Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

A depth-suitable and water-stable trap for CO_2 capture

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Experimental

Materials

Tetraethylammonium chloride (98%), tetramethylammonium chloride (99%), octanoicacid (99%), 1,4-cyclohexanedicarboxylic acid (98%), 1,3,5-benzenetricarboxylic acid (99%) and sodium sulfite (98%) were supplied by Innochem Co., Ltd. Methyltrioctylammonium chloride (99%), dipotassium hydrogen phosphate (99%), tetrabutylammonium bromide (99%) and tripotassium phosphate (99%) were obtained from J&K Co., Ltd. Tributyldodecylphosphonium bromide (98%) and 2,2-dimethylbutyric acid (98%) were purchase from Aladdin Co., Ltd. Tributyl-n-octylphosphonium bromide (98%) was got from TCI Co., Ltd. Butyltriethylammonium bromide (97%) and Phenolphthalein (98%) were obtained from Alfa Aesar Co., Ltd. 2-Ethylhexanoic acid (99%) and 2-propylpentanoic acid (99%) were supplied by Acros Co., Ltd. Trimethylbutylammonium chloride (97%) and tributylhexdecylphosphonium bromide (97%) were obtained from Ark Co., Ltd. Tribytylhexylphosphonium bromide (99%)was got from Centre for Green Chemistry and Catalysis, LICP, CAS. CO_2 (99.999%), SO_2 (99.9%) and H_2S (99.9%) were supplied by Beijing Analytical Instrument Factory. Other reagents were all analytical grade and were provided by Sinopharm Chemical Reagent Co., Ltd. All reagents were used as received.

Carboxylates synthesis and characterization

All carboxylates are synthesized and dried before using following the procedures reported in literatures.[25,29] Representative carboxylate ionic liquid were characterized by ^{1}H-NMR, ESI-MS and IR. ^{1}H-NMR were presented in Fig. S3a and Fig. S7. IR were presented in Fig. S8. ESI-MS: tetrabutylammonium 2-ethylhexanoate (+: 242.3, -: 143.2), tributylhexylphosphonium 2-ethylhexanoate (+: 287.3, -: 143.2), tributyloctylphosphonium 2-ethylhexanoate (+: 315.3, -: 143.2), tributyldodecylphosphonium 2-ethylhexanoate (+: 371.4, -: 143.2), methyltrioctylammonium 2-ethylhexanoate (+: 368.4, -: 143.2), tributylhexylphosphonium 2-propylpentanoate (+:287.3, -: 143.2).

Absorption study

The phase behavior studies were carried out in glass bottles with magnetic stir. CO_2 (SO_2 or H_2S) was provided with balloons.

In a typical absorption test, carboxylates and water needed were added in. The bottle was connected with balloon, and kept stirring for 12 hrs. The sorption tests at 80 ^{o}C were carried out in an oil bath. All CO_2 sorptions are determined by titrating with NaOH solution, phenolphthalein as detector, after replacement of CO_2 in bottle's up space with air five times.

In separation of surfactant test, 50 mg tributylhexadecylphosphonium bromide, 16 mg sodium 2-ethylhexanoate and 5 g water were added in a bottle, kept stirring until the solution is clear. CO_2 was injected with a speed about 20 ml/min, and the solution

became completely opaque in three minutes. Then the opaque mixture was exposed to air and kept stirring, and the solution became clear again in several minutes.

Sample preparation and characterization

For sample of sodium carbonate plus 1,4-cyclohexanedicarboxylic acid, 0.106 g sodium carbonate, 0.172 g 1,4-cyclohexanedicarboxylic acid and 1 ml ethanol were added in bottle, then sealed with cap and kept stirring for 12 hrs. After ethanol in the mixture was brought out with CO_2 flow, the solid left in the bottle was tested with XRD.

For other solids from 1,4-cyclohexanedicarboxylic acid, 1,3,5-benzenetricarboxylic acid react with sodium sulfite, dipotassium hydrogen phosphate and tripotassium phosphate are prepared as follows: 2 mmol carboxylic acid, corresponding weight of salts and 2 ml ethanol were added in bottle and kept stirring for 12 hrs, than ethanol is removed by rotary evaporation.

