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A Benzobisimidazolium-Based Fluorescent and Colorimetric Chemosensor for CO_2

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Supporting Information

ABSTRACT: A new sensor for the fluorescent and colorimetric detection of CO_2 is described. The system utilizes fluoride to activate a tetrapropyl benzobisimidazolium salt and operates in the absence of an exogenous base. On the basis of spectroscopic and theoretical analyses, the mode of action of the present system is ascribed to the fluoride-induced formation of an N-heterocyclic carbene intermediate that reacts with CO_2 to form an imidazolium carboxylate.

Carbon dioxide is a known greenhouse gas and linked to global climate change.[1] As such, there is a need to detect CO_2 selectively and to quantify its concentration in anthropogenic gas streams (e.g., flue gas, syngas, biogas, etc.) that typically contain high CO_2 levels before release into the atmosphere.[1] Improved CO_2 gas detection strategies could also prove beneficial for other applications, including agricultural production, hypercapnia assessment, and environmental analysis.[2] Common methods for CO_2 detection include Severinghaus-type potentiometric sensors, GC-MS, and IR spectroscopic techniques.[2b] Although state-of-the-art, these methods are generally expensive, rely on bulky instrumentation, are often intolerant to interferents, and, in some cases, are unsuitable for real-time measurements of gas streams.[2,3] In contrast, optical CO_2 gas sensors based on fluorescence changes are attractive due to their simple and inexpensive construction, high sensitivity, rapid sensing capabilities, and ability to operate at ambient temperature.[4] Unlike previous optical methods for CO_2 sensing, which depend primarily on the acidic properties of CO_2, we describe here a new strategy that provides a direct, chemical-based approach for detecting CO_2. As detailed below, the method allows for both the fluorescent and colorimetric sensing of CO_2.

Recently, it was shown that N-heterocyclic carbenes (NHCs), which are often obtained by deprotonating the corresponding imidazolium salts, are capable of activating CO_2 to form imidazolium carboxylates.[5] However, these systems require dry and air-free conditions, and lack the features needed to be useful as CO_2 sensors. We thus sought to use an NHC system that would allow the aforementioned chemistry to be carried out under less rigorously controlled environments.

The chemistry of imidizolium-based sensors has developed rapidly over the past decade, particularly for anion recognition.[6] When an imidazolium species interacts with an anion, a strong $(C-H)^+\cdots X^-$ hydrogen bond is formed. Such types of bonds, along with electrostatic effects, are thought to provide the basis for the observed molecular recognition properties. However, we considered that they might also serve to activate an imidazolium group for interaction with CO_2 by forming what might be viewed as an incipient NHC (without the addition of external bases). If this occurred within the context of a relatively acidic imidazolium system and displayed protonation-dependent absorption or emission features in the visible portion of the electronic spectrum, it could provide the basis of a new class of optical-based CO_2 sensors. As detailed below, we successfully realized such a detection scheme using tetrapropyl benzobisimidazolium salts (**TBBI**, Scheme 1).

Bielawski[7] and Hahn[8] reported that benzobisimidazolium (**BBI**) salts can act as biscarbene ligands for metal ions and, in some cases, are fluorescent.[9] Recently, a BBI derivative has also been shown to act as a redox partner in an anion-switched electron transfer process involving an electron-rich calix[4]-pyrrole.[10] Collectively, these studies have served to establish that the electronic properties intrinsic to BBI cations may be tuned through structural modification.

