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Supporting Information

A squaraine-based sensor for colorimetric detection of CO_2 gas in aqueous medium through an unexpected recognition mechanism

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Detection Limit [1]**.** The detection limit was calculated on the basis of the UV-Vis titration. The UV-Vis spectrum of **SQM** (7.5 μM) in MeCN-H_2O (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:

$$\text{Detection limit} = 3\sigma/k \quad (1)$$

Where σ is the standard deviation of blank measurement, and k is the slope between the absorbance versus the volume of pure CO_2 gas (V_{CO2}).

References

[1] S. Samanta, S. Goswami, M. N. Hoque, A. Rameshm and G. Das, *Chem. Commun.*, 2014, **50**, 11833.

‡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 $[NBu_4]F$ in MeCN. Inset: The corresponding plots of absorbance at indicated wavelengths versus additional $[NBu_4]F$.

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 CO_2 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_2O (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-H_2O (V : V = 90 : 10).

Fig. S8 The absorbance of **SQM** (7.5 μM) at 627 nm in MeCN-H_2O with different volume fractions of H_2O after addition of 20 eq TBD (the black bar) followed by bubbling 5 mL CO_2 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 CO_2 gas in MeCN-H_2O (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 CO_2 gas in MeCN-H_2O (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-H_2O (V : V = 90 : 10)

with addition of TBD in positive mode.

Fig. S13 The mass spectrometry analysis of **SQM** in MeCN-H_2O (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_2O (V : V = 90 : 10) with addition of NaOH in positive mode.

Fig. S15 The mass spectrometry analysis of **SQM** in MeCN-H_2O (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_2O (V : V = 90 : 10).

Fig. S17 The mass spectrometry analysis of **SQM** in MeCN-H_2O (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.

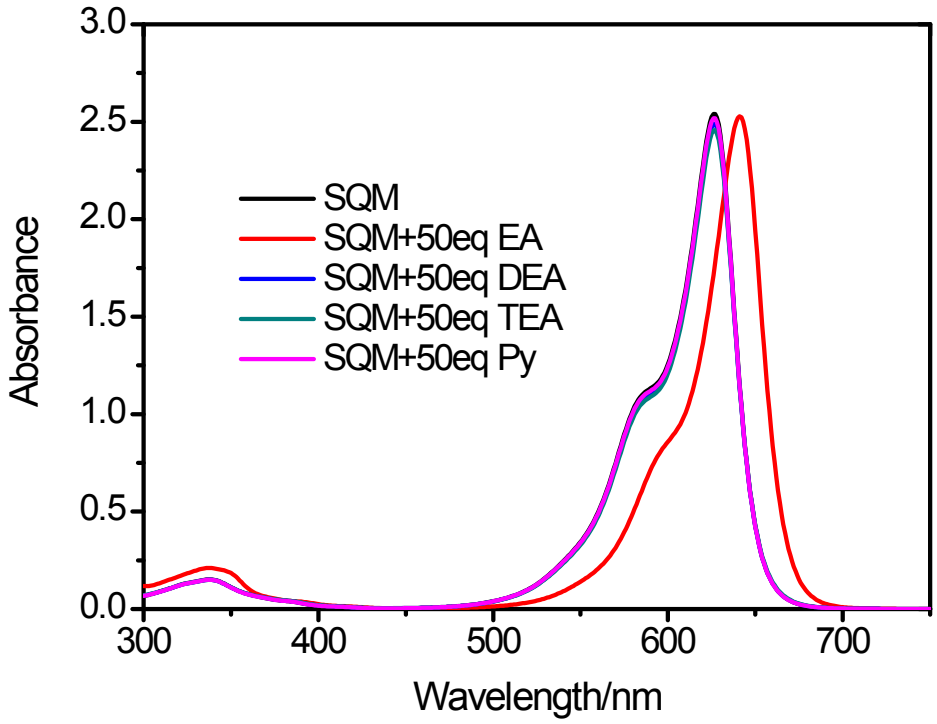

Fig. S1 UV-Vis spectral changes obtained during the course of titrating sensor **SQM** (7.5 μM) with 50-fold weak base EA, DEA, TEA and Py in MeCN respectively.

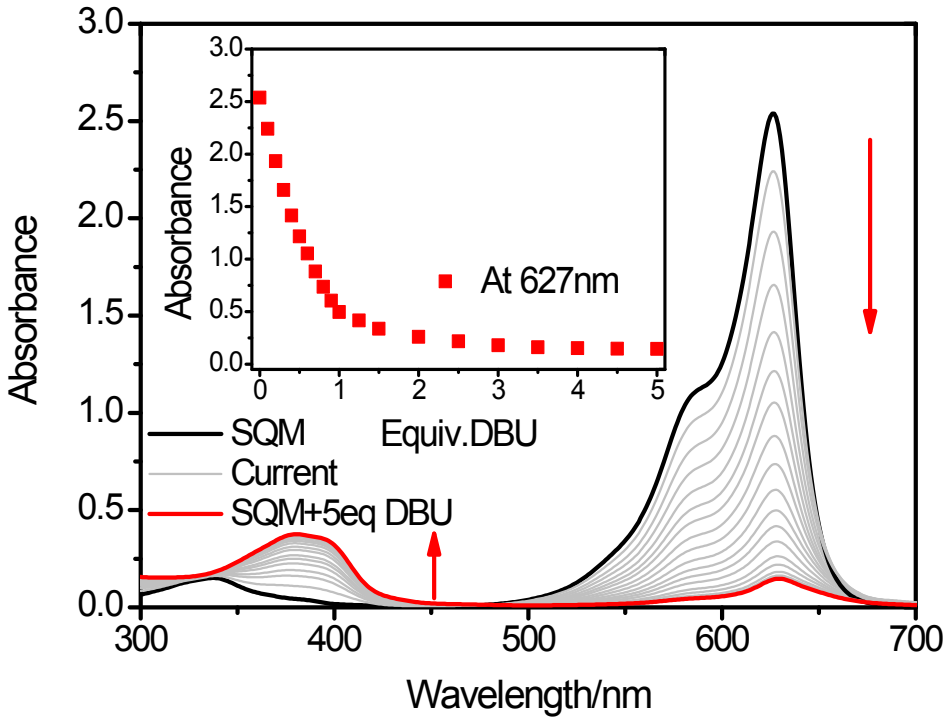

Fig. S2 UV-Vis spectral changes obtained during the course of titrating sensor **SQM** (7.5 μM) with DBU in MeCN. Inset: The corresponding plots of absorbance at indicated wavelengths versus additional DBU.

