Dalton Transactions

Cite this: Dalton Trans., 2012, 41, 5217

Aminoanthraquinone-based chemosensors: colorimetric molecular logic mimicking molecular trafficking and a set-reset memorized device[†]

Navneet Kaur*^{*a*} and Subodh Kumar^{*b*}

Received 17th November 2011, Accepted 8th February 2012 DOI: 10.1039/c2dt12201d

The synthesis, photophysical properties, protonation and metal–ion coordination features of a family of four (**3–6**) anthraquinone-based schiff base derivatives are reported. The outstanding UV-vis absorption properties of the 1-aminoanthraquinone chromophore allowed the efficient visual detection and quantification of Cu^{2+} and/or Ni²⁺ in buffered aqueous solution. Analysis of spectrophotometric data with SPECFIT yielded the macroscopic and microscopic stability constants of the complexes. Furthermore, the different optical output signals (*i.e.* absorbance) observed with addition of various metal ions to a solution of **6** can be used for mimicking the operation of a traffic signal and "Set–Reset" molecular level information processing device.

Introduction

Recently, the development of new artificial chemosensors for the recognition of physiologically and environmentally important analytes has attracted considerable attention.^{1–3} Among the various detection methods available, UV-vis and fluorescence spectroscopy still remain the most frequently used modes due to their high sensitivity and easy operational use. More recently, a new chemosensor design concept of "single sensor for multiple analytes" has emerged, that is the analysis of more than one analyte by one receptor using a single detection method or an array of detection methods.^{4–7} There are mainly two methods to realize this concept. One method is by combination of multichromogenic units into a single receptor,⁸ and the other one is by using a variety of detection methods such as UV-vis and fluorescence.^{4,9}

Recently, the development of molecular logic gates¹⁰ and photonic devices¹¹ based on the optical sensing of specific analytes has emerged an attractive research area for unconventional computing. The chemically encoded information was converted into fluorescent signals as the output, which results in development of molecular level logic gates such as AND, OR, NOR, INHIBIT, XOR, YES, NOT, and XNOR logic gates. The integration of these molecular logic gates at molecular level is

related to the integration and processing of binary data of conventional microprocessor systems.¹² Conventional silicon based devices have the limitation that they can only be miniaturized down to the nanoscale.13 Therefore, the development of materials for information storage and retrieval at the molecular level is a promising choice to overcome this limitation.¹⁴ The sequential integration of molecular logic gates is an important step for the realization of information storage processes (memory devices).¹⁵ Sequential logic circuits, which are functions of both past and present inputs, operate through a feedback loop in which one of the outputs of the device operates as an input and is memorized as a "memory function". Van der Boom et al.¹⁶ reported molecular level random access memory (RAM) using "Set-Reset"/"Flip-Flop" functions based on surface-confined osmium polypyridyl complexes using chemical reagents as inputs. Chemical devices such as molecular keypad locks,¹⁷ set-reset logic devices^{15,16,18} and molecular trafficking¹⁹ have been mimicked by sequential integration of molecular logic gates. Recently, Pischel^{18c} highlighted the importance of sequential logic circuits with memory function in molecular computing. Thus, intelligent molecules which are capable of producing sequential logic operations are extremely interesting. However there are only a few reports about "set-reset" logic devices^{15,16,18} where the memorized unit²⁰ has been mimicked by sequential integration of molecular logic gates.

An anthraquinone chromophoric system may be important as a chemosensor because its optical properties can be significantly perturbed by chemical stimuli. It is also important to note that the carbonyl group of 9,10-anthraquinone ligands is known to interact with various metal ions to cause a pronounced color change.^{21,22} Also, different anthraquinones bearing electron-rich coordinating sites at 1/1,8 or 1,4 positions have been investigated by our group for their metal-sensor behavior through color change. In all the chemosensors, Cu²⁺-induced deprotonation of the amine NH of anthracene-9,10-dione has been observed,

^aDepartment of Chemistry, Panjab University, Chandigarh, 160 014 Punjab, India. E-mail: neet_chem@yahoo.co.in; Fax: +91 172 2545074; Tel: +91 172 2541435

^bDepartment of Chemistry, Guru Nanak Dev University, Amritsar, 143 005 Punjab, India. E-mail: subodh_gndu@yahoo.co.in; Fax: +91 183 2258820; Tel: +91 183 2258802-09 Ext. 3206

[†]Electronic supplementary information (ESI) available: Changes in absorption spectrum of chemosensors **3**, **5** and **6** upon addition of various metal ions, absorption curves for molecular scale implementation of "traffic on", "traffic off" and "Set–Reset" with addition of different inputs. See DOI: 10.1039/c2dt12201d



Scheme 1 Synthesis of chemosensors 3–5



Scheme 2 Synthesis of chemosensor 6

resulted in a ~100 nm bathochromic shift (from $\lambda_{max} = 500$ nm to $\lambda_{\text{max}} = 600 \text{ nm}$) of the absorption band (Fig. S1a, ESI⁺) along with color change of the solution from red to blue. This red shift has been attributed to Cu²⁺ induced deprotonation of amine NH of anthracene-9,10-dione moioety.²³ Simulation of the spectral data shows the formation of ML (log β 7.0 ± 0.5) and M₂L₃ (log β 25.0 ± 0.8) species. The addition of Ni²⁺ to the solution of chemosensor 3 resulted in deprotonation of the NH of both the anthracene-9,10-dione moiety and the -OH group by which two new bands appeared at λ_{max} 700 nm and 445 nm, repectively.^{23e} Simultaneously, the absorption bands lying at λ_{max} 500 nm and 415 nm decreased (Fig. S1b, ESI⁺). The spectral changes with addition of Cu²⁺ and Ni²⁺ are similar to those obtained in the case of chemosensor 2^{23e} The presence of other heavy metal ions, alkali and alkaline earth metal ions caused nominal changes in the absorption spectra of 3.

