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Fluorescence indicator displacement detection based on pillar[5]arene-assisted dye deprotonation†

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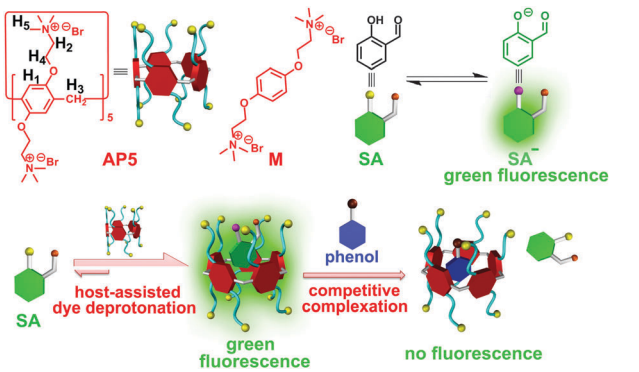
Fluorescence indicator displacement detection based on pillar[5]arene-assisted dye deprotonation was reported.

With the fast development of host–guest chemistry,[1] analyte-responsive macrocyclic host/dye systems have been widely investigated with the aim of constructing highly sensitive and selective chemsensors.[2] Fluorescent dyes with high affinities for macrocycles in aqueous solution can show remarkable fluorescence changes upon host–guest complexation.[2] When an analyte is added to a solution of a host/dye complex, the analyte displaces the fluorescent dye from the complex and the solution recovers to the initial fluorescence condition. This phenomenon is broadly termed as host/dye fluorescence indicator displacement (FID), as the occurrence of such an event is totally determined by the competition between the tested analyte and the indicator for the binding site of the host.[3] Previously reported examples of host/dye pairs for FID are focused on neutral guests and cation receptors, including cyclodextrins, calixarenes and cucurbiturils,[2–4] which are able to recognize compounds of biological and environmental relevance such as diamines and acetylcholines. Correspondingly, anion receptor/dye systems have been rarely investigated due to the lack of macrocycles that selectively bind anionic dyes.[5] This greatly restricts the types of analytes and hinders the development of supramolecular chemosensors. Thus it is necessary to explore new classes of anion receptor-type macrocycles to construct new host/dye systems, not only for fundamental research, but also for practical applications.

Here we aimed to develop a new anion-receptor/dye pair for FID. In search of a macrocyclic host, our attention was drawn to an emerging class of artificial macrocycles, pillararenes. Over the past eight years, pillar[*n*]arenes have attracted more and more interest from researchers because of their outstanding ability to selectively complex various guests.[6] Especially, host–guest recognition motifs based on water-soluble pillar[*n*]arenes are most appealing, because they can be extensively applied in biomedical research such as cell imaging and drug delivery.[7] Among these water-soluble pillar[*n*]arenes, cationic pillar[*n*]arenes aroused our interest, because they were able to recognize a series of anionic guests such as ATP,[8] 2,4-dinitrophenylphosphate[9] and sodium 1-octanesulfonate.[10] Inspired by these studies, in the present work we designed a turn-on fluorescence switch based on host–guest complexation between a pH-sensitive dye (salicylaldehyde) and a water-soluble cationic pillar[5]arene (**AP5**) (Scheme 1). Salicylaldehyde is weakly fluorescent in its neutral form (**SA**), but exhibits strong fluorescence in its deprotonated form ($\mathbf{SA}^-$). When **AP5** was added to a solution of salicylaldehyde at neutral pH, the transformation from **SA** to $\mathbf{SA}^-$ occurred due to the different association constants between $\mathbf{AP5}\supset\mathbf{SA}$ and $\mathbf{AP5}\supset\mathbf{SA}^-$. The complexation-assisted dye deprotonation and deaggregation effects caused a pronounced fluorescence enhancement of the solution. We further employed this turn-on fluorescence switch for FID detection of phenolic contaminants, including chlorophenols.

First, ^{1}H NMR spectroscopy was employed to investigate the host–guest complexation of **AP5** and salicylaldehyde. Since the



Scheme 1 Chemical structures and cartoon presentations of **AP5**, **SA**, $\mathbf{SA}^-$ and **M** and illustration of the fluorescence indicator displacement process.

