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Reversible covalent chemistry of CO_2

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Reversible reaction of CO_2 with fluorescently active amines in polar aprotic solvent rapidly results in carbamic acids, which significantly enhances the solution fluorescence.

Extensive carbon dioxide (CO_2) circulation in atmosphere, industry, transport, and agriculture requires its systematic monitoring under a variety of climates and conditions, and necessitates the development of improved methods of CO_2 chemical fixation.[1] Fast, quantitative and reliable CO_2 sensors are also needed in anesthesiology and physiology, for measuring cardiovascular system exchange rates, and for gas concentration determination in blood during surgery.[1,2] Current CO_2 sensors are mostly electrochemical and monitor pH changes in solution upon bicarbonate formation or changes in ionic conduction in the solid state.[2] Being in general an unreactive molecule, CO_2 combines rapidly with amines, at ordinary temperatures and pressures; the resulting carbamate salts are thermally unstable and release CO_2 upon heating.[3] These processes are of practical importance: polymer-supported amines are used to remove CO_2 from gas streams[4] and can be used for CO_2 sensing.[5] We apply dynamic covalent interactions between primary amines and CO_2 for reversible assembly of novel light-emitting molecular devices and describe here our surprising findings in the chemistry of these processes. These may open new opportunities for the construction of novel nanostructures and materials upon reversible CO_2 fixation.

The sequence of binding events involving CO_2 and amines was studied by UV–vis, fluorescence and ^{1}H and ^{13}C NMR spectroscopy and depicted on Fig. 1. Bubbling CO_2 through solutions of 1-aminomethylnaphthalene **1** or 1-aminomethylpyrene **2** in polar aprotic solvent such as DMSO or DMF did not change their UV–vis spectra but resulted in strong fluorescence enhancement, thus directly reporting on the CO_2 entrapment (Fig. 2).

Upon excitation with λ_{ex} = 282 and 341 nm for **1** and **2** respectively, CO_2 yielded intense, broad emission at λ_{em} ~ 336 and 380 nm, respectively. At the same time, free amines **1** and **2** only weakly emit fluorescence under these conditions.

Photoinduced electron transfer (PET) quenching of excited aromatic fluorophores by intramolecular amino groups has been known for years.[6] PET in derivatives of arylmethylamines constitutes the basis of pH switching of fluorescence: upon protonation, the lone pair on the nitrogen atom is no longer available for the excitation quenching.† In a single case, reversible PET quenching was demonstrated for some arylmethylamines upon exposure to CO_2 in dioxane, however no chemistry of the process was studied.[7]

When performed in the NMR tube in DMSO-d_6, the above experiments resulted in quite significant transformation of the spectra (Fig. 3). In particular, prior to the CO_2 exposure, benzylic CH_2 protons of **1** and **2** were seen as singlets at 4.19 and 5.09 ppm, respectively. After the CO_2 bubbling, these were transformed into doublets (J = 6.0 Hz) at 4.63 and 4.91 ppm, respectively. In both cases, a very broad signal appeared at ~ 10.7 ppm, which was assigned to the C(O)OH. The carbamate NH signals also emerged as triplets (J = 6.0 Hz) at 7.37 and 7.54 ppm, respectively. Integration of the high resolution ^{1}H NMR spectra clearly indicated the formation of the 1 : 1 amine–CO_2 adducts, carbamic acids **3** and **4** (Fig. 1, and 3). Carbamic acids are usually considered highly unstable.[3,4] Upon formation, they typically release CO_2 to yield the corresponding free amines. In addition, the acidic OH proton may further be transferred to the second amine molecule with the formation of the corresponding alkylammonium carbamic salts. According to the ^{1}H NMR spectra, neither process was observed in our experiments, and carbamic acids **3** and **4** existed in DMSO and DMF solutions for hours. The corresponding ^{13}C NMR C=O signals were found at 158 ppm (DMSO-d_6).

Bubbling N_2 through the above DMSO solutions of **3** and **4** resulted in loss of CO_2, even at room temperature. The fluorescence emission decreased as well. Initially, free amines **1** and **2** were formed (^{1}H NMR), which rapidly abstracted the acidic OH protons from the remaining carbamic acids **3** and **4**, respectively, and partially precipitated as carbamate salts **5** and **6**.

