A squaraine-based sensor for colorimetric detection of CO$_2$ gas in aqueous medium through an unexpected recognition mechanism

Jianqi Sun$^{a,b}$, Xiangjuan Zheng$^a$, Xinjie Wu$^a$, Dong Li$^a$, Guomin Xia$^a$, Shuxian Yu$^a$, Qiming Yu and Hongming Wang$^a$

$^a$ College of Chemistry and Institute for Advanced Study, Nanchang University, Nanchang, Jiangxi 330031, China

$^b$ College of Chemistry and Environmental Engineering, Jiujiang University, Jiujiang, Jiangxi 332005, China

Detection Limit\cite{1}. The detection limit was calculated on the basis of the UV-Vis titration. The UV-Vis spectrum of SQM (7.5 $\mu$M) in MeCN-H$_2$O (V : V = 90 : 10) was measured 12 times, and the standard deviation of blank measurement was achieved. To gain the slope, the absorbance at 627 nm versus amount of pure CO$_2$ gas was plotted. The detection limit was calculated using the following equation:

$$\text{Detection limit} = \frac{3\sigma}{k}$$

Where $\sigma$ is the standard deviation of blank measurement, and $k$ is the slope between the absorbance versus the volume of pure CO$_2$ gas ($V_{CO_2}$).

References


$\dagger$ These authors contributed equally to this work.
Captions:

**Fig. S1** UV-Vis spectral changes obtained during the course of titrating sensor SQM (7.5 μM) with 50-fold weak base EA, DEA, TEA and Py in MeCN respectively.

**Fig. S2** UV-Vis spectral changes obtained during the course of titrating sensor SQM (7.5 μM) with DBU in MeCN. Inset: The corresponding plots of absorbance at indicated wavelengths versus additional DBU.

**Fig. S3** UV-Vis spectral changes obtained during the course of titrating sensor SQM (7.5 μM) with TMG in MeCN. Inset: The corresponding plots of absorbance at indicated wavelengths versus additional TMG.

**Fig. S4** UV-Vis spectral changes obtained during the course of titrating sensor SQM (7.5 μM) with [NBu₄]F in MeCN. Inset: The corresponding plots of absorbance at indicated wavelengths versus additional [NBu₄]F.

**Fig. S5** UV-Vis spectral changes obtained during the course of titrating sensor SQM (7.5 μM) with (a) 2-fold TBD; (b) 5-fold DBU in MeCN then bubbled with different volumes of CO₂ gas in a sealed cuvette.

**Fig. S6** (a) UV-Vis spectral changes obtained during the course of titrating sensor SQM (7.5 μM) with DBU in MeCN-H₂O (V : V = 90 : 10); (b) then bubbled with different volumes of CO₂ gas in a sealed cuvette. Inset: The corresponding plots of absorbance at indicated wavelengths versus additional DBU or volume of CO₂ gas.

**Fig. S7** UV-Vis spectrum of precursor SQ (7.5 μM) in MeCN-H₂O (V : V = 90 : 10).

**Fig. S8** The absorbance of SQM (7.5 μM) at 627 nm in MeCN-H₂O with different volume fractions of H₂O after addition of 20 eq TBD (the black bar) followed by bubbling 5 mL CO₂ gas (the green bar) in a sealed cuvette.

**Fig. S9** The absorbance of SQM (7.5 μM) at 627 nm with the addition of TBD (20 eq) versus the volume of pure CO₂ gas in MeCN-H₂O (V : V = 90 : 10).

**Fig. S10** The absorbance of SQM (7.5 μM) at 627 nm with the addition of DBU (20 eq) versus the volume of pure CO₂ gas in MeCN-H₂O (V : V = 90 : 10).

**Fig. S11** The mass spectrometry analysis of SQM in MeCN with addition of TBD in positive mode.

**Fig. S12** The mass spectrometry analysis of SQM in MeCN-H₂O (V : V = 90 : 10)
with addition of TBD in positive mode.

**Fig. S13** The mass spectrometry analysis of **SQM** in MeCN-H$_2$O (V : V = 90 : 10) with addition of TBD followed by CO$_2$ gas in positive mode.

**Fig. S14** The mass spectrometry analysis of **SQM** in MeCN-H$_2$O (V : V = 90 : 10) with addition of NaOH in positive mode.

**Fig. S15** The mass spectrometry analysis of **SQM** in MeCN-H$_2$O (V : V = 90 : 10) with addition of NaOH followed by CO$_2$ gas in positive mode.

**Fig. S16** The absorbance of **SQM** (7.5 μM) at 627 nm with the addition of NaOH (300 eq) versus the volume of pure CO$_2$ gas in MeCN-H$_2$O (V : V = 90 : 10).

**Fig. S17** The mass spectrometry analysis of **SQM** in MeCN-H$_2$O (V : V = 90 : 10) with addition of TBD followed by CO$_2$ gas in negative mode.

