Sensors & Actuators: B. Chemical 292 (2019) 88–93

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Squaraine-hydrazine adducts for fast and colorimetric detection of aldehydes in aqueous media

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ARTICLE INFO

Keywords:
Squaraine dyes
Aggregation
Colorimetric and fluorescence
Chemosensors
Aldehydes detection

ABSTRACT

Capitalizing on the nucleophilic addition of hydrazine toward the central cyclobutenyl core and affinity of aldehydes to hydrazine group, two water-soluble squaraine dyes (SQOH and SQPY) were synthesized as sensitive colorimetric and fluorescent chemosensors for aldehydes. The color change from blue to colorless and back to blue these sensors underwent was readily observed, even by the naked eyes. The response was fast (less than 1 s) and the detection limit for formaldehyde as an example was about 60 μM. In contrast to the previous nucleophilic attack to squaraines and the other amine references studied, this work underwent a whole ON-OFF-ON sensing circle based on the characteristics of hydrazine. Meanwhile, the different photophysical properties of the two squaraines related to their different structures were also demonstrated. Importantly, a possible sensing mechanism is proposed suggesting these types of dyes hold great potential in the area of rapid, sensitive, and convenient detection of aldehydes.

1. Introduction

Aldehydes are an important class of chemicals that play important roles in numerous industrial and biological systems. They are naturally contained in foods such as fruits and vegetables, dairy products, and various beverages, and sometimes used as flavoring compounds in E-cigarette aerosols and food manufacturing since it has a fruit-like flavour [1,2]. It is also known that generation of volatile aldehydes is one of the main causes of beer flavour deterioration during both brewing and storage [3–6]. While some aldehydes, including formaldehyde (HCHO), acetaldehyde, and benzaldehyde, are considered as well-known pollutant and poses a great threat to human health because of its carcinogenic and mutagenic properties [7–11]. A high concentration of acetaldehyde in wine during the brew process causes suppression of yeast function and decrease of alcohol fermentation rate [4]. Therefore, the establishment of a highly sensitive and selective method of detecting aldehydes in aqueous media is of great importance in the fields of chemical, environmental, and industrial sciences.

In the sensing of aldehydes, colorimetric and fluorescence methods are advantageous by virtue of their simplicity, high sensitivity, real-time detection, low cost, and ability to provide *in situ* and real-time information [12–19]. Over the past decade, various fluorescent reagents such as oligothiophene, coumarin, dimethylquinoline, naphthalimide, BODIPY, squaraines, etc have been developed for the detection of aldehydes [18–25]. However, some of the reported fluorescent probes suffer from drawbacks including long reaction time, fluorescence turn-off, and nonlinear calibration curves, which limit their practical use. Hence, development of efficient colorimetric or fluorescent sensing materials for detecting aldehydes remains a significant challenge.

Squaraines (SQs) with resonance stabilized zwitterionic structure exhibit narrow and intense absorption and fluorescence in the near-infrared region [26–28]. One attractive feature of the electron-deficient cyclobutene ring of SQs is its susceptibility to attack by sterically unencumbered nucleophiles, which leads to a loss of π-conjugation and the subsequent bleaching of the solution. A number of SQs have been reported in recent years as colorimetric and fluorescent probes for detecting nucleophilic anions such as thiols, fluorides, and cyanides [29–36]. Among these, Martínez-Máñez and co-workers reported a squaraine–thiol conjugate for sensitive and selective detection of Hg^{2+} in aqueous media based on the strong thiophilic affinity of Hg^{2+} and the subsequent regeneration of the squaraine dye [37]. Anslyn et al.

