Coordination effect-regulated CO_2 capture with alkali metal onium salts/crown ether system

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1. General experimental methods:

Caution

Experiments using compressed gase (CO_2) are potentially hazardous and must only be carried out by using the appropriate equipment and under rigorous safety precautions.

Materials

All the reagents used in this work are purchased from Sigma-Aldrich Company and directly used without further purification. CO_2 with a purity of 99.99% is commercially available.
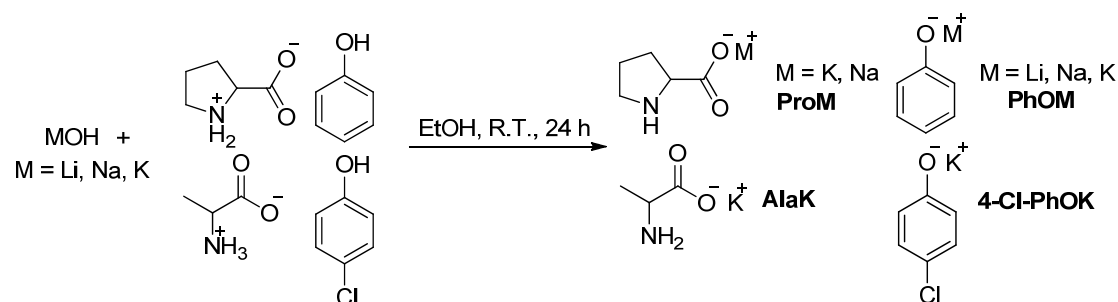
Experimental methods

^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 MHz spectrometer (^{1}H NMR, 300 MHz, ^{13}C NMR, 75 MHz) in $CDCl_3$, the chemical shifts were referenced to the residual solvent. FTIR data were obtained using a Bio-Rad Excalibur FTS-3000 spectrometer.

General procedure for absorption and desorption of CO_2

In a typical procedure, CO_2 capture was carried out in a glass container with an inner diameter of 10 mm. The absorbents were charged into the reactor at room temperature. Then, a needle was used for CO_2 bubbling, which was inserted in the bottom of the flask. The absorption reaction was conducted at 25 °C with a CO_2 bubbling rate of 80 mL/min. The amount of CO_2 absorbed was determined by an analytical balance with an accuracy of ± 0.0001 g every five minutes. In a typical desorption of CO_2, N_2 of atmospheric pressure is bubbled through the absorption system at 50 °C using the same equipment and procedure as CO_2 capture. Absorption/desorption is determined by several cycles of repeated experiments.

2. Synthesis of alkali metal onium salts:

The alkali metal onium salts were prepared from the neutralization of various amino acids or phenols with alkali metal hydroxides. For example, in a typical procedure for the synthesis of ProK, equimolar proline was added to an ethanolic solution of KOH. Then, the mixture was stirred at room temperature for 24 h. Subsequently, EtOH was distilled off at 70 °C under vacuum. The obtained solid was washed with ethyl ether three times and dried under vacuum at 80 °C for 24 h.

3. Characterization of ProK/18-crown-6/PEG300 and 4-Cl-PhOK/18-crown-6/PEG300 (^{1}H, ^{13}C NMR and FT-IR) before and after CO_2 capture

18-crown-6

^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.64 (s, 24H);

ProK

^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.77 (t, ^3J = 7.8 Hz, 1H), 3.21-3.29 (m, 1H), 2.96-3.05 (m, 1H), 2.11-2.21 (m, 1H), 1.81-1.99 (m, 3H);

ProK/18-crown-6

^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.61-3.62 (m, 25H), 3.05-3.13 (m, 1H), 2.81-2.89 (m, 1H), 2.03-2.16 (m, 1H), 1.86-1.97 (m, 1H), 1.58-1.72 (m, 2H);

ProK/18-crown-6/PEG300

^{1}H NMR (CDCl$_3$, 300 MHz) δ 3.44-3.58 (m, 78H), 2.94-3.01 (m, 1H), 2.73-2.82 (m, 1H), 1.92-2.04 (m, 1H), 1.79-1.88 (m, 1H), 1.49-1.65 (m, 2H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ **177.7**, 77.2, 72.0, 71.9, 69.3-69.7, 61.0, 60.2, 60.1, 46.0, 30.4, 25.1.

