Fluorescent Chemosensor for Detection and Quantitation of Carbon Dioxide Gas

Yang Liu,[†] Youhong Tang,[†] Nikolay N. Barashkov,[‡] Irina S. Irgibaeva,[§] Jacky W. Y. Lam,[†] Rongrong Hu,[†] Dinara Birimzhanova,[§] Yong Yu,[†] and Ben Zhong Tang*,[†]

Department of Chemistry, Institute of Molecular Functional Materials, The Hong Kong University of Science and Technology (HKUST), Hong Kong, China, Micro-Tracers, Inc., San Francisco, California 92124, United States, and Department of Chemistry, L. N. Gumiliyov Eurasian National University, Astana, Kazakhstan

Received October 8, 2009; E-mail: tangbenz@ust.hk

Abstract: CO_2 sensing is of great societal implications, as CO_2 is a component of gas mixtures from many natural and anthropogenic processes with huge impacts on globe climate and human well-being. Herein we report a CO_2 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 CO_2 sensing process is specific, quantitative, and interferent tolerant.

CO_2 sensing is of great importance to occupational hygiene, public health, and societal welfare. For example, checking for blackdamp, a gas mixture containing 5−20% CO_2, in enclosed spaces such as mines, sewers, wells, tunnels, and ships (submarines) is required by safety regulations.[1] Volcanic gases typically contain 10−40% of CO_2.[2] Monitoring the variations in CO_2 levels in the gas mixtures released from dormant craters, hot springs, and seafloor "smoking chimneys" may help capture the early signs of a volcano, earthquake, or tsunami. Many anthropogenic gases (flue gas, syngas, biogas, etc.) are mixtures with high CO_2 contents (some being as high as 50%).[1] Quantification of their CO_2 concentrations serves as quality control to ensure their proper functions in the industrial processes and as a safeguard against their notorious effects on global climate change through the scrubbing processes before they are discharged as waste streams into the atmosphere.[1]

Electrochemical (EC) and IR methods are generally used for CO_2 sensing.[3] EC sensors commonly work at high temperatures (300−800 °C) and are thus power-hungry and unsuitable for use in potentially flammable and explosive locations. IR sensors, on the other hand, are bulky and expensive. The interference of CO is a thorny problem, as it absorbs at the similar wavelengths in the IR spectral region and it usually coexists with CO_2 in the gas mixtures. Moreover, both EC and IR chemosensors are cross-sensitive to water. GC−MS can also be used to analyze CO_2, but the process is costly and time-consuming. Field-effect transistors based on carbon nanotubes and inorganic semiconductors are promising for gas-detection applications,[4] but the devices require fabrication of complex equipment and processes.

For real-world applications, a CO_2 sensor should ideally be 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 CO_2
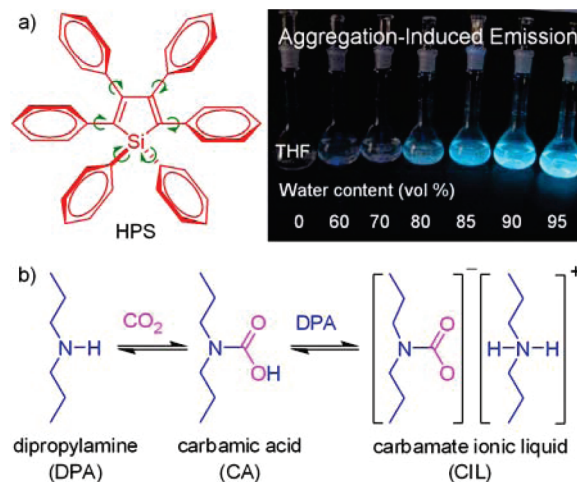

Figure 1. (a) 1,1,2,3,4,5-Hexaphenylsilole (HPS) is nonemissive when its molecules are dissolved in THF but becomes strongly fluorescent when the luminogens are aggregated in the THF/water mixtures with high water contents. (b) Formation of carbamate ionic liquid (CIL) by bubbling CO_2 gas through dipropylamine (DPA) liquid.

concentration range, instead of merely at ppm level. Herein we report a new fluorescent CO_2-chemosensing scheme that meets most of the requirements discussed above.

We have recently discovered a novel photophysical effect of aggregation-induced emission (AIE).[5] 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 CO_2 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 CO_2 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 CO_2 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 CO_2 gas. Photoluminescence (PL) spectrum of HPS was intensified with increasing the volume of CO_2 gas (Figure 2b). After being bubbled with 25 mL of CO_2 gas, the HPS mixture emitted a very bright green light.