Powder XRD analysis was performed on the X-ray diffractometer (Model D/MAX2500, Rigaka) with Cu-Kα radiation. ^{1}H NMR analysis was carried out on Bruck Avance III 400 HD NMR spectrometer. The SEM characterizations were carried out using an HITACHI SU-8020. Infrared Radiation (IR) spectroscopy was recorded on Bruker Tensor-27 FT-IR Spectrometer.

All DFT calculations were performed with the Gaussian 09 package,[30] using the B3-LYP functional and 6-31G+(d) basis set.

References:

29 Suarez, P. A. Z., Dullius, J. E. L., Einloft, S., de Souza R. F. and J. Dupont, *Polyhedron*, 1996, **15**, 1217–1219 (1996).

30 Frisch, M. J. et al. Gaussian 09, Revision A.01, Gaussian, Inc., Wallingford, CT, 2009.

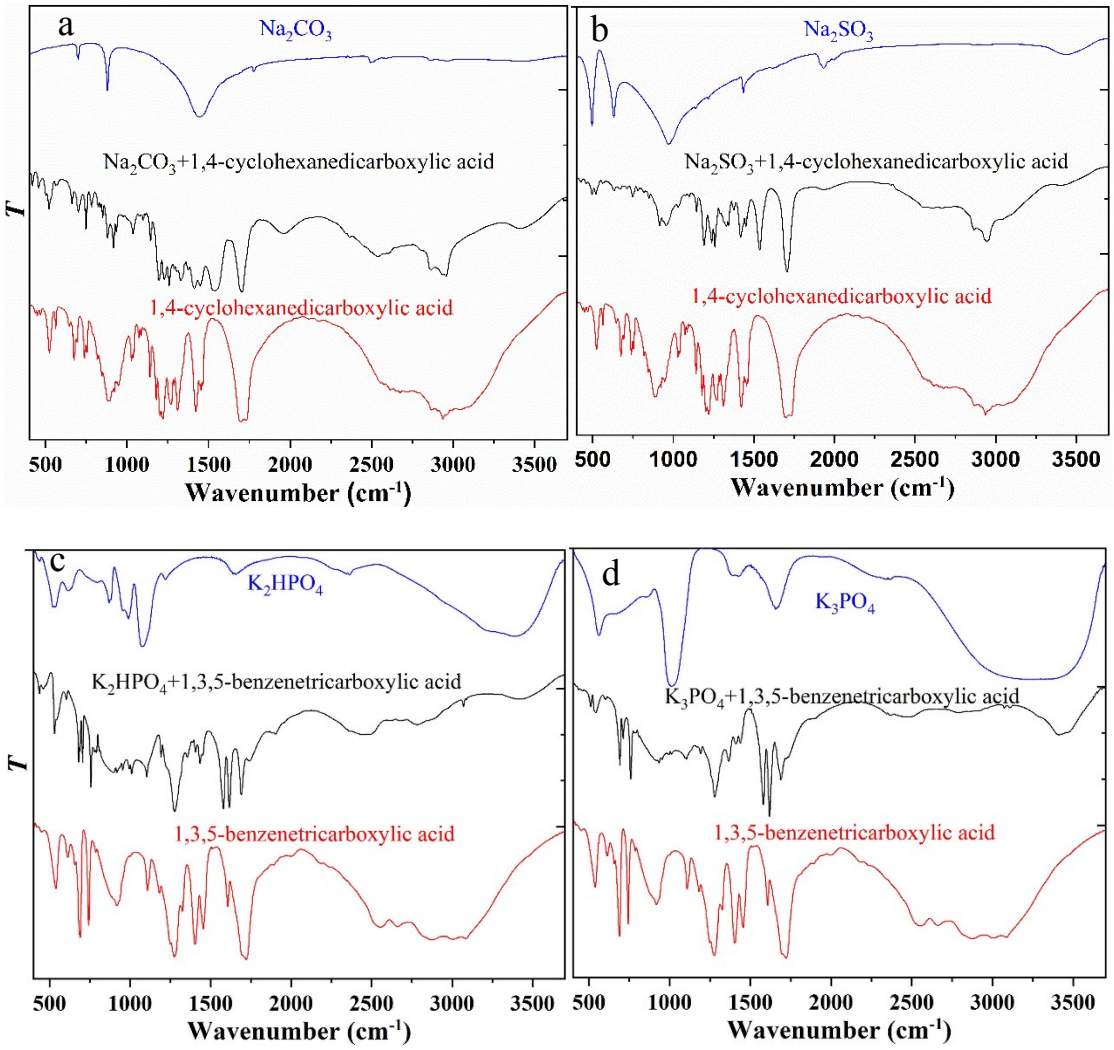


Fig. S1 IR test of united hydrogen bonds products.

