Supporting information

The reaction between CO_2 and chloroform in anion-functionalized ionic liquids with the formation of trichloroacetates

Mingzhe Chen, Congyi Wu, and Dezhong Yang *

School of Science, China University of Geosciences, Beijing 100083, China

Corresponding author:

Dezhong Yang, Email: yangdz@cugb.edu.cn

Experimental Sections

Materials and Characterization

N-ethyl-N,N-dimethyl-N-(2-methoxyethyl)ammonium bromide ([$MOEN_{211}$][Br], 99%) was purchased from Lanzhou Green Chemistry Co. Ltd. $CHCl_3$ (99%), imidazole (98%), pyrazole (98%), and 1,2,4-triazole (98%) were purchased from Innochem (Beijing) China. CO_2 (99.995%) and N_2 (≥99.99%) were supplied from Beijing ZG Special Gases Science Co. Ltd. (Beijing, China). Ambersep 900(OH) ion exchange resin was obtained from Alfa Aesar. FTIR spectra were collected on a Nicolet 6700 spectrometer with an attenuated total reflection (ATR) accessory. ^{1}H NMR (400 MHz) and ^{13}C NMR (100.6 MHz) spectra were recorded on a Bruker spectrometer with DMSO-d_6 or $CDCl_3$ as the references. When DMSO-d_6 was used as the solvent, the chemical shift values were obtained using the peaks of DMSO-d_6 (H: 2.50 ppm; C:39.52 ppm) as references. When $CDCl_3$ was used as the solvent, the peaks of TMS were used as references. When DMSO-d_6 and $CDCl_3$ were both contained in the samples, the peaks of DMSO-d_6 (H: 2.50 ppm; C:39.52 ppm) were used as references. $CHCl_3$ was dried at room temperature by 4Å molecular sieve prior to use.

Synthesis of ILs

Synthesis of [$MOEN_{211}$][Triz] and [N_{2222}][Triz]: The synthesis of [$MOEN_{211}$][Triz] was using the methods reported in the literature with some modifications.[1, 2] At first, the aqueous solution of [$MOEN_{211}$][OH] was obtained by flowing the solution of [$MOEN_{211}$][Br] in water through a column containing the Ambersep 900(OH) ion exchange resin. After that, equimolar 1,2,4-triazole was added into the solution of [$MOEN_{211}$][OH] ([$MOEN_{211}$][OH]: 1,2,4-triazole = 1:1), and above mixture was stirred at room temperature for about 2 hours. Then, [$MOEN_{211}$][Triz] was obtained after removing water in the mixture using a rotary evaporator. [$MOEN_{211}$][Triz] was further dried under vacuum at 70 °C prior to use. The method of synthesizing [N_{2222}][Triz] was similar to that of [$MOEN_{211}$][Triz].

The methods of synthesizing [$MOEN_{211}$][Im] and [$MOEN_{211}$][Pyr] were also similar to that of [$MOEN_{211}$][Triz].

Absorption of CO_2

The CO_2 absorption procedures can be found in our previous work.[3, 4] CO_2 was bubbled by a long steel needle into the absorbents (IL or DMSO-d_6 solution of IL) contained in a glass tube, and another short needle was used for CO_2 outlet. The weight change of the glass tube before and after CO_2 capture was measured and used to calculate the capacity of absorbents.

The preparation of NMR and FTIR samples

The samples of IL+DMSO-d_6 and IL+DMSO-d_6+CO_2:

The DMSO-d_6 solutions of IL before and after CO_2 capture were used directly to record NMR and FTIR spectra. The concentration of $[MOEN_{211}][Triz]$ and $[N_{2222}][Triz]$ in DMSO-d_6 before CO_2 capture was 40 wt% and 20 wt%, respectively.

The samples of $[MOEN_{211}][Triz]+CO_2+CDCl_3$:

After the absorption of CO_2 by $[MOEN_{211}][Triz]$ reached saturation, $CDCl_3$ was added into the mixture $[MOEN_{211}][Triz]+CO_2$ to obtain $[MOEN_{211}][Triz]+CO_2+CDCl_3$, which was stirred at room temperature for about 20 min. The concentration of $[MOEN_{211}][Triz]$ in $[MOEN_{211}][Triz]+CO_2+CDCl_3$ mixture was about 40 wt%.

The sample of $[MOEN_{211}][Triz]+CDCl_3$ was obtained by mixing $[MOEN_{211}][Triz]$ and $CDCl_3$ at room temperature, and the concentration of $[MOEN_{211}][Triz]$ was 40 wt%.

The samples of IL+DMSO-d_6+$CHCl_3$ and IL+DMSO-d_6+CO_2+$CHCl_3$:

The samples of IL+DMSO-d_6+$CHCl_3$ were prepared by adding $CHCl_3$ into IL+DMSO-d_6 solutions, and the molar ratio of $CHCl_3$ to IL was 2:1.

