Chemical Science

RSCPublishing

EDGE ARTICLE

View Article Online
View Journal

Cite this: DOI: 10.1039/c3sc51132d

CB[8]-based rotaxane as a useful platform for sensitive detection and discrimination of explosives†

Wei Zhu, Weina Li, Chen Wang, Jiecheng Cui, Haowei Yang, Yin Jiang
and Guangtao Li*

Received 26th April 2013
Accepted 12th June 2013

DOI: 10.1039/c3sc51132d

www.rsc.org/chemicalscience

Based on a naphthalene-threaded cucurbit[8]uril (CB[8]) rotaxane structure on a solid substrate, a new strategy for rapid, fully reversible, and highly sensitive detection of a broad class of explosives was developed by using one receptor. Due to the unique confinement effect and size exclusion of the CB[8] cavity, it is found that the intercalation of an explosive compound in the constructed rotaxane can significantly influence the photophysical property of the naphthalene core in the confined nanocavity of CB[8]. Dependent on the electronic structures and the sizes of explosive compounds, the fluorescence of the naphthalene core would be quenched or enhanced to different extents, leading to the direct detection and discrimination of distinctively different groups of trace explosives in the vapor phase, especially including the challenging aliphatic nitro-organics (RDX, HMX and PETN). Control experiments were performed to show the different sensing behaviors between the common organic vapors and nitrate-based explosives, which made it easy to realize the discrimination between target analytes and interferents. Due to the surface-attached sensing elements, a rapid response was also achieved in this system. Moreover, the non-covalent nature of the resulting heteroternary complex indicates that the trapped target molecules in the rotaxane structure are facilely removable by simply washing, demonstrating an excellent regeneration of the constructed explosive sensors for real-world application. The performed experiments suggested that the rotaxane structure-based sensing protocol opened a new way to develop a new kind of explosive sensors enabling a richer identification of threats.

1 Introduction

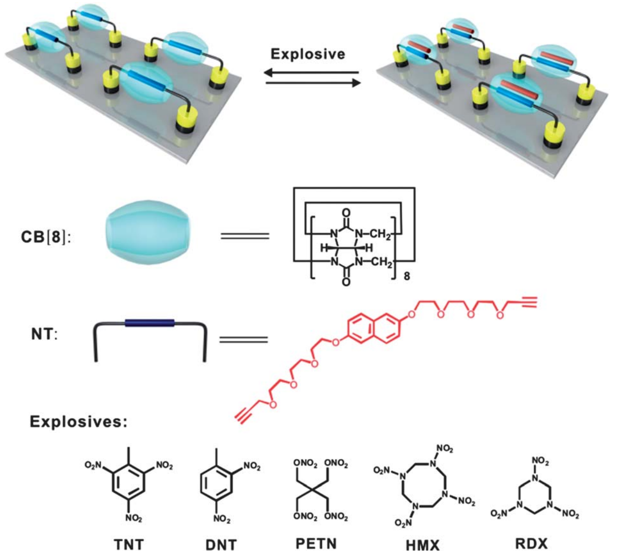
Rapid detection and discrimination of hidden explosives are very important aspects concerning homeland security, environmental and humanitarian safety.[1] In this respect, nitrated aromatics (*e.g.* TNT and DNT), nitramines (*e.g.* RDX and HMX), and nitrate esters (*e.g.* PETN) are three classes of the most commonly used energetic compounds,[2] which are directly associated with modern bombs in terrorist attacks or other criminal intents. In the past years, although numerous methods have been proposed for sensing these explosives, most of the works are limited to the detection of nitroaromatic compounds.[2] In contrast, due to their low-volatility and weak binding to the sensory materials, which arises from their highly three dimensional structures and lack of π–π interaction, directly detecting aliphatic nitro-organics such as RDX, HMX and PETN, in particular in the vapor phase, is very difficult and remains a great challenge.[3] Additionally, since their physicochemical properties differ from each other significantly, the development of a sensor for broad-class explosive detection is also a serious challenge.[3a] Many current sensors are only specific for one class of explosives, which reduce their overall utility. Therefore, developing a chemosensor that has a broad responsive range for different sorts of explosives would present a significant advance for this field, as it would enable a richer identification of threats.[3a]

Cucurbit[n]urils (CB[n], $n = 5$–8 glycoluril units) are a class of barrel-shaped macrocyclic hosts possessing a hydrophobic cavity accessible through both identical carbonyl-fringed portals for guest molecules.[4] These unique structural features make them very useful as versatile synthetic receptors and building blocks for construction of supramolecular architectures and functional chemical systems.[5] In particular, in comparison with CB[6] and CB[7] that typically bind to one equivalent guest molecule, the larger homologue CB[8] is able to simultaneously accommodate two guests. A more remarkable characteristic of CB[8] is that the binding can occur sequentially and the resulting CB[8]·X complex of the first guest (X) then can serve as a receptor for the second guest (Y).[6] Taking advantage of the rare binding ability of CB[8] to form a heteroternary

---

Key Lab of Organic Optoelectronic and Molecular Engineering, Department of Chemistry, Tsinghua University, Beijing, 100084, P. R. China. E-mail: lgt@mail.tsinghua.edu.cn; Tel: +86-010-62792905

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c3sc51132d



Scheme 1 Schematic illustration of the construction of CB[8]-based rotaxane on solid substrate for selective detection and discrimination of explosives in the vapor phase.

complex, in this work, we reported a novel strategy for selective detection and discrimination of explosives based on naphthalene-core-threaded CB[8] rotaxane structure (Scheme 1). To achieve a good sensing system with fast response and good sensitivity, the synthesized CB[8]-based rotaxane structure that is generated by a three-step approach was first grafted onto the solid substrate surface. During the detection process, interestingly, it was found that the intercalation of the explosive compound (the third component) in the constructed rotaxane would significantly influence the photophysical property of the naphthalene core in the confined nanocavity of CB[8].

