



# An alkali-free approach for recyclable detection and accurate quantification of carbon dioxide gas



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## ARTICLE INFO

### Article history:

Received 16 October 2016

Received in revised form

28 December 2016

Accepted 30 December 2016

Available online 31 December 2016

### Keywords:

Carbon dioxide

Squaraine

Colorimetric sensor

Alkali-free

DFT

## ABSTRACT

CO<sub>2</sub> gas monitoring is of great realistic significance, as CO<sub>2</sub> is a component of gas mixtures from many natural and man-made processes with huge impacts on globe climate and environment change. In this work, a squaraine-based colorimetric method without any alkali media for recyclable CO<sub>2</sub> gas detection has been developed in pure alcohols. Furthermore, this CO<sub>2</sub>-assay scheme permits quantitation of its amount over the whole concentration range (0–100%) and holds a limit of detection of approximate 26 ppm in MeOH. Combining theoretical analyses, a plausible sensing mechanism was particularly depicted.

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## 1. Introduction

As we all know, carbon dioxide (CO<sub>2</sub>) is a key greenhouse gas blamed for inducing and aggravating a series of natural disasters including the well-known global climate change [1–4]. As such, that the practicable strategies for CO<sub>2</sub> accurately monitoring and quantifying in the atmosphere would make a lot of importance in disaster prediction and prevention around the world [5–8]. As a prerequisite, it is urgent to develop low-cost, sensitive, resettable detectors that can be used to quantitatively monitor the CO<sub>2</sub> concentration in the gas emission processes and as a safeguard against their notorious effects on global climate change [9–15].

Realistically, compared with classical instrumental GC–MS, electrochemistry and IR sensors [16,17], recently prevailed optical CO<sub>2</sub> gas detection has received considerable interest in virtue of the outstanding advantages such as technical simplicity, high sensitivity and excellent compatibility with “in situ” and “on time” monitoring [18,19]. In fact, numerous optical probes have been designed and applied to detect and even quantify CO<sub>2</sub> gas based on different sensing mechanisms, and the outcomes of many optical assay systems were even visible to the naked eye. For instance, Tang’s group reported a new fluorescent CO<sub>2</sub>-

chemosensing scheme based on aggregation-induced emission by increasing the polarity and viscosity in dipropylamine (DPA) liquid with CO<sub>2</sub> bubbling [20]. Yoon’s group detailedly demonstrated an N-heterocyclic carbene-based sensor for colorimetric detection of CO<sub>2</sub> gas [21]. Recently, they further developed a colorimetric and fluorescent turn-on CO<sub>2</sub> sensor with high selectivity that relies on a polydiacetylene, PDA-1, functionalized with amines and imidazolium groups [22]. Moreover, they subsequently reported an anion-activated chemosensor system, NAP-chol 1, which permitted dissolved CO<sub>2</sub> gas to be detected in organic media via simple color changes or through ratiometric differences in fluorescence intensity [23]. In 2013, Martínez-Máñez et al. first developed a squaraine-based approach for the chromogenic sensing of CO<sub>2</sub> gas using silica nanoparticles functionalized with amino and thiol moieties [24].

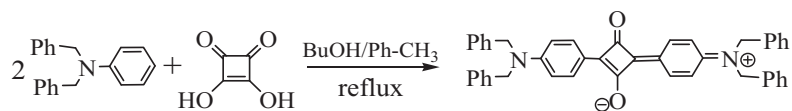
Although state-of-the-art, these “so called” responses are generally required to involve additional alkali media such as fluorides, amidines and amines for CO<sub>2</sub> capture or sensor activation. Considering the low reactivity of CO<sub>2</sub> molecule, the direct optical recognition of CO<sub>2</sub> gas in the absence of any alkalic additions seems hard to accomplish for researchers up to now. However, for potential application to colorimetric detection of CO<sub>2</sub>, it is urgent to search a new method for highly sensitive detection and accurate quantification of CO<sub>2</sub> in absence of any alkalic additions [25,26].

In view of the excellent optical properties [27–34], squaraine dyes have been extensively developed for a number of technologically relevant applications so far, including solar cell sensitizer,

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**Scheme 1.** The synthesis of receptor **SQ**.

metal ions chemosensor as well as biological imaging reagent [35–40]. More recently, our group has also reported a series of squaraine-based chemosensors for the “naked-eye” detection of CO<sub>2</sub> gas in the presence of F<sup>−</sup> [41–43]. In this paper, we further developed a facile **SQ**-based colorimetric method for CO<sub>2</sub> quantitative detection in alcohols without any base added. Results revealed that the deep colored **SQ** will fade away gradually, but colorimetrically restore after a stream of CO<sub>2</sub> gas bubbling in alcohols only. Moreover, this minimalist CO<sub>2</sub>-assay system features an operational simplicity, high sensitivity and instant responsiveness as well as excellent repeatability, and is able to “naked-eye” detect and quantify CO<sub>2</sub> gas over a wide concentration range at room temperature. On the base of theoretical calculation, a plausible sensing mechanism was proposed to illustrate how the receptor **SQ** works as a CO<sub>2</sub> qualitative colorimetric probe in the present system.

## 2. Experimental

### 2.1. Chemicals and reagents

3,4-Dihydroxy-3-cyclobutene-1, 2-dione and Dibenzylaniline were purchased from Energy-Chemical (China). All other common chemicals and solvents of analytical reagent grade were obtained from different commercial suppliers and used as received unless otherwise stated.

