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Naked-eye recognition of Cu^{II}, Zn^{II} and acetate ion by the first guanine-based difunctional chromoinophore

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ABSTRACT

The first guanine-based difunctional colorimetric receptor 8-[(4-nitrophenyl)azo]guanine (receptor 1) was designed, synthesized and characterized by IR, UV–vis, ^{1}H NMR and mass spectrometric analysis. The synthesized receptor 1 was able to recognize Cu^{II}, Zn^{II} and acetate ion through visible color changes in its DMSO and DMSO-H_2O (95:5, v/v) solution. The binding affinity of the receptor 1 with the chosen analytes has been estimated in terms of binding constants through non-linear fittings of corresponding UV–vis titration data while the binding mode of the same was studied through ^{1}H NMR spectral studies.

1. Introduction

The recognition of cations and anions through strategically designed receptors have been a field of extensive and intensive research for last few decades in view of their crucial roles in the physiology and biochemistry of living systems [1–4]. Among the various available methods for the detection of analytes the naked-eye detection is preferentially used method as it does not involve either costly instruments or any pretreatment of the sample [5]. Literature survey revealed that most of the synthetic receptors sense either cation [6–8] or anion [9–12]. There are only few synthetic receptors which are able to sense the cation and anion both [13–20]. The binding moieties of the difunctional receptors for cations [14,21,22,17,19,23] are usually cyclic compounds such as crown ether, porphyrin and calix[4]arene or calix[4]pyrrole, while the same for anions include urea/thiourea [24], imidazole [25], indole [26], pyrrole, amide and guanidyl [27], etc. The chemical synthesis of these type of receptors is a bit difficult. The chemoreceptor being presented through this communication involves a very simple reaction like diazonium coupling of 4-nitrobenzenediazonium chloride at C8 position of guanine.

The receptor 1 possesses electron rich and deficient pockets in the form of purine and 4-nitroazobenzene respectively and hence is able to act as an intramolecular charge transfer (ICT) probe. The objectives behind construction of present receptor over guanine were two folds. The first one was to exploit the –NH functionalities of guanine for supramolecular interactions with anionic analytes while utilizing the diazonium nitrogens along with imidazolic nitrogen of guanine for the binding purpose with cationic analytes was the second objective. Our objective was very much fulfilled in the sense that the receptor 1 was able to detect the acetate from a mixture of acetate, benzoate and formate on one hand while it was also able to detect Cu^{II} and Zn^{II} on the other hand through different visible color changes in DMSO and DMSO-H_2O (95:5, v/v) solution also. In this context it is worth to mention that the earlier N-substitution studies [28] over guanine in DMSO/DMSO-H_2O could enable it to recognize only acetate ion and that too in the UV region only.

The anionic analytes under present study include the carboxylate anions in view of their interactions particularly of acetate with purine bases and nucleosides resulting into disruption of the guanine–cytosine base pair [29]. Besides its biological importance the acetate ion also play important roles in a number of chemical industries such as plastic, pharmaceutical and food [30]. On the other hand M^{II} ions of 3d series from d^5-d^{10} and Cd^{II} Hg^{II}, Pb^{II} were chosen as cationic analytes in view of their important roles as trace metals in living system as well as their toxicity towards our environment, respectively [31–33]. Among the cations only Cu^{II} and Zn^{II} were discriminated by the receptor 1 through different colorimetric changes. Cu^{II} proteins are involved in oxygen binding, electron transfer and the activation of small molecules [34,35] while Zn^{II} is well known for its role as a co-factor in

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several enzymes and towards protein synthesis and cell division besides its role in the functioning of immune system [36,37]. To the best of our knowledge the receptor 1 is the first ever colorimetric receptor constructed over guanine and it is our yet another effort to synthesize receptors on the frame work of nucleic acid bases having potential to recognize cations and anions both [25,38].

2. Experimental

2.1. Apparatus

The IR Spectrum for the receptor 1 was recorded on JASCO-FTIR Spectrophotometer while ^{1}H NMR spectra were recorded on a Bruker-400 Avance NMR Spectrometer and JEOL AL 300 FT NMR Spectrometer. Mass spectrometric analysis was carried out on a MDS Sciex API 2000 LCMS spectrometer. Electronic spectra were recorded at room temperature (298 K) on a UV-1700 pharmaspec spectrophotometer with quartz cuvette (path length = 1 cm).

2.2. Materials

All reagents for synthesis were purchased from Sigma–Aldrich and were used without further purification. The DMSO of HPLC grade for UV–vis experiments was purchased from Spectrochem Pvt. Ltd., Mumbai, India.

2.3. General methods

All titration experiments were carried at room temperature. For the UV–vis titrations a 5×10^{-5} M solution of the receptor and solutions of tetrabutylammonium salts of the respective anions and chloride salt of metals were prepared in DMSO/DMSO-H_2O (95:5, v/v). The binding constants were calculated by using nonlinear least-squares curve-fitting procedure through Origin software. The ^{1}H NMR titrations were carried out in DMSO-d_6 using tetramethylsilane (TMS) as an internal reference standard. For the ^{1}H NMR spectral titrations the 5×10^{-3} M solutions of the receptor 1 and the varying equivalents of tetrabutylammonium acetate as well as the chloride salts of Cu^{II} and Zn^{II} were separately prepared in DMSO-d_6. The optimized structures were fully refined in the gas-phase at the DFT level with the Gaussian 03 package [39], B3LYP/6-31G** basis set.

