A simple chemosensor for Hg^{2+} and Cu^{2+} that works as a molecular keypad lock†

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A new chemosensor which can detect Hg^{2+} in water and Hg^{2+}/Cu^{2+} in acetonitrile and its application as a molecular keypad lock using Cu^{2+} and F^- as ionic inputs are demonstrated.

Use of a molecular-scale keypad lock as a data security device is an attractive research goal in the area of unconventional computing, as it offers a new approach for protecting information at the molecular level.[1] A molecular keypad lock is a device which can be opened only by the proper combination and sequence of chemical inputs. Very recently researchers have started exploring the possibility of mimicking the function of silicon chips and building electronic devices using organic/inorganic molecules based on their spectral/redox responses towards an external stimulus. Research in this area has gained momentum with the idea of developing purpose built molecules in the nano scaled dimension which have the ability to respond to changes in the surrounding environment.[2] The first and smallest unimolecular rectifier in the 2 or 3 nm dimension was reported by Aviram *et al.*[3] But the function of a security device like a keypad lock at the molecular level is yet to be mimicked. In cryptography, an encrypt/decrypt function allows access to secret messages using a password to decrypt the encrypted algorithm. Such molecular devices, capable of authorizing password entries, are of significance for information protection.[4]

Furthermore, the development of fluorescent chemical sensors for heavy transition metal (HTM) ions[5] and the integration of these into molecular level devices is an active area of research.[6] Therefore, the dual application of a single molecular entity to the detection of toxic HTM ions and the integration of these HTM ions as chemical-driven molecular machines would be of future interest in molecular computing.[7]

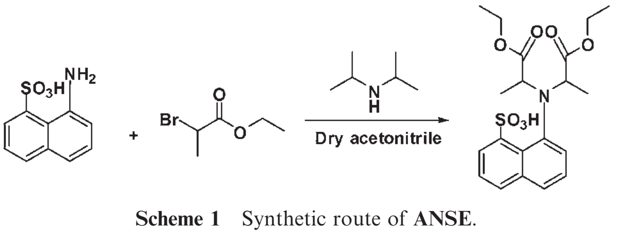
In the present paper, we show that an anion (F^-) and a cation (Cu^{2+}) can be used as ionic inputs for demonstrating security codes using a 1-**A**mino-8-**N**aphthalene **S**ulfonic acid **E**ster (**ANSE**) based chemosensor. A reconfigurable molecular security device has been achieved whose fluorescence is in the *ON* state in response to a specific sequence of ionic inputs, which makes this molecular-level security device work.

ANSE was synthesized (Scheme 1) by reacting 1-amino-8-naphthalenesulfonic acid and ethyl 2-bromopropionate (see ESI†). Water soluble **ANSE** has a naphthalene moiety as the signaling unit, which is covalently bound to an ONO-donor receptor functionality. **ANSE** was found to bind selectively to Hg^{2+} in aqueous solution and to Cu^{2+}/Hg^{2+} in acetonitrile solution and could be used for detection of these two cations in the respective solvents at a ppb level of concentration. The detection of Hg^{2+} in aqueous solution is of prime importance owing to its proven toxicity.[8] Furthermore, detection of HTM ions such as Hg^{2+} in an aqueous environment is difficult due to its effective hydration and the high stabilization energy of the solvated cation.[5b] Binding of Hg^{2+} in aqueous solution caused an efficient fluorescence quenching of **ANSE** *via* enhanced spin–orbit coupling.[9]

The electronic spectrum of **ANSE** in water has a maximum at 340 nm due to the charge transfer transition between the donor amine center and the acceptor naphthalene moiety. However, on binding to Hg^{2+}, a new transition band appeared at longer wavelength (381 nm) due to the ligand to metal charge transfer (LMCT) transition (Fig. 1). Addition of various other metal ions did not result in any detectable spectral change (see ESI†).