ProK/18-crown-6/PEG300 + CO$_2$

^{1}H NMR (CDCl$_3$, 300 MHz) δ 3.98 (s, 1H), 3.56-3.70 (m, 82H), 3.19-3.29 (m, 2H), 2.25 (s, 1H), 1.97-2.09 (m, 1H), 1.70-1.79 (m, 2H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 175.9, 157.7, 77.2, 72.3, 72.1, 69.5-70.0, 60.8, 60.5, 46.4, 28.9, 24.1.

4-Cl-PhOK

^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.11 (s, 1H), 7.08 (s, 1H), 6.71 (s, 1H), 6.68 (s, 1H);
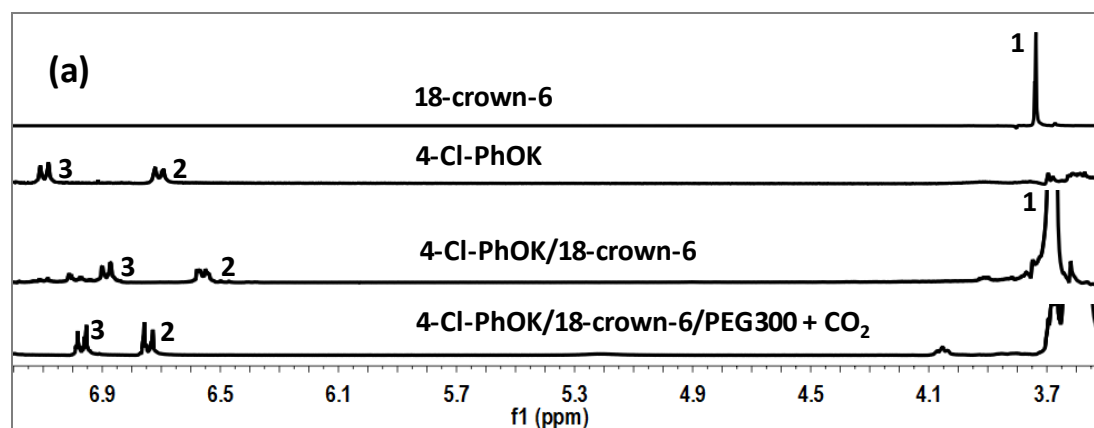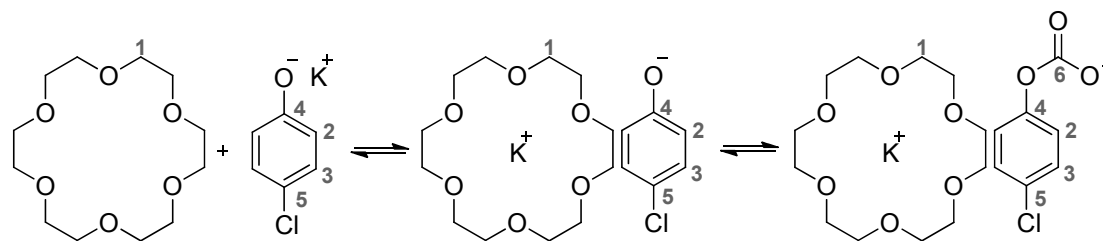
4-Cl-PhOK/18-crown-6

^{1}H NMR (CDCl$_3$, 300 MHz) δ 6.86-6.90 (m, 2H), 6.53-6.57 (m, 2H), 3.60 (s, 84H);

4-Cl-PhOK/18-crwon-6/PEG300

^{1}H NMR (CDCl$_3$, 300 MHz) δ 6.99 (s, 1H), 6.96 (s, 1H), 6.76 (s, 1H), 6.73 (s, 1H), 3.56-3.70 (m, 140H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 165.1, 129.2, 128.0, 119.0, 115.8, 77.2, 72.3, 72.2, 72.18, 69.5, 69.9, 60.4-60.6.

