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A novel squaraine dye with squaramide as a scaffold and the colorimetric detection of amine

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Abstract

A novel unsymmetrical squaramide-linked squaraine dye (SQ) has been synthesized through squaramide **3** and semisquaraine **6**. The molecular structure of SQ has been characterized by ^{1}H NMR, IR and MS. Due to the influence of the hydrogen bond and the solvent effect, SQ exhibits unique spectral properties compared with typical squaraine dyes. For its excellent ability of binding primary amine, SQ is a promising receptor of recognizing primary amine.

Keywords: Squaraine dye; Squaramide; Hydrogen bond; Receptor

As the growing demand for simple, rapid and flexible online analyses of a variety of chemical compounds, the development of new colorimetric receptor that allow naked-eye detection without the use of any spectroscopic instrument is a field of current interest.

Be a superior performance of near-infrared dyes, squaraines have been applied widely in fields such as cation recognition [1], biochemicallabeling [2], optical recording [3], and photovoltaics [4]. Recently, Ros-Lis *et al*. [5] reported a chromomeric response sensor to volatile amines and thiols. With a two-step ship-in-the-bottle way, they put squaraine dye into the supercages of zeolite Y and got the hybrid material Z30-SQ. The blue colour of the Z30-SQ material was faded by reacting with the thiol and amine derivatives.

Secondary squaramides have considerable potential as hydrogen bond donors and acceptors [6]. They have been used for wide ranging applications such as anion receptor [7–9], cation recognition [10,11], chiral ligand [12,13]. Herein we reported a novel squaraine (SQ) with squaramide as a scaffold. With the influence of squaramide skeleton, the SQ exhibits some unique spectral properties as a promising receptor of primary amine.

1. Experimental

The synthesis of SQ is shown in Scheme 1. The aniline derivatives **2** and **5** were prepared according to the literature [14,15]. Squaramide **3** was synthesized by direct condensation of diethyl squarate and aniline derivative **2**.

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Semisquaraine **6** was prepared by condensation of aniline derivative **5** and squaric acid dichloride. SQ was synthesized through condensation of squaramide **3** and semisquaraine **6** in *n*-heptanol under reduced pressure.

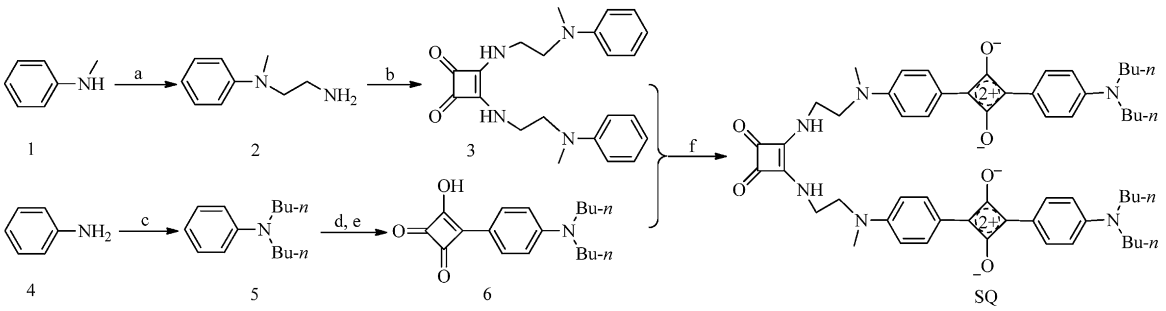
Squaramide **3**: diethyl squarate (0.34 g, 2 mmol) was dissolved in ethanol (10 mL) and then aniline derivative **2** (0.60 g, 4 mmol) in ethanol (5 mL) was added. The resulting solution was stirred over night at ambient temperature. The crude product was precipitated out. After filtration the filter residue was chromatographed on a column of silica gel with chloroform/methanol (100:6, v/v) to give **3** (0.71 g, 94%) as a white solid, mp 220–221 °C. IR (KBr, cm^{-1}): 3434, 3179, 2934, 1803, 1633, 1600, 1572, 1506, 1480, 1429, 1369, 1338, 744, 689. ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.88 (s, 6H), 3.46 (t, 4H, J = 6.2 Hz), 3.63 (br, s, 4H), 6.62 (t, 2H, J = 7.2 Hz), 6.73 (d, 4H, J = 8.4 Hz), 7.13–7.17 (m, 4H), 7.44 (br, s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 38.5, 41.3, 53.4, 112.5, 116.4, 129.4, 149.5, 168.5, 183.0. ESI-MS: m/z 379.0 ($[M+H]^+$), 377.3 ($[M-H]^-$).

