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A fluorescence-based cyclodextrin sensor to detect nitroaromatic explosives

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We report the use of a cyclodextrin inclusion complex (CIC) in fluorescence sensing to provide a method to classify energetic nitroaromatic compounds. A CIC was prepared by the inclusion of 9,10-bis(phenylethynyl)anthracene (BPEA) with γ-cyclodextrin (CD) (BPEA/CD) in water with 5% tetrahydrofuran by volume. The inclusion behaviour of BPEA with γ-CD was studied by fluorescence spectroscopy. The effect of α- and β-CD with BPEA was also studied. In this system, the inclusion complex BPEA/CD acted as the host and the guests were the explosives 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), 2,4,6-trinitrophenyl-*N*-ethylnitramine (Tetryl), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazine (HMX) and pentaerythritoltetranitrate (PETN). The binding of TNT, RDX, Tetryl, HMX and PETN with CD/BPEA was studied for the potential use of BPEA/CD in a sensing application. Experiments were also conducted with explosives and BPEA in the absence of CD. The optical response found for the explosives TNT, RDX, Tetryl, HMX and PETN with BPEA/CD was modelled with a modified Stern–Volmer relationship. This investigation showed successful classification of aromatic and non-aromatic explosives. The approach using a CD-based fluorescence sensor has the potential to be a sensing technology for the detection of nitroaromatic explosives.

Keywords: TNT; RDX; HMX; Tetryl; PETN; BPEA

Introduction

Reliable detection of trace explosive materials has become a focal point in security screening methods. Research efforts to date for the detection of explosives have been substantial. Nevertheless, identifying and distinguishing related explosives using current sensing methods is still an enormous challenge (*1–3*). Further, even though much effort has been directed to the detection of explosives (*4*), there is a lack of simple and convenient methods. Our efforts have focused on sensing the five commonly used explosives: 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) (Chart 1). Prior to this work, we reported a simple method to detect explosives using UV–visible spectroscopy (*5*). Fluorescence quenching-based chemical detection represents one of the most sensitive and convenient methods employed in explosive detection (*1*, *6*). Herein, we present a molecular chemosensor for the direct fluorescent detection of TNT and Tetryl, as well as for discrimination of aromatic and non-aromatic explosives by a cyclodextrin (CD) host.

CDs have been the subject of much study in the field of supramolecular chemistry due to their ability to bind a variety of organic compounds. CDs are cyclic oligosaccharides, the most common of which (designated α, β and γ) consist of six, seven and eight glucose units, respectively. The internal cavities of these near cylindrical compounds vary in the order $\alpha < \beta < \gamma$ (*7*). What makes CDs interesting is their ability to extract and bind hydrophobic molecules from aqueous solution, because their cavities are less polar than water. Taking advantage of these unique molecules is the object of enormous research (*8*). Building on our earlier UV–visible study that probed hydrophobic interactions (*5*), we became interested in creating a fluorescent detection mode for use in a sensor for explosives due to the generally higher sensitivity of fluorescence.

Many dyes/fluorophores form inclusion complexes with CD in aqueous solution (*9*). CDs are spectroscopically inert, but they can be transformed into spectroscopically active hosts that signal guest binding by covalent introduction of a chromophore or fluorophore (*8a*). Our goal was to create a sensor by complexation of a fluorescent molecule with the CD, where the CD simultaneously non-covalently binds the guest and the fluorophore. We selected 9,10-bis(phenylethynyl)anthracene (BPEA) for our current study. BPEA has a high quantum yield for fluorescence (*10*), and it has been widely used in chemiluminescent formulations (*11*). Due to its remarkably high emission efficiency in the visible region, good solubility in a variety of solvents and thermal stability (*12*), we thought that BPEA would be a good

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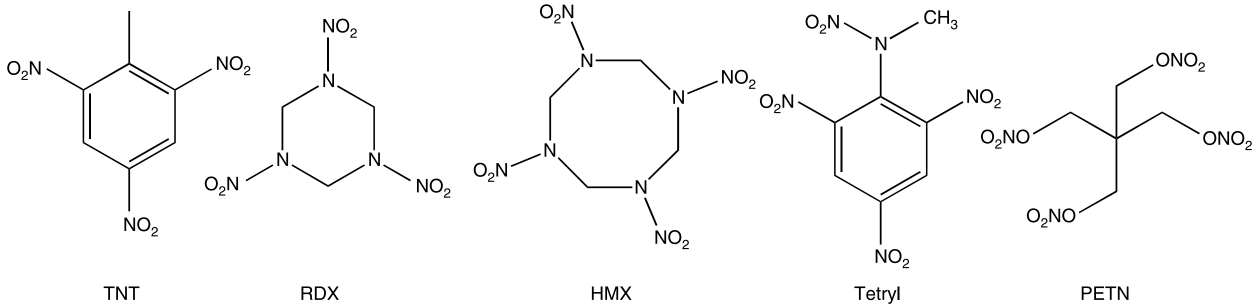