4-Cl-PhOK/18-crown-6/PEG300+CO$_2$

^{1}H NMR (CDCl$_3$, 300 MHz) δ 6.95-6.99 (m, 2H), 6.73-6.76 (m, 2H), 3.55-3.70 (m, 94H); ^{13}C NMR (CDCl3, 75 MHz) δ 158.7, 157.4, 128.0, 120.3, 117.2, 77.2, 71.9, 69.4-69.8, 60.5.
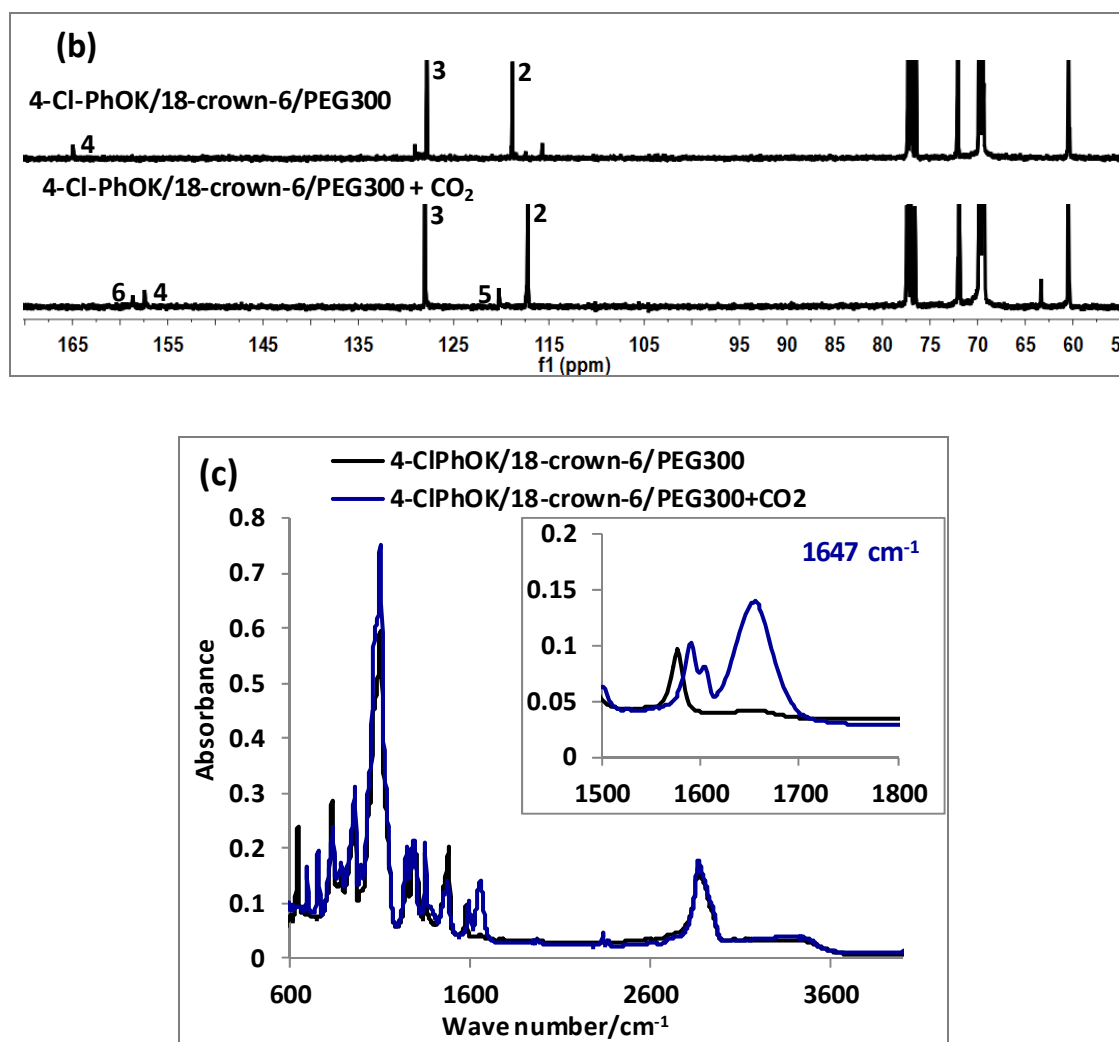
Figure S1. (a) ^{1}H NMR spectra (CDCl$_3$, 300 MHz) of 18-crown-6, 4-Cl-PhOK, 4-Cl-PhOK/18-crown-6 and 4-Cl-PhOK /18-crown-6/PEG300+CO$_2$ (from top to bottom); (b) ^{13}C NMR spectra (CDCl$_3$, 75 MHz) of 4-Cl-PhOK /18-crown-6/PEG300 before (top) and after (bottom) CO$_2$ absorption. (c) FT-IR spectrum of 4-Cl-PhOK /18-crown-6/PEG300 before (black line) and after (blue line) CO$_2$ absorption.