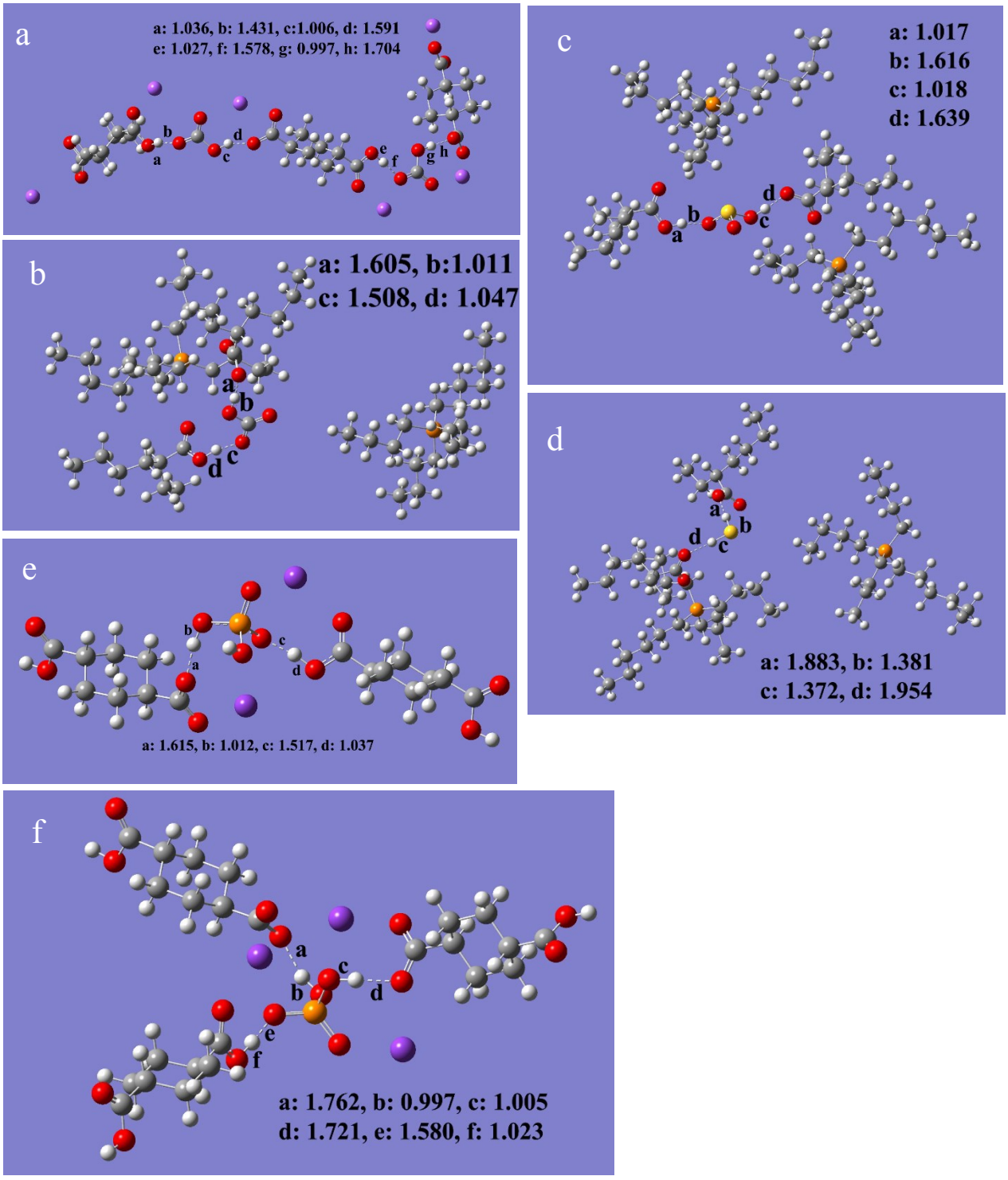
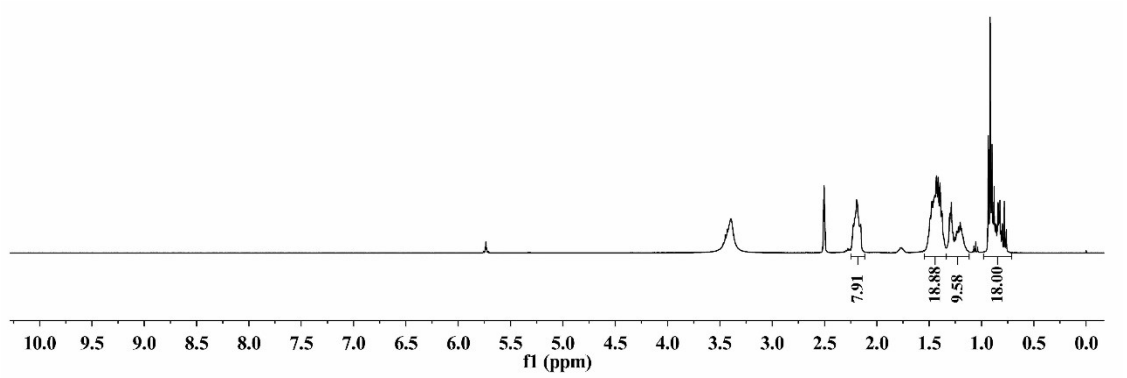