For Hg^{2+}, the spectrophotometric titration profile could be fitted to a 1 : 1 binding model, and the association constant evaluated was $3.10\ (\pm 0.07) \times 10^3\ M^{-1}$. This agreed well with the value of $2.09\ (\pm 0.05) \times 10^3\ M^{-1}$ obtained from fluorescence ($\tau_{ANSE} = 5.2 \pm 0.016$ ns, $\chi^2 = 1.13$) titration monitored at 489 nm as a function of the $[Hg^{2+}]$. For **Hg^{2+}–ANSE** complex, the naphthalene-based triplet state was found to be short lived ($\tau = 2.6 \pm 0.03$ ns, $\chi^2 = 1.19$), which could be explained by the shorter HOMO–LUMO gap and favored spin–orbit coupling.

In acetonitrile solution, the results obtained were little more complicated. Intraligand charge transfer spectra for **ANSE** appeared at 352 nm (Fig. 2). A new absorption band appeared



Scheme 1 Synthetic route of **ANSE**.

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† Electronic supplementary information (ESI) available: Synthetic details, optical and fluorescence spectra of **ANSE**. Photographs showing the detectable color changes. Table revealing the excited state properties of **ANSE** and its complexes with Hg^{2+} and Cu^{2+}, associated fluorescent decay traces, fluorescence spectra with different sequences of ionic inputs at different time intervals. See DOI: 10.1039/b807290f

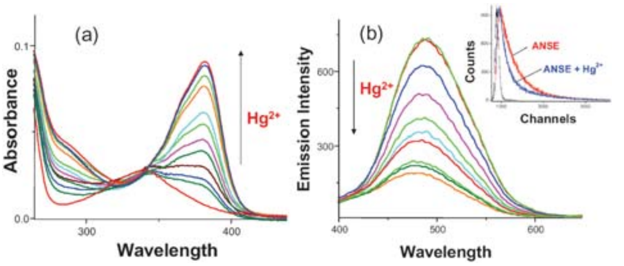

Fig. 1 (a) UV–Vis ([**ANSE**] = 1.5 × 10^{-5} M) and (b) fluorescence spectra ([**ANSE**] = 3.0 × 10^{-6} M) in water in the presence of varying [Hg^{2+}] (0–1.6 × 10^{-3} M); λ_{ext} = 340 nm, slit width 7/7. Inset: Fluorescence decay profile of **ANSE** in the presence and absence of Hg^{2+} [λ_{ext} = 340 nm]. The trace shown in black represents the laser source response time.

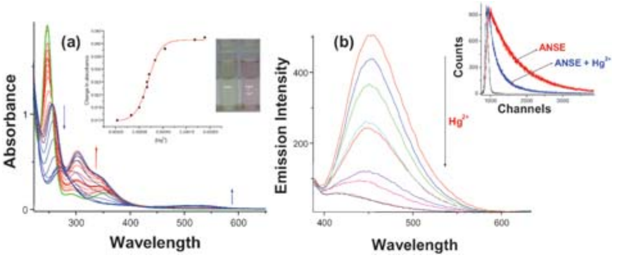

Fig. 2 (a) UV–Vis spectra of **ANSE** (3.3 × 10^{-5} M) in the presence of varying [Hg^{2+}] (0–1.89 × 10^{-4} M) in acetonitrile. Inset: Change in absorbance of **ANSE** at 525 nm as a function of [Hg^{2+}]. (b) Fluorescence spectra of **ANSE** (4.0 × 10^{-6} M) (λ_{exc} = 352 nm) in the presence of varying [Hg^{2+}] (0–2.6 × 10^{-5} M) in acetonitrile. Inset: Fluorescence decay profile of **ANSE** in the presence and absence of Hg^{2+} using laser excitation source of 340 nm.

