Colorimetric Recognition of d^{10} Metal Ions through an Adenine-Based ICT Probe

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We report hereby use of *p*-nitrophenyltriazenopurine, (PNTP) as a colorimetric receptor for recognition of d^{10} metal ions in DMSO through visible color changes. All the chosen metal ions showed 1:1 stoichiometry with PNTP. Among the chosen metal ions Hg^{II} was most preferred by PNTP.

Highly accurate sensing of cations and anions is an urgent need of ours today for many areas of technology, including biological, clinical, environmental, and waste management applications.[1,2] The colorimetric chemosensors have attracted considerable attention since they provide immediate qualitative signal, which allows direct naked-eye detection of cations/anions due to some specific color changes of solution.[3] The selection of metal ions in this communication is based on their important roles in enzymatic/environmental areas.[4–6] Zinc acts as a co-factor in various enzymes and plays an important role in protein synthesis and cell division besides its role in the functioning of the immune system.[7] The environmental havoc produced by Cd^{II} and Hg^{II} are well known in the form of itai-itai[8] and minamata[9] disease respectively. The selective sensing protocols for heavy metal ions such as Cd^{II} and Hg^{II} are critical owing to their high toxicity.[10,11] These heavy metal ions have detrimental effects on humans, causing impairment in brain development, renal dysfunction, calcium metabolism disorders, chronic inflammation to the heart and kidney, and impairing reproductive systems.[12,13] Extensive studies have been carried out on the development of protocols for the determination of biologically relevant metal ions.[14,15] Most of them are disadvantageous in terms of cost and hence not suitable for routine analysis. One accurate available method for low level determination of heavy metals is AAS, but it involves expensive instrumentation and sample pretreatment that is time consuming and inconvenient also. Hence, there is a critical need for the development of selective, portable, and inexpensive diagnostic tools for determination of heavy metals.

In our previous communication[16] we reported synthesis, characterization, and application of *p*-nitrophenyltriazenopurine (PNTP) for the binding of some anions, particularly PF_6^- as its tetrabutylammonium salt. The application of triazenes for the spectrophotometric determination of d^{10} metal ions particularly Cd^{II} and Hg^{II} is well documented in the literature.[17] PNTP contains triazene as its π unit in its D–π–A system hence it was thought worthwhile to explore the possibility of interactions of this reagent with Zn^{II}, Cd^{II}, and Hg^{II}. The sensing ability of PNTP for cations and anions both may be attributed to the simultaneous presence of triazene[17] as well as imidazole moiety.[18]

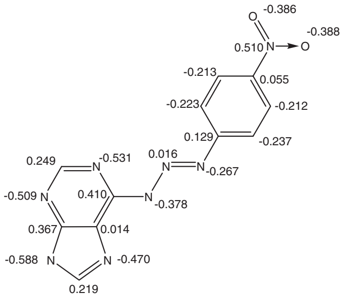

Figure 1. Charges obtained from NBA using B3LYP/6-31G** optimized geometry of PNTP.

The structural optimization and computation of atomic charges from natural bond orbital analysis (NBA) for PNTP with B3LYP/6-31G** through density functional theory (DFT) clearly proved that it possesses electron-rich and -deficient pockets simultaneously within the same framework. That is why PNTP is a fit case for its potential application as an ICT probe.[19] The optimized structure with NBA charges on different atoms of PNTP has been given in Figure 1. The sum total of NBA charges on various fragments of PNTP indicated that the purine moiety is electron rich in comparison to the *p*-nitrophenyl group. Both of these units are attached with triazene moiety. Hence there will be a natural flow of electron density from purine (D) to *p*-nitrophenyl (A) group through triazene (D–π–A).

The absorption spectrum of the PNTP was characterized by the presence of absorption maxima at 398 nm along with a broad band at 575 nm in DMSO while in nujol mull the broad band at 575 nm was not observed. The peak at 398 nm is assigned to the *p*-nitrophenyl moiety of PNTP while the broad band at 575 nm is due to intramolecular charge transfer (ICT) from electron-rich purine to electron-deficient *p*-nitrophenyl through triazene. It is worthy to mention that the ICT band of PNTP at 575 nm was observed only in polar aprotic solvents like DMSO, DMF and not in other non-polar aprotic solvents like chloroform. Hence, the polarity of the solvent may be taken as responsible for decreasing the energy barrier for ICT which ultimately may lead to an increase in the solvent relaxation time and finally giving rise to a new peak at 575 nm in the light of a recent literature report.[20] Nevertheless, intermolecular hydrogen bonding between PNTP (through imidazolic –NH–) and polar aprotic solvents through $X = O$ (where $X = S$ for DMSO and $X = C$ for DMF) may be yet another probable reason behind the genesis of the 575 nm peak of PNTP in its UV–vis spectrum in DMSO.[21]

Addition of 1 equivalent of Zn^{II}, Cd^{II}, and Hg^{II} as their chloride salts respectively to the 5×10^{-5} M solution of PNTP in DMSO produced visible color changes as well as changes in its UV–vis spectral bands (Figures 2a and 2b). This observation clearly proved the sensitivity of PNTP towards chosen metal ions.