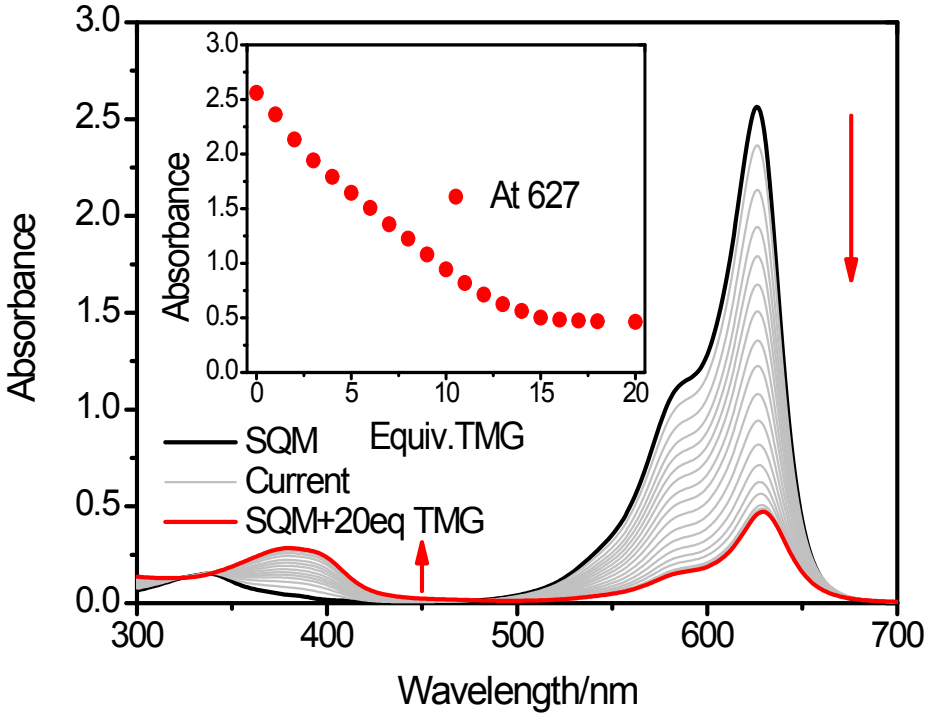

Fig. S3 UV-Vis spectral changes obtained during the course of titrating sensor **SQM** (7.5 μM) with TMG in MeCN. Inset: The corresponding plots of absorbance at indicated wavelengths versus additional TMG.

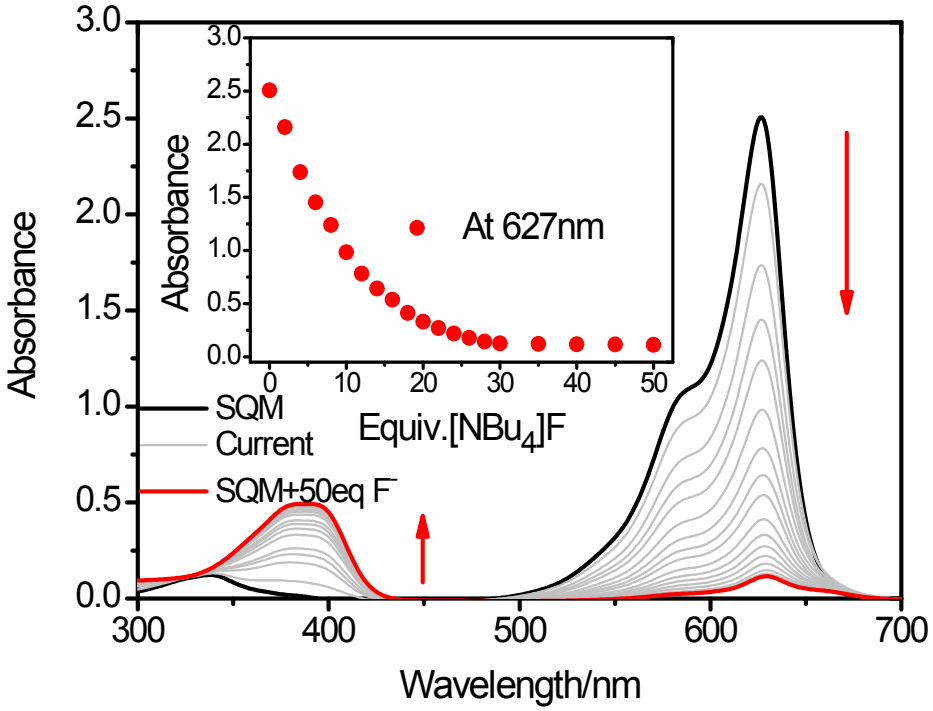

Fig. S4 UV-Vis spectral changes obtained during the course of titrating sensor **SQM** (7.5 μM) with $[NBu_4]F$ in MeCN. Inset: The corresponding plots of absorbance at indicated wavelengths versus additional $[NBu_4]F$.

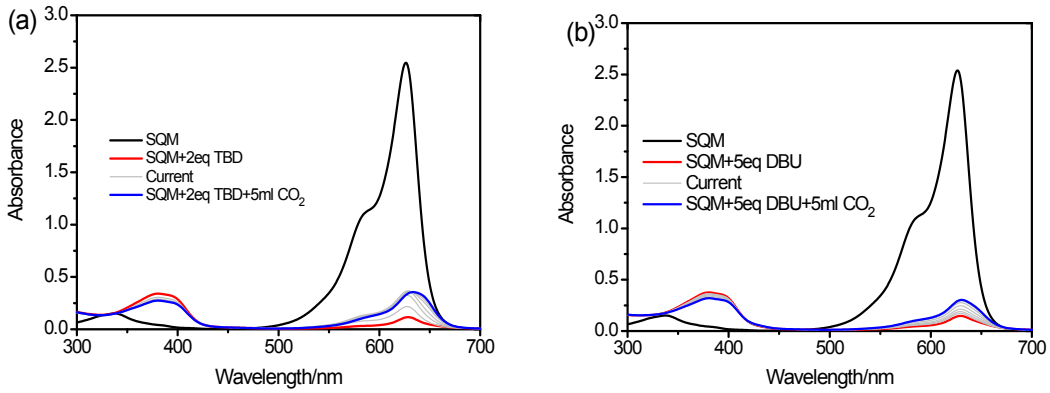

Fig. S5 UV-Vis spectral changes obtained during the course of titrating sensor **SQM** (7.5 μM) with (a) 2-fold TBD; (b) 5-fold DBU in MeCN then bubbled with different volumes of CO_2 gas in a sealed cuvette.