2.4. Synthesis of 8-[(4-nitrophenyl)azo]guanine (receptor 1)

For the synthesis of receptor 1 the literature procedure was adopted [40]. A solution of 4-nitobenzenediazonium chloride (10 mmol) was prepared by the dissolution of 4-nitroaniline (690 mg, 5 mmol) in hot distilled water (3 mL) followed by addition of conc. HCl (1 mL). On cooling this solution to 0 °C a solid white cake was formed which was dissolved by addition of 5 mL of distilled water. To this solution a cooled aqueous solution of sodium nitrite (370 mg, 5% excess) in 2 mL of distilled water was added slowly with constant stirring maintaining the temperature of the reaction mixture around 0 °C. The resulting 4-nitrobenzenediazonium salt solution was added dropwise to a solution of guanine (0.75 g, 5 mmol) in 0.62N sodium hydroxide (40 mL) around 0 °C while stirring maintaining the pH between 10 and 11. The stirring was further continued for 15 min followed by neutralization of reaction mixture to pH 7 by dropwise addition of 1.0N HCl. The resulting brown colored precipitate was filtered, washed thoroughly with chloroform, water and finally dried under vacuum. Receptor 1: Mp 265 °C (decomposed); FAB MS m/z = 301.33 Calc. for $C_{11}H_8N_8O_3$ = 300.23; IR/cm^{-1}: 3392, 3300, 3132, 1697, 1583, 1517, 1476, 1424, 1392, 1332, 1244, 1188, 1148, 1101, 1003, 909, 856, 783, 725; ^{1}H NMR (DMSO-d_6): 13.27 (s, 1H, –N_9H), 11.01 (s, 1H, –N_1H), 8.42–8.44 (d, 2H, Ar–H), 8.02–8.04 (d, 2H, Ar–H) and 7.00 (s, 2H, –NH_2); UV–vis/nm (DMSO/DMSO-H_2O): 503 nm.

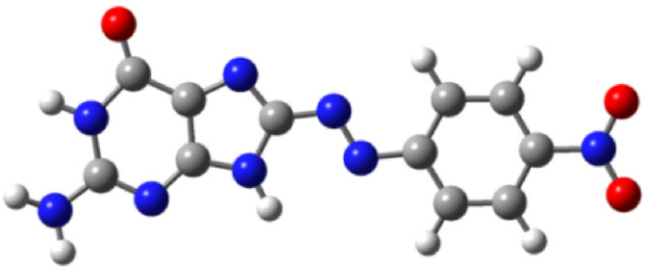

Fig. 1. Energy-minimized structure of receptor calculated by B3LYP method with the 6-31G** basis set.

3. Results and discussion

The IR, ^{1}H NMR spectra of the receptor 1 along with DFT calculations suggested that receptor 1 exist in the form of tautomer 1 (Fig. 1) out of its four possible tautomers (see ESI; Fig. 1).

3.1. UV–vis spectral studies

The 5×10^{-5} M DMSO solution of the receptor 1 was of red color and exhibited a strong intramolecular charge transfer (ICT) band at 503 nm due to HOMO–LUMO transition (Fig. 2).

The solution of receptor 1 underwent visible changes on the respective additions of one equivalent of tetrabutylammonium salts of acetate, benzoate and formate (Fig. 3a). Similar additions of M^{II} of 3d series from d^5-d^{10} as well as Cd^{II}, Hg^{II} and Pb^{II} as their chloride salts (Cl^- does not complex with receptor 1; see ESI; Fig. 2) produced a variety of responses (see ESI; Fig. 3). Mn^{II} and Fe^{II} did not produce any significant visible color change. While Co^{II} and Ni^{II} produced violet color on the other hand Cu^{II} produced blue and Zn^{II} produced purple color (Fig. 3b). Among the Cd^{II}, Hg^{II} and Pb^{II} only Hg^{II} produced almost same color change to that of Co^{II} and Ni^{II}. However addition of 100 equivalents of Cd^{II} did produce a naked-eye change (Fig. 7a). Thus receptor 1 is able to distinguish Cu^{II} and Zn^{II} out of above-mentioned M^{II} ions.

For having a detailed idea about the binding pattern and binding constant the UV–vis spectral titrations between receptor 1 and corresponding analytes were performed separately. For the titra-

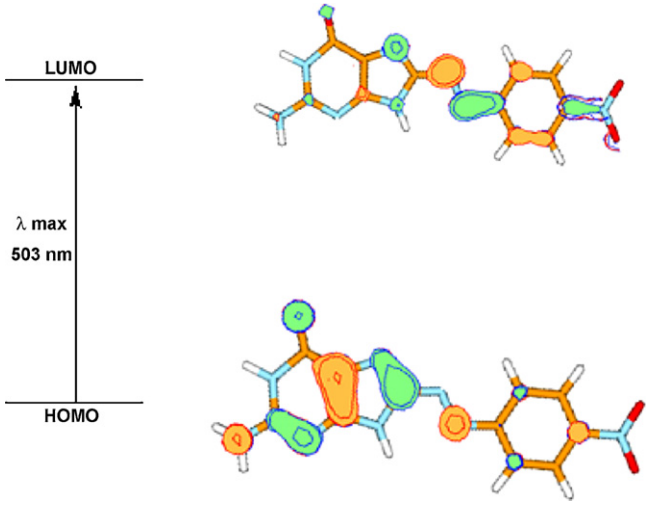

Fig. 2. Representation of HOMO–LUMO transition of receptor 1.