Depending on the electronic structures and the sizes of explosive compounds, the fluorescence of the naphthalene core would be quenched or enhanced to different extent, leading to the direct detection and discrimination of distinctively different groups of trace explosives in the vapor phase, especially including the challenging aliphatic nitro-organics (RDX, HMX and PETN). The sensing mechanism toward the fluorescence quenching was attributed to form the host stabilized charge transfer (CT) complexes, whereas, enhancement effect was probably attributed to the 'rigidifying effect' where the encapsulated bulky guest molecule limited the motions (vibration, torsion *etc.*) of the naphthalene core and reduced its final nonradiative decay processes and thus increased the intensity of the fluorescence. Control experiments were performed to show the different sensing behaviors between the common organic vapors and nitrate-based explosives, which made it easy to realize the discrimination between target analytes and interferents. Moreover, the non-covalent nature of the resulting heteroternary complex indicates that the trapped target molecules in the rotaxane structure are facilely removable by simply washing, demonstrating an excellent regeneration of the constructed explosive sensors for real-world application.

2 Experimental section

Synthesis of 2,6-bis[2-(2-(2-hydroxyethoxy)ethoxy)ethoxy]-naphthalene

2,6-Dihydroxynaphthalene (2.29 g, 14.0 mmol) was added to a suspension of K_2CO_3 (5.94 g, 42.9 mmol) in dry DMF (50 ml). The suspension was heated to 70 °C under nitrogen and stirred for a further 30 min. A solution of 2-(2-(2-chloroethoxy)ethoxy)-ethoxyethanol (5.0 g, 62.3 mmol) in DMF (10 ml) was added dropwise over 1 h. Heating was continued for a further 3 days. The mixture was cooled, and the solid inorganic residues were filtered off *in vacuo* and washed with DMF. The DMF was removed *in vacuo*, and the resultant solid was taken up into CH_2Cl_2 (50 ml) and washed with saturated Na_2CO_3 (2×30 ml) and H_2O (2×30 ml). The organic layer was dried ($MgSO_4$), filtered under gravity, and the CH_2Cl_2 was removed *in vacuo*. MS: $C_{22}H_{32}O_8$ ($M = 424.49$), ESI-ms(+): m/z (+) = 447.29 $[M + Na]^+$, ^1H NMR (300 MHz, $CDCl_3$): δ 7.70 (2H, d, $J = 9$ Hz), 7.28 (2H, S), 7.13(2H, d, $J = 9$ Hz), 4.17 (4H, t, $J = 4$ Hz), 3.80 (4H, t, $J = 4$ Hz), 3.61 (4H, t, $J = 3$ Hz), 3.56 (4H, t, $J = 3$ Hz), 3.48 (4H, t, $J = 4$ Hz), 3.43 (4H, t, $J = 4$ Hz), 3.37 (2H, broad, S).

Synthesis of 2,6-bis(2-(2-(2-(prop-2-ynyloxy)ethoxy)ethoxy)-ethoxy)naphthalene (NT) and 2-(2-(2-((6-(2-(2-(2-(prop-2-yn-1-yloxy)ethoxy)ethoxy)ethoxy)naphthalene-2-yl)oxy)ethoxy)-ethoxy)ethanol (NT-1)

Solid NaH (362 mg, 15.1 mmol) was added to the solution of 2,6-bis[2-(2-(2-hydroxyethoxy)ethoxy)ethoxy]naphthalene (1.60 g, 3.78 mmol) in dry DMF (50 ml). The resulting suspension was stirred at 23 °C until the evolution of gas ceased. A solution of propargyl bromide in xylene (80%) by weight, (4.20 ml, 37.8 mmol) was injected using a syringe. The mixture was stirred at 23° for 4 days. The reaction was stopped by the addition of MeOH, and the solvent were removed *in vacuo*. Crude brown oil was first filtered through a plug of silica, eluting with Me_2CO, and then subjected to chromatography on silica (hexane/EtOAc = 50/50) to provide a white solid. MS: $C_{28}H_{36}O_8$ ($M = 500.24$), ESI-ms(+): m/z (+) = 523.27 $[M + Na]^+$, ^1H NMR (300 MHz, $CDCl_3$): δ 7.61 (2H, d, $J = 9$ Hz), 7.16 (2H, d, $J = 9$ Hz), 7.10 (2H, S), 4.20–4.23 (8H, m), 3.92 (4H, t, $J = 5$ Hz), 3.37–3.77 (m, 8H), 3.70–3.72 (m, 8H), 2.42 (2H, t, 2 Hz). MS: $C_{25}H_{34}O_8$ ($M = 462.53$), ESI-ms(+): m/z (+) = 485.2 $[M + Na]^+$, ^1H NMR (300 MHz, $CDCl_3$): δ 7.61 (2H, d, $J = 9$ Hz), 7.16 (2H, d, $J = 9$ Hz), 7.10 (2H, S), 4.20–4.23 (6H, m), 3.92 (4H, t, $J = 5$ Hz), 3.70–3.80 (14H, m), 3.62 (2H, t, 4 Hz), 3.48 (1H, s), 2.42 (1H, t, 2 Hz).

