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GRAPHICAL ABSTRACT

Dipicrylamine as Colorimetric Sensor for Anions: Experimental and Computational Study

Ravi Gunupuru, Manoj K. Kesharwani, Ashish Chakraborty, Bishwajit Ganguly, Parimal Paul

Text for table of content:

Dipicrylamine exhibited bared-eye detectable colorimetric sensing of F^-, OAc^- and $H_2PO_4^-$, out of a large number of anions. Interestingly, F^- binds with one of the phenyl carbon of dipicrylamine.

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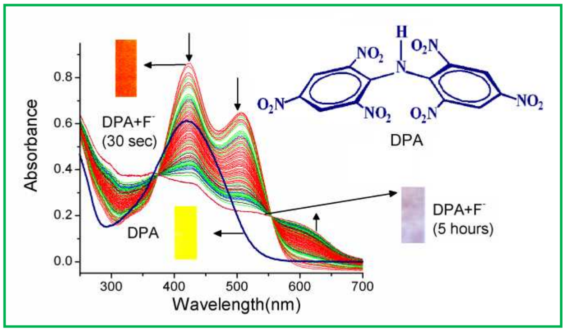

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ARTICLE

Dipicrylamine as Colorimetric Sensor for Anions: Experimental and Computational Study†

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Dipicrylamine (2,4,6-2',4',6'-hexanitrodiphenylamine, DPA) has been used for detection and extraction of metal ions, especially potassium, however its capability as anion sensor has not been reported so far. It contains a secondary amine (N-H), the proton of which can make H-bonding with anions and this property has been exploited to investigate the capability of DPA as anion sensor. Out of a large number of anions used for this study, F^-, OAc^-, $H_2PO_4^-$ exhibited strong interaction with sharp colour change in acetonitrile. The DPA-anion recognition event was monitored by UV-vis, NMR and ESMS studies, apart from distinct colour change, detectable by bared-eye. Detail investigation revealed that the anions first interact with the N-H proton through H-bonding and then deprotonation takes place forming DPA^--TBA^+ (tetrabutylammonium) complex. The rate constants of these complex formation have been determined from time dependent UV-vis spectral change and the order of the observed rate constants is $F^- > OAc^- > H_2PO_4^-$. For F^-, the NMR and ESMS data indicated the interaction of F^- with one of the carbon or its attached proton of one of the benzene rings. Computational study suggests that F^- ion binds with one of the phenyl carbon instead of the –CH hydrogen of DPA^-.

Introduction

The development of optical sensors for selective recognition of anions is an emerging area in chemistry, as anions play important role in many chemical and biological processes.[1] In recent years, special attention has given to anions such as fluoride, phosphate, acetate, etc.[2] Fluoride has been considered by the US National Academy of Science as an essential nutrient, daily intake of 1-3 mg of fluoride prevents dental caries,[2g] however long-term intake of higher amount causes acute toxic effect and even death was reported.[2h] Phosphate is again considered as an essential nutrient required for critical biological reactions that maintain the normal homoeostatic control of the cell. However, excessive retention of phosphate in the body can cause toxicity resulting in a wide range of cellular and tissue injuries.[2i] Acetate is a common anion in biology and at low concentration generally not harmful for the body, in fact some salts of acetate are use as food additive, however, increased acetate level is harmful to human body.[2j] Therefore, because of clinical and environmental reasons early detection of these ions in the environment is desirable.[2] For detection/estimation of anions, different instrument based analytical and spectroscopic techniques are available.[3] All these instrument based techniques require sophisticated analytical instruments, many of these techniques are not simple and suitable for quick and online analysis, some methods require lengthy processes for sample preparation and some of the methods need large amount of samples. As alternative, considerable efforts have been made to develop sensor based colorimetric and fluorescent molecular probes for the recognition of anions.[1,2] Among these, the colorimetric method is more attractive because of its simplicity and bare-eye detection.[1,2,4]

For designing of anion sensors, various noncovalent interactions such as hydrogen-bonding, anion-π and reactions like hydrogen abstraction, electron transfer etc. are mainly considered.[5] Molecules containing amide and amine groups, particularly secondary amine having proton(s) with acidic character can effectively interact with anions and can function as anion sensors.[5,6] Systems with very strong hydrogen bonding sometimes may lead to proton abstraction,

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†Electronic supplementary information (ESI) available: Figs. S1 – S10 (UV-Vis, mass, NMR and computationally optimized structures).

which in turn exhibit colour change due to charge transfer (CT) transition.[5g] Electron deficient organic compounds with π-system having strong positive quadrupole moment can also make effective anion-π interaction functioning as chromogenic sensors.[2d] Recently, a number of anion sensors have been reported, operation of which is based on anion induced single/double electron transfer processes.[5i,5j]. All of these interactions and charge/electron transfer processes lead to perturbation to their photophysical properties resulting in fluorescent/colour changes allowing the anion to be detected.