4. Scanning thermogravimetric analysis (TGA) and reusability of the 4-Cl-PhOK/18-crown-6/PEG300 system
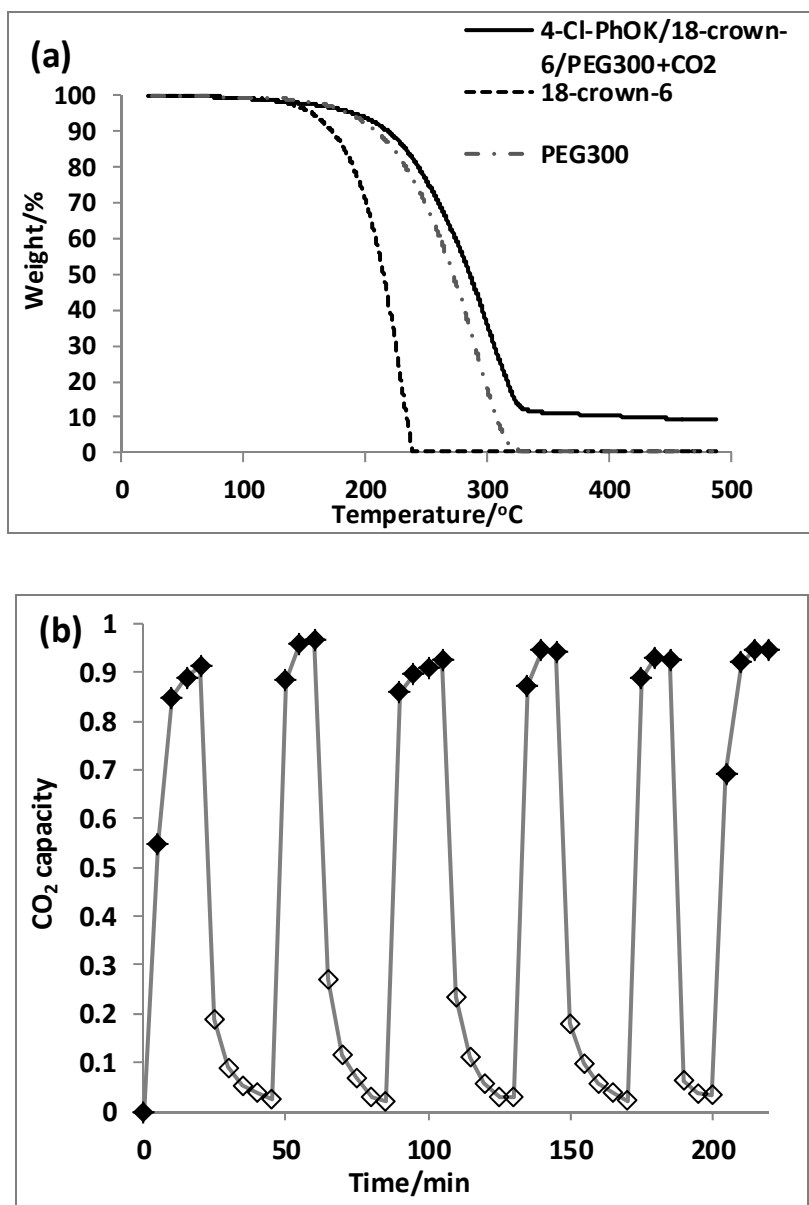
Figure S2. (a) Scanning thermogravimetric analysis (TGA) results for 4-Cl-PhOK /18-crown-6/PEG300+CO_2 with a 10 $^\circ$C min^{-1} temperature ramping rate to 500 $^\circ$C. (b) Six consecutive cycles of CO_2 absorption ($\blacklozenge$ 15 min, 25 $^\circ$C, CO_2) and release ($\lozenge$ 20 min, 80 $^\circ$C, N_2) by 4-Cl-PhOK/18-crown-6/PEG300 system, data were obtained every 5 min.

5. IR spectra of other absorption systems before and after CO₂ capture