Chart 1. Explosives.

sensor for our study, and thus, we converted non-fluorescent CD into a fluorescent binding ensemble of BPEA/CD.

The fluorescent BPEA/CD ensemble was studied for the binding and inclusion ability of the analytes TNT, RDX, Tetryl, HMX and PETN. Molecular size and shape of the guest have a large role to play in deciding the mode of inclusion of explosives in a BPEA/CD complex. In addition, for a given guest, the stoichiometry, stability and structure of the CD complex will depend on which of the three CDs is used. The cavity size of γ-CD is large enough to accommodate 2:1 complexes (*7*). We exploited the 2:1 stoichiometry to sense explosives by a quenching process. To model the quenching, we used a modified Stern–Volmer relationship, which led to a method of classification of analytes/explosives.

Experimental

Materials and methods

α-, β- and γ-CDs and BPEA were purchased from Aldrich Chemical Company (St Louis, MO, USA) and used without purification. TNT, RDX, HMX and Tetryl were all supplied as 1000 $\mu g\,ml^{-1}$ acetonitrile solutions in sealed glass vials from Ultrascientific (North Kingstown, RI, USA). PETN was obtained as 1000 $\mu g\,ml^{-1}$ in methanol in sealed glass vials from Accustandard (New Haven, CT, USA). Tetrahydrofuran (THF) was obtained from Fischer Scientific (Pittsburgh, PA, USA). Both water and THF were degassed prior to use via bubbling with N_2 for 2 h. Single-cuvette fluorescent measurements were made using a Photon Technology International Quanta Master spectrofluorimeter.

Fluorescence titrations

Titration 1 (binding of BPEA with CD – BPEA/CD)

The solvent H_2O–5% THF served as a blank. A cuvette with 2 ml solution of BPEA as a guest (99 μM) was prepared. The host stock solution was identical to the cuvette solution but with CD (9.9 mM). The host stock solution was added in aliquots to the cuvette and the intensity was recorded between aliquots. The intensity between the original solution of the guest and the final addition of the host was determined. The change in intensity between each addition of the host was plotted against the concentration of the host added.

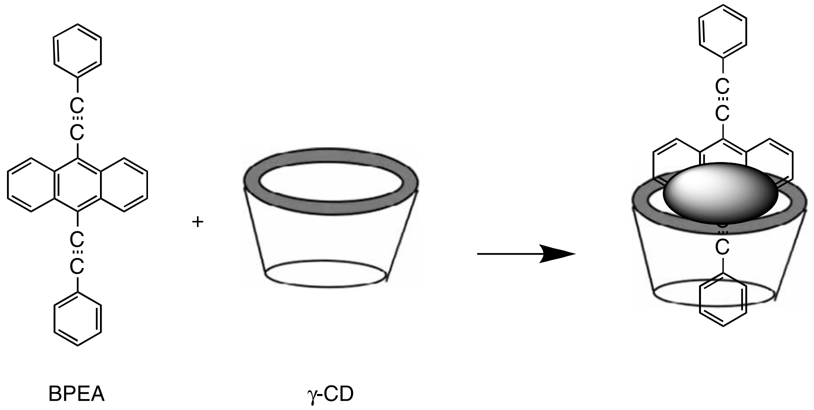
Titration 2 (binding of BPEA/CD with explosives)

The solvent H_2O–5% THF served as a blank. A cuvette with 2 ml solution of BPEA/CD as a host, where [BPEA] = 99 μM and [CD] = 9.9 mM, was prepared. The guest stock solution was identical to the cuvette solution but with added explosive. The guest stock solution was added in aliquots to the cuvette and the intensity was recorded between aliquots. The intensity between the original solution of the host and the final addition of the guest was determined. The change in intensity between each addition of the guest was plotted against the concentration of the guest added.