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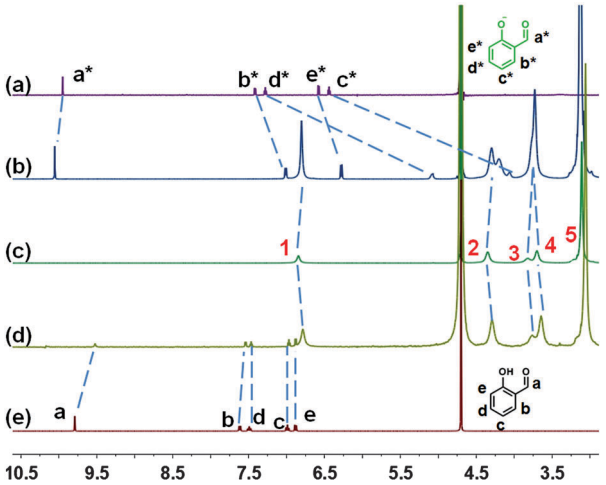

Fig. 1 Partial ^{1}H NMR spectra (400 MHz, D_2O, 293 K): (a) 5.00 mM **SA**$^-$ (pD = 11.0); (b) a mixture of 5.00 mM **SA**$^-$ and **AP5** (pD = 11.0); (c) **AP5** (5.00 mM); (d) a mixture of 5.00 mM **SA** and **AP5** (pD = 4.0); (e) 5.00 mM **SA** (pD = 4.0). The pD value of the solution was adjusted by adding DCl or NaOD.

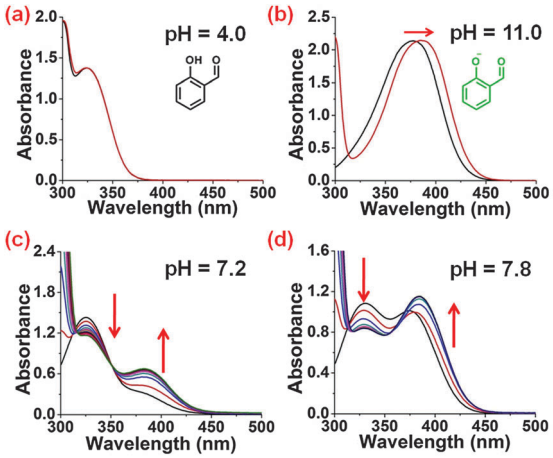

Fig. 2 UV-vis spectra of (a) **SA** (5.00×10^{-4} M) at pH = 4.0 and (b) **SA**$^-$ (5.00×10^{-4} M) at pH = 11.0 in the absence (black) and presence (red) of 1 equiv. of **AP5**. Successive titration of **AP5** into the solution of the dye at (c) pH = 7.2 and (d) pH = 7.8. The pH value of the solution was adjusted by adding HCl or NaOH.

acid dissociation constant (pK_a) of salicylaldehyde is ~8.3,[11] only **SA** needs to be considered at pH = 4.0 and only **SA**$^-$ needs to be considered at pH = 11.0. Therefore, the host–guest interactions between **AP5** and salicylaldehyde in neutral and deprotonated states can be studied individually at these two different pH values. Upon addition of **AP5** to a solution of **SA**$^-$, all signals related to phenyl protons of **SA**$^-$ shifted upfield remarkably and peaks corresponding to H_{b^*} and H_{d^*} on **SA**$^-$ became broad (Fig. 1, spectra a–c). These phenomena indicated that these protons resided in the cavity of **AP5** and were shielded by the π-rich cavity upon the host–guest complexation.[12] On the other hand, peaks related to protons H_{1-5} on **AP5** also displayed slight chemical shift changes due to the host–guest interactions between **AP5** and **SA**$^-$.[13] The 2D NOESY NMR spectrum of a solution of **AP5** and **SA**$^-$ exhibited NOE cross-peaks between protons H_{1-4} of **AP5** and aromatic protons H_{b^*,d^*,e^*} as well as aldehydic protons H_{a^*} on **SA**$^-$, indicative of phenyl ring inclusion in the cavity of **AP5** (Fig. S9, ESI†). Moreover, a mole ratio plot demonstrated that the binding stoichiometry of **AP5** and **SA**$^-$ was 1 : 1 (Fig. S12, ESI†). The association constant (K_{ass}) of **AP5**⊃**SA**$^-$ was calculated to be $(2.01 \pm 0.21) \times 10^4$ M^{-1} by isothermal titration calorimetry (ITC) (Fig. S13, ESI†). Similarly, the host–guest complexation between **AP5** and **SA** was also investigated in D_2O (pD = 4.0) by ^{1}H NMR and 2D NOESY NMR spectroscopy (spectra c–e in Fig. 1, and Fig. S4, ESI†). Notably, the K_{ass} value of **AP5**⊃**SA** was calculated to be $(2.76 \pm 0.75) \times 10^3$ M^{-1}, showing a significant decrease in comparison with that of **AP5**⊃**SA**$^-$ (Fig. S5–S8, ESI†), by a factor of 7.

