REGULAR ARTICLE

Hydrazone derivatives appended to diphenylphosphine oxide as anion sensors

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Abstract. Phosphine substituted hydrazones with or without nitro substituents were synthesized and characterized by multinuclear NMR, FT-IR, UV-Vis spectroscopy and single crystal X-ray diffraction. The anion recognition properties of phosphine oxides $\{Ph_2P(O)C_6H_4CHNNHPh\}$ (**2**) and $\{Ph_2P(O)C_6H_4CHNNHC_6H_3(2,4-NO_2)_2\}$ (**4**) with anions (F^-, Cl^-, Br^-, I^-, CH_3COO^- and $H_2PO_4^-$) were investigated. The selectivity towards these anions is attributed to the hydrogen bonding capability of the NH bond. Competitive titrations have shown that the binding ability of fluoride with **4** is not influenced by the presence of other anions.

Keywords. Hydrazones; phosphine oxides; anion recognition; colorimetric sensing.

1. Introduction

Anions play a major role in day-to-day life. However, over-accumulation of some of the biologically important ions such as fluoride, acetate and phosphate leads to various metabolic disorders.[1] For example, change in the fluoride ion level causes fluorosis, nephrolithiasis and kidney failure and acetate ion accumulation leads to tissue damage. Efforts are being made to find inexpensive, rapid, reliable and simple methods to detect these ions in solution.[2] Considerable efforts have been devoted to expand the library of molecules which can change one or more of their properties such as color (colorimetric),[2a] fluorescence (fluorescent)[2a,3] or redox potentials (electrochemical)[4] when subjected to analytes. These molecules have an intrinsic key design element for selective binding to analytes through hydrogen bonding or aurophilic interactions. Colorimetric anion detection is of particular interest which would allow detection by the naked eye without resorting to any analytical instrumentation.[5a−e] In the absorption spectra of colorimetric chemosensors, a bathochromic or hypsochromic shift is usually accompanied by a visual color change.[2c,6]

Chemosensors which exploit hydrogen bonding capability should have suitable H-bonding moieties like -OH and –NHR (NH$_2$) groups. The main problem with recognition studies is that water cannot be used as a medium. Thus, artificial neutral receptors typically containing one or more NH fragments and their interactions with anions must be investigated in aprotic solvents like CHCl$_3$, CH$_3$CN, and dimethylsulphoxide (DMSO).[6a,7] Generally, phenols,[8] amides,[9] urea,[10] guanidine,[11] and pyrroles,[12a] are reported to be good hydrogen bond donors and have been studied extensively. Hydrazones with the >C=N-NH-C< skeleton are preferred due to their modularity, easy synthesis, and stability towards hydrolysis.[12b] The tendency of the acidic NH proton to form hydrogen bonding is used for sensing applications.[6a,13] Molecules such as anthracene,[8,14] indole,[15] salicylaldehyde,[13c] pyrene,[16] terpyridine,[17] and calixarene,[18] containing hydrazone moiety have been employed in anion recognition studies. However, phosphine derivatives despite several of them showing remarkable flexibility towards oxidation, quaternization and metallation have not been explored for anion recognition studies.[19] As a continuation of our interest in designing novel phosphorus based ligands for photophysical studies[20] and catalytic applications,[21] herein we report the utility of phosphine oxide-appended hydrazone-based chemosensor with good association constants for the recognition of fluoride, acetate and dihydrogen phosphate anions. Details on the effect of water on anion recognition are also included.

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2. Experimental

2.1 *General*

Phenylhydrazine, 2,4-dinitrophenylhydrazine (DNPH), tetra-butylammonium salts were purchased from Aldrich and used without further purification. 2-Diphenylphosphinobenzaldehyde, $Ph_2PC_6H_4CHNNHPh$ (**1**)[22a] and $Ph_2PC_6H_4CHNNHC_6H_3(2,4-NO_2)_2$ (**3**)[22b] were synthesized according to the published procedures. The NMR spectra were recorded at the following frequencies: 400 MHz (^{1}H), 162 MHz (^{31}P) and 100 MHz (^{13}C) using Bruker AV 400 spectrometer. The spectra were recorded in $CDCl_3$ (or DMSO-d_6) solutions with $CDCl_3$ (or DMSO-d_6) as an internal lock; chemical shifts of ^{1}H and ^{13}C NMR spectra are reported in ppm downfield from tetramethylsilane (TMS), used as an internal standard. The chemical shifts of ^{31}P NMR spectra are referred to 85% H_3PO_4 as external standard. The microanalyses were performed using Carlo Erba Model 1112 elemental analyzer. Mass spectra were recorded using Waters Q-Tof micro (YA-105). The melting points were observed in capillary tubes and are uncorrected. Absorption spectra were recorded with a Perkin-Elmer Lambda-35 spectrometer manufactured by ISS, USA instruments.