Synthesis of 3-azidopropyltriethoxysilane

3-chloropropyltriethoxysilane (5.0 g, 20.85 mmol), sodium azide (5.0 g, 76.92 mmol) and 60 ml of dry DMF were heated to 90 °C under a N_2 atmosphere for 8 h. The boiling materials were removed by distillation under reduced pressure, after which 50 ml of diethyl ether was added to the cooled mixture and the precipitated salts were removed by filtration. Diethyl ether removal and the oil were subjected to chromatography on silica to provide as a colorless liquid. ^1H NMR (300 MHz, $CDCl_3$): δ 3.83 (q, $J = 7$ Hz, 6H; CH_3CH_2O), 3.27 (t, $J = 7$ Hz, 2H; CH_2N_3), 1.72 (m, 2H; $SiCH_2CH_2$), 1.23 (t, $J = 7$ Hz, 9H, CH_3CH_2O), 0.70 (m, 2H; $SiCH_2$).

Fabrication of CB [8]-NT film

A mixture of CB[8] (2 ml, 0.1 mM), methyl viologen (0.3 ml, 4 mM) and NT (50 μl, 2 mM) were heated at 65° for 10 min, then $CuSO_4$ (15 μl, 1 mM), sodium ascorbate (15 μl, 5 mM) and DMF (200 μl) were added to form a solution. After an azide-quartz wafer was immersed into the solution for a 30 min reaction, the CB[8]-MV^{2+}-NT film was formed. Before the detection process, the molecules MV^{2+} were extracted to form the desired structure.

Fabrication of NT film as reference

A mixture of deionized water and NT (50 μl, 2 mM) were heated at 65° for 10 min, then $CuSO_4$ (15 μl, 1 mM), sodium ascorbate (15 μl, 5 mM) and DMF (200 μl) were added to form a solution. After an azide-quartz wafer was immersed into the solution for 30 min reaction, the NT film was formed.

Explosives detection

The prepared film was inserted into a glass vials (10 ml) at RT containing solid analytes and cotton gauze, which prevented the direct contact of the film with the analyte and helped to maintain a constant saturated vapor pressure. After exposure at the specified time, the fluorescence spectra were measured immediately at an excitation wavelength of 239 nm.

3 Results and discussion

3.1 Characterization

Three-step approach was employed for the construction of CB [8]-based rotaxane structure on solid substrate, as shown in Scheme 1. Scheme S1 in the ESI† shows the detailed procedure. Firstly, as a threaded molecule 2,6-dioxynaphthalene derivative (NT) carrying alkyne-terminated glycol chains was synthesized by using a standard synthetic method. Then, naphthalene NT was mixed with equimolar CB[8] along with excess methyl viologen (MV) in water to form a water-soluble pseudorotaxane CB[8]·NT·MV. Under this condition, the equilibrium lies predominantly or overwhelming in favor of the pseudorotaxane CB[8]·NT·MV owing to its extremely high overall binding constant up to 10^{12} M^{-2} in aqueous solution.[7] In fact, only the mass peak of the formed heteroternary complex was detected in the performed sample without the signature signal of the naphthalene NT (Fig. 1A), clearly indicating that all naphthalene is exclusively threaded in CB[8], assisted by viologen molecule. Upon the mixing of these three components, the color of the solution was changed from colorless to light purple (Fig. S1†). UV/vis spectroscopy also showed the typical formation of the charge transfer (CT) interaction at 524 nm between MV and naphthalene mediated by CB[8] (Fig. 1B), confirming that the naphthalene core of the compound NT stayed in the cavity of CB[8].[8] To further confirm the formation of the 1 : 1 : 1 inclusion complex, NMR technique has been employed. In comparison with the ^{1}H NMR of MV (Fig. 1C), the α-and β-protons of the viologen moiety in the CB[8]-NT-MV system shifted upfield from 8.98 to 8.89, and 8.44 to 8.23, respectively. Also, three different protons of the naphthalene moiety shifted upfield from 7.92 to 6.59, 7.47 to 5.93, and 7.32 to 5.73, respectively. These results clearly confirmed that the synthesized naphthalene derivate is exclusively threaded in CB[8] assisted by the viologen molecule and a strong CT complex with the viologen moiety inside the cavity of CB[8] formed in solution.[9] These results provided a prerequisite for the construction of the desired CB[8] rotaxane on solid surface. Finally, an azide-modified quartz wafer was immersed into the solution of the formed pseudorotaxane CB[8]·NT·MV for surface immobilization using catalyzed azide-alkyne cycloaddition. It should be noted that, besides the addition of a catalytic amount of $CuSO_4$ and sodium ascorbate, the addition of a small amount of DMF (5%) in the reaction medium is crucial for successful implementation of the mentioned click reaction. The probable reason may be that the presence of DMF offers a favorable environment for alkyne units to extend into the reaction medium. In addition, to ensure the anchoring of both terminal alkyne moieties of pseudorotaxane CB[8]·NT·MV on the surface simultaneously, a lower concentration of the pseudorotaxane (10^{-6} M) was used in our case. Indeed, under optimized preparation conditions, the construction of the desired NT-threaded rotaxane on a solid substrate was achieved. After the extraction of MV molecules, the fluorescence of the naphthalene core in the cavity of CB[8] was restored (Fig. 2A), and the resulting CB[8]·NT complex can act as a receptor for the reversible binding of proper guest molecules as demonstrated by using MV (Fig. 2B).

