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Polydiacetylene-Based Colorimetric and Fluorescent Chemosensor for the Detection of Carbon Dioxide

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Ⓢ *Supporting Information*

ABSTRACT: We developed a colorimetric and fluorescent turn-on carbon dioxide sensor that relies on a polydiacetylene, **PDA-1**, functionalized with amines and imidazolium groups. The pendant amines react with CO_2 under basic conditions to form carbamoate anions, which partially neutralize the polymer's positive charges, inducing a phase transition. **PDA-1** allows for the selective sensing of CO_2 with high sensitivity, down to atmospheric concentrations. Naked-eye detection of CO_2 is accomplished either in water solutions of **PDA-1** or in the solid state with electrospun coatings of **PDA-1** nanofibers.

The toxicity of carbon dioxide, which acts mostly as an asphyxiant, is a significant concern for the safety of workers who operate in confined spaces.[1] It is most famous as the blackdamp of mining incidents, but may occur in environments as varied as sewers, grain silos, ship holds, spacecrafts, and submarines. Carbon dioxide is also released in large quantities by volcanic activity and, as a result of its density being greater than that of air, can accumulate in low-lying pockets called mazuku that cause harm to people and fauna alike. The dangers of CO_2 are most vividly illustrated by the liminic eruptions of Lake Monoun (1984) and Lake Nyos (1986), which caused deaths by asphyxiation by the thousands.

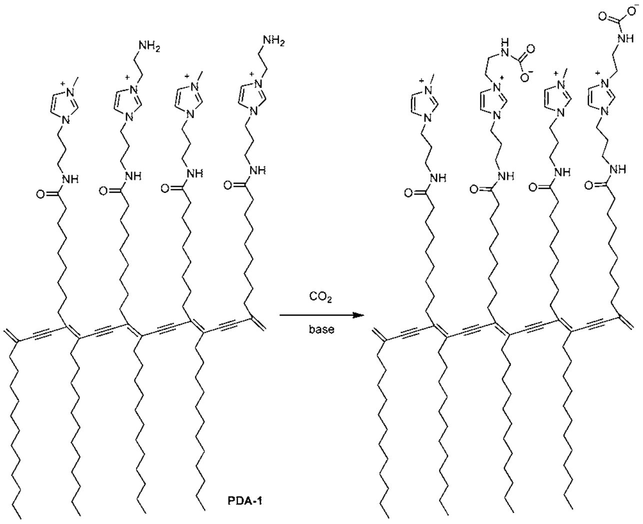
In economically privileged nations, workers and citizens are in large part protected from these risks by the installation of suitable ventilation systems, gas scrubbers, and CO_2 sensors that can trigger alarms. Those include sensors based on electrochemical measurements, mass spectrometry, gas chromatography, and most commonly nondispersive infrared sensors.[2,3] These sensors nonetheless suffer from high costs, the need for power sources, and their considerable bulk, which combine to make their operation in the field difficult. In this communication, we present our efforts to develop a sensor for the naked-eye detection of CO_2 that does not require an external power source and is sufficiently simple and inexpensive to be within reach of less wealthy populations.

Optical sensors for CO_2 have been reported by us[4] and others,[5] but fail to satisfy the above-mentioned criteria. Many of those rely on the pH change induced by the hydration of CO_2 to carbonic acid, and therefore suffer from low selectivity. Other synthetic receptors for CO_2 require organic solvents, a disadvantage which we sought to avoid due to their cost, toxicity, and environmental impact.

Polydiacetylenes (PDAs) exhibit a characteristic blue-to-red phase transition that can be triggered when stimuli disrupt the effective polymer conjugation length, typically by inducing a change in the preferred backbone conformation.[6] This unique property of PDAs has been adopted in the development of various chemosensors.[7]

Our sensor design relies on the reaction of CO_2 with alkylamines tethered to the imidazolium PDA to induce the blue-to-red phase change. In the presence of an added base, carbamic acid salts that partially neutralize the polymer's positive charges are generated, affecting the solvation of the side chains and resulting in changes to the backbone conformation. The signal change is maximized by the covalent linking of the carbamoates to prevent their diffusion away from the polymer (Scheme 1).

