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Reversible CO_2 Capture by Unexpected Plastic-, Resin-, and Gel-like Ionic Soft Materials Discovered during the Combi-Click Generation of a TSIL Library

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The reversible capture of CO_2 is a prominent feature in schemes for the mitigation of causative agents in global warming.[1] Already important in the purification of natural gas and in breathing-air recirculation systems, it is often achieved on large scales by passing a contaminated gas through an aqueous amine solution, with which the entrained CO_2 reacts.[2] Unfortunately, this approach is dogged by the volatility of the amines, which are gradually lost into the gas stream. Consequently, if reactive capture is to be an element of future CO_2 management technologies, there is an urgent need to develop systems in which the scavenger is both nonvolatile and affordable.

Task-specific ionic liquids (TSILs)[3] and liquid salt hydrates are promising materials of little-to-no volatility for CO_2 separations, but their development for this use is still in its infancy.[4,5] Accordingly, pressing toward new scavenging ionics is a worthwhile endeavor, especially when a range of materials potentially useful at different point sources of emission may result. However, it is imperative that these efforts also focus on the creation of materials that can be prepared rapidly and economically and preferably in a modular fashion to facilitate the tuning of their structures and properties. In this light, we have applied two highly regarded synthetic paradigms, combinatorial chemistry and click chemistry,[6] to this multi-faceted challenge. We believe the resulting collection of 63 CO_2-philic salts is the first library designed to achieve reactive gas capture. And, while the majority of the compounds are new TSILs, our intended target, we are pleased to report the serendipitous isolation of 16 others which are intrinsically resin-, plastic-, or gel-like, all of which capture CO_2 in these forms.[7] While the water[8] and LMOG (low molecular weight organogelator)-induced[9] formation of ionic liquid (IL) gels is known, as

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(1) See: www.fossil.energy.gov/programs/sequestration/capture/.
(2) Kohl, A.; Nielsen, R. *Gas Purification*, 5th ed.; Gulf: Houston, 1997; Chapters 1, 2, and 14.
(3) (a) Lee, S.-G. *Chem. Commun.* **2006**, 1049−1063. (b) Davis, J. H., Jr. *Chem. Lett.* **2004**, *33*, 1072−1077.
(4) For CO_2 capture by and/or the synthesis of amine-functionalized TSILs, see: (a) Zhang, J.; Zhang, S.; Dong, K.; Zhang, Y.; Shen, Y.; Lv, X. *Chem.—Eur. J.* **2006**, *12*, 4021−4026. (b) Fukumoto, K.; Yoshizawa, M.; Ohno, H. *J. Am. Chem. Soc.* **2005**, *127*, 2398−2399. (c) Bates, E. D.; Mayton, R. D.; Ntai, I.; Davis, J. H., Jr. *J. Am. Chem. Soc.* **2002**, *124*, 4194−4195. (d) Davis, J. H., Jr. U.S. Patent 7,208,605, 2007.
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(6) Kolb, H. C.; Finn, M. G.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 2004−2021.
(7) Pending a detailed investigation of the micro/nanoscale structure of these materials, we use here the terms *plastic*, *resin*, and *gel* solely to convey a *sense* of their macroscopic characteristics.
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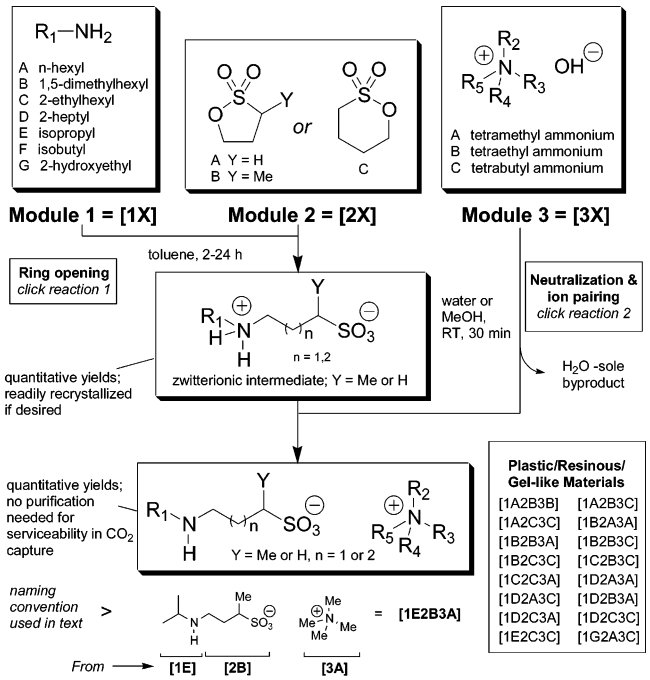
Scheme 1. Synthesis of the New CO_2-philic Materials