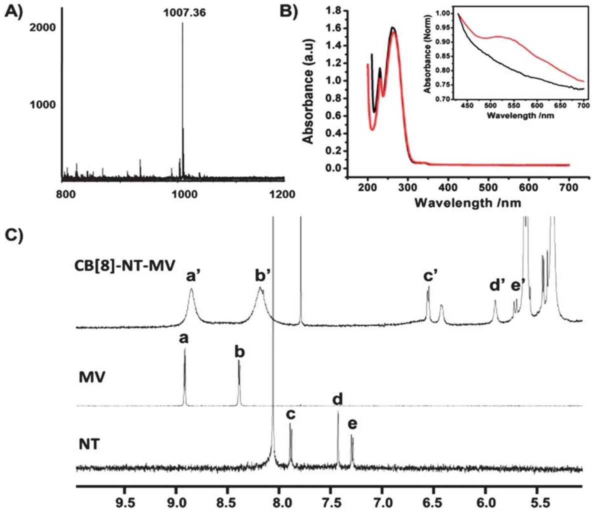


Fig. 1 (A) ESI-MS spectrum of the formed CB[8]·NT·MV host–guest complexes in water; (B) UV-vis spectrum of the formed CB[8]·NT·MV complex in solution in comparison with that of NT·MV without CB[8]; (C) ^{1}H NMR spectra (600 MHz, D_2O/DMF-d_7) of NT and methyl viologen in the presence of the CB[8] cavity (1 : 1 : 1 equiv.) (top), methyl viologen (middle), and NT (bottom) in solution of D_2O/DMF-d_7.

In our work, as a control experiment, the synthesized naphthalene derivative without CB[8] was also anchored on the surface using the same procedure, whereas none of the phenomena described above were observed. Herein, both of the

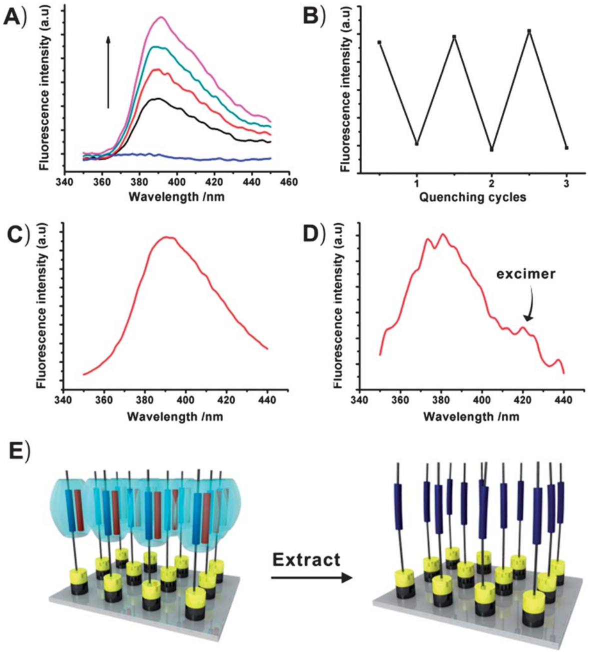


Fig. 2 (A) Fluorescence evolution of CB[8]·NT·MV structure on a substrate with the gradual removal of the trapped MV molecule; (B) reversible change of the fluorescence of the CB[8]-NT-MV structure on the substrate upon trapping and removal of an MV molecule; (C) fluorescence emission of the film with the rotaxane structure where the naphthalene core is in the confined nanocavity of CB[8]; (D) fluorescence emission of the film with pseudorotaxane structure after the extraction of MV molecule; (E) schematic illustration of the extraction process to demonstrate the unstable pseudorotaxane structure.

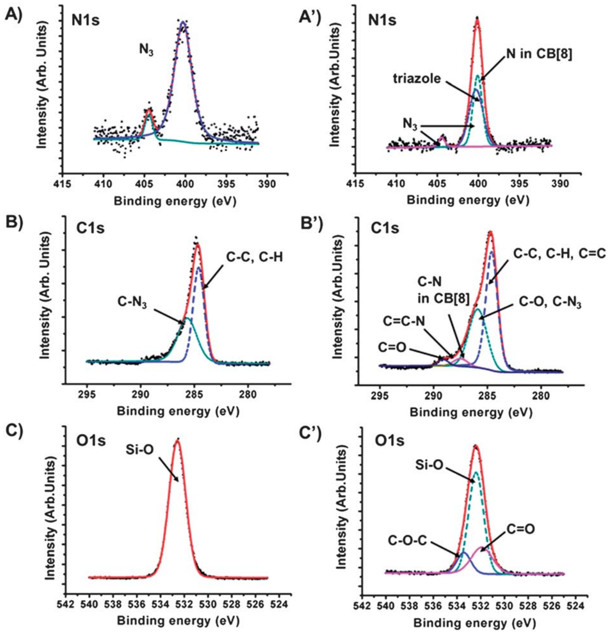


Fig. 3 Comparison of the high-resolution XPS spectra of the N1s C 1s and O1s of azide-modified substrate before (A–C) and after (A′–C′) click reaction.

terminal alkyne groups of the pseudorotaxane CB[8]·NT·MV that were simultaneously attached on the surface were the key factor to obtain a stable structure for analyte sensing. To prove this point, the attachment of one terminal alkyne moiety (NT-1) of pseudorotaxane CB[8]·(NT-1)·MV onto the substrate was carried out. In this case, the extraction of the MV molecule to form the (NT-1)-threaded CB[8] structure also caused the removal of the CB[8] macrocycle, due to the weak hydrophobic interactions between the naphthalene core and CB[8] cavity. As shown in Fig. 2D, the characteristic emission peak at 420 nm which represents the presence of the NT–NT excimer appeared,[10] indicating that the naphthalene cores were no longer isolated by the CB host molecule and thus the formation of the unstable and undesired pseudo-rotaxane structure (Fig. 2E).