Results and discussion

Binding of CD with BPEA

The binding of BPEA with CD forms a cyclodextrin inclusion complex (CIC), which is the basis for the sensor. The fluorescence enhancement in aqueous media of CD–dye inclusion complexes (*9*, *13*) has been observed in a number of studies. In other situations, a diminution of fluorescence is noted (*14*, *15*). In our study, a CIC was prepared from the inclusion of BPEA with γ-CD in water with 5% THF by volume (Scheme 1). We observed a decrease in the fluorescence intensity as described previously. The fluorescence of a cuvette with 2 ml solution of BPEA as a guest (99 μM) was recorded via excitation at 495 nm. The host stock solution was identical to the cuvette solution but with CD (9.9 mM). The host stock solution was added in aliquots to the cuvette and the



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

fluorescence intensity was recorded between aliquots. The intensity of the maximum difference between the original solution of the BPEA and that found after the addition of CD was determined. The change in intensity between each addition of CD was plotted against the concentration of CD added to the solution. The intensity of the BPEA emission became saturated as the concentration of γ-CD increased, as shown in Figure 1. We used the saturation point for making a (BPEA/CD) sensor for the differentiation of explosives (see below).

We carried out the same experiment for the inclusion of BPEA except using α- and β-CD. The central cavity diameter of α-, β- and γ-CD is 5.3, 6.5 and 8.3 Å, respectively, and the height of the CD cavity is 7.9 Å (*7*). The fluorophore for inclusion is BPEA, the diameter of the anthracene moiety is 7.3 Å and the height of the phenyl ring moiety is 2.7 Å (*11d*). The phenyl ring moiety is definitely bound in α-, β- and γ-CD. Because of the smaller cavity of α- and β-CD, the anthracene ring in BPEA is not able to bind these two compounds.

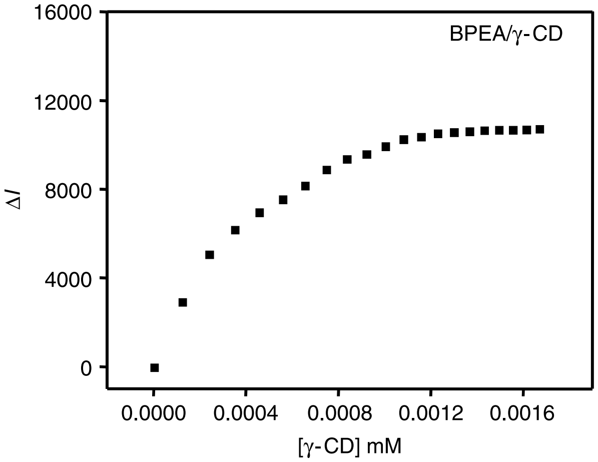


Figure 1. A plot of concentrations of γ-CD against change in intensity of BPEA (99 μM in H_2O–5% THF).

We observed that there were little to no changes in intensities even in the presence of high concentrations of α- and β-CD. But, in γ-CD, we demonstrate that, from the above physical characteristics, the inclusion of the anthracene ring in BPEA can occur. The current experimental study also evidenced the changes in intensities when BPEA was included in γ-CD.

Binding of BPEA/CD with TNT

TNT is widely used among explosives in the modern world. This widespread use of nitroaromatics makes them an important target class for detection (*16–18*). The BPEA/CD complex was studied to detect the explosive TNT. As an example, 2 ml solution of BPEA/CD as a host, where [BPEA] = 99 μM and [CD] = 9.9 mM, was added to a cuvette. The guest stock solution was identical to the cuvette solution but with TNT. We observed strong fluorescence quenching by TNT. The intensity of the maximum difference between the fluorescence of the original solution of BPEA/CD and the final addition of TNT was determined. The change in intensity was plotted versus [TNT] and the intensity saturated as [TNT] increased (Figure 2). As a control, we also carried out the same titration experiment but without the presence of γ-CD. In the absence of CD, the quenching and the saturation were also observed, but not to as great an extent as in the presence of CD. This indicates that BPEA is more effectively quenched by TNT in the presence of CD. There are reports (*19*, *20*) stating that CD encapsulation reduces the quenching effect when smaller α- and β-CDs were used. This was attributed to the protection of the fluorophore from the quencher by binding to the CD. In our system, we observed an increase in the quenching by TNT in the presence of γ-CD, where the cavity is larger than α- and β-CD. This provides evidence that TNT is able to bind to CD in the presence of BPEA, possibly in a stacking orientation with BPEA.