A key feature of BBI-based fluorophores is that functionalization of the C1 position of the imidazolium rings can serve to tune the photophysical properties displayed by these salts, as manifested by changes in the respective.[9] Considering these factors, we hypothesized that chemical modification of the C1 positions of **BBI** derivatives would permit the construction of a working optical CO_2 sensor. In particular, we envisioned that addition of a fluoride anion, which is considered to be a weak

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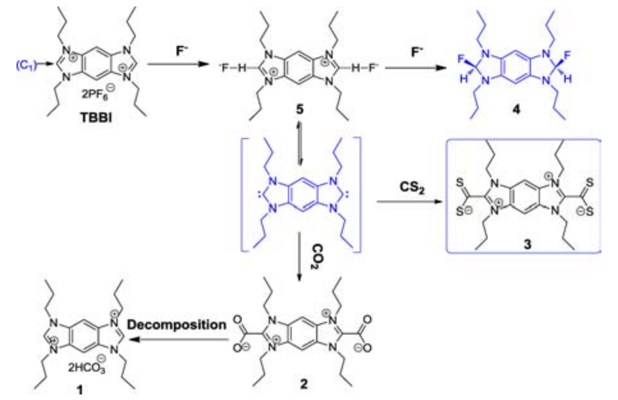
Scheme 1. Proposed Reactions That Occur When TBBI Is Treated First with F^- and Then Either CO_2 or CS_2



base, would produce a species possessing partial NHC character[11] and therefore would allow for reaction with CO_2; the associated changes in optical features would then enable detection. To test this hypothesis, we synthesized a specific organic-soluble NHC precursor, namely **TBBI** (Scheme 1).

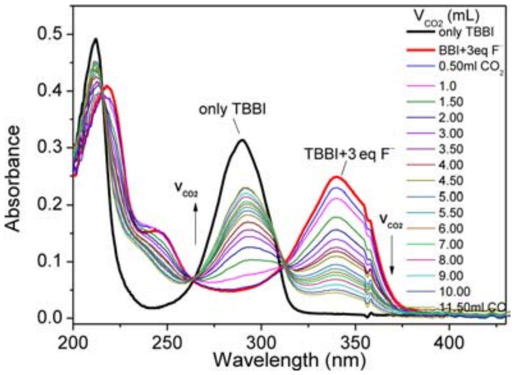


Figure 1. UV spectra of **TBBI** (15.0 μM, 3.0 mL) recorded in CH_3CN in the presence of TBAF (3.0 equiv of F^-) and then bubbling with different volumes of CO_2.

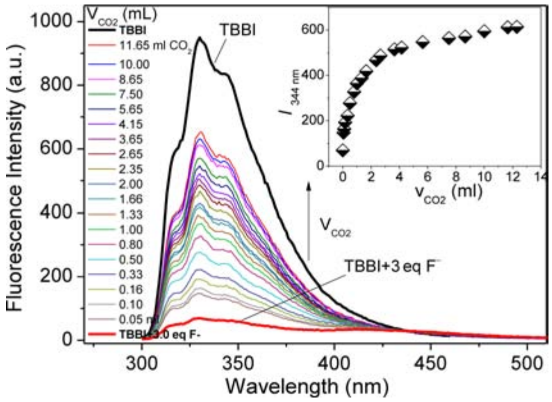


Figure 2. Changes in the fluorescence titration spectral features of **TBBI** (15.0 μM) in CH_3CN observed upon the addition of TBAF (3.0 equiv) and then bubbling with different volumes of CO_2 with excitation at 290 nm. Inset: plot of the fluorescence intensity I_{344nm} of a solution consisting of **TBBI** and 3.0 equiv of TBAF versus various volumes of CO_2 with excitation effected at 290 nm.

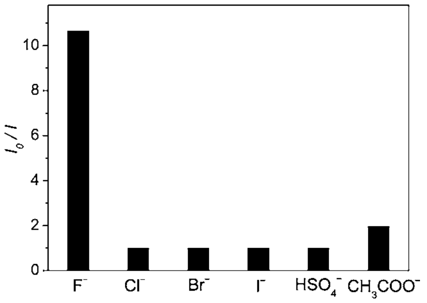


Figure 3. Fluorescence responses of **TBBI** (15.0 μM) with the addition of 3.0 equiv of various anions, F^-, Cl^-, Br^-, I^-, HSO_4^-, and CH_3COO^-, in CH_3CN. The black bars represent the I_0/I ratios at 344 nm after addition of anions to solutions of **TBBI** (15 μM) with excitation at 290 nm.