The attachment of the constructed sensor structure on a solid substrate was firstly confirmed by QCM technique. As shown in Fig. S2,† it was found that, upon addition of the complex in the reaction medium, a fast negative shift (*ca.* 3 Hz) of frequency was observed, indicative of the immobilization of the threaded complex (CB[8]·NT·MV) onto the azide-functionalized substrate. Moreover, the constructed rotaxane structure was further confirmed by using XPS technique. Fig. 3 shows the comparison of XPS data of the azide-modified quartz wafer before and after the click reaction described above. In the case of the used substrate, the characteristic azide double-peak structure was observed as shown in Fig. 3A. The double-peak structure is indicative of the azide as the smaller peak is seen at 404.5 eV and the larger peak is seen at 400.3 eV, in agreement with previously reported results for azide peak location.[11] The ratio of areas of the two peaks is not exactly 1 : 2 as expected for surface azides, the difference in areas can be attributed to the well-known degradation of the middle nitrogen during the XPS analysis process. The C1s signal (Fig. 3B) was deconvoluted and fitted to two peaks assigned to *C*–C/*C*–H (284.6 eV), and *C*–N_3 (285.7 eV). The O1s signal (Fig. 3C) was fitted to one peak (532.8 eV), which was consistent with the presence of the Si–*O* species on the surface. All these results prove a good grafting of azide functional groups on the substrate surface by treatment using 3-azidopropyltriethoxy silane. The subsequent click reaction with the formed pseudorotaxane CB[8]·NT·MV led to a clear change in the XPS spectra (Fig. 3A′–C′). The N1s signal of the azide group became weaker, and the N1s signal (400.3 eV) of the 1,2,3-triazole formed during the cycloaddition click reaction is observed (Fig. 3A′). Further, the carbon signal (288.5 eV) of the formed 1,2,3-triazole is also detectable (Fig. 3B′). The characteristic XPS signals of the threaded CB[8] molecules are found at 289.1 eV for C–*N* (Fig. 3A′), at 289.1 eV for *C*=O (Fig. 3B′) and at 531.9 eV for C=*O* (Fig. 3C′), respectively, which are consistent with the values in literature.[12] Following the similar data processing method in Gopalan's work,[13] the surface density of CB[8]-based rotaxanes was calculated to be about 5.61×10^{13} molecules per cm^2, less than the monolayer coverage.

The presence of the threaded CB[8] molecule on the surface was further corroborated by Fourier-transform Infrared Reflection Absorption Spectroscopy (FT-IRRAS). The characteristic C–N and C=O stretch absorptions of the immobilized CB[8] molecules are clearly evident at 1442 cm^{-1} and 1714 cm^{-1},[14] respectively (Fig. S3 in ESI†). Also, the dominating peak at

1105 cm^{-1}, which was assigned to the C–O–C stretch, confirms the existence of the NT molecule. It should be noted that the XPS signal of the terminal alkyne is not detectable in the performed XPS analysis, indicating that under the optimized click reaction conditions described above both terminal alkyne groups of the pseudorotaxane CB[8]·NT·MV were simultaneously attached on the surface, affording the desired rotaxane structure as shown in Scheme 1. Indeed, thoroughly washing the modified substrate using different solvents didn't lead to any changes of the XPS signals of the attached CB[8] molecules.

3.2 Explosive detection and discrimination

The naphthalene core in the confined nanocavity of CB[8] retains its optical properties as in bulky solution (Fig. S4†) and exhibits strong fluorescence emission in the range from 350 nm to 450 nm. Interestingly, we found that the naphthalene core-threaded CB[8] rotaxane structure on solid surface can serve as a unique receptor for selective detection and discrimination of explosives. In our work, the CB[8] rotaxane-attached substrates were exposed to saturated vapors of different explosives at room temperature, including TNT (5.8×10^{-6} torr) and DNT (1.1×10^{-4} torr),[1c] for varied periods of time (10 s, 30 s, 60 s, 120 s, 300 s, 600 s), and PETN (1.4×10^{-8} torr), RDX (4.6×10^{-9} torr) and HMX (8.0×10^{-11} torr),[1c] for varied periods of time (0 min, 1 min, 3 min). As shown in Fig. 4, depending on the explosive used, the constructed rotaxane shows a clearly different optical response. For nitroaromatics (TNT and DNT), the fluorescence of the naphthalene core was gradually quenched with increased exposure (Fig. 4A and B). Due to the formation of host stabilized charger transfer complexes, the constructed sensor shows a fast response. Unexpectedly, the presence of trace aliphatic explosives like RDX and HMX induced the opposite response of the optical property of the naphthalene, and instead of quenching, fluorescence enhancement to varying degrees was detected (Fig. 4C). In the case of bulky PETN, however, the fluorescence of the naphthalene core in CB[8] remains unchanged even with prolonged exposure (Fig. 4D). As expected for the surface sensing elements, all described responses are fast and take several seconds. Compared with the reported explosive sensors, our constructed sensor also exhibits a good sensitivity.[1–3] In the case of TNT in vapor phase, the detection limit could reach ppt level, as shown in Fig. S6.† Moreover, the trapped explosive molecules in the rotaxane structure can be facilely removed by simply washing, and the sensing ability of the constructed rotaxane is completely regenerable (Fig. 4F). As a control experiment, the synthesized naphthalene derivative (NT) without CB[8] macrocycle was attached on the substrate using the same preparation procedure in this work. The distinctly dissimilar sensing behavior described above was not observed in the control case (Fig. S5†), indicating that the confined nanospace provided by CB is critical for the sensing and discrimination of explosives in the constructed rotaxane structure. In our work, the secondary effect arising from the impurity in the used explosives was excluded. All the obtained results were reproducible.