Fig. S2 Spatial conformation of united hydrogen bonds products.
a~g are got from DFT calculation [DFT/B3-LYP, 6-31+G(d)]. (**a**) sodium 1,4-Cyclohexanedicarboxylate + CO_2 + H_2O; (**b**) Tributylhexylphosphonium 2-ethylhexanoate (**1**) + CO_2 + H_2O; (**c**) **1** + SO_2 + H_2O; (**d**) **1** + H_2S; (**e**) 1,4-Cyclohexanedicarboxylic acid + K_2HPO_4; (**f**) 1,4-Cyclohexanedicarboxylic acid + K_3PO_4.

a



b

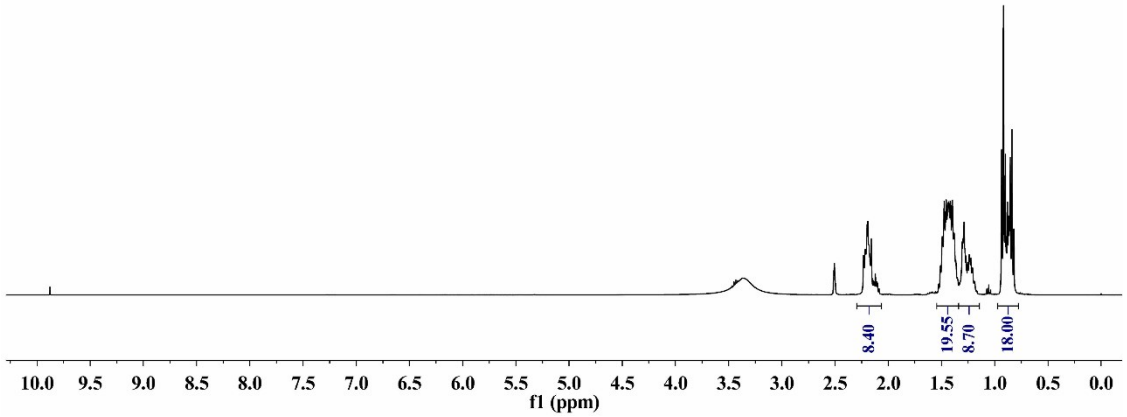


Fig. S3 ^{1}H NMR study of carboxylates absorbing SO_2. a) Tributylhexylphosphonium 2-ethylhexanoate (**1**) In DMSO-d6; b) Top phase in **1** + water + SO_2 system in DMSO-d6.