Semisquaraine **6**: to a solution of aniline derivative **5** (0.68 g, 3.3 mmol) in benzene (25 mL) was added squaric acid dichloride (0.51 g, 3.4 mmol), and then the reaction mixture was refluxed for 6 h. After cooling to room temperature, the mixture was poured into ice water, washed three times with water, dried with Na_2SO_4, filtered, and concentrated under reduced pressure to afford dark oil which was changed into yellow solid as kept in refrigerator. The yellow solid was dissolved in the mixture of dichloromethane (25 mL) and acetone (5 mL), 2 mol/L hydrochloric acid (3 mL) and trifluoroacetic acid (3 mL) were added and then refluxed over night. The solvent was removed under reduced pressure to give dark oil which was changed into yellow solid upon the addition of methanol. After filtration the crude product was washed adequately with methanol and anhydrous ether to give **6** (0.49 g, 49%) as a yellow powder, mp 203–204 °C (literature [16] 258 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.90 (t, 6H, J = 7.2 Hz, CH_3), 1.27–1.36 (m, 4H, CH_2), 1.49 (s, 4H, CH_2), 3.38 (s, 4 H, CH_2), 6.86 (s, 2H, ArH), 7.86 (s, 2H, ArH) (literature [17] ^{1}H NMR (300 MHz, DMSO-d_6): δ 0.88 (t, 6H, J = 7.5 Hz, CH_3), 1.29 (m, 4H, CH_2), 1.46 (s, 4H, CH_2), 3.43 (s, 4H, CH_2), 6.81 (s, 2H, ArH), 7.83 (s, 2H, ArH)).

Squaraine dye (SQ): squaramide **3** (15.2 mg, 0.04 mmol) and semisquaraine **6** (24.0 mg, 0.08 mmol) were added to a three-necked flask equipped with a Dean-stark trap. *n*-Heptanol (20 mL) was added and the reaction mixture was refluxed under reduced pressure for 8 h. The solvents were removed under reduced pressure and the crude product was chromatographed twice on a column of silica gel with chloroform/methanol (20:1, v/v) to give SQ (9.2 mg, 24%) as a green solid, mp >300 °C. IR (KBr, cm^{-1}): 3436, 2923, 1623, 1580, 1385, 1187. ^{1}H NMR (400 MHz, $CDCl_3$:CD_3OD (v/v) = 1:1): δ 0.98 (t, 12H, J = 7.0 Hz), 1.35–1.41 (m, 8H), 1.63 (br, s, 8H), 3.14 (s, 6H), 3.57 (br, s, 8H), 3.77 (br, s, 8H), 5.34 (s, 2H), 6.70 (d, 4H, J = 8.0 Hz), 6.75 (d, 4H, J = 7.6 Hz), 8.10 (d, 4H, J = 7.6 Hz), 8.15 (d, 4H, J = 8.4 Hz). ESI-MS: m/z 947.1 ($[M+H]^+$) 945.3 ($[M-H]^-$).

2. Results and discussion

The spectra data of SQ in different solvents are listed in Table 1. Compared with bis[4-(dibutylamino)phenyl]-squaraine (BDPSQ) of which the absorption maximum is in the range from 640 to 645 nm in various solvents, the long wavelength band absorption maximum of SQ (in the range from 635 to 639 nm in various solvents) shows a blue-shift of around 5 nm, indicating distinguished intermolecular hydrogen bond interactions between anilino N at squaraine moiety and NH at squaramide moiety. With the flexible alkyl linkage between squaraine moiety and squaramide



Scheme 1. Synthesis of squaraine dye SQ. (a) 2-Bromoethylamine hydrobromide, KI, *n*-BuOH; (b) diethyl squarate, EtOH, reflux; (c) *n*-C_4H_9Br, K_2CO_3, KI, DMF; (d) squaric acid dichloride, benzene, reflux; (e) HCl, TFA, CH_2Cl_2, acetone, reflux; (f) *n*-heptanol, −0.09 MPa, reflux.

Table 1
Absorption and emission spectral data of SQ in various solvents.