Dipicrylamine (2,4,6-2',4',6'-hexanitrodiphenylamine, DPA, Fig. 1) contains a secondary amine group, the proton of which is readily deprotonable (pK = 2.62)[7] and this molecule has been extensively used for recognition and selective extraction of alkali and alkaline earth metal ions, specially potassium.[8-10] Crystal structures of DPA and computational study on the intermolecular interactions revealed that after deprotonation the partial delocalization of the resultant negative charge mediated by the aromatic rings that facilitates coordination of the oxygen atoms of the nitro group to suitable metal ions.[11] The six nitro groups that are flexible and can interact and adjust in the space facilitates intermolecular interaction to form network structure encapsulating metal ions in the cavities.[12] Though substantial work on this molecule (DPA) has been done to investigate its complexation property with metal ion, yet its interaction with anions has not been reported. Since this molecule contains N-H, which is potential to interact with anions through H-bonding, therefore we wanted to exploit this property of DPA to investigate its capability as anion sensor, which has not been reported so far.

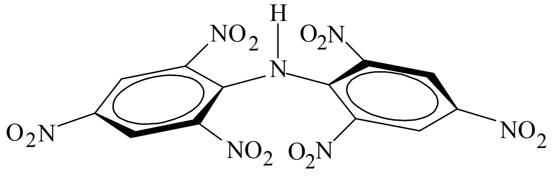


Fig. 1 Structural drawing of dipicrylamine (DPA)

In this paper we report interaction of DPA with a wide range of anions in acetonitrile, which revealed strong interaction with F^-, OAc^-, $H_2PO_4^-$ with sharp colour change. Detail investigation has been made with the aid of UV-vis, NMR spectroscopy and quantum chemical calculations have been employed to investigate the site of interaction with the anion and to rationalize the experimental observation.

Results and discussion

The interaction of different anions with DPA has been assessed by UV-vis spectral change and also by colour change, detectable by bare-eyes. Details of the experimental procedure for recording UV-vis spectral change for various anions are given in the Experimental Section. Out of ten anions (F^-, Br^-, Cl^-, ClO_4^-, OAc^-, I^-,HSO_4^-, NO_3^-, BF_4^- and $H_2PO_4^-$) used for this study, only three anions, F^-, OAc^- and $H_2PO_4^-$ exhibited immediate colour change along with substantial UV-vis spectral change, whereas other anions did not exhibit any significant change either in colour or in UV-vis spectra. We also tested CN^- and N_3^- in acetonitrile, in which CN^- exhibited slow colour change from yellow to orange with high concentration of anion whereas N_3^- did not show any change. The UV-vis spectral change was not straight forward, the acetonitrile solution of DPA exhibits a single band at 420 nm (ε = 2.73x10^4) and after addition of TBAF there was substantial enhancement of the intensity (40 %) of this band with slight red shift of the λ_{max} to 425 nm and a new strong band grew at 508 nm. This spectral change was completed within 30 sec, after that the spectra gradually changed again and the intensity of the 425 and 508 nm bands decreased with growing of a new broad band of low intensity around 600 nm showing two clear isosbestic points at 555 and 374 nm. This change was continued for almost 5 hrs, the spectrum of DPA, the intermediate spectrum recoded after 30 sec of addition of TBAF and the final spectrum recoded after 5 h is shown in Fig. 2. The colour

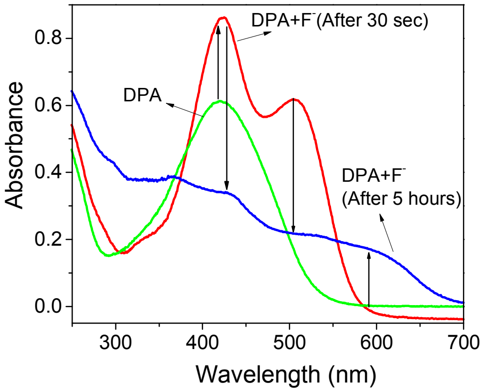
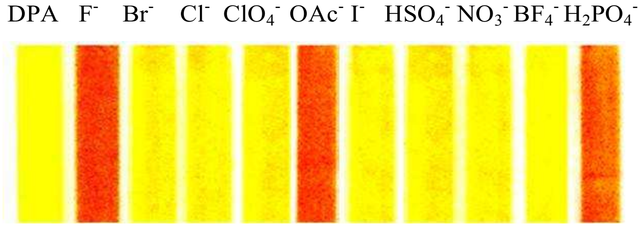


Fig. 2 UV-vis spectra of DPA in acetonitrile (2.5x10^{-5}M) before and after addition of TBAF.



After 12 hours

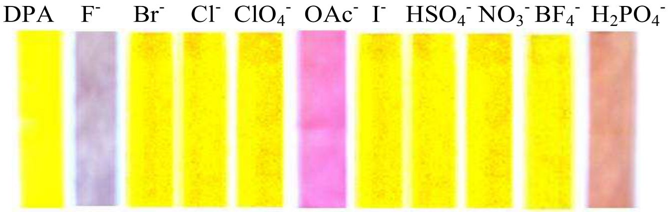


Fig. 3 Colour change of the acetonitrile solution of DPA (2.5x10^{-4} M) before and after addition of various anions (2.5x10^{-2} M), recorded within 20 minutes and after 12 h of addition.