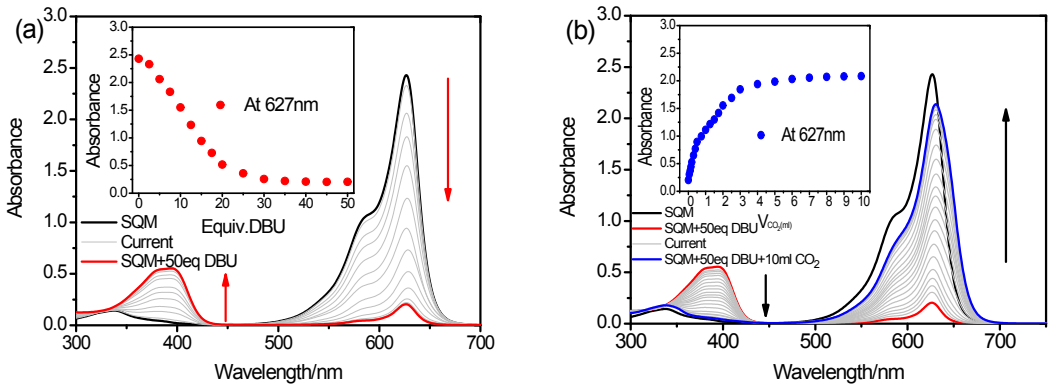

Fig. S6 (a) UV-Vis spectral changes obtained during the course of titrating sensor **SQM** (7.5 μM) with DBU in MeCN-H_2O (V : V = 90 : 10); (b) then bubbled with different volumes of CO_2 gas in a sealed cuvette. Inset: The corresponding plots of absorbance at indicated wavelengths versus additional DBU or volume of CO_2 gas.

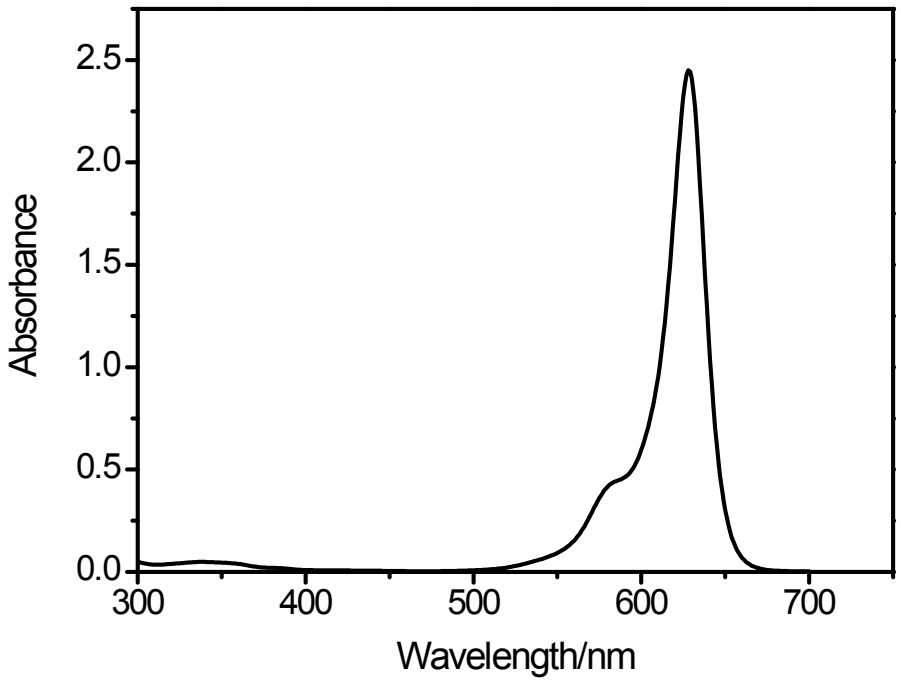

Fig. S7 UV-Vis spectrum of precursor **SQ** (7.5 μM) in MeCN-H_2O (V : V = 90 : 10).

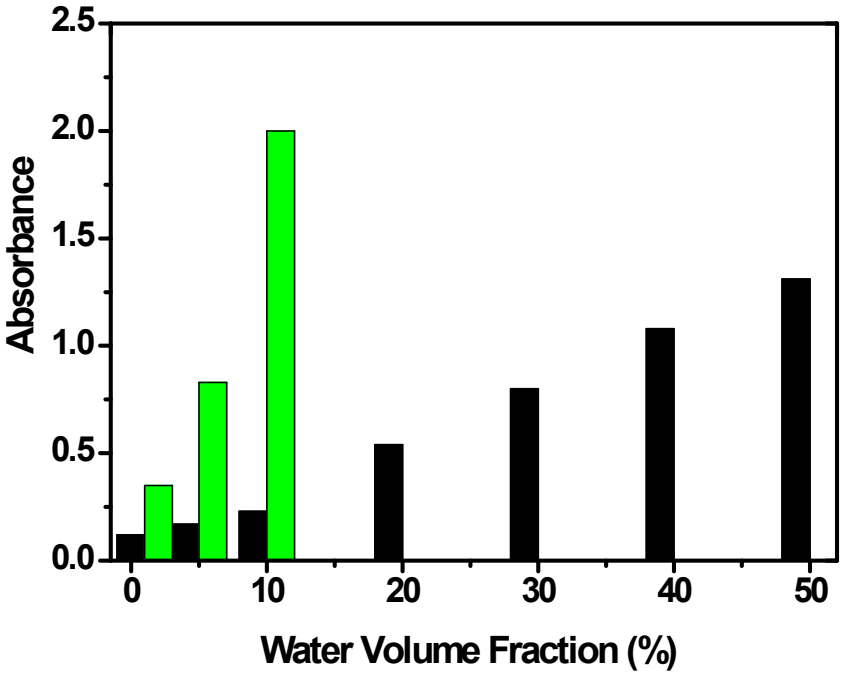

Fig. S8 The absorbance of **SQM** (7.5 μM) at 627 nm in MeCN-H_2O with different volume fractions of H_2O after addition of 20 eq TBD (the black bar) followed by bubbling 5 mL CO_2 gas (the green bar) in a sealed cuvette.

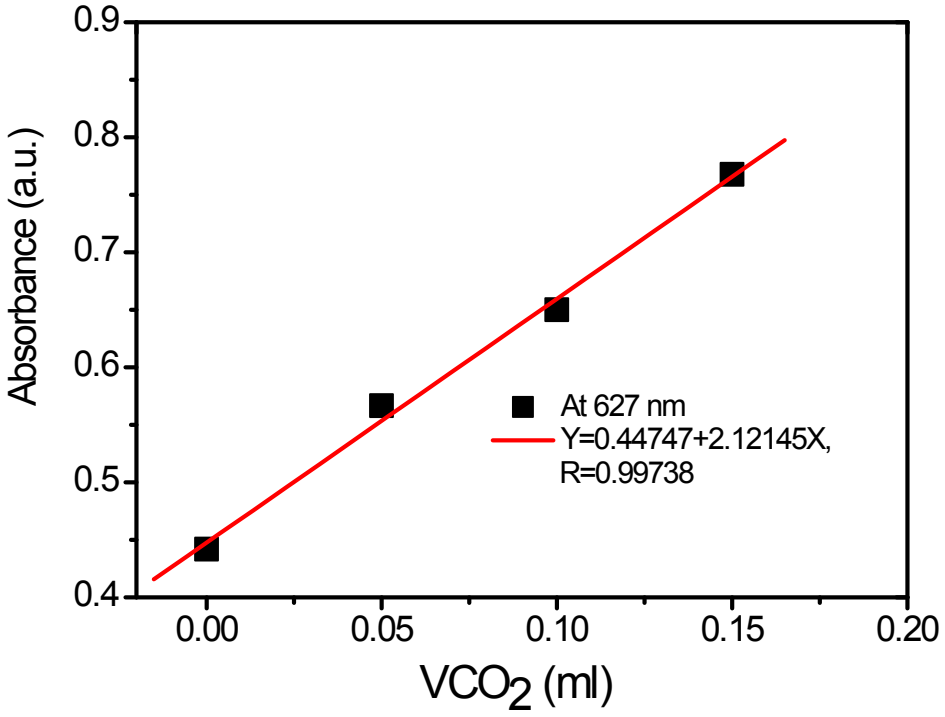

Fig. S9 The absorbance of **SQM** (7.5 μM) at 627 nm with the addition of DBT (20 eq) versus the volume of pure CO_2 gas in MeCN-H_2O (V : V = 90 : 10).

