



Short communication

Colorimetric fluorescence response to carbon dioxide using charge transfer dye and molecular rotor dye in smart solvent system



Young-Jae Jin, Byong-Cheon Moon, Giseop Kwak*

School of Applied Chemical Engineering, Major in Polymer Science and Engineering, Kyungpook National University, 1370 Sankyuk-dong, Buk-ku, Daegu 702-701, South Korea

ARTICLE INFO

Article history:

Received 2 April 2016

Received in revised form

3 May 2016

Accepted 5 May 2016

Available online 7 May 2016

Keywords:

Colorimetric fluorescence

Charge transfer

Molecular rotor

Carbon dioxide

Smart solvent system

ABSTRACT

Combination of a charge transfer dye and a molecular rotor dye in a smart solvent system resulted in a remarkable colorimetric fluorescence (FL) response to carbon dioxide (CO₂). Nile Red and allyl-2-cyano-3-(1,2,3,5,6,7-hexahydropyrido[3,2,1-ij]quinolin-9-yl)acrylate (ACHQA) were used as the charge transfer dye and molecular rotor dye, respectively, and an equivalent molar mixture of 1,8-diazabicyclo-[5.4.0]-undec-7-ene (DBU) and 1-propanol was chosen as the smart solvent system. Nile Red and ACHQA in the DBU/1-propanol solvent mixture emitted red light mainly due to Nile Red, whereas the FL color gradually turned to green with the increasing amount of CO₂ injected. The FL color reverted into the initial state by simultaneously bubbling N₂ gas and heating at 50 °C.

© 2016 Elsevier Ltd. All rights reserved.

Carbon dioxide (CO₂) detection is required in many fields for chemical, clinical, and environmental monitoring [1]. IR spectroscopic and electrochemical detection methods have been used for CO₂ sensing [2]. However, such direct detection methods suffer from strong interferences from water vapor and carbon monoxide (CO) gas, and require complicated and expensive optical instruments. To overcome these problems, many highly sensitive and convenient CO₂ sensors have been developed as platforms for fiber- and film-optics [3]; their sensing mechanisms have been based mostly on pH sensitivity. These sensors work exclusively in the presence of water, since these dyes induce pH changes and display an output signal only when CO₂ reacts with water to produce carbonic acid. Accordingly, the CO₂ sensitivity is highly dependent on the relative humidity. In solid-state applications, sensor systems need not only a hydrophobic matrix that can act as a proton barrier and reduce the cross-sensitivity to pH, but also a phase-transfer agent to solubilize the pH indicator in the hydrophobic matrix. Therefore, the development of new types of optical CO₂ sensor systems that are not based on pH indicators may open new avenues in this field, providing more facile and simpler detection methods.

Some secondary and tertiary amines react with CO₂ gas and convert to carbonate ionic liquids in the presence of alcohols or to carbamate ionic liquids in themselves. As a result, their physical properties, such as their polarity and viscosity, are significantly changed to higher values. Desorption of CO₂ by nitrogen (N₂) bubbling and/or heating at a relatively low temperature makes it possible to revert to the original value levels. Thus, such amine/alcohol mixtures can be referred to as smart solvent systems [4]. The reversible changes in polarity and viscosity may be recognized by the naked eye with the aid of some specific functional dyes [5]. On the one hand, polarity changes can be visualized by charge transfer dyes. Usually, the fluorescence (FL) emission of charge transfer dyes decreases remarkably in intensity (non-radiative FL decay) and simultaneously shifts to longer wavelengths (red-shift) with the increasing polarity of the solvent. On the other hand, viscosity changes can be visualized by molecular rotor dyes. Generally, the FL emission of molecular rotor dyes increases markedly in intensity (radiative FL decay) as the solvent viscosity increases, due to the restriction of intramolecular rotation. We thus envisioned that, if both a charge transfer dye and an molecular rotor dye are dissolved in an amine/alcohol mixture and their FL bands do not overlap, the FL emission of the charge transfer dye will be dominant in the less polar and viscous solution (that is, before reaction with CO₂) while, after reaction with CO₂, the FL emission of the charge transfer dye will disappear and, instead, the FL emission

* Corresponding author.

