Rapid DNT Fluorescent Films Detection with High Sensitivity and Selectivity

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Abstract

In this study, we designed and synthesized two small fluorescent molecules, TCAC and TCA. Their spin-coated films were used as fluorescent sensors for 2, 4-dinitrotoluene (DNT) vapor. Compared with TCAC, which has carbazole units at the end of the hexyl side chains, TCA films exhibited better sensitivity and selectivity to DNT vapor with good reutilization in 30 s. Furthermore, TCA was performed to detect trace DNT by contact mode approach for real-time field and visualized detection with good performances.

1. Introduction

Detection of trace explosives such as 2, 4, 6-trinitrotoluene (TNT) and 2, 4-dinitrotoluene (DNT) is of great significance due to their serious threat to homeland security and public safety [1-3]. So far, the common techniques detected trace explosives mainly include gas chromatography mass spectrometry (GC-MS) [4,5], X-ray imaging [6], ion mobility spectroscopy (IMS) [7], surface-enhanced Raman spectroscopy [8,9], and electrochemical methods [10,11]. But these technologies usually exhibit some disadvantages such as high cost, complicated operation and time-consuming. Specially, the poor portability makes these techniques not suitable for the real-time field detection. Compared with these techniques, fluorescence detection shows low cost, good portability,

high sensitivity and selectivity. Besides that, the fluorescent films could be easily incorporated into a handheld device for the real-time field detection of explosives [12]. Up to date, many fluorescent materials have been used for explosives detection, such as conjugated polymers [13], luminescent metal-organic frameworks [14], bio-inspired materials [15], aggregation induced emission (AIE) materials [16,17], nanomaterials [18] and so on. The main mechanism ascribes to the photoinduced electron transfer (PET) [19]. Based on this mechanism, some fluorescent materials are designed with electron rich groups to enhance the electron donating ability [20]. In addition, the morphology of the sensing films is another key to influence the sensing performances, thus, some designed molecules with "big" units in the backbone or sidechains are designed to achieve the porous films, which benefit the diffusion of the explosives and improve the contact of the sensing materials and the explosives [21].

DNT is toxic and may cause anemia, abnormal liver function, cataract development and skin irritation [22,23]. It has been list of stress control pollutants by United States Environmental Protection Agency (US EPA) [24]. The detection of DNT is of great importance and deserved exploring. Firstly, DNT has similar chemical structure with TNT. It is the major impurity and the decomposition product of TNT. The saturated vapor pressure of DNT (411 ppb) is much higher than TNT (9.15 ppb), thus, the small quantities of DNT that contained in TNT hold the dominating vapor, which can serve as the marker for TNT vapor detection [25]. So rather than attempting to detect low vapor pressure of TNT directly, researchers often focus on detecting DNT vapor [26,27]. Secondly, the selective detection between DNT and TNT is still a challenge, which is due to their similar chemical structure. Finally, the rapid detection of DNT is extremely

needed for the practical application. As we know, it takes long time for the passengers at airports for security checks, and the working efficiency is urgently needed to be improved through the rapid detection [28]. Thereby, the detection of DNT with high sensitivity and selectivity deserve further exploration, however, less attention are paid to this study.

Herein, we designed and synthesized two fluorescent molecules, TCAC and TCA (Scheme 1), their spin-coated films are used as the fluorescent sensor to DNT. The difference between TCAC and TCA is the sidechains, which might make their spin-coated films exhibit distinguishing sensing performance to DNT. And the results show that TCA, which has hexyl as the sidechains, is a rapidly responsive, highly selective and real-time fluorescent sensor to DNT.

2. Experimental

2.1. Materials and methods

All chemicals and solvents were purchased from commercial sources. Reactions were all conducted under argon atmosphere. $^1\text{H-NMR}$ spectra were recorded on a Bruker AVANCZ 500 spectrometer at 500 MHz, using CDCl_3 as the solvent at 298 K, and tetramethylsilane (TMS) as the internal standard. Ultraviolet-visible (UV-vis) absorption spectra were recorded on a model UV-3100 spectrophotometer. Fluorescence spectra were performed using a model RF-5301PC spectrophotometer.