at 301 nm until one mol equiv. of Hg^{2+} was added, along with a distinct hump at around 344 nm. Two isosbestic points at 233 and 256 nm were also observed. A new absorption band at around 344 nm was presumably due to the LMCT transition, which was found to appear at 389 nm in a more polar solvent like water. Beyond one mol equiv. of [Hg^{2+}], a distinctly different spectral pattern was observed—a decrease in absorbance intensity in the wavelength region of 280–400 nm along with two stronger absorption bands at 302, 349 nm were observed, while a much weaker band at 525 nm appeared. These changes were associated with an isosbestic point at 412 nm. This signified the formation of a new species, which was in equilibrium with the **Hg^{2+}–ANSE** complex. The spectroscopic titration profile shows 2 : 1 complex formation between **Hg^{2+}** and **ANSE**. Binding constants for the 1 : 1 ({**Hg–ANSE**}$^{2+}$) and 2 : 1 ({**$(Hg)_2$ANSE**}$^{2+}$) complex formation (K_a^1 = (6.0 ± 0.1) × 10^4 M^{-1} and K_a^2 = (1.6 ± 0.05) × 10^4 M^{-2}) were evaluated from the plots of the changes in absorbance at 302 and 525 nm, respectively. The nature of the binding of the additional $Hg^{2+}{}_{solvated}$ to **Hg^{2+}–ANSE** is not clearly understood, but presumably it gets weakly associated to one of the two acetate functionalities and favors the LMCT transition. The relatively lower binding constant in aqueous solution presumably reflects the efficient solvation of Hg^{2+} in water.

In contrast, Cu^{2+} was found to form a 1 : 1 complex with **ANSE** and the association constant was found to be 5.21 (±0.03) × 10^5 M^{-1} with a new absorption band at 523 nm (Fig. 3) owing to the LMCT transition. The fluorescence maximum of **ANSE** at 450 nm in acetonitrile was found to be completely quenched on addition of 2 equiv. of Hg^{2+} and 1 equiv. of Cu^{2+} (Fig. 2 and see ESI†). Time resolved fluorescence studies (using a 340 nm laser source and monitoring 450 nm as λ_{ems}) revealed a single exponential decay for **ANSE** emission and the lifetime was found to be 11.2 (±0.018) ns (χ^2 = 1.012). In presence of excess (≥ 3.0 mol equiv.) of Hg^{2+}, a biexponential and faster decay of the excited state was observed owing to the narrower HOMO–LUMO gap (τ_1 = 1.2 (±0.044) ns (25.99%), τ_2 = 5.4 (±0.03) ns (74.01%) (χ^2 = 1.1268)). However, for Cu^{2+}, an even faster but single exponential decay was observed, τ = 3.3 (±0.02) ns (χ^2 = 1.217).

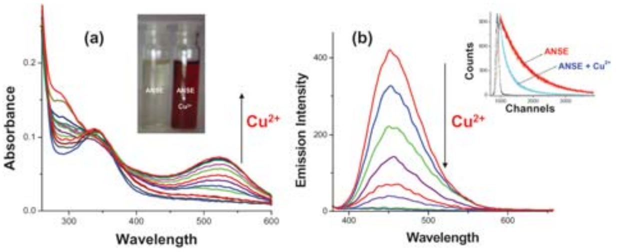

Fig. 3 (a) UV–Vis spectra of **ANSE** (3.3 × 10^{-5} M) upon addition of one equiv of Cu^{2+} in acetonitrile. (b) Fluorescence spectra of **ANSE** (2.0 × 10^{-6} M) (λ_{exc} = 352 nm) in the presence of varying [Cu^{2+}] (0–8.0 × 10^{-6} M) in acetonitrile. Inset: Fluorescence decay profile of **ANSE** in the presence and absence of Cu^{2+} using laser excitation source of 340 nm.

To reveal the sequence dependence of the emission output signal, Cu^{2+} (2.5 equiv.) and F^- (17.5 equiv.) were selected as inputs (Fig. 4). For the first input sequence, F^- and Cu^{2+} were used as inputs A and B, respectively. Emission maxima in acetonitrile, as well as the emission lifetime (τ = 11.0 ± 0.017 ns, χ^2 = 1.01) remained almost unchanged and signified no binding of Cu^{2+} to **ANSE**. Presumably excess F^- (input A) preferentially complexed Cu^{2+} (input B) ions and thereby restricted the coordination of Cu^{2+} to **ANSE**. Thus, the emission behavior of **ANSE** remained unchanged (Fig. 4).