2.2 *Synthesis*

2.2a Synthesis of {$Ph_2P(O)C_6H_4CHNNHPh$} (2): An aqueous solution of hydrogen peroxide (30%) (0.0065 mL, 0.0574 mmol) was added dropwise to a solution of {$Ph_2PC_6H_4CHNNHPh$} (**1**) (0.017 g, 0.044 mmol) in THF (20 mL) at room temperature and the mixture was stirred for six hours. After evaporating the solvent under reduced pressure, the product was extracted with chloroform and dried with Na_2SO_4. The solvent was evaporated and the residue obtained was washed with petroleum ether and dried under vacuum to yield an analytically pure product of **2** as a yellow solid. Yield: 79% (0.014 g). M.p.: 169–172°C. Anal. Calcd. for $C_{25}H_{21}N_2PO$: C, 75.74; H, 5.34; N, 7.07%. Found: C, 75.31; H, 5.19; N, 6.89%. ^{31}P{^{1}H}NMR ($CDCl_3$): δ 36.8 (s).^{1}H NMR ($CDCl_3$): δ 8.90 (s, NH, 1H), 8.45 (d, 1H, $^4J_{HH}$ = 2.2 Hz), 7.64–6.83 (m, 19H, ArH). ^{13}C NMR ($CDCl_3$): δ 144.4, 139, 136.4, 135.7, 134.0, 133.8, 132.1, 132.0, 129.2, 129.0, 128.8, 128.7, 128.6, 128.3, 125.8, 120.0, 112.7. ^{1}H NMR (DMSO-d_6): δ 11.50 (s, NH, 1H), 8.35 (d, 1H, $^4J_{HH}$ = 2.8 Hz), 7.64-6.83 (m, 19H, ArH). IR (KBr): $\nu_{(C=N)}$ 1603, $\nu_{(N-H)}$ 3054 cm^{-1}. HRMS (ESI, m/z) (M+ Na) found 419.1284, $C_{25}H_{21}N_2PONa$ requires 419.1284.

2.2b Synthesis of {$Ph_2P(O)C_6H_4CHNNHC_6H_3(2,4-NO_2)_2$} (4): An aqueous solution of H_2O_2 (30%) (0.0065 mL, 0.0574 mmol), was added dropwise to a solution of {$Ph_2PC_6H_4CHNNHC_6H_3(2,4-NO_2)_2$} (**3**) (0.021 g, 0.044 mmol) in THF (15 mL) at room temperature and the mixture was stirred for 6 h. After evaporating the solvent, the product was extracted with chloroform and dried with Na_2SO_4. The solvent was evaporated and the residue obtained was washed with petroleum ether and dried under reduced pressure to yield an analytically pure product of **4** as a yellow solid. Yield: 85% (0.018 g). M.p.: 241–243°C. Anal. Calcd. for $C_{25}H_{19}N_4O_5P.H_2O$: C, 59.52; H, 4.19; N, 11.11%. Found: C, 59.29; H, 4.51; N, 11.36%. ^{31}P{^{1}H}NMR ($CDCl_3$): δ 38.8 (s). ^{13}C NMR ($CDCl_3$): δ 145.3, 145.2, 144.4, 135.1, 135.0, 134.7, 134.6, 132.6, 132.1, 131.1, 130.4, 129.8, 129.7, 129.1, 128.6, 123.4, 117.1. ^{1}H NMR ($CDCl_3$): δ 11.25 (s, NH, 1H), 9.10 (d, 1H, $^4J_{HH}$ = 2.6 Hz), 8.718 (d, 1H, $^3J_{HH}$ = 5.7 Hz), 8.20 (dd, 1H, $^3J_{HH}$ = 2.6 Hz,$^3J_{HH}$ = 9.6 Hz), 7.99 (dd, 1H, $^3J_{HH}$ = 4.0 Hz,$^3J_{HH}$ = 7.1 Hz), 7.72 (d, 1H, $^3J_{HH}$ = 9.6 Hz), 7.75–7.27 (m, 4H, ArH), 6.98 (dd, 1H, $^3J_{HH}$ = 4.3 Hz,$^3J_{HH}$ = 7.7 Hz). ^{1}H NMR (DMSO-d_6): δ 11.77 (s, NH, 1H), 9.18 (d, 1H, $^4J_{HH}$ = 4.0 Hz), 8.81 (d, 1H, $^3J_{HH}$ = 2.6 Hz), 8.23 (dd, 1H, $^3J_{HH}$ = 2.6 Hz,$^3J_{HH}$ = 9.6 Hz), 8.01 (d, 1H, $^3J_{HH}$ = 4.0 Hz). IR (KBr): $\nu_{(C=N)}$ 1618, $\nu_{(N-H)}$ 2927, $\nu_{(NO2)}$ 1525 and 1333 cm^{-1}. HRMS (ESI, m/z) (M) found 487.1169, $C_{25}H_{19}N_4O_5P$ requies 487.1166.

2.3 *X-ray Crystallography*

Crystals of each of the compounds in the present work suitable for X-ray crystal analysis were mounted on a Mitegen loop with a drop of paratone oil and placed in the cold nitrogen stream of the Oxford Cryostream attachment of the Bruker D8 Venture diffractometer. Hemispheres of data were collected with 0.5° ω scans under the control of the APEX2 program suite. The raw data were reduced to F[2] values using the SAINT+ software and a global refinement of unit cell parameters using *ca*. 6058–9823 reflections chosen from the full data sets were performed. Multiple measurements of equivalent reflections provided the basis for an empirical absorption correction as well as a correction for any crystal deterioration during the data collection (SADABS).[23] The structures of **3** and **4** were solved by direct methods. Hydrogen atoms attached to carbon were placed in calculated positions while those attached to nitrogen were placed in locations derived from difference maps and their coordinates adjusted to give N–H = 0.90 Å. All were included as riding contributions with isotropic displacement parameters tied to those of the attached non-hydrogen atoms. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1440702 (compound **3**), 1440703 (compound **4**).