In order to have a deeper insight of the sensing phenomenon the UV–vis titrations were performed by the interaction of

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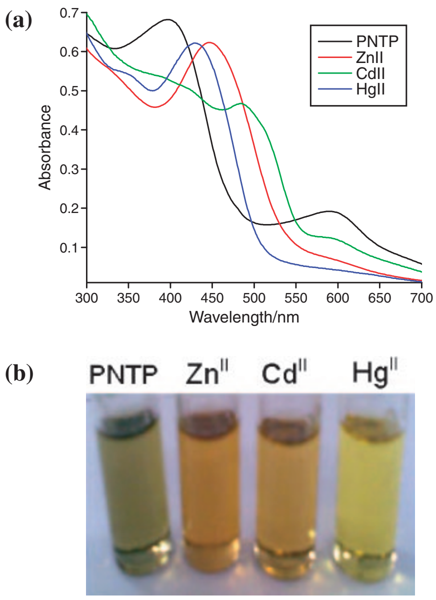

Figure 2. (a) UV–vis spectra of PNTP and corresponding changes on addition of 1 equivalent of Zn^{II}, Cd^{II}, and Hg^{II}. (b) Visible color changes of DMSO solution of PNTP on addition of 1 equivalent of Zn^{II}, Cd^{II}, and Hg^{II}. (I) The counter ions in all the cases were chloride ions. (II) 5×10^{-5} M DMSO solution of PNTP was used for 2a and 2b.

5×10^{-5} M DMSO solution of PNTP with Zn^{II}, Cd^{II}, and Hg^{II} in the range of 0.20–2 equivalents each as their chloride salts. The corresponding UV–vis titration curves have been shown in Figures 3a–3c.

Clear changes in the UV–vis absorption characteristics of PNTP as its DMSO solution on the addition of d^{10} metal ions can be noted from the above titration curves. The addition of Hg^{II} leads to a clear vanishing of the 575 nm peak of PNTP with the origin of a new peak at 436 nm and an isosbestic point at 418 nm. On the other hand the addition of Zn^{II} and Cd^{II} to PNTP under similar conditions lead only partial vanishing of 575 nm peak with the origin of a new peak at 446 and 483 nm respectively. The isosbestic points in these two cases were marked on 424 and 438 nm respectively. The occurrence of isosbestic points for all the three metal ions clearly proved their binding with PNTP and existence of only one species i.e., corresponding metal complexes at respective equilibria. Interestingly in all the cases the absorption peak of PNTP at 398 nm suffered a regular hypochromic shift on concomitant addition of 0.2–2 equivalents of Zn^{II}, Cd^{II}, and Hg^{II}. This very hypochromic shift in the 398 nm peak of PNTP was chosen for the calculation of the corresponding binding constants. Satisfactory results for the binding constants with the correlation coefficients over 0.99 were obtained (Table 1) for all three analytes. The nonlinear curve fitting of the titration data on 1:1 metal/ligand binding confirmed 1:1 host/guest ratio between PNTP with all the chosen metal ions. The binding constants (K_{ass}) and correlation coefficients (R) were obtained by a nonlinear least-squares analysis of A versus C_H and C_G using the following equation from the literature[22] in the ORIGIN 7.0 software:

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

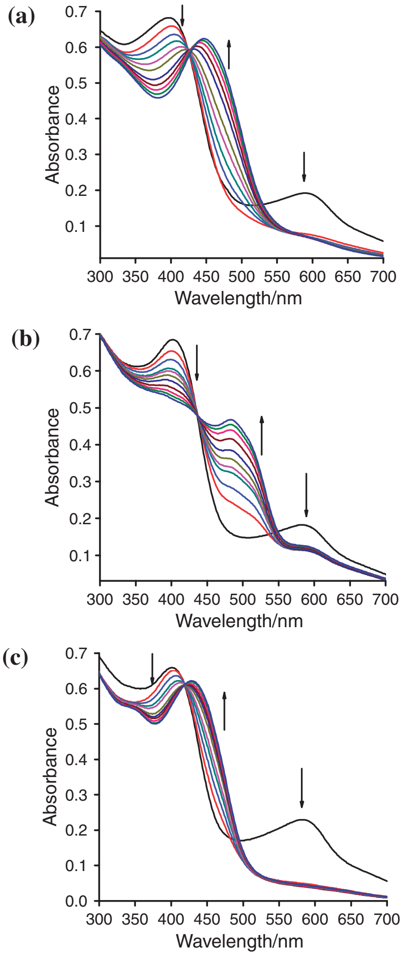

Figure 3. UV–vis titration curves of PNTP with d^{10} metal ions: (a) Zn^{II}, (b) Cd^{II}, and (c) Hg^{II}.

