Fluorescent Chemosensor for Detection and Quantitation of Carbon Dioxide Gas

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Abstract: CO2 sensing is of great societal implications, as CO2 is a component of gas mixtures from many natural and anthropogenic processes with huge impacts on global climate and human well-being. Herein we report a CO2 assay scheme over a wide concentration range, utilizing a fluorogen with an aggregation-induced emission feature and a liquid with tunable polarity and viscosity. The CO2 sensing process is specific, quantitative, simple, quick, and tolerant to interferents, especially CO and water. It will be even better if the outcome of the test is visible to the naked eye, which will aid on-site decision-making. The assay kit should be portable and energy- and cost-effective, with a working calibration curve covering a wide CO2 concentration range, instead of merely at ppm level. Herein we report a new fluorescent CO2-chemosensing scheme that meets most of the requirements discussed above.

We have recently discovered a novel photophysical effect of aggregation-induced emission (AIE).7 Hexaphenylsilole (HPS), for example, is nonluminescent in solutions but highly emissive as aggregates (Figure 1). It has been proved experimentally and theoretically that restriction of intramolecular rotations (RIR) of its multiple phenyl rotors in the aggregate accounts for the AIE effect.6 It is known that bubbling CO2 through an amine yields a carbamate ionic liquid (CIL), which is accompanied by increases in polarity and viscosity.7 It is thus envisioned that purging an amine solution of HPS with a stream of CO2 gas may turn on the light emission of HPS, because its molecules may cluster in and its RIR process may be activated by the polar and viscous CIL.5

We screened a series of amines. Bubbling large volumes of CO2 gas through HPS solutions in DEA, BA, Pip, and Py caused no recognizable changes in the emission of HPS (Figure 2a). A green light, however, was emitted from a DPA solution of HPS immediately after it had been bubbled with a small volume of CO2 gas. Photoluminescence (PL) spectrum of HPS was intensified with the test is visible to the naked eye, which will aid on-site decision-making. The assay kit should be portable and energy- and cost-effective, with a working calibration curve covering a wide CO2 fold) of CO2 gas to drive the reaction to far to the right as possible.

Figure 1. (a) 1,1,2,3,4,5-Hexaphenylsilole (HPS) is nonemissive when its molecules are dissolved in THF but becomes strongly fluorescent when the luminogens are aggregated in the THF/water mixtures with high water contents. (b) Formation of carbamate ionic liquid (CIL) by bubbling CO2 gas through dipropylamine (DPA) liquid.
Addition of an increasing amount of the CIL into a DPA solution of HPS resulted in a monotonic increase in its PL intensity (Figure S1). Clearly, it is the CIL that has affected the emission of HPS. A linear line ($R = 0.9988$) was obtained for the semilog plot of the PL intensity vs the fraction of CIL (Figure 3a).

It is of practical value to quantify the fraction of CO$_2$ ($f_{\text{CO}_2}$) in a gas mixture. CO$_2$/N$_2$ mixtures were used as a model system in this work to check how the PL of HPS responses to variations in $f_{\text{CO}_2}$. The CO$_2$/N$_2$ mixtures with different CO$_2$ contents were bubbled through HPS solutions in DPA at a fixed rate for a fixed time. As shown in Figure S2,$^8$ the PL spectrum of HPS was intensified monotonically with increasing amount of CO$_2$. The log $I = f_{\text{CO}_2}$ plot gives a linear line over the whole concentration range (Figure 3b). This calibration line enables quantitation of CO$_2$ under various conditions, particularly for the gas mixtures with very high CO$_2$ contents, such as black-damp and volcano gases.

Since the conventional CO$_2$-sensing processes are susceptible to water and it has been reported that bicarbonate formation is involved in the reaction of amine with CO$_2$ in the presence of water,$^9$ we prepared moisturized CO$_2$ gas by sublimation of dry ice cubes immersed under water and used it to examine the effect of water on the performance of our sensing scheme. Purgung a DPA solution of HPS with the moisturized gas gave data nearly identical to those obtained by using dry CO$_2$ as the bubbling gas (Figure 4a). Furthermore, we directly added water droplets into DPA solutions of HPS. The results were virtually the same within experimental error, even in the presence of a large amount of water (100 µL). The addition of the water droplets exerted little effect on the viscosity of the CIL system (Figure S3).$^8$ Though bicarbonate is probably formed in the reaction of DPA with the humidified CO$_2$ gas, it should be noted that the bicarbonate is also an ionic liquid (BIL; Scheme S1).$^8$ The collective effects of the viscosity, polarity, and solubility of the BIL on the light emission of HPS are possibly similar to those of the CIL, which explains why the performance of the CO$_2$-sensing process is little affected by the presence of water.

