid.<sup>1</sup> These features noted in the FTIR spectrum offered the prelim proofs to confirm the identity of the final product as [DDBIM][Cl]. This was further confirmed by the  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra recorded for the as synthesised samples of [DDBIM][Cl]. Fig S.1 1(b) and (c) depict sample  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra recorded over the freshly synthesised samples of [DDBIM][Cl]. The spectroscopic signatures;

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  0.84 (m, 3H), 1.21 (m, 18H), 0.98 (s, 1H), 1.90 (m, 2H), 4.44 (m, 2H), 5.38 (s, NH), 7.35(s, 1H), 7.53 (s, 1H), 7.77 (s, 1H), 8.66 (s, 1H), 8.92 (s, 1H)

$^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm), 131.51(s), 127.09 (dd), 123.86(dd), 123.38(dd), 119.34(dd), 113.22(dd), 110.39(dd), 47.87(s), 45.86 (dd), 32.01 (dd), 29.85 (dd), 29.69 (dd), 29.62 (dd), 29.52 (dd), 29.43 (dd), 29.20 (dd), 26.87 (dd), 22.79 (dd), 14.23 (d)

clearly confirm the identity of the final product as being [DDBIM][Cl]. The synthesis of [DDMIM][Cl] was carried out following an earlier reported procedure<sup>2</sup> for this SAIL.



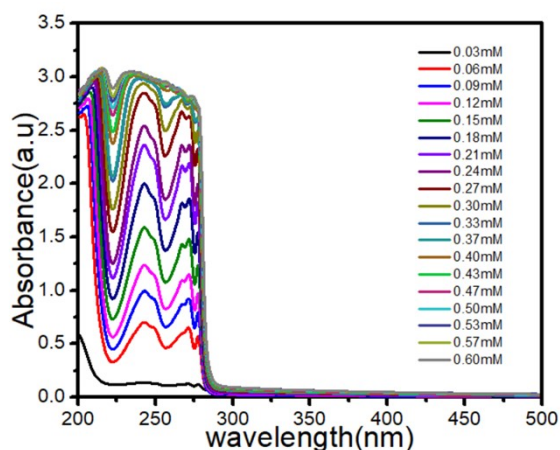


(c)

Fig. S1. (a) FTIR (b)  $^1\text{H}$  NMR (c)  $^{13}\text{C}$  NMR spectra recorded for freshly prepared samples of [DDBIM][Cl]

1.5) Determination of *cmc* via UV-Vis investigations:

For the spectrophotometric estimation of the *cmc*, concentration dependence of the absorbance behaviour of SAIL, [DDBIM][Cl] in 0.1 M PBS solutions was monitored in the UV-visible range (200-360 nm). The UV-vis spectra were recorded for changing concentrations of SAIL in 0.1 M PBS and Fig. S2 depicts a sample set of UV-Vis spectra recorded during such investigations. The depicted spectra exhibit an absorption behaviour typical to that of imidazolium based ionic liquids. The absorbance corresponding to the imidazolium specific absorption bands as noted in these spectra plotted as a function of the SAIL concentration exhibited a behaviour typical of amphiphilic imidazolium based ionic liquids.<sup>3</sup> The plots revealed a typical linear dependence of absorbance over concentration in the pre-micellar region with almost a SAIL concentration independent absorbance for the post-micellar concentrations of the SAIL. The absorbance vs concentration data for post and pre-micellar concentrations fits linear regression making a sharp intersect. The concentration corresponding to the point of intersection is found to be specific for the SAIL and represents the onset of micellization process or the *cmc* of the ionic liquid.<sup>2</sup> The *cmc* value estimated for the chosen SAILs by this method was observed to be in close agreement with the value estimated from the tensiometric and conductometric investigations carried for these SAIL solutions.



