Pattern recognition based identification of nitrated explosives†

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We report an effective approach for the identification of nitro explosives by the reaction of an electron-acceptor with an electron-donor with and without the addition of γ-cyclodextrin (γ-CD). A charge-transfer complex was prepared in acetonitrile by the reaction of the nitro explosive TNT as an electron acceptor with the donor *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (TMPD). The complex TNT/TMPD converts gradually into $\text{TNT}^{\bullet -}/\text{TMPD}^{\bullet +}$ in water with 5% acetonitrile by volume. The inclusion behavior of $\text{TNT}^{\bullet -}/\text{TMPD}^{\bullet +}$ with γ-CD was studied by UV-visible spectroscopy. The effect of α- and β-CD with $\text{TNT}^{\bullet -}/\text{TMPD}^{\bullet +}$ was also studied. Similar experiments were also carried out for $\text{RDX}^{\bullet -}/\text{TMPD}^{\bullet +}$ with γ-CD. The binding of $\text{TNT}^{\bullet -}/\text{TMPD}^{\bullet +}$ and $\text{RDX}^{\bullet -}/\text{TMPD}^{\bullet +}$ with γ-CD were compared for the application of the complexes in a sensor array. Subsequently, the visible absorption spectra of nitro explosives as analytes, such as TNT, RDX, HMX and Tetryl with TMPD in the presence and absence of γ-CD, were measured with time. We worked with the same analytes with a second electron donor tetrakis(dimethylamino)ethylene (TDAE) using 96-well plate experiments. Pattern recognition analysis was applied to analyze the data collected and it showed successful discrimination of the nitro explosives. This work represents the simplest colorimetric chemical sensor technique to be used in monitoring the range of common nitro explosives.

Introduction

Chemical sensors for the rapid detection of explosives are gaining importance because they have potential applications in real life scenarios.[1–5] Various methods of explosive agent detection are currently available, ranging from simple to sophisticated mass spectrometry methods. Though highly sensitive, mass spectrometry is expensive and requires sophisticated instrumentation. Absorption based detection is among the simplest methods, and several kinds of color change chemical sensors have been developed for rapid detection of explosives.[6,7] In this paper, we discuss a novel and simple method for the detection and differentiation of nitro explosives by specific color reactions using host–guest and charge-transfer (CT) acceptor/donor complexes.

Electron acceptor and donor complexes have been extensively studied in biological to photophysical and photochemical fields, and are now effectively applied in the field of color change chemical sensors.[8] Our goal was to create acceptor/donor complexes with nitro explosives that give color patterns that are diagnostic of the identity of the explosive. In these acceptor/donor complexes we choose *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (TMPD) and tetrakis(dimethylamino)ethylene (TDAE) as donors (Chart 1); The ease of removal of electrons from the amino function makes it possible to study their oxidation reaction pathways. In particular TMPD and TDAE, among various amine compounds, have received considerable attention because of their CT photoionization process.[9–14] The absorption properties of intermolecular CT transitions, and the association behavior of the complexes, depend on the ionization potential of the donor. TMPD and TDAE have low ionization potential, thereby acting as powerful electron donors.[15]

In our study, the electron acceptor molecules were explosives such as: 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazine (HMX), 2,4,6-trinitrophenyl-*N*-ethylnitramine (Tetryl), and pentaerythritoltetranitrate (PETN). These acceptors differ in size, position of their substituents and reduction potentials (Chart 1). The goal of this study was differentiate the nitro explosives using e-acceptor/e-donor complexes with and without the use of a cyclodextrin.

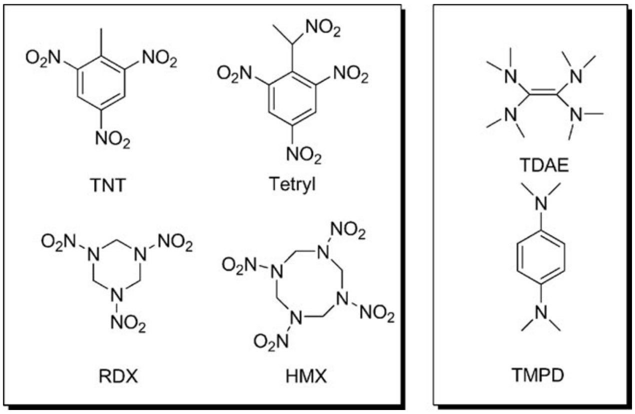

Chart 1

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† Dedicated to Professor Jerry Atwood on the occasion of his 65th birthday.