However, the UV-Vis spectrum of **4** exhibited absorption bands at λ_{max} 485 nm due to anthraquinone moiety and at λ_{max} 435 nm due to hydroxyquinoline moiety. Addition of Cu²⁺ to the solution of **4** (50 μ M; CH₃OH : H₂O 4 : 1; pH 7.0 \pm 0.1; 10 mM HEPES) resulted in a ~100 nm bathochromic shift of the absorption band along with color change of the solution from red to blue. Simulation of the spectral data shows the formation of ML (log β 7.1 \pm 0.5) and M₂L (log β 11.9 \pm 0.5) species. However, addition of Ni²⁺, Co²⁺ and Zn²⁺ to a solution of **4** resulted in a hypsochromic shift of the 435 nm absorption band to 410 nm (Fig. 1) but the 485 nm band due to the

Results and discussion

The photophysical studies of chemosensor 2 have already been discussed in ref. 23*e*. However, in order to study the role of extended π -conjugation and the presence of other hetero atoms (N) in the azo-methine unit, the chemosensors 3–6 were synthesized.

which was responsible for the drastic color changes.²³ However, in anthraquinone based derivatives having Schiff base linkages, π -electron delocalization and alcohol deprotonation are mainly responsible for the signal generation as a consequence of cation binding events. Herein, we report different anthraquinone based Schiff base derivatives that can detect Cu²⁺ and Ni²⁺ differen-

tially by visible color changes. The diverse photometric

responses *i.e.* regulation of Cu^{2+} (input 2) and Ni²⁺ (input 3) at

variable pH range (input 1) observed in the case of chemosensor **6** mimics the trafficking mechanism (*vide infra*). Molecular

trafficking represents a phenomenon in which the information is

processed and transmitted with signals in a specific manner at the molecular level. The synthetic systems in which the information is processed and transmitted in a specific manner are

helpful in rationalizing intricate aspects of inter- and intracellular metal trafficking. In addition to this, encoding binary digits of logic conventions, we have proposed a logic circuit for designing a molecular traffic signal with incorporation of an R–S (Reset–Set) latch^{16a} circuit *i.e.* a circuit comprising cross coupled NOR

logic gates which responds to a sequence of input pulses. Nearly all digital electronic devices (microprocessors, digital clocks, mobile phones, cordless telephones, electronic calculators, *etc.*) are designed on such sequential circuits. Thus, the significant role played by trafficking in day to day life and the application

of latch circuits raised our interest in the development of a mol-

ecular system mimicking the trafficking mechanism.



Synthesis of chemosensors 3–5

Stirring 1-(2-Aminoethylamino)anthracene-9,10-dione $(1a)^{23a}$ with different aromatic aldehydes in ethanol resulted in the formation of azo-methine derivatives 3–5, dark red solids (Scheme 1).

Similarly, stirring of $1b^{23b}$ with 2-hydroxy benzaldehyde in ethanol gave chemosensor 6 (Scheme 2).

A. Photophysical studies of chemosensors 3-6

A1. Metal ion binding studies of chemosensors 3–6. Chemosensor 3 showed two bands at 500 nm and 415 nm due to the anthraquinone moiety and the hydroxynaphthalene group, respectively. Addition of Cu^{2+} to solution of chemosensor 3 (50 μ M; CH₃OH:H₂O 4:1; pH 7.0 \pm 0.1; 10 mM HEPES)



Fig. 1 Effect of different metal ions on UV-vis spectrum of chemosensor 4.

anthraquinone moiety remained unaffected. Therefore, the presence of an additional binding site *i.e.* nitrogen in the azomethine unit of chemosensor **4** in comparison with **2** leads to preferable binding of Ni²⁺ with the 8-hydroxyquinoline unit and did not cause Ni²⁺ induced deprotonation of the aryl NH observed in the case of chemosensors **2** and **3**. The presence of other metal ions did not cause any notable change in the absorption spectrum of **4**.

The absorption spectrum of chemosensor **5** (50 μ M), which lacks an –OH group, showed only nominal changes in its absorption maxima and absorbance in the visible region on addition of 0.001 M Na⁺, K⁺, Ca²⁺, Mg²⁺, Ba²⁺, Co²⁺, Cd²⁺, Zn²⁺ and Ni²⁺. However, the addition of Cu²⁺, even in equimolar quantities to **5** caused switching of the absorption band from λ_{max} 492 nm to 600 nm with a bathochromic shift of ~100 nm. This resulted in a visible change in color from red to blue (Fig. S2, ESI[†]).

Chemosensor **1b**, possessing two aminoethylamino appendages, has been found to bind with two Cu^{2+} ions in a stepwise manner and on binding with Cu^{2+} showed emergence of two new absorbance bands with red shift of nearly 150 and 265 nm, respectively.^{23b} These bands were associated with different color changes dependent on the concentration of Cu^{2+} ions. So, keeping in view these results, chemosensor **6** with two azomethine-ethylamino appendages at the 1 and 8 position of the anthraquinone moiety was then synthesized, which would be significantly more sensitive Cu^{2+} sensor than **2**.^{23a,b}

The absorption spectrum of **6** (25 μ M; CH₃OH : H₂O 4 : 1; pH 7.0; 10 mM HEPES) showed λ_{max} at 530 nm which on addition of equimolar quantities of Cu²⁺, Ni²⁺ or Co²⁺ showed a bathochromic shift of the absorption band, but within a few minutes precipitation took place. So, due to the poor solubility of the metal complexes in aqueous-methanol, further photophysical studies were done in either CH₃CN : H₂O or THF : H₂O mixtures.