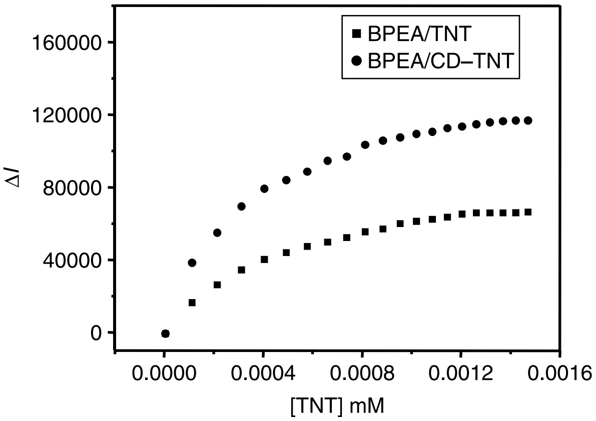


Figure 2. A plot of concentrations of TNT against change in intensity of BPEA (99 μM in H_2O–5% THF) in the absence and presence of γ-CD (9.9 mM).

Mechanism of quenching by TNT with CD/BPEA

To investigate the mechanism of quenching by TNT (Q), the measured fluorescence intensities in the presence as well as absence of TNT were determined. The Stern–Volmer equation (*21*) (Equation (1)) is useful in the quantitative measurement of fluorescence quenching; F_0 is the initial fluorescence measured in the absence of the quencher, F is the fluorescence intensity at a given concentration of Q and K_{sv} is the Stern–Volmer constant,

$$\frac{F_0}{F} = 1 + K_{sv}[Q]. \tag{1}$$

Quenching data are presented as plots of F_0/F vs. $[Q]$. A linear Stern–Volmer plot is generally indicative of a fluorophore being accessible to the quencher. But in the present study, the Stern–Volmer plot for TNT slopes downwards (Figure 3(A)). The downward curvature towards the x-axis of the plot indicates two separate mechanisms or populations of fluorophores involved in quenching (*21a*).

Commonly, one models downward curvature by postulating two populations of fluorophores, one of which is accessible (a) to quenchers and the other being inaccessible or buried (b). The total fluorescence in the absence of the quencher (F_0) is given by

$$F_0 = F_{0a} + F_{0b}, \tag{2}$$

where the subscript ‘0’ refers to the fluorescence intensity in the absence of the quencher. In the presence of the quencher, the intensity of the accessible fraction (f_a) is decreased according to the Stern–Volmer equation, whereas the buried fraction is not quenched. Therefore, the observed intensity is given by

$$F = \left(\frac{F_{0a}}{1 + K_a[Q]}\right) + F_{0b}, \tag{3}$$

where K_a is the Stern–Volmer quenching constant of the accessible fraction and $[Q]$, the concentration of the quencher. Subtracting Equation (3) from Equation (2) yields

$$\Delta F = F_0 - F = F_{0a}\left(\frac{K_a[Q]}{1 + K_a[Q]}\right). \tag{4}$$

Inversion of Equation (4) followed by division into Equation (2) yields

$$\frac{F_0}{\Delta F} = \frac{1}{f_a K_a[Q]} + \frac{1}{f_a}, \tag{5}$$

where f_a is the fraction of the initial fluorescence that is accessible to the quencher,

$$f_a = \left(\frac{F_{0a}}{F_{0b} + F_{0a}}\right). \tag{6}$$

This modified form of the Stern–Volmer equation allows f_a and K_a to be determined graphically (Figure 3(B)). A plot of $F_0/\Delta F$ vs. $1/[Q]$ yields f_a^{-1} as the intercept and $(f_a K)^{-1}$ as the slope. A Y intercept may be understood intuitively. The intercept represents the extrapolation to infinite quencher concentration ($1/[Q] = 0$). The value of $F_0/(F_0 - F)$ at this quencher concentration represents the reciprocal of the fluorescence that was quenched. We observed that K_{sv} was $3.53 \times 10^3\ M^{-1}$ for the quenching of BPEA/CD with TNT. In the absence of CD, the quenching of BPEA by TNT had a K_{sv} value of $2.22 \times 10^3\ M^{-1}$. Hence, quenching is increased with CD, indicating a static quenching mechanism that is assisted by CD.