2.2. Synthesis of TCAC and TCA

TCAC: $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 8.06 (t, 8 H), δ 7.95 (m, 2 H), δ 7.83 (m, 2 H), δ 7.72 (m, 4 H), δ 7.49 (m, 1 H), δ 7.37 (m, 16 H), δ 7.32 (m, 4 H), δ 7.25 (m, 4 H), δ 7.18 (m, 9 H), δ 7.10 (m, 3 H), δ 7.02 (m, 1 H), δ 4.15 (m, 8 H), δ 1.92 (m, 8 H), δ 1.70

(m, 8 H), δ 1.15 (m, 16 H), δ 0.76 (m, 8 H). ^{13}C -NMR (125 MHz, CDCl_3): δ 130.03, 127.68, 127.35, 127.04, 126.05, 125.54, 125.02, 123.52, 120.31, 119.92, 118.68, 108.61, 42.93, 40.24, 29.69, 28.79, 26.86, 23.74. MALDI-TOF-MS: 1504.8. Calcd. for $\text{C}_{112}\text{H}_{102}\text{N}_4$: N: 3.73 %, C: 89.44 %, H: 6.84 %. Found: N: 3.63 %, C: 89.59 %, H: 6.97 %.

TCA: ^1H -NMR (500 MHz, CDCl_3): δ 7.98 (d, 2 H), 7.91-7.75 (m, 6 H), 7.54-7.33 (m, 14 H), 2.09-1.98 (m, 8 H), 1.20-1.06 (m, 24 H), 0.89-0.71 (m, 20 H). ^{13}C NMR (126 MHz, CDCl_3): δ 150.95, 140.79, 127.42-126.74, 124.99, 122.92, 119.73, 40.49, 31.57, 29.69, 23.91, 22.53, 14.04. MALDI-TOF-MS: 843.31. Calcd. for $\text{C}_{64}\text{H}_{74}$: C: 91.15 %, H: 8.85 %. Found: C: 91.44 %, H: 8.86 %.

2.3. Preparation of Spin-coated films

The films of TCAC and TCA were fabricated by spin-coated on quartz substrates with a rate of 1500 rpm and a concentration of 0.5 mg mL^{-1} in THF. Then the films were in vacuum at 45°C for 10 min to remove the residual solvents.

2.4. Fluorescence detection of explosives vapor

The explosives powder was put into the quartz cell bottom, then a suitable filter paper was put on the powder to prevent the direct contact between the films and the powder, finally, the quartz cell was sealed. After 60 min, the films were put into the cell. The fluorescence spectra were recorded as a function of exposed time under the excitation light at 360 nm.

To study the reusability of the spin-coated films, after being exposed to explosives vapor, the films were immersed into methanol for 60 min, and then dried in vacuum oven at 45 °C for 1 h. The fluorescence emission of films could be recovered.

3. Results and discussion

Scheme 1. The synthetic routes of TCAC and TCA.

TCAC and TCA were synthesized through Suzuki reaction according to the previous literatures [1]. Their molecular structures are shown in Scheme 1. As can be seen, TCAC and TCA have the same rigid backbone composed of anthracene and fluorene groups but different sidechains. TCA has four hexyl sidechains, while TCAC has carbazole groups at the end of the hexyl sidechains, which could enhance the donating ability [29]. TCAC and TCA have the same backbone composed of anthracene and fluorene groups. The rigid anthracene groups could not only reduce the π stacking of molecules but also create a loose microstructure to benefit the diffusion of explosives vapor and enhance the contact between the sensing materials and explosives.

The absorption spectrum of TCAC in THF displays main absorption bands located at 294, 308, 332, 346, 360, 379 and 399 nm, respectively (Figure S1). The bands at 294, 332 and 346 nm are attributed to the transition of the carbazole groups, the band at 308 nm is attributed to the electronic transition of fluorene groups, and the bands at 360, 379 and 399 nm are attributed to π - π^* transition of the anthracene group. TCA exhibits similar absorption bands of fluorene and anthracene groups. The PL spectra of TCAC and TCA exhibit the same blue emission located at 435 nm in THF (Figure 1). However, comparing PL spectra of the films with those in solution, red-shifts of 2 nm for TCA and 7