The CIL-based sensing scheme is free of the CO-interfering problem, because it is well-known that CO does not react with amine.$^{10}$ It thus becomes clear that our fluorescent CO$_2$-sensing process is highly resistant to the common interferences of water and CO.

Figure 2. (a) Photographs of HPS solutions ($\sim$37 µM) in the amines (2 mL) bubbled with CO$_2$ gas (45 mL); DEA = diethylamine, BA = butylamine, Pip = piperidine, Py = pyridine. (b) PL spectra and photographs of HPS in DPA before and after bubbling with different volumes of CO$_2$ ($V_{\text{CO}_2}$). All the photographs were taken under UV illumination.

Figure 3. Plots of PL intensities ($I$) of HPS versus fractions of (a) CIL ($f_{\text{CIL}}$) and (b) CO$_2$ ($f_{\text{CO}_2}$) in a DPA/CIL and (c) CO$_2$/N$_2$ mixtures. Inset in panel (a): photographs of HPS in the DPA/CIL mixtures, whose CIL fractions (vol %) are given by the numbers on the sample vials.

Figure 4. (a) Plot of $I/I_0$ ratio versus amount of water added into HPS solution in DPA (2 mL). $I$ and $I_0$ are the PL intensities after and before bubbling with CO$_2$, respectively. (b) Change of viscosity ($\eta$) with $f_{\text{CIL}}$ in DPA/CIL mixture (cf, Figure 3a). (c) Size distribution of nanoparticles of HPS formed after its solution in DPA was bubbled with CO$_2$. Inset: TEM image of the HPS nanoparticles.
To gain insights into the operating mechanism of the sensing process, we carried out spectroscopic and microscopic analyses. NMR and IR spectra verified that the CO$_2$ bubbling had resulted in the formation of CIL (Figures 3c and S88), accompanying which the viscosity of the CIL became increased logarithmically (Figures 3b and S78). Measurements with a TEM microscope and a ζ potential analyzer revealed that the molecules of HPS were aggregated into nanoparticles with an average diameter ($D$) of ~100 nm in the CIL mixture (Figures 3c and S88).

The above experimental results suggest a working mechanism for the CO$_2$ sensing process as follows. In the very dilute DPA solution of HPS (~37 μM), its six phenyl rotors undergo active intramolecular rotations, which effectually annihilate its excited states nonradiatively. Bubbling DPA liquid with CO$_2$ gas results in the formation of a viscous and polar CIL with poor solvating power toward HPS. It is well-known that a viscous medium hampers intramolecular motion and that a polar solvent induces hydrophobic solutes to aggregate. Both of these two effects activate the RIR process of HPS, thereby blocking its nonradiative decay channels and turning on its light emission in the CIL mixture. The viscosity and polarity are increased with an increase in CO$_2$ volume, thus enabling the gas quantitation. DEA, BA, Pip, and Py failed to serve as media for the CO$_2$-detection scheme. The reason is not clear at present. One possibility is that the changes in the viscosity and polarity of the systems caused by the CO$_2$ purging were not big enough to induce the fluorogenic HPS molecules to aggregate.

In summary we developed a simple CO$_2$-assay scheme in this work. It visualizes the presence of CO$_2$ and permits quantitation of its amount over the whole concentration range (0~100%). It is free of the problems often encountered in the conventional CO$_2$-sensing systems. Our scheme is particularly appealing to the mega sciences with huge societal impacts, such as volcanology and seismology, where field tracking of the gas mixtures with high CO$_2$ contents plays a crucial role in disaster prediction and prevention.

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Supporting Information Available: Experimental procedures, PL spectra of HPS in the DPA/CIL mixtures, reaction scheme of DPA with moisturized CO$_2$, effect of water on CIL viscosity, spectral data of CIL, viscosity change with purging time, and TEM images of HPS particles formed in the CIL. This material is available free of charge via the Internet at http://pubs.acs.org.

References

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