Owing to the existence of ten cationic trimethylammonium groups on its two rims, **AP5** was a suitable host for the anionic guest **SA**$^-$ because of electrostatic driving forces for complexation. On the other hand, there existed a prototropic equilibrium between **SA**$^-$ and **SA** in aqueous solution. Considering that **AP5** preferred to encapsulate **SA**$^-$, the corresponding prototropic equilibrium between **SA**$^-$ and **SA** could be modulated by **AP5**.

To confirm the above-mentioned hypothesis, UV-vis titrations were carried out at room temperature in water at different pH values. As shown in Fig. 2a, **SA** showed an absorption peak at 325 nm and no obvious shift was observed upon addition of 1 equiv. of **AP5**. On the contrary, **SA**$^-$ afforded a notable red shift upon encapsulation by **AP5** (~9 nm, from 376 nm to 385 nm in Fig. 2b). Notably, when **AP5** was successively titrated into a solution of the dye at pH = 7.2, in the intermediary pH range around pK_a of salicylaldehyde, a well-defined isosbestic point was clearly observed at 350 nm (Fig. 2c). The absorption peak at 325 nm gradually decreased while a new peak at 385 nm appeared, indicating that the concentration of **SA** decreased while the concentration of **SA**$^-$ increased. Meanwhile the color of the solution changed to light-green finally (Fig. S37, ESI†). Similar changes in absorbance spectra were monitored in Fig. 2d. Upon gradual addition of **AP5** to a solution of the dye at pH = 7.8, the peak corresponding to **SA**$^-$ showed a marked increase in intensity accompanied with a decrease in intensity for the peak of **SA**. Furthermore, a continuous bathochromic shift was clearly observed in the titration process. These results confirmed that **AP5** assisted the transformation from **SA** to **SA**$^-$ because of its stronger binding to **SA**$^-$.

Interestingly, salicylaldehyde is one of the simplest pH dependent fluorescent dyes and its deprotonated form has much stronger fluorescence than its neutral form in water.[14] Therefore, upon complexation with **AP5**, the solution of salicylaldehyde experiences a pronounced fluorescent enhancement due to its complexation-induced deprotonation.

The fluorescence intensity of salicylaldehyde in the presence and absence of **AP5** was measured in phosphate buffer solution (PBS) at pH = 7.2 (Fig. 3). As expected, when **AP5** was added to the solution of salicylaldehyde, the fluorescence intensity at 502 nm was enhanced significantly. We also measured the fluorescence of the dye in the presence of β-cyclodextrin and cucurbit[7]uril (Fig. 3a) and no fluorescence changes were observed, suggesting that these

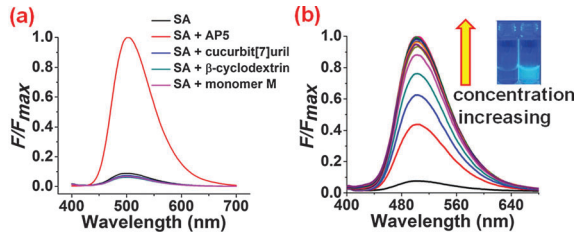

Fig. 3 (a) Fluorescence spectra of dye (0.500 mM) with monomer **M** (3.50 mM), β-cyclodextrins (3.50 mM), cucurbit[7]urils (3.50 mM) and **AP5** (3.50 mM) in PBS (λ_{ex} = 370 nm, λ_{em} = 502 nm, pH = 7.2); (b) the changes in fluorescence intensity of dye (0.500 mM, pH = 7.2, λ_{ex} = 370 nm, λ_{em} = 502 nm) upon gradual addition of **AP5** (0.00, 0.10, 0.30, 0.60, 1.00, 1.50, 2.00, 2.50, 3.00, 4.00, 5.00, 6.00, 7.00 equiv.) in PBS. The inset photograph shows the corresponding fluorescence enhancement in water upon excitation at 365 nm using a UV lamp at 298 K for 0.500 mM salicylaldehyde in the absence and presence of 3.50 mM **AP5**.