In separate experiments, carbamate salts **5** and **6** were quantitatively prepared upon bubbling CO_2 through solutions of **1** and **2** in less polar $CHCl_3$, MeCN or THF. Their structure was confirmed by high resolution ^{1}H NMR, ^{13}C NMR and elemental analysis.‡ In particular, benzylic CH_2 protons were seen in DMSO-d_6 as two separate signals: a singlet at 4.22 and a doublet at 4.62 ppm (J = 5.5 Hz) for **5**, and a singlet at 4.48 and a doublet at 4.90 ppm (J = 5.5 Hz) for **6** (Fig. 3). The carbamate

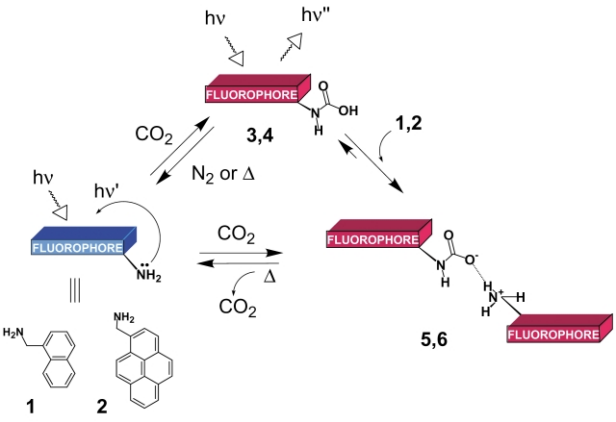

Fig. 1 Reversible covalent bonding of CO_2.

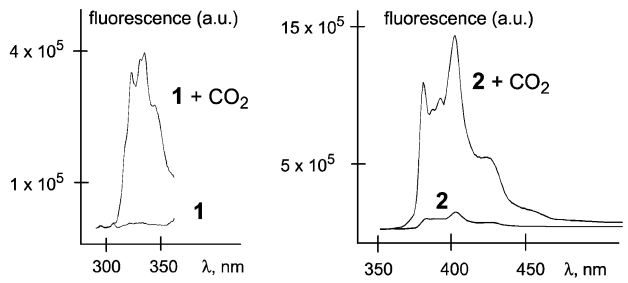

Fig. 2 Fluorescence measurements with **1** and **2** (λ_{ex} = 282 and 341 nm, respectively) in DMF before and after saturation with CO_2. All solutions were deoxygenated with N_2 prior measurements; [**1**] = [**2**] = 10^{-6} M.

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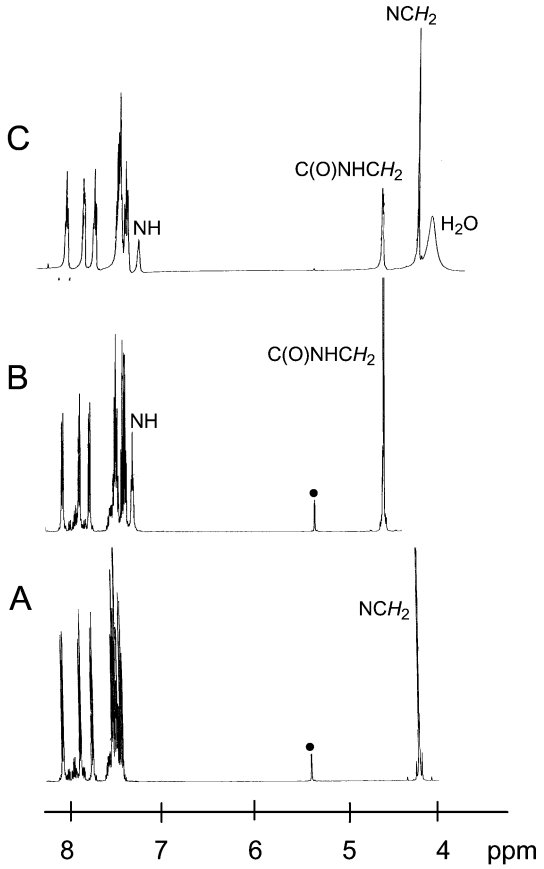

Fig. 3 CO_2 induced spectral changes of 1-aminomethylnaphthalene **1**. A and B: ^{1}H NMR spectra (500 MHz, DMSO-d_6, 295 K) of **1** before and after saturation with CO_2, respectively. C: ^{1}H NMR spectrum of carbamate salt **5**. The NH and benzylic CH_2 signals are assigned. The impurity signal is marked '●'. The initial solutions were deoxygenated with N_2 prior to measurements.