**Fig.S2** A sample set of UV-Vis spectra recorded for aqueous solutions of [DDBIM][Cl] at changing concentrations.

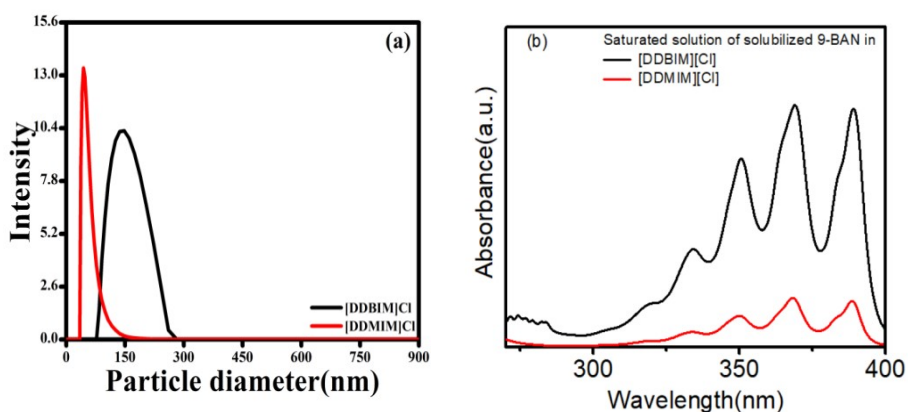
#### 1.6. Micellar Size and BAN solubilisation investigations:

Dynamic light scattering (DLS) investigations were carried out over the aqueous micellar solutions of the [DDMIM][Cl] and [DDBIM][Cl] SAILS to reveal the degree of polydispersity and the sizes of the constituent micelles. The DLS measurements suggested a hydrodynamic radius of ca. 137 nm for [DDBIM][Cl] micelles, compared to the size of 42 nm for [DDMIM][Cl] micelles (Fig S3(a)). This large size of [DDBIM][Cl] micelles compared to that of the [DDMIM][Cl] micelles is well expected in light of our tensiometric and conductometric investigations that suggest better stability of the former on account of stronger interactions among monomers and a strong counterion binding in these micelles. The relative differences in the surface activity, self-aggregation tendency, size and stability of the constituent micelles of the [DDMIM][Cl] and [DDBIM][Cl] SAILS, clearly imply that the aqueous micellar solution of the later SAIL should be much better at dissolving hydrophobic organic species in water than the [DDMIM][Cl] SAIL.<sup>4</sup> This was confirmed by our detailed UV-Vis solubilization investigations that were carried out to reveal and compare the solubilizing capacity of [DDMIM][Cl] and [DDBIM][Cl] SAILS with 9-Bromoanthracene (BAN) as a model halohydrocarbon. A three-step solubilization procedure<sup>3</sup> was employed for the estimation of BAN solubilizing potential of the aqueous micellar solutions of [DDMIM][Cl] and [DDBIM][Cl] SAILS. In order to solubilize 9-bromoanthracene (9-BAN), 1 mM solution of [DDBIM][Cl] in 0.1 M phosphate buffer (pH 7) was chosen. 9-BAN was added to the vial to saturate the solution. The sample vial was stirred for a period of 12 hours on a magnetic stirrer with sample maintained at a temperature of  $25 \pm 0.5$  °C. This is the period at which in the peaks corresponding to concentration of BAN in the solution as monitored spectrophotometrically showed maximum absorption. Afterwards, the sample vial containing 9-BAN was left for sedimentation and then decanted. The decant was centrifuged at 13400 rpm for 15 minutes to remove any undissolved analyte. The concentration of 9-BAN solubilized in 1 mM [DDBIM][Cl] was determined spectrophotometrically. Fig. S3(b), depicts the sample UV-Vis spectra recorded for BAN-saturated aqueous micellar solutions of [DDMIM][Cl] and [DDBIM][Cl] SAILS. The depicted UV-Vis spectra show the presence of all the BAN-

specific absorption bands. Importantly while the position of the BAN-specific absorption bands seems to be the same in [DDMIM][Cl] and [DDBIM][Cl] SAILS, the intensity of these bands recorded for BAN saturated [DDBIM][Cl] micellar solutions is almost six times the intensity observed for BAN saturated [DDMIM][Cl] micellar solutions. Using the known molar extinction coefficient of BAN for the  $\lambda_{\text{max}}$  of 388 nm as calculated in our previous work<sup>2</sup>, the saturation concentration of BAN for aqueous micellar solutions of [DDBIM][Cl] was estimated to be ca. 250  $\mu\text{M}$ , this is more than 6 times the value (40  $\mu\text{M}$ ) observed for the aqueous micellar solutions of [DDMIM][Cl]. In view of these observations, it is safe to conclude that while the site of solubilization for the BAN is similar in the [DDMIM][Cl] and [DDBIM][Cl] micelles, the BAN solubilizing capacity of the latter is almost six times that of the former. These above-presented results from our tensiometric, conductometric, DLS and UV-Vis spectrophotometric investigations besides establishing the amphiphilic and self-aggregation potential of [DDMIM][Cl] and [DDBIM][Cl] SAILS, clearly establish that the surface activity, micellar stability and halocarbon solubilization capacity of former SAIL<sup>4</sup> is much better than the latter.

