

## Electronic Supplementary Information

### Alkaline polymer electrolytes containing pendant

#### dimethylimidazolium groups for alkaline membrane fuel cells

*Xiaocheng Lin<sup>a</sup>, John R. Varcoe<sup>b</sup>, Simon D. Poynton<sup>b</sup>, Xuhao Liang<sup>a</sup>, Ai Lien Ong<sup>b</sup>,  
Jin Ran<sup>a</sup>, Yan Li<sup>a</sup>, Tongwen Xu<sup>a,\*</sup>*

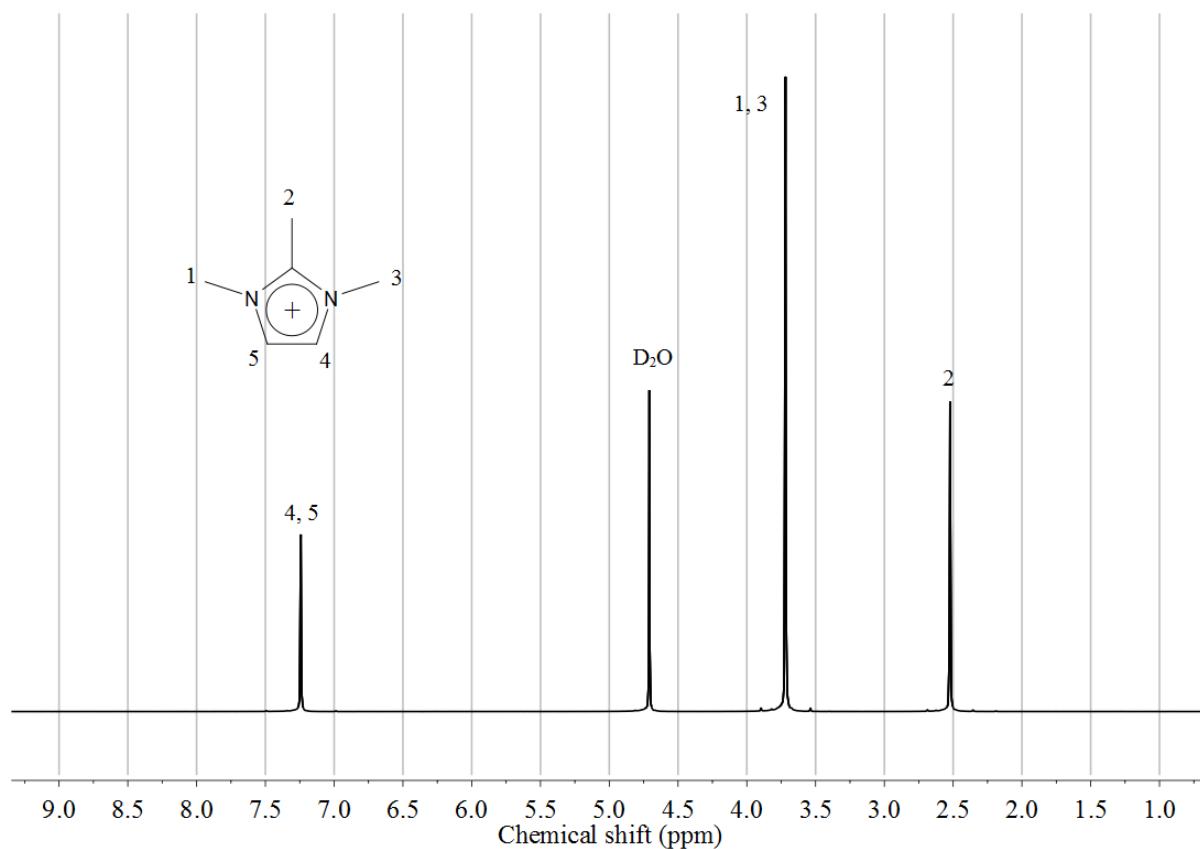
<sup>a</sup> School of Chemistry and Material Science, University of Science and Technology of China, Hefei, Anhui, 230026, P. R. China