3. Results and Discussion

3.1 *Synthesis*

The reaction of 2-diphenylphosphinobenzaldehyde with phenylhydrazine or 2,4-dinitrophenylhydrazine in ethanol under refluxing conditions produced compounds **1** and **3** in 76 and 92% yield, respectively, as microcrystalline solids as shown in Scheme 1. The corresponding oxide derivatives were obtained by treating
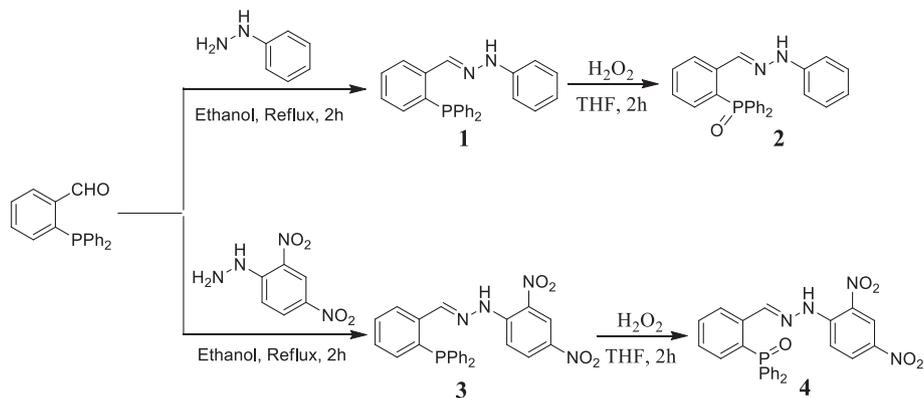
Scheme 1. Synthesis of compounds **1**–**4**.

1 and **3** with hydrogen peroxide in tetrahydrofuran at room temperature. Compounds **1**–**4** were characterized by mass spectrometry, IR and conventional multinuclear NMR techniques. The ^{31}P{^{1}H}NMR spectra of **1** and **3** showed single resonances at -12.8 and -12.2 ppm, whereas the corresponding oxides **2** and **4** showed single resonances at 36.8 and 38.8 ppm, respectively.

The ^{1}H NMR spectra of compounds **2** and **4** were recorded in both CDCl$_3$, a hydrogen bond donating solvent (HBD) and DMSO-d_6, a hydrogen bond accepting solvent (HBA) and are shown in Figure 1. In the ^{1}H NMR spectrum of **2** in CDCl$_3$, the imine CH proton appeared as a doublet at 8.37 ppm, whereas the NH proton appeared as a singlet at 8.64 ppm. Similarly, the ^{1}H NMR spectrum of **4** in CDCl$_3$ showed a doublet at 9.1 ppm for the imine CH proton. The change of 2.6 ppm shift of the NH proton for **4** (singlet

at 11.2 ppm) when compared to **2** (8.6 ppm) confirms the presence of strong intramolecular hydrogen bonding between NH and NO$_2$ groups in **4**. The ^{1}H NMR spectra recorded in DMSO-d_6 for compounds **2** and **4** were found to be similar except for the NH proton which underwent a downfield shift in both the cases compared to that recorded in CDCl$_3$. The chemical shift due to the NH proton in compound **2** appeared at 8.6 ppm in CDCl$_3$, whereas in DMSO-d_6 it was shifted to 10.6 ppm with a 2 ppm downfield shift and similar trends were observed in the case of compound **4** as well. Additionally, when the solvent was changed from CDCl$_3$ to DMSO-d_6, the magnitude of the downfield shift of the NH proton was much larger for **2** compared to that of **4** (Figure 1). This is due to the strong intermolecular hydrogen bonding interaction present between the hydrazone NH of **2** and the oxygen atom of the solvent. On the other hand, hydrazone NH in **4** being
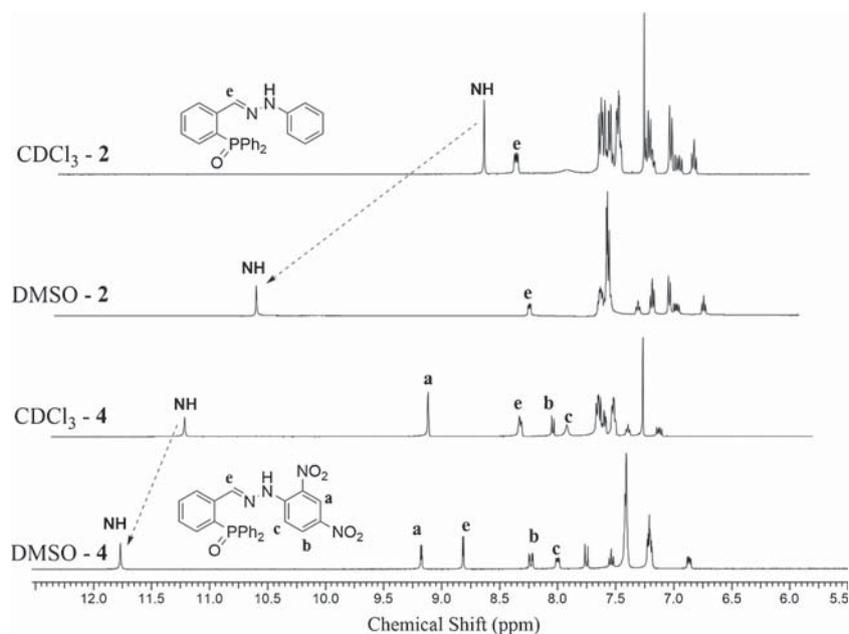
Figure 1. Comparison of ^{1}H NMR spectra of compounds **2** and **4** in CDCl$_3$ and DMSO-d_6.
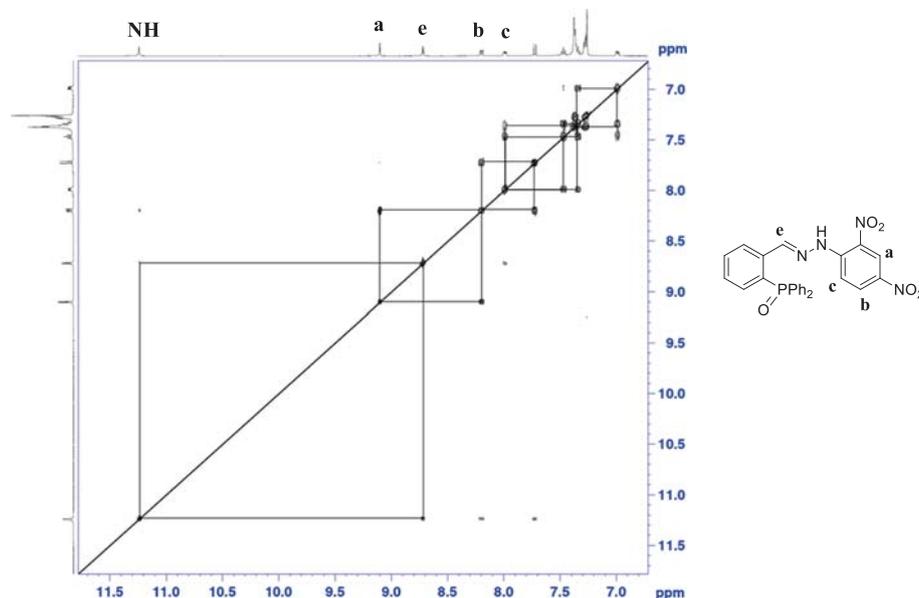
Figure 2. ^{1}H–^{1}H correlation spectrum of compound **4** in CDCl$_3$.