E-mail address: gkwak@knu.ac.kr (G. Kwak).

of the molecular rotor dye will appear in the much more polar and viscous ionic liquid solution. The schematic illustration of this concept is shown in Fig. 1.

To verify this conceptual idea, we examined an equivalent molar amine/alcohol mixture as the CO₂-sensitive smart solvent system. 1,8-Diazabicyclo-[5.4.0]-undec-7-ene (DBU) and 1-propanol were chosen as the amine and the alcohol, respectively. Nile Red and allyl-2-cyano-3-(1,2,3,5,6,7-hexahydropyrido[3,2,1-ij]quinolin-9-yl)acrylate (ACHQA) were selected as the charge transfer dye and molecular rotor dye, respectively. ACHQA was newly synthesized in this study as a 9-(2-carboxy-2-cyanovinyl)julolidine (CCVJ) derivative, as described in the experimental section (see the Supporting Information). Nile Red and ACHQA were dissolved in the DBU/1-propanol mixture at a concentration of 5.0×10^{-5} M. Fig. 2 shows the UV-vis absorption and FL emission spectra of Nile Red and ACHQA in the DBU/1-propanol mixture. Nile Red exhibits its absorption maximum wavelength at 543 nm in the smart solvent

system before CO₂ injection, whereas the absorption maximum peak of ACHQA cannot be clearly identified probably due to its relatively low absorptivity. Nile Red shows a very strong FL emission with a maximum at 610 nm in the smart solvent system before CO₂ injection, whereas ACHQA displays a relatively weak FL emission with a maximum at 489 nm in the same smart solvent system. Before CO₂ injection, the smart solvent system emits red light mainly due to Nile Red. On the other hand, the red-light emission of Nile Red immediately disappears after CO₂ injection owing to the increase in polarity, and the green-light emission from ACHQA becomes predominant owing to the increase in viscosity. The two facts that 1) the viscosity of smart solvent system remarkably increases when reacting with an excess amount of CO₂ and 2) the FL intensity of ACHQA significantly increases with an increase in solvent viscosity are clearly shown and described in more detail (Figs. S1 and S2). This suggests that red-to-green FL colorimetric sensing of CO₂ is possible by the coexisting charge transfer dye and molecular rotor dye in the smart solvent system. Although the FL emission band of ACHQA slightly overlaps the absorption band of Nile Red in the smart solvent system, the possibility of Förster resonance energy transfer (FRET) between ACHQA and Nile Red is eliminated by diluting the solution appropriately (concentration = 5.0×10^{-5} M). ACHQA does not display any significant Stokes shift, even in the carbonate ionic liquid state of DBU/1-propanol after CO₂ injection, due to its twisted intramolecular charge transfer characteristics [5], whereas the absorption band of Nile Red is significantly attenuated and shifted to a longer wavelength due to its high dipole moment (dipole moment at ground state: $\mu_g \sim 8.2 \pm 1.0$ Debye) [6]. Thus, the possibility of FRET between ACHQA and Nile Red in the polar ionic liquid solution after the injection of CO₂ is almost completely discarded regardless of the concentration. The FL excitation spectra measurement confirmed that FRET does absolutely not occur between the Nile red and ACHQA in the dilute solution (Fig. S3). Notably, the FL color of the smart solvent system changes gradually with the increasing amount of CO₂ injected (Fig. 3). The red emission color changes to pink (CO₂/smart solvent system mol% ~20%), white (~30%), and light green (>40%) with the CO₂ molar ratio. This provides the possibility of naked eye determination of the amount of CO₂ without the need for analytical equipment. As expected, the green light-emission gradually disappears by simultaneously bubbling N₂ gas and heating at 50 °C (Fig. 4), and the initial red-light emission is completely restored due