macrocycles were incapable of modulating the prototropic equilibrium between $\mathbf{SA}^-$ and **SA**. Furthermore, negligible change in fluorescence intensity was monitored upon addition of the cationic monomer **M** into a solution of dye, emphasizing the key role of the macrocyclic scaffold of **AP5**. These results suggested that two driving factors were indispensable for the emergence of fluorescence effects: (i) the inclusion offered by the hydrophobic cavity of the macrocycle and (ii) the electrostatic interactions between the phenoxide anion of salicylaldehyde and the positively charged groups on the pillararene backbone.[15] Detailed fluorescence titration of the dye with **AP5** is shown in Fig. 3b. The fluorescence intensity increased by approximately 15-fold in the presence of **AP5**. Moreover, the significant green fluorescence was clearly visualized under UV light (the inset photograph in Fig. 3b).

Then pH titrations of salicylaldehyde in the presence and absence of **AP5** were performed to display changes in fluorescence intensity at different pH values (Fig. S16, ESI†). As expected, the free dye salicylaldehyde was pH-sensitive. When the solution pH was higher than 7, deprotonation of the dye resulted in increased fluorescence. Its pK_a value was calculated to be 8.25, consistent with the previously documented pK_a value, 8.3.[11] Upon complexation with **AP5**, the pK_a value of salicylaldehyde showed a decrease of 0.90 unit. This pK_a shift indicated that the host efficiently assisted dye deprotonation and facilitated the fluorescence emission under relatively acidic conditions. Notably, in basic aqueous solution of $\mathbf{SA}^-$ (pH > 10), a 6-fold fluorescence enhancement was observed upon addition of **AP5**, because the encapsulation of the dye hindered dye aggregation, also leading to a remarkable fluorescence intensity increase.[2a]

To further understand the host–guest complexation induced pK_a shift, a four-state model was proposed (Scheme S2, ESI†).[16] Accordingly, the thermodynamic results for the supramolecular system are consistent with four simultaneous pathways: (i) the complexation of **SA** with **AP5**, K_{sa}; (ii) the complexation of $\mathbf{SA}^-$ with **AP5**, K_{sa^*}; (iii) deprotonation of the uncomplexed dye **SA**, K_{a1}; (iv) deprotonation of the complexed dye **AP5**⊃**SA**, K_{a2}. According to eqn S1 (ESI†), in the presence of **AP5**, the shifted pK_{a2} value was calculated to be 7.40 and the resultant ΔpK_a value was 0.85, in good agreement with the result of fluorescence measurements. This confirmed that upon complexation by **AP5**, salicylaldehyde becomes a ~7 ($10^{0.85}$) times stronger acid than its free form. The stereoelectronic restrictions and the hydrophobic environment originating from the rigid host have a pronounced effect on the prototropic equilibrium of the dye inside the macrocyclic cavity.

The significant fluorescence response of salicylaldehyde upon complexation with **AP5** allowed its implementation for FID detection (Fig. 4). A typical displacement titration is displayed in Fig. 5a using 2,4,6-trichlorophenol (**G6**) as a strong competitive guest. When **G6** was injected into a mixed PBS solution of the dye and **AP5** (pH = 7.2), the expected decrease in the fluorescence intensity was clearly observed. The phenomenon suggested that upon addition of **G6**, the fluorescent dye slipped out of the cavity of **AP5** and a more stable host–guest complex **AP5**⊃**G6** formed due to the higher binding affinity of **G6** to **AP5**. The "turn-off" fluorescence changes by the addition of **G6** were also easily visualized by the naked eye using a simple UV-lamp (the inset photograph in Fig. 5a).