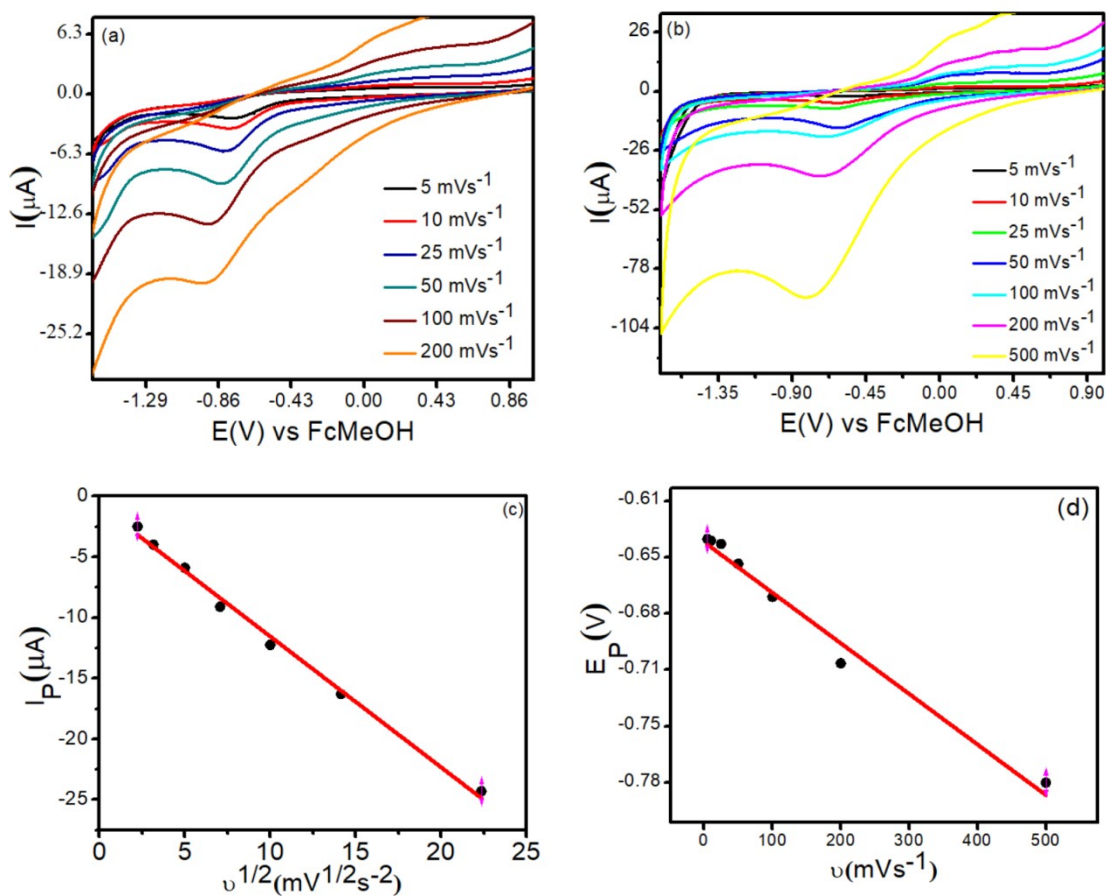
**Table S1:** Showing comparison of surface activity and size of [DDBIM][Cl] and [DDMIM][Cl]

SAIL	CMC(mM)	$\gamma_{\text{cmc}}$ (mN/m)	$\bar{r}$ ( $\mu\text{M}/\text{m}^2$ )	$A_{\text{min}}$ ( $\text{nm}^2$ )	$\beta$
[DDMIM][Cl]	12.49mM	46.19 $\pm$ 0.3	2.91 $\pm$ 0.03	0.57 $\pm$ 0.1	0.28
[DDBIM][Cl]	0.25mM	43.23 $\pm$ 0.3	5.51 $\pm$ 0.03	0.30 $\pm$ 0.1	0.71