### 2.2. Instruments and measurements

Absorption spectrometry was performed using Lambda 750 UV/Vis/NIR Spectrometer of PerkinElmer. <sup>1</sup>H NMR spectra were recorded with a Bruker AVANCE 500 spectrometer with use of the deuterated solvent as the lock and TMS as an internal reference. Elemental analysis was performed on Elementar Vario EL III. Mass spectrometry analysis was performed with a Q Exactive mass spectrometer (Thermo Fisher Scientific, USA). All solvents used in titrations were redistilled in fresh.

### 2.3. Synthesis

Deep green solid **SQ** was synthesized according to the literature [44] (Scheme 1), and the structure was confirmed by its NMR, mass spectrometric analysis (see Supporting Information).

Dibenzylaniline (547 mg, 2 mmol) was mixed with squaric acid (114 mg, 1 mmol) and dissolved in a 1:1 toluene/*n*-butanol mixture. The reaction was heated to reflux with azeotropic removal of water. After 2 h, the reaction mixture was cooled to room temperature and bright green microcrystals of pure product formed spontaneously. These crystals were filtered and washed with 2-propanol to yield the desired product **SQ** in yields 29% (181 mg, 0.29 mmol). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>-d<sub>1</sub>) ppm 7.19 (d, *J* = 7.46 Hz, 8H), 6.87 (d, *J* = 8.93 Hz, 4H), 7.30 (d, *J* = 6.94 Hz, 4H), 7.38–7.33 (m, 8H), 4.78 (s, 8H), 8.36 (d, *J* = 8.99 Hz, 4H). <sup>13</sup>C NMR can not be obtained due to its poor solubility. Anal. Calcd for **SQ**: C, 84.59; H, 5.81; N, 4.48. Found: C, 84.56; H, 5.84; N, 4.44. HRMS calcd for [**SQ**–H]<sup>−</sup> 623.2704; found 623.2704.

### 2.4. Computational method

All calculations were performed using the Gaussian 09 package [45]. Theoretical calculation for the geometrical optimization of receptor was performed at the density functional theory (DFT) level using the B3LYP [46–48]. The 6–311G (d, p) basis sets were employed all atoms. All reactants and intermediates had no imaginary frequency, and the transition states were ascertained by vibrational analysis with only one imaginary frequency mode. The zero-point energy was calculated by using the vibrational frequencies. In the case of transition states, the vibration was associated with a movement in the direction of the reaction coordinate. Intrinsic reaction coordinate calculations, at the same level of theory, were performed to ensure that the transition states led to the expected reactants and products. The solvent effects have been considered using a relatively simple self-consistent reaction field (SCRF) method, based on the polarizable continuum model (PCM) [49–51]. The solvent used in this calculation is DMF. The values of the relative energies with zero-point energy correction (ΔE<sub>0</sub>) were calculated and used on the basis of the total energies of the stationary points. All the kinetic studies were carried out under pseudo-first-order method. The temperature to be used for our calculation is 298.15 K.

## 3. Results and discussion

### 3.1. UV/Vis spectral test of **SQ** in alcohols/chloroform mixtures

The UV–vis spectral analysis of squaraine dyes were generally carried out in aprotic solvents like DMSO, THF, CH<sub>3</sub>CN and so on. Accidentally, we discovered that the deep cyan solution of **SQ** in CHCl<sub>3</sub> will gradually fade away into a colorless mixtures when increasing the volume fractions of MeOH at room temperature, and the intensity at the maximum absorbance (630 nm) of colored **SQ** underwent a significant decrease from 1.89 to nearly 0 (Fig. 1a). The same variation of **SQ** in CHCl<sub>3</sub> solution was also observed when increasing the volume fractions of ethanol (EtOH, Fig. 1b). Whereafter, we screened a series of common alcohols in the laboratory and the spectral profiles were depicted in Fig. 2b. The results revealed that the intensity at 630 nm of **SQ** decreased in *n*-propanol (*n*-PrOH, 0.43) and *n*-butanol (*n*-BuOH, 0.62), whereas *i*-propanol, trifluoroethanol, benzyl alcohol caused no recognizable decolorations with just a slight decrease to 1.80, 1.84, 1.80, respectively. For comparison, we also recorded the UV–vis spectra of receptor **SQ** in CHCl<sub>3</sub> with different volume fractions of *n*-PrOH (Fig. S1a), *n*-BuOH (Fig. S1b), and ethanethiol (EtSH, Fig. S2).

For convenience, the corresponding plots of absorbance at 630 nm wavelength of **SQ** versus their volume fractions in alcohols (thiol)/CHCl<sub>3</sub> mixtures were particularly depicted in Fig. 2a, which displayed visually that the bleaching effect of EtSH was much more obvious than that of all the other four tested alcohols. As shown, the value of absorbance at 630 nm wavelength of **SQ** in CHCl<sub>3</sub> decreased from 1.89 to 0.48 and the mixtures turned into colorless with just addition of 10% EtSH, whereas adding equivalent alcohols caused an unnoticeable decoloration with a negligible decrease of the absorbance only. For other four alcohols, all of them caused a well-recognizable decoloration as long as increasing the volume fractions of alcohols in mixtures, and the color of mixtures

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