

# A Benzobisimidazolium-Based Fluorescent and Colorimetric Chemosensor for CO<sub>2</sub>

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## S Supporting Information

**ABSTRACT:** A new sensor for the fluorescent and colorimetric detection of CO<sub>2</sub> 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<sub>2</sub> to form an imidazolium carboxylate.

Carbon dioxide is a known greenhouse gas and linked to global climate change.<sup>1</sup> As such, there is a need to detect CO<sub>2</sub> selectively and to quantify its concentration in anthropogenic gas streams (e.g., flue gas, syngas, biogas, etc.) that typically contain high CO<sub>2</sub> levels before release into the atmosphere.<sup>1</sup> Improved CO<sub>2</sub> gas detection strategies could also prove beneficial for other applications, including agricultural production, hypercapnia assessment, and environmental analysis.<sup>2</sup> Common methods for CO<sub>2</sub> detection include Severinghaus-type potentiometric sensors, GC-MS, and IR spectroscopic techniques.<sup>2b</sup> 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.<sup>2,3</sup> In contrast, optical CO<sub>2</sub> 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.<sup>4</sup> Unlike previous optical methods for CO<sub>2</sub> sensing, which depend primarily on the acidic properties of CO<sub>2</sub>, we describe here a new strategy that provides a direct, chemical-based approach for detecting CO<sub>2</sub>. As detailed below, the method allows for both the fluorescent and colorimetric sensing of CO<sub>2</sub>.

Recently, it was shown that N-heterocyclic carbenes (NHCs), which are often obtained by deprotonating the corresponding imidazolium salts, are capable of activating CO<sub>2</sub> to form imidazolium carboxylates.<sup>5</sup> However, these systems

require dry and air-free conditions, and lack the features needed to be useful as CO<sub>2</sub> 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 imidazolium-based sensors has developed rapidly over the past decade, particularly for anion recognition.<sup>6</sup> When an imidazolium species interacts with an anion, a strong (C–H)<sup>+</sup>...X<sup>−</sup> 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<sub>2</sub> 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<sub>2</sub> sensors. As detailed below, we successfully realized such a detection scheme using tetrapropyl benzobisimidazolium salts (TBBI, Scheme 1).

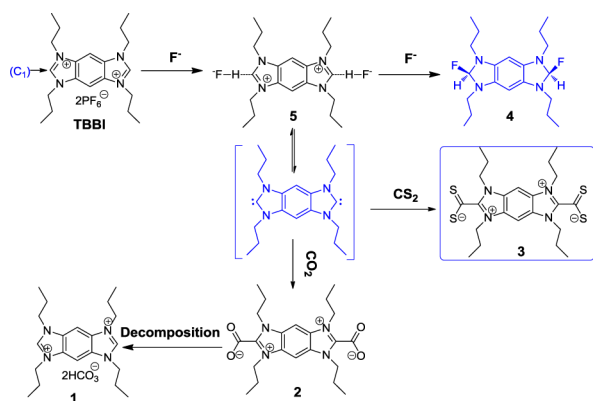
Bielawski<sup>7</sup> and Hahn<sup>8</sup> reported that benzobisimidazolium (BBI) salts can act as biscarbene ligands for metal ions and, in some cases, are fluorescent.<sup>9</sup> Recently, a BBI derivative has also been shown to act as a redox partner in an anion-switched electron transfer process involving an electron-rich calix[4]-pyrrole.<sup>10</sup> 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.<sup>9</sup> Considering these factors, we hypothesized that chemical modification of the C1 positions of BBI derivatives would permit the construction of a working optical CO<sub>2</sub> sensor. In particular, we envisioned that addition of a fluoride anion, which is considered to be a weak

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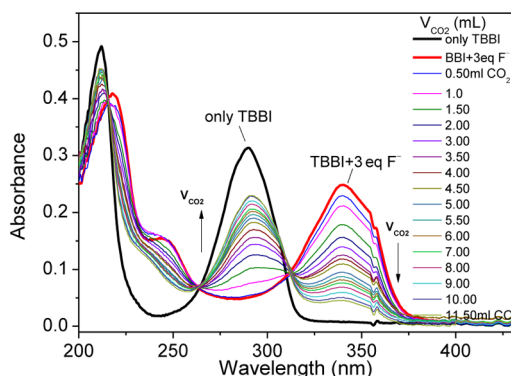
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**Scheme 1.** Proposed Reactions That Occur When TBBI Is Treated First with  $F^-$  and Then Either  $CO_2$  or  $CS_2$



base, would produce a species possessing partial NHC character<sup>11</sup> 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).

