ORGANIC LETTERS
2012
Vol. 14, No. 13
3244–3247

Reusable Amine-Based Structural Motifs for Green House Gas (CO_2) Fixation

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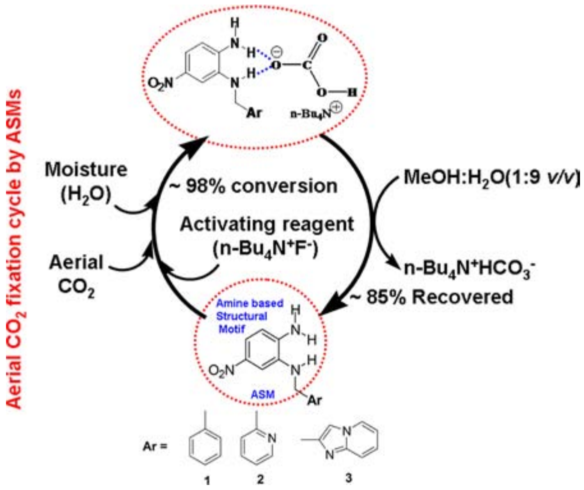
Received March 30, 2012

ABSTRACT



A series of compounds with an amine based structural motif (ASM) have been synthesized for efficient atmospheric CO_2 fixation. The H-bonded ASM–bicarbonate complexes were formed with an in situ generated HCO_3^- ion. The complexes have been characterized by IR, ^{13}C NMR, and X-ray single-crystal structural analysis. ASM–bicarbonate salts have been converted to pure ASMs in quantitative yield under mild conditions for recycling processes.

Carbon dioxide is a critical green house gas that is responsible for global warming. The last few decades have witnessed enormous attention to minimize the excess CO_2 in air, and attempts have been made to measure the quantity of CO_2 uptakes by various methods.[1] Different methods were developed for capturing aerial carbon dioxide to combat the problem of global warming.[2] Among different methods, porous materials consisting of metal–organic frameworks (MOFs) have been reported with a remarkable CO_2 adsorption capability.[3] Most MOFs utilized for these applications are very expensive and moisture sensitive. One such example is the MOFs composed of

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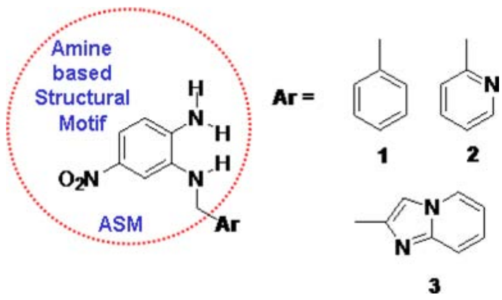
10.1021/ol301241k

transition-metal complexes which can absorb CO_2 from the air and then convert the gas into bicarbonate or carbonate salts.[4] At present, aminodisiloxanes,[2] green- MOFs,[3a] neutral organic cages,[5a,b] various amine solutions,[5c,d] aminosilicas,[6] ionic liquids,[7] etc. have been commonly used as efficient CO_2 absorbents from the flue gases via a chemical reaction between the amines and CO_2 molecules under variable conditions. However, high energy is needed for recovering these amines for the recycling process.[5c,d,6,7]

An alternative solution to reduce the excess atmospheric CO_2 is to utilize amine-based structural motifs (ASMs) because ASMs act as an effective reusable aerial carbon dioxide absorbent. Only a few receptors were reported as an efficient green house gas (CO_2) fixation in the basic medium [in the presence of TBOH (n-$Bu_4N^+OH^-$) or TBAF (n-$Bu_4N^+F^-$)], where CO_2 is converted to bicarbonate/carbonate and can form a strongly H-bonded receptor-bicarbonate/carbonate complex. For example, simple naphthalimide-based receptors having aromatic secondary amine are capable for colorimetric sensing of fluoride ion, and this has been used for aerial carbon dioxide fixation in presence of activating reagent TBAF or TBOH in DMSO solvent.[8] The urea-based receptor is also capable for atmospheric carbon dioxide fixation in the presence of TBAF in acetonitrile solvent.[9] Recently, a reusable neutral receptor was reported for efficient fixation of atmospheric CO_2 by carbonate complex formation in the presence of TBOH in DMSO solvent.[10] Among these developments, a systematic study with primary amine-based compounds suitable for green house gas fixation has not been investigated.