The detection limit in MeCN-H_2O (V : V = 90 : 10) (3.0 ml) was calculated to be about $1.59*10^{-6}$ M (ca. 39.0 ppm, 1atm, 25°C)

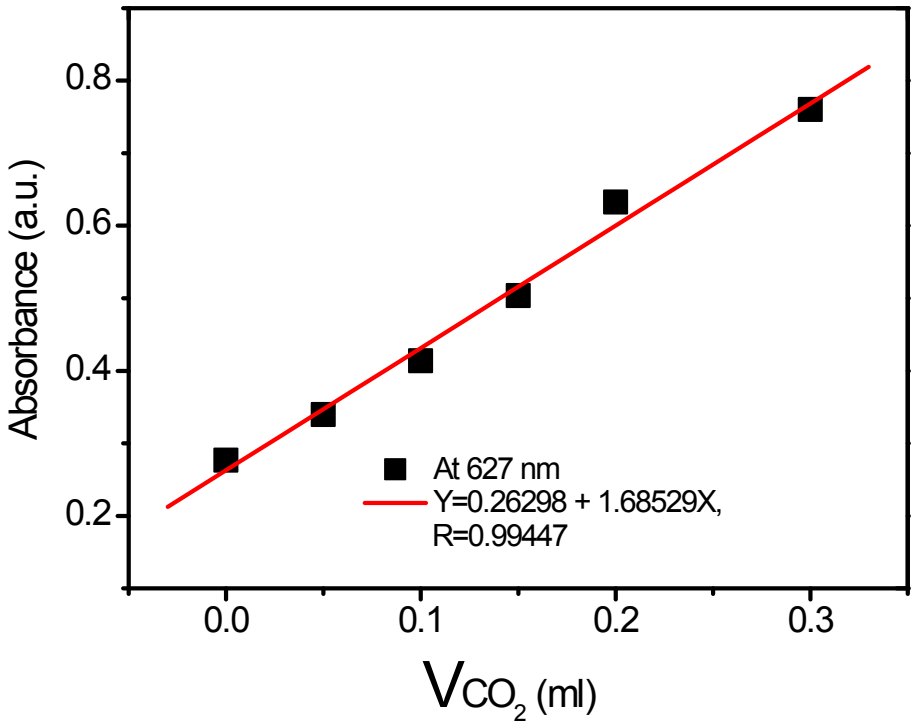

Fig. S10 The absorbance of **SQM** (7.5 μM) at 627 nm with the addition of DBU (20 eq) versus the volume of pure CO_2 gas in MeCN-H_2O (V : V = 90 : 10).

The detection limit in MeCN-H_2O (V : V = 90 : 10) (3.0 ml) was calculated to be about $2.0*10^{-6}$ M (ca. 49.1 ppm, 1atm, 25°C)

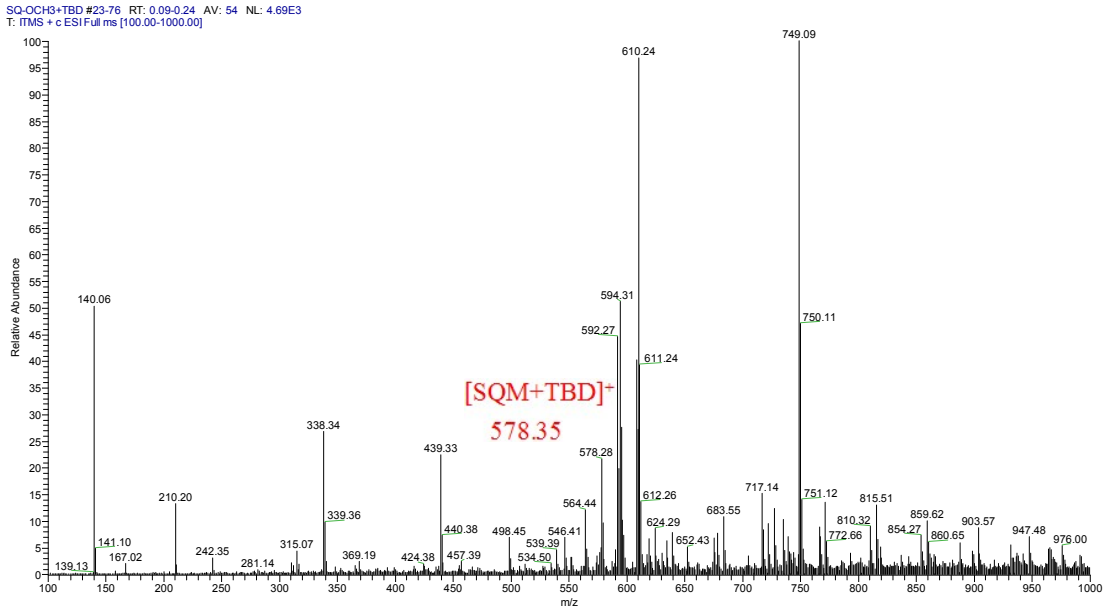

Fig. S11 The mass spectrometry analysis of **SQM** with addition of TBD in MeCN in positive mode.