change noted at the intermediate stage after addition of anions and that after 12 h are shown in Fig. 3. For OAc^- and $H_2PO_4^-$, the UV-vis spectral changes are similar but rate of change was considerably slow and the final spectrum is different from that of F^-. For OAc^-, the intermediate spectrum was optimum after 9 min and for $H2PO_4^-$ it was after 36 min; and the final spectra were recorded after 12 and 24 hrs for OAc^- and $H_2PO_4^-$, respectively. The final spectrum for OAc^- exhibited a weak shoulder around 640 nm, a sharp band at 540 nm and the original band of DPA (420 nm) appeared at 416 nm with low intensity (Fig. 4). For $H_2PO_4^-$, the weak shoulder appeared around 620 nm, the new band appeared at 508 nm and the original band of DPA appeared almost at the same position (422 nm) with slightly low intensity (Fig. 5). These observations suggest that all the three anions first interacted with the DPA forming an intermediate compound, which further transformed slowly into a stable compound, the nature of final spectra also suggest that the end products for OAc^- and $H_2PO_4^-$ anions are probably similar but they are different from that of F^-. The time dependent spectral changes from intermediate to final spectra for F^- and OAc^- are shown in Figs. 6 and 7 respectively and the same for $H_2PO_4^-$ is submitted as electronic supplementary material (ESI, Fig. S1). The clean spectral changes with sharp isosbestic points for all three cases also suggest that there is no side reaction to form any other product.

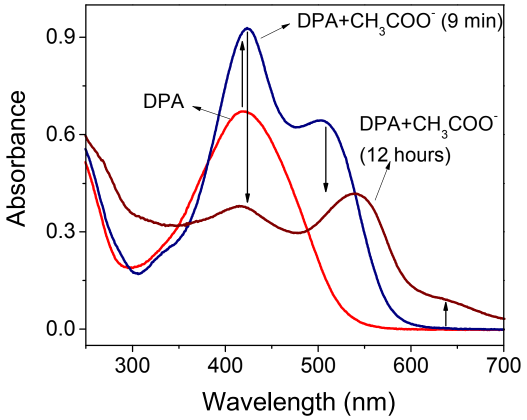


Fig. 4 UV-vis spectra of DPA in acetonitrile (2.5x10^{-5}M) before and after addition of TBA(OAc).

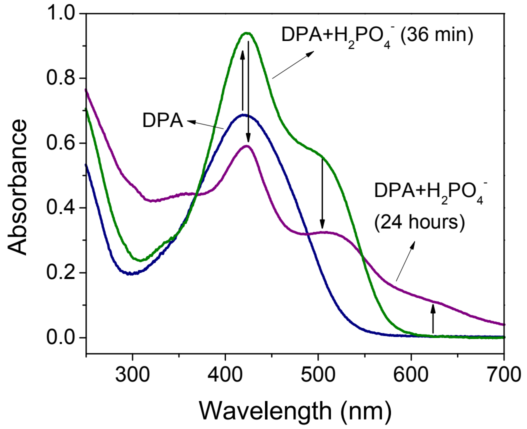


Fig. 5 UV-vis spectra of DPA in acetonitrile (2.5x10^{-5}M) before and after addition of TBA(H_2PO_4).

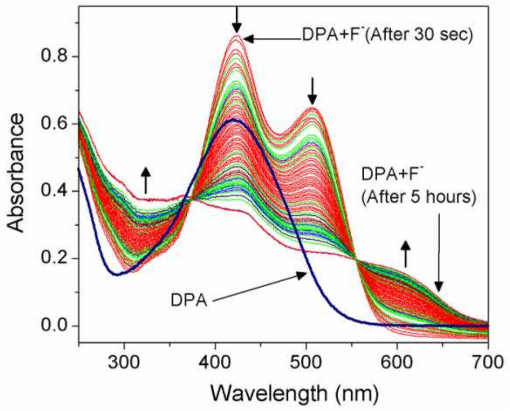


Fig. 6 UV-vis spectral change of DPA in acetonitrile (2.5x10^{-5} M) as a function of time after addition of TBAF (2.5x10^{-3} M).

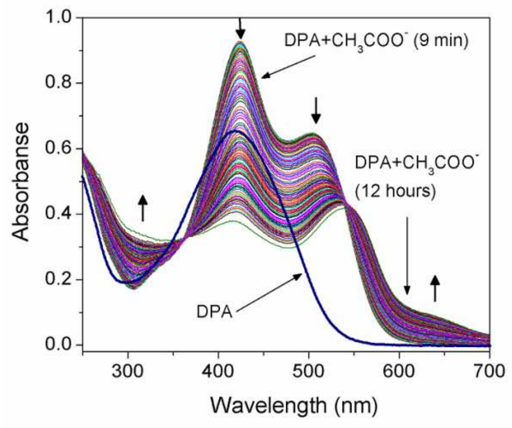


Fig. 7 UV-vis spectral change of DPA in acetonitrile (2.5x10^{-5} M) as a function of time after addition of TBA(OAc) (2.5x10^{-3}M).