Fig. 3. Visible color changes of receptor 1 solution upon addition of 5 equivalents of each (a) anions; from left to right, receptor 1; with acetate; benzoate and formate and (b) cations; from left to right, with Cu^{II} and Zn^{II}.

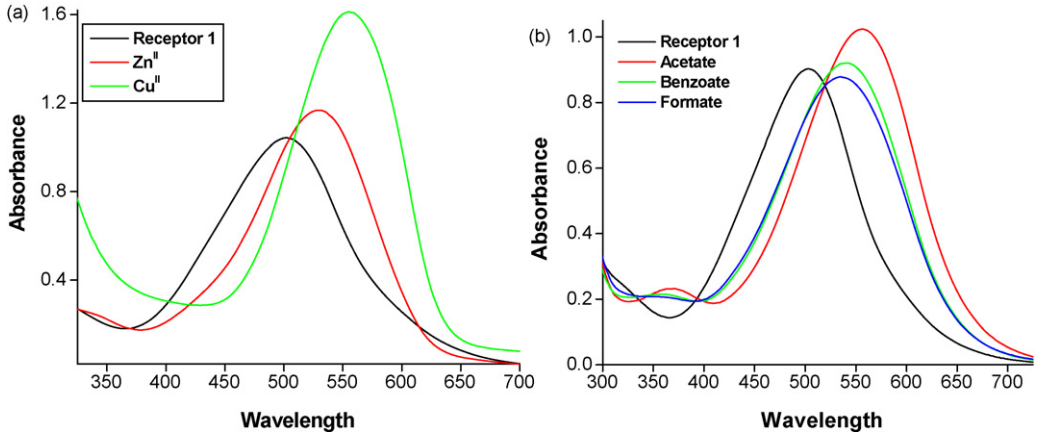

Fig. 4. The comparative UV–vis spectral changes of receptor 1 upon addition of 10 equivalents of (a) cations (Cu^{II}, Zn^{II}) and (b) anions.

tion purposes 0–10 equivalents of the respective analytes as their DMSO solutions were added to the 5×10^{-5} M DMSO solution of the receptor 1. The comparative UV–vis spectral changes for the individual Cu^{II}, Zn^{II} and anion have been given in Fig. 4.

3.1.1. Cation binding studies

The UV–vis absorption band of the receptor 1 at the 503 nm was gradually shifted to the higher wavelength with increasing intensity on the concomitant additions of Cu^{II} (Fig. 5a).

This trend was maintained till the addition of 1 equivalent when the 503 nm band was shifted finally to 555 nm (red shift of 52 nm). Further additions of Cu^{II} did not affect either spectral pattern or naked-eye appearance of the solution. The color of the solution changed from red to blue at this stage (Fig. 3b). Similarly Zn^{II} also perturbed the UV–vis spectrum of the receptor 1 (Fig. 5b) but to a smaller extent (red shift of 25 nm) with the color change from red to purple (Fig. 3b). Thus the receptor 1 was able to recognize Cu^{II} and Zn^{II} at the level of 10^{-5} M concentration on the basis of their different visible color changes as well as different extents of bathochromic shifts in the 503 nm band of the receptor 1. The single isosbestic points for Cu^{II} at 525 nm while for Zn^{II} at 320 nm were observed indicating their chemical interactions with the receptor 1. The spectral pattern for Co^{II} and Ni^{II} followed to that of Hg^{II} (see ESI; Fig. 4) while Mn^{II}, Fe^{II} and Pb^{II} did not produce any significant visible/spectral changes (see ESI; Figs. 3 and 5).

The stoichiometries for cationic host–guest interaction were confirmed to be 1:1 from the Job plots (Fig. 6) which was further supplemented by ESI-MS of a representative Zn^{II} complex as its