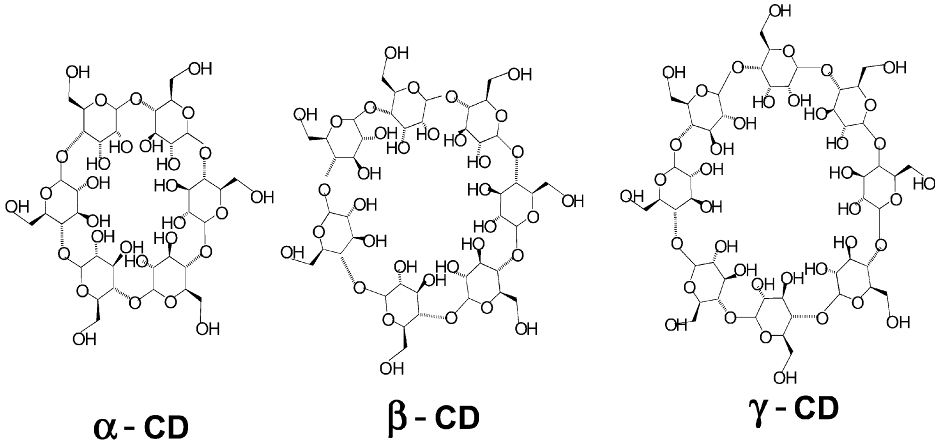


Fig. 1 Chemical structures of the α-, β- and γ-cyclodextrins (CD).

Supramolecular chemistry involves the study of intermolecular interactions, and the majority of studies are of the host–guest type.[16–19] Among potential hosts for explosives, CDs seem to be optimal. The three major CDs are torus-like macrocyclic rings built up from six (α-), seven (β-), or eight (γ-) glucopyranose units (Fig. 1). The cavity size varies depending upon the number of glucopyranose units and the order is α- < β- < γ-CD. CDs cavities are hydrophobic, and are well known to encapsulate various hydrophobic guest molecules.

CDs form inclusion complexes if there is a good match between the size of both analyte and cavity.[20–24] The 1 : 1 (guest : CD) stoichiometry is the most common type of CD complex. However, the cavity size of γ-CD is large enough[25] to accommodate two guests thereby giving complexes of 2 : 1 stoichiometry. We prepared CT complexes with nitro explosives as acceptors and TMPD as a donor and studied the inclusion properties with γ-CD. We used the host–guest association to create patterns of the nitrated explosives using UV-visible spectrophotometry. We also carried out the reactions without cyclodextrin. In these studies we used TDAE as a donor, and nitro explosives as acceptors, employing a 96-well plate for analysis.

Experimental

Materials and methods

α-, β- and γ-cyclodextrins and *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine were purchased from Aldrich Chemical Company and were used without further purification. TNT, RDX, HMX and Tetryl were all supplied as 1000 μg mL^{-1} acetonitrile (MeCN) solutions in sealed glass vials from Ultra Scientific. PETN was as 1000 μg mL^{-1} in methanol in sealed glass vials from Accustandard. In our studies all the reagent solutions were made using H_2O–5% MeCN for the reactions. All the reactions were performed under concentrations: [nitro explosive/TMPD] = 0.09 mM; [CD] = 0.09 M at room temperature 25 °C. Distilled, deionized, and filtered water was used in the studies. Acetonitrile (optima grade) was obtained from Fischer Scientific and used without further purification. Both water and MeCN are degassed prior to use *via* bubbling with N_2 for 2 h.

UV-Vis titrations

All the titrations were performed using the DU 800 UV-visible spectrophotometer (Beckman) in conjunction with a PC controlled system. The control of the instrument, data handling, and data reduction capabilities, are contained within the confines of the PC. The PC runs windows 2000 as an operating system.

A UV-Vis titration proceeded as follows: the solvent H_2O–5% MeCN served as a blank. A cuvette with 1 ml of a solution of (nitro explosive)$^{\bullet -}$/TMPD$^{\bullet +}$ as a guest (0.09 mM) was recorded. The host stock solution was identical to the cuvette solution but with CD (0.09 M). The host stock solution was added in aliquots to the cuvette and the spectrum was recorded between aliquots. The wavelength of maximum difference between the original solution of guest, and the final addition of host, was determined. The change in absorbance between the each addition of host was plotted against the volume of host added to the solution.

UV-Vis time variations

The time variation experiments were conducted with a DU 800 UV-visible spectrophotometer (Beckman) in conjunction with PC controlled system. Two types of experiments were measured: (a) nitro explosive/TMPD in MeCN and, (b) nitro explosive/TMPD (0.09 mM) plus CD (0.09 M) in H_2O–5% MeCN. MeCN was a blank solution for (a) and H_2O–5% MeCN as a blank for (b). The absorption spectra were recorded in a definite time interval. Each experiment of type (a) and (b) were repeated five times. Data were analyzed with principal component analysis (PCA).

96-Well plate experiments

All 96-well plate experiments were performed in a Molecular Devices quartz 96-well plate. Nitro-explosives (1.13 mM) and tetrakis(dimethylamino)ethylene (TDAE) (1.13 mM) were added to each well of the 96 well plate. MeCN was added so that the total volume was 280 μl. Ten μl of each donor–acceptor solution was then removed and diluted to 280 μl in a 96-well plate. Analytes (2.25 mM) and TMPD (2.25 mM) were added to each well. Solvents (H_2O, MeCN and $C_2H_4Cl_2$) were added until the total volume was 280 μl. Blank measurements were obtained for both TDAE and TMPD in the absence of explosives. Four replicates were obtained for each explosive/donor in each solvent.