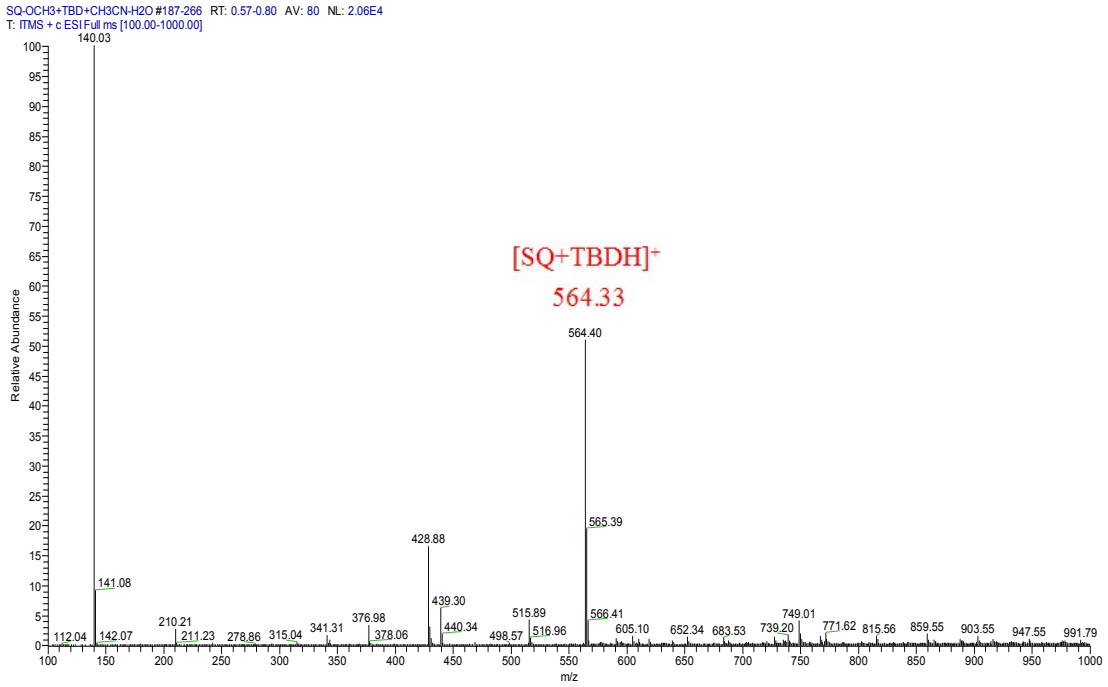

Fig. S12 The mass spectrometry analysis of **SQM** in MeCN-H_2O (V : V = 90 : 10) with addition of TBD in positive mode.

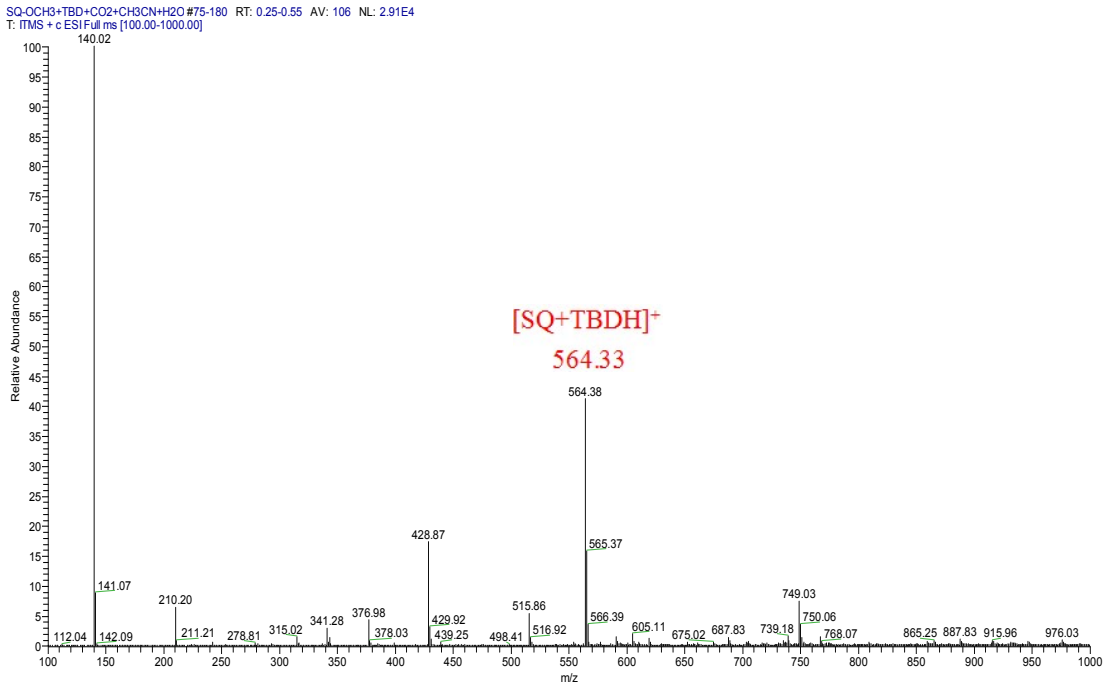

Fig. S13 The mass spectrometry analysis of **SQM** in MeCN-H_2O (V : V = 90 : 10) with addition of TBD followed by CO_2 gas in positive mode.

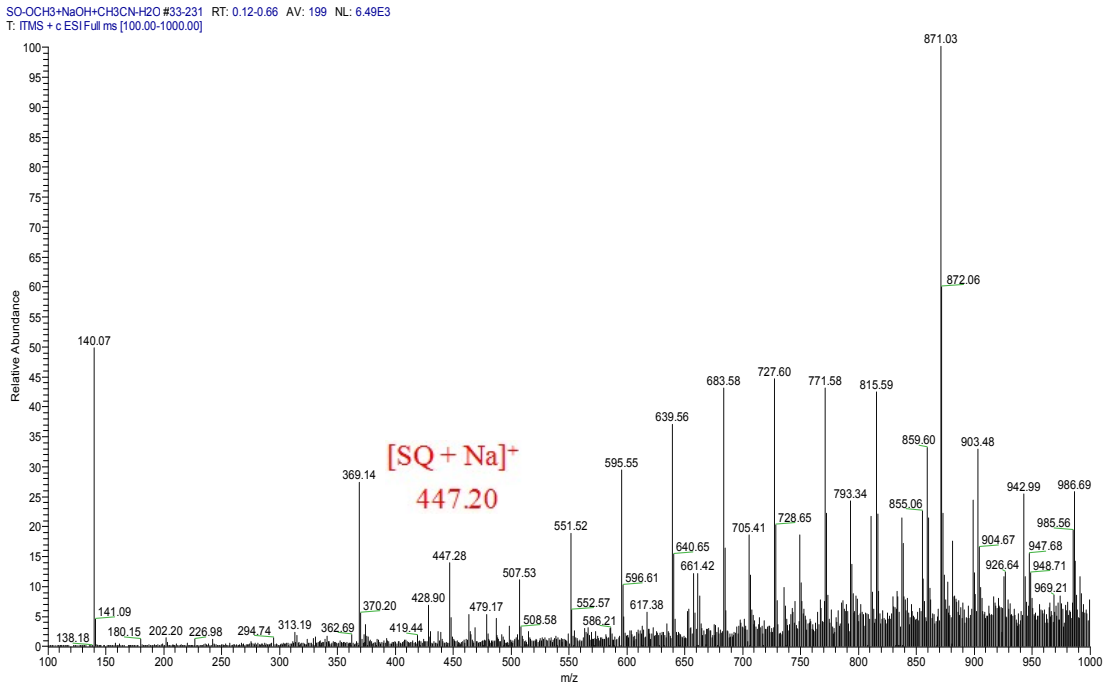

Fig. S14 The mass spectrometry analysis of **SQM** in MeCN-H_2O (V : V = 90 : 10) with addition of NaOH in positive mode.