We prepared a CIL by purging DPA with a large excess (160 fold) of CO_2 gas to drive the reaction to far to the right as possible
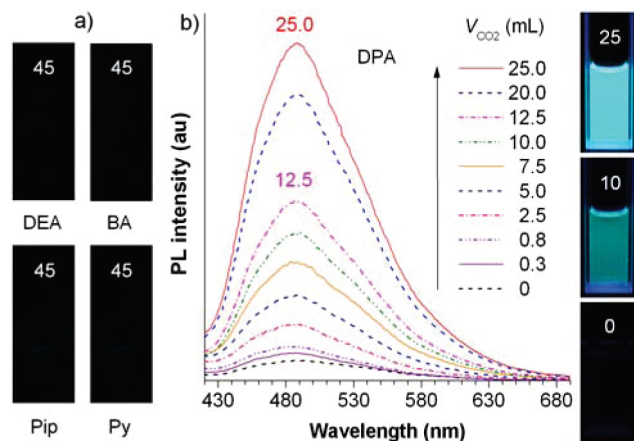
Figure 2. (a) Photographs of HPS solutions (~37 μM) in the amines (2 mL) bubbled with CO_2 gas (45 mL); DEA = diethylamine, BA = butylamine, Pip = piperidine, Py = pyridine. (b) PL spectra and photographs of HPS in DPA before and after bubbling with different volumes of CO_2 (V_{CO2}). All the photographs were taken under UV illumination.
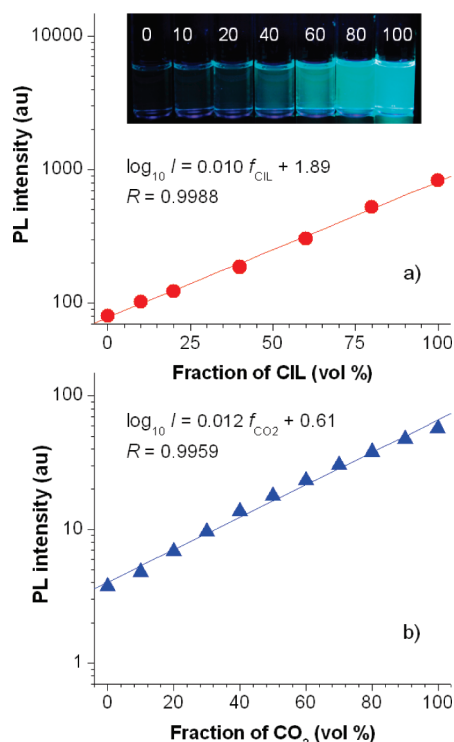

Figure 3. Plots of PL intensities (*I*) of HPS versus fractions of (a) CIL (f_{CIL}) and (b) CO_2 (f_{CO2}) in a) DPA/CIL and (c) CO_2/N_2 mixtures. Inset in panel (a): photographs of HPS in the DPA/CIL mixtures, whose CIL fractions (vol %) are given by the numbers on the sample vials.

(cf, Figure 1b). 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).[8] 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_{CO2}) 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_{CO2}. 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 monotonously with increasing amount of CO_2. The log $I - f_{CO2}$
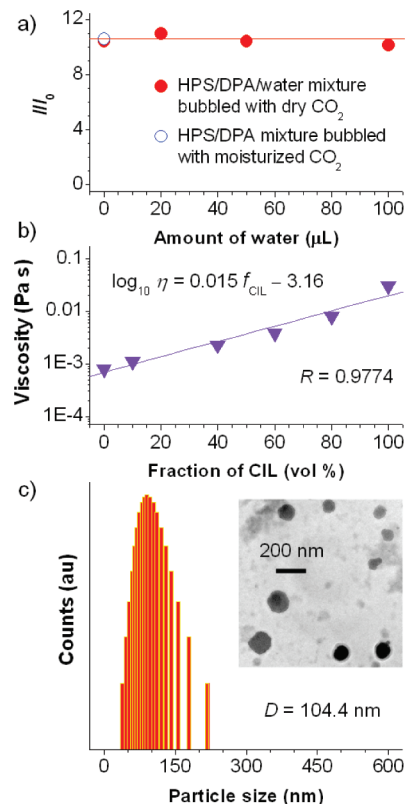

Figure 4. (a) Plot of I/I_0 ratio versus amount of water added into HPS solution in DPA (2 mL). *I* and I_0 are the PL intensities after and before bubbling with CO_2, respectively. (b) Change of viscosity (η) with f_{CIL} in DPA/CIL mixture (cf, Figure 3a). (c) Size distribution of nanoparticles of HPS formed after its solution in DPA was bubbled with CO_2. Inset: TEM image of the HPS nanoparticles.

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. Purging 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.

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 S4−S6[8]), accompanying which the viscosity of the DPA solution was increased logarithmically (Figures 3b and S7[8]). 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 S8[8]).