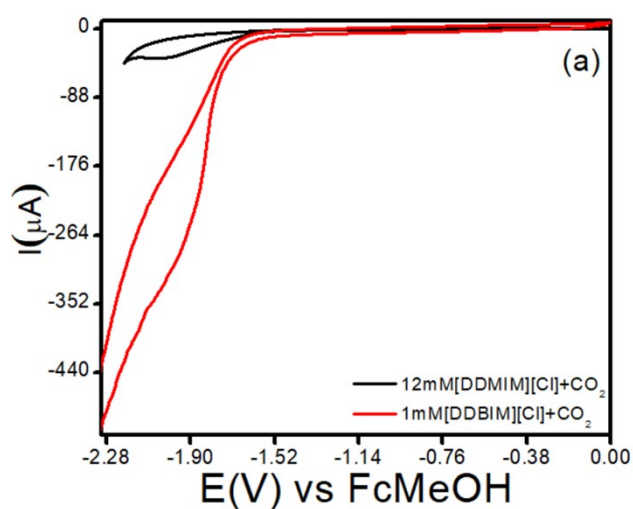


**Fig S3.** a) Typical size distribution the [DDBIM][Cl](black line) and of [DDMIM][Cl] micelles (red line) as observed for the aqueous micellar solution of these SAIL in DLS investigations b) Absorbance spectra recorded over BAN saturated aqueous micellar solutions of [DDBIM][Cl] and [DDMIM][Cl].

## 1.7 Electrochemistry

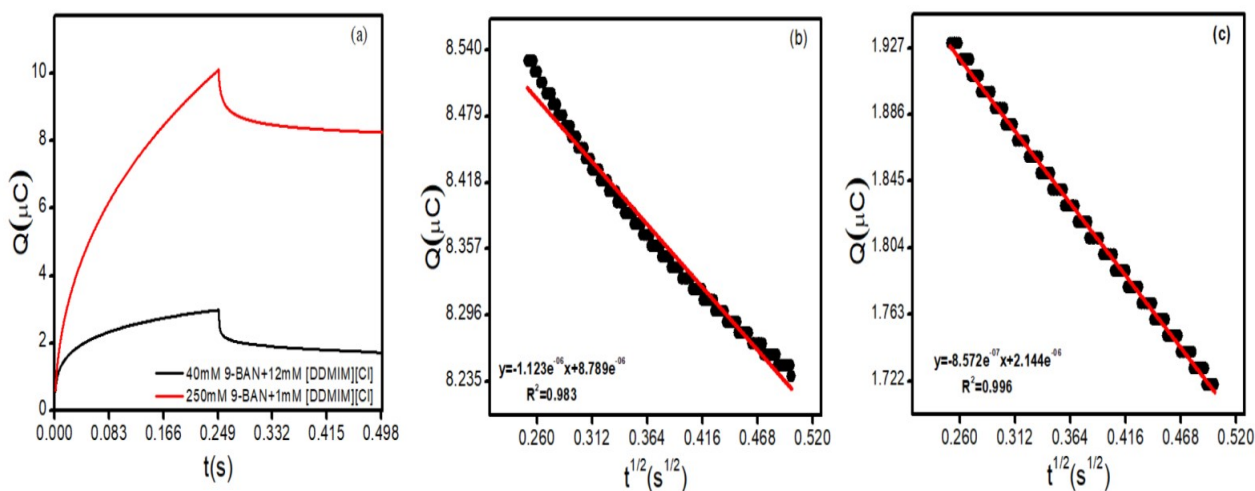


**Fig.S4.** CVs recorded at changing scan rates for 9-Bromoanthracene(9-BAN) saturated aqueous micellar solutions of [DDBIM][Cl] in 0.1 M PBS (a) in absence and (b) in presence of  $\text{CO}_2$  (c) shows variation of  $I_p$  as a function of square root of scan rate ( $v^{1/2}$ ) and (d) shows variation of  $E_p$  as a function of  $v$