The UV-vis spectra were also recorded with varying amount of anions, from 2 to 1000 molar equivalent and it was noted that the pattern of spectral changes are independent of molar equivalent of anions added but the rate of change enhanced with increasing the amount of anions added. It may be noted that the initial change, that is enhancement of intensity of the 420 nm band with little red shift and growing of a new band at 508 nm are similar for all of the three anions, F^-, OAc^- and $H_2PO_4^-$ (Figs. 2, 4 and 5) and this change is due to formation of hydrogen-bonded complex between N-H of DPA and anions.[2d,4c,4e,4f] The next slow change, which drastically reduced the intensity of the 425 and 508 nm bands and new bands grew in the region 600 to 650 nm, as mentioned above and shown in Figs. 2, 4 and 5, is assigned to deprotonation of N-H of DPA and complex formation between DPA^- and TBA salts of the anions. As the spectral changes exhibited clean isosbestic points, therefore it may be assumed that there was no significant side reaction(s) and on this basis we tried to fit the data of change in absorbance as a function of time to the first order rate equation, $\ln|A - A_\infty| = -kt + \ln|A_0 - A_\infty|$, where A_0 is the initial absorbance and A_∞ is the absorbance when the reaction is completed, to evaluate the observed rate constant for comparison among three systems. The plot for F^- monitoring the band at 508 nm is shown in Fig. 8 and similar plots for OAc^- and $H_2PO_4^-$ are submitted as ESI (Figs. S2 and S3). It may be noted that the fittings are very good ($R^2 = 0.998$) and the observed rate constant thus calculated at two different wavelengths (424 and 508 nm) are summarized in Table 1. The observed rate constants at two wavelengths are close and it is in the deceasing order of $F^- > OAc^- > H_2PO_4^-$, the trend is similar to their pKa values for OAc^- and $H_2PO_4^-$, 4.8 (OAc^-) > 2.12 ($H_2PO_4^-$), however F^- (3.2) did not follow the order, which is probably due to the reaction of F^- with the aromatic ring, which discussed in detail in the section, computational study. However, to check whether DPA^- interacts with F^- or not, K^+ and Ca^{2+} salts of DPA were prepared and allowed to interact with TBAF in aqueous media, as the DPA^- salts are soluble in water. The UV-vis spectral changes for both the salts (Figs S4 and S5, ESI) are similar to that of F^-, which again suggest interaction of F^- with DPA^-.

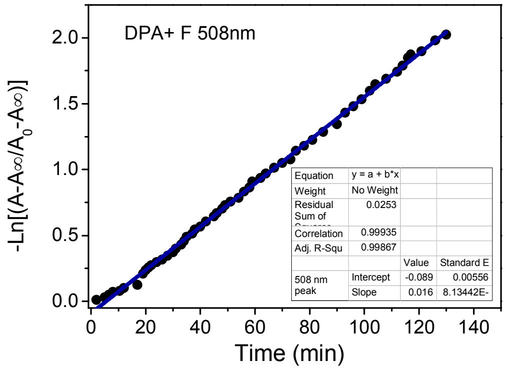


Fig. 8 Plot of the first order rate equation to determine observed rate constant from UV-vis spectral change of DPA as a function of time after addition of TBAF.

Table 1 Observed rate constant for the reaction of DPA with anions in acetonitrile, calculated at two different wavelengths

Anions	Rate constant (*k*) Sec^{-1}	
	424 nm	508 nm
F^-	0.0159	0.0160
OAc^-	0.0102	0.0101
$H_2PO_4^-$	0.00118	0.0012

Mass spectrometry

ESMS is a soft ionisation technique and useful to investigate intermolecular interaction in solution. It was therefore decided to perform mass analysis of the solution upon addition of anions. This analysis has done by LC-MS after addition of anions into the DPA solution following the method described in the experimental section and the data obtained are also given there. For F^-, two strong peaks were observed at *e/m* values of 438.33 and 720.85 (Fig. S6), which correspond to the compound $[DPA^-]^-$ and compound of composition $[DPA^-+TBA^++HF_2^-]^-$, respectively. For OAc^- and $H_2PO_4^-$, the highest and strong peaks were noted at 1118.36 and 1118.53, respectively and they are correspond to the composition $[2DPA^-+TBA^+]^-$ (calculated value 1118.87). Apart from these peaks, the OAc^- anion exhibited two other peaks at *e/m* 556.61 and 661.76, which corresponds to $[DPA+OAc^-+HOAc]^-$, and $[DPA+OAc^- +NaOAc+2CH_3CN]^-$, respectively; and $H_2PO_4^-$ ion exhibited four peaks at *e/m* 534.37, 632.38, 971.78 and 1069.74, (Fig. S7), which correspond to $[DPA+H_2PO_4^-]^-$, $[DPA+H_2PO_4^-+H_3PO_4]^-$, $[DPA+ H_2PO_4^-+ H_3PO_4+TBAH_2PO_4]^-$ and $[2DPA+H_2PO_4^-+H_3PO_4]^-$, respectively. ESMS is a soft ionization technique and mass of the assembly including solvents associated by weak intermolecular interaction is often observed.[13] The mass data, therefore confirmed the interaction of anions with the DPA molecule and in all the three cases the N-H of the DPA is finally deprotonated to form DPA^- and it is stabilized by the interaction with the cation TBA^+. In a few cases, as mentioned above, the proton of the amino group of the DPA paired up with anion through N-H…O (oxygen from OAc^- or $H_2PO_4^-$) H-bonding interaction, the other molecules including solvents are probably associated with the assembly by short contact.[2a,2b,5,6]