Furthermore, a series of phenol derivatives (Fig. 4) were employed as analytes in FID detection. Addition of phenols in the same molar amounts to the **AP5**/salicylaldehyde complex resulted in varying degrees of dye displacement, as recorded by fluorescence spectroscopy. As shown in Fig. 5b, the decrease in fluorescence intensity showed the following sensitivity order: phenol < monochlorophenols < dichlorophenol < trichlorophenol. With the increasing number of chlorine substituents,

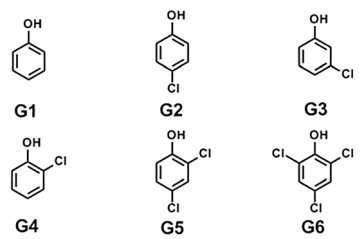

Fig. 4 The tested analytes in the fluorescence indicator displacement experiments.

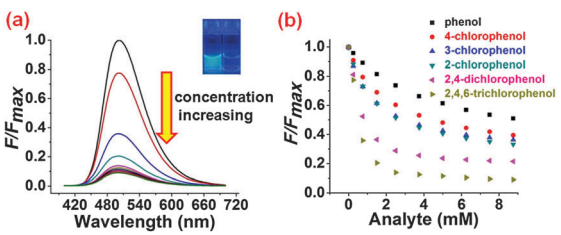

Fig. 5 (a) Fluorescence titration for the competitive displacement of salicylaldehyde (0.500 mM) from **AP5** (1.00 mM) by **G6** (0, 0.250, 0.750, 1.50, 2.50, 3.75, 5.00, 6.25, 7.50, 8.75 mM) in PBS at pH 7.2 (λ_{ex} = 370 nm, λ_{em} = 502 nm). The inset photograph shows the corresponding fluorescence quenching in water upon excitation at 365 nm using a UV lamp at 298 K for a mixture of 0.500 mM salicylaldehyde and 1.00 mM **AP5** in the absence and presence of 8.75 mM **G6**. (b) Displacement efficacy after successive titration of different phenolic compounds into solutions containing 0.500 mM salicylaldehyde and 1.00 mM **AP5**.

Table 1 The acid dissociation constant (pK_a) of analytes[17] and their independent association constants (K_{ass}) with **AP5** in PBS at pH = 7.2

Guest	pK_a	K_{ass} (M^{-1})
G1	9.92	$(1.49 \pm 0.29) \times 10^3$
G2	9.37	$(2.54 \pm 0.41) \times 10^3$
G3	8.79	$(2.72 \pm 0.41) \times 10^3$
G4	8.52	$(2.91 \pm 0.52) \times 10^3$
G5	7.90	$(7.03 \pm 1.54) \times 10^3$
G6	5.99	$(1.39 \pm 0.24) \times 10^5$
Salicylaldehyde	8.25	$(3.11 \pm 0.59) \times 10^3$

binding affinity with **AP5** is enhanced (Table 1), leading to higher dye displacement efficacy. There are two reasons for this: (i) the introduction of more electron-withdrawing substituents causes a decrease in pK_a, so that more of the anionic form of the phenol will exist in aqueous solution at a given pH, and as a consequence, the overall electrostatic interactions between the host and the guest will be enhanced; (ii) the incorporation of electron-withdrawing groups will result in intensified electron-deficiency of the phenyl ring of the phenol, strengthening the charge-transfer interaction with the electron-rich cavity of **AP5**. These two factors determine the binding affinity between **AP5** and the phenol, subsequently affecting the dye displacement efficacy.

In conclusion, we reported a novel turn-on fluorescence switch based on host–guest complexation between the pH-sensitive dye salicylaldehyde and cationic pillar[5]arene **AP5**. A surprising finding was that **AP5** modulates the acid–base equilibrium of salicylaldehyde, which led to an approximate 0.90 unit pK_a decrease for the dye. The complexation-induced dye deprotonation and deaggregation resulted in a remarkable fluorescence enhancement of the dye solution. Furthermore, the turn-on fluorescence switch was employed for FID detection of phenols and chlorophenols. In fact, this reported FID system can be further applied in detecting anionic compounds of biological and environmental relevance such as nucleic acids and endogenous phenol derivatives.

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