Table 1. Binding Constants K_a/M^{-1} of PNTP with Chosen Metal Ions

Cations[a]	K_a/M^{-1} [b]	R[c]
Zn^{II}	$1.38 \pm 0.24 \times 10^5$	0.99117
Cd^{II}	$2.28 \pm 0.42 \times 10^5$	0.99090
Hg^{II}	$6.09 \pm 1.25 \times 10^5$	0.99244

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

Where, A is the absorption intensity and C_H and C_G are the corresponding concentrations of the host and guest; C_0 is the initial concentration of the host. The corresponding results are listed in Table 1.

A perusal of the binding constants indicated the order of preference of PNTP among chosen metal ions as:

$$Hg^{II} > Cd^{II} > Zn^{II} \quad (2)$$

Since the guest species are the d^{10} metal ions hence the triazene unit of PNTP is expected to be the most susceptible site for their binding on the similar line of earlier literature reports.[23] The results of DFT calculations given in Table 2 categorically established that out of the various possibilities of the chelate formation the six-membered one is the most

Table 2. Total Energies and M–N Bond Lengths on the Basis of DFT Calculations for Various Possible MCl_2–PNTP Chelates

Chelate	Energy/au	Bond distances/Å	
Six membered	−3711.99977491	2.06690 (N_2–Zn)	2.13324 (N_{13}–Zn)
Five membered	−3711.99282258	2.01795 (N_8–Zn)	3.81824 (N_{11}–Zn)
Four membered	−3711.97998709	2.05321 (N_{13}–Zn)	3.12582 (N_{11}–Zn)

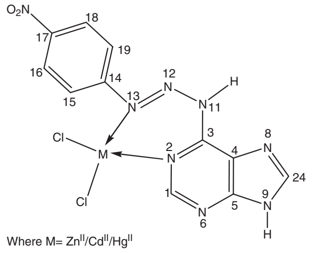

Figure 4. Chemical structure images of the d^{10} M^{II} ions on binding with PNTP.

preferred on the basis of its most negative total energy as well as the bond lengths of M–N(13) and M–N(2).

Hence the chemical structure images for the species of Zn^{II}, Cd^{II}, and Hg^{II} with PNTP may be given as shown in Figure 4. As it can be seen in Figure 4 that the chosen metal ions undergo binding with PNTP through two sites viz., N(13) and N(2) which belong to the triazene i.e., π unit (responsible for electron transfer from donor to acceptor) and purine (donor unit) respectively. Hence, the process of intramolecular charge transfer from purine (D) to *p*-nitrophenyl (A) through triazene is being affected which is responsible for the spectral and visible changes in PNTP described above and finally makes the basis for the naked-eye sensing of the selected metal ions under present study.

The highest affinity of PNTP for Hg^{II} may be understood in terms of its softest[24] nature among the chosen metal ions. On the other hand Zn^{II} and Cd^{II} are almost neck to neck with each other with a slight edge of Cd^{II}. The binding ability of the d^{10} metal ions evidenced by their respective binding constants (Table 1) seems to follow their relative softness.[24] The change of counter anions from chloride to sulphate or nitrate of the selected metal ions did not affect their binding characteristics with PNTP. The experimental details along with discussions regarding the sensing ability of PNTP towards a particular ion in the various possible sets of the mixtures of chosen metal ions have been given as the supplementary materials along with this communication.

Hence, the present communication establishes clearly that visible color changes and UV–vis spectral patterns along with binding constants distinguish the selectivity of PNTP towards chosen metal ions. The solution of PNTP is dark yellow in DMSO. Addition of Hg^{II} to the PNTP solution produced a yellow color which can be easily distinguished from those of Zn^{II} and Cd^{II}. Addition of Zn^{II} and Cd^{II} to the PNTP solution produced almost similar color (light orange) but their corresponding UV–vis spectral pattern is able to differentiate them on the basis of the appearance of a new peak at 446 and 483 nm respectively. At the same time the PNTP is a unique type of chemosensor having ability to bind with anions[16] and cations.

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Supporting Information

Competition experiments of PNTP with d^{10} metal ions. This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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