Data processing

Data processing[26] for analysis was done using XL STAT (VERSION 2007.6).

Results and discussion

The chemical structures of α-, β- and γ-CDs are shown in Fig. 1, and their central cavities have diameters of 4.5–5.3, 6.0–6.5 and 7.5–8.3 Å, respectively.[27] Complexation of guests within the cavity of CDs results in changes in various spectral properties of both the guest and CD itself.[28] The effect of CDs on the spectral properties of guest molecules have led to their use as reagents in various spectrometric analysis, including UV-visible spectrophotometry, fluorescence and phosphorescence methods, and nuclear magnetic resonance spectroscopy.[29]

Binding of CD with TNT through CT complex formation (UV-visible titration)

2,4,6-Trinitrotoluene (TNT) is one of the most commonly used explosives in the modern world. Its chemistry has been studied extensively by a variety of means.[30] As observed from Chart 1, TNT has three C-nitro groups on the aromatic nucleus and hence it acts as a strong electron acceptor. Studies have shown that TNT forms complexes with strong electron donors.[31] In our study, we noticed that TNT (obtained as MeCN solution) formed an interaction with TMPD, a strong donor,[13] and we observed this by appearance of a new band in the absorption spectrum. The appearance of the new band indicates the formation of CT complexes.[32–34] This could be noticed from the absorption measurement at 504 nm (Fig. 2—black line). CT complexes are also known as π–complexes, and in this case the TMPD acts as the π donor while TNT acts as the π acceptor, in which the former supplies an electron to the later.

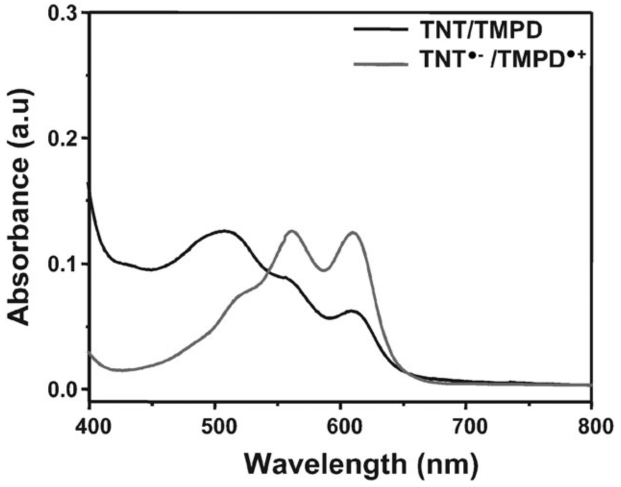


Fig. 2 Absorption spectra of TNT/TMPD (black) in MeCN and $TNT^{\bullet -}/TMPD^{\bullet +}$ (gray) in H_2O–5% MeCN.

After forming the TNT/TMPD CT complex in pure MeCN, the reaction solution was diluted into 0.09 mM in H_2O–5% MeCN. This results in formation of the radical ions $TNT^{\bullet -}$ and $TMPD^{\bullet +}$. The solution became an intense violet color due to the radical cation of TMPD. The absorbance of 504 nm for the TNT/TMPD CT complex in the low polarity solvent MeCN immediately changes into a violet color ($TNT^{\bullet -}$, $TMPD^{\bullet +}$) due to the higher polarity solvent H_2O (Fig. 2–gray line).

It seems reasonable to assume that radical ions are formed in a stepwise process, namely,

$$\mathrm{TNT} + \mathrm{TMPD} \rightleftarrows \mathrm{TNT/TMPD} \qquad (1)$$

$$\mathrm{TNT/TMPD} \rightleftarrows \mathrm{TNT}^{\bullet -}/\mathrm{TMPD}^{\bullet +} \qquad (2)$$

CT complexes have been categorized into two groups, *viz.*,

(a) weak complexes involving but little charge transfer from donor to acceptor, and

(b) strong complexes with the capacity to separate as free ion-radicals.

As Mulliken explained, weak CT complexes (Ψ_N) containing one donor molecule combined with one acceptor molecule are approximated represented by the wave function;[35]

$$\Psi_N = a\Psi_0(\mathrm{A, D}) + b\Psi_1(\mathrm{A}^-, \mathrm{D}^+) \qquad (3)$$

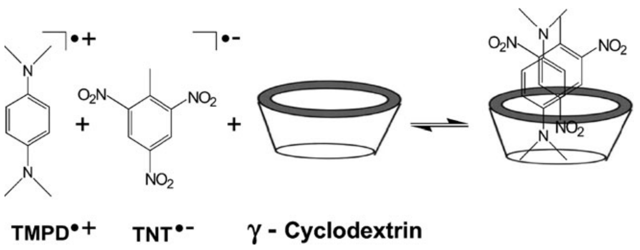
where A is the acceptor and D the donor; Ψ_0 the wave function for the non-ionic state of D and A, in which they may be linked either by a hydrogen bond, by dipole–dipole interaction forces, or by any others forming part of the classical "van der Waals forces", Ψ_1 is the wave function of the combined state, corresponding to complete transfer of one electron from D to A, and *a* and *b* are coefficients.