IR and ^1H NMR study

The deprotonation of DPA upon interaction with anion was also confirmed from IR and ^1H NMR spectroscopy. The IR spectrum of DPA exhibits a strong and sharp peak at 3242 cm^{-1} due to ν(N-H), which disappeared when the DPA solution was treated with TBAF. For investigation of the details of DPA-anion interactions, ^1H NMR study was carried out, details of the experimental procedure and the ^1H and ^{13}C NMR data are given in the Experimental Section. DPA in acetonitrile exhibited two singlet at δ 9.05 (4 H) and 10.61 (1 H) due to four equivalent aromatic protons and the N-H proton, respectively. After addition of TBA^+ salts of the anions, in all the three cases the singlet observed for aromatic protons at δ 9.05 was shifted to the upfield region at δ 8.72, 8.72 and 8.985 for F^-, OAc^- and $H_2PO_4^-$, respectively. The time dependent NMR spectra for OAc^- and $H_2PO_4^-$, the first one of which was recorded within minutes after addition of anions and then after 1, 4 and 24 hrs, exhibited that for $H_2PO_4^-$ the upfield shift observed in the first spectrum recorded upon addition of anion remained almost same upto 24 h (Fig. 9). For OAc^-, the situation is similar to that of $H_2PO_4^-$, except some small peaks (not well resolved) grew in the later stage (Fig. S8), which is probably due to formation of a minor species. However, for F^-, apart from the upfield shift of the singlet, new singlets at δ 5.28 and 5.02 and a few new peaks in the range δ 8.51 to 8.72 have grown after the addition of the anion (Fig. 10). The new peaks in this spectrum were growing with time at the expense of the original singlet and it continued for almost 24 h, beyond that no further change is noted during the testing period of 96 hrs. From NMR data it

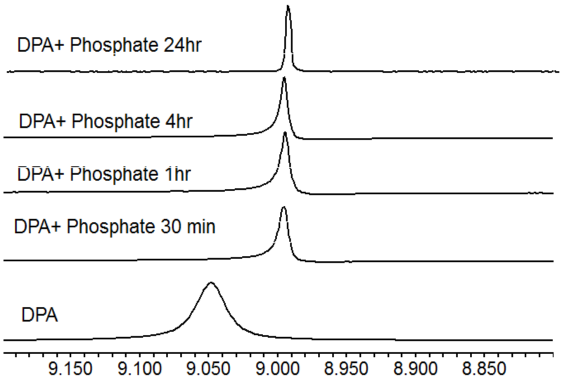


Fig. 9 ^{1}H NMR spectral change of DPA recorded after addition of TBA(H_2PO_4) in CD_3CN.

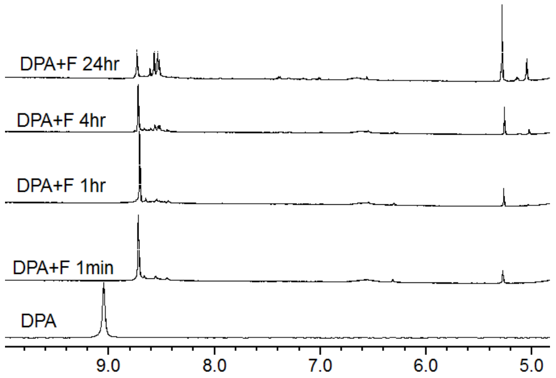


Fig. 10 ^{1}H NMR spectral change of DPA recorded after addition of TBAF in CD_3CN.

is concluded that the shielding of the singlet in all three case in the first instant after addition of anions is due to deprotonation of the N-H proton of the DPA to form DPA$^-$, the negative charge on the nitrogen atom is delocalized on two benzene rings, which resulted in shielding of the protons attached with the benzene rings causing upfield shift of the singlet. The other important conclusion is that for OAc$^-$ and $H_2PO_4^-$ anions, the four aromatic hydrogen atoms of DPA remained equivalent even after deprotonation of N-H group, in other words DPA molecule remained intact (except deprotonation) but for F$^-$ ion, the four protons are no longer equivalent and at least one of the protons is affected either by some reaction in the benzene ring or by some other strong interaction with some highly electronegative moiety, as the new signal appeared at substantially high field region, δ 5.28 and 5.02 (Δδ = 3.77 and 4.03 ppm). As the interaction of N-H with fluoride genrates HF_2^-,[2a] and it is dificult to observe this signal at room temperatue, therefore low temperature (-20 °C) ^{1}H NMR spectrum was recorded and the signal appeared at 16.05 (Fig. S9) is assigned to the proton of HF_2^-.[2a] ^{13}C NMR spectra of DPA before and after addition of anions (F$^-$, OAc$^-$ and $H_2PO_4^-$) were also recorded, DPA exhibits four signals at δ 117.33, 126.52, 134.55 and 141.77, as expected from four type of carbon atoms in this molecule. However, after addition of F$^-$, five peaks at δ 118.26, 125.19, 133.09, 139.85 and 143.48 appeared in the aromatic region (Fig. 11) but for OAc$^-$ and $H_2PO_4^-$ anions, four peaks with slight change in chemical shifts compared to free DPA were noted. Both the ^{1}H and ^{13}C NMR data thus suggest that the F$^-$ ion might have interacted with one of the electron deficient carbon or proton attached to the carbon of the aromatic ring and the equivalent nature of the two rings is lost. To investigate this phenomenon, computational study was undertaken to explain the observation.