In this endeavor, we have clearly outlined a systematic study toward green house gas fixation by primary amine-based synthetic compounds and their reusuability. In order to produce an efficient green house gas (CO_2) absorbent at room temperature and atmospheric pressure, we have designed and synthesized simple neutral organic molecules of low molecular mass from commercially available simple starting materials (PNOPDA, Supporting Information). We have also examined the indispensable role of ASMs toward green house gas fixation processes. After the action of activating reagent TBAF, the receptors are capable of efficient aerial CO_2 fixation and form H-bonded bicarbonate complexes (like $\{n\text{-}Bu_4N^+[\mathbf{1}\cdot HCO_3]^-\}$, $\{n\text{-}Bu_4N^+[\mathbf{2}\cdot HCO_3]^-\}$, and $\{n\text{-}Bu_4N^+[\mathbf{3}\cdot HCO_3]^-\}$). These bicarbonate complexes were characterized by X-ray single-crystal diffraction, IR, and ^{13}C NMR analysis. We have also verified the possibilities of carbon dioxide fixation in the presence of other anions such as Cl^-, Br^-, I^-, AcO^-, NO_3^-, ClO_4^-, NO_2^-, HSO_3^-, and HSO_4^-. It is important to note that our amine-based receptors never form carbamate salts in the presence of atmospheric carbon dioxide as was reported in previous reports.[5c,d,6,7] To the best of our knowledge, we have synthesized amine-based structural motifs (ASMs, Scheme 1) for efficient uptake of atmospheric carbon dioxide without the formation of carbamate salts. The ASM−bicarbonate complexes are formed with good quantitative yield and can be recovered at room temperature for reusable purposes.[10]

Scheme 1. Chemical Structures of ASMs **1**−**3**



Compounds **1**−**3** (Scheme 1) have been synthesized according to our published procedure.[11] Detailed synthetic schemes and characterizations are provided in the Supporting Information. Our preliminary investigation on ASMs has been done in the presence of various anions (~2 equiv) in acetonitrile solvent. These solutions were used for atmospheric carbon dioxide fixation at room temperature. Solutions were placed under ether diffusion systems for ~1−2 days. Reddish sticky materials were obtained and separated from F^-, Cl^-, and AcO^- anion-containing solutions. These sticky materials were easily separated from the binary solution system (CH_3CN/Et_2O) by simply decanting the solvent mixture and evaporating under air. The sticky material was then dissolved in acetonitrile solvent and placed under an ether diffusion system. Unfortunately, after several trials Cl^- and AcO^- anion-containing systems could not produce crystals even after a prolonged time. However, after a considerable time (~ 2 days), fluoride-containing compounds (**1**−**3**) can easily form air-stable red crystals ($\{n\text{-}Bu_4N^+[\mathbf{1}\cdot HCO_3]^-\}$, $\{n\text{-}Bu_4N^+[\mathbf{2}\cdot HCO_3]^-\}$, and $\{n\text{-}Bu_4N^+[\mathbf{3}\cdot HCO_3]^-\}$) with high quantitative yields (Table S1, Supporting Information). These crystals were suitable for single-crystal X-ray diffraction analysis.[12−14] ASM−bicarbonate hydrogen-bonded complex formation occurs by capturing in situ generated HCO_3^- ions. The presence of bicarbonate in all crystals