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https://doi.org/10.1016/j.snb.2019.04.138
Received 10 February 2019; Received in revised form 12 April 2019; Accepted 27 April 2019
Available online 29 April 2019
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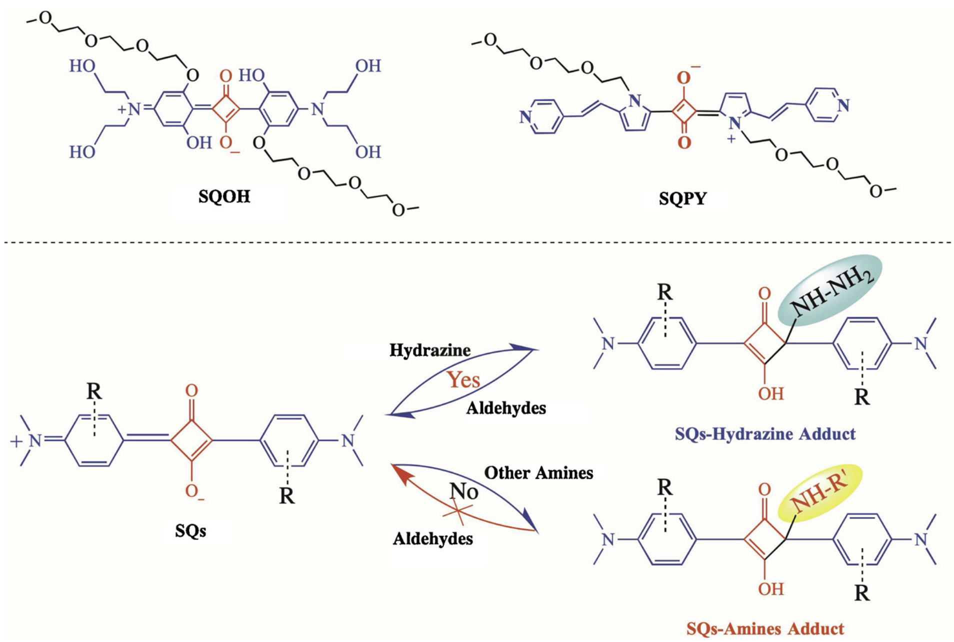

Fig. 1. Chemical structures of the SQs (SQOH and SQPY) and schematic illustration of the possible sensing mechanism of the SQ-hydrazine system for detecting aldehydes in aqueous media.

reported the pattern-based discrimination of thiols and metal ions using a single squaraine indicator [38]. Recently, the extension of this methodology has been achieved for chromo- and fluorogenic "switching-on" response toward some other analytes such as carbon dioxide, formaldehyde, pyrophosphate, and chemical warfare agents, etc [34,39–44].

Herein, we developed two symmetrical SQs, namely SQOH and SQPY, for the highly sensitive detection of aldehydes in aqueous media based on the "on-off-on" sensing concept [16,38]. Briefly, addition of various amines can bleach the characteristically blue SQs to the corresponding colorless SQ-amine adducts. Addition of aldehydes to the adducts resulted in the retroversion of the parent SQs that can be colorimetrically detected, especially in the most effective SQ-hydrazine system. The chemical structures of the SQs and proposed sensing mechanism are depicted in Fig. 1 [44]. This is an interesting sensing strategy based on the adduct of SQs-hydrazine for detecting aldehydes. Moreover, the sensing concept presented here was employed in quantifying total aldehydes in beer, yielding satisfactory results.

2. Experimental section

2.1. Synthesis of squaraine dyes

As depicted in Fig. 1 and Scheme S1, dyes SQOH and SQPY were obtained *via* a condensation reaction between the related intermediates and squaric acid in a mixture of 1-butanol/toluene (1/1, v/v) using a Dean-Stark apparatus, where the water that formed was removed continuously [45–48]. The chemical structure and purity of the related compounds were confirmed by NMR and high-resolution mass spectroscopy. An overview of the synthetic procedures and molecular characterization details are presented in the Supporting Information (c.f. Figs. S1–S8).

3. Results and discussion

3.1. Characterization and photophysical properties of the squaraine dyes

Initially, both SQs exhibited good solubility in common organic solvents, yielding a characteristically blue solution with intense absorption maximum as well as fluorescence emission maxima bands in the far-red spectral region [47,48]. The main linear absorption features for SQOH and SQPY in tetrahydrofuran (THF) were narrow absorption centered at 640 nm and 680 nm, respectively (π-π^* transition). As shown in Fig. 2a and b, SQPY exhibited red-shifted maximum fluorescence emission at 691 nm with a typically small Stokes shift ($\Delta\lambda = 11$ nm), while SQOH displayed fluorescence emission at 663 nm in THF.

