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Separations Using Carbon Dioxide

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Separation processes are central to the chemical, materials, energy, and pharmaceutical industries. Traditional separations involve distillations, extractions, membrane transport processes, crystallizations, and various chromatographic techniques, but today molecular recognition is becoming an area of emerging importance. The impact of molecular receptors in chemistry and separation technology has been very impressive.[1,2] A great number of chemically, industrially and biologically significant molecules and ions have been complexed. At the same time, separations through molecular recognition still pose a number of problems. Most of “host−guest” complexes exist in solution and often break or dissociate upon separation.[2] The use of large quantities of solvents, that may often be toxic, is also of great concern. In polymeric materials, functionalized with molecular recognition sites, complexation events take place not in homogeneous solution but at the solid−liquid or gas−solid interface and, often, are not effective. We describe here a separation strategy, which combines selective solution complexation by macrocyclic receptors *and*, recently described by us, CO_2-induced molecular switching, leading to effective precipitation.[3,4] Earlier, we established that unique materials could be prepared from CO_2 and primary amines, especially derived from amino acids.[3] CO_2 reacts rapidly with amine building blocks, at normal temperatures and pressures, with the formation of alkylammonium $-^+NH_3 \cdots O^-C(O)NH-$ carbamate salts.[5] The carbamate formation is rapid at room temperature, and loss of CO_2 from the formed ammonium salt can be readily achieved upon gentle heating (~60 °C) or simply by addition of HCl or TFA.[6] These carbamate materials can therefore be called supramolecular. Supramolecular polymers represent a novel class of macromolecules, in which monomeric units are held together by reversible forces.[7]

Our separation strategy involves supramolecular polymers and is presented in Figure 1. Receptors can be prepared that also possess multiple primary amino groups capable of reacting with CO_2. After complexation of target species by these receptors, CO_2 is introduced (room temperature, 1 atm) and reacts with the terminal amino groups of the receptors. As the result, *cross-linked* carbamate polymers will form and precipitate. These polymers incorporate the target complexes within their structures. The process will thus *separate* the complexed species from the bulk solution and uncomplexed species. The precipitated materials can be collected and stored. On the other hand, they can release CO_2 and dissociate back to monomers upon heating or the addition of acid and subsequently release the complexed species in its pure form.

To prove the principle, dibenzo-18-crown-6 derivative **1** was prepared (Figure 2); it is also functionalized with two *l*-lysine fragments on the periphery (see Supporting Information for the experimental procedures). It was established already by C. J. Pedersen that dibenzo-18-crown-6 ether can selectively extract potassium (K^+) cations in the presence of other cations.[8] More recently we showed that free lysine ε-amino groups readily react with CO_2 in apolar solution.[3] To work with amino acids is convenient. They are readily available either from commercial sources or via one or two synthetic steps, utilizing conventional peptide protocols. They are chiral and biologically friendly and can be easily functionalized on the periphery.

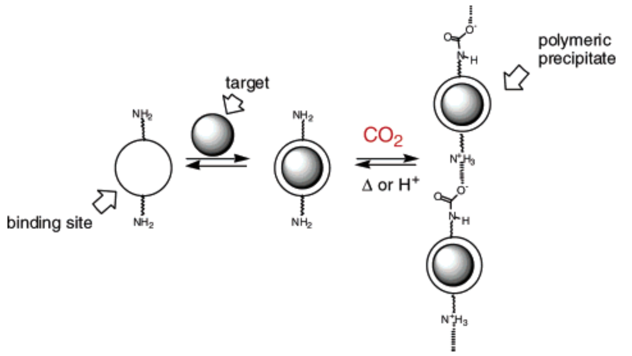

Figure 1. Separation strategy uses CO_2 as a cross-linking agent in the formation of supramolecular carbamate polymers.

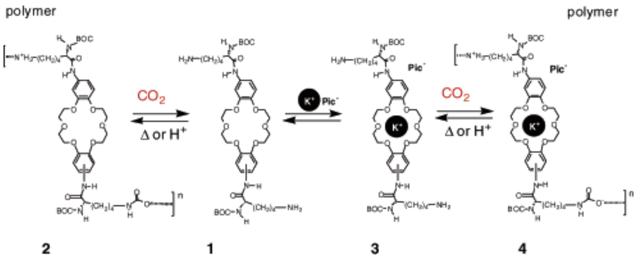

Figure 2. Reaction with CO_2 leads to the formation of insoluble ($CHCl_3$) supramolecular polymeric materials **2** and **4**, which can be separated by simple filtration. Polymer **4** also separates K^+Pic^- by complexation. Polymers **2** and **4** can dissociate back to the corresponding monomers upon heating or addition of acid.

Reaction of CO_2 with crown ether **1** in $CHCl_3$ leads to the formation of ammonium carbamate salt **2**. While insoluble in $CHCl_3$, **2** can be dissolved in DMSO-d_6 and fully characterized. The ^1H NMR spectrum clearly shows two 1:1 signals at 2.51 and 2.87 ppm, which correspond to two different α-CH_2N methylene groups from the carbamate and ammonium ends (Figure 3). The spectrum also showed a signal at 6.42 ppm corresponding to the carbamate NH proton. In the COSY spectrum, a cross-peak between the carbamate NH signal and the carbamate α-CH_2N methylene group at 2.87 ppm can be clearly seen. To further prove carbamate salt formation, ^{13}C-labeled CO_2 ($^{13}CO_2$) was bubbled through a solution of **1** in $CHCl_3$. A strong signal of ^{13}C-labeled carbamate carbonyl group in **2** appeared at 159.6 ppm. These data are in agreement with the previously published spectral data for alkylammonium carbamates.[3,5] The reaction between the primary amino groups in crown ether **1** and CO_2 takes place smoothly and quantitatively, and supramolecular polymer **2** forms.[9]