In weak complexes, $a \gg b$ and the eqn (3) becomes

$$\Psi_N \cong a\Psi_0\,(\mathrm{A, D}) \qquad (4)$$

In the system of TMPD (donor) with electron acceptor (A), free paramagnetic ions $TMPD^+$ and A^- are the favored species for the systems in ionizing solvents such as water or methanol.[36] Now $b \gg a$ and $\Psi_N \cong \Psi_1(\mathrm{A}^-, \mathrm{D}^+)$. The solvent effects alter the nature of acceptor/donor interactions, and polar solvents increase the amount of charge transferred.

In the present research work, in MeCN the weak CT complex of TNT/TMPD was formed (eqn (1) and (4)). In the study of this complex interacting with CD as described below, we changed MeCN to the more polar medium (H_2O–5% MeCN). We consequently observed that the CT complex TNT/TMPD dissociated into the corresponding radical ions $TNT^{\bullet -}$ and $TMPD^{\bullet +}$, as in eqn (2). These radical



Scheme 1 Proposed inclusion complex in the cavity of γ-CD.

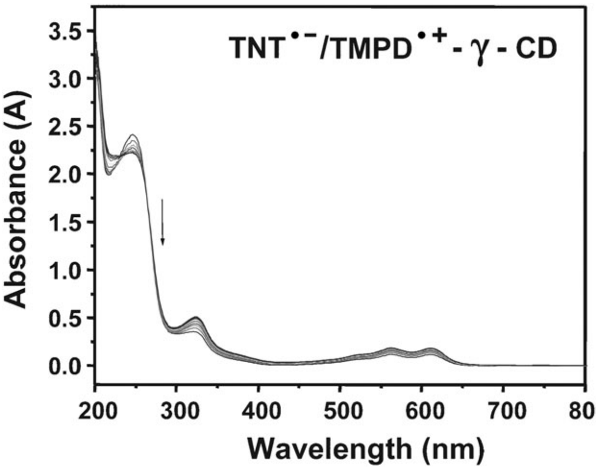


Fig. 3 Absorption spectra of increasing concentrations of γ-CD in TNT$^{\bullet-}$/TMPD$^{\bullet+}$ in H_2O–5% MeCN.

ions could be accommodated by γ-CD due to its large cavity size giving complexes of 2 : 1 (Scheme 1).

To the solution of intense violet color (TNT$^{\bullet-}$, TMPD$^{\bullet+}$) we increased the concentration of γ-CD and measured the absorbance by UV-Vis spectrophotometry (Fig. 3). The intensity of violet color became saturated as the concentration of γ-CD increased (Fig. 4).

As a control we also carried out the same titration experiment, but without addition of γ-CD. In the absence of γ-CD the intensity of violet color increased also (Fig. 4). This means that the separated acceptor/donor ions continue to increase over the time of the titration.[37,38] However, γ-CD can bind two aromatic rings at a time, most probably in a stacked orientation.[39] In our study, the experimental observation of a saturation of violet color leads us to conclude that the CT complex of TNT/TMPD is bound in the γ-CD cavity. In the hydrophobic cavity of γ-CD the complex exists in the CT state rather than the separated ions. This means that the γ-CD preferentially binds the CT complex (Fig. 4).

We carried out the same experiment of the inclusion of TNT$^{\bullet-}$/TMPD$^{\bullet+}$ using the same procedure with and without α- and β-CD. We observed that there were little to no changes in intensities, even in the presence of high concentrations of α and β-CD (Fig. 5 and 6).

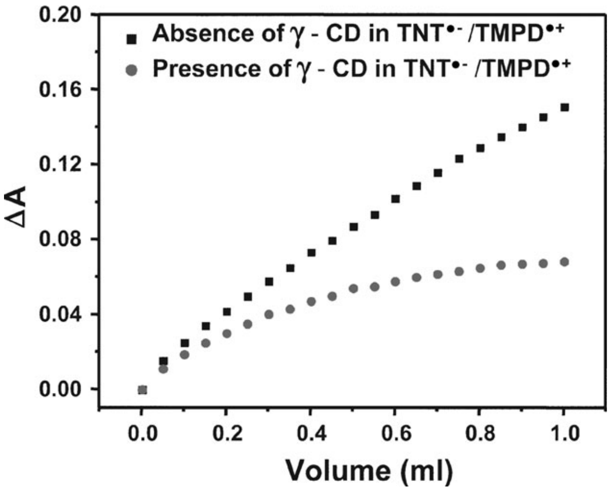


Fig. 4 A plot of volume against change in absorbance of TNT$^{\bullet-}$/TMPD$^{\bullet+}$ (H_2O–5% MeCN) in the absence and presence of γ-CD.