In aqueous solution, SQOH did not aggregate and exhibited a characteristic sharp and intense absorption band of the monomeric squaraine chromophore at *ca.* 640 nm ($\varepsilon = 1.70 \times 10^5$ L/M, c.f. Fig. S9) with relatively strong far-red fluorescence at 667 nm ($\Phi_F = 0.03$) [28,29]. Meanwhile, the strong absorption of SQPY at 616 nm is assigned as H-aggregates with a broad shoulder at approximately 682 nm for the SQ monomer [49]. The ability of SQOH to avoid aggregation can be attributed largely to the ethoxyether substituents adjacent to the squaraine core, and, perhaps, to a lesser extent the ethanol terminal moieties. In other words, functionalization of triethylene glycol chains close to the squaraine core not only provide enhanced solubility, it significantly attenuates squarainyl intramolecular interactions, preventing aggregation in aqueous media [26–29].

3.2. Sensing performance of the SQs to different amines and aldehydes

Subsequently, in order to compare the chemical stability of SQOH and SQPY, both dyes were treated with various primary amines, including hydrazine hydrate ($N_2H_4{\cdot}H_2O$), ethanolamine, methylamine, and β-phenylethylamine, as well as the secondary amines diethylamine and urea. Fig. 2c shows that addition of 500-fold N_2H_4 results in > 90% decrease in the absorption intensity, along with a distinct blue-to-colorless change in solution. In contrast to urea and diethylamine with less than 6% decrease of the original intensity at 640 nm, all the primary amines bleached the SQs rapidly and hydrazine has the most effective attack (c.f. Fig. 2d). It is known that decrease of the main absorption band can be ascribed to the addition of nucleophilic amines to the central cyclobutene core. Meanwhile, a new absorption band at *ca.* 300 nm corresponding to a semi-squaraine showed up and increased proportionally [29–36,44]. We also evaluated ammonia and NaOH at similar concentrations and got moderate bleaching effects.