Scheme 1. Structure of the PDA-1 Studied in This Work, and Proposed Origin of the CO_2-Induced Color Change



The preparation of the sensory polymer **PDA-1** is shown in Scheme 2. Imidazolyldiyne **1** was allowed to react with 2-(Boc-amino)ethyl bromide under reflux to give the amine-tethered monomer **2** in 90% yield. While **2** is dispersed in water, homopolymerization under UV irradiation results in insoluble polymers. To remediate this lack of solubility, diynes **2** and **3** (1:1 ratio) were copolymerized to afford stable blue solutions of **PDA-1**. Transmission electron microscopy analysis shows that it possesses a fibrous structure (Figure S1).

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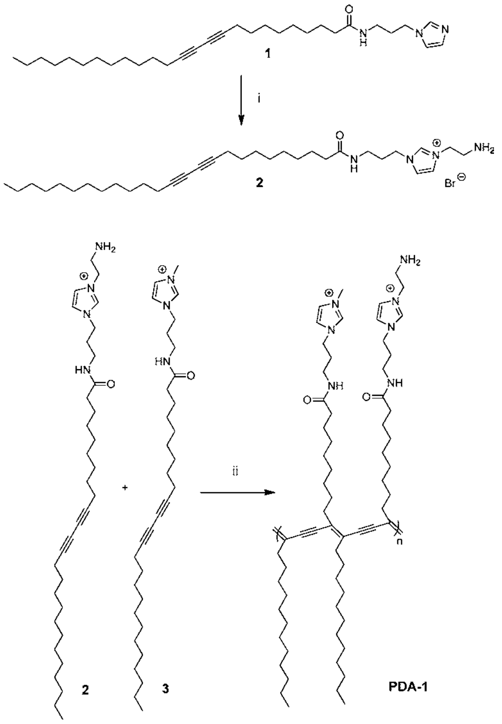
Scheme 2. Preparation of PDA-1[a]



[a]Conditions: (i) 2-(Boc-amino)ethyl bromide, CH_3CN, reflux. (ii) *hν* 254 nm, 30 s.

Reaction of the tethered amine with CO_2 to form carbamoate salt releases a proton, which is then captured by another amine site. The ammonium ions generated are unreactive toward CO_2, and their positive charge cancels out the newly formed anionic carbamoate sites. As a result, a solution of **PDA-1** in water does not change color after exposure to CO_2 gas (Figure S2). To solve this problem, triethylamine (TEA, 0.5% v/v) is added as a base to deprotonate the nascent ammonium carbamoate. The external base does not interact with **PDA-1** in the absence of CO_2, as evidenced by the lack of change in its visible spectra, and the original blue color of the solution remains (Figure S3).

The sensory response of **PDA-1** toward CO_2 is immediately apparent upon bubbling small volumes of the gas into sample cuvettes containing aqueous solutions of the polymer in the presence of TEA (Figure 1). The color change from brilliant blue to red is sufficiently clear to the untrained, naked eye for the unmistakable detection of CO_2. These features are attributed to the growth of a new absorption peak near 540 nm, together with the decrease in intensity of the absorption maximum of pristine **PDA-1** at 623 nm, and are consistent with the blue-to-red phase transition of PDAs. Spectral changes saturate after the addition of ca. 0.75 mL of gas. At that stage a small portion of the now-red polymer precipitates. This behavior is consistent with the postulated sensing mechanism: as anionic carbamoate sites are incorporated, aggregation with neighboring cationic polymer particles occurs, and the resulting zwitterionic polymer loses some of its water solubility.

The CO_2-induced phase transition of **PDA-1** is also readily monitored by its fluorescence signal (Figure 2). Pristine blue-phase **PDA-1** solutions are only weakly luminescent. Upon introduction of CO_2, fluorescence emission centered at 560 nm is briskly enhanced up to 5.9-fold until signal saturation is reached, as in the colorimetric detection scheme. Given that the red-phase **PDA-1** generated in the presence of CO_2 has a broad absorption band centered near 540 nm, an inexpensive AAA battery-powered green (532 nm, ≤5 mW) laser pointer constitutes an excellent light source for naked-eye fluorimetric detection of CO_2 in the field. The yellow emission of red-phase **PDA-1** after contact with CO_2 is easily distinguished from the green light scattered from pristine blue-phase **PDA-1** (Figure 3).