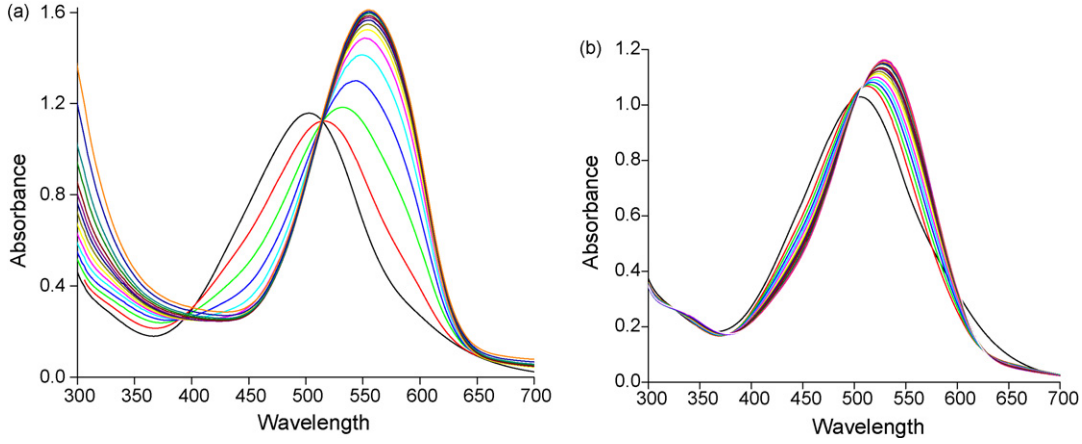

Fig. 5. Changes in UV–vis spectra of receptor 1 upon concomitant addition of (a) Cu^{II} and (b) Zn^{II}.

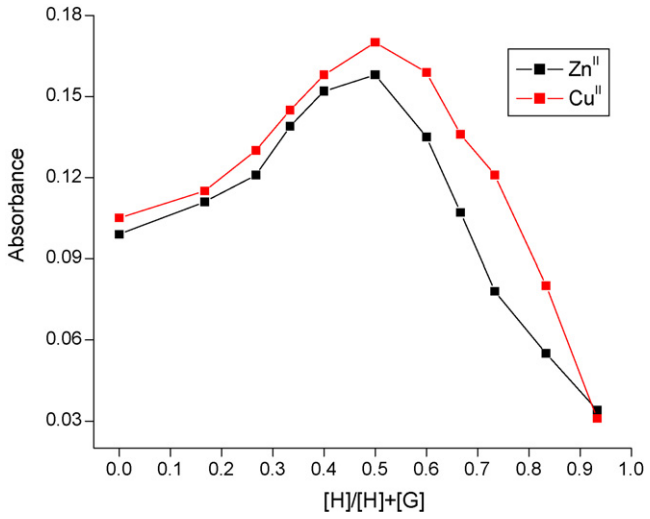

Fig. 6. Job Plots of Cu^{II} and Zn^{II} with receptor 1 showing 1:1 stoichiometry.

chloride salt with receptor 1 (see ESI; Fig. 6) showing a peak at m/z 437.4 (Calc. for $C_{11}H_8N_8O_3ZnCl_2$ = 436.53) corresponding to the 1:1 complex.

The binding constants for the complexes between receptor 1 and metal ions (Cu^{II} and Zn^{II}) in DMSO (Table 1) were determined by the non-linear fittings (see ESI; Fig. 7) of the corresponding titration data in 1:1 binding equation as reported in literature [41].

$$A = A_0 + (A_{lim} - A)/2C_0\{C_H + C_G + 1/K - [(C_H + C_G + 1/K)^2 - 4C_HC_G]^{1/2}\}$$

A perusal of the binding constants (Table 1) suggested a comparative stronger binding of Cu^{II} with the receptor 1 in comparison to Zn^{II} which is also manifested in terms of a higher extent of bathochromic shift in the 503 nm band of the receptor 1 on addition of Cu^{II}. This observation is justified in terms of smaller size of Cu^{II} in comparison to Zn^{II}.

Although the gradual addition of Cd^{II} (up to 10 equivalents) to the 5×10^{-5} M DMSO solution of the receptor 1 (Fig. 7a) did not produce any distinct visible color change but the 503 nm band of the receptor 1 shifted to 511 nm which was finally shifted to 495 nm on the addition of large excess (100 equivalents) of Cd^{II} to the same solution of receptor 1 (Fig. 7b). The color of the solution at this stage was orange (Fig. 7b). No isosbestic point was observed in this case suggesting an ill defined binding between Cd^{II} and receptor 1 (Fig. 7c).

The red shift in the UV–vis spectrum of the receptor 1 with Cu^{II} and Zn^{II} both may be understood in terms of their interactions with imidazolic (N_7) and azo (N_{11}) donors of the receptor 1 (see ESI; Fig. 8a and b).

As it can be seen in Fig. 8 that imidazolic and azo nitrogens are situated over HOMO and LUMO of receptor 1 respectively hence their interactions with cations will result into their stabilisation. Since the imidazolic nitrogen is the part of aromatic system while the azo nitrogen is not hence the donor ability of the previous one will be comparatively poor than the later one. In other words, there will be less stabilisation of HOMO in comparison to LUMO leading to decrease in their energy gap and finally will lead to bathochromic shift in the ICT of receptor 1. The comparative higher red shift for Cu^{II} may be understood in terms of its smaller size which allowed it for a comparatively higher extent of bonding with azo nitrogen and thus stabilising the LUMO of the receptor further (Fig. 9).

Nevertheless, the addition of Cd^{II} to the receptor 1 at the similar level of Cu^{II} and Zn^{II} lead to a very small extent of bathochromic shift which may be a consequence of the poor extent of binding of Cd^{II} with the same donor sets which is also supported by the non-occurrence of any isosbestic point in this case as mentioned above (Fig. 7c). The blue shift in the 503 nm band of the receptor 1

Table 1
Binding constants (K) of receptor 1 with metal ions.