Accordingly, considering aldehydes could react with the

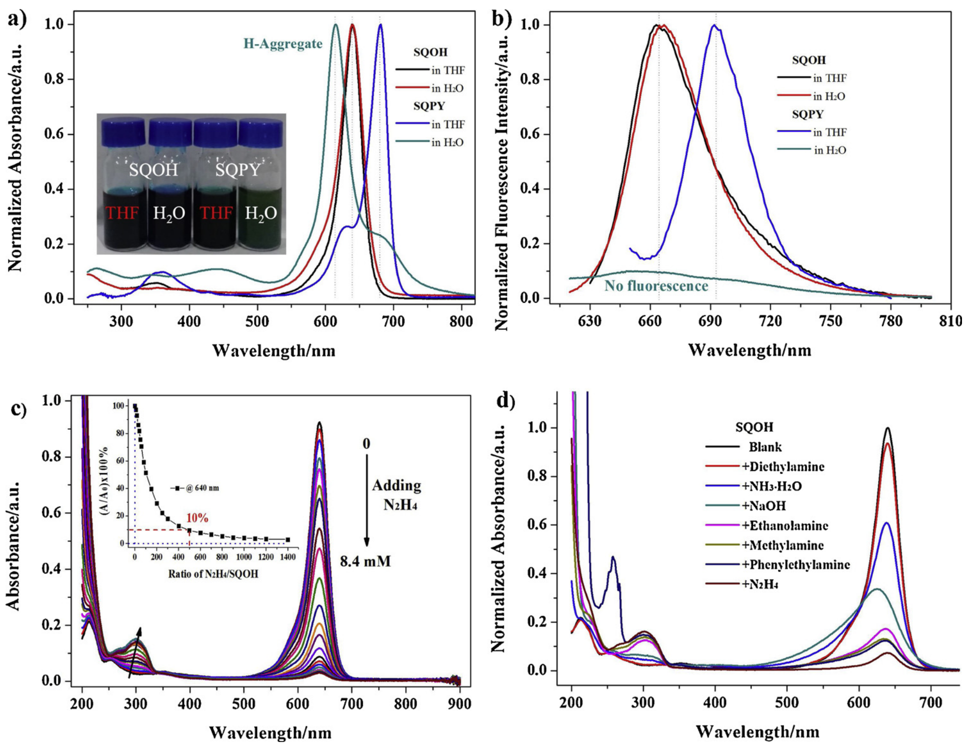

Fig. 2. UV–vis absorption (a) and fluorescence spectra (b) of dyes SQOH and SQPY in THF and aqueous solution; c) UV–vis spectral changes of SQOH upon increasing amount of N_2H_4 (range from 0 to 8.4 mM) in distilled water. Inset shows the corresponding plots of absorption intensity *versus* the N_2H_4 concentration; d) UV–vis spectral changes of SQOH (6.0 μM) upon addition of different amines and basic interferents (3.0 mM).

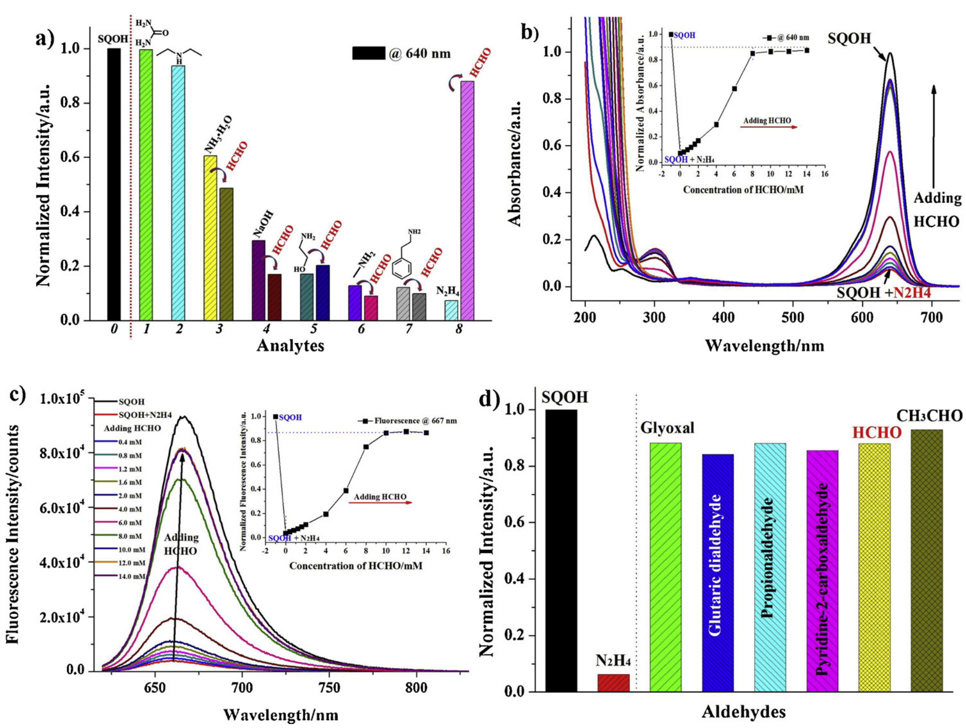

Fig. 3. a) Normalized absorption intensity changes of SQOH upon adding different amines first and the recovery efficiency by adding HCHO. Absorption changes (b) and fluorescence emission changes (c) of the SQOH-hydrazine system upon addition of HCHO (0–14.0 mM). Inset show the corresponding plots between the intensity and HCHO concentration; d) Absorption intensity changes of the SQOH-Hydrazine system upon adding different aldehydes.

corresponding SQ-amine adducts and reverse the bleaching reaction, the parent SQOH could be regenerated by adding aldehydes to a SQOH-hydrazine adduct solution. As depicted in Fig. 3b and c, titration of HCHO to the SQOH-hydrazine adduct showed an obvious increase of the absorption band at 640 nm. Addition of excess HCHO can completely scavenge the hydrazine, evidenced by a 23-fold increase in absorption intensity and 86% recovery in the emission intensity of the original SQOH. This response was obtained in less than 1 s, implying the fast response of the adduct to HCHO. Furthermore, the solution exhibited a visual color change from colorless to blue, easily distinguished by the naked eye or quantitatively analyzed with the aid of a portable spectrometer (c.f. Fig. S10). The high sensitivity of this chemosensor in aqueous solution afforded a detection limit of 60 μM for HCHO based on fluorescence detection. We know that the concentration of the dyes and the analytes play an important effect in the practical detecting applications. Based on the above analyses, the optimal bleaching ratio for hydrazine to the SQs and the maximum recovery ratio of adding HCHO to the adducts was 500 and 1650, respectively.