TBBI was prepared in ca. 60% yield from benzobisimidazole,[9a] by reacting with 1-iodopropane in CH_3CN followed by anion exchange with PF_6^- (see SI). The UV absorbance and fluorescence spectra of **TBBI** were recorded, and the effect of added F^- was examined. As shown in Figure 1, a solution of **TBBI** (15 μM) in acetonitrile showed a characteristic absorbance band centered at 290 nm. In the presence of 3.0 equiv of F^- ion (added as the tetrabutylammonium salt, TBAF), the absorption band at 290 nm bathochromically shifted to 344 nm, an effect ascribed to formation of strong $(C-H)^+\cdots F^-$ bonds. At the same time, an efficient fluorescence quenching was observed upon excitation at 290 nm (Figure 2). Further examination revealed that **TBBI** exhibited a high selectivity for the fluoride anion over other halide anions (Figures 3 and S1).

Next, the **TBBI** solution containing F^- was exposed to CO_2 gas. When the solution obtained by treatment with 3.0 equiv of TBAF was bubbled with increasing volumes of CO_2 (as governed by a mass flow controller), the intensity of the spectral feature at 290 nm (cf. the original solution of **TBBI** in Figure 1) was seen to increase, while the signal observed at 344 nm, assigned to **TBBI** with F^-, decreased. These spectral changes gave rise to an isosbestic point, localized at 312 nm in the absorption spectra (Figure 1).

Analogous effects were observed in the corresponding fluorescent emission spectra, as shown in Figure 2. Specifically, the addition of F^- (as TBAF) to an acetonitrile solution of **TBBI** (15 μM, 3.0 mL) caused a sharp decline in the emission spectral intensity arising from the bisimidazolium cation (excitation at 290 nm). On the other hand, a marked increase in the fluorescence intensity (λ_{max} = 330 nm) was observed upon exposure to increasing concentrations of CO_2 gas (as inferred from bubbling with increased volumes at a fixed rate for a fixed time). After being bubbled with about 12 mL of CO_2 gas, the mixture was saturated, and no additional changes in the emission features were observed. The saturation curve is shown in the inset of Figure 2, which also provides a representative plot of the fluorescence intensity (I_{344nm}) of a solution of **TBBI**·F^- (**5**) in CH_3CN versus the volume of CO_2 bubbled through the solution. The optical changes induced by exposure to CO_2 were immediate on the laboratory time scale.

From these data, we concluded that the spectroscopic changes were strongly dependent on the CO_2 concentration and that the aforementioned approach effectively established a new method for CO_2 detection. The CO_2 detection limit of this system was calculated to be ca. 30 ppm (cf. Figure S2). The good sensitivity combined with the ability to conveniently conduct fluorescence-based analyses are attractive and distinguish this system from alternative CO_2 detection strategies.

To obtain additional insight into the underlying mechanism of the sensing process, various chemical studies were carried out. **TBBI** (50 mg) was added to a solution of TBAF (3 equiv) in CH_3CN. After bubbling with a large volume of CO_2 gas, a white precipitate formed which was assigned to the bis-NHC−CO_2 adduct **2**. Unfortunately, the putative adduct was not stable in solution and quickly decomposed to form the stable imidazolium hydrogen carbonate salt **1** (Scheme 1). The stability of the proposed NHC-derived CO_2 adducts, such as 1,3-disubstituted 2-imidazolium carboxylates, is known to be affected by many factors, including temperature, the bulkiness of the N-substituent, and the polarity of the solvent.[5] Very recently, Taton and Vignolle demonstrated that reversible hydrolysis reactions involving imidazolium carboxylates and imidazolium HCO_3^- salts are possible, with the specifics depending in part on the water content of the solvent system employed.[12a] One of the more convenient methods for effecting the decomposition of NHC−CO_2 adducts into the corresponding imidazolium HCO_3^- salt involves exposure to a traditional Krapcho polar aprotic solvent (e.g., DMSO).[12] Presumably, such decomposition occurs spontaneously in the case of **2**. An effort was therefore made to characterize the daughter product, salt **1**. Since this latter species proved insoluble in acetonitrile, DMSO-d_6 was chosen to allow the presumed formation and decomposition reactions of **2** to be followed by ^{1}H NMR spectroscopy. Subsequent spectroscopic characterization of salt **1** (vide infra) provided support for the reaction chemistry summarized in Scheme 1.