Cations[a]	K (M^{-1})[b]	R^2 [c]
Cu^{II}	$(4.12 \pm 0.40) \times 10^5$	0.9995
Zn^{II}	$(2.63 \pm 0.58) \times 10^4$	0.9939

[a] The cations were used as their chloride salts.
[b] The data were calculated from UV–vis titrations in DMSO.
[c] The data values of R were obtained by the results of nonlinear curve fitting.

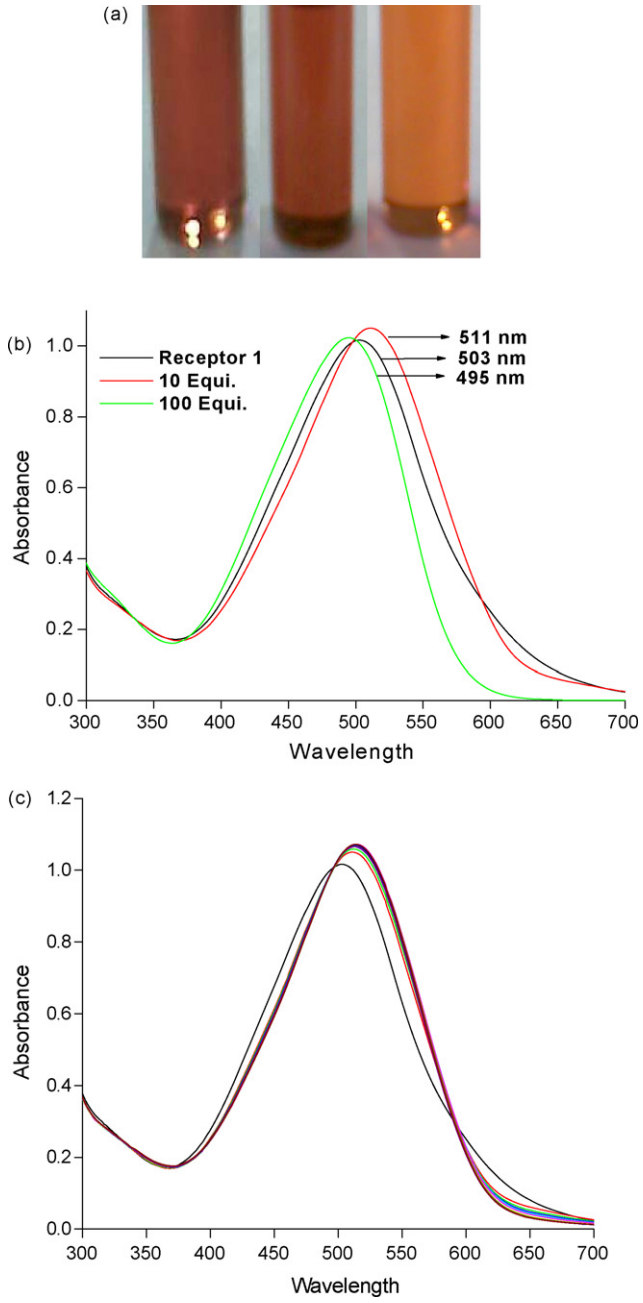

Fig. 7. (a) Visible color changes of receptor 1; from left to right: receptor 1, upon addition of 10 and 100 equivalents of Cd^{II}, (b) changes in UV–vis spectra of receptor 1 upon addition of 10 and 100 equivalents of Cd^{II}, (c) UV–vis spectrum of receptor 1 upon concomitant addition of Cd^{II} ion (0–10 equivalent).

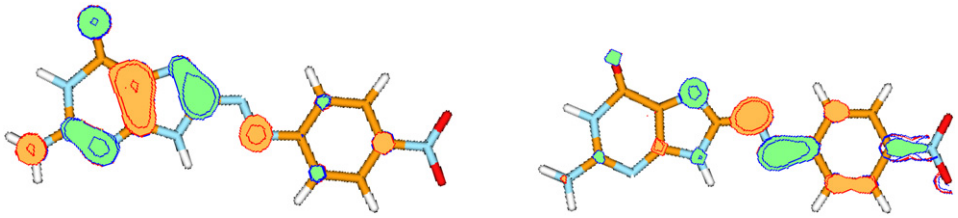

Fig. 8. HOMO and LUMO orbitals of receptor 1 calculated by B3LYP method with the 6-31G** basis set.

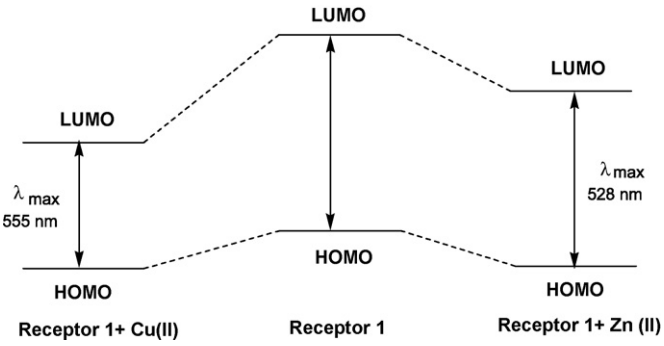

Fig. 9. Variation in HOMO and LUMO energy levels of receptor 1 in the presence of Cu^{II} and Zn^{II}.