With gradual addition of Co^{2+} to **6** (25 μ M; pH 7.0; 10 mM HEPES: CH₃CN : H₂O 4 : 1), two new bands at λ_{max} 700 nm and 365 nm appeared and color of the solution underwent a visible change from purple to blue. The decrease in absorbance at λ_{max} 530 nm and increase at λ_{max} 700 nm and 365 nm achieved their maximum values up to ~25 μ M of Co²⁺, and addition of further Co²⁺ led to only nominal changes in their absorption spectra (Fig. S3a, ESI†). On the other hand, on addition of 2.5 μ M Ni²⁺ to a solution of sensor **6** (25 μ M; pH 7.0; 10 mM HEPES; CH₃CN : H₂O 4 : 1), the emergence of a new broad peak between λ_{max} 700 nm–780 nm along with

another peak at λ_{max} 385 nm was observed. The intensity of the new peaks increased gradually with increasing concentration of Ni²⁺ up to 25 μ M and then a plateau was achieved. However, a concomitant decrease in absorbance at λ_{max} 530 nm with the addition of Ni²⁺ was observed (Fig. S3b, ESI†). All these absorbance changes resulted in a visual change in color of the solution from purple to blackish blue.

The titration fitting of the spectra obtained by titration of **6** (25 μ M) with Co²⁺ or Ni²⁺ at pH 7.0 \pm 0.1 in CH₃CN : H₂O (4 : 1) shows the formation of ML and M₂L₃ species as described in eqn (1) and (2).

$$\mathbf{6} \xrightarrow[\log\beta_{M2L3}=22.6\pm0.3]{\text{Co}^{2+}} (\text{Co}^{2+})_2 \cdot \mathbf{6}_3 \xrightarrow[\log\beta_{ML}=6.4\pm0.1]{\text{Co}^{2+}} \text{Co}^{2+} \cdot \mathbf{6}$$
(1)

$$\mathbf{6} \xrightarrow[\log\beta_{\text{M2L3}}=24.0\pm0.4]{\text{Ni}^{2+}} (\text{Ni}^{2+})_2 \cdot \mathbf{6}_3 \xrightarrow[\log\beta_{\text{ML}}=7.0\pm0.2]{\text{Ni}^{2+}} \text{Ni}^{2+} \cdot \mathbf{6}$$
(2)

Contrary to changes observed with the addition of Co^{2+} and Ni^{2+} , the addition of Cu^{2+} to a solution of **6** (25 μ M; pH 7.0; CH₃CN : H₂O 4 : 1) results in precipitation due to separation of Cu²⁺-complex, which did not allow estimation of Cu²⁺ ions. Moreover, addition of Cu²⁺ caused a visual change in color from red to blue.

The addition of other metal ions (25 μ M) viz. Na⁺, K⁺, Ca²⁺, Mg²⁺, Ba²⁺, Sr²⁺, Cd²⁺ and Zn²⁺ to the solution of **6** (25 μ M; pH 7.0; 10 mM HEPES: CH₃CN : H₂O 4 : 1) did not show any visible color change or absorbance changes in the UV-vis spectra (Fig. 2).

In order to avoid the micro-precipitaion caused by addition of Cu^{2+} , the photophysical studies were performed in THF : H₂O (4 : 1) mixtures. Addition of Cu^{2+} to a solution of **6** (25 μ M; THF : H₂O 4 : 1; pH 7.0 \pm 0.1; 0.1 mM HEPES) resulted in a decrease in absorbance at λ_{max} 530 nm with the appearance of two new bands at λ_{max} 640 nm and 700 nm along with a color change of the solution from purple to blue. Addition of Co^{2+} or Ni²⁺ to a solution of **6** (25 μ M; THF : H₂O 4 : 1; pH 7.0 \pm 0.1; 0.1 mM HEPES) resulted in similar effects as those obtained in the case of CH₃CN : H₂O mixture (Fig. S4, ESI†). Here, Cu²⁺ induced deprotonation of both aryl NH and –OH groups as similar types of absorption curves were obtained in the case of **6** upon addition of Co²⁺ and Ni²⁺ (similar association constants, Table 1).

Simulation of the spectral data shows the formation of ML and M_2L_3 species (Table 1). Significantly, the analysis of UV-vis



Fig. 2 Effect of different metal ions on the absorption spectrum of 6.

Table 1 log β values of 6-M²⁺ complexes in THF : H₂O 4 : 1 at pH 7.0 ± 0.1

M ²⁺	$\log \beta_{ m ML}$	$\log \beta_{M2L3}$
$\begin{array}{c} Cu^{2+} \\ Co^{2+} \\ Ni^{2+} \end{array}$	6.2 ± 0.1 5.4 ± 0.1 5.2 ± 0.1	$\begin{array}{c} 21.6 \pm 0.3 \\ 19.6 \pm 0.4 \\ 19.7 \pm 0.2 \end{array}$

spectral data obtained by titration of **6** with Cu^{2+} [in THF : H₂O (4:1)] and Co^{2+} , Ni²⁺ [both in CH₃CN : H₂O (4:1) and THF : H₂O (4:1)] shows the formation of mainly 1:1 complexes. All these complexes have log *K* values at 5.6 ± 0.5. This situation was quite favorable for estimation of Cu^{2+} and Co^{2+} or Ni²⁺ in a similar manner as that observed with the help of chemosensor **2**. However, keeping the solutions of **6**–M²⁺ for more than 5 h led to precipitation of complexes in the case of Cu^{2+} . So, the simultaneous estimation of metal ions could not be performed.

A2. Effect of pH on 3–6 and their metal complexes. In order to probe the nature of species formed during complexation of 3-6 with M^{2+} , a series of pH and UV-vis titrations were performed and the respective spectral data were analyzed using an iterative method on multi-wavelength data using the programme Specfit/32.²⁶ The pKa values of chemosensors 3-6 were determined by observing the changes in their UV-vis spectra upon titration of solutions of 3-6 with HCl or NaOH solutions, separately.

Due to the poor solubility of chemosensor 3 in aqueous DMSO or CH_3OH under acidic and basic conditions, the effect of pH on 1 : 1 solutions of $M^{2+} - 3$ could not be evaluated.