After CO_2 absorption by IL+DMSO-d_6 solution reached saturation, $CHCl_3$ was added into the carbon-captured solution to obtain the mixture IL+DMSO-d_6+CO_2+$CHCl_3$, which was stirred at room temperature for about 20 min. The molar ratio of added $CHCl_3$ to IL in IL+DMSO-d_6+CO_2 was 2:1.

The method of preparing the sample of $[N_{2222}][Triz]$ +DMSO-d_6+CO_2+$CDCl_3$ was similar to that of $[N_{2222}][Triz]$ +DMSO-d_6+CO_2+$CHCl_3$.

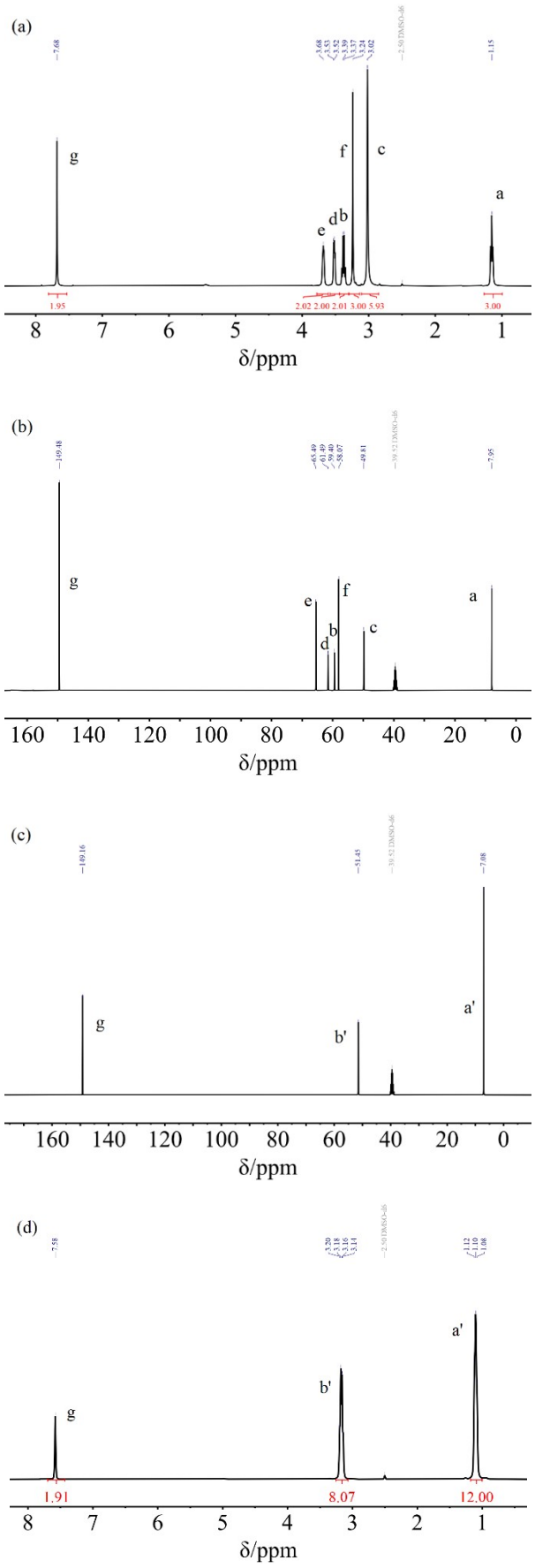

Fig. S1 The NMR spectra of [$MOEN_{211}$][Triz] (a and b) and [N_{2222}][Triz] (c and d) in DMSO-d_6.

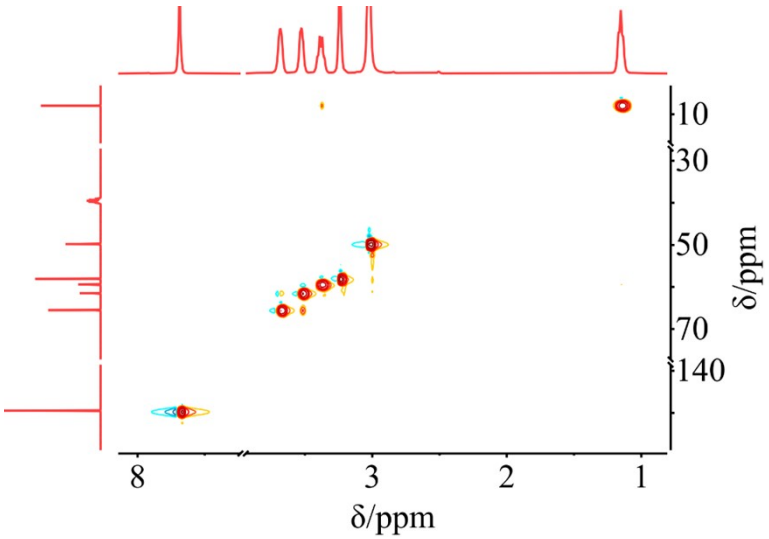

Fig. S2 The ^{1}H-^{13}C HSQC NMR spectra of $[MOEN_{211}][Triz]$ in DMSO-d_6.