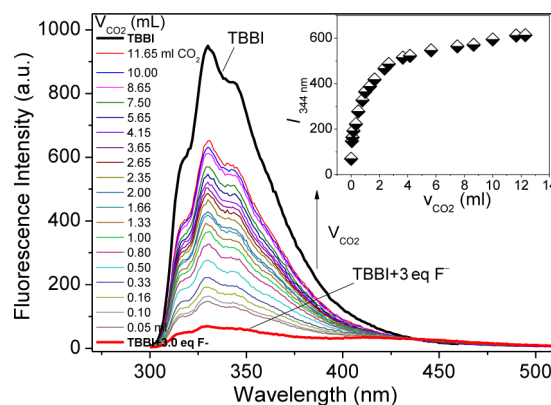
**TBBI** was prepared in ca. 60% yield from benzobisimidazole,<sup>9a</sup> by reacting with 1-iodopropane in  $CH_3CN$  followed by anion exchange with  $PF_6^-$  (see SI). The UV absorbance and fluorescence spectra of **TBBI** were recorded, and the effect of added  $F^-$  was examined. As shown in Figure 1, a solution of



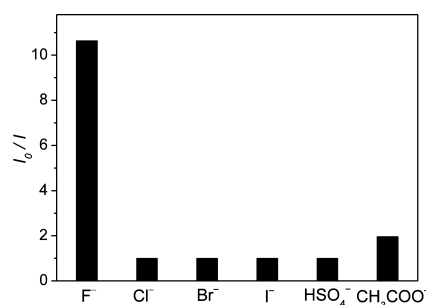
**Figure 1.** UV spectra of **TBBI** (15.0  $\mu M$ , 3.0 mL) recorded in  $CH_3CN$  in the presence of TBAF (3.0 equiv of  $F^-$ ) and then bubbling with different volumes of  $CO_2$ .

**TBBI** (15  $\mu M$ ) 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



**Figure 2.** Changes in the fluorescence titration spectral features of **TBBI** (15.0  $\mu M$ ) 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  $\mu M$ ) 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  $\mu M$ ) with excitation at 290 nm.

changes gave rise to an isosbestic point, localized at 312 nm in the absorption spectra (Figure 1).

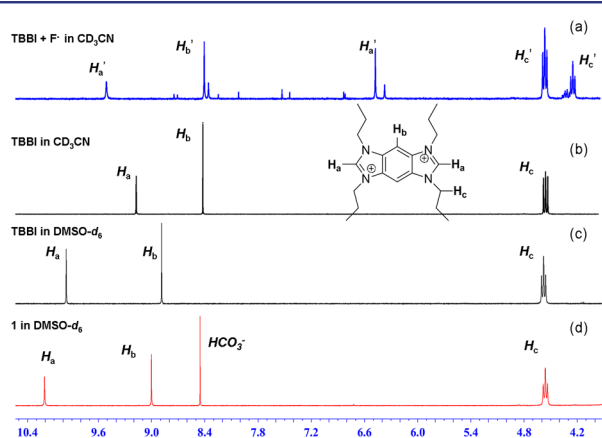
Analogous effects were observed in the corresponding fluorescent emission spectra, as shown in Figure 2. Specifically, the addition of  $F^-$  (as TBAF) to an acetonitrile solution of **TBBI** (15  $\mu M$ , 3.0 mL) caused a sharp decline in the emission spectral intensity arising from the bisimidazolium cation (excitation at 290 nm). On the other hand, a marked increase in the fluorescence intensity ( $\lambda_{max} = 330$  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<sub>2</sub> 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<sub>3</sub>CN. After bubbling with a large volume of CO<sub>2</sub> gas, a white precipitate formed which was assigned to the bis-NHC–CO<sub>2</sub> 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<sub>2</sub> 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.<sup>5</sup> Very recently, Taton and Vignolle demonstrated that reversible hydrolysis reactions involving imidazolium carboxylates and imidazolium HCO<sub>3</sub><sup>−</sup> salts are possible, with the specifics depending in part on the water content of the solvent system employed.<sup>12a</sup> One of the more convenient methods for effecting the decomposition of NHC–CO<sub>2</sub> adducts into the corresponding imidazolium HCO<sub>3</sub><sup>−</sup> salt involves exposure to a traditional Krapcho polar aprotic solvent (e.g., DMSO).<sup>12</sup> 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*<sub>6</sub> was chosen to allow the presumed formation and decomposition reactions of **2** to be followed by <sup>1</sup>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 <sup>1</sup>H NMR spectrum of the white precipitate formed after **TBBI** was first exposed to TBAF and



**Figure 4.** Partial <sup>1</sup>H NMR spectra of (a) **TBBI** recorded after the addition of TBAF in CD<sub>3</sub>CN; (b) **TBBI** in CD<sub>3</sub>CN; (c) **TBBI** in DMSO-*d*<sub>6</sub>; (d) salt **1** in DMSO-*d*<sub>6</sub>.