Addition of acid and base to a solution of **4** caused small changes (~10%) in absorbance with a ~15 nm bathochromic shift in basic medium. However, the absorbance at λ_{max} 400 nm gradually increased on increasing the pH from 2 to 12, without causing any change in the color of the solution. Titration fitting of the data shows the step-wise tri-protonation of **4** to form LH–LH₃ species (eqn (3)). Here, L represents the monoanion formed by deprotonation of phenolic OH in **4**.

$$4 \xrightarrow{H^+}{}_{\log\beta_{LH}9.0\pm0.02} 4H^+ \xrightarrow{H^+}{}_{\log\beta_{LH2}13.9\pm0.1} 4H^{2+} \xrightarrow{H^+}{}_{\log\beta_{LH3}16.1\pm0.4} 4H^{3+} (3)$$

The combination of pH and UV-vis titration of 1:2 solution of 4-Cu²⁺ suggests deprotonation of the aryl amine NH and shows the formation of M_2LH_{-1} and $M_2LH_{-1}(OH^-)$ and MLH species (eqn (4)).

$$2(Cu^{2+}) + 4 \frac{H^{*}}{\log\beta 21.6 \pm 0.2} (Cu^{2+})_{2} \cdot 4(2H^{2+}) \frac{-H^{*}}{\log\beta 0.2 \pm 0.04} (Cu^{2+})_{2} \cdot 4H_{.1} \log\beta 8.7 \pm 0.1 - H^{*} (4) (Cu^{2+})_{2} \cdot 4H_{.1}(OH^{-})$$

In the case of chemosensor **5**, only a small hypsochromic shift (~15 nm) of the λ_{max} was observed in the acidic region. Titration fitting of these data shows the formation of LH (log β 9.6 ± 0.1), LH₂ (log β 17.4 ± 0.2) and LH₃ (log β 20.4 ± 0.2). The combination of pH and UV-vis titration of 1 : 1 solution of **5** and Cu²⁺



Fig. 3 (a) Effect of pH on absorbance of **6**; (b) Plot of absorbance of **6** (25 μ M) at λ_{max} 530 nm and 385 nm with change in pH. The points refer to experimental values and solid line refers to curve fitting.

suggests deprotonation of the aryl amine NH and shows the formation of different complexes as described in eqn (5).

$$\begin{array}{c|c} Cu^{2+} + 5 \underbrace{H^{+}}_{\text{log}\beta 14.3 \pm 0.2} Cu^{2+} & 5 & \underbrace{-H^{+}}_{\text{log}\beta 7.8 \pm 0.2} Cu^{2+} & 5H_{.1} \\ & & \\$$

Fig. 3 shows the changes for **6** upon pH titration. Sensor **6** on variation in pH from 2–12 showed only small changes at λ_{max} 530 nm with a ~15 nm bathochromic shift in basic region (pH 7–12). However, significant changes in absorbance values at λ_{max} 385 nm were observed with changes in pH. On lowering the pH from 12, the absorption band at λ_{max} 385 nm gradually decreased till pH 9.0 and on further lowering the pH, no change in spectrum was observed (Fig. 3). However, this change in absorbance at λ_{max} 385 nm did not lead to any visible color change in **6**. The analysis of these pH induced changes in the absorbance of **6** through iterative titration fitting shows the stepwise protonation of **6** (eqn (6)).

$$6 \xrightarrow{H^{+}} 6 H^{+} \xrightarrow{H^{+}} 6 H^{+} \xrightarrow{H^{+}} 6 H^{2+} \xrightarrow{H^{+}} 6 H^{2+} \xrightarrow{H^{+}} 6 H^{3+} 6$$

Insight into formation of various species during titration of **6** with Co^{2+} or Ni^{2+} has been provided by using a combination of pH and UV-vis titrations of solutions of **6** – M^{2+} (1:1) in CH₃CN : H₂O 4:1. The evaluation of the spectral data obtained by pH and UV-vis titration of the solution of **6**–Co²⁺ (1:1) (eqn (7), Fig. 4a) shows that chemosensor **6** at pH 6.5 starts forming MLH₋₁ and above pH 10.0 forms MLH₋₁(OH⁻). However, in



Fig. 4 Species distribution of **6** as a function of pH for a system containing (a) $6-\text{Co}^{2+}(1:1;25 \,\mu\text{M})$; (b) $6-\text{Ni}^{2+}(1:1;25 \,\mu\text{M})$.

the acidic region *i.e.* at pH \leq 6.0, MLH starts forming and it remains stable between pH 2 and 6. The 1 : 1 solution of **6**–Ni²⁺ also shows the formation of MLH, MLH₋₁ and MLH₋₁(OH⁻) species (eqn (8), Fig. 4b).

$$Co^{2+} + 6 \xrightarrow{H^{+}}_{\log\beta 35.1 \pm 0.1} Co^{2+} \cdot 6H \xrightarrow{-H^{+}}_{\log\beta 21.6 \pm 0.1} Co^{2+} \cdot 6H_{-1}$$

$$\log\beta \ 10.9 \pm 0.1 / - H^{+}$$

$$Co^{2+} \cdot 6H_{-1}(OH^{-})$$
(7)

$$Ni^{2+} + 6 \xrightarrow{H^{+}}_{\log\beta 18.7 \pm 0.2} Ni^{2+} \cdot 6H \xrightarrow{-H^{+}}_{\log\beta 6.01 \pm 0.2} Ni^{2+} \cdot 6H_{-1}$$

$$\log\beta 5.1 \pm 0.2 \int_{-H^{+}}^{-H^{+}} Ni^{2+} \cdot 6H_{-1}(OH^{-})$$
(8)

Thus, the combination of pH and UV-vis titrations reveals that **6** forms only 1:1 complexes with Co^{2+} , Ni^{2+} and Cu^{2+} and, as initially envisaged, M₂L complexes are not formed. This is quite remarkable that two arms of azomethine amino functionality do not encapsulate two metal ions.