Fluorescence quenching can occur by static and dynamic processes (*21a*). Both static and dynamic quenching require molecular contact between the fluorophore and the quencher. Static processes are the result of quenching by a bound complex, which is supported by the data for BPEA/CD bound with TNT. For static quenching, the diffusion rate of the quencher is not a factor and the fluorescence lifetime can be saturated by increasing [TNT]. For purely dynamic quenching, the excited state is quenched by a collision with TNT, and hence, the lifetime is reduced with added TNT. If the Stern–Volmer plot (F_0/F vs. $[Q]$) is linear, it indicates that only one type of quenching, either static or dynamic, is dominant. Situations in which the two processes are competitive give rise to nonlinear Stern–Volmer relationships. In our study of the quenching by TNT of the BPEA/CD complex, we observed non-linearity when F_0/F is plotted against

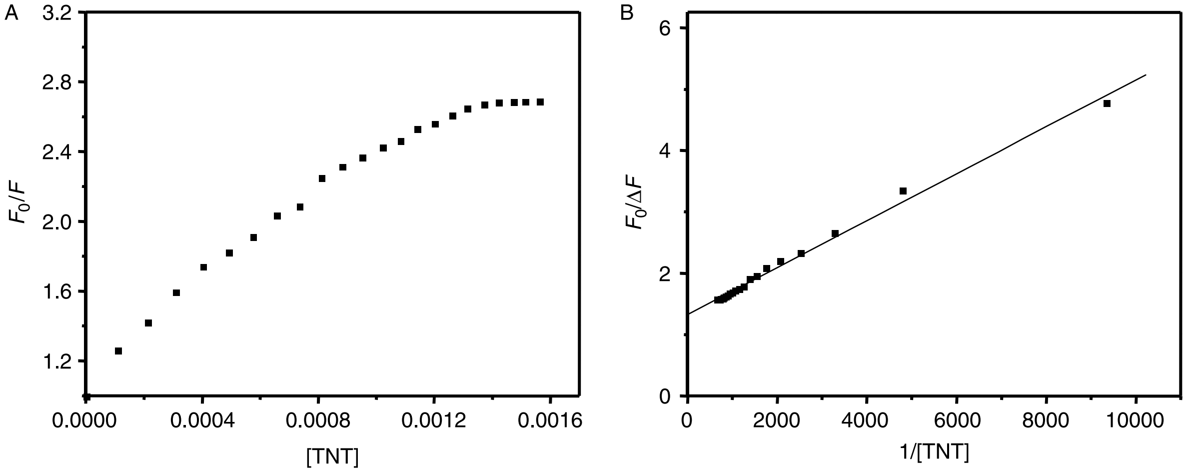


Figure 3. (A) Stern–Volmer. (B) Modified Stern–Volmer plots for TNT quenching the sensor BPEA/CD.

[TNT]. Hence, there is the possibility of both static and dynamic quenching. Static quenching is in accord with host–guest complexation. So, we conclude that TNT quenches the BPEA/CD complex by both static and dynamic quenching. In the absence of CD, we also observed non-linearity. Hence, we conclude that both static and dynamic processes are possible even without CD. The BPEA and TNT aggregate to some extent without CD. But in the presence of CD, the value of K_{sv} for the quencher TNT is 1.6 times higher than that in the absence of CD (Table 1). We interpret this to support complexation of TNT with BPEA, but CD increases the complexation due to a weak encapsulation of both BPEA and TNT.

Binding of RDX, Tetryl, HMX and PETN with CD/BPEA

RDX is the explosive used in C4, and it has attracted considerable attention due to its unique properties (*1*, *22*). The molecule consists of three NO_2 groups bonded to the nitrogen atoms of a triazine ring (Chart 1). RDX was studied in a manner analogous to TNT, but it showed no response to BPEA/CD (Figure 4). Control experiments were carried out in the absence of CD, and RDX did not quench BPEA in the absence of CD. Hence, TNT and RDX act differently with the sensor BPEA/CD. The cross-reactivity indicates that similar differences may exist with the other nitro explosives.

Table 1. K_{sv} (M^{-1}) values measured with the addition of various explosives.