are reactions of CO_2 with aminated polymers[10] and the CO_2 induced formation of gels and other soft matter,[11] we believe these new ionic soft materials[12] are novel as native substrates for CO_2 capture. The added value of their unique macroscopic characteristics is especially apparent in the ease with which they are applied and adhere to glass, plastics, textiles, or metals, facilitating the use of various objects to support them.

The materials from which they are made, primary amines, sultones, and quaternary ammonium hydroxides, are commodity chemicals. In addition, their modular nature lends them to combinatorial assembly by an inexpensive process: two high-yielding, atom-efficient *click* reactions[6,13] (Scheme 1) that produce water as the sole byproduct, require minimal amounts of cheap and benign solvents, are frequently rapid, and usually require no heating or cooling. Further, the materials produced in this fashion are serviceable for CO_2 capture without purification,[6] an advantage of enormous value for any material, the development of which for large-scale use may be envisioned.

The heart of each new material is its anion, most formal homotaurine derivatives related to Zwittergent-type detergents. However, where the latter are zwitterions incorporating quaternary nitrogen centers from sultone ring-opening by tertiary amines, our use of primary amines leads to anions bearing secondary amine groups. We stress that this distinction is *not* trivial. Rather, the presence of a lone pair and a hydrogen atom on the nitrogen are requisite features for the capture of CO_2 as a carbamate, the principal mechanism by which certain widely used industrial scrubbing amines (e.g., MEA and DEA) function.[2] In turn, the amine-provided alkyl group exerts an influence on the properties of the final products. For example, anions derived from [1A]−[1D] appear more apt to form resinous/plastic materials while those from [1E]−[1G] more generally produce TSILs.

The second synthetic step is often done in water/wet methanol, resulting in residual water in the products at levels similar to those in certain amino-acid based TSILs described by Ohno et al.[4b] For example, one sample of [1B2A3C] contained 3.96% water after initial solvent stripping, while 2 days of storage over P_2O_5(s) reduced this to 1.93%. Gravimetric measurements during hydration/dehydration cycles (no CO_2), along with visual/manual evaluations of the plastic, resin, and gel-like materials, indicate that most retain their overall macroscopic character as such even upon some variation in water content. And, while some deliquesce, they do so slowly and *only* when maintained for prolonged periods in a sealed vessel above a reservoir of water.

To demonstrate the potential utility of surface-supported deposits of the plastic/resinous materials, [1B2A3A] was used to create a prototype pass-through device for reversible CO_2 capture (Figure 1). On exposing the resin to a flow of CO_2 for 12 h, it became frosted, consistent with CO_2 absorption (vide infra). Subsequent passage of hot water (∼80 °C) through the coil while subjecting the sample to mechanical vacuum resulted in CO_2 extrusion and a return of the resin to its original appearance. To our knowledge, these compounds are the first non-polymeric plastic or resinous materials used to capture CO_2, making them interesting counterparts to SAWD (solid amine/water desorption) technology.[14]

Gravimetric measurements intended to quantify CO_2 uptake by the soft phases gave erratic results (Supporting Information), likely a result of mass fluctuations from water loss into the dry gas stream and concurrent CO_2 uptake by the scavenger. Nevertheless, CO_2 uptake by any of the salts, which occurs even when they are left open to air, is confirmed in a variety of fashions. After CO_2 exposure, evidence is manifest in the visible increase in the viscosities (sometimes solidification) of those that are liquids and the opaque, frosted appearance of the soft materials. Similarly, TSIL samples charged with indicator dye change from sapphire to bright green in color on exposure to the gas (graphical abstract).[15] Dye-charged soft phases also respond in this fashion, suggesting a potential for their development as apply-anywhere colorimetric CO_2 sensors. Unambiguous evidence of CO_2 binding is provided by Fourier transform infrared (FTIR), ^{13}C NMR, and electrospray ionization mass spectrometry (ESI-MS; Figure 2). Representative of the new