Figure 4d shows the partial ^{1}H NMR spectrum of the white precipitate formed after **TBBI** was first exposed to TBAF and then bubbled with CO_2 in DMSO-d_6. The spectrum may be compared with the spectrum recorded before the CO_2 gas was introduced, i.e., that of the pure **TBBI** salt recorded in CD_3CN and DMSO-d_6 (Figure 4b,c) and a mixture of **TBBI** and F^- in CD_3CN (Figure 4a). ^{1}H NMR spectral analysis revealed that the signal assigned to the imidazolium proton (H_a), observed at 9.21 ppm in the spectrum of **TBBI** in CD_3CN, shifted to lower field upon the addition of F^- (as TBAF). In addition, the new signal at 6.64 ppm appeared upon the addition of F^-. The spectroscopic change was ascribed to the formation of the **TBBI**−F adduct **4** (Scheme 1 and Figure S3). After bubbling with CO_2, the solution produced by exposure of **TBBI** to F^- (3 equiv) gave rise to the presumed salt **1** (Figure 4d). The spectrum of this latter species was found to resemble that of the original **TBBI** precursor, with the exception that a new signal at 8.45 ppm (DMSO-d_6) was observed and assigned to the HCO_3^- anion.[12b] Collectively, these data provides support for the notion that the salt formed in the sequential manner described above was indeed **1**.

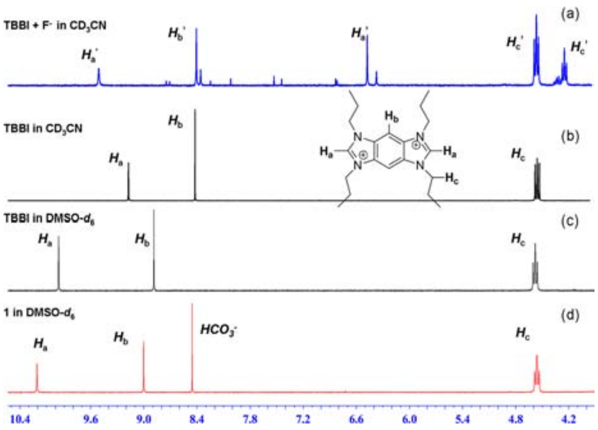


Figure 4. Partial ^{1}H NMR spectra of (a) **TBBI** recorded after the addition of TBAF in CD_3CN; (b) **TBBI** in CD_3CN; (c) **TBBI** in DMSO-d_6; (d) salt **1** in DMSO-d_6.

Further support for the above assignments was obtained from ^{13}C and ^{19}F NMR spectral analyses of **TBBI** in the presence of first fluoride ions and then exposure to CO_2. A comparison of the ^{13}C NMR spectra of **TBBI** and the presumed salt **1** as recorded in DMSO-d_6 (Figure S4) revealed that the proton signal of **C1** at 146.5 ppm in **TBBI** was still present. However, a new signal at 165.6 ppm was observed and assigned to HCO_3^- anion of **1**, in agreement with literature data.[12a] The ^{19}F NMR resonances of the PF_6^- counteranion appeared as a doublet between −70 and −73 ppm. Upon the addition of fluoride to **TBBI**, a single signal, corresponding to free F^-, was seen at −127.4 ppm; there was also a new signal appearing at −144.6 ppm which resulted from formation of the imidazolium adduct **4** (Figure S5). These data were further supported by a series of mass spectral analyses (see SI).