already engaged in intramolecular hydrogen bonding with the NO$_2$ group, showed only an additional down-field shift of 0.5 ppm. The specific signal assignments for **4** were carried out by recording the ^{1}H–^{1}H COSY NMR spectrum (Figure 2).
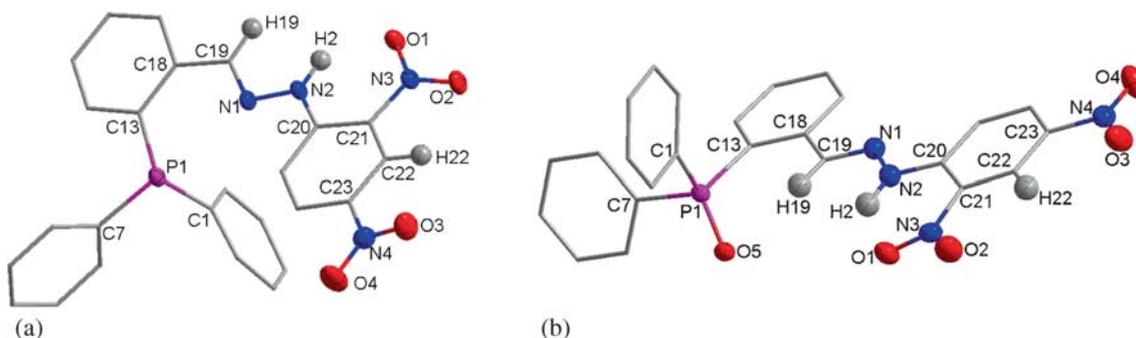
3.2 *Molecular structures of 3 and 4*

The single crystals suitable for X-ray diffraction studies were obtained by slow diffusion of petroleum ether into chloroform solutions of **3** and **4** at room temperature. Perspective views of the molecular structures of **3** and **4** with the atom numbering schemes are shown in Figure 3. The crystallographic data and the details of the structure determination are given in Table S1 (in Supplementary Information), while the selected bond lengths and bond angles are listed in Table 1. Compound **3** crystallized with a chloroform molecule, whereas **4** included a water molecule in the lattice. No significant differences were observed in bond parameters of **3** and **4**.

The imine NH is involved in intramolecular hydrogen bonding interaction with the oxygen of the *ortho*-substituted nitro group as evidenced by the bond distances (O1-H2) of 1.9708(14) Å and 1.994(12) Å for **3** and **4**, respectively, which probably play a crucial role in the planarization of the benzylidene fragment of the molecule. The dihedral angles (C19-N1-N2-C20) 171.40(18)° and 177.75(15)° of **3** and **4**, respectively, indicate the planar arrangement of hydrazone units. The C-P-C angles in both **3** and **4** are in the range of 98.86(9)° to 107.26(8)°, confirming the tetrahedral geometry around phosphorus atom.

3.3 *Photophysical properties of 2 and 4*

The UV-Vis spectral behavior of compounds **2** and **4** examined in solvents of varying polarity are presented in Figure 4 and Table 2. Compound **4**, due to the presence of two nitro units which lead to more π-delocalization, absorbs at a longer wavelength than **2**.

Figure 3. Molecular structures of compounds **3** and **4**. Some of the hydrogen atoms have been omitted for clarity.

Table 1. Selected Bond lenghts (Å) and Bond angles (°) of compounds **3** and **4**.

	Bond length (Å)			Bond angles (°)	
	3	**4**		**3**	**4**
N1-N2	1.379(2)	1.369(2)	C1-P1-C13	101.74(9)	107.1(8)
N1-C19	1.278(3)	1.274(2)	C19-N1-N2	115.64(16)	115.92(15)
N2-C20	1.356(2)	1.355(2)	C20-C21-N3	121.89(17)	122.30(16)
N3-O1	1.242(2)	1.242(2)	C20-N2-N1	118.59(16)	118.27(15)
N3-O2	1.231(2)	1.224(2)	N2-H2-O1	127.99(11)	127.99(11)
O1-H2	1.9708(14)	1.994(12)	C22-H22-O2	98.33(12)	98.33(12)
O2-H22	2.3451(14)	2.3316(15)	C1-P1-O5	–	113.47(7)
O3-H22	2.4351(17)	2.4304(17)			
O5-H19	–	2.5729(14)			
P1-O5	–	1.4961(12)			
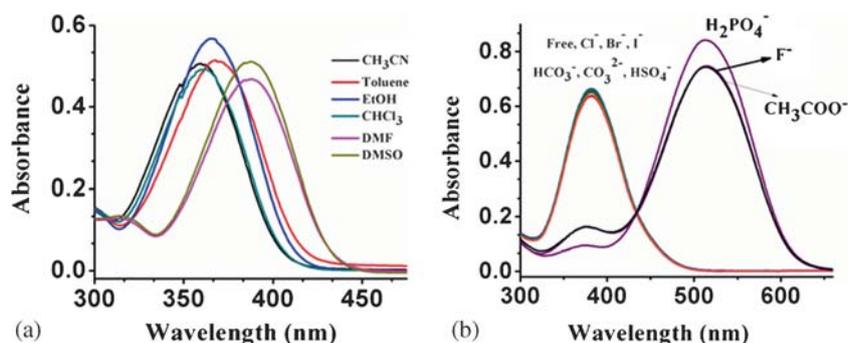
Figure 4. Absorption spectra of **4** (2×10^{-5} M): (a) in various solvents, and (b) in the presence of various anions (50 equivalents) in CH_3CN.