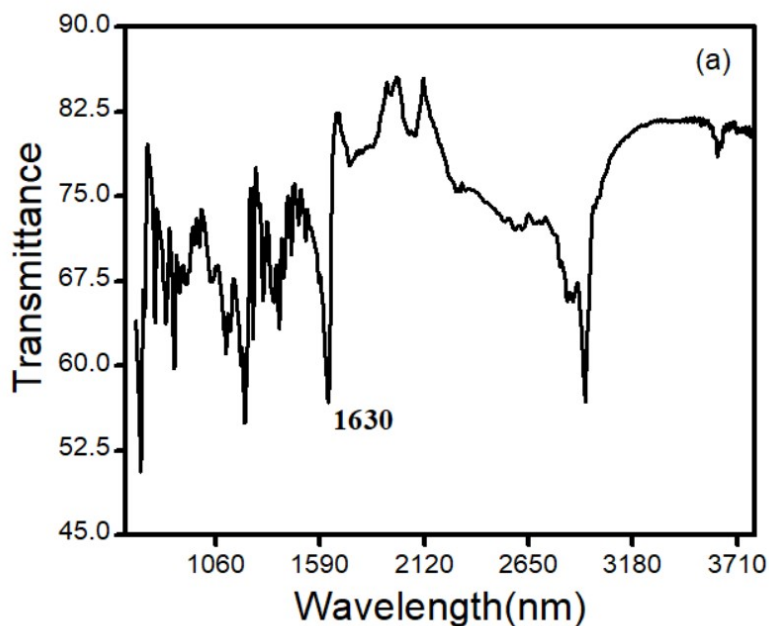
**Fig.S5.** CVs recorded over a glassy carbon electrode for the carbon dioxide saturated 1 mM [DDBIM][Cl] (the black trace) and 12mM [DDMIM][Cl] (red trace) with 0.1M PBS as the supporting electrolyte. The potential scan rate was 50  $\text{mVs}^{-1}$