As a control experiment, CS_2, an isoelectronic analogue of CO_2, was added to **TBBI** in the presence of fluoride. Upon addition, a distinct white to red color change, consistent with the formation of an imidazolium dithiolate, was observed. Moreover, ^{1}H NMR spectroscopic analysis of the reaction mixture revealed that the proton signal, H_a, which was assigned to an imidazolium ring resonance disappearred, while the proton signals corresponding to H_b of the benzyl unit shifted upfield to ca. 7.94 ppm (Figure S6). Collectively, these observations provided support for the conclusions that F^- may serve to activate the imidazolium group and that the free carbene form is then produced in solution. Such a unique activation process allows for direct reaction with CO_2 or CS_2 without recourse to an external base (Scheme 1). It should be pointed out, however, that a suitable number of fluoride anion equivalents is needed to activate the precursor and form the reactive NHC speices. Addition of excess F^- to **TBBI** leads to the corresponding imidazolium adducts (e.g., **4**; Figure S3). We thus propose that other anions, such as OAc^- and CN^-, may also active the imidazolium rings via deprotonation, although perhaps less effectively than the fluoride anion. To the extent that this is true, alternative bases could be used to implement the present CO_2 sensing strategy (Figure S7).

Finally, to increase our understanding of the sequence of chemical transformations that occurred when **TBBI** was exposed to F^- followed by CO_2, a reaction coordinate energy diagram was proposed and calculated using density functional theory (Figure 5). The reaction between **TBBI** and TBAF was found to be barrierless for the step leading to the formation of the (F−H)···(NHC) complex. This finding leads us to suggest that bisimidazolium derivatives, such as **TBBI**, may be more efficient than monotopic analogues in generating NHCs. The reaction of CO_2 with the free NHC (Step A) and the subsequent reaction of H_2O with the NHC−CO_2 adduct were also investigated. A small energy barrier (1.1 kcal/mol) was calculated for Step A, a finding that leads us to predict that the NHC−CO_2 adduct formed quickly after the initial species was exposed to CO_2 gas. Moreover, decomposition of the corresponding NHC−CO_2 adduct **2** (Step B) was calculated to be exothermic, with a relatively small barrier of 16.8 kcal/

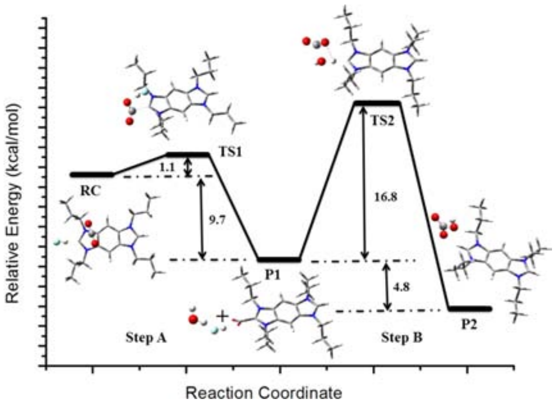


Figure 5. Energy profiles for the reactions of **TBBI** with TBAF, followed by CO_2 and subsequently H_2O. The numbers listed are in kcal/mol and calculated at the DFT level of theory.

mol.[13] Collectively these calculations supported our experimental findings: the $TBBI^+F^-$ complex reacts with CO_2, and the corresponding NHC−CO_2 quickly decomposes in the presence of water to form an imidazolium salt.

In summary, we have developed a novel optical-based CO_2 sensor that utilizes tetrapropyl benzobisimidazolium salts. The system features a high selectivity for fluoride, a low limit of detection, fast response times, and provides for both fluorescence and colorimetric outputs. Although our demonstration used fluoride anion, we believe that other basic species could be used to activate the starting bisimidazolium system for subsequent reaction with CO_2. Likewise, we believe that further structural modifications may enhance the already high sensitivity or enable the detection of other species.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed experimental procedures, NMR analysis, additional spectral data, and complete ref 13. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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