## p-Nitrophenyl Triazenyl Purine: First Adenine-based Colorimetric Anion Sensor

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6-[(2*E*)-3-(4-Nitrophenyl)triaz-2-en-1-yl]-9*H*-purine (*p*-nitrophenyl triazenyl purine, PNTP) has been synthesized and evaluated for sensing the anions  $PF_6^-$ ,  $HSO_4^-$ ,  $CIO_4^-$ , and  $BF_4^-$  as their tetrabutylammonium salts in DMSO. This is the first example of any adenine-based anion sensor. The addition of 2 equivalents of  $PF_6^-$ ,  $HSO_4^-$ ,  $CIO_4^-$ ,  $cIO_4^-$ , and  $BF_4^-$  to the  $2 \times 10^{-5} \text{ mol dm}^{-3}$  DMSO solution of PNTP at room temperature produced visible color changes and perturbation of UV–vis spectral pattern of PNTP in terms of absorbance at 398 and 575 nm in reciprocal patterns. The sensing ability of PNTP was found to be best for  $PF_6^-$  among all the chosen anions.

Anions play numerous indispensable roles in biological and chemical processes,<sup>1,2</sup> as well as contributing significantly to environmental pollution.<sup>3</sup> The majority of enzyme substrates and a good number of co-factors are anionic.<sup>4</sup> Anionic pollutants such as phosphate, nitrate, chromate, and dichromate lead to disruption of aquatic life cycles.<sup>5</sup> Radioactive pertechnate from the nuclear fuel cycle is also hazardous from the environment view point.<sup>6</sup> Hence, development of suitable anion sensors for the visual selection and quantification has been a matter of intensive and extensive research since 1968, when Park and Simmons<sup>7</sup> described the first synthetic receptor capable of encapsulating chloride anions. Since the decade of ninety of the last century, the chemical literature has witnessed an upsurge in the field of optical chemo sensing for the recognition of anions. Several review articles and a number of good papers appeared time to time in highly reputed journals describing latest development in this area.<sup>8-10</sup> The anion sensors which have been designed for the last decades ranged from polyamides,<sup>11</sup> urea-thiourea bases,<sup>12</sup> calixarenes,<sup>13</sup> hydrazone derivatives,<sup>14</sup> Ru<sup>III</sup> Schiff base complexes,<sup>15</sup> 8-hydroxyquinoline azo nitrobenzene, their transition-metal complexes,<sup>16</sup> etc. The anion sensor PNTP being reported under present communication is the first of its kind because no adenine-based colorimetric anion sensor has been reported in the literature so far. The adenine is an important constituent of nucleic



Scheme 1.

acid and since PNTP has been constructed upon it hence it may be considered as biofriendly molecule. Reactions of benzenediazonium ion with adenine<sup>17</sup> described under Scheme 1 made the basis for the designing of PNTP.

The diazo substitution on the amino group of adenine resulted into a downfield shift ca. 1 unit in the chemical shift value of exo and endo -NH- in comparison to adenine. Out of exo and endo -NH- the previous one i.e., the exo one is liable to get involved in intramolecular hydrogen bonding with N-7 atom of PNTP.<sup>17</sup> Thus, PNTP possesses a very good potential binder functionality for the anions in the form of imidazolic -NH- (endo -NH-) with the chemical shift value of 13.6 ppm. Presence of *p*-nitrophenyl, a signaling unit in PNTP further makes it suitable as a sensor in the light of recent literature report.<sup>18</sup> A possible chemical structure image of PNTP having binding with anion may be given as Figure 1.

The selected anions under present communication i.e.,  $HSO_4^-$ ,  $CIO_4^-$ ,  $BF_4^-$ , and  $PF_6^-$  as their tetrabutylammonium salts have their biological relevance.<sup>19</sup>

For the synthesis of PNTP the literature procedure was adopted.<sup>17</sup> This involved dissolution of *p*-nitroaniline (690 mg, 5 mmol) in hot distilled water (3 mL) followed by addition of conc. hydrochloric acid (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. This was followed by slow addition of cooled aqueous solution of sodium nitrite (370 mg, 5% excess) in 2 mL of distilled water. The temperature of the reaction mixture was kept at 0 °C during the addition process. The p-nitrobenzenediazonium salt solution was added drop wise to a solution of adenine (337.5 mg, 2.5 mmol) in 0.62 M sodium hydroxide (20 mL) at 0 °C. The pH was adjusted to 10-11 by the drop wise addition of sodium hydroxide. After the addition of NaOH, the solution was stirred for further 15 min. followed by neutralization to pH 7 with 0.5 M hydrochloric acid. The precipitate formed was filtered, washed thoroughly with chloroform, water, and methanol, and finally air-dried for few hours and ultimately stored in a refrigerator at low temperature. PNTP: mp 120 °C (decomposed); MS [M - H]: 283.3;  $IR/cm^{-1}$ : 3337, 3108, 2115, 1599, 1517, 1400, 1342, 1246, 1201, 1164, 1109, 940, 859, 752, 691, 642, 538; <sup>1</sup>HNMR: (DMSO-d<sub>6</sub>): 13.6 (1H) (Endocyclic -NH-); 8.6–7.3 (7H) (C<sub>2</sub>H and C<sub>8</sub>H, Ar-H + Exocyclic -NH-); UV-vis/nm (DMSO): 398, 575.