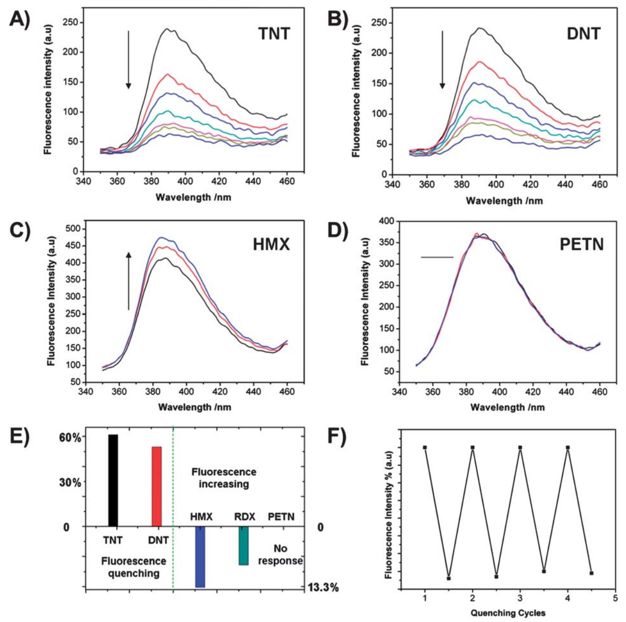


Fig. 4 Time-dependent fluorescence intensity of the NT-threaded CB[8] rotaxane on solid substrate upon exposure to saturated vapor TNT (A), DNT (B), HMX (C) and PETN (D) at room temperature; (E) the detected fluorescence attenuation and enhancement of TNT, DNT, HMX, RDX and PETN for time of 3 min; (F) regeneration of the constructed sensors in case of TNT.

Usually, the observed fluorescence attenuation and enhancement can be explained by the donor–acceptor electron-transfer mechanism. Scheme S2 in ESI† displays the band gap energies of the donor (naphthalene NT) and the acceptors (TNT, DNT, PETN, RDX, HMX), which were calculated by using density-functional theory (DFT) at the B3LYP/6-31G(d) level for the optimized geometries.[15] It is clear that for all the tested analytes the energy gaps are large enough to provide an appropriate thermodynamic driving force and photoinduced electron transfer should be possible between the NT and explosive molecules resulting in fluorescence quenching of the former (NT). In practice, however, naphthalene is hardly used for the detection of explosives, and an effective quenching effect is not detectable as confirmed in our control experiments (Fig. S5†). In contrary, in the case of the naphthalene threaded CB[8] rotaxane (Scheme 1) which is a kind of host stabilized charge transfer complex, the confinement of the analyte (*e.g.* TNT or DNT) inside the CB[8] nanocavity may promote the close association of aromatic explosive molecules with a naphthalene core through π–π interactions, and thereby facilitates an efficient electron transfer process resulting in fluorescent quenching of naphthalene. Different from aromatic explosives, another mechanism should be responsible for the observed fluorescence enhancement in the case of aliphatic counterparts. Due to their three-dimensional molecular structure and lack of π–π interaction and subsequently tight binding interaction,[3] the restricted nanospace provided by CB[8] cannot lead to an efficient orbital overlap of the naphthalene core and the trapped aliphatic explosives necessary for electron transfer. But, the incorporation of such a bulky guest in the constructed CB[8] rotaxane reduces the free-volume of the CB[8] confined space, and actually exerts a similar rigidifying effect on the motions (vibrations, torsions *etc.*) of the naphthalene core in the CB[8] cavity. Then, non-radiative decay processes should be slowed and the fraction of excited species decaying radiatively should increase, resulting in increased intensity of fluorescence.[16] Clearly, the degree of the observed enhancement should be dependent on the size of the included guest. Besides the confinement effect, the size exclusion effect of the carbonyl-fringed portals in CB[8] structure provides another mechanism of molecular selectivity. The guest molecules that are smaller than the CB[8] apertures can be included, but larger molecules cannot. In Table 1, the molecular size of a series of guest molecules and CB[8] had been given. Indeed, in agreement with the obtained results the explosives with smaller size, *e.g.* TNT (167.75 Å^3), DNT (150.12 Å^3), HMX (201.21 Å^3), RDX (152.51 Å^3) can get into the nanocavity of the CB[8] macrocycle, leading to different changes of the photophysical properties of the naphthalene core depending on the electronic structures and the molecular sizes of the explosives. Conversely, for larger molecules like PETN (244.69 Å^3), the size exclusion of CB[8] makes no opportunity for such an analyte to enter the interior of CB[8] and blockades the optical response of the naphthalene inside. In addition, large naphthalenediimide molecule, which is a well-known effective quencher for naphthalene,[17] was also employed to test the responsive behavior of the protected naphthalene in CB[8] cavity.

As expected, due to its larger molecular size, the size exclusion of CB[8] inhibits such an analyte from entering the interior of CB[8] and blockades the optical response of the naphthalene inside (Fig. S7†). This result implies that, based upon molecular size and shape, the described findings can be also utilized to discriminate a couple of different classes of compounds besides explosives. In Fig. 5, the optimized structures of CB[8]-NT-TNT, DNT, RDX, and HMX had been calculated based on MM calculations. It was found that due to the enhanced intermolecular interactions by CB cavity, the optimized structure of the ternary structure proved the possibility of our CB[8]-NT system for explosive sensing. Moreover, the formation of complexation of CB[8]-naphthalene-RDX and CB[8]-naphthalene-HMX could also be confirmed by ESI-MS measurements (Fig. S8†), where the NT molecule was replaced by 2,6-dihydroxynaphthalene for clarity.

Table 1 Molecular size of the guest molecules and CB[8]

	a/Å	*b*/Å	*c*/Å
TNT	7.91	7.83	2.85
DNT	7.97	6.53	2.74
RDX	6.91	6.28	4.74
HMX	8.83	7.24	4.84
PETN	8.82	9.14	6.80
Naphthalene-diimide	10.03	7.74	1.00
CB[8][a]	6.9	8.8	9.1

[a] The values quoted for *a*, *b*, and *c* for CB[8] take into account the van der Waals radii of the relevant atoms. The size of other molecules are determined based on the optimized structure which are calculated by using density-functional theory at the B3LYP/6-31G(d) level.