Fax: (+86) 0551-3601592, E-mail: [twxu@ustc.edu.cn](mailto:twxu@ustc.edu.cn)

<sup>b</sup> Department of Chemistry, Faculty of Engineering and Physical Sciences, The University of Surrey, Guildford GU2 7XH, United Kingdom

### 1. Synthesis of 1,2,3-Trimethylimidazolium iodide (TIMI)

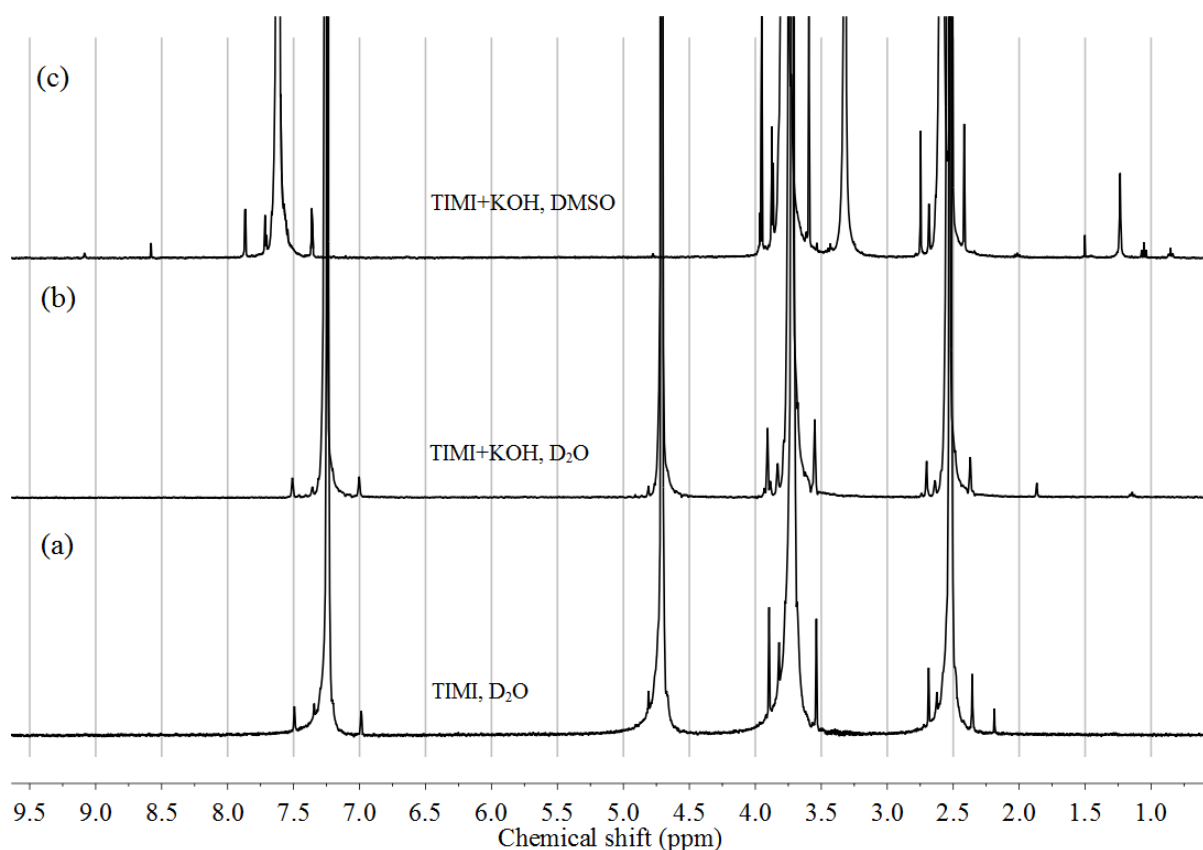
A small molecule analogue (1,2,3-Trimethylimidazolium iodide (TIMI)) was synthesized to study the possible decomposition mechanism of DIm-PPO AEMs in the alkaline environment with high pH. Specifically, 1, 2-dimethylimidazole (DIm) (5.0 g, 52.0 mmol) was dissolved in 150 mL acetone and then methyl iodide (CH<sub>3</sub>I) (16.2 mL, 260.0 mmol) was added drop-wise to the stirred solution. After stirring at room temperature for 24 hours, the white solid (TIMI) was filtered and washed with acetone, and dried under vacuum. [1] The <sup>1</sup>H NMR (Figure S1) spectrum of TIMI has been investigated and is consistent with the preconceived structure according to the reference [2].