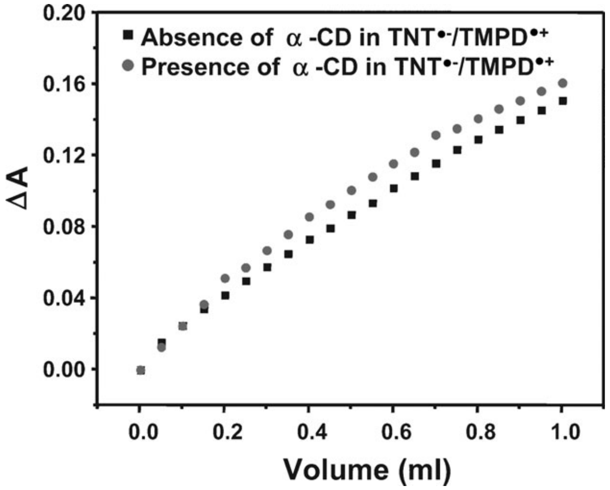


Fig. 5 A plot of volume against change in absorbance of TNT$^{\bullet-}$/TMPD$^{\bullet+}$ (H_2O–5% MeCN) in the absence and presence of α-CD.

We observed the titrations are essentially identical in the presence and absence of α- and β-CD. So we could conclude that there was no encapsulation of TNT$^{\bullet-}$/TMPD$^{\bullet+}$ in their cavities.

These observations suggest that the large cavity of γ-CD is suitable to encapsulate TNT$^{\bullet-}$ and TMPD$^{\bullet+}$, and when they are close in contact[37,39] in a hydrophobic environment, the CT complex is preferred.

Binding of CD with RDX through CT complex formation

Cyclictrimethylenetrinitramine (hexahydro-1,3,5-trinitro-1,3,5-triazine), better known as RDX, is a powerful explosive used in C4. It has attracted considerable attention due to its unique properties.[40,41] The molecule consists of three NO_2 groups bonded to the nitrogen atoms of a triazine ring (Chart 1).

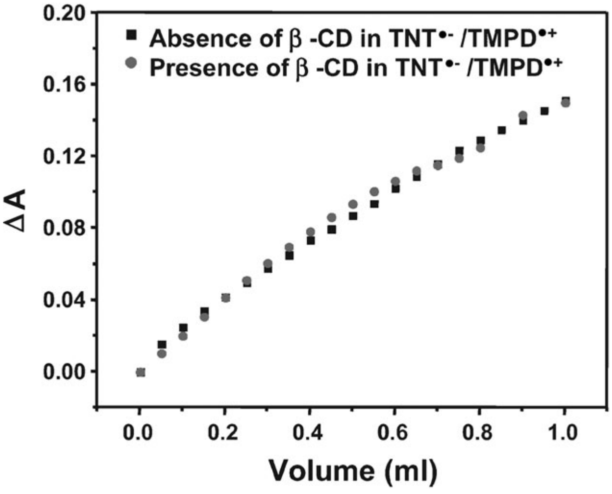


Fig. 6 A plot of volume against change in absorbance of TNT$^{\bullet-}$/TMPD$^{\bullet+}$ (H_2O–5% MeCN) in the absence and presence of β-CD.

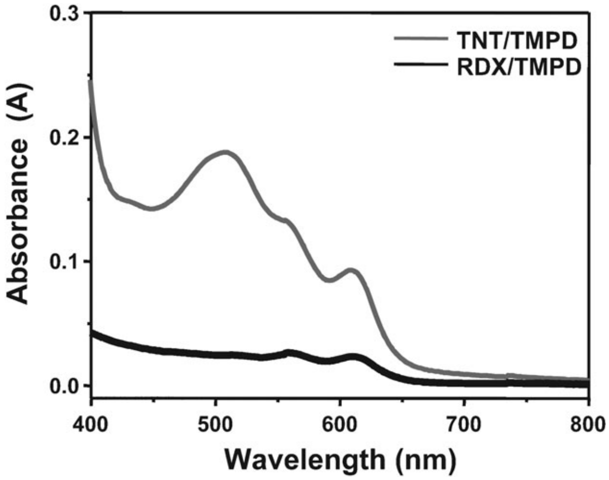


Fig. 7 Absorption spectra of TNT/TMPD (gray) and RDX/TMPD (black) in MeCN.

A solution of RDX in MeCN was studied with TMPD in a manner analogous to TNT. Similar to TNT/TMPD, the RDX/TMPD CT complex was formed, but it showed a very weak absorbance (Fig. 7). It is known that N–NO_2 groups are weaker electron acceptors compared to C–NO_2 groups.