Table 2. The photophysical data for compounds **2** and **4** in different solvents.

| Solvent	Dielectric constant	**2**			**4**		
		λ_{abs} (nm)	$\log (\varepsilon_{max}/M^{-1}cm^{-1})$	FWHM (nm)	λ_{abs} (nm)	$\log (\varepsilon_{max}/M^{-1}cm^{-1})$	FWHM (nm)
Toluene	2.4	366	4.65	56	382	4.82	72
Chloroform	4.8	363	4.69	56	380	4.91	73
Ethanol	24.5	371	4.70	57	377	4.87	76
Acetonitrile	37.5	360	4.70	49	379	4.90	73
DMF	36.7	372	4.70	59	394	4.86	79
DMSO	46.7	372	4.67	59	396	4.83	80

Also, a slight bathochromic shift was observed in the absorption band in compounds **2** and **4** in hydrogen bond accepting solvents such as DMSO and dimethyl-formamide (DMF). Absorption bands obtained at 363 and 380 nm for **2** and **4**, respectively, in $CHCl_3$ are bathochromically shifted by 9 and 16 nm in DMSO (Table 2). Similar to the NMR experiments, compound **4** experienced slightly larger red shift than **2** when the solvent was changed from $CHCl_3$ to DMSO (Figure 4a). Hydrogen bonding interactions between the NH group and the solvent resulting in the reduction of the HOMO–LUMO gap thereby stabilizing the energy states is the main reason for the red shifts observed for **2** and **4** in DMSO/DMF. The larger red

shift observed for compound **4** supports the stronger hydrogen bonding interaction between the solvent and compound **4**.

3.4 *Chemosensing applications*

Chromophores substituted with dinitrophenylhydrazone units have been extensively explored for anion binding studies. High selectivity is a prerequisite for an excellent chemosensor. In order to test the ability of compounds **2** and **4** to sense anions such as F^-, Cl^-, Br^-, I^-, N_3^-, NO_3^-, HSO_4^-, ClO_4^-, HPO_4^{2-}, $H_2PO_4^-$, HCO_3^-, CH_3COO^-, qualitative analyses were carried out by adding excess of anions to **2** and **4** in CH_3CN with
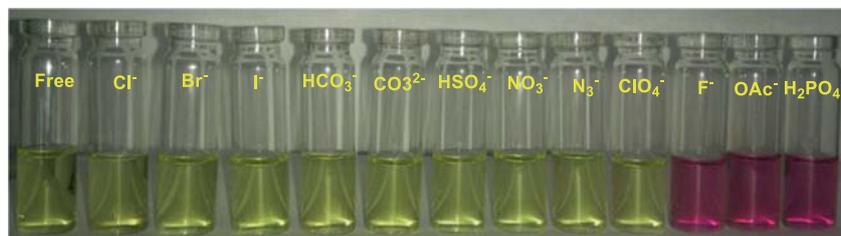
Figure 5. Visual changes upon addition of two or more equivalents of various anions (as tetrabutylammonium salts) to sensor **4** (2×10^{-5} M) in acetonitrile.
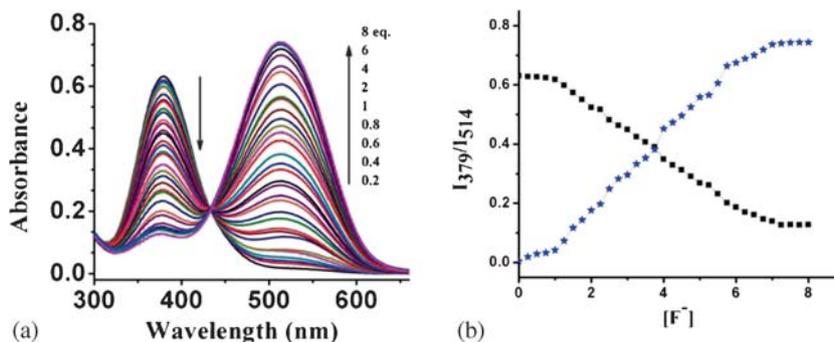

Figure 6. (a) Absorption spectra of receptor **4** (2×10^{-5} M) with different concentrations of F^- (TBAF) (0–8 equivalents) in CH_3CN. Arrows indicate the direction of increasing anion concentration. (b) A plot of I_{379} and I_{514} (data shown in 'a') *vs.* $[F^-] \times 10^{-6}$ M.

parallel monitoring of the changes using absorption spectroscopy. The spectrum of compound **2** remained unchanged upon addition of 50 equivalents of anions (F^-, Cl^-, Br^-, I^-, $H_2PO_4^-$, CH_3COO^-). This indicated very weak or no interaction between compound **2** and these anions and hence, further systematic anion sensing experiments were not carried out.