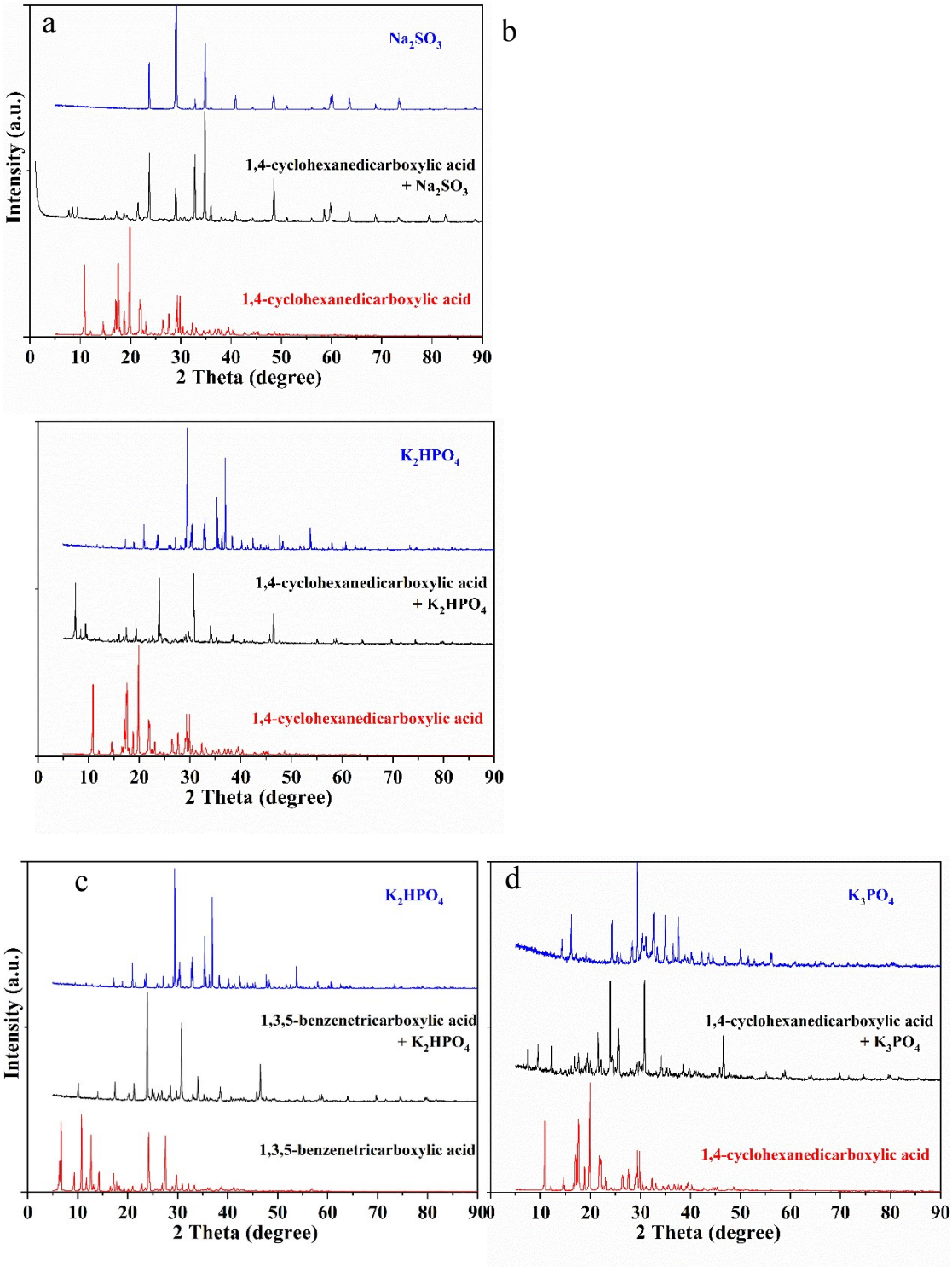


Fig. S4 Powder XRD patterns of united hydrogen bonds products.