Solvent	λ_{1max} (nm)	ε_1 (mol^{-1} cm^{-1} L)	λ_{2max} (nm)	ε_2 (mol^{-1} cm^{-1} L)	ε_1:ε_2	Φ[a]	λ_{em} (nm)
CH_3OH	638	1.97×10^5	268	0.36×10^5	5.47:1	0.0096	663
CH_3CN	635	1.94×10^5	266	0.41×10^5	4.73:1	0.0181	660
CH_3CH_2OH	639	1.97×10^5	267	0.36×10^5	5.47:1	0.0219	658
$CHCl_3$	639	2.32×10^5	266	0.34×10^5	6.82:1	0.072	655
i-PrOH	639	1.44×10^5	267	0.24×10^5	6.00:1	0.0391	652
THF	639	2.14×10^5	259	0.45×10^5	4.76:1	0.107	653

[a] Fluorescence quantum yields were determined using Rhodamine B as the standard.

moiety, SQ exhibits a typical squaramide absorption (in the range from 259 to 268 nm in various solvents) in the short wavelength band with the ε value 30% higher than that of BDPSQ. Due to the structural flexibility [17] and asymmetry [18], SQ displays a weak emission in red region (from 653 to 663 nm in organic solvents) with only around 10% quantum yield of BDPSQ.

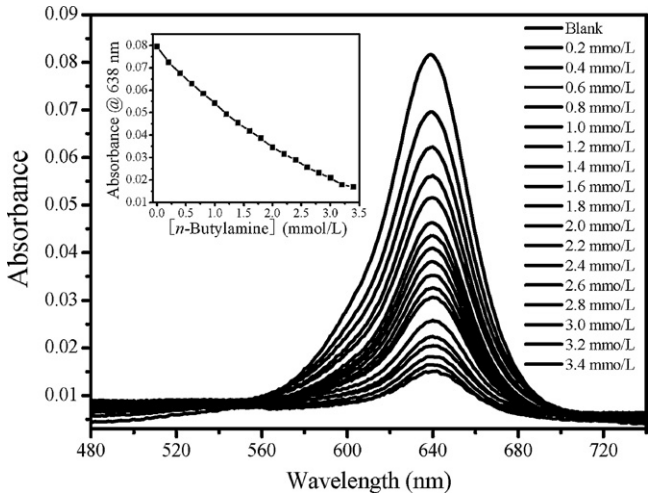


Fig. 1. Absorption spectra of SQ (0.6 μmol/L) upon the addition of *n*-butylamine (0–3.4 mmol/L) in *i*-propanol. *Inset*: the binding isotherm of SQ at 638 nm upon the addition of *n*-butylamine.

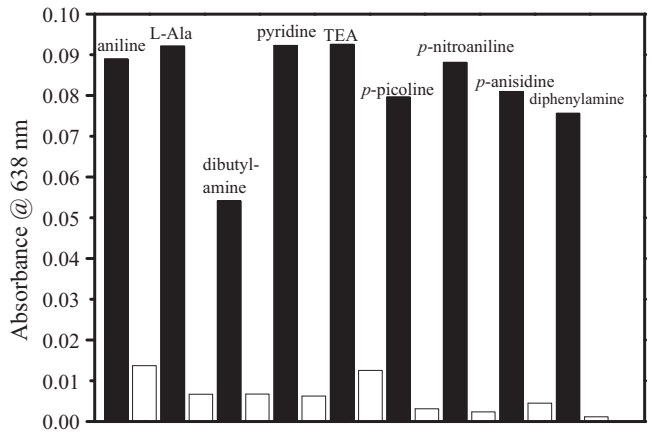


Fig. 2. The competition experiments of *n*-butylamine (3.5 mmol/L) in *i*-propanol solution of SQ (0.6 μmol/L) to various nucleophilic reagents (3.5 mmol/L). Black bars represent the addition of the 3.5 mmol/L competing nucleophilic regents to a 0.6 μmol/L solution of SQ. White bars represent the subsequent addition of 3.5 mmol/L *n*-butylamine to the solution.

The *n*-butylamine titration of SQ was shown in Fig. 1. Upon the addition of amine, the absorption peak of SQ diminished proportionally. Preliminary studies show that *n*-butylamine, as a strong nucleophilic reagent, can attack the dye at the electron-deficient central four-membered squaric acid ring, which destroys the conjugation of squaraine moiety of SQ, leading its bleaching [19–21]. The competition experiments show that other nucleophilic reagents, such as triethylamine, aniline, *p*-nitroaniline, *p*-anisidine, diphenylamine, pyridine, *p*-picoline and L-ALA have low interference in the detection of primary amine because the nucleophilicity of these reagents is not very high. Only dibutylamine, an aliphatic secondary amine, can combine with SQ competitively and has some disturbance to the primary amine detection. So SQ has a potential application in the selective detection of aliphatic primary amine in the presence of tertiary amine, aromatic amine, pyridine derivative and amino acid (see Fig. 2).

In conclusion, we have synthesized a novel squaraine dye based on squaramide. With the influence of the hydrogen bond and the solvent polarity, SQ exhibits remarkable difference in photophysical properties. Amine titration experiment shows that SQ can act as a new receptor of recognizing primary amine in alcohol. Future studies on SQ are still in progress.

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