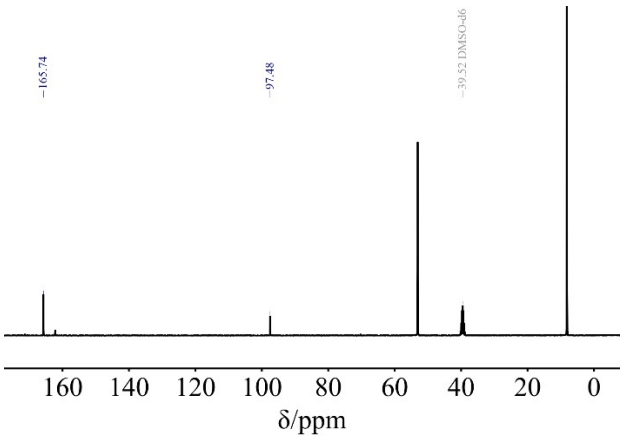

Fig. S3 The ^{13}C NMR spectra of $[N_{2222}][Cl]$: CCl_3COONa (1:1) in the solvent containing D_2O and DMSO-d_6.

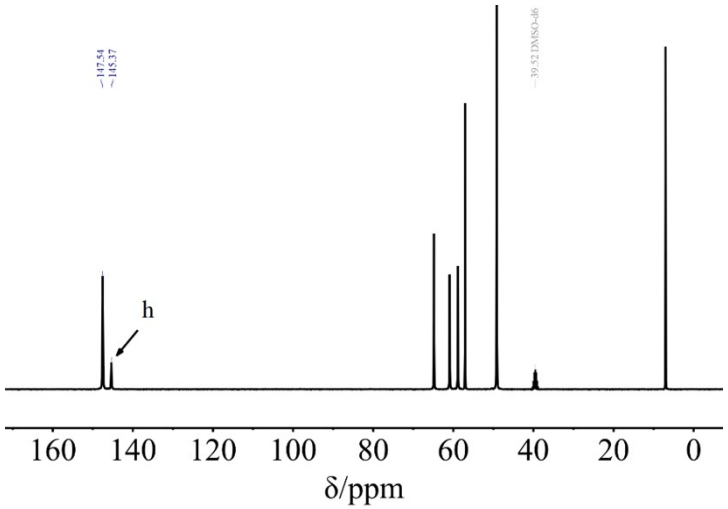

Fig. S4 The ^{13}C NMR spectra of $[MOEN_{211}][Triz]+CO_2$ using DMSO-d_6 as the external solvent.

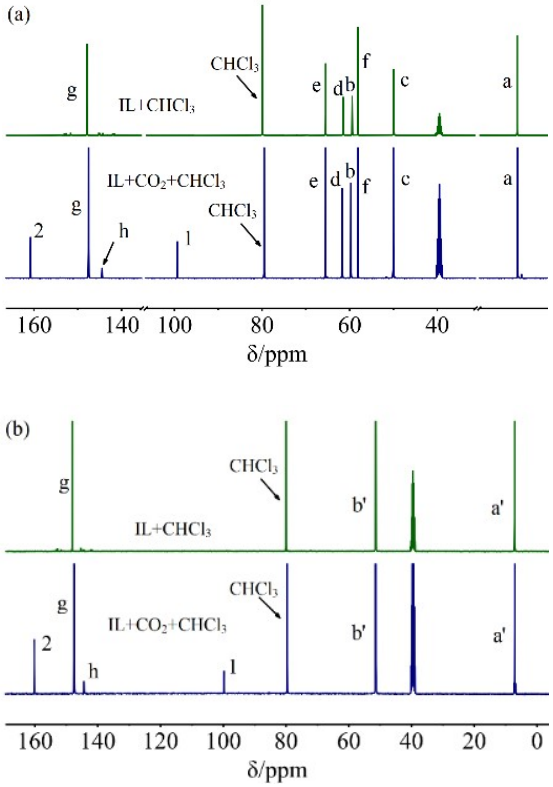

Fig. S5 The ^{13}C NMR spectra of $[MOEN_{211}][Triz]+CHCl_3$ (a) and $[N_{2222}][Triz]+CHCl_3$ (b) with and without CO_2 in DMSO-d_6.