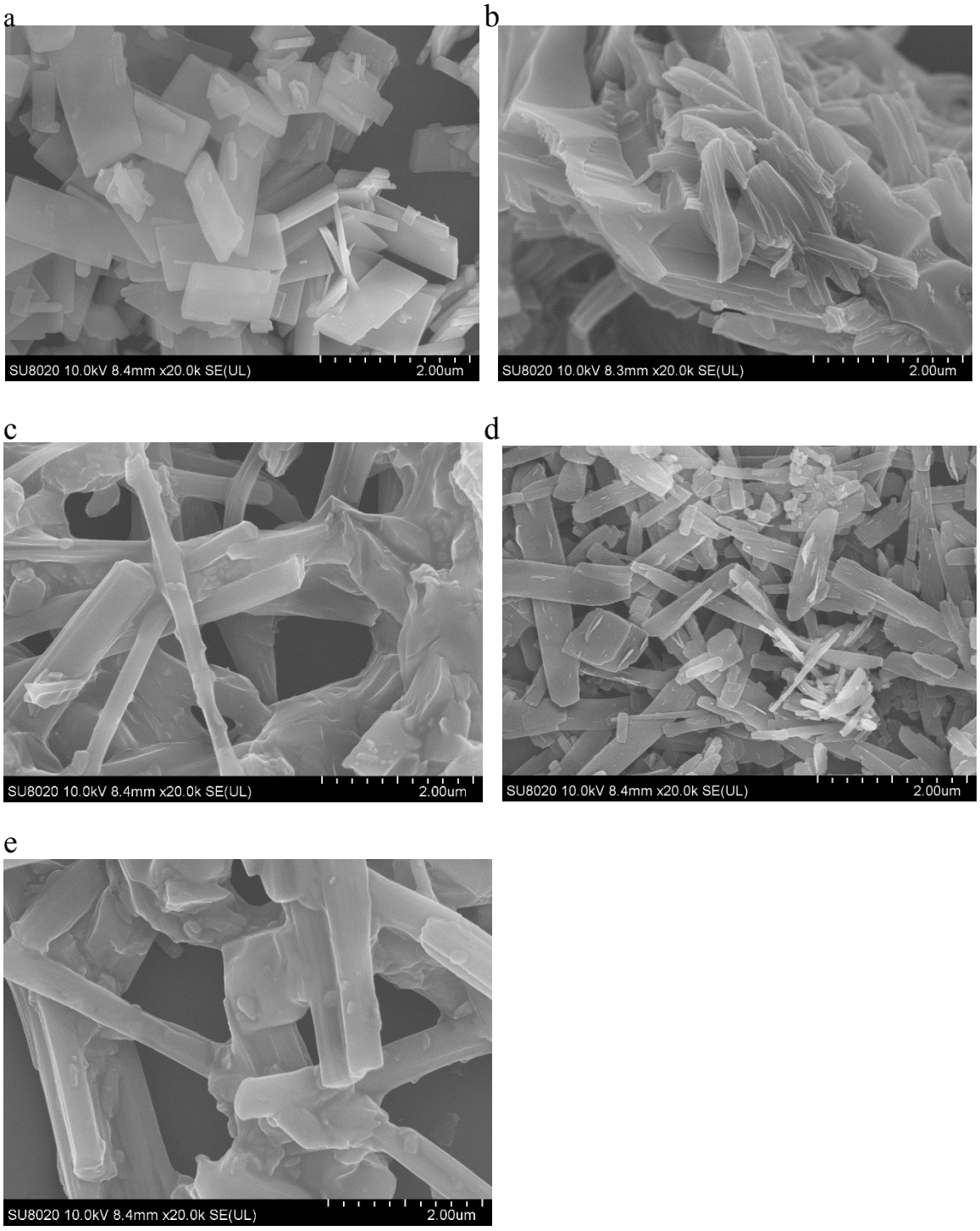


Fig. S5 SEM photos of united hydrogen bonds products.
(**a**) 1,3,5-Benzenetricarboxylic acid + K_2HPO_4; (**b**) 1,4-Cyclohexanedicarboxylic acid + Na_2SO_3; (**c**) 1,4-Cyclohexanedicarboxylic acid + K_2HPO_4; (**d**) 1,3,5-Benzenetricarboxylic acid + Na_2SO_3; (**e**) 1,4-Cyclohexanedicarboxylic acid + K_3PO_4.