The metal ion interaction induced blue²⁴ and red^{23,25} shifts in a chromophore are marked with the respective decrease or increase in electron-donating abilities of the substituents participating in interactions. In chemosensors **3–6**, the red shift in the case of Cu²⁺ and Ni²⁺ (or Co²⁺ in the case of chemosensor **6** only) points to aryl NH deprotonation.

B. Elaboration of molecular logic gates using chemosensor 6

The diverse photometric responses observed upon addition of Cu^{2+} and Ni^{2+} to the solution of chemosensor 6 (Fig. 5) at

different pH values are helpful in mimicking the traffic mechanism. To elaborate molecular trafficking based on Boolean arithmetic, we envisaged Cu2+, Ni2+ and pH as inputs (pH values greater than 6 and less than 6 are taken as 0 and 1, respectively); Table 2 is constructed based on binary logic. Input 1 (pH) is designated red signal, input 2 (Cu^{2+}) is designated yellow signal, input 3 (Ni^{2+}) is designated green signal (Fig. 6). As the green light in a traffic signal indicates permission to move forward and the red light is a warning signal to stop, so, in a similar way, the output in the absorption spectrum at 800 nm with high absorbance values (> 0.8) correlates with movement of 'traffic on' and low absorbance values (< 0.3) correlates with movement of 'traffic off'. At high pH values (pH values > 5), in the absence of any chemical input, 6 shows no absorption peak at 800 nm *i.e.* output is "0" (Table 1). By operation of input 3 (Ni²⁺ ions) to 6 at high pH values (pH values >5), a new absorption band with an absorbance of 0.11 is observed and the output becomes "1"



Fig. 5 Changes in the absorbance spectrum of 6 (25 μ M; THF : H₂O 4 : 1; pH 7.0 \pm 0.1) on addition of different metal ion solutions.

 Table 2
 Boolean arithmetic operation on chemosensor 6

In 1 pH	$In 2 \\ Cu^{2+}$	<i>In</i> 3 Ni ²⁺	Output at $\lambda = 800 \text{ nm}$
0	0	0	0
0	0	1	1
0	1	0	0
0	1	1	0
1	0	0	0
1	0	1	0
1	1	0	0
1	1	1	0



Fig. 6 Assignment of traffic signal colors to different inputs.

Table 3 Truth table for the memory unit for two input signals Set $\rm (H^{+})$ and Reset $\rm (Cu^{2+})$

Reset In 1 Cu ²⁺	Set In 2 H ⁺	Output at $\lambda = 490$ nm
0	0	1
1	0	0
0	1	1
1	1	1



(Table 2). Thus input 3 corresponds to the green color, which directs the traffic to move (Fig. S5, ESI[†]).

By operation of input 2 (Cu^{2+} ions) to 6 at high pH values (pH values > 5), no band appears at 800 nm (weak absorption near 800 nm with an absorabance value of 0.01) i.e. the output is "0" (Table 2). Input 2 corresponds to the yellow color which directs the traffic to get prepared to stop and defines the 'low' value of absorbance (Fig. S6, ESI⁺). On sequential addition of both the inputs, *i.e.* when input 2 (Cu^{2+} ions) follows input 3 $(Ni^{2+} \text{ ions})$ at high pH values (pH values > 5), a very small absorption peak with an absorbance value of 0.02 appears *i.e.* the output is "0" (Table 2). Hence input 2 is added afterwards, which means finally the yellow signal glows, which directs the traffic to get prepared to stop (Fig. S7, ESI⁺). At low pH values (pH values < 5), the absorption intensity of **6** at 800 nm is very low in the absence or presence of any of the chemical inputs *i.e.* at low pH values (pH values < 5) the output is "0" (Table 2). Thus, the pH value less than 5 corresponds to the red signal, which directs that traffic must stop (Fig. S8, ESI[†]).

Also, molecular switching using Cu^{2+} and H^+ as chemical inputs has been integrated into sequential logic circuits with memory function in a feedback loop which mimics a "Set-Reset" molecular level information processing device. Here, In 2 is "0" when the pH value is 7 and In 2 is "1" when the pH value is less than 4. Without addition of "Set" or "Reset" inputs i.e. In 1 and In 2, the output is "read" out optically as high absorption intensity at 490 nm. When "Set" input is high $(In \ 2 = 1)$, the system "writes" and "reads" "logic state 1" with high absorbance at 490 nm (Table 3, Fig. S9, ESI⁺). The stored information was "erased" by the "Reset input" (In 1 = 1) with low absorption intensity at 490 nm and system write and save "logic state 0" (Fig. S9, ESI[†]). For evaluating the multiple "rewriting" ability of chemosensor 6, many write-erase cycles were performed which showed that write-erase cycles could be repeated many times with the same solution without any appreciable reduction in intensity in the absorption spectra. These reversible sequences of "Set-Reset" logic operations in a feedback loop demonstrate the memorized state of the system with "Write-Read-Erase-Read" functions with an optical output signal at 490 nm (Fig. 7).

Conclusions

In conclusion, we synthesized chemosensors **3–6** based on aminoanthraquinone derivatives having schiff base linkages and evaluated them using absorption (UV-vis) studies. Chemosensor **3** undergoes color and absorption changes with addition of $Cu^{2+}-Ni^{2+}$ but has poor solubility in aqueous DMSO or CH₃OH

Fig. 7 The feedback loop showing reversible logic operations for the memory element with two inputs (Set and Rest) possessing "write–Read–Erase–Read" functions with optical output signals.

under strong acidic or basic conditions. However, chemosensors 4 and 5 undergo significant absorption changes when Cu^{2+} ions are added, with a small hypsochromic shift (~25 nm) observed with the addition of Ni²⁺, Co²⁺ and Zn²⁺ to a solution of 4. On the other hand, chemosensor 6, possessing two hydroxybenzene units, gives color and absorption changes with the addition of Cu^{2+} or Co^{2+} . Furthermore, the different optical output signals (*i.e.* absorbance) observed with addition of various metal ions to a solution of 6 can be used for mimicking the operation of a traffic signal and "Set–Reset" molecular level information processing device.