**Fig. S18** Partial $^1$H-NMR spectra obtained during the course of titrating sensor **SQM** (5.0 mM) with NaOH followed by CO$_2$ in DMSO-$d_6$.

**Fig. S19** $^1$H NMR spectrum of **SQM**

**Fig. S20** $^{13}$C NMR spectrum of **SQM**

**Fig. S21** The mass spectrometry analysis of **SQM** in MeCN in positive mode.
Fig. S1 UV-Vis spectral changes obtained during the course of titrating sensor SQM (7.5 μM) with 50-fold weak base EA, DEA, TEA and Py in MeCN respectively.
**Fig. S2** UV-Vis spectral changes obtained during the course of titrating sensor **SQM** (7.5 μM) with DBU in MeCN. Inset: The corresponding plots of absorbance at indicated wavelengths versus additional DBU.
**Fig. S3** UV-Vis spectral changes obtained during the course of titrating sensor SQM (7.5 μM) with TMG in MeCN. Inset: The corresponding plots of absorbance at indicated wavelengths versus additional TMG.
**Fig. S4** UV-Vis spectral changes obtained during the course of titrating sensor SQM (7.5 μM) with [NBu₄]F in MeCN. Inset: The corresponding plots of absorbance at indicated wavelengths versus additional [NBu₄]F.
**Fig. S5** UV-Vis spectral changes obtained during the course of titrating sensor **SQM** (7.5 μM) with (a) 2-fold TBD; (b) 5-fold DBU in MeCN then bubbled with different volumes of CO₂ gas in a sealed cuvette.
Fig. S6 (a) UV-Vis spectral changes obtained during the course of titrating sensor SQM (7.5 μM) with DBU in MeCN-H$_2$O (V : V = 90 : 10); (b) then bubbled with different volumes of CO$_2$ gas in a sealed cuvette. Inset: The corresponding plots of absorbance at indicated wavelengths versus additional DBU or volume of CO$_2$ gas.
Fig. S7 UV-Vis spectrum of precursor SQ (7.5 μM) in MeCN-H₂O (V : V = 90 : 10).
Fig. S8 The absorbance of SQM (7.5 μM) at 627 nm in MeCN-H₂O with different volume fractions of H₂O after addition of 20 eq TBD (the black bar) followed by bubbling 5 mL CO₂ gas (the green bar) in a sealed cuvette.
Fig. S9 The absorbance of SQM (7.5 μM) at 627 nm with the addition of DBT (20 eq) versus the volume of pure CO₂ gas in MeCN-H₂O (V : V = 90 : 10).

The detection limit in MeCN-H₂O (V : V = 90 : 10) (3.0 ml) was calculated to be about 1.59*10^-6 M (ca. 39.0 ppm, 1atm, 25°C)
**Fig. S10** The absorbance of SQM (7.5 μM) at 627 nm with the addition of DBU (20 eq) versus the volume of pure CO₂ gas in MeCN-H₂O (V : V = 90 : 10).

The detection limit in MeCN-H₂O (V : V = 90 : 10) (3.0 ml) was calculated to be about 2.0*10⁻⁶ M (ca. 49.1 ppm, 1 atm, 25°C)
Fig. S11 The mass spectrometry analysis of SQM with addition of TBD in MeCN in positive mode.
Fig. S12 The mass spectrometry analysis of SQM in MeCN-H$_2$O (V : V = 90 : 10) with addition of TBD in positive mode.
Fig. S13 The mass spectrometry analysis of SQM in MeCN-H$_2$O (V : V = 90 : 10) with addition of TBD followed by CO$_2$ gas in positive mode.
Fig. S14 The mass spectrometry analysis of SQM in MeCN-H₂O (V : V = 90 : 10) with addition of NaOH in positive mode.
Fig. S15 The mass spectrometry analysis of SQM in MeCN-H$_2$O (V : V = 90 : 10) with addition of NaOH followed by bubbling CO$_2$ gas in positive mode.
**Fig. S16** The absorbance of SQM (7.5 μM) at 627 nm with the addition of NaOH (300 eq) versus the volume of pure CO₂ gas in MeCN-H₂O (V : V = 90 : 10).

The detection limit in MeCN-H₂O (V : V = 90 : 10) (3.0 ml) was calculated to be about 1.20*10⁻⁶ M (ca. 29.4 ppm, 1 atm, 25°C)
Fig. S17 The mass spectrometry analysis of SQM in MeCN-H₂O (V : V = 90 : 10) with addition of TBD followed by CO₂ gas in negative mode.
Fig. S18 Partial $^1$H-NMR spectra obtained during the course of titrating sensor SQM (5.0 mM) with NaOH followed by CO$_2$ in DMSO-$d_6$. 
Fig. S19 $^1$H NMR spectrum of SQM
Fig. 20 $^{13}$C NMR spectrum of SQM
Fig. 21 The mass spectrometry analysis of SQM in MeCN in positive mode.