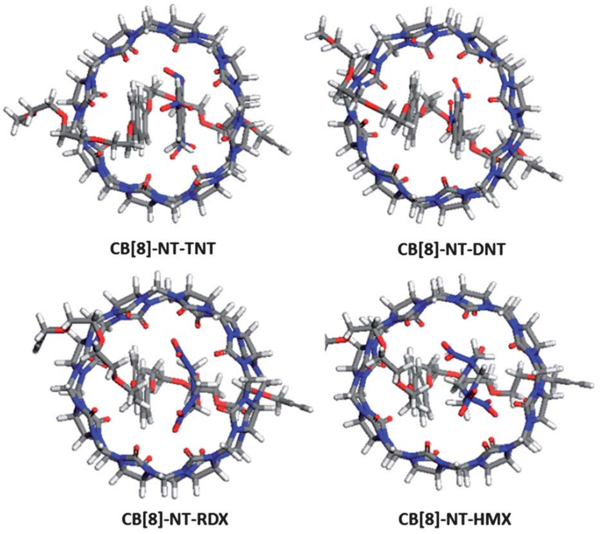


Fig. 5 Optimized structures of CB[8]-NT-nitrated explosives (TNT, DNT, RDX and HMX) based on MM calculations.

To provide new evidence for the proposed mechanism described above, thioflavin T (ThT), a well-known chromophore for its dramatic fluorescent enhancement upon binding to a restricted host space,[18] was employed to construct sensor device. It is found that significant enhancement of sensing performance was detected with ThT-based structure in Fig. S9.† In comparison with the initial result, fluorescence response increased by 434% in the case of RDX. This result clearly indicates that the strategy described in our paper could afford more sensitive and competent sensors with enhanced discrimination of trace explosives when appropriate flexible chromophores are integrated with CB[8] macrocycle.

In this work, control experiments were performed by using conventional organic vapors (*e.g.* toluene, THF, CH_2Cl_2 and ethanol) as interferents. We found that the used organic vapors could induce, to some extent, the change of the fluorescence intensity of the protected naphthalene in CB[8] cavity (Fig. S10†). However, quite different from the phenomena observed in the cases of explosives, the fluorescence of the protected naphthalene in CB[8] immediately recovered upon the exposure of the used sensors to air. This result indicates that the detection of the explosives can be easily discriminated from the interferent organic vapors.

The preliminary results described above are encouraging. Based on the unique confinement effect and size exclusion of CB[8] in the constructed rotaxane structure, direct detection and discrimination of distinctively different groups of trace explosives in the vapor phase are realized by using one single host structure, especially including the challenging aliphatic nitro-organics (RDX, HMX and PETN). The surface-anchored sensing element is especially favorable to sensing efficiency. Compared with the reported explosive sensors, our constructed sensor also exhibited a good sensitivity. However, like most of other sensors reported in the literature, it may still be difficult to use one single sensor or method to realize the detection and discrimination of all the explosives in a real complicated environment. Mimicking the mammalian olfactory system, the construction of sensor array using the developed sensor as sensor element may be the best and most reliable way to achieve the detection and discrimination in a complicated environment. The related work is ongoing in our lab. Additionally, although our new concept was tested with CB[8], in principle it should be used as a general and effective sensing scheme for creating various sensors in other synthetic molecular-sized nanocavities, for example in metal-organic frameworks (MOFs).

4 Conclusions

In summary, based on a NT-threaded CB[8] rotaxane structure on solid substrate, a new strategy for rapid, fully reversible, and highly sensitive detection of a broad class of explosives was developed by using one receptor. Due to the unique confinement effect and size exclusion of CB[8] nanocavity, it is found that, depending on the electronic structures and the sizes of explosives, the photophysical property of the naphthalene core in the confined CB[8] cavity shows different changes upon contact with the tested analyte, leading to the direct detection and discrimination of different groups of trace explosives, including the challenging aliphatic nitro-organics (RDX, HMX and PETN). In recent years, a fluorescence-based sensing scheme has been extensively explored for the detection of explosives. However, chemosensors capable of detection and discrimination of a broad range for explosives classes, especially in the vapor phase, are rare.[3e] Therefore, we believe that our findings would open a new way to design and develop a new kind of explosive sensors enable a richer identification of threats.

Acknowledgements

We gratefully acknowledge the nancial support from the National Science Foundation of China (no. 21025311, 21121004, 21261130581 and 91027016), Ministry of Education (2011Z01014), MOST Program (2011CB808403, 2013CB834502) and the transregional project (TRR61). We also thank Prof. Feng Liu in Perking University for the QCM characterization.

Notes and references

1 (*a*) S. W. Thomas, G. D. Joly and T. M. Swager, *Chem. Rev.*, 2007, **107**, 1339–1386; (*b*) D. T. McQuade, A. E. Pullen and T. M. Swager, *Chem. Rev.*, 2000, **100**, 2537–2574; (*c*) J. C. Sanchez and W. C. Trogler, *J. Mater. Chem.*, 2008, **18**, 3143–3156; (*d*) S. J. Toal and W. C. Trogler, *J. Mater. Chem.*, 2006, **16**, 2871–2883; (*e*) T. Naddo, Y. Che, W. Zhang, K. Balakrishnan, X. Yang, M. Yen, J. Zhao, J. S. Moore and L. Zang, *J. Am. Chem. Soc.*, 2007, **129**, 6978–6979; (*f*) Y. Che, D. E. Gross, H. Huang, D. Yang, X. Yang, E. Discekici, Z. Xue, H. Zhao, J. S. Moore and L. Zang, *J. Am. Chem. Soc.*, 2012, **134**, 4978–4982; (*g*) A. Ponnu, N. Y. Edwards and E. V. Anslyn, *New J. Chem.*, 2008, **32**, 848–855; (*h*) P. Anzenbacher Jr, L. Mosca, M. A. Palacios, G. V. Zyryanov and P. Koutnik, *Chem.–Eur. J.*, 2012, **18**, 12712–12718.