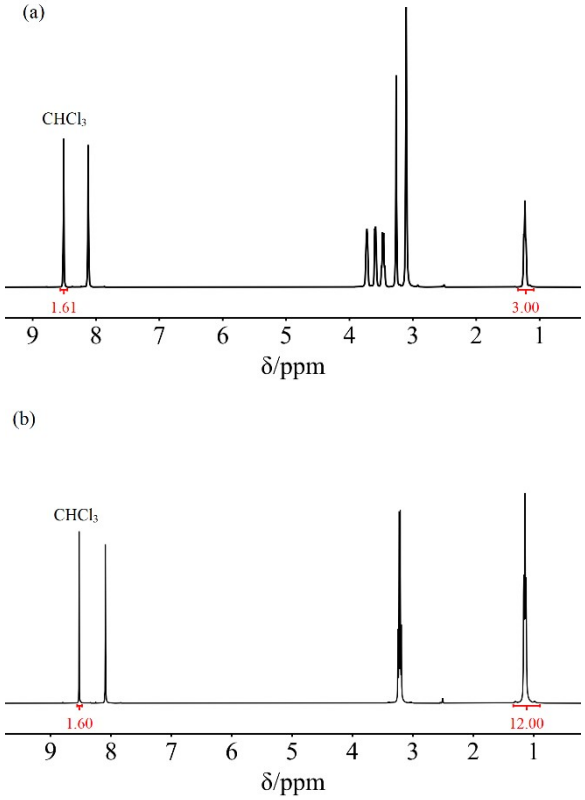

Fig. S6 The ^{1}H NMR spectra of $[MOEN_{211}][Triz]+CO_2+CHCl_3$ (a) and $[N_{2222}][Triz]+CO_2+CHCl_3$ (b) in DMSO-d_6.

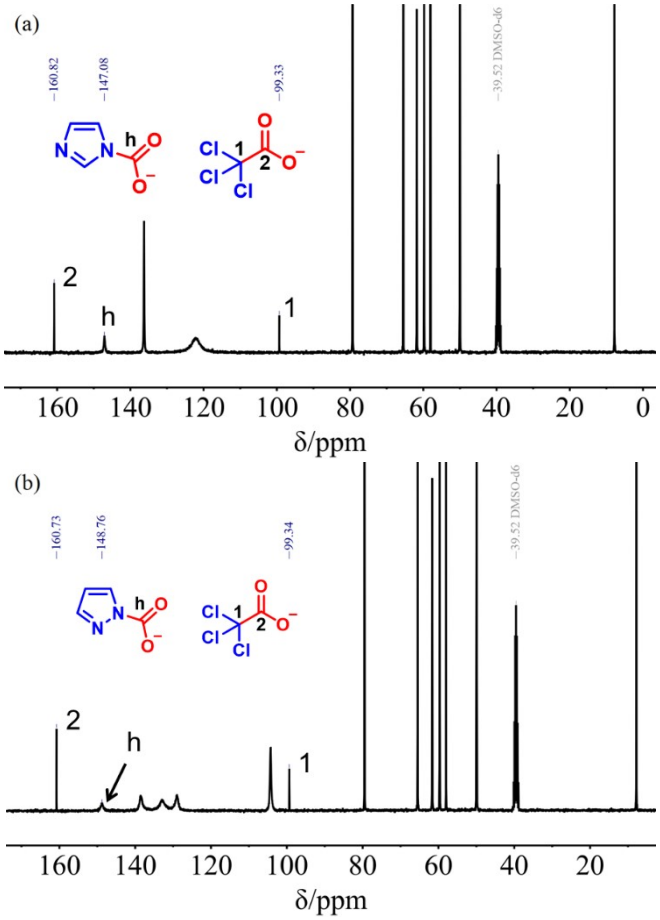

Fig. S7 The ^{13}C NMR spectra of $[MOEN_{211}][Im]+CO_2+CHCl_3$ (a) and $[MOEN_{211}][Pyr]+CO_2+CHCl_3$ (b).

References

1. C. Wang, X. Luo, H. Luo, D.-e. Jiang, H. Li and S. Dai, *Angew. Chem. Int. Ed.*, 2011, **50**, 4918-4922.
2. Y. Huang, G. Cui, Y. Zhao, H. Wang, Z. Li, S. Dai and J. Wang, *Angew. Chem. Int. Ed.*, 2017, **56**, 13293-13297.
3. D. Yang, M. Lv and J. Chen, *Chem. Commun.*, 2019, **55**, 12483-12486.
4. M. Chen, Y. Zhou, Q. Lu and D. Yang, *Chem. Commun.*, 2024, **60**, 7061-7064.