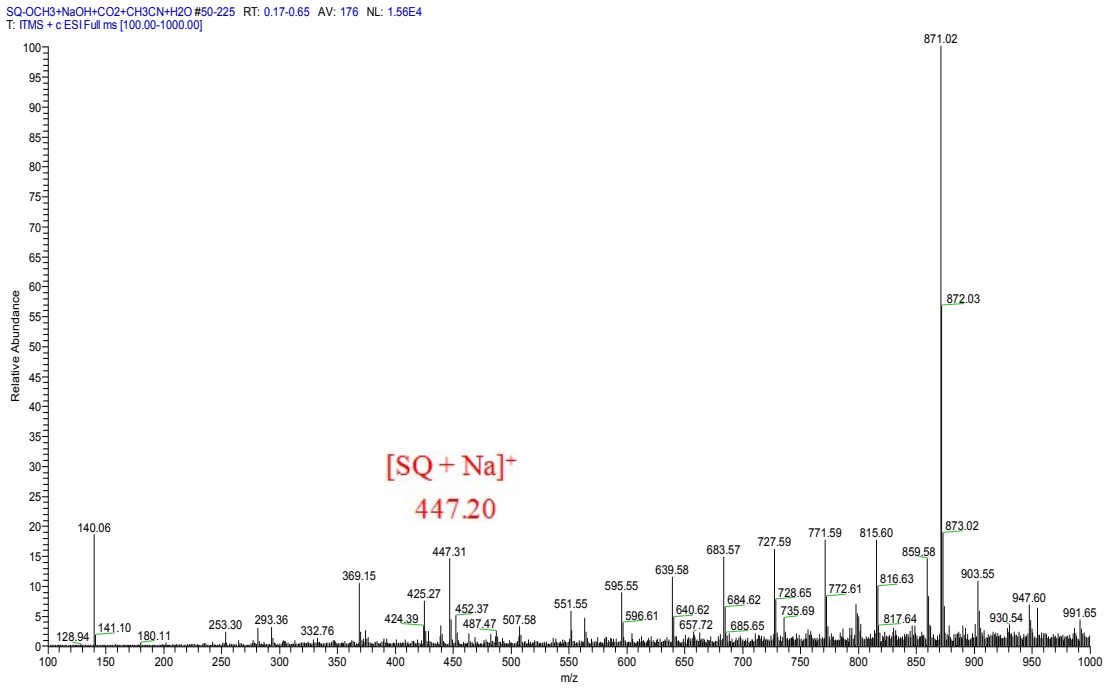

Fig. S15 The mass spectrometry analysis of **SQM** in MeCN-H_2O (V : V = 90 : 10) with addition of NaOH followed by bubbling CO_2 gas in positive mode.

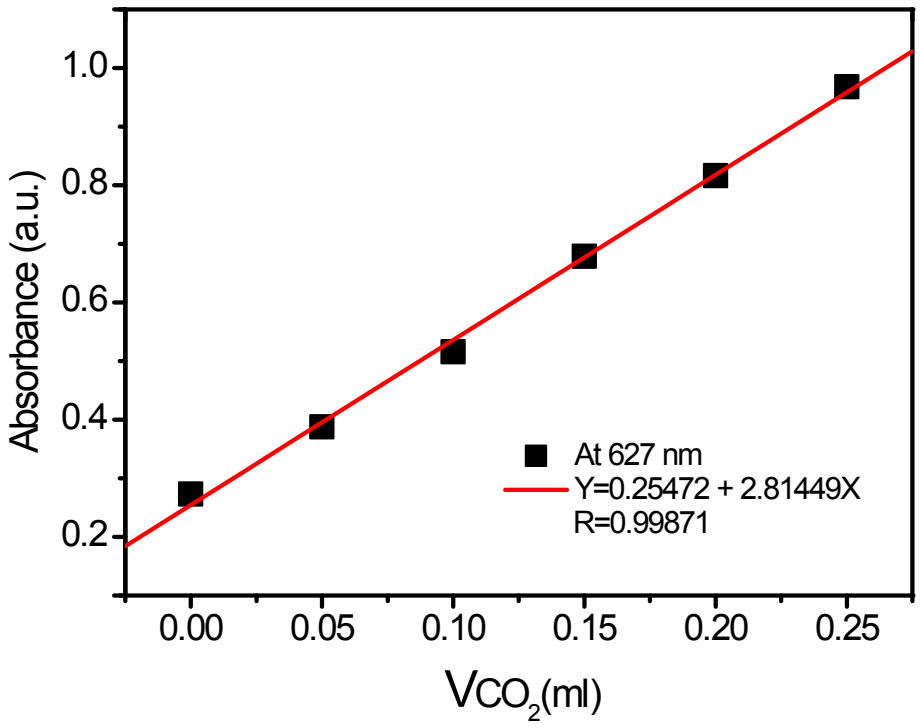

Fig. S16 The absorbance of **SQM** (7.5 μM) at 627 nm with the addition of NaOH (300 eq) versus the volume of pure CO_2 gas in MeCN-H_2O (V : V = 90 : 10).

The detection limit in MeCN-H_2O (V : V = 90 : 10) (3.0 ml) was calculated to be about $1.20*10^{-6}$ M (ca. 29.4 ppm, 1atm, 25°C)