2 Y. Salinas, R. Martinez-Manez, M. D. Marcos, F. Sancenon, A. M. Costero, M. Parra and S. Gil, *Chem. Soc. Rev.*, 2012, **41**, 1261–1296.

3 (*a*) M. E. Germain and M. J. Knapp, *Chem. Soc. Rev.*, 2009, **38**, 2543–2555; (*b*) A. Lan, K. Li, H. Wu, D. H. Olson, T. J. Emge, W. Ki, M. Hong and J. Li, *Angew. Chem.*, 2009, **121**, 2370–2374; *Angew. Chem., Int. Ed.*, 2009, **48**, 2334–2338; (*c*) A. D. Hughes, I. C. Glenn, A. D. Patrick, A. Ellington and E. V. Anslyn, *Chem.–Eur. J.*, 2008, **14**, 1822–1827; (*d*) T. L. Andrew and T. M. Swager, *J. Am. Chem. Soc.*, 2007, **129**, 7254–7255; (*e*) M. E. Germain and M. J. Knapp, *J. Am. Chem. Soc.*, 2008, **130**, 5422–5423; (*f*) S. Pramanik, C. Zheng, X. Zhang, T. J. Emge and J. Li, *J. Am. Chem. Soc.*, 2011, **133**, 4153–4155.

4 (*a*) J. W. Lee, S. Samal, N. Selvapalam and K. Kim, *Acc. Chem. Res.*, 2003, **36**, 621–630; (*b*) L. Lagona, P. Mukhopadhyay, S. Chakrabarti and L. Isaacs, *Angew. Chem.*, 2005, **117**, 4922–4949; *Angew. Chem., Int. Ed.*, 2005, **44**, 4844–4871; (*c*) D. T. Dang, *Chem. Sci.*, 2012, **3**, 2679–2684; (*d*) F. Biedermann, U. Rauwald, J. M. Zayed and O. A. Scherman, *Chem. Sci.*, 2011, **2**, 279–286; (*e*) R. Hota, K. Baek, G. Yun, Y. Kim, H. Jung, K. M. Park, E. Yoon, T. Joo, J. Kang, C. G. Park, S. M. Bae, W. S. Ahn and K. Kim, *Chem. Sci.*, 2013, **4**, 339–344.

5 (*a*) W. M. Nau and O. A. Scherman, *Isr. J. Chem.*, 2011, **51**, 492, special issue for cucurbit[*n*]uril chemistry; (*b*) M. M. Boyle, R. A. Smaldone, A. C. Whalley, M. W. Ambrogio, Y. Y. Botros and J. F. Stoddart, *Chem. Sci.*, 2011, **2**, 204–210.

6 (*a*) H. J. Kim, H. Heo, W. S. Jeon, E. Lee, J. Kim, S. Sakamoto, K. Yamaguchi and K. Kim, *Angew. Chem.*, 2001, **113**, 1574–1577; *Angew. Chem., Int. Ed.*, 2001, **40**, 1526–1529; (*b*) V. Ramalingam and A. R. Urbach, *Org. Lett.*, 2011, **13**, 4898–4901.

7 (*a*) U. Rauwald and O. A. Scherman, *Angew. Chem.*, 2008, **120**, 3904–3907; *Angew. Chem., Int. Ed.*, 2008, **47**, 3950–3953; (*b*) Y. Liu, Y. Yu, J. Gao, Z. Wang and X. Zhang, *Angew. Chem.*, 2010, **122**, 6726–6729; *Angew. Chem., Int. Ed.*, 2010, **49**, 6576–6579.

8 A. Trabolsi, M. Hmadeh, N. M. Khashab, D. C. Friedman, M. E. Belowich, N. Humbert, M. Elhabiri, H. A. Khatib, A. Albrecht-Gary and J. F. Stoddart, *New J. Chem.*, 2009, **33**, 254–263.

9 D. Zou, S. Andersson, R. Zhang, S. Sun, B. Akermark and L. Sun, *J. Org. Chem.*, 2008, **73**, 3775–3783.

10 J. S. Yang and T. M. Swager, *J. Am. Chem. Soc.*, 1998, **120**, 11864–11873.

11 S. Prakash, T. M. Long, J. C. Selby, J. S. Moore and M. A. Shannon, *Anal. Chem.*, 2007, **79**, 1661–1667.

12 Q. An, G. Li, C. Tao, Y. Li, Y. Wu and W. Zhang, *Chem. Commun.*, 2008, 1989–1991.

13 P. Paoprasert, J. W. Spalenka, D. L. Peterson, R. E. Ruther, R. J. Hamers, P. G. Evans and P. Gopalan, *J. Mater. Chem.*, 2010, **20**, 2651–2658.

14 K. Kim, J. W. Lee, Y. H. Ko and K. Kim, *Chem. Commun.*, 2004, 848–849.

15 (*a*) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648; (*b*) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.

16 (*a*) L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne and J. T. Hupp, *Chem. Rev.*, 2012, **112**, 1105–1125; (*b*) A. C. Bhasikuttan, H. Pal and J. Mohanty, *Chem. Commun.*, 2011, **47**, 9959–9971.

17 S. V. Bhosale, C. H. Jani and S. J. Langford, *Chem. Soc. Rev.*, 2008, **37**, 331–342.

18 L. M. Tolbert, A. Baldridge, J. Kowalik and K. M. Solntsev, *Acc. Chem. Res.*, 2012, **45**, 171–181.