This is evident from Fig. 7 where RDX/TMPD showed a very weak absorbance compared to the absorbance of the TNT/TMPD complex. Thus, TNT and RDX behaved differently when mixed with the strong electron donor TMPD in MeCN.

However, when the weak RDX/TMPD CT complex in MeCN solution was diluted to 0.09 mM in H_2O–5% MeCN, the intense violet color formed indicative of electron transfer from TMPD to RDX and the formation of $TMPD^{\bullet+}$ and $RDX^{\bullet-}$. Analogously to the study with TNT, the complex with γ-CD was studied by checking for the saturation of the violet color. As a control, we also carried out the same titration without γ-CD. We observed that there little to no difference in intensities in the presence and absence of γ-CD as shown in Fig. 8. Therefore, separate ions $RDX^{\bullet-}$ and $TMPD^{\bullet+}$ are not encapsulated in the cavity of γ-CD. Even with addition of high concentrations of γ-CD there was little encapsulation of $RDX^{\bullet-}$ and $TMPD^{\bullet+}$ within the γ-CD cavity.

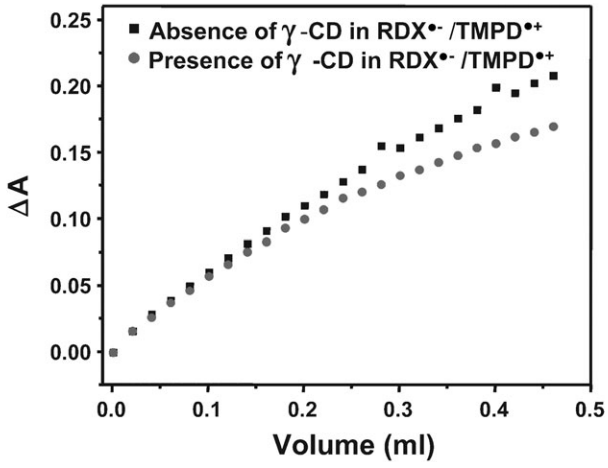


Fig. 8 A plot of volume against change in absorbance of $RDX^{\bullet-}$/$TMPD^{\bullet+}$ (H_2O–5% MeCN) in the absence and presence of γ-CD.

This study also showed that the effect of γ-CD is not to simply complex TMPD and thereby protect it from oxidation by the acceptors. If this were occurring, there would again be protection from RDX, which we do not observe. Hence, TNT and RDX act differently in the presence and absence of γ-CD. The cross reactivity indicates that similar differences may exist with the other nitro explosives. Therefore, based on the above findings, we expanded our study to the detection of explosives by the use of a sensor array using γ-CD.

UV-Vis—variation with time

As shown in Fig. 4–6 and 8, the separated acceptor/donor ions increase in concentration over time, and increase over the time scale of a titration. Therefore to create a sensor array using CD and UV-Vis titration methods, we needed to use the time course variations in the array based analysis. In the UV-Vis time interval method, we included the other two explosives, Tetryl, which is a nitro aromatic, and HMX, which is a nitramine (Chart 1).[42]

Sensor arrays generate a great deal of data in a very short time. For this reason, one often uses pattern recognition protocols to simplify the output and analysis. The pattern analysis methods used herein were principal component analysis (PCA) and linear discriminant analysis (LDA).[43] Often two or three principal components provide an adequate representation of the data, which is convenient for graphical display.[44]

The time course reactions were studied for four nitrated explosives as analytes: TNT, RDX, HMX and Tetryl, with TMPD in the presence and absence of γ-CD using UV-Vis spectrophotometry. In the absence of γ-CD we simply mixed the analyte as received with TMPD in the same concentrations in MeCN. The absorbance of the solution was measured for 40 min. The intensities of the λ_{max} of analyte/TMPD were measured. In the presence of γ-CD, a solution of analyte with TMPD at 0.09 mM was prepared in H_2O–5% MeCN. To the solution, a host stock solution (analyte/TMPD (0.09 mM) plus γ-CD (0.09 M)) was added, and the absorbance was measured for 40 min. The time course experiments in the presence and absence of γ-CD with TMPD and each analyte was repeated five times and was found to be very reproducible. Then we developed an array format consisting of four columns, each column being the absorbances at two different maximum wavelengths after 40 min in the presence and absence of γ-CD, and twenty rows for five analytes. The result of PCA using the entire data set is shown in Fig. 9.