Experimental

General considerations

Melting points were determined in capillaries and are uncorrected. ¹H NMR spectra were recorded on JEOL Al 300 MHz instrument using CDCl₃ solution containing tetramethylsilane (TMS) as an internal standard. The chemical shifts are reported in δ values relative to TMS and coupling constants (*J*) are expressed in Hz. ¹³C NMR spectra were recorded at 75 MHz and values are reported relative to CDCl₃ signal at δ 77.0. Chromatography was performed with silica gel 100–200 mesh and the reactions were monitored by thin layer chromatography (TLC) with glass plates coated with silica gel HF-254. FAB mass spectra were recorded as normal ion [MF-Linear]. The pH of the solutions was maintained by using (*N*-[2-hydroxyethyl] piperazine-*N*'-2-ethanesulphonic acid (HEPES) buffer (10 mM).

Photophysical studies

All the solvents were of analytic grade and were used after distillation. The solutions of metal ions were prepared in distilled water. All pH measurements were made with an equip-tronics pH-Meter. UV-vis spectroscopy experiments were carried out on a Shimadzu UV-1601 PC UV-vis Spectrophotometer by using slit widths of 1.0 nm and matched quartz cells. In the case of visible absorption spectra as a function of pH, aliquots of acid or base were added manually with the help of a micropipette. Enough time was allowed after the addition of metal ion or acid or base in order for the pH of the mixture to reach the equilibrium. All absorption scans were saved as ACSII files and were

View Article Online

further processed in ExcelTM to produce all of the graphs shown. Solutions of **3–5** were typically 50 μ M and that of **6** was 25 μ M.

Synthesis of chemosensor 2

1-(2-aminoehylamino)anthracene-9,10-dione (1a) (532 mg, 2 mmol) was dissolved in ethanol and then 1-hydroxynaphthalene-2-carbaldehyde (413 mg, 2.4 mmol) was added to the solution. The reaction mixture was stirred at 60 °C for 7 h. After completion of the reaction, the solid formed was filtered and then crystallized from ethanol to give pure **3**.

Similarly, the stirring of **1a** with different aldehydes in ethanol gave chemosensors **4–5**.

Chemosensor 3. Dark red solid; 70%; m.p. 195 °C; FAB mass M^+ m/z 421 (M^+ + 1); IR v_{max} (KBr) 1635 (C=O), 1654 (C=O), 3430 (NH-OH) cm⁻¹; ¹H NMR (CDCl₃): δ 3.77 (q, J = 6.0 Hz, 2H, CH₂), 3.99 (t, J = 6.0 Hz, 2H, CH₂), 6.99 (d, J = 9.0 Hz, 1H, ArH), 7.11-7.22 (m, 2H, ArH), 7.28-7.34 (m, 1H, ArH), 7.54-7.62 (m, 3H, ArH), 7.65-7.74 (m, 3H, ArH), 7.88 (d, J = 7.4 Hz, 1H, ArH), 8.15–8.21 (m, 2H, ArH), 8.94 (s, 1H, CH), 9.97 (bs,1H, NH, exchanges with D_2O); ¹³C NMR (normal/DEPT-135) (CDCl₃): δ 43.45 (CH₂), 54.57 (CH₂), 96.13 (C), 113.67 (C), 116.31 (CH), 117.62 (CH), 118.45 (CH), 122.88 (CH), 122.99 (CH), 126.66 (CH), 126.80 (CH), 127.77 (CH), 129.11 (CH), 132.93 (CH), 133.03 (C), 133.23 (C), 133.88 (CH), 134.77 (C), 135.47 (CH), 136.38 (CH), 151.34 (C), 160.43 (CH), 171.55 (C), 183.53 (C), 185.34 (C); Found C 77.27; H 4.9; N 6.46%. C₂₇H₂₀N₂O₃ requires C 77.13; H 4.79; N 6.66%.

Synthesis of 3-Ni complex

Chemosensor **3** (420 mg, 1 mmol) was dissolved in THF and the aqueous methanol solution of Ni(ClO₄)₂ (365 mg, 1 mmol) was added to this with stirring. The pH of the solution was maintained at 8.0 and it was allowed to stand at 25 °C for two days. The solid formed was filtered and washed well with CH₃OH– CH₂Cl₂. The solid was dried in air to get Ni²⁺ complex of **3**.

Complex 3–Ni²⁺. Dark green solid; 75%; m.p. 280 °C (C₂H₅OH–CHCl₃); FAB mass M⁺ m/z 479 (M⁺ + 1) ¹H NMR (CDCl₃): δ 3.27 (t, J = 6.9 Hz, 2H, CH₂), 3.65 (t, J = 6.9 Hz, 2H, CH₂), 7.06–7.22 (m, 5H, ArH), 7.39–7.47 (m, 2H, ArH), 7.64 (t, J = 6.9 Hz, 2H, ArH), 7.70–7.77 (m, 2H, ArH), 8.18 (d, J = 7.8 Hz, 1H, ArH), 8.22 (s, 1H, ArH), 8.31 (d, J = 8.1 Hz, 1H, ArH).

Chemosensor 4. Dark red solid; 70%; m.p. 120 °C; FAB mass M⁺ m/z 422 (M⁺ + 1); ¹H NMR (CDCl₃): δ 3.80 (t, J = 5.7 Hz, 2H, CH₂), 3.99 (t, J = 5.7 Hz, 2H, CH₂), 6.96 (d, J = 8.7 Hz, 1H, ArH), 7.11–7.19 (m, 2H, ArH), 7.41–7.46 (m, 1H, ArH), 7.51–7.60 (m, 2H, ArH), 7.67–7.77 (m, 2H, ArH), 7.98 (d, J = 8.4 Hz, 1H, ArH), 8.20–8.27 (m, 3H, ArH), 8.88 (s, 1H, CH), 9.94 (bs,1H, NH, exchanges with D₂O); ¹³C NMR (normal/DEPT-135) (CDCl₃): δ 43.43 (CH₂), 58.27 (CH₂), 113.67 (C), 116.11 (CH), 117.92 (CH), 118.45 (CH), 126.66 (CH), 126.83 (CH), 127.67 (CH), 128.05 (CH), 128.95 (C), 129.11 (C), 129.87 (CH), 132.93 (CH), 133.03 (C), 133.93 (CH), 134.18

(C), 134.77 (C), 135.47 (CH), 136.38 (CH), 148.10 (C), 151.84 (C), 160.43 (CH), 170.55 (C), 183.23 (C), 185.14 (C); Found C 74.27; H 4.68; N 10.10%. $C_{26}H_{19}N_3O_3$ requires C 74.10; H 4.54; N 9.97%.