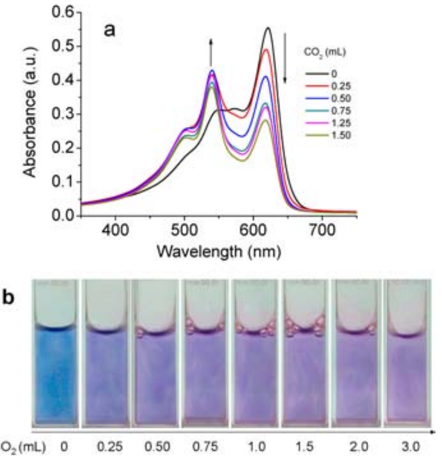


Figure 1. (a) UV/vis spectral changes of **PDA-1** in aqueous solution (25 *μ*M, containing 0.5% TEA) after bubbling with different volumes of CO_2. (b) Photos of the aqueous **PDA-1** solutions with different volumes of CO_2.

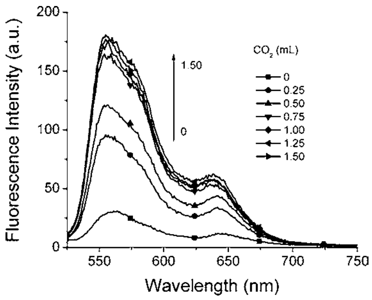


Figure 2. Fluorescence spectra changes of **PDA-1** solution (25 *μ*M, containing 0.5% TEA) after bubbling with different volumes of CO_2. Excitation wavelength, 500 nm; slit widths, 5/5 nm.

The **PDA-1**/TEA system is sufficiently sensitive to allow for detection of atmospheric CO_2 (ca. 400 ppm). Upon exposure to air in the presence of the external base, **PDA-1** undergoes its characteristic blue-to-red phase transition within 30 min, as evidenced by UV–vis and fluorescence spectroscopy (Figure S4).

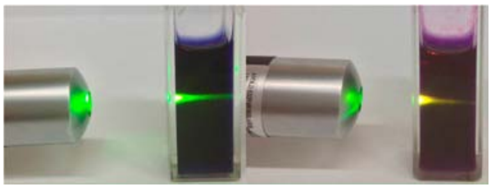


Figure 3. Fluorescence changes of **PDA-1** solution (1 mM, containing 0.5% TEA) before (left) and after (right) bubbling CO_2, illuminated with a simple green (532 nm) laser pointer for high-sensitivity naked-eye fluorescence detection.

Cationic imidazolium groups play a significant role in the blue-to-red phase transition in response to CO_2. When solutions of **PDA-NH_2**,[8] which has a backbone similar to that of **PDA-1** and primary amine side chains but lacks imidazolium moieties, are sparged with CO_2 in the presence of TEA, only minimal changes in spectral properties may be discerned (Figure 4), and the blue color remains unchanged. Therefore, the appended primary amines and the mere formation of carbamoate anions[9] are not sufficient to induce a PDA phase transition. To gather additional insight, we synthesized model compounds **5** and **7** and followed by ^1H NMR their reaction with CO_2 in D_2O containing 1.0 equiv of TEA (Figures 5, S5, and S6). Given the acidity of the imidazolium hydrogen,[10] TEA catalyzes the hydrogen−deuterium exchange of **7** to give deuterated **8**. By contrast, when **5** is reacted in with CO_2 in D_2O in the presence of 1.0 equiv of TEA, no significant deuterium−hydrogen exchange at the 2-position of the imidazolium is observed on a comparable time scale (minutes). This implies that the catalytic effect of TEA on the hydrogen−deuterium exchange has been neutralized by protonation with a Brønsted acid significantly stronger than the imidazolium. These observations are consistent with the proposed mechanism in which TEA acts as a Brønsted base to deprotonate the incipient ammonium carbamoate or the tautomeric carbamoic acid.