NH signals were seen as triplets (J = 5.5 Hz) at 7.32 and 7.53 ppm, respectively.

Analogous results were obtained when CO_2 was used as dry ice. Fine suspensions of both precipitates **5** and **6** appeared to be strongly fluorescent upon exposure to UV light of the appropriate excitation wave length.

When solutions of **1** and **2** were exposed to the laboratory air, carbamates **5** and **6** precipitated within minutes (in $CHCl_3$, MeCN or THF).

At the same time, carbamates **5** and **6** are stable compounds and cannot be transformed to amines **1** and **2** by simply bubbling N_2 through their solutions. On the other hand, loss of CO_2 from **5** and **6** was readily achieved within several minutes upon heating. Thus, **5** and **6** were transformed (> 90%) back to amines **1** and **2** upon refluxing in toluene (80 °C, 1–2 h).

In summary, information about reversible covalent binding of CO_2 can be conveniently transmitted *via* light signals (Fig. 1). Besides this sensory role and due to the reversibility, such behavior have a potential for information processing since the emission can be switched between two distinguishable, amine/carbamic acid states. These findings also open wider possibilities towards more complex light-emitting devices and functional nanostructures and materials, including crown ethers, hemicarcerands, capsules,[8] and gels,[9] which involve CO_2 chemical fixation and based on its reversible[10] covalent bonding to amines. We are currently preparing these structures and will report on due to the course.

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Notes and references

† In our hands, fluorescence intensity of **1** and **2** significantly (~10 times) increased upon addition of TFA (5% v/v) to their MeCN solutions.

‡ NMR spectra were obtained on a JEOL Eclipse (500 MHz) and Bruker 300 MHz NMR spectrometers; fluorescence was measured on Jobin YvonFluoroMax 3 and SpexFluorimeter-1404 0.85m spectrometers. Selected spectra for **3**: ^{1}H NMR (DMSO-d_6): δ 8.13 (d, J 9.0 Hz, 1 H), 7.94 (d, J 9.0 Hz, 1 H), 7.83 (d, J 9.0 Hz, 1 H), 7.6–7.4 (m, 4 H), 7.37 (t, J 6.0 Hz, 1 H), 4.62 (d, J 6.0 Hz, 2 H). ^{13}C NMR (DMSO-d_6): δ 158.1 (C=O). Selected ^{1}H NMR (DMSO-d_6) data for **4**: δ 8.5–8.0 (m, 9 H), 7.54 (t, J 6.0 Hz, 1 H), 4.91 (d, J 6.0 Hz, 2 H). Selected data for **5**: mp 105 °C (decomp.); ^{1}H NMR (DMSO-d_6): δ 8.12 (2 × d, J 8.0 Hz, 2 H), 7.93 (d, J 8.0 Hz, 2 H), 7.81 (2 × d, J 8.0 Hz, 2 H), 7.6–7.4 (m, 8 H), 7.32 (t, J 5.5 Hz, 1 H), 4.62 (d, J 5.5 Hz, 2 H), 4.22 (s, 2 H). ^{13}C NMR (DMSO-d_6): δ 158.5 (C=O). Anal. Calc. for $C_{23}H_{22}N_2O_2 \cdot 0.2H_2O$: C, 76.30; H, 6.24; N, 7.74. Found: C, 76.20; H, 6.59; N, 7.76%. Selected data for **6**: mp 80–95 °C (decomp.); ^{1}H NMR (DMSO-d_6): δ 8.5–8.0 (m, 18 H), 7.53 (t, J 5.5 Hz, 1 H), 4.90 (d, J 5.5 Hz, 2 H), 4.48 (s, 2 H). Anal. Calc. for $C_{35}H_{26}N_2O_2$: C, 82.98; H, 5.17; N, 5.53. Found: C, 83.03; H, 5.47; N, 5.35%.

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