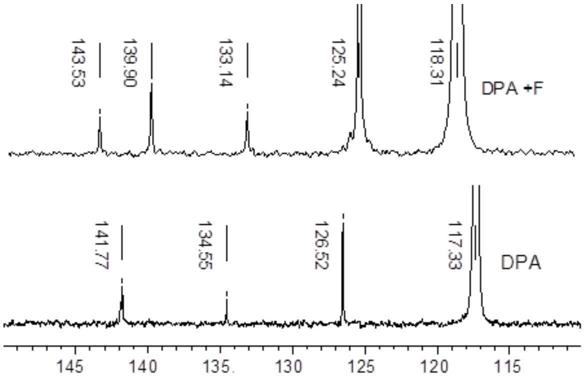


Fig. 11 ^{13}C NMR spectral change of DPA recorded after addition of TBAF in CD_3CN.

Computational study

Quantum chemical calculations have been performed to examine the mode of interactions of F$^-$ ion with DPA molecule. Geometries were optimized with RHF/6-31+G* level of theory,[14] and single point energy calculations were performed with B3LYP/6-31+G** and M06/6-31+G** methods.[15,16] Experimental results (*vide supra*) suggest that F$^-$ ion deprotonate the amine nitrogen instantly, which results into the formation of DPA anion (**1**) (Fig. 12). Therefore, calculations were performed with **1**. DPA anion (**1**) can interact with anion via –CH···anion interactions or/and through anion-π type

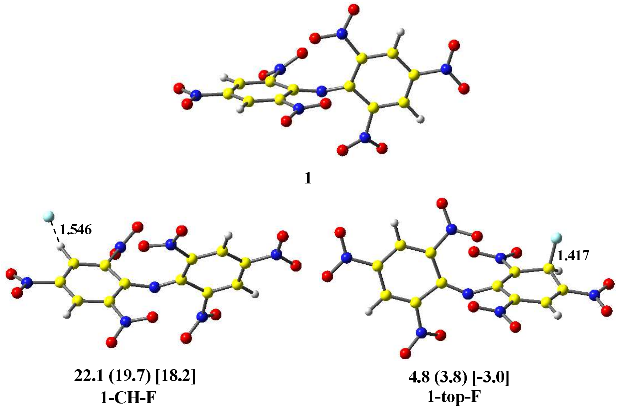


Fig. 12 RHF/6-31+G* optimized geometries, calculated fluoride ion affinities (kcal/mol) and important distances (Å). B3LYP/6-31+G**//RHF/6-31+G* and M06/6-31+G**//RHF/6-31+G* calculated fluoride ion affinities are given in parentheses and square brackets respectively. (yellow = carbon; blue = nitrogen; red = oxygen; white = hydrogen; cyan = fluoride).

interactions between anion and phenyl ring. The possible modes of interactions have been examined in this study. The interactions of anions with electron deficient arenes are reported in the literature.[17] Calculated binding energies with all the studied levels suggest for the repulsive interactions of F^- ion with -CH hydrogen of phenyl ring (**1-CH-F**) (Fig. 12). However, optimization of geometry with F^- ion at the centre of phenyl rings leads to the geometry which shows interaction of F^- ion with –CH carbon of phenyl ring (**1-top-F**). M06/6-31+G**//RHF/6-31+G* calculated results suggest for -3.0 kcal/mol binding energy for **1-top-F**. These calculated results suggest that preferably F^- ion binds with phenyl carbon instead of the –CH hydrogen of DPA anion **1** (Fig. 12).

The observed repulsive interaction of F^- ion with **1** is presumably due to the interaction between two anions that is DPA^- anion (**1**) and F^- ion. To circumvent this situation, we have performed the calculation using [DPA anion-TBA] complex (**2**) (Fig. 13). It is worth to note that in experimental study tetrabutylammonium salt of fluoride ion was used. Further, mass spectra study also suggests for the complex formation between DPA and TBA anions (*vide supra*). The calculated binding energies with **2** suggest for an attractive interaction of the F^- ion at both the sites, i.e., with –CH hydrogen (**2-CH-F**) and –CH carbon (**2-top-F**) of phenyl ring (Fig. 14). The F^- ion interacts to –CH hydrogen of **1** with -46.3 kcal/mol with M06/6-31+G**//RHF/6-31+G* level of theory (**2-CH-F**), however, F^- ion showed much stronger interaction (-58.3 kcal/mol) with the –CH carbon of **1** at the same level of theory. These results suggest for the binding of F^- ion with –CH carbon more preferentially than the –CH hydrogen.