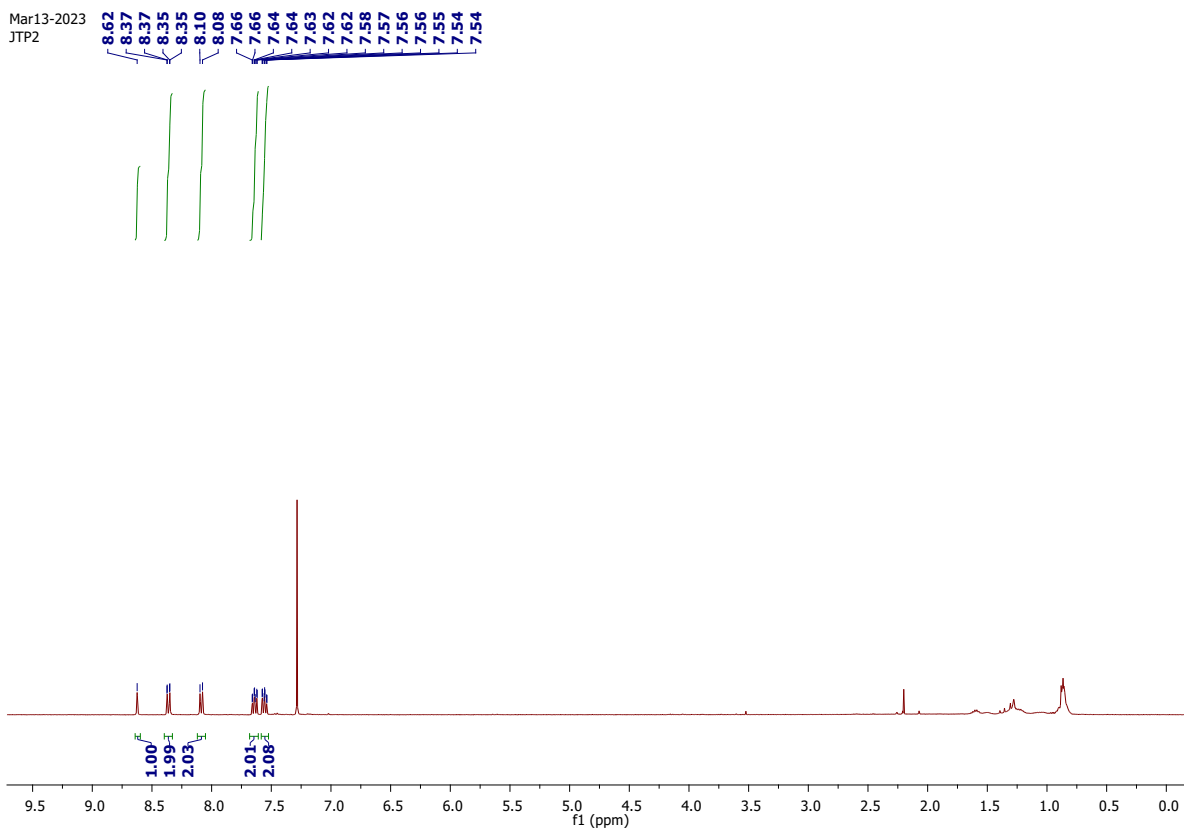


**Fig.S6.** a) Large amplitude potential step chronocoulograms recorded over bare glassy carbon electrode for 9-BAN saturated aqueous micellar solutions of [DDMIM][Cl] (black trace) and 1mM [DDBIM][Cl](red trace) with 0.1 M phosphate buffer solution acting as the supporting electrolyte. Respective Cottrell plots corresponding to the chronocoulometric data b) [DDBIM][Cl] and c) [DDMIM][Cl].

## 2. Characterization of the products



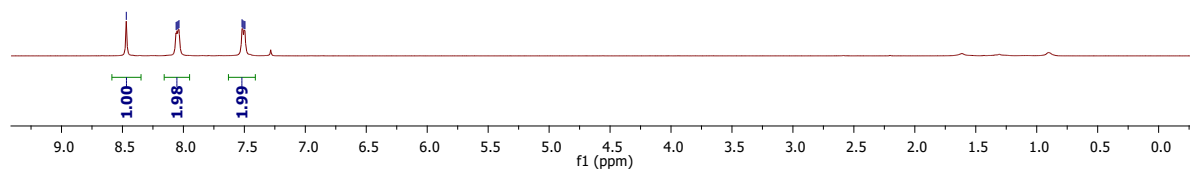
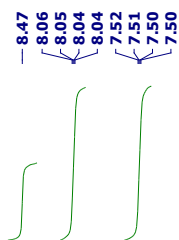
**Fig S7.** FTIR spectrum of the product recovered from BAN saturated aqueous micellar solution of the [DDBIM][Cl] electrolysed in presence of CO<sub>2</sub>. The potentiostatic electrolysis was carried in an H-type electrolysis cell at a potential chosen from the CV records recorded for the said mixture.



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.62 (s, 1H), 8.36 (dd,  $J = 8.8, 0.8$  Hz, 2H), 8.09 (d,  $J = 8.5$  Hz, 2H), 7.68 – 7.61 (m, 2H), 7.59 – 7.52 (m, 2H).

**Fig. S8.**  $^1\text{H}$  NMR FTIR spectrum of the product recovered from BAN saturated aqueous micellar solution of the [DDBIM][Cl] electrolysed in presence of  $\text{CO}_2$ . The potentiostatic electrolysis was carried in an H-type electrolysis cell at a potential chosen from the CV records recorded for the said mixture.

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$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.47 (s, 1H), 8.04 (dd,  $J = 8.8, 0.8$  Hz, 1H), 7.5(d,1H)

**Fig. S9.**  $^1\text{H}$  NMR FTIR spectrum of the product recovered from BAN saturated aqueous micellar solution of the [DDBIM][Cl] electrolysed in absence of  $\text{CO}_2$ . The potentiostatic electrolysis was carried in an H-type electrolysis cell at a potential chosen from the CV records recorded for the said mixture.

#### References:

1. S. A. Dharaskar, M. N. Varma, D. Z. Shende, C. K. Yoo and K. L. Wasewar, *The Scientific World Journal*, 2013, **2013**.
2. S. A. Pandit, S. A. Bhat, M. A. Rather, F. A. Sofi, P. P. Ingole, Z. M. Bhat, M. O. Thotiyl, K. A. Bhat, S. U. Rehman and M. A. Bhat, *Green Chemistry*, 2021, **23**, 9992-10005.
3. E. Fuguet, C. Ràfols, M. Rosés and E. Bosch, *Analytica Chimica Acta*, 2005, **548**, 95-100.
4. J. Wan, R. Fukuda, M. Hada and H. Nakatsuji, *The Journal of Physical Chemistry A*, 2001, **105**, 128-133.