Figure 1. Chemical structure image of PNTP attached with anion.

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**Figure 2.** Absorption spectra of solutions containing PNTP  $(2 \times 10^{-5} \text{ mol dm}^{-3})$  and 2 equiv. of different anions in DMSO (300–700 nm).



**Figure 3.** Relative absorbance of solutions containing PNTP  $(2 \times 10^{-5} \text{ mol dm}^{-3})$  and 2 equiv. of different anions in DMSO at 398 (A) and 575 nm (B).

In order to study the binding of the chosen anions with PNTP the UV-vis spectrophotometric studies were performed. The addition of 2 equiv. of  $PF_6^-$ ,  $HSO_4^-$ ,  $CIO_4^-$ , and  $BF_4^-$  to the  $2\times 10^{-5}\,\text{mol}\,\text{dm}^{-3}$  DMSO solution of PNTP produced visible color changes. In each case the counter cation was tetrabutylammonium ion. The UV-vis spectra of the above solutions were recorded at the room temperature in the range 300-700 nm. In the absence of anions, the absorption spectrum of PNTP is characterized by the presence of two maxima at 398 and 575 nm respectively. The addition of anions produced hypochromic and hyperchromic shift at 398 and 575 nm respectively in the UV-vis spectrum of the DMSO solution of PNTP (Figure 2). However, the hyperchromic shift is much more pronounced as compared to hypochromic one as it is evinced through the histogram pattern of relative absorbance of PNTP at 398 and 575 nm in the presence of 2 equiv. of chosen anions (Figures 3a and 3b).

In order to establish the stoichiometry between the anion and the host the UV-vis spectral pattern of the  $2 \times 10^{-5}$  mol dm<sup>-3</sup> DMSO solution of PNTP was studied at 575 nm on the successive addition of 1-10 equiv. of the respective anions. The corresponding UV-vis spectral pattern for the complexation of PNTP with anions obtained from the absorption titration experiments showed a stoichiometry of 2:1 (anion/host) for oxy anions i.e., HSO<sub>4</sub><sup>-</sup> and  $ClO_4^-$  while 3:1 (anion/host) for non oxy anions i.e.,  $BF_4^-$  and PF6<sup>-</sup>. The difference in chemical structures of PNTP-non oxygenated anions (PF6- and BF4-) and PNTP-oxygenated anions (HSO<sub>4</sub><sup>-</sup> and ClO<sub>4</sub><sup>-</sup>) is again reflected in terms of DELTA absorbance of 10 (anion/host) which is 1.2 and 0.5 respectively which is nothing but a consequence of difference of electronegativity between central and surrounding atoms of the concerned anions. It is worth to mention that the spectral pattern of UV-vis titration of chosen anions showed two distinct patterns (Figure 4). For oxy anions only one maximum is observed while for non oxy anions two maxima are observed. Among the non oxy anions the pattern for  $PF_6^-$  is a bit different than  $BF_4^-$  (Figure 4). A perusal of increase in absorbance of  $2 \times 10^{-5}$  molar DMSO solution of PNTP



Figure 4. Absorbance changes of host PNTP  $(2 \times 10^{-5} \text{ M})$  monitored at 575 nm upon addition of (TBA)HSO<sub>4</sub>, (TBA)ClO<sub>4</sub>, (TBA)BF<sub>4</sub>, and (TBA)PF<sub>4</sub>.

at 575 nm on addition of 2 equiv. of different anions indicated following binding order among the anions.

$$PF_6^- > HSO_4^- > ClO_4^- > BF_4^-$$
 (1)

Hence,  $PF_6^-$  is most preferred by PNTP while  $BF_4^-$  is least preferred among the chosen anions. Thus, it may also be concluded at this stage that among the octahedral and tetrahedral anionic moieties it is the octahedral one ( $PF_6^-$ ) which is preferred over the tetrahedral ones ( $HSO_4^-$ ,  $CIO_4^-$ , and  $BF_4^-$ ) by PNTP. Among the tetrahedral ones the oxy anions i.e.,  $HSO_4^-$  and  $CIO_4^-$  are preferred over  $BF_4^-$ . This observation is just reverse to the basicity order of these three anions.<sup>20</sup>

Thus, the present communication reports synthesis, characterization and evaluation of *p*-nitrophenyl triazenyl purine (PNTP) for  $PF_6^-$ ,  $HSO_4^-$ ,  $CIO_4^-$ , and  $BF_4^-$ , as their tetrabutylammonium salt. All of them perturbed the UV–vis spectral pattern of the DMSO solution of PNTP in terms of absorbance and produced visible color changes. Among the chosen anions the response of  $PF_6^-$  was the best because the absorbance change in this case was maximum, almost 10 times to that of original value of PNTP at 575 nm. At the same time the visible color change also was most intense for this very anion.

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