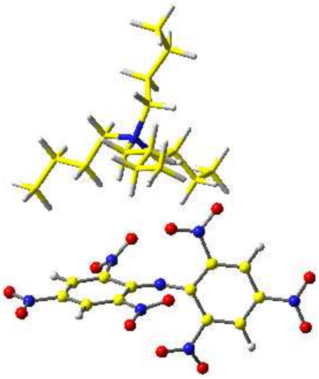


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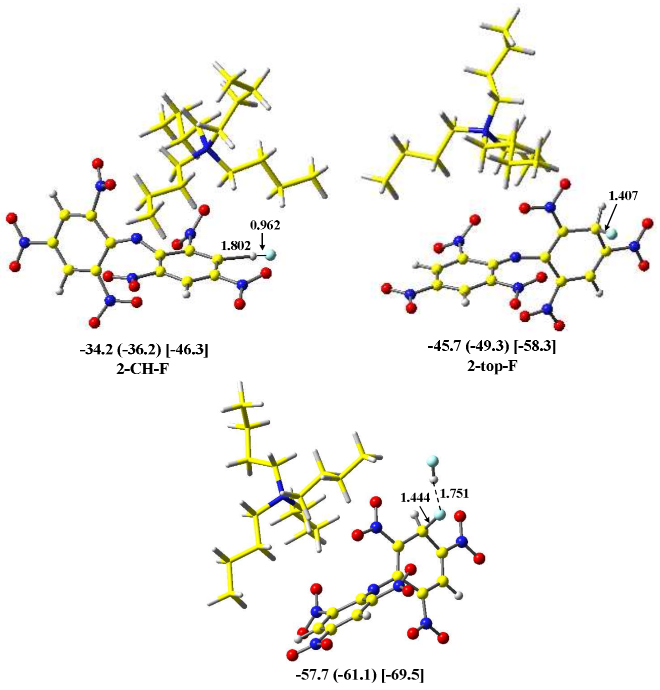
Fig. 13 RHF/6-31+G* optimized geometry of 2 (yellow = carbon; blue = nitrogen; red = oxygen; white = hydrogen.

The mass spectroscopy study reveals that DPA with tetrabutyl ammonium salt of fluoride can form $[DPA^-+TBA^++HF_2^-]^-$ (*vide supra*). Therefore, there is a possibility for additional interaction of C-F fluoride with HF molecule via intermolecular hydrogen bonding. It is likely that HF can from in the solution through the deprotonation of –N-H hydrogen in DPA. We have examined this possibility and the calculated results show that such a binding mode of F^- with **1** is much higher (-69.5 kcal/mol) (**2-top-F-HF**) at M06/6-31+G** level of theory than the previous binding modes (Fig. 14). We have also examined two additional possibilities of binding of two F^- ion with one DPA molecule, i.e., interaction of two fluoride ions with –CH carbons of each phenyl rings (**2-2F-top**) and, interaction of one F^- ion at –CH carbon and second F^- with –CH hydrogen (**2-2F-top-CH**) (Fig. S10, ESI). The calculated interaction energies for these two possibilities are lower than **2-top-F-HF** (Fig 14 and Fig. S10, ESI).

Further, to see the influence of solvent on fluoride ion affinity, single point energy calculations were performed in the acetonitrile solvent medium with B3LYP/6-31+G** and M06/6-31+G** methods using conductor-like polarisable continuum salvation model (CPCM).[18] The calculated fluoride ion affinities in the solvent medium are smaller in energy than the gas phase calculated energies, however, **2-top-F-HF** shows highest binding energies with both levels of theory (Table 1). These results are also in support of the preferential binding of F^- ion with –CH carbon of phenyl ring.

Table 1: Calculated fluoride ion affinities (kcal/mol) in acetonitrile solvent medium using CPCM salvation model.

	B3LYP/6-31+G**	M06/6-31+G**
1-CH-F	1.33	-0.15
1-top-F	-0.66	-7.59
2-CH-F	14.17	3.94
2-top-F	-1.60	-10.97
2-top-F-HF	-7.90	-16.32



-34.2 (-36.2) [-46.3]
2-CH-F

-45.7 (-49.3) [-58.3]
2-top-F

-57.7 (-61.1) [-69.5]
2-top-F-HF

Fig. 14 RHF/6-31+G* optimized geometries, calculated fluoride ion affinities (kcal/mol) and important distances (Å). B3LYP/6-31+G**//RHF/6-31+G* and M06/6-31+G**//RHF/6-31+G* calculated fluoride ion affinities are given in parentheses and square brackets respectively. (yellow = carbon; blue = nitrogen; red = oxygen; white = hydrogen; cyan = fluoride).

Conclusions

The property of dipicrylamine as colorimetric sensor for anions has been investigated. In acetonitrile, it exhibited strong interaction with F^-, OAc^-, $H_2PO_4^-$ out of a large number of anions tested and the interaction resulted in sharp colour change. Initial colour change for all the three anions are similar but with time distinct colour difference for all the three anions was noted. The DPA-anion interaction was followed by UV-vis, NMR (^{1}H and ^{13}C) and ESMS studies, which revealed that in the first step, anions form H-bonding interaction with the N-H proton of DPA and then deprotonation of N-H takes place forming complex between DPA^- and TBA^+. The spectral change for complex formation is slow and the observed rate constants for the formation of these complexes have been determined from UV-vis spectral change and the order of observed rate is $F^- > OAc^- > H_2PO_4^-$. However, F^- interacts with one of the carbon of a phenyl ring, which has been suggested by NMR and ESMS study and further it has been confirmed by quantum chemical calculations.