As shown in Fig. 9, the first principle component (PC1) carries about 62.46% of the variance while the second principle component (PC2) carries 35.52%. Altogether 97.98% of the whole variance in the data is carried by these two components. Excellent clustering of all the analytes was achieved. The tight clustering of repetitious data relative to the separation of each analyte demonstrates good resolution. The results clearly demonstrate that the technique reproducibly allows the

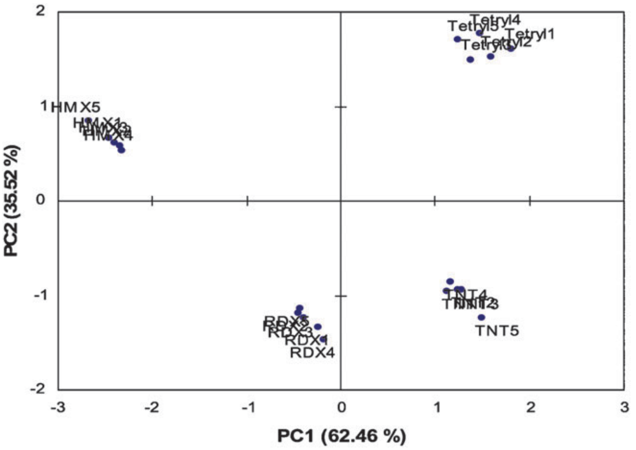


Fig. 9 Two-dimensional PCA plot for selective explosives TNT (4.40 mM), RDX (4.50 mM), HMX (3.38 mM) and Tetryl (3.48 mM) in MeCN.

discrimination of the explosives, while the method is inexpensive and rapid.

The variance along the PC axes of Fig. 9 carries information about the analysis. Apparently, TNT and Tetryl act similarly due to their near identical scores along PC1. The most obvious similarity is their greater tendency to undergo electron acceptance from the TMPD donor. Yet, along the PC2 axis we find RDX and TNT, and separately HMX and Tetryl, with nearly identical scores. The similarities here are not as clear, but potentially size is a determining factor. HMX and Tetryl are larger, and this would affect their ability to be associated with the γ-CD. Irrespective of the reasons behind the discrimination, it is clear that the combination of host–guest chemistry with γ-CD coupled with the associated modulation of charge transfer leads to a powerful method of analysis. However, we were interested in finding out if a similar analysis without γ-CD could also be successful, and therefore we proceeded in array studies minus the γ-CD. As now described, this also works but with much lower discriminatory power between RDX and HMX.

Assays with TMPD and TDAE in the absence of cyclodextrin

Given the success of the study with TMPD and cyclodextrin, we next assessed the ability of a second electron donor to form charge-transfer complexes with the analytes in a variety of solvents. TDAE was chosen for this purpose. Shown in Fig. 10(A) are vials containing equimolar amount of TDAE (2.25 mM) and our explosive analytes (2.25 mM). We observed that the nitroaromatics TNT (burgundy) and tetryl (orange) were nicely discriminated from the nitramines, which showed different intensities of yellow color upon addition of TDAE. These color changes are shown along with PETN, which appears as a colorless solution. Corresponding UV-Vis changes for equimolar solutions of the explosives with TDAE (40 μM) are shown in Fig. 10(B). LDA was performed on a data matrix consisting of the analytes (rows) and absorbance values at the wavelengths showing the greatest differences in absorbance values of the analytes (columns). Two discriminant functions (F1 and F2) accounted for 100% of the variance in the data set. A scores plot (Fig. 11) of F1 *vs.* F2 features classification of TNT and Tetryl, however, RDX and HMX have overlapping score values and hence are not classified, in keeping with the raw data. A cross-validation assessment method, known as the leave-one-out,[45] showed 100% classification of all observations in the data set.

To improve the discriminatory properties of our array with respect to the nitramines, we included TMPD in a variety of

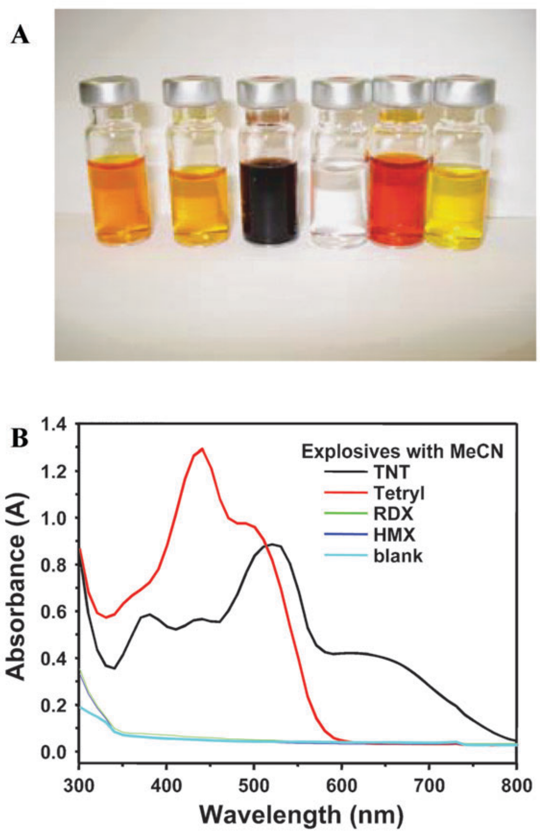


Fig. 10 (A) Vials containing 2.25 mM TDAE and 2.25 mM explosives (from left to right): RDX, HMX, TNT, PETN, Tetryl and blank. (B) Absorbance spectra of TDAE with TNT, Tetryl, RDX and HMX in MeCN.