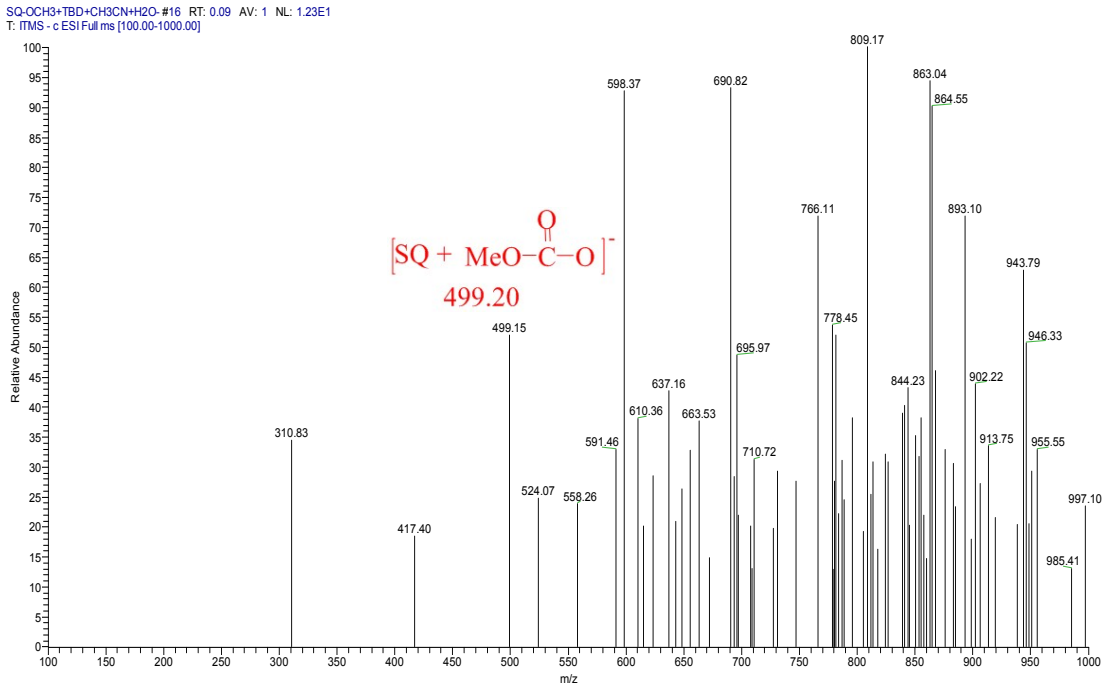

Fig. S17 The mass spectrometry analysis of **SQM** in MeCN-H_2O (V : V = 90 : 10) with addition of TBD followed by CO_2 gas in negative mode.

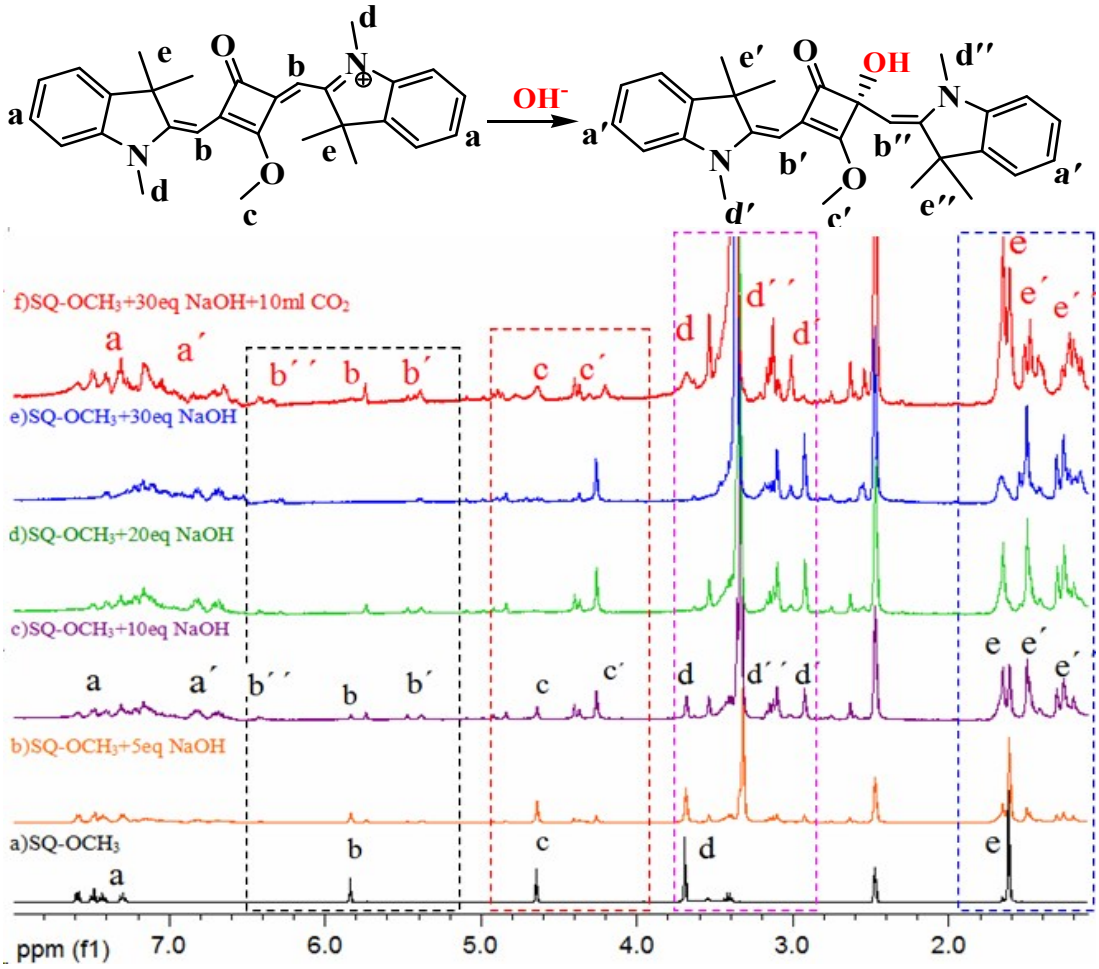

Fig. S18 Partial ^{1}H-NMR spectra obtained during the course of titrating sensor **SQM** (5.0 mM) with NaOH followed by CO_2 in DMSO-d_6.