Experimental

Materials

Dipicrylamine was prepared in the laboratory following the modified reported procedure.[19] Tetrabutylamminium salts of all the anions were purchased from Sigma-Aldrich and Fluka. All the solvents were purchased from Merck, Fischer Scientific and were purified by standard procedure before use.

Instrumentation

The UV-Vis spectra were recorded on a CARY 500 scan Varian spectrophotometer. NMR spectra were recorded on a model DPX 200 and Advance II 500 MHz Bruker FT-NMR instruments using TMS as internal standard. Mass spectra were recorded on a Q-TOF Micro^{TM} LC-MS instrument. Infrared spectra were recorded on a Perkin-Elmer spectrum GX FT-system as KBr pellets.

Interaction with anions by UV-Vis study

Interaction of DPA with various anions was followed by UV-Vis spectral change and also by visualization of colour change with bare-eyes. In a typical experiment, stock solution of DPA (5×10^{-5} M) and that of tetrabutylammonium (TBA) salts (5×10^{-3} M) of a series of anions (F^-, Br^-, Cl^-, ClO_4^-, OAc^-, I^-, HSO_4^-, NO_3^-, BF_4^-, $H_2PO_4^-$) were prepared in freshly distilled acetonitrile. Then 2 mL of stock solution of DPA and 2 mL of stock solution of each anion were taken in a 5 mL volumetric flask, so that the effective concentration of DPA was 2.5×10^{-5} M and that of anion was 2.5×10^{-3} M. The absorbance spectra of DPA (2.5×10^{-5}) and the resulting solutions upon addition of anions were recorded. Significant spectral change was noted for F^-, OAc^- and $H_2PO_4^-$, whereas for other anions no significant spectral change was noted. The spectral changes for these three ions are interesting and recorded as a function of time till the saturation. Details of it discussed in the Results and Discussion section. The colour changes just after addition of anions and after completion of reaction were also photographed.

Mass spectroscopy

For recording mass spectra, 1 mL stock solution of DPA and 1 mL stock solution of the anions (F^-, OAc^- and $H_2PO_4^-$) were mixed and the mass spectra of the resulting solutions were recorded within 10 minutes of addition and also after 24 h. Mass data: *e/m* for F^-, 438.33, $[DPA^-]^-$, (calculated 438.20) and 720.85, $[DPA^- + TBA^+ + HF_2^-]^-$, (calculated 719.68); for OAc^-, 438.08, $[DPA^-]^-$, (calculated 438.20) 556.61, $[DPA + OAc^- + HOAc]^-$, (calculated 558.30); 661.76, $[DPA + OAc^- + NaOAc + 2CH_3CN]^-$, (calculated 662.40) and 1118.36, $[2DPA^- + TBA^+]^-$ (calculated 1118.87) and for $H_2PO_4^-$, 534.37, $[DPA + H_2PO_4^-]^-$, (calculated 536.20); 632.38, $[DPA + H_2PO_4^- + H_3PO_4]^-$, (calculated 634.19); 971.78, $[DPA + H_2PO_4^- + H_3PO_4 + TBAH_2PO_4]^-$, (calculated 973.65); 1069.74, $[2DPA + H_2PO_4^- + H_3PO_4]^-$, (calculated 1073.40); 1118.53, $[2DPA^- + TBA^+]^-$ (calculated 1118.87).

NMR spectral study

The ^{1}H and ^{13}C NMR spectra of DPA before and after addition of anions (F^-, OAc^- and $H_2PO_4^-$) were recorded in CD_3CN. In a typical experiment, 2 mg of DPA dissolved in 0.5 mL of CD_3CN was added tetrabutylammonium salts of the anions (solid, 20 molar equivalents) and the spectra were recorded at different time interval up to 24 h of addition. ^{1}H NMR data (CD_3CN): DPA, δ 10.61 (1 H, NH) and 9.05 (4 H, Ar-H); after 24 h of addition of anions (only aromatic protons): for F^-, δ 8.72, 8.61, 8.58, 8.53. 8.51, 5.28 and 5.02; for OAc^-, δ 8.73 and for $H_2PO_4^-$, δ 8.985; ^{13}C NMR data (CD_3CN): DPA, δ 117.33, 126.52, 134.55 and 141.77; after 24 h of addition of anions (only aromatic protons): for F^-, δ 118.26, 125.19, 133.09, 139.85 and 143.48; for OAc^-, δ 117.03, 123.86, 131.79 and 138.55 and for $H_2PO_4^-$, δ 117.41, 124.17, 132.08 and 138.13.

Computational methods

All geometries were fully optimized in the gas phase with restricted Hartree−Fock method[14] using the 6-31+G* basis set. To calculate the energies with a higher basis set, single point energy calculations were performed at the B3LYP/6-31+G** M06/6-31+G** levels[15,16] using RHF/6-31+G* optimized geometries. The choice of M06 method is based on its reliability towards calculations of non-bonding intercations.[16] Further, single point energy calculations were performed in acetonitrile (ε=35.688) using conductor-like polarisable continuum salvation model (CPCM).[18] This approach describes the solvent reaction field by means of apparent polarization charge distribution on the cavity surface. All calculations were performed with the Gaussian 09 suite program.[20]

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