The addition of F^-, CH_3COO^- and $H_2PO_4^-$ ions to compound **4** led to the change in the color of the solution from yellow to pink, thus enabling detection by the naked eye, whereas no color change was observed in the presence of other anions (Figure 5). Concomitantly, the addition of F^-, CH_3COO^- and $H_2PO_4^-$ ions to **4** resulted in a remarkable bathochromic shift (160 nm) in the absorption maxima while other anions listed above did not show any change in the absorption peak maximum. This indicated that compound **4** acts as an optical sensor for F^-, CH_3COO^- and $H_2PO_4^-$ ions (Figure 5) and hence, the absorption spectral titration of compound **4** with increasing amounts of F^-, CH_3COO^- and $H_2PO_4^-$ ions was carried out. The systematic changes in the UV spectrum of receptor **4** on addition of increasing amounts of tetrabutylammonium fluoride (TBAF) in CH_3CN are shown in Figure 6(a). The addition of F^- to CH_3CN solution of **4** resulted in gradual disappearance of the absorption band at 379 nm with

concomitant appearance of a new band at 514 nm and a clear isosbestic point at 433 nm indicating that receptor **4** acts as an F^- sensor in solution. This was also clearly evident in the plot which shows the changes in the absorption bands at 379 and 514 nm versus the amount of F^- ion (Figure 6(b)). Similar absorption spectral changes with clear isosbestic points were also noted for the systematic addition of CH_3COO^- (Figure S1(a) in SI) and $H_2PO_4^-$ (Figure S1(b) in SI) ions to receptor **4** supporting the conclusion that compound **4** also acts as a sensor for these two anions.

The initial hydrogen bonding interaction and then the removal of the NH proton of the dinitrophenylhydrozone group by F^-, CH_3COO^- and $H_2PO_4^-$ ions may be the reason for large bathochromic shifts of the absorption maximum of receptor **4**.[11] This kind of interaction results in increasing the electron density on nitrogen. Further delocalization of electron density from the nitrogen to the dinitrophenyl groups leads to a more stable structure. Thus, the rearrangement of electrons in the whole molecule takes place with π-electron delocalization being extended all over the molecule, resulting in substantial red shift. A Job plot analysis of sensor **4** with F^- interaction supports the 1:1 binding stoichiometry (Figure 7). Similar isosbestic points in the range of 426–447 nm were obtained for CH_3COO^- and $H_2PO_4^-$
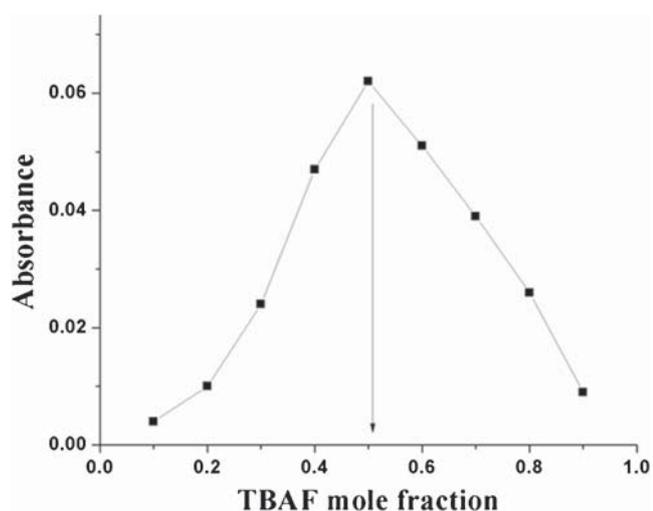
Figure 7. Job's plot of **4** (at 514 nm) with TBAF. The total concentration of the host and guest is 1.0×10^{-4} mol L^{-1} in CH$_3$CN.

anions. The binding ability of receptor **4** with acetate is the strongest among the studied anions. However, on the basis of equilibrium or pKa values, F$^-$ is needed in a slightly larger concentration than CH$_3$COO$^-$ for binding with the receptor.

The nature of the interaction between the analytes and receptor **4** was confirmed by performing ^{1}H NMR titration in DMSO. The spectral changes on addition of TBAF are presented in Figure 8. On gradual increment of F$^-$ ion concentration, complete disappearance of the

NH signal at 11.5 ppm was observed supporting the deprotonation mechanism. Removal of NH proton by anions increases the electron density which is delocalized in the 2,4-dinitrophenyl moiety thereby making the entire molecule electron-rich. This creates a shielding effect leading to upfield shifts of protons near the anion binding site, for example, H^a (Figure 8). Also, negligible shifts were observed for other protons which are distant from the anion binding site. Thus, through ^{1}H NMR titration studies, it is ascertained that NH was involved in binding with F$^-$ ion and the subsequent deprotonation will increase the electron density through delocalization in the molecule leading to a large red shift of the absorption band and upfield shifts in the ^{1}H NMR spectrum.