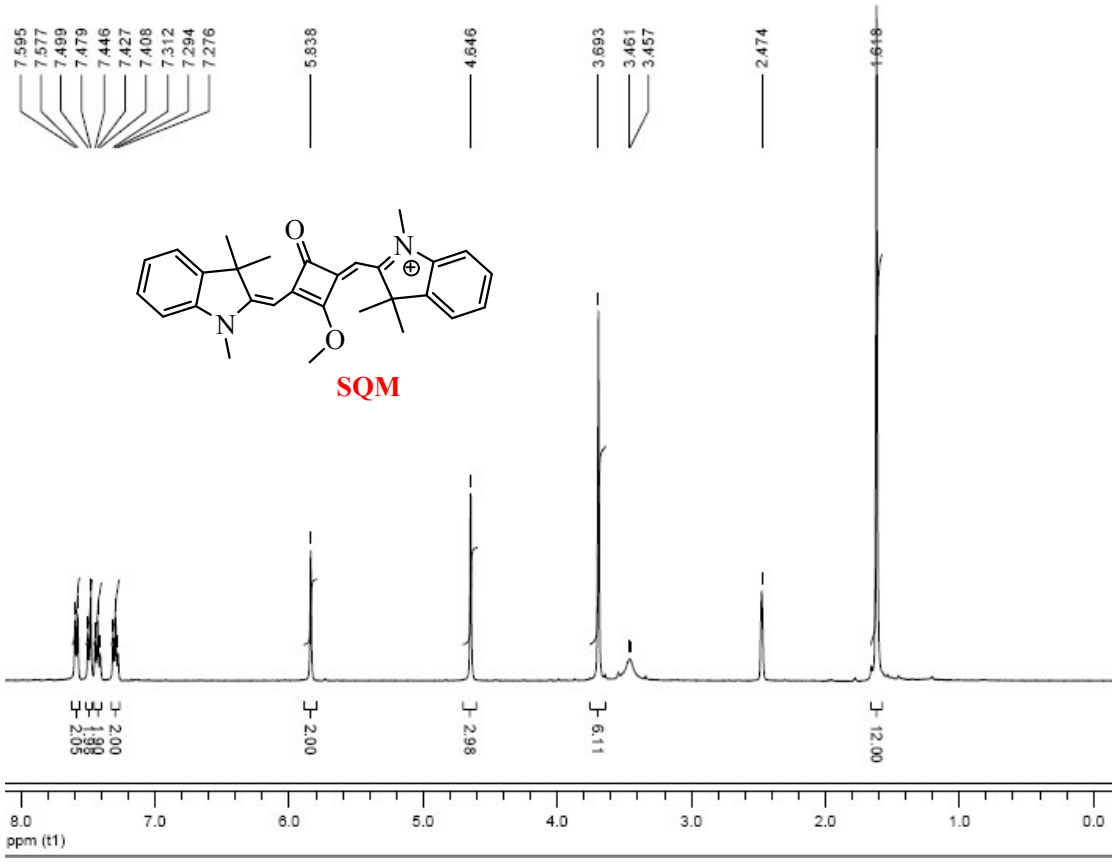

Fig. S19 ^{1}H NMR spectrum of **SQM**

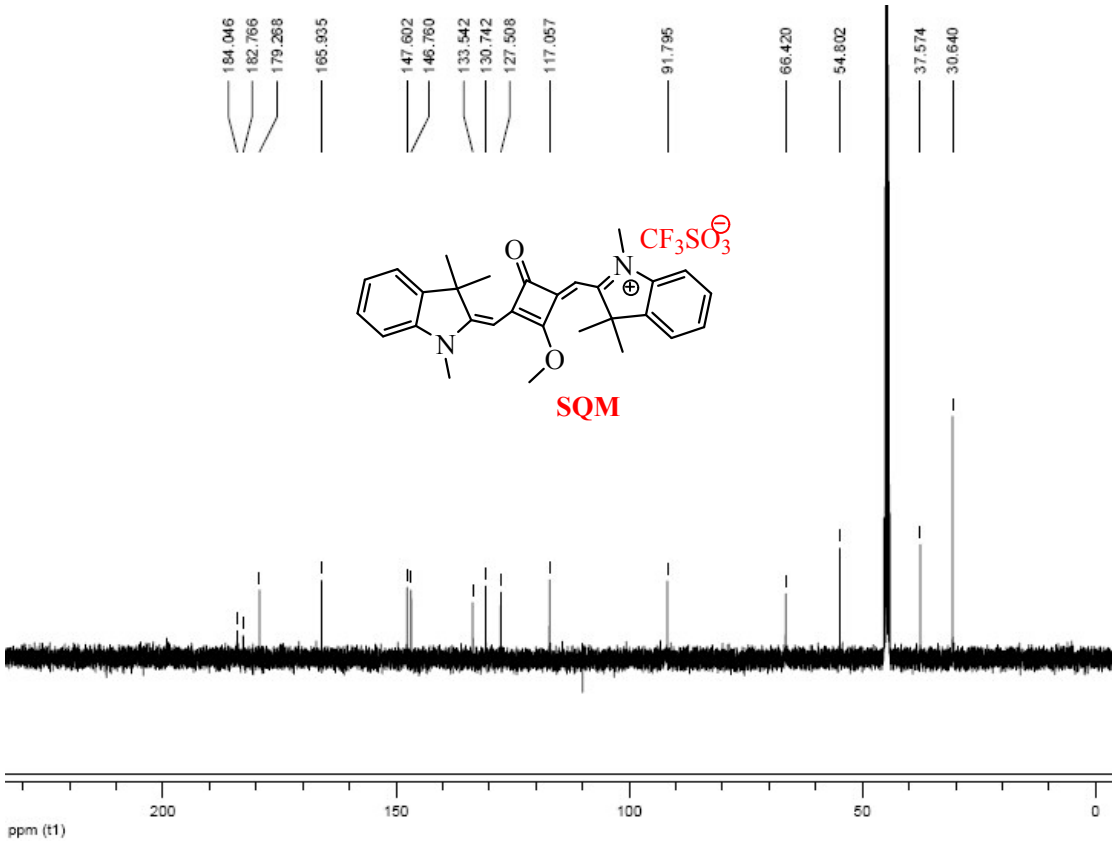

Fig. 20 ^{13}C NMR spectrum of **SQM**

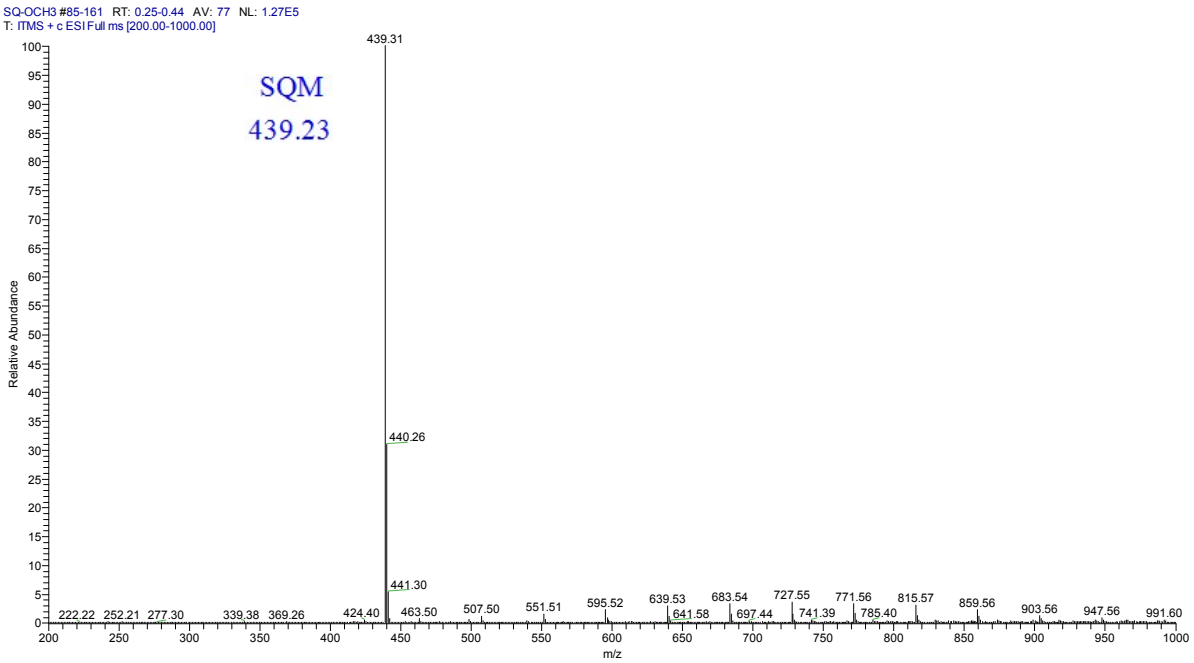

Fig. 21 The mass spectrometry analysis of **SQM** in MeCN in positive mode.