Quenchers	BPEA/CD	BPEA
TNT	3.53×10^3	2.22×10^3
RDX	No quenching	No quenching
Tetryl	1.91×10^3	1.47×10^3
HMX	No quenching	No quenching
PETN	No quenching	No quenching

To better understand the response of the BPEA/CD sensor, experiments were conducted with Tetryl (*23*), which is a nitroaromatic compound, HMX (*24*), which is a nitramine, and PETN (*25*), all using the same procedure. The response to Tetryl was as with TNT in the quenching of BPEA/CD. As with TNT, Tetryl has a higher change in intensity in the presence of CD than in the absence of CD (Figure 4). We also did not observe a linear Stern–Volmer plot for Tetryl when F_0/F was plotted against [Tetryl]. We applied the modified Stern–Volmer equation to determine K_{sv}. The K_{sv} value is somewhat higher for Tetryl in the presence of CD ($1.91 \times 10^3\ M^{-1}$) than in the absence of CD ($1.47 \times 10^3\ M^{-1}$). The other two explosives, HMX and PETN, showed no response to the sensor. We conclude that

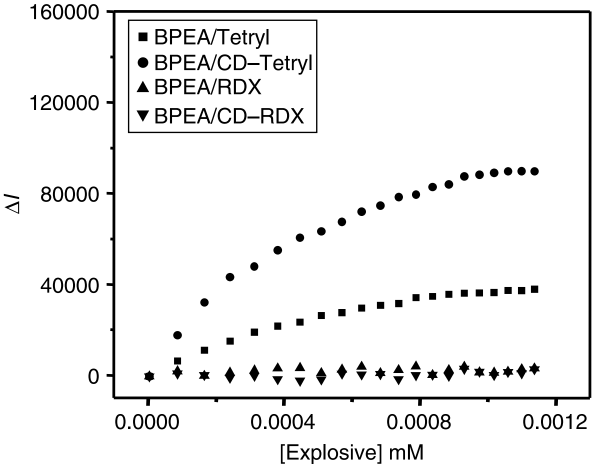


Figure 4. A plot of concentrations of explosive (RDX and Tetryl) against change in intensity of BPEA (99 μM in H_2O–5% THF) in the absence and presence of γ-CD (9.9 mM).

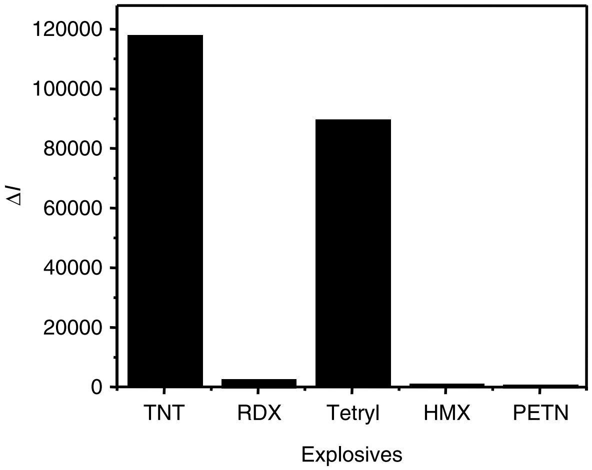


Figure 5. Change in emission profiles of explosives with the sensor BPEA/CD.

the non-aromatic explosives RDX, HMX and PETN neither bind with BPEA/CD nor able to quench free BPEA.

Figure 5 shows the change in emission resulting from the quenching of BPEA/CD by the explosives TNT, RDX, Tetryl, HMX and PETN. When we compare the quenching of the explosives TNT and Tetryl in the presence of CD, the quenching of TNT with the sensor BPEA/CD was moderately higher than that of Tetryl. One explanation is that TNT is slightly better accommodated than Tetryl in the CD cavity, which leads to the higher K_{sv}.

Conclusion

The inclusion behaviour of BPEA with γ-CD was explored as a potential sensor of nitro explosives. The complexation of BPEA with CDs with a suitable cavity size was reported. The complex BPEA/CD differentiates aromatic explosives TNT and Tetryl from RDX, HMX and PETN by using their differential quenching ability with the sensor. The aromatic explosives TNT and Tetryl were able to quench BPEA/CD, while the non-aromatic explosives RDX, HMX and PETN showed no response. A modified Stern–Volmer equation was applied to describe the sensing ability of explosives by the sensor. In addition, quenching interactions as measured by K_{sv} were enhanced by the CD-complexed fluorophore by 1.6 times for TNT and 1.3 times for Tetryl than in the absence of γ-CD. Particularly when we compare TNT and Tetryl in the presence of γ-CD, K_{sv} for TNT is 1.8 times higher than that of Tetryl, possibly due to better fit in the γ-CD cavity.

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