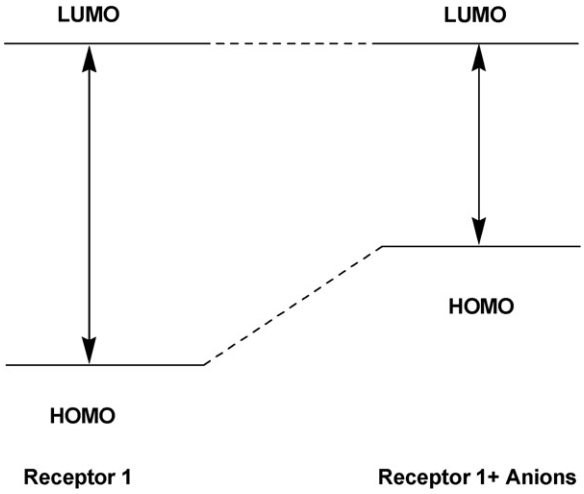

Fig. 11. Variation in HOMO and LUMO energy levels of receptor 1 in the presence of carboxylate anions.

on addition of higher equivalents of Cd^{II} (100 equivalents) may be a consequence of its coordination with N_7 and O_6 hence stabilising the HOMO (as N_7 and O_6 both are situated on HOMO; Fig. 8) and not affecting LUMO leading to a larger energy gap between HOMO and LUMO ultimately causing the blue shift in the UV–vis spectrum of the receptor 1.

3.1.2. Anion binding studies

The chosen carboxylate anions were taken as their tetrabutylammonium salts. The corresponding titration curves for the individual anions have been given in Fig. 10.

The gradual addition of the acetate ion to the receptor 1 solution lead red shifting of 503 nm band to 555 nm producing naked-eye change from red to blue (Fig. 3a). This bathochromic shift may be understood as the outcome of the interaction of receptor 1 with acetate through –NH's of its purine moiety. Since the HOMO is spread over the purine part (Fig. 8) hence its interaction with acetate will make it further electron rich and hence will destabilise it leading to decrease in the HOMO–LUMO energy gap of the receptor 1 (Fig. 11). Which is ultimately reflected in terms of bathochromic shift.

The similar type of bathochromic shifts to lesser extents were also observed on the respective concomitant additions of benzoate (37 nm) and formate (30 nm) to the 5×10^{-5} M DMSO solution of the receptor 1 (Fig. 10b and c). The extent of bathochromic shifts for acetate, benzoate and formate followed their relative basicity order [42]. Hence, receptor 1 differentiated acetate from benzoate and formate on the basis of spectral characteristics and naked-eye changes of receptor 1 on their respective additions. However, benzoate and formate could not be differentiated on the basis of naked-eye change only because their respective additions to the DMSO solution of the receptor 1 produced purple color for both the cases (Fig. 3a). In order to confirm the specificity of the receptor 1 towards acetate a matrix of acetate, benzoate and formate in DMSO was added to the 5×10^{-5} M DMSO solution of the receptor 1. The naked eye change was same as it was with the acetate individually. There were three well-defined isosbestic points at 332, 392 and 520 nm in all the cases with a variation of 1 or 2 nm indicating a neat interconversion between the receptor 1 and its complexes with chosen anions (Fig. 10).

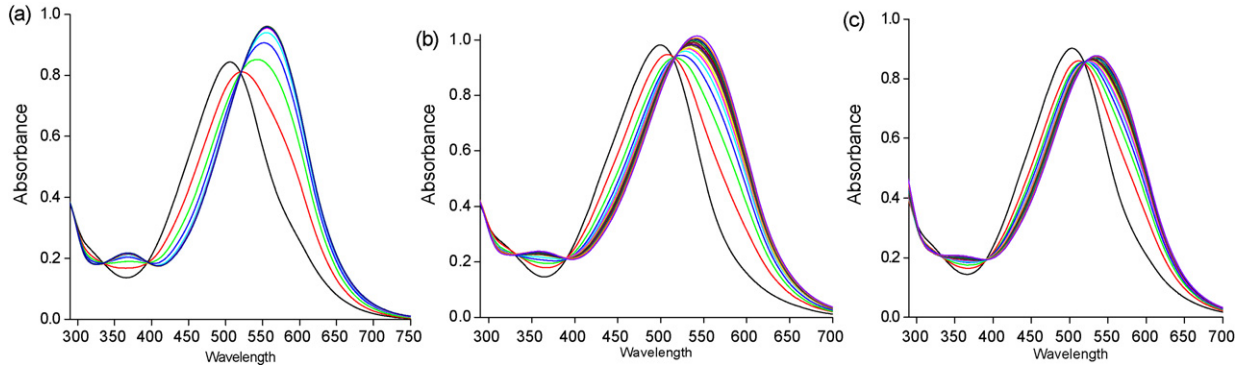

Fig. 10. Changes in UV–vis spectra of receptor 1 upon concomitant addition of carboxylate anions (a) acetate, (b) benzoate and (c) formate.

Table 2
Binding constants (K) of receptor 1 with anions.