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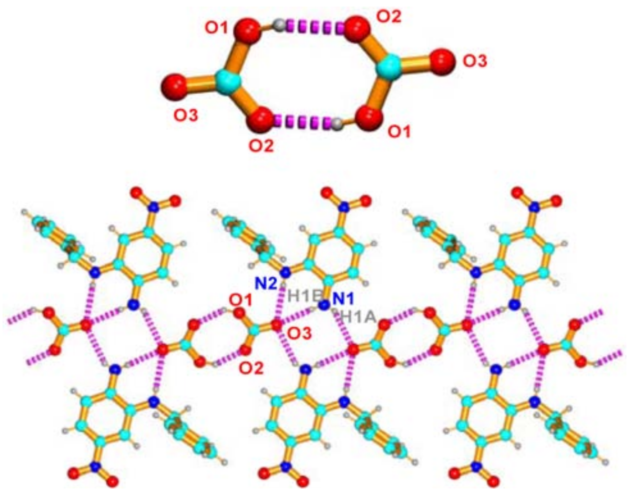


Figure 1. Bicarbonate dimer (top); **1**−bicarbonate adduct formed through aerial CO_2 fixation (bottom).

ensures the obvious conversion of atmospheric CO_2 to HCO_3^- in the presence of TBAF.[9]

Single-crystal X-ray diffraction data reveal that bicarbonate-containing complexes are structurally similar due to the presence of ASMs. The crystal structure analysis shows that **1**·HCO_3^-, **2**·HCO_3^-, and **3**·HCO_3^- complexes are crystallized in the space groups P_{21}/n, P-1, and P-1, respectively. Moreover, in each ASM−bicarbonate complex one bicarbonate anion is engaged to form a bifurcated hydrogen bond with two amine hydrogens. Each ASM-bound HCO_3^- ion donates as well as accepts hydrogens from another ASM-bound HCO_3^- ion. This gives rise to a dimer or a polymer by means of other interactions, which again depends on their variable molecular backbones. The X-ray single-crystal structure descriptions (ORTEP: Figures S1−S3, Supporting Information) of the complexes are summarized in Table S2 (Supporting Information). Relevant geometrical parameters correspond to H-bonding interactions in all crystalline complex salts ({n-Bu_4N^+[**1**·HCO_3]$^-$}, {n-Bu_4N^+[**2**·HCO_3]$^-$}, and {n-Bu_4N^+[**3**·HCO_3]$^-$}) are presented in Table S3 (Supporting Information).

The smallest molecular unit (compound **1**) efficiently absorbs atmospheric CO_2 and forms an H-bonded bicarbonate complex ({n-Bu_4N^+[**1**·HCO_3]$^-$}). The structure of the **1**·HCO_3^- complex shows that compound **1** is bound to bicarbonate anion through strong H-bonding interactions, where the O3 atom of HCO_3^- anion is bound through a bifurcated H-bond with two amine (N1 and N2) hydrogen atoms (Figure 1, Table S3 (Supporting Information), distances N1(−H1B)···O3 2.889 and N2···O3 2.971 Å). Each **1**-bound HCO_3^- ion donates and accepts hydrogens from another **1**-bound HCO_3^- ion and forms a dimer (Figure 1, distance O1···O2 2.586 Å). Each dimer is then connected with another dimer via H-bonding interactions between the aromatic primary amine (N1 atom) and bicarbonate anion (O3 atom). This generates a supramolecular polymer (Figure 1, distance N1(−H1A)···O3 2.970 Å).

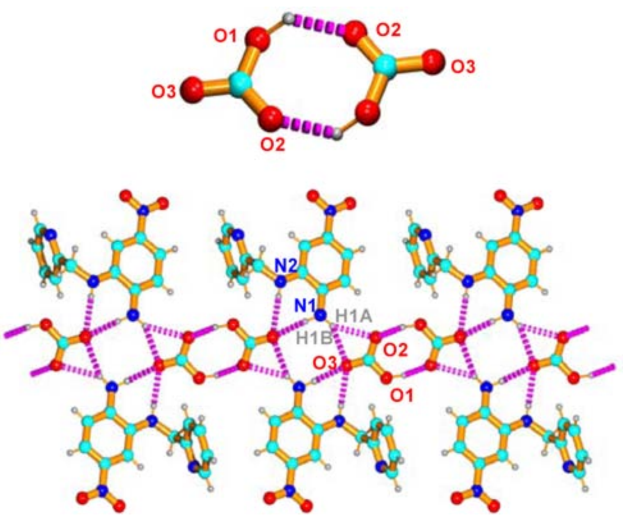


Figure 2. Bicarbonate dimer (top); **2**−bicarbonate adduct formed during aerial CO_2 fixation process (bottom).