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(12) *Ionic Soft Matter: Modern Trends in Theory and Applications*; Henderson, D., Holovko, M., Trokhymchuk, A., Eds.; NATO Science Series II, No. 206; Springer: Dordrecht, 2005.
(13) The neutralization reaction, with its concomitant *ionic* bond formation between the newly generated amine-functionalized anion and the quaternary ammonium cation, appears to meet all of the defining criteria (ref 5) for categorization as a click reaction save for the stereospecificity condition, which is (arguably) moot in this instance.
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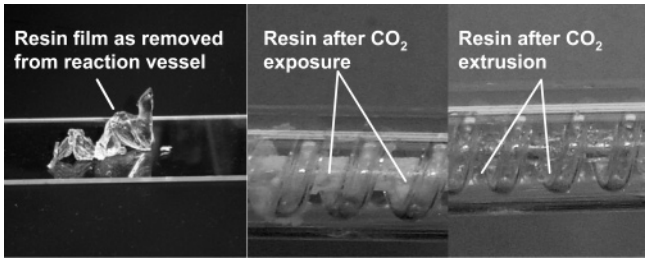

Figure 1. [1B2A3A] is "sliced" and removed in strips from the reaction vessel as a moldable transparent film. It can be applied to the coils of a spiral condenser fitted with gas adapters at each end to create a simple, recyclable, pass-through CO_2 absorber.

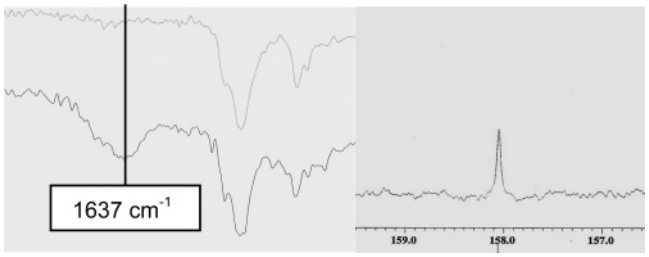

Figure 2. [1B2A3C] and CO_2: left, FTIR spectra (CO region) before [upper] and after [lower] CO_2 exposure; right, carbamate/carbamic acid carbon resonance at 158 ppm (^{13}C NMR).

compounds vis-à-vis its response to CO_2, [1B2A3C] undergoes marked changes in its ^{13}C spectrum when treated with a stream of CO_2, the most important of which is the appearance of a new signal at 158 ppm. The latter is consistent with the CO_2-supplied carbon atom of a newly formed carbamate (or, possibly, carbamic acid) group within the anion, the presence of which is also manifested by a broad but substantial C═O absorption (FTIR) centered at 1637 cm^{-1}.[4a,c,11b] Clinching evidence for the covalent incorporation of CO_2 into the anion structure is provided by the negative-mode ESI-MS, which produces a peak for an ion with the proper mass (294) for a $[2A3C-CO_2]^-$ adduct. Further implicating a carbamate as an intermediate in CO_2 capture by these salts, the latter fragments (ESI-MS^2) to form $[2A3C]^-$ ($m/e = 250$), specifically consistent with the loss of CO_2. Notably, the intensity of the peaks from the CO_2-containing ions diminishes with residence time in the MS, providing further verification of the reversibility of the binding.

The potential value of the combined reactivity and physical characteristics of the new ionic soft materials is clear even in the absence of understanding the origins of the latter. Nevertheless, an investigation into the basis of these physical properties is in order as is work to devise a reliable means for quantifying CO_2 uptake by them. An aggressive expansion of the present library is also anticipated as is an elaboration of this general approach to the synthesis of soft ionics. Future work will also address the development of means to tune the energetics of CO_2 binding and release by the salts.

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Supporting Information Available: Tabular summary of new salts and their capacities for CO_2 capture, CO_2 uptake experiment details, representative syntheses, spectra, and details and results of the water saturation experiments (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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