Anions[a]	K (M^{-1})[b]	R^2 [c]
CH_3COO^-	$6.32 \pm 1.41 \times 10^5$	0.9977
$C_6H_5COO^-$	$1.37 \pm 0.06 \times 10^5$	0.9997
$HCOO^-$	$1.03 \pm 0.06 \times 10^5$	0.9994

[a] The anions were used as their tetrabutylammonium salts.
[b] The data were calculated from UV–vis titrations in DMSO.
[c] The data values of R were obtained by the results of nonlinear curve fitting.

The UV–vis titration data for all the anions were best fitted for 1:1 (host/guest) stoichiometry (see ESI; Fig. 9) and the corresponding binding constants between receptor 1 and carboxylate ions have been given in Table 2. The binding constants also followed the relative basicity of the chosen anions, i.e., for acetate it was highest while for formate it was lowest.

A comparison of the binding constant of acetate with receptor 1 under present study with the earlier similar studies involving N-substitution over guanine [29], clearly established the superiority of C8 substitution over N-substitution on guanine for the sensing purposes of the carboxylate anions. It is worth to mention that the naked-eye and spectral characteristics of receptor 1 with fluoride (as its tetrabutylammonium salt) under similar conditions was almost same to that of acetate (see ESI; Fig. 10) hence receptor 1 will not be able to discriminate between acetate and fluoride from their mixture.

Hence, on the basis of above discussions it is clear that both cations and anions are able to modulate the ICT of the receptor 1. Among the anions the acetate is the best one while Cu^{II} and Zn^{II} are among the cations which modulate the ICT of the receptor 1 in characteristically different way than the rest of the chosen cations. Although Cd^{II} also affects the ICT of the receptor 1 in its own characteristic way but it is identifiable through receptor 1 at higher concentrations (10^{-3} M while Cu^{II} and Zn^{II} at 10^{-5} M) than Cu^{II} and Zn^{II}.

There is fundamental difference between the recognition mechanism of the receptor 1 for anion and cation. The anions being electron rich develop hydrogen bonding through –NH of the receptor 1 hence increasing electron density on HOMO hence destabilising it finally decreasing the HOMO–LUMO gap. On the other hand cations being able to accept electron density from the receptor 1 affecting its HOMO and LUMO both but certainly to the LUMO one to higher extent leading to decrease in HOMO–LUMO gap. Nevertheless, the receptor 1 is also able to recognize the acetate through visible color change from the matrix of acetate, benzoate and formate at the level of their 10^{-5} M concentrations establishing the high specificity of receptor 1 towards acetate among the chosen carboxylate anions. All the above sensing studies with cations and anions were also performed in DMSO-H_2O (95:5, v/v) with almost same naked-eye changes but the corresponding binding constants were not determined.

3.2. ^1H NMR titration studies

To further look into the nature of host–guest interactions, ^1H NMR titration experiments of receptor 1 with tetrabutylammonium acetate and M^{II} (Zn^{II} and Cu^{II} as their chloride salts) were carried out in 5×10^{-3} M DMSO-d_6 solution.

3.2.1. ^1H NMR titrations experiment with cations

The gradual additions of Zn^{II} (0–2 equiv.) to the receptor solution resulted into marginal upfield shifting of $-N_1H$ and $-NH_2$ protons whereas a marginal downfield shifting of $-N_9H$ proton of the receptor 1 (see ESI; Table 1) which was constantly maintained throughout the addition of Cu^{II}. Hence, the possibility of involvement of $-NH_2$ group in binding with Zn^{II} was categorically ruled out because in that situation there would have been a downfield shifting of $-NH_2$ protons. The downfield shifting of $-N_9H$ and phenyl protons in the vicinity of azo group supported the involvement of N_7 and N_{11} in coordination with Zn^{II} (see ESI; Fig. 8) as we proposed above on the basis of UV–vis spectral studies. The similar studies with Cu^{II} lead broadening in the ^1H NMR signals of the receptor 1 in view of paramagnetic nature of the same.

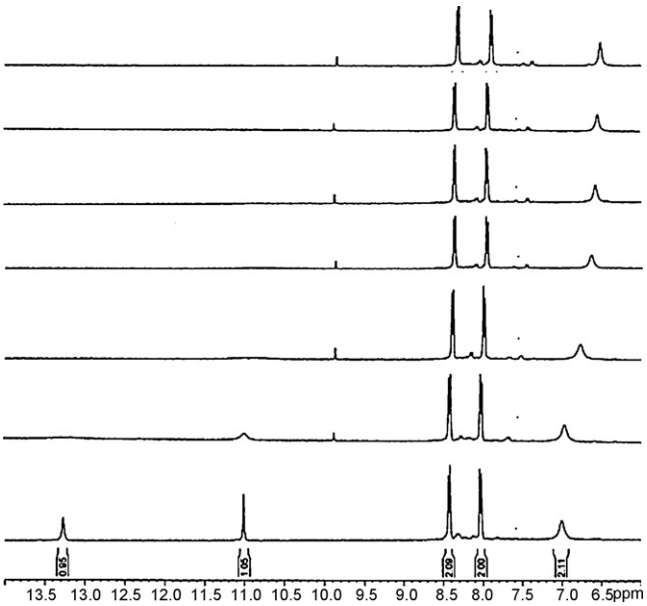

Fig. 12. Partial ^1H NMR spectra of receptor 1 (5×10^{-3} M) in DMSO-d_6 with tetrabutylammonium acetate; from bottom to up: receptor 1; 1 + 0.25 equiv. acetate; 1 + 0.5 equiv. acetate; 1 + 0.75 equiv. acetate; 1 + 1.0 equiv. acetate; 1 + 1.5 equiv. acetate and 1 + 2.0 equiv. acetate.