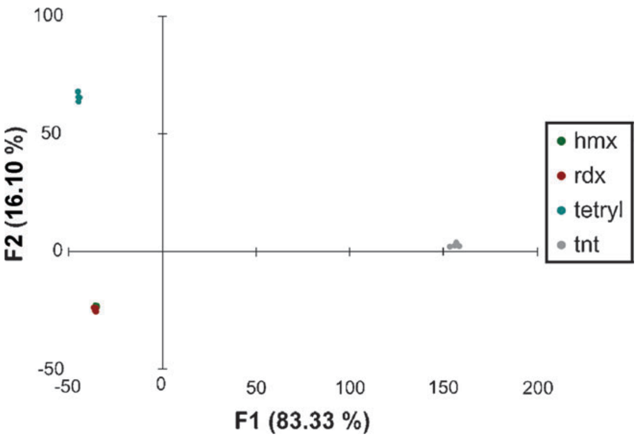


Fig. 11 Scores plot of F2 *vs.* F1 for TNT, RDX, HMX and Tetryl with an array based on donor–acceptor complexes formed by TDAE.

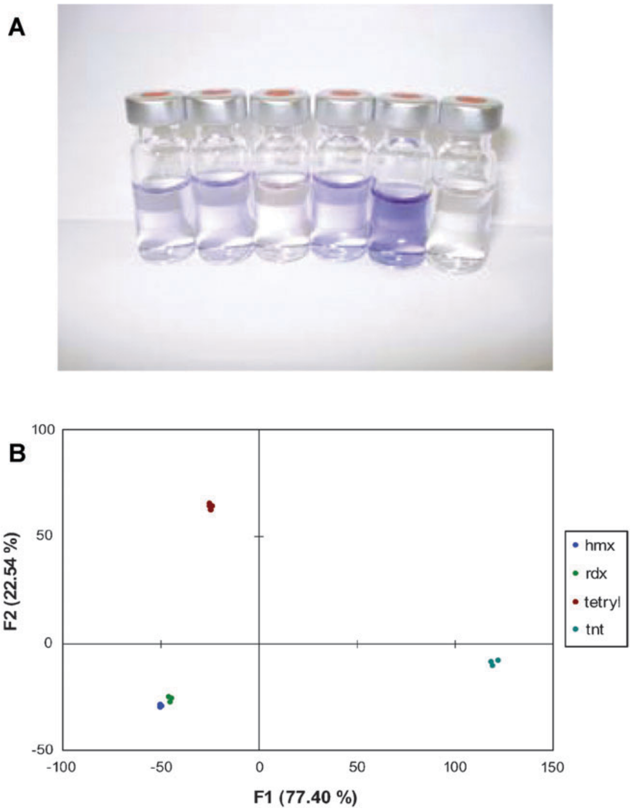


Fig. 12 (A) Vials containing 2.25 mM TMPD and 2.25 mM explosives (from left to right): RDX, HMX, TNT, PETN, Tetryl and blank. (B) Scores plot of F2 *vs.* F1 for TNT, RDX, HMX and Tetryl with an array based on acceptor–donor complexes formed from TMPD and TDAE.

solvents (H_2O, CH_3CN and $CH_2H_4Cl_2$) alongside TDAE, with the expected result of changing the position and intensity of the UV-Vis bands resulting from the formation of the charge-transfer complexes. Different intensities of a blue–violet color are formed upon mixing equimolar quantities of our explosive analytes with TMPD and TDAE. A linear discriminant scores plot of F1 *vs.* F2 (Fig. 12) features classification of all our explosive analytes. The result is accompanied by a 100% classification of all observations in the data set by the leave-one-out method.

Conclusion

The inclusion behavior of CT complexes, $TNT^{\bullet -}/TMPD^{\bullet +}$ and $RDX^{\bullet -}/TMPD^{\bullet +}$ with γ-cyclodextrin was determined. The non-inclusion complex of $TNT^{\bullet -}/TMPD^{\bullet +}$ with α- and β-cyclodextrins was also studied. The complexation of TNT-TMPD in cyclodextrins with a suitable cavity size was reported. We used the differences in time course evolution of CT-complexes to separate the analytes of explosives TNT, RDX, HMX and Tetryl using PCA. A very good clustering of the analytes illustrated the ability of the array to discriminate the explosives. Further, we worked with the same analytes with TDAE. LDA was applied, and found the ability of array in the discrimination of explosives was found to be good exception for RDX and HMX. In conclusion, we have created a simple color change array, that when coupled with pattern recognition leads to complete classification of the analytes. Also, we found the discrimination of explosives in the absence of cyclodextrin using 96-well plate experiments. Both systems can serve as the methods for the classification and identification of explosives.

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