**Figure S1.** <sup>1</sup>H NMR spectrum of TIMI.

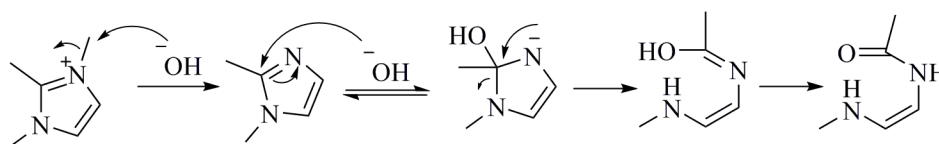
## 2. Alkaline stability of TIMI in KOH aqueous solution

TIMI(1.0g) was dissolved in 8 mL of 2mol dm<sup>-3</sup> KOH aqueous solution firstly. The resultant solution was stirred for 7 days at 60 °C. The mixture was extracted with ether (5 mL) for 4 times. Then, dried over Na<sub>2</sub>SO<sub>4</sub> was added to the ether solution and keep for 12 hours. After that, the ether was removed by evaporation to get the final products.



**Figure S2.**  $^1\text{H}$  NMR spectra of (a) TIMI and (b,c) the products of TIMI after treatment (in  $\text{D}_2\text{O}$  and DMSO respectively)

As shown in Figure S2, it is found that most of TIMI would maintain stable even after immersing in  $2\text{mol dm}^{-3}$  KOH aqueous solution at  $60\text{ }^\circ\text{C}$  for 7 days. For the decomposed part, the signals at 8.58 and 9.08 ppm appear at DMSO but disappear at  $\text{D}_2\text{O}$  should be assigned to the reactive protons of the decomposed product and may be attributed to the proton of amide and enamine (may form intermolecular hydrogen bonding interaction enamine ( $\text{CO}\cdots\text{HN}$ )) groups, respectively. To this end, a possible degradation mechanism is shown in Figure S3. It is noted that TIMI should firstly lose a methyl at C1 or C3 position under the attack of  $\text{OH}^-$  and then its ring will open at C2 position after the further attack to form a product with amide and enamine groups. The results are consistent with the FT-IR spectra, which show that DIm-PPO AEMs would lose the whole DIm cations at C1 position. Moreover, it seems that the degradation of TIMI is different from those of imidazolium without C2 substitution. For the latter, imidazolium ring should be attacked by  $\text{OH}^-$  at C2 position and open directly [1, 3]. These may be the reason why DIm-PPO AEMs shows the better alkaline stabilities than Im-PPO AEMs herein (especially in low temperature).



**Figure S3.** Possible decomposition mechanism of TIMI in KOH solution

**References:**

- [1] O.D. Thomas, K.J.W.Y. Soo, T.J. Peckham, M.P. Kulkarni, S. Holdcroft, Anion conducting poly(dialkyl benzimidazolium) salts, *Polymer Chemistry*, 2 (2011) 1641-1643.
- [2] N. Kumar, R. Jain, Convenient syntheses of bulky group containing imidazolium ionic liquids, *Journal of Heterocyclic Chemistry*, 49 (2012) 370-374.
- [3] Y. Ye, Y.A. Elabd, Relative Chemical Stability of Imidazolium-Based Alkaline Anion Exchange Polymerized Ionic Liquids, *Macromolecules*, 44 (2011) 8494-8503.