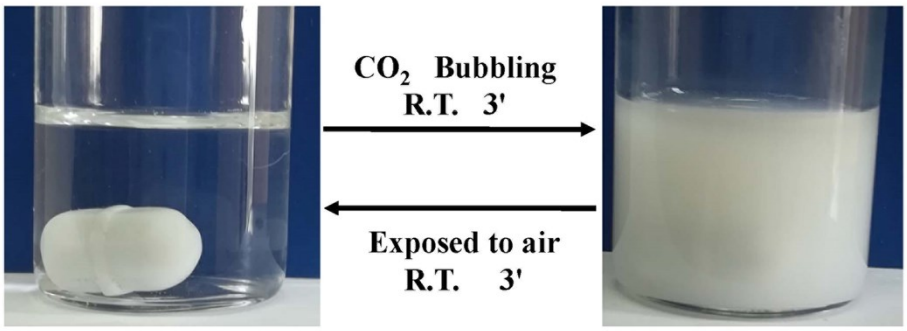


Fig. S6. Some surfactants separation from water.
50 mg tributylhexadecylphosphonium bromide and 16 mg sodium 2-ethylhexanoate in 5 g water.

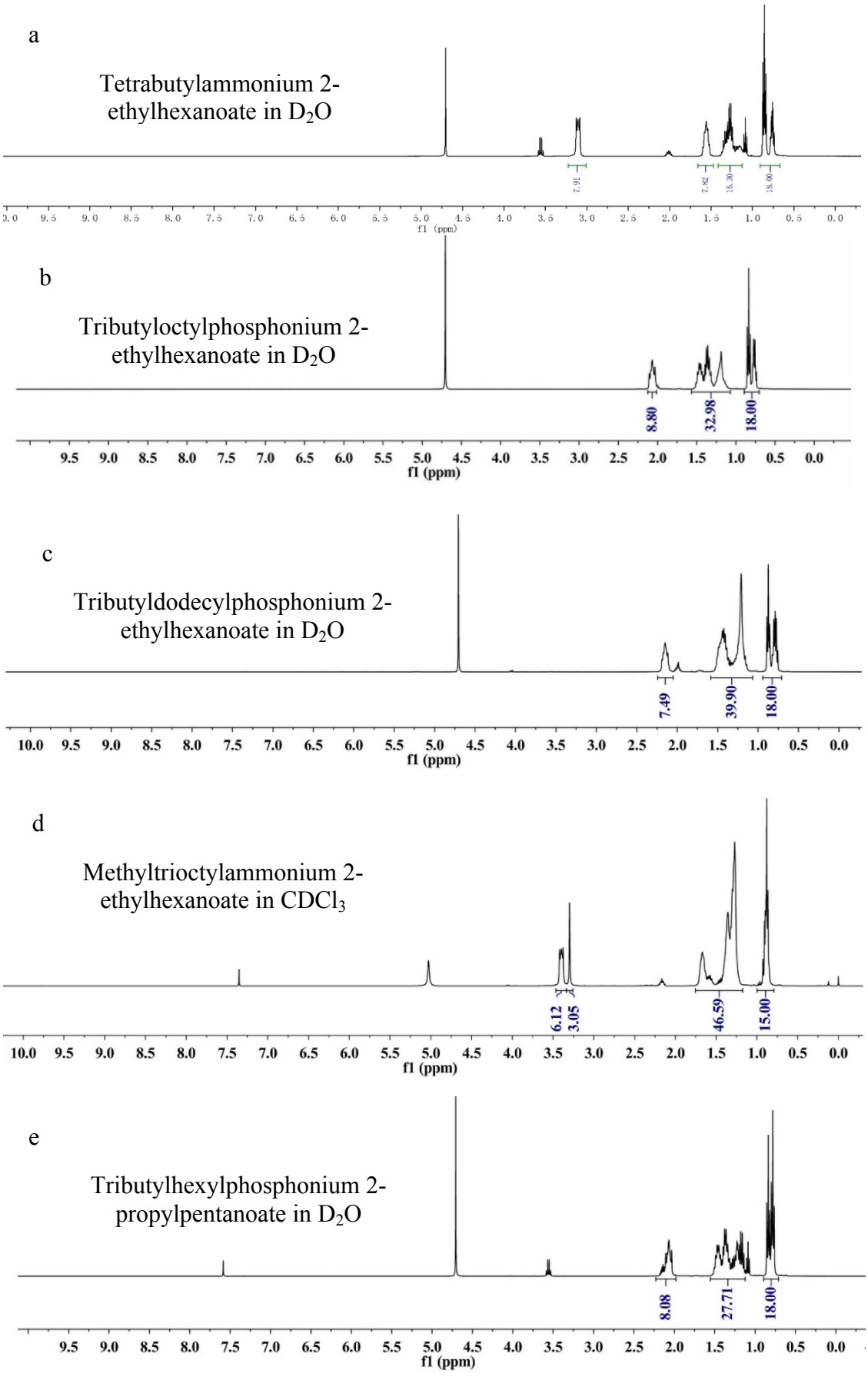


Fig. S7 ^{1}H NMR of carboxylate ionic liquids.