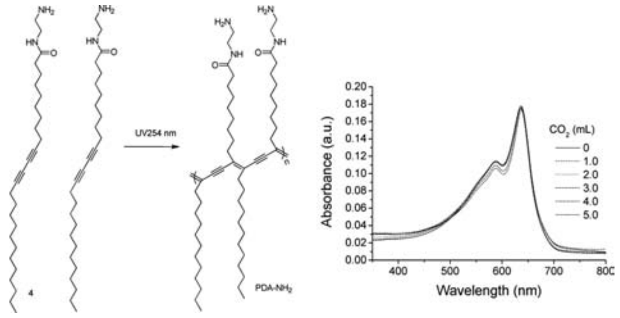


Figure 4. Chemical structure of **PDA-NH_2**, and spectra of **PDA-NH_2** solution (25 μM) bubbled with different volumes of CO_2 in the presence of TEA (0.5%).

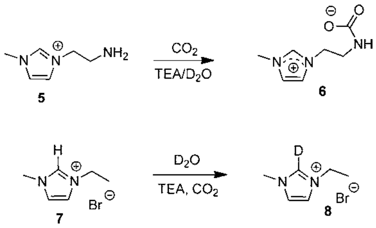


Figure 5. Reaction of model compounds **5** and **7** with CO_2 in D_2O in the presence of TEA (1.0 equiv).

The colorimetric and fluorimetric detection of CO_2 with solutions of **PDA-1** satisfies the criteria of simplicity, portability, and affordability that were our initial objectives. Nevertheless, for a number of applications, solid-state sensing may be superior to the sparging of the gas samples in water solutions of the polymer. For these purposes, admixtures of diynes **2**, **3**, and poly(ethylene oxide) were electrospun on aluminum plates, air-dried, and finally irradiated with UV light (254 nm) to result in a surface coating of blue-phase **PDA-1** nanofibers. Upon exposure to a CO_2 atmosphere and TEA vapors, a blue-to-red color change that parallels solution behavior is immediately observed (Figure 6). These results illustrate the potential of **PDA-1** for the development of simple colorimetric strips for CO_2 analogous to the widely used pH paper.

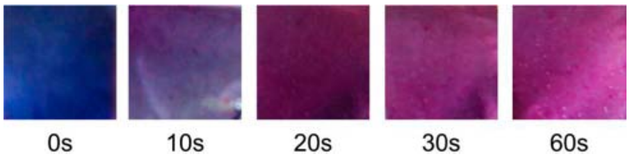


Figure 6. Time-dependent color changes of **PDA-1**-embedded electrospun microfibers in a CO_2 atmosphere saturated with TEA vapor.

In summary, we have developed a chemical sensor for carbon dioxide based on a polydiacetylene, **PDA-1**. Detection of CO_2 is made possible by the unique microstructure of **PDA-1**, which combines imidazolium cations with primary amines that react with CO_2 to form carbamoate anions in the presence of an external base. Naked-eye colorimetric CO_2 detection is possible both in aqueous solutions and on surfaces coated with electrospun fibers of **PDA-1**. The photophysical characteristics of **PDA-1** allow for the fluorimetric naked-eye detection of CO_2 using widely available battery-powered green laser pointers as light source. Because of their simplicity and low cost, and the avoidance of toxic organic solvents, CO_2 sensors based on **PDA-1** may be useful in locations and socio-economic environments where existing sensors would have been unthinkable.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Equipment and measurements; synthesis of monomer **2** and compound **8**; preparation of **PDA-1** solution and its nanofibers; spectra of **PDA-1** solutions with CO_2 and with TEA (0.5%); UV/vis and fluorescence spectra changes of **PDA-1** solution (with 0.5% TEA) exposed to air; CO_2-induced ^1H NMR spectral changes of compounds **5** and **6**; and ^1H NMR and ^{13}C NMR spectra of monomer **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

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Notes

The authors declare no competing financial interest.

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