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Efficient fluorescent chemosensors for HSO₄⁻ based on a strategy of anion-induced rotation-displaced H-aggregates[†]

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A novel fluorometric sensing strategy based on the anion-induced rotation-displaced H-aggregates of styrylindolium dyes was employed to enhance the selectivity of fluorescent chemosensors for HSO_4^- detection. The marvelous anion-induced H-aggregate strategy opens new routes to simple synthesis of receptors for tetrahedral anionic species.

Motivated by applications in medical diagnostics, environmental and industrial monitoring, and nuclear waste cleanup,¹ the selective sensing of anions by fluorometric methods² has been the subject of intensive research effort. Compared with the receptor-based metal ions and small-sized anions sensing,^{2a} the design of receptors with the complementary conformation for the detection of tetrahedral anionic species, such as SO_4^{2-} , HSO_4^{-} , $H_2PO_4^{-}$, HPO_4^{2-} *etc.*, is quite challenging because of their extremely large hydration energy according to the Hofmeister bias.³ Thus, it is highly desirable to seek novel, simple and efficient paradigms to realize the high selectivity and sensitivity for anion detection.

It is known that the intriguing optical properties of J- and H-aggregates are of significant interest for organic dyes conceived by supramolecular approaches.⁴ To date, the photophysical properties of J-aggregates have been widely utilized to develop novel fluorescent and colorimetric chemosensors for chemical detections, or to develop photosensitizers for photographic applications.⁵ Comparatively, the applications of the optical properties of H-aggregates are rare due to their blue shifted absorption bands and fluorescence quenching properties.⁶ In 2006, Würthner *et al.*⁷ reported an example of fluorescent H-aggregates composed of slight rotation-displaced merocyanine dyes.

Enlightened by Würthner's work,⁷ we reported herein a novel strategy for anionic receptor design by taking full advantage of the fluorescent properties of the anion-induced rotation-displaced

H-aggregates of the dyes. In this paper, 4-hydroxystyrylindolium derivatives **L1** and **L2** were chosen as sensitive and selective chemosensors for HSO_4^- anions based on the following considerations: (i) a hydroxyl on the *para*-position of the dye offers an anion binding site *via* hydrogen bonding; (ii) the charged indolium moiety donates a positive charge for electrostatic interactions with the anionic guest; (iii) the steric hindrance arising from the spatial orientation of the dye's 3,3-dimethyls prevents them from the formation of an anion-induced face-to-face H-aggregate. Based on this idea, we developed successfully **L1** and **L2** as selective chemosensors for HSO_4^- anions Scheme 1.

Firstly, the photophysical properties of the dyes were elucidated by UV/Vis absorption and fluorescence spectra in the absence and in the presence of various anions in H2O-EtOH (1:1, v/v). L1 showed the characteristic intense charge-transfer band occurring in the long-wavelength region between 400 and 560 nm, which peaked at 541 nm (ε = 1.18 × 10⁵ M⁻¹ cm⁻¹) (Fig. S1, ESI⁺). It is interesting to note that the addition of 10.0 equiv. of HSO₄⁻ into the red solutions of L1 immediately generated a yellow solution with a new absorption band centred at 434 nm ($\varepsilon = 5.81 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$), which matched perfectly those of classical H-type dimer aggregates with a pronounced hypsochromic shift.8 However, no obvious absorption and colour changes arose from the addition of other anions, such as PO₄³⁻, HPO₄²⁻, H₂PO₄⁻, NO₃⁻, SO₄²⁻, Cl⁻, CO₃²⁻, F⁻, and Ac⁻. To understand the HSO₄⁻-induced aggregation, the absorption spectra of the styrylindolium dyes L2-L4 were also investigated under conditions identical to those used for L1. Similar to L1, the electronic absorption spectra of L2 in aqueous ethanol



Scheme 1 Structures of the styrylindolium dyes L1-L4.

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Fig. 1 Photograph of **L1** (a and b) and **L2** (c and d) in the presence of various anions. (a) and (c) Color changes in the presence of different anions; (b) and (d) fluorescence changes under UV 365 nm excitation in the presence of different anions. (a)–(d) From right to left, (10.0 equiv.) of PO_4^{3-} , HPO_4^{2-} , $H_2PO_4^{-}$, NO_3^{-} , SO_4^{2-} , HSO_4^{-} , CI^- , CO_3^{2-} , F^- , Ac^- and **L1** or **L2** alone in H_2O –EtOH (1 : 1, v/v).