Receptor **1** was then used for the extraction of K^+Pic^- from water to $CHCl_3$. The extraction process was monitored by conventional

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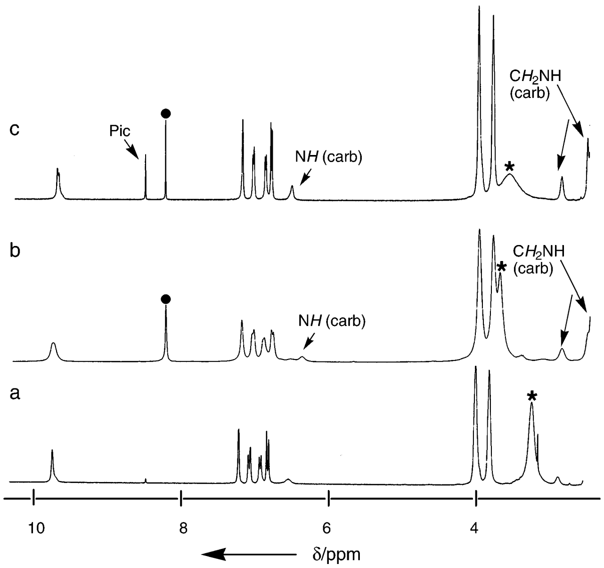

Figure 3. Selected portions of the ^{1}H NMR spectra (500 MHz, DMSO-d_6, 295 K), of (a) crown ether **1**; because of the sensitivity of **1** to the air CO_2, impurities of carbamate **2** can be seen; (b) carbamate polymer **2**, prepared from **1** and CO_2 in $CHCl_3$ and redissolved in DMSO-d_6; (c) polymeric complex **4**, prepared from **3** and CO_2 in $CHCl_3$ and redissolved in DMSO-d_6. The residual $CHCl_3$ and H_2O signals are marked "●" and "*", respectively. The assignments were performed by COSY experiments.

Figure 4. (left) Extraction of K^+Pic^- by receptor **1** from water to $CHCl_3$; formation of complex **3**. (right) Formation of carbamate polymer **4** from complex **3** in $CHCl_3$ upon bubbling CO_2 gas. The $CHCl_3$ layer was used as is, with no prior drying.

absorption spectroscopy, yielding up to 67% of the complex **3** (Figure 2). Then CO_2 was introduced, which quickly reacted with the lysine ϵ-amino groups and cross-linked complex **3** into insoluble material **4** (Figure 4). The precipitate was collected by filtration, dried, and analyzed. As in the case with polymer **2**, the formation of ammonium carbamate salt **4** takes place. The ^{1}H NMR spectrum in DMSO-d_6 clearly shows two 1:1 signals at 2.54 and 2.89 ppm, which correspond to two different α-CH_2N methylene groups from the carbamate and ammonium ends. The spectrum also showed a signal at 6.59 ppm corresponding to the carbamate NH proton. This was further confirmed by the COSY experiment, clearly showing a cross-peak between the carbamate NH signal and the carbamate α-CH_2N methylene group at 2.89 ppm.[10] More important however, ^{1}H NMR and absorption spectroscopies confirm the presence of K^+Pic^- in **4** (Figure 3c and Supporting Information).

Carbamate **4** was found to be quite stable when stored refrigerated for ~4 months. The reversibility of carbamate formation was proven by simply heating a suspension of **4** in $CHCl_3$ to temperatures ~50 °C and simultaneous bubbling N_2 through this solution for 1−2 min or addition of TFA. Under these conditions, polymer **4** dissociated with the release of CO_2, and monomeric host−guest complex **3** formed, from which the K^+ guests could be separated by simply washing with water. We believe, that the same principles and protocols will apply to other receptors and their guests, both ionic and neutral.

In conclusion, the proposed strategy is promising. It involves structural switching, which works together with molecular recognition. The architecture and complexation properties of the separating materials can be programmed through synthesis at the stage of their monomers. In contrast to known separating polymers and materials, which impose significant phase-transfer restrictions on complexation, the proposed here receptors complex guests in solution, as monomers, and only polymerize upon reaction with CO_2. Because of effective precipitation, large quantities of solvent can be recovered.

The storage is accomplished without the use of solvent, which is also preferred. Another important feature is the guest release, which can be easily accomplished upon dissociation of carbamates. For the first time CO_2 gas can be used as a building block. Considering the significance of CO_2 in industry and the environment, the strategy may, one day, offer means for creating environmentally responsive processes for separation, storage, and release.[11]

Acknowledgment. Financial support is acknowledged from the Petroleum Research Fund.

Supporting Information Available: Experimental procedures and spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) In contrast to $CHCl_3$, the reaction between CO_2 and **1** in DMSO-d_6 leads to the formation of carbamic acid **8** (Scheme 2 in Supporting Information). Rather stable in solution, acid **8** was characterized by ^{1}H, ^{13}C, and COSY NMR spectroscopy. Particularly characteristic are the new triplet at 6.65 ppm, belonging to the −NHC(O)OH protons, and significant shift of corresponding α-CH_2N methylene protons to the lower field (2.88 ppm) in the ^{1}H NMR spectrum. A carbonyl signal at 158 ppm in the ^{13}C NMR spectrum represents clear evidence for carbamic acid formation.

(10) Since the extraction and subsequent carbamate polymer formation were performed only on a small scale suitable for UV−vis measurements, no satisfactory ^{13}C NMR spectrum of **4** could be obtained at this stage.

(11) Experiments are now in progress to test the selectivity of receptor **1** for K^+ over Li^+, Na^+, and Cs^+. The corresponding picrates have been used, showing a reproducible preference toward K^+, which was however lower than for dibenzo-18-crown-6.

JA0672369