We further examined whether the other relevant adducts could react with HCHO to give positive results. Interestingly, the switching-on

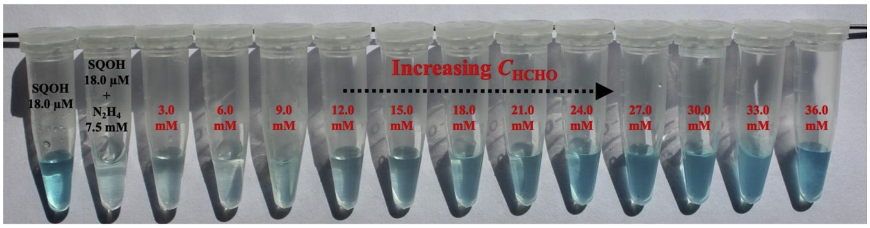

Fig. 4. Solution color changes of the SQOH-N_2H_4 adduct by adding different concentrations of HCHO (from left to right: 0–36 mM).

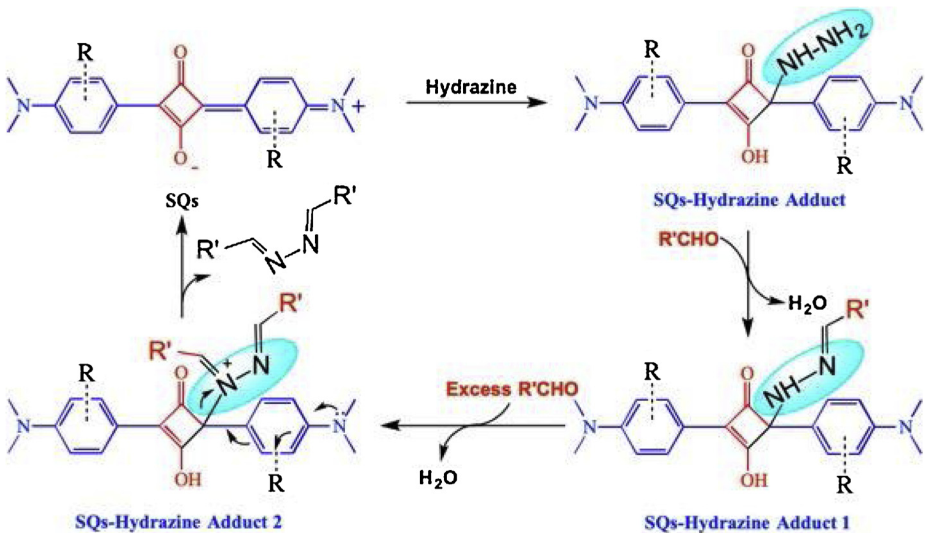

Fig. 5. Schematic diagram depicting the realization of colorimetric and fluorescent signaling of aldehydes based on the SQs-N_2H_4 adduct.

signal by HCHO could be obtained only in the SQ-hydrazine system. Furthermore, we inspected the spectra changes of the SQOH-hydrazine adduct toward different aldehydes such as acetaldehyde (c.f. Fig. S11), glyoxal, glutaric dialdehyde, propionaldehyde and pyridine-2-carboxaldehyde in aqueous solutions and the same results were obtained (c.f. Fig. 3d). The results show that all the aldehydes can cause the regeneration of SQOH, clearly demonstrating the crucial role played by the hydrazone in the SQ-hydrazine adduct. Meanwhile, the same concentrations of alcohol, ethyl acetate, and ketone derivatives showed no obvious effect to the detecting process, suggesting the selectivity of the SQ-hydrazine adduct to aldehydes (c.f. Fig. S12).