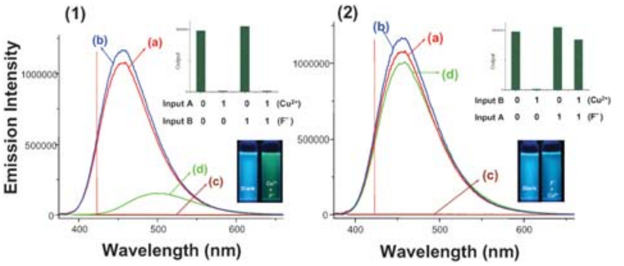

Fig. 4 Emission output of **ANSE**, following excitation at 352 nm with different input sequences: (1) Cu^{2+} as first input A followed by F^- as second input B; (2) F^- as first input A followed by Cu^{2+} as second input B. (a) Emission of **ANSE** (4.0 × 10^{-5} M) in acetonitrile upon addition of (b) F^- (7.0 × 10^{-4} M) and (c) Cu^{2+} (1.0 × 10^{-4} M). (d) 2.5 equiv. of Cu^{2+} + 17.5 equiv. of F^-. The corresponding emission output bar diagram at 422 nm is shown in an inset. Insets for (1) and (2) show photographs of the emission changes for two different sequences of ionic inputs.

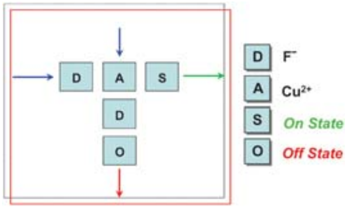

Fig. 5 Fluorescent keypad to access a secret code at 422 nm with different input sequences.

On reversal of the input sequence, *i.e.* for Cu^{2+} as input A and F$^-$ as input B, a new green fluorescence with λ_{ems} at 500 nm ($\tau = 4.8 \pm 0.009$ ns, $\chi^2 = 0.99$) was observed. Presumably, coordination of F$^-$ to the Cu^{2+}-center in **Cu^{2+}–ANSE** enhances stabilization of the $d_{x^2-y^2}$ and destabilization of the d_{z^2}. This reduces the possibility of emission quenching through participation of the d_{z^2} orbital of the Cu^{2+} ion. Furthermore, coordination of the cationic Cu^{2+}-center to **ANSE** is expected to lower the energy of the LUMO of the naphthalene-based chromophore and this is expected to reduce the HOMO–LUMO gap and could account for the longer wavelength emission as compared to **ANSE**. When Cu^{2+} was used, the fluorescence of **ANSE** was found to be completely quenched, while for F$^-$ a very small change in the fluorescence spectra was observed.

To simplify the input sequence as a password and **ANSE** as a keypad lock, inputs Cu^{2+} and F$^-$ were designated as "A" and "D", respectively. For the first input sequence "D" followed by "A" gave emission *ON* at 422 nm and it created a secret code "DAS" (S defines *ON* state). When the input sequence is reversed, *i.e.* the first input is "A" and the second input is "D", fluorescence was in the *OFF* state at 422 nm. Thus, this sequence and the wrong entry "ADO" (O defines the *OFF* state) failed to open the keypad lock (Fig. 5). This demonstrates that one can use "DAS" as a security code to open an **ANSE** fluorescent lock at 422 nm. Use of numerical digits (0–9) as PIN numbers in a two-digit password allows a total of 90 different combinations. The choice becomes wider (650 different combinations) when individual letters (A–Z), each signifying a specific ionic input, are used as PIN numbers. Thus, access codes would be made possible by assigning the correct starting (F$^-$) and ending (Cu^{2+}) ions to two specific letters (D and A, respectively) and different ions to all of the other letters, to ensure that only one code would work. But there are many combinations to try and this adds to the complexity of cracking the keypad lock.

In conclusion, a sensor for biologically important ions such as Hg^{2+} and Cu^{2+} has been used at a molecular level and this fluorescent lock may be used for security devices, which would allow access using specific ionic keys as a password.

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