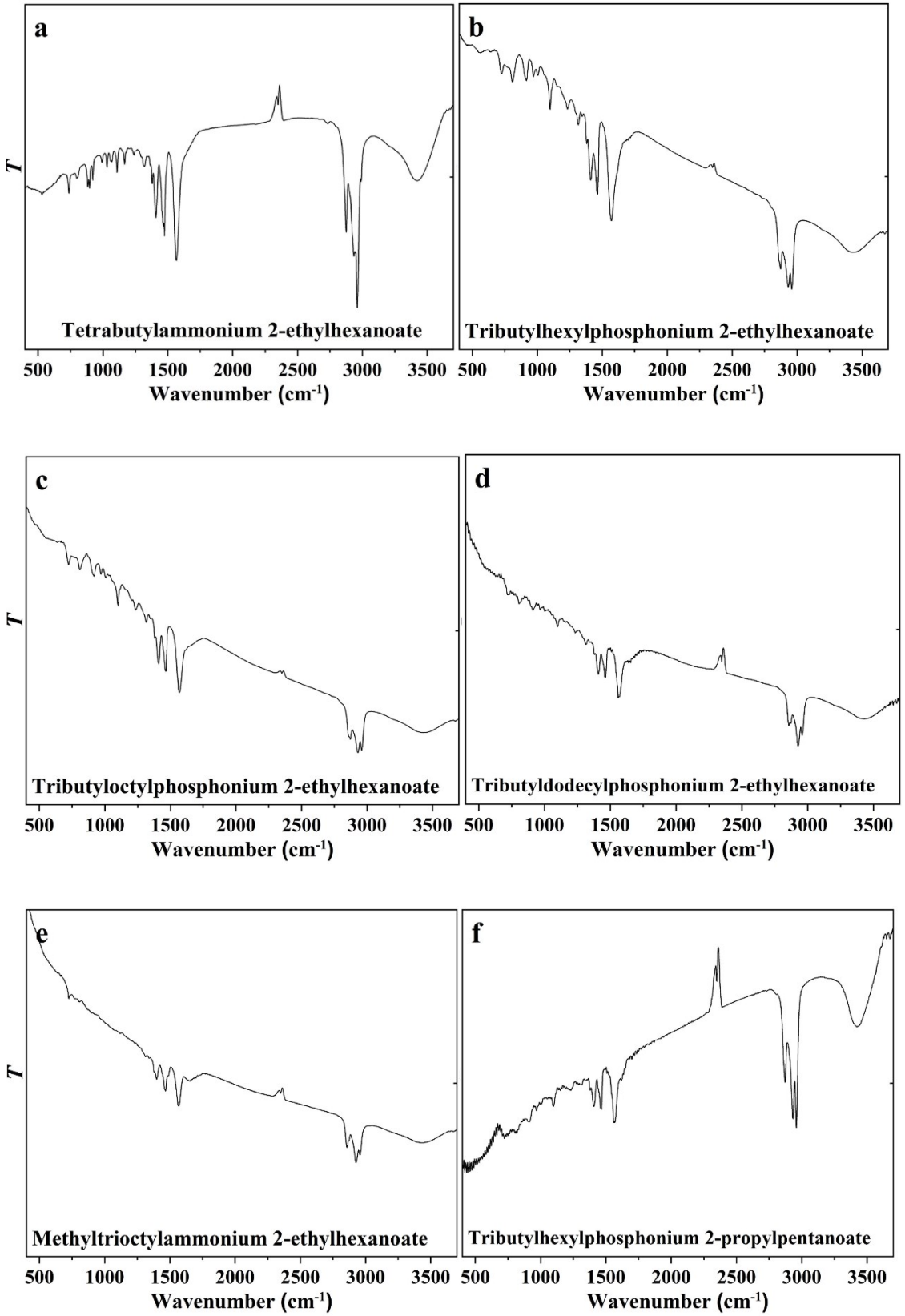


Fig. S8 IR of carboxylate ionic liquids.