showed the characteristic charge-transfer band positioned at 580 nm ($\varepsilon = 1.19 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$), which was hypsochromically shifted to 448 nm upon the addition of HSO₄⁻ (Fig. S2, ESI⁺). Thus, the HSO₄⁻-induced unique absorption changes of L1 and L2 indicated that they can be used as selective chemosensors for HSO₄⁻. Meanwhile, the interesting features of HSO₄⁻-induced colour changes of L1 and L2 revealed that they can serve as selective visible chemosensors for HSO₄⁻. As shown in Fig. 1, only HSO₄⁻ induced a prominent colour change (Fig. 1a and c). At the same time, fluorescence of L1 and L2 also showed a characteristic colour change in the presence of HSO4- when excited under a hand-UV lamp at 365 nm (Fig. 1b and d). While in the case of a styryl moiety with a hydroxyl at the 3-position, however, L3 and L4 didn't show a hypsochromically shifted absorption band, which indicated that the structure is unfavourable for the formation of HSO₄⁻-induced H-aggregates (Fig. S3 and S4, ESI⁺).

To gain a general understanding of the fluorescence properties of the anion-induced aggregates, fluorescence spectra of the dyes were recorded by excitation at the maximum absorption band of the H-aggregates. Under these conditions, both L1 and L2 showed a prominent blue-shifted fluorescence enhancement upon the addition of 10 equiv. of HSO₄⁻ anions (Fig. S5 and S6, ESI⁺). However, the addition of 10 equivalents of other anions has no obvious effect on the fluorescence intensity. Upon excitation at the isosbestic point of L1 at 476 nm, it showed a monomer emission band centered at 568 nm (Fig. S7, ESI⁺). Upon the addition of various anions, only HSO₄⁻ induced a blue-shifted emission, whereas other anions afforded no obviously fluorescent changes. The inset of Fig. S7 (ESI[†]) exhibits the dependence of the intensity ratios of L1 at 528 nm to that at 568 nm (I_{528}/I_{568}) on the anions, which showed specific selectivity toward HSO₄⁻ among all the examined anions. Upon excitation at the isosbestic point of L2 at 501 nm, however, only a similar blue-shifted fluorescence enhancement at 562 nm as those excited at the maximum absorption band of the aggregation was observed (Fig. S8, ESI⁺). The HSO₄⁻-induced H-aggregates exhibited significant enhanced or ratiometric fluorescence changes, suggesting that L1 and L2 may be useful as fluorescent chemosensors.

To qualitatively assess the thermodynamic parameters for their aggregation processes, the HSO_4^- -induced H-aggregates of L1 were studied by temperature-dependent electronic absorption



Scheme 2 The proposed HSO₄⁻⁻-induced rotation-displaced H-aggregate of L via hydrogen bondings, charge interactions and π - π interactions.

spectroscopy (Fig. S9, ESI⁺). Upon increasing the temperature, the transformation from the aggregates to the monomeric species was observed, thus revealing the reversibility of the anion-induced aggregation process. On the other hand, although the concentration-dependent absorption spectra^{6,12} of the free chemosensor L1 increased nonlinearly at 434 nm provided additional evidence for the formation of aggregates under higher concentrations, prominent changes are not observed, indicating that the HSO₄⁻ anion played a key role in inducing the aggregation (Fig. S10, ESI⁺). Accordingly, we hypothesized that the HSO₄⁻ was firstly bonded with the free chemosensor L1 via hydrogen bonding to form a L1·HSO₄⁻ complex, then it was further aggregated in a head-to-tail fashion via intermolecular π - π interactions and electrostatic interactions to form an H-aggregate (Scheme 2). It has been reported that functionalization of the dye's electron-donor moiety with bulky groups induced displacement of the monomer into a slip-stacked arrangement in the solid state.13

To obtain further insight into the bonding properties of HSO_4^- with L1 and L2, the absorption and fluorescence spectra of the dyes upon titration with HSO_4^- were obtained in $H_2O-EtOH$ (1:1, v/v). As shown in Fig. 2a, upon addition of HSO_4^- (0–25.5 equiv.), a significant decrease in the absorption band of L1 at 541 nm and an increase in the new band at 434 nm was observed. Two distinct isosbestic points at 268 nm and 476 nm were observed, indicating the formation of a new complex between L1 and HSO_4^- . The absorption bands at 541 and 434 nm linearly decreased and increased up to a 4:1 [HSO_4^-]/[L1] ratio, respectively (Fig. S11, ESI†). Moreover, the absorbance at 434 nm remains constant in the presence of more than 5.0 equivalents of HSO_4^- anions (inset of Fig. 2a). The absorbance ratio R (A_{434}/A_{541}) increased upon increasing the concentration of HSO_4^- , which also allowed the use of L1



Fig. 2 (a) Absorption spectra of **L1** (10.0 μ M) to increasing concentrations of HSO₄⁻ in H₂O–EtOH (1:1, v/v). Inset: the absorbance changes of **L1** at 434 nm as a function of the HSO₄⁻ concentration. (b) Fluorescent titration spectra of **L1** (6.0 μ M) in the presence of different concentrations of HSO₄⁻ in EtOH–H₂O (1:1, v/v). Inset: plot of the emission ratio *R* upon HSO₄⁻ titration of **L1**, wherein *R* is defined as the ratio of the emission intensities at the two wavelengths [*I*_{528nm}/*I*_{568nm} for **L1**]. $\lambda_{ex} = 476$ nm.