Chemosensor 5. Dark red solid; 72%; m.p. 135 °C; FAB mass $M^+ m/z$ 406 ($M^+ + 1$); ¹H NMR (CDCl₃): δ 3.80 (q, J = 5.7 Hz, 2H, CH₂), 4.10 (t, J = 5.7 Hz, 2H, CH₂), 7.20 (d, J = 8.1 Hz, 1H, ArH), 7.53–7.62 (m, 3H, ArH), 7.70–7.77 (m, 3H, ArH), 7.86 (d, J = 7.8 Hz, 1H, ArH), 8.11 (d, J = 8.4 Hz, 1H, ArH), 8.21–8.25 (m, 4H, ArH), 8.63 (s, 1H, CH), 10.02 (bs,1H, NH, exchanges with D₂O); ¹³C NMR (normal/DEPT-135) (CDCl₃): δ 43.42 (CH₂), 60.23 (CH₂), 113.34 (C), 115.8 (CH), 118.00 (CH), 118.48 (CH), 126.64 (CH), 126.74 (CH), 127.54 (CH), 127.71 (CH), 128.83 (C), 129.62 (CH), 129.83 (CH), 132.88 (CH), 132.96 (C), 133.88 (CH), 134.69 (C), 134.96 (C), 135.19 (CH), 183.81 (C), 185.00 (C); Found C 77.17; H 4.68; N 10.26%. C₂₆H₁₉N₃O₂ requires C 77.02; H 4.72; N 10.36%.

Synthesis of chemosensor 6

1,8-di(2-aminoehylamino)anthracene-9,10-dione (**1b**) (648 mg, 2 mmol) was dissolved in ethanol and then 2-hydroxybenzaldehde (610 mg, 5 mmol) was added to the solution. The reaction mixture was stirred for 6-8 h at 60 °C. After completion of the reaction, the solid was filtered and was crystallized from ethanol to give pure **6**.

Chemosensor 6. Dark purple solid; 75%; m.p. 165 °C ($C_2H_5OH-CHCl_3$); FAB mass M⁺ m/z 533 (M⁺ + 1); ¹H NMR (CDCl_3): δ 3.64 (q, J = 6.0 Hz, 4H, CH₂), 3.89 (t, J = 6.0 Hz, 4H, CH₂), 6.87 (t, J = 8.1 Hz, 2H, ArH), 6.96 (d, J = 8.1 Hz, 2H, ArH), 7.06 (d, J = 8.4 Hz, 2H, ArH), 7.23 (d, 2H, ArH), 7.32 (t, J = 8.7 Hz, 2H, ArH), 7.48 (t, J = 8.1 Hz, 2H, ArH), 7.53 (t, J = 6.3 Hz, 2H, ArH), 7.48 (t, J = 8.1 Hz, 2H, ArH), 7.53 (t, J = 6.3 Hz, 2H, ArH), 8.39 (s, 2H, CH), 9.77 (bs, 2H, NH, exchanges with D₂O), 13.1 (bs, 2H, OH, exchanges with D₂O); ¹³C NMR (normal/DEPT-135) (CDCl₃): δ 43.34 (CH₂), 58.66 (CH₂), 115.35 (C), 116.98 (CH), 117.60 (CH), 118.69 (CH), 118.79 (C), 131.51 (CH), 132.43 (CH), 134.27 (CH), 134.68 (CH), 150.89 (C), 160.96 (C), 166.78 (CH), 184.31 (C), 186.24 (C); Found C 72.27; H 5.42; N 10.46%. C₃₂H₂₈N₄O₄ requires C 72.16, H 5.30; N 10.52%.

References

- 1 R. Martínez-Mánez and F. Sancenón, Chem. Rev., 2003, 103, 4419.
- J. F. Callan, A. P. de Silva and D. C. Magri, *Tetrahedron*, 2005, 61, 8551.
 A. P. de Silva, H. Q. N. Gunaratne, T. Gunnlaugsson, A. J. M. Huxley, C.
- P. McCoy, J. T. Rademacher and T. E. Rice, *Chem. Rev.*, 1997, 97, 1515.
- 4 M. Schmittel and H. W. Lin, Angew. Chem., Int. Ed., 2007, 46, 893.
- 5 N. Singh, R. C. Mulrooney, N. Kaur and J. F. Callan, *Chem. Commun.*, 2008, 4900.
- 6 N. Singh, N. Kaur, C. N. Choitir and J. F. Callan, *Tetrahedron Lett.*, 2009, 50, 4201.
- 7 H. J. Jung, N. Singh, D. Y. Lee and D. O. Jang, *Tetrahedron Lett.*, 2010, **51**, 3962.
- 8 H. Komatsu, D. Citterio, Y. Fujiwara, K. Minamihashi, Y. Araki, M. Hagiwara and K. Suzuki, Org. Lett., 2005, 7, 2857.
- 9 D. Jiménez, R. Martínez-Mánez, F. Sancenón and J. Soto, *Tetrahedron Lett.*, 2004, 45, 1257.
- (a) K. Szaciłowski, Chem. Rev., 2008, 108, 3481; (b) S. Ozlem and E. U. Akkaya, J. Am. Chem. Soc., 2009, 131, 48; (c) U. Pischel, Angew.