Compound **2** is structurally similar to that of compound **1**. We may expect that compound **2** could form similar type of bicarbonate complex ({n-Bu_4N^+[**2**·HCO_3]$^-$} as that of **1** {n-Bu_4N^+[**1**·HCO_3]$^-$}) through aerial CO_2 fixation. Most importantly, it was found that compound **2** also forms similar type of bicarbonate complex as that of **1** (Figure 2, distances N1(−H1B)···O3 2.913, N2···O3 2.939, O1···O2 2.582, N1(−H1A)···O3 3.059, and N1(−H1A)···O2 3.196 Å). Only hydrogen bond distances are different (Table S3, Supporting Information) due to their minor structural differences. Interestingly, the hydrogen atoms of amine are found to be suitable for H-bonding interaction with bicarbonate anion through the formation of strong bifurcated adduct. In the case of compound **3**, a comparatively large aromatic subunit was attached with the basic backbone in order to examine the indispensable role of ASMs toward atmospheric carbon dioxide fixation. Compound **3** similarly forms a bicarbonate complex through aerial carbon dioxide fixation. In the structure of **3**·HCO_3^- complex (Figure 3), one bicarbonate anion (O3 atom) is bound with two amine nitrogen atoms (N1 and N2 atoms) through a similar type of bifurcated H-bond (Table S3 (Supporting Information), distances N1(−H1B)···O3 2.879 and N2···O3 3.009 Å). Each **3**·HCO_3^- unit donates and accepts hydrogens from another **3**·HCO_3^- unit and generates a dimer (Figure 3, distance O1···O2 2.607 Å) and polymer (Figure 3, distance N1(−H1A)···O3 3.074 and N1(−H1A)···O2 3.316 Å). In contrast to **1**·HCO_3^- and **2**·HCO_3^- complexes, here 1D polymer is extended to supramolecular 2D sheet through π-interactions (Figures S4 and S5, Table S4, Supporting Information).

The presence of bicarbonate anions in all crystalline complexes has been further confirmed by ^{13}C NMR measurement (Figure S6, Supporting Information). The appearance of a new peak (δ) at 159−160 ppm (compared

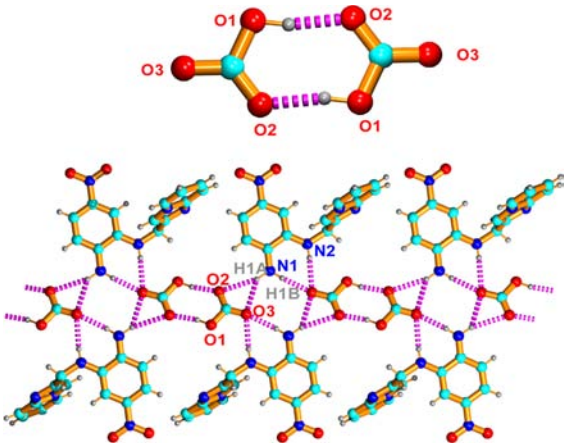
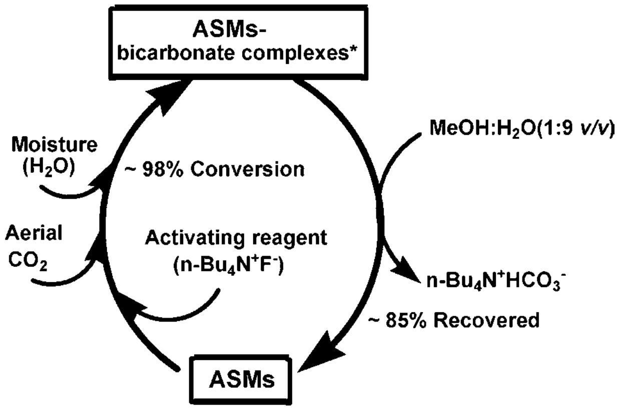