3.3. Detection of aldehydes

Compared to traditional sensing systems for HCHO, the colorimetric method based on squaraine-hydrazine adduct is relatively easy to implement and inexpensive, since it offers a convenient "mix-and-detect" protocol for homogeneous detection and does not require complicated synthesis, strict storage conditions, and expensive equipment (c.f. Fig. 4). Similar results were obtained for SQPY and confirmed the bleaching process (c.f. Figs. S13–S15). Relative to the non-fluorescent H-aggregates of SQPY, the emission intensity of SQOH decreased faster, which indicates that SQOH is a more sensitive probe for aldehydes than SQPY.

3.4. The sensing mechanism

According to the discussion aforementioned, primary amines undergo a nucleophilic addition at the double bond that is proximate to the cyclobutene ring in SQs. This double bond in resonance stabilized SQ is delocalized adjacent to the aniline or pyrrole ring, and the reaction preferentially occurs on one of these electrophilic centers instead of the carbonyl group in the core [50]. Upon addition of aldehydes, the initial emission band gradually emerged and, concomitantly, the semi-squaraine peak at 300 nm disappeared, which agreed well with the expected recovery of the adduct to the original squaraine [29–36,44].

In order to validate the reaction mechanism of SQOH with N_2H_4, we confirmed *via* HRMS that the fluorescence increase resulted from conversion of the SQ-N_2H_4 adduct to the original SQ upon adding the aldehydes to the adduct system. The APCI-HRMS showed that a new peak emerged at m/z 797.3701 for [SQOH + H^+]. Additionally, the ESI-HRMS displayed new peaks appearing at m/z 797.3708 (M + H^+) and 819.3522 (M + Na^+), corresponding to the parent SQOH (c.f. Fig. S16). These results are consistent with the hydrazine-initiated chemical conversion shown in Fig. 1 and the proposed sensing mechanism depicted in Fig. 5. The specificity of the SQ-hydrazine adduct originates from the so-called α-effect which is, in fact, the repulsion between the unshared pairs of electrons of the nucleophilic nitrogen atoms [51,52]. Some previous studies have reported the nucleophilic addition of amines to the central squaraine core [53–55].

The formation of carbonyl compounds has been widely used to monitor the degradation in the quality of foods and beverages, including beer. Oxidation occurs readily in beer at elevated temperatures, and subsequently its flavor quality decreases. Among oxidation products, carbonyl compounds such as acetaldehyde and diacetyl have been considered to be responsible for off-flavors caused during the production and storage of beer [11,56]. After demonstrating excellent responsiveness to aldehydes and exceptional selectivity in aqueous solution, we tested the ability of SQOH to quantify the total aldehydes in beers. Based on the relationship of acetaldehyde concentration with the recovery efficiency of SQOH (c.f. Fig. S11), total aldehydes content in a beer sample was evaluated to be around 100 mM, and the aldehydes content increased with the higher storage temperature and longer oxidative degradation in open air (c.f. Fig. S17).

4. Conclusions

In conclusion, water-soluble squaraine dyes SQOH and SQPY were successfully designed and synthesized for sensing aldehydes. SQOH did not form aggregates in aqueous condition, and exhibited intense absorption with a maximum peak at 640 nm and relatively strong fluorescence. These signals could selectively disappear in the presence of amines and switch-on by adding aldehydes to the adduct. The detection limit of the SQOH-hydrazine adduct for HCHO was around 60 μM. A sensing mechanism of the SQs for detecting aldehydes was proposed. We envision that this work provides a simple, sensitive, and convenient method for the rapid and naked eye detection of aldehydes, with great potential for the development of squaraine-based HCHO detection system. Future work will focus on improving the detection limit of this class of probe and realize the concise detection for aldehydes through developing novel SQs by structural modification.

Notes

The authors declare no competing financial interest.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (21527802, 21673133, and 21820102005), 111 project (B14041), Program for Changjiang Scholars and Innovative Research Team in University (IRT-14R33), the Fundamental Research Funds for the Central Universities (GK201803024) and the Open Fund of Shaanxi Joint Laboratory of Graphene (Northwestern Polytechnical University, 2019SJLG-01). KDB acknowledges support from the National Science Foundation (CHE-1726345).

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.snb.2019.04.138.

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