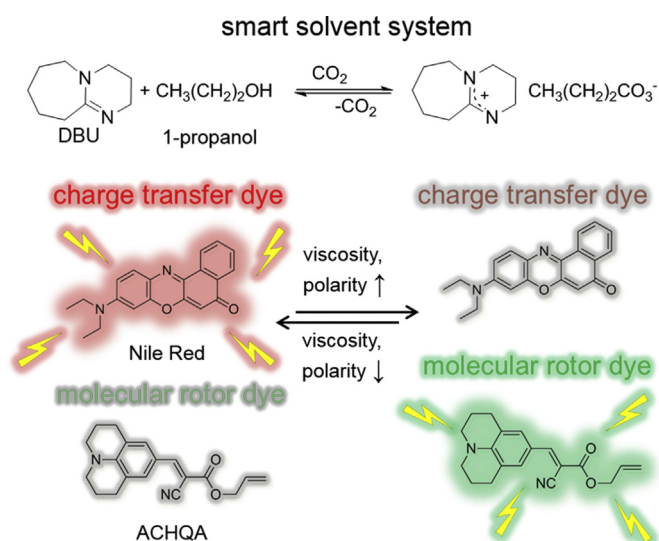


Fig. 1. Chemical structures and conceptual FL response mechanism of the charge transfer dye (Nile Red) and molecular rotor dye (ACHQA) to CO₂ in the smart solvent system (equivalent molar DBU/1-propanol mixture).

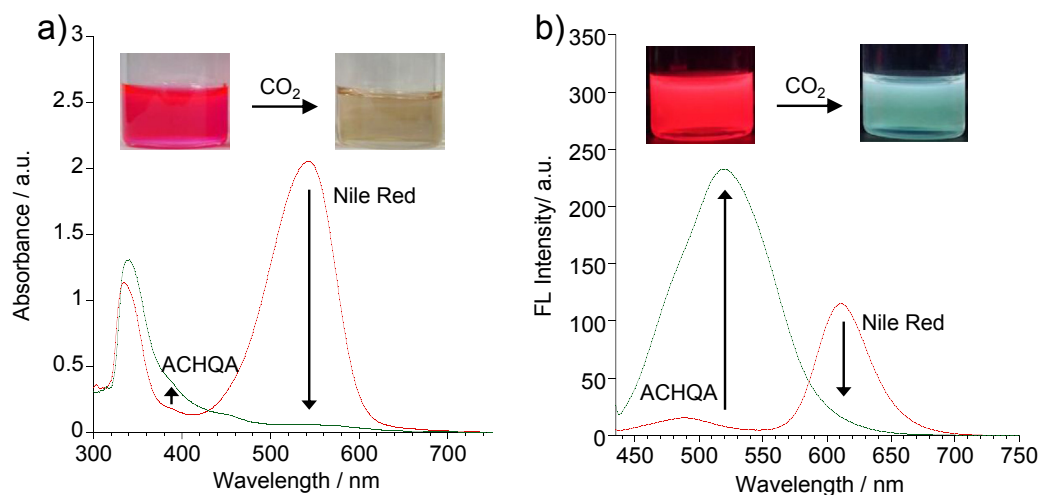


Fig. 2. a) UV-vis absorption and b) FL emission (excited at 430 nm) spectra of Nile Red and ACHQA coexisting in the DBU/1-propanol mixture (5.0×10^{-5} M) before and after injection of an excess amount of CO₂. Insets: photographs of the solution under a) ambient light and b) UV light (excited at >365 nm). In this study, dry ice was used as the CO₂ source for experimental convenience.

Download English Version:

<https://daneshyari.com/en/article/175343>

Download Persian Version:

<https://daneshyari.com/article/175343>

[Daneshyari.com](https://daneshyari.com)