In order to study the selective binding ability of fluoride ion towards **4** in the presence of other anions, the UV–Vis spectral interference experiment was carried out (Figure 9). The spectral response of **4** upon the addition of a mixture of anions is almost the same as the addition of only F$^-$ ions, clearly indicating the selectivity of receptor **4** for F$^-$ anions. Owing to the hydrogen bonding interaction, the recognition and/or sensing of the anions was performed in noncompetitive organic solvents such as acetonitrile and DMSO.[24] In aqueous solution, the hydrogen bonding interaction between the hydrazone and analytes was significantly weakened due to the presence of competing water molecules. Figure 10 shows the absorption response of
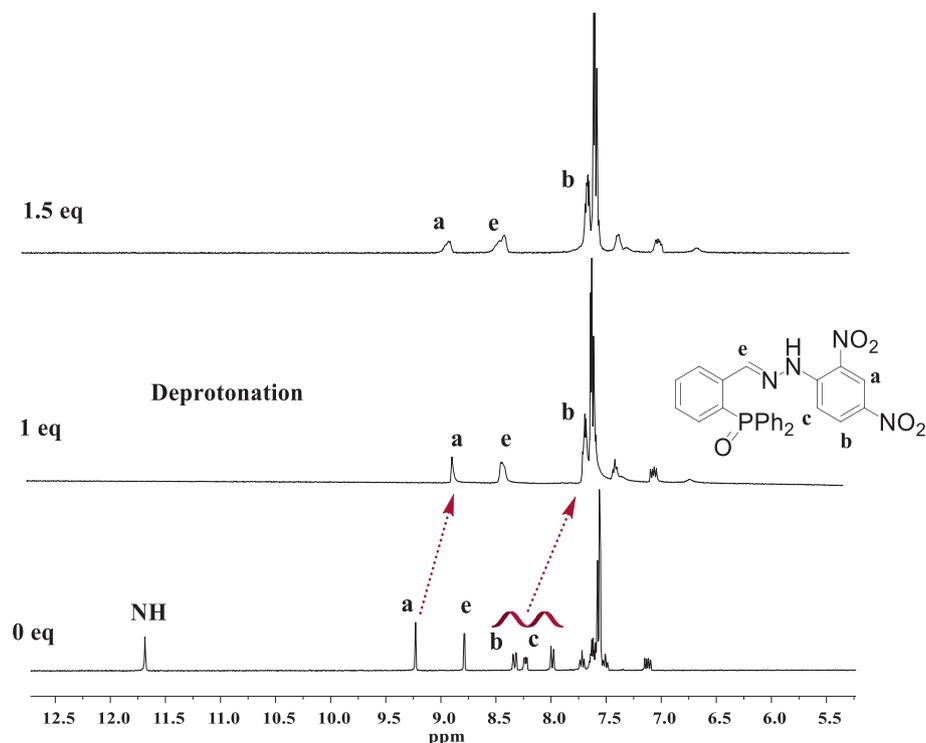
Figure 8. Partial ^{1}H NMR spectrum of receptor **4** (2×10^{-5} M) in the presence of 1.5 equivalents of F$^-$ ion in DMSO-d_6.

receptor **4** in the presence of 50 equivalents of various anions in CH$_3$CN/water (9/1) system. Addition of water molecules disturbs the hydrogen bonding and thus a very small change in the absorption spectra was observed as compared to that in CH$_3$CN solution.

Since water has a considerable effect, it is necessary to study the effect of its content on the stability of the host-guest complex. In order to asses this, to a
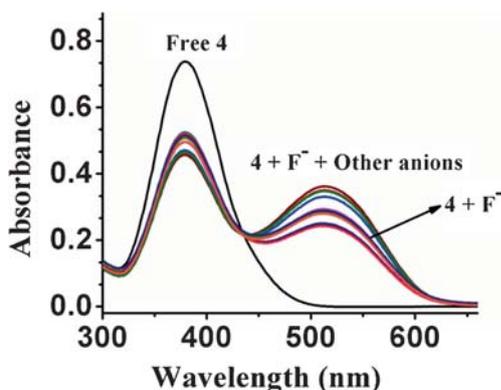

Figure 9. Absorption spectra of receptor **4** for competitive titration in presence of four equivalents of F$^-$ ions and various other anions (50 equivalents) in CH$_3$CN.

2×10^{-5} M solution of **4** in CH$_3$CN, ten equivalents of TBAF was added (hereafter this solution is referred as **4-F$^-$**). The systematic addition of water led to visible color change and the corresponding absorption spectral changes are shown in Figure 11. When 1% water was added to the **4-F$^-$** system, which was obtained upon treatment of **4** with 10 equivalents of fluoride ion in acetonitrile, the absorption spectrum resembled to that of **4** indicating that the hydrogen bonding interactions were disrupted by water molecules (Scheme 2). In the presence of water molecules, the **4-F$^-$** complex was no longer stable and, upon dissociation of the F$^-$ ions, free **4** was restored indicating the possible utility of **4-F$^-$** as a potential sensor for the determination of water content.[25] Hydroxide ions are also potential hydrogen bond facilitators similar to water molecules. The absorption spectra of receptor **4** when titrated with various concentrations of tetrabutylammonium hydroxide are depicted in Figure 10b. Similar to F$^-$, CH$_3$COO$^-$ and H$_2$PO$_4^-$, hydroxide (OH$^-$) ions also show gradual increase in the absorbance at 514 nm and gradual decrease in the absorbance at 379 nm.