3.2.2. ^1H NMR titrations experiment with anions

^1H NMR titration experiments of receptor 1 with tetrabutylammonium acetate have been shown in Fig. 12 and the observed peaks with their chemical shifts in δ ppm along with the corresponding assignments have been given in Table 3.

The receptor 1 possesses two –NHs, i.e., $-N_1H$ and $-N_9H$ absorbing at 11.01 and 13.27 δ ppm respectively indicating that $-N_9H$ is more polar than $-N_1H$. On addition of first aliquot (0.25 equiv.) of acetate as its tetrabutylammonium salt the $-N_9H$ was shifted towards acetate represented through equilibrium (i) as follows;

$$LH_2 + {}^-OAc \rightleftarrows LH^- + HOAc \quad \text{(i)}$$

The same is reflected in terms of a small peak at 9.87 δ ppm in the ^1H NMR spectra (Fig. 12). At the same time the $-N_1H$ signal

Table 3
Changes in chemical shifts (δ, ppm) of receptor 1 during ^1H NMR titration experiment upon concomitant addition of tetrabutylammonium acetate.

[Acetate] (equivalents)	$-N_9H$	$-N_1H$	Ar–H		Ar–H		$-NH_2$
0.00	13.270	11.011	8.439	8.418	8.044	8.022	7.002
0.25	–	10.997	8.433	8.413	8.037	8.017	6.968
0.50	–	–	8.409	8.387	8.007	7.986	6.778
0.75	–	–	8.389	8.356	7.980	7.959	6.645
1.00	–	–	8.378	8.415	7.965	7.944	6.585
1.50	–	–	8.365	8.343	7.946	7.924	6.543
2.00	–	–	8.333	8.312	7.911	7.889	6.520

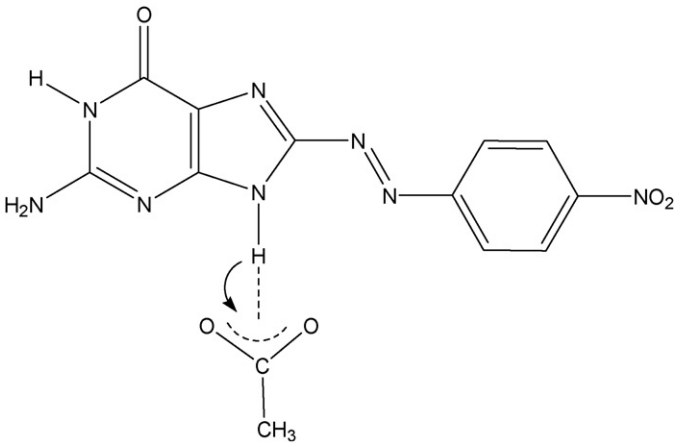

Fig. 13. Chemical structure image of receptor 1 attached with acetate ion.

got broadened because by the shifting of $-N_9H$ in favour of acetate the electron density on donor (purine) of the receptor 1 increases hence the $-N_1H$ sticks with nitrogen and is able to experience its quadrupolar effect. On addition of next aliquot of acetate the $-N_1H$ was also shifted towards acetate resulting into the yet another type of ion dipole interaction represented through equilibrium (ii) as given below;

$$LH^- + {}^-OAc \rightleftarrows L^{2-} + HOAc \quad \text{(ii)}$$

The equilibrium (ii) is the less favoured one in comparison to equilibrium (i) as it involves two negatively charged species on the left hand side. The ion dipole interaction between L^{2-} and HOAc is reflected in the form of yet another small peak at ~7.5 δ ppm (Fig. 12). Hence out of two equilibria (i) and (ii) it is the first one which is dominating and responsible for the selective naked-eye sensing of acetate through receptor 1. The $-NH_2$ protons along with the aromatic protons shifted upfield due to through-bond effect [43] during the entire course of titration. The upfield shifting of $-NH_2$ protons excluded its possibility to be involved in hydrogen bonding interaction with acetate which is reverse to the earlier pattern involving N-substitution over the guanine [28,29,44–46]. Hence on the basis of ^1H NMR in association with UV–vis spectral titration studies between receptor 1 and acetate following chemical structure image (Fig. 13) may be proposed for the selective naked-eye sensing of acetate through receptor 1.

4. Conclusion

In summary we have constructed a difunctional colorimetric receptor over the skeleton of guanine by C8 substitution through coupling with diazonium salt of 4-nitroaninline. This strategy introduced the naked-eye sensing ability in the guanine towards Cu^{II} and Zn^{II} as well as recognition of acetate ion from the matrix of acetate, benzoate and formate. However, the Cd^{II} could also be recognized by the receptor 1 but at comparatively higher concentration. The C8 substitution over the guanine under present study made it more potent towards its interaction with carboxylate ion as compared to earlier N-substitutions which is clearly established through above discussions.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.talanta.2010.01.005.

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