for the detection of HSO_4^- by ratiometric absorbance methods (Fig. S12, ESI[†]). From the sigmoidal curves, the apparent dissociation constant (K_d) 7.04 × 10⁻⁵ M (R = 0.997) is obtained. Stoichiometry for L1 and the HSO_4^- complex was evaluated on the basis of the Job's plot and was found to be 1:1 (Fig. S13, ESI[†]). Similar experiments were also conducted with L2, and the results imply that L2 is also a good chemosensor for HSO_4^- anions (Fig. S14, ESI[†]). The K_d derived from the titrations was found to be 3.91 × 10⁻⁵ M (R = 0.998) (Fig. S15, ESI[†]). Job plots obtained from fluorescence titrations indicated a 1:1 stoichiometry for the receptor- HSO_4^- interaction (Fig. S16, ESI[†]).

By excitation at the maximum absorption band of the aggregates, both L1 and L2 showed a fluorescence enhancement with the increase of HSO₄⁻ concentrations (Fig. S17 and S18, ESI⁺). The $K_{\rm d}$ values 5.81 \times 10⁻⁵ M (R = 0.993) for L1 and 4.29 \times 10⁻⁵ M for L2 (R = 0.998) were obtained according to the titration spectra, respectively. Upon excitation at the isosbestic point at 476 nm in the presence of different concentrations of HSO₄⁻, however, a unique ratiometric fluorescent change was observed for L1. It is known that from ratiometric fluorescent measurements changes in the ratio of the emission intensities at two wavelengths can be observed.¹⁴ This measurement circumvents adverse effects on fluorescence signals by the single wavelength detections and gives an increased accuracy and reproducibility for analyte detection.9-11 To investigate the possibility of using L1 as a ratiometric HSO₄⁻ sensor, continuous fluorescence titrations of the dye with increasing amounts of HSO₄⁻ were carried out. As shown in Fig. 2b, L1 exhibited a characteristic emission band at 568 nm. The addition of HSO₄⁻ anions to a solution of L1 induced a remarkable ratiometry since the emission band centred at 528 nm of H-aggregates increases as its monomer emission declines. A well-defined isoemission point at 550 nm was also observed, indicating the formation of a new complex between L1 and HSO₄⁻. The emission intensity at 568 nm (I_{568}) (Fig. S19, ESI⁺) and the intensity ratio R (I_{528}/I_{568}) (Fig. S20, ESI[†]) increased upon the gradual addition of HSO4⁻, which allowed the detection of HSO4⁻ by both single wavelength and dual-wavelength measurements of fluorescence emission. From the sigmoidal curves in Fig. S19 and Fig. S20 (ESI⁺), apparent dissociation constants 5.86 \times 10⁻⁵ M (R = 0.991) and 6.68×10^{-5} M (R = 0.992) are obtained, respectively.

To survey the strategy of the anion-induced H-aggregates for practical applicability in anion detection, further experiments to study HSO_4^- -selective sensing were carried out with L1 and L2 by excitation at 476 nm in the presence of the above-mentioned anions. Upon addition of HSO_4^- anions, the solution still displayed a distinct fluorescence enhancement, indicating that they showed good selectivity and sensitivity toward HSO_4^- over other competitive anions (Fig. S21, ESI⁺). The evaluated proper pH conditions of L1 and L2 indicated that L1 can be used from pH 4.5 to pH 8.0, and L2 can be used from pH 5.8 to pH 10.0 for HSO_4^- determination (Fig. S22, ESI⁺). From the changes in HSO_4^- -dependent fluorescence intensity (Fig. S23, ESI⁺), the detection limits of L1 and L2 were estimated to be 1.0×10^{-7} and 1.0×10^{-6} M, respectively.

In conclusion, a novel strategy based on the optical signal changes of anion-induced rotation-displaced H-aggregates to enhance the sensitivity and selectivity for anion sensing has been developed. The strategy based on the use of styrylindolium dyes as chromophores provided a simple and efficient way for the selective recognition of HSO_4^- , an interesting tetrahedral anion owing to its established role in biological and industrial areas and its harmfulness for human health as well.¹⁵ The chemosensors showed significant fluorescence signal changes with high sensitivity and selectivity toward HSO_4^- , allowing its selective detection in the presence of a wide range of the environmentally relevant competing anions. With smart structural design, we anticipate that this paradigm, by taking advantage of the anion-induced rotation-displaced H-aggregates, provides a very simple way for designing anion-selective chemosensors.

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