Chem., Int. Ed., 2007, **46**, 4026; (*d*) A. P. de Silva and N. D. McClenaghan, *Chem.–Eur. J.*, 2004, **10**, 574.

- 11 (a) A. P. de Silva, N. D. McClenaghan and C. P. McCoy, Molecular level electronics, imaging and information, energy and environment, in *Elec*tron Transfer in Chemistry, ed. V. Balzani, Wiley-VCH, Weinheim, 2001, vol. 1; (b) Molecular Devices and Machines. A Journey into the Nano world, ed. V. Balzini, M. Venturi and A. Credi, Wiley-VCH, Wienheim, 2003; (c) Unconventional Computing 2005: From Cellular Automata to Wetware, ed. C. Teuscher and A. Adamatzky, Luniver, C. Press, Beckington, U.K., 2005.
- 12 R. J. Mitchell, *Microprocessor Systems: An Introduction*, Macmillan, London, 1995.
- 13 (a) D. Goldhaber-Gordon, M. S. Montemerlo, J. C. Love, G. J. Opiteck and J. C. Ellenbogen, *Proc. IEEE*, 1997, **85**, 521; (b) M. Schultz, *Nature*, 1999, **399**, 729; (c) D. A. Muller, T. Sorsch, S. Moccio, F. H. Baumann, K. Evans-Lutterodt and G. Timp, *Nature*, 1999, **399**, 758.
- (a) A. J. Bard, Integrated Chemical Systems: A Chemical Approach to Nanotechnology, Wiley, New York, 1994; (b) Molecular Machines (special issue), Acc. Chem. Res., 2001, 34, 409–522; (c) R. M. Metzger, Acc. Chem. Res., 1999, 32, 950; (d) J. M. Tour, Acc. Chem. Res., 2000, 33, 791; (e) V. Balzani, A. Credi, F. M. Raymo and J. F. Stoddart, Angew. Chem., Int. Ed., 2000, 39, 3348; (f) C. Joachim, J. K. Gimzewski and A. Aviram, Nature, 2000, 408, 541; (g) J. R. Heath, Pure Appl. Chem., 2000, 72, 11.
- 15 (a) M. M. Mano and C. R. Kime, Logic and Computer Design Fundamentals, Prentice-Hall, Upper Saddle 5 River, 4th edn, 2000; (b) G. Periyasamy, J. P. Collin, J. P. Sauvage, R. D. Levine and F. Remacle, Chem.-Eur. J., 2009, 15, 1310; (c) R. Baron, A. Onopriyenko, E. Katz, O. Lioubashevski, I. Willner, W. Sheng and H. Tian, Chem. Commun., 2006, 2147.
- 16 (a) G. de Ruiter, E. Tartakovsky, N. Oded and M. E. van der Boom, Angew. Chem., Int. Ed., 2010, 49, 169; (b) G. de Ruiter, L. Motiei,

J. Choudhury, N. Oded and M. E. van der Boom, Angew. Chem., Int. Ed., 2010, 49, 4780.

- (a) M. Kumar, R. Kumar and V. Bhalla, *Chem. Commun.*, 2009, 7384;
 (b) M. Kumar, A. Dhir and V. Bhalla, *Org. Lett.*, 2009, 11, 2567;
 (c) D. Margulies, C. E. Felder, G. Melman and A. Shanzer, *J. Am. Chem. Soc.*, 2007, 129, 347;
 (d) J. Andreasson, S. D. Straight, T. A. Moore, A. L. Moore and D. Gust, *Chem.-Eur. J.*, 2009, 15, 3936.
- (a) M. Kumar, R. Kumar and V. Bhalla, Org. Lett., 2011, 13, 366;
 (b) M. Kumar, A. Dhir and V. Bhalla, Chem. Commun., 2010, 46, 6744;
 (c) U. Pischel, Angew. Chem., Int. Ed., 2010, 49, 1356.
- 19 M. Kumar, A. Dhir and V. Bhalla, Chem. Commun., 2010, 46, 6744.
- 20 (a) S. Giordani and F. M. Raymo, Org. Lett., 2003, 5, 3559; (b) F. M. Raymo and S. Giordani, Org. Lett., 2001, 3, 3475; (c) F. M. Raymo, R. J. Alvarado, S. Giordani and M. A. Cejas, J. Am. Chem. Soc., 2003, 125, 2361.
- 21 J. Butler and B. M. Hoey, Br. J. Cancer, 1987, 55, 53.
- 22 M. W. Remold and A. H. E. Kramer, J. Soc. Dyers Colour., 1980, 96, 122.
- 23 (a) S. Kumar and N. Kaur, *Supramol. Chem.*, 2006, **18**, 137; (b) N. Kaur and S. Kumar, *Dalton Trans.*, 2006, 3766; (c) N. Kaur and S. Kumar, *Tetrahedron*, 2008, **64**, 3168; (d) N. Kaur and S. Kumar, *Tetrahedron Lett.*, 2006, **47**, 4109; (e) N. Kaur and S. Kumar, *Chem. Commun.*, 2007, 3069; (f) N. Kaur and S. Kumar, *Tetrahedron Lett.*, 2008, **49**, 5067.
- 24 C. Lu, Z. Xu, J. Cui, R. Zhang and X. Qian, J. Org. Chem., 2007, 72, 3554.
- (a) Z. Xu, X. Qian, J. Cui and R. Zhang, *Tetrahedron*, 2006, 62, 10117;
 (b) Z. Xu, X. Qian and J. Cui, *Org. Lett.*, 2005, 7, 3029;
 (c) M. Boiocchi, L. D. Boca, D. E. Gomez, L. Fabbrizzi, M. Licchelli and E. Monazani, *J. Am. Chem. Soc.*, 2004, 126, 16507.
- 26 Titration data is fit with programme *Specfit/32*, which analyzes multiwavelength data using an iterative method to obtain the association constant in terms of free or unbound M^{2+} .