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 effectively 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.[5,6] 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.[2]

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

(1) Pierantozzi, R. In *Encyclopedia of Chemical Technology*, 4th ed.; Kroschwitz, J. I. , Ed.; Wiley: New York, 1991; Vol. 4, pp 803−822.
(2) Laursen, L. *Science* **2010**, *328*, 410, and references therein.
(3) (a) Neethirajan, S.; Jayas, D. S.; Sadistap, S. *Food Bioprocess Technol.* **2009**, *2*, 115. (b) Lin, J. *Trac-Trends Anal. Chem.* **2000**, *19*, 541. (c) Wolfbeis, O. S.; Weis, L. J.; Leiner, M. J. P.; Ziegler, W. E. *Anal. Chem.* **1988**, *60*, 2028. (d) Hitchman, M. J.; Park, M. U.S. Patent 6,365,022, 2002. (e) Safinya, K. A.; Tarvin, J. A. U.S. Patent 4,994,671, 1991. (f) Tchakarov, B. J. DiFoggio, R.; Forgan, S. W.; Fanini, O. N.; Hunziker, J. C.; Civarolo, M. F. U.S. Patent 6,218,662, 2001. (g) Mills, A.; Hamilton, M. WO/9 105 252, 1991.
(4) For example:(a) Barsan, N.; Weimar, U. *J. Electroceram.* **2001**, *7*, 143. (b) Star, A.; Han, T.-R.; Joshi, V.; Gabriel, J-C. P.; Grüner, G. *Adv. Mater.* **2004**, *16*, 2049.
(5) (a) Luo, J.; Xie, Z.; Lam, J. Y.; Cheng, L.; Chen, H.; Qiu, C.; Kwok, H.; Zhan, X.; Liu, Y.; Zhu, D.; Tang, B. Z. *Chem. Commun.* **2001**, 1740. (b) Hong, Y.; Lam, J. W. Y.; Tang, B. Z. *Chem. Commun.* **2009**, 4332. (c) Liu, J.; Lam, J. W. Y.; Tang, B. Z. *J. Inorg. Organomet. Polym. Mater.* **2009**, *19*, 249. (d) Liu, J.; Lam, J. W. Y.; Tang, B. Z. *Chem. Rev.* **2009**, *109*, 5799.
(6) (a) Zhao, Z.; Wang, Z.; Lu, P.; Chan, C. Y. K.; Liu, D.; Lam, J. W. Y.; Sung, H. Y.; Williams, I. D.; Ma, Y.; Tang, B. Z. *Angew. Chem., Int. Ed.* **2009**, *48*, 7608. (b) Liu, Y.; Tao, X.; Wang, F.; Dang, X.; Zou, D.; Ren, Y.; Jiang, M. *J. Phys. Chem. C* **2008**, *112*, 3975. (c) An, B. K.; Kwon, S. K.; Jung, S. D.; Park, S. Y. *J. Am. Chem. Soc.* **2002**, *124*, 14410. (e) Yeh, H. C.; Yeh, S. J.; Chen, C. T. *Chem. Commun.* **2003**, 2632. (f) Chen, J.; Law, C. W.; Lam, J. W. Y.; Dong, Y. P.; Lo, S. F.; Williams, I. D.; Zhu, D.; Tang, B. Z. *Chem. Mater.* **2003**, *15*, 1535. (g) Yu, G.; Yin, S.; Liu, Y.; Qiu, C.; Chen, J.; Xu, X.; Sun, X.; Ma, D.; Zhan, X.; Peng, Q.; Shuai, Z. G.; Tang, B. Z.; Zhu, D. B.; Fang, W.; Luo, Y. *J. Am. Chem. Soc.* **2005**, *127*, 6335. (h) Liu, L.; Zhang, G.; Xiang, J.; Zhang, D.; Zhu, D. *Org. Lett.* **2008**, *10*, 4581. (i) Pu, K. Y.; Liu, B. *Adv. Funct. Mater.* **2009**, *19*, 277. (j) Li, Z.; Dong, Y. Q.; Lam, J. W. Y.; Sun, J.; Qin, A.; Häuβler, M.; Dong, Y. P.; Sung, H. H. Y.; Williams, I. D.; Kwok, H. S.; Tang, B. Z. *Adv. Funct. Mater.* **2009**, *19*, 905.
(7) (a) Jessop, P. G.; Heldebrant, D. J.; Li, X.; Eckert, C. A.; Liotta, C. L. *Nature* **2005**, *436*, 1102. (b) Phan, L.; Andreatta, J. R.; Horvey, L. K.; Edie, C. F.; Luco, A. L.; Mirchandani, A.; Darensbourg, D. J.; Jessop, P. G. *J. Org. Chem.* **2008**, *73*, 127.
(8) See Supporting Information.
(9) (a) Sayari, A.; Belmabkhout, Y. *J. Am. Chem. Soc.* **2010**, *132*, 6312. (b) Serna-Guerrero, R.; Da'na, E.; Sayari, A. *Ind. Eng. Chem. Res.* **2008**, *47*, 9406.
(10) (a) Yamada, T.; Lukac, P. J.; George, M.; Weiss, R. G. *Chem. Mater.* **2007**, *19*, 967. (b) Phan, L.; Chiu, D.; Heldebrant, D. J.; Huttenhower, H.; John, E.; Li, X.; Pollet, P.; Wang, R.; Eckert, C. A.; Liotta, C. L.; Jessop, P. G. *Ind. Eng. Chem. Res.* **2008**, *47*, 539.

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