then bubbled with CO<sub>2</sub> in DMSO-*d*<sub>6</sub>. The spectrum may be compared with the spectrum recorded before the CO<sub>2</sub> gas was introduced, i.e., that of the pure **TBBI** salt recorded in CD<sub>3</sub>CN and DMSO-*d*<sub>6</sub> (Figure 4b,c) and a mixture of **TBBI** and F<sup>−</sup> in CD<sub>3</sub>CN (Figure 4a). <sup>1</sup>H NMR spectral analysis revealed that the signal assigned to the imidazolium proton (H<sub>a</sub>), observed at 9.21 ppm in the spectrum of **TBBI** in CD<sub>3</sub>CN, shifted to lower field upon the addition of F<sup>−</sup> (as TBAF). In addition, the new signal at 6.64 ppm appeared upon the addition of F<sup>−</sup>. The spectroscopic change was ascribed to the formation of the **TBBI**–F adduct **4** (Scheme 1 and Figure S3). After bubbling

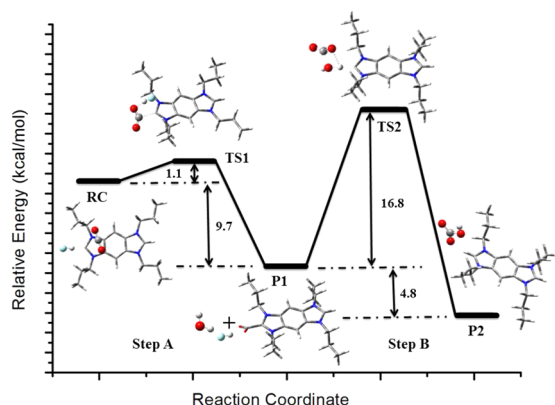
with CO<sub>2</sub>, the solution produced by exposure of **TBBI** to F<sup>−</sup> (3 equiv) gave rise to the presumed salt **1** (Figure 4d). The spectrum of this latter species was found to resemble that of the original **TBBI** precursor, with the exception that a new signal at 8.45 ppm (DMSO-*d*<sub>6</sub>) was observed and assigned to the HCO<sub>3</sub><sup>−</sup> anion.<sup>12b</sup> Collectively, these data provides support for the notion that the salt formed in the sequential manner described above was indeed **1**.

Further support for the above assignments was obtained from <sup>13</sup>C and <sup>19</sup>F NMR spectral analyses of **TBBI** in the presence of first fluoride ions and then exposure to CO<sub>2</sub>. A comparison of the <sup>13</sup>C NMR spectra of **TBBI** and the presumed salt **1** as recorded in DMSO-*d*<sub>6</sub> (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<sub>3</sub><sup>−</sup> anion of **1**, in agreement with literature data.<sup>12a</sup> The <sup>19</sup>F NMR resonances of the PF<sub>6</sub><sup>−</sup> counteranion appeared as a doublet between −70 and −73 ppm. Upon the addition of fluoride to **TBBI**, a single signal, corresponding to free F<sup>−</sup>, 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<sub>2</sub>, an isoelectronic analogue of CO<sub>2</sub>, 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, <sup>1</sup>H NMR spectroscopic analysis of the reaction mixture revealed that the proton signal, H<sub>a</sub>, which was assigned to an imidazolium ring resonance disappeared, while the proton signals corresponding to H<sub>b</sub> of the benzyl unit shifted upfield to ca. 7.94 ppm (Figure S6). Collectively, these observations provided support for the conclusions that F<sup>−</sup> 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<sub>2</sub> or CS<sub>2</sub> 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 species. Addition of excess F<sup>−</sup> to **TBBI** leads to the corresponding imidazolium adducts (e.g., **4**; Figure S3). We thus propose that other anions, such as OAc<sup>−</sup> and CN<sup>−</sup>, may also activate 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<sub>2</sub> sensing strategy (Figure S7).

Finally, to increase our understanding of the sequence of chemical transformations that occurred when **TBBI** was exposed to F<sup>−</sup> followed by CO<sub>2</sub>, 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<sub>2</sub> with the free NHC (Step A) and the subsequent reaction of H<sub>2</sub>O with the NHC–CO<sub>2</sub> 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<sub>2</sub> adduct formed quickly after the initial species was exposed to CO<sub>2</sub> gas. Moreover, decomposition of the corresponding NHC–CO<sub>2</sub> 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<sub>2</sub> and subsequently H<sub>2</sub>O. The numbers listed are in kcal/mol and calculated at the DFT level of theory.

mol.<sup>13</sup> Collectively these calculations supported our experimental findings: the TBBI<sup>+</sup>F<sup>−</sup> complex reacts with CO<sub>2</sub>, and the corresponding NHC–CO<sub>2</sub> quickly decomposes in the presence of water to form an imidazolium salt.

In summary, we have developed a novel optical-based CO<sub>2</sub> 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<sub>2</sub>. 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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