Figure 3. Bicarbonate dimer (top); **3**−bicarbonate adduct formed during aerial CO_2 fixation process (bottom).

with ASMs itself, $\delta < 150$ ppm) in all complexes ensures the presence of bicarbonate anion in each complex. Further information regarding the existence of bicarbonate anions in all complexes was obtained from solid-state IR spectral measurements (Figures S7−S9, Supporting Information). The presence of new band (compared with ASMs itself) at ~1680−1702 cm^{-1} in all complexes indicates the presence of H-bonded bicarbonate anion.[11] Minor spectral differences (^{13}C NMR and IR) in the bicarbonate complexes are the reflections of their negligible X-ray single-crystal structural alternations.

For the commercialization of ASMs for the CO_2 fixation cycle, we have investigated its reusuability. To reuse the ASMs for further CO_2 fixation processes, we have treated the bicarbonate complexes ($\{n\text{-}Bu_4N^+[\mathbf{1}\cdot HCO_3]^-\}$, $\{n\text{-}Bu_4N^+[\mathbf{2}\cdot HCO_3]^-\}$, and $\{n\text{-}Bu_4N^+[\mathbf{3}\cdot HCO_3]^-\}$) with MeOH/$H_2O$ solvent mixture (1:9 v/v). The neutral uncomplexed ASMs are insoluble in water, whereas the $n\text{-}Bu_4N^+HCO_3^-$ salt is highly soluble in water. Therefore, the ASM−bicarbonate complexes were immediately crashed out under the binary solvent mixture (MeOH/H_2O), and the ASM residues were separated out from the solution, filtered off, and washed with distilled water. Pure ASMs **1**−**3** were obtained in almost quantitative yields (Table S1, Supporting Information) and could be reused for further carbon dioxide fixation processes (Scheme 2).

Scheme 2. Aerial CO_2 Fixation Cycle by ASMs



[*] Bicarbonate complexes are $\{n\text{-}Bu_4N^+[\mathbf{1}\cdot HCO_3]^-\}$, $\{n\text{-}Bu_4N^+[\mathbf{2}\cdot HCO_3]^-\}$, and $\{n\text{-}Bu_4N^+[\mathbf{3}\cdot.HCO_3]^-\}$.

The purity of recovered ASMs has been checked by IR, NMR, and mass spectral analysis.

In conclusion, we have established a potential chemical route for selective atmospheric CO_2 fixation (Scheme 2). To achieve this, we have synthesized some predesigned ASMs of very low molecular mass with high CO_2 fixation ability. The formation of ASM−bicarbonate complexes ($\{n\text{-}Bu_4N^+[\mathbf{1}\cdot HCO_3]^-\}$, $\{n\text{-}Bu_4N^+[\mathbf{2}\cdot HCO_3]^-\}$, and $\{n\text{-}Bu_4N^+[\mathbf{3}\cdot HCO_3]^-\}$) and regeneration of ASMs under mild conditions clearly establishes the potential of reversible binding. Using this fundamental concept and by adopting proper methods it is possible to reduce the green house gas (CO_2) as well as global warming by efficient CO_2 absorbent (having ASMs) on a large scale.

Acknowledgment. This work is supported by grants from DST, India (Project No. SR/S1/PC/26/2008), to N.G. S.D. and S.J. acknowledge UGC for fellowships. We are thankful to Dr. J. L. Mynar of UC, Berkeley, for editing the manuscript.

Supporting Information Available. Material and methods, synthesis and characterization, experimental details, Figures S1−S13, and Tables S1−S4. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.