Even though only the hydrazone unit is involved in the mechanism of anion recognition, the phosphine
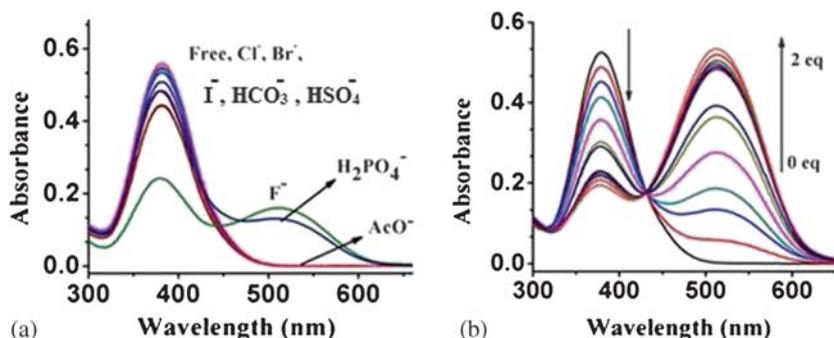
Figure 10. (a) Absorption spectra of receptor **4** (5×10^{-6} M), in presence of various anions in 9:1 CH$_3$CN/H$_2$O system. (b) Absorption spectra of receptor **4** with different concentrations of tetrabutylammonium hydroxide solution in CH$_3$CN.
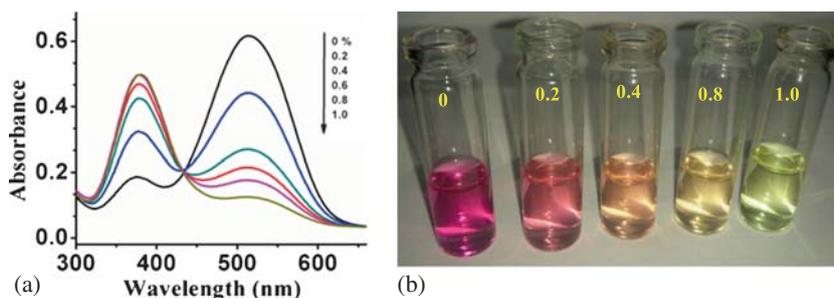
Figure 11. The changes in the absorption spectrum of the **4-F$^-$** system as a function of water content. (a) Absorption response of **4-F$^-$** to addition of water. (b) Photograph showing the color changes on addition of water.
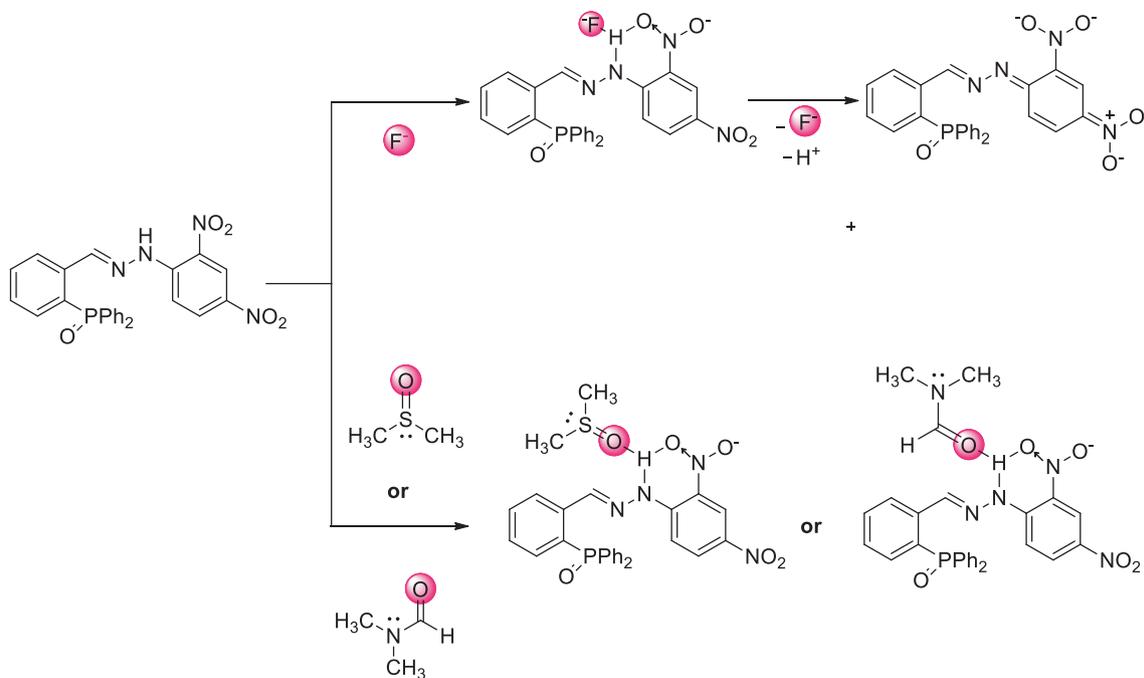
Scheme 2. Intermolecular hydrogen bonding interaction of compound **4** with fluoride anion and solvents.

moieties in **1**–**4** could lead to the use of such molecules in a wide spectrum of applications. Compounds **1** and **3** with soft phosphorus atoms along with the imine nitrogen are potential ligands for forming chelate complexes. The platinum group metal complexes formed with such ligands have the added advantage due to the availability of NH group in close proximity to the P atom that it can perform as a proton sponge during various steps of catalytic processes. Also, compounds with P=O moiety can coordinate to inner transition metals such as lanthanides. The lanthanide complexes are generally luminescent and one of their applications being chemosensing for halides and HCO_3^-, cations like Zn^{2+}, and chiral molecules.[26] The exploration of transition and inner transition metal chemistry of **1**–**4** which enhances their ability for various applications is under study.

4. Conclusions

The anion recognition property of the hydrazone substituted phosphine oxides $\{Ph_2P(O)C_6H_4CHNNHPh\}$ (**2**) and $\{Ph_2P(O)C_6H_4CHNNHC_6H_3(2,4\text{-}NO_2)_2\}$ (**4**) with biologically important anions (F^-, Cl^-, Br^-, I^-, CH_3COO^- and $H_2PO_4^-$) have been studied by UV–Visible and ^1H NMR titration experiments. The introduction of NO_2, a colorimetric group along with electron-withdrawing effect, strengthens the binding ability of receptor **4** with anions. Compound **2** without NO_2 shows no interaction with studied anions.

The interaction of the artificial receptors with F^-, CH_3COO^- and $H_2PO_4^-$, causes the visible color change which makes the receptor **4** as colorimetric sensor. The colorimetric properties of these sensors are ascribed to the hydrogen bond formation and to the colorimetric nitro group. In addition, the binding ability of fluoride with receptor is not influenced by the existence of other anions. We have made several transition metal complexes of both phosphine and phosphine-oxide derivatives to look into the influence of metals ions on anion recognition properties including the reversibility. The details will be published in due course.

Supplementary Information (SI)

Crystallographic information of compounds **3** and **4**, absorption spectra, NMR (^1H, ^{31}P and ^{13}C) and IR spectra for compounds **1**–**4** are provided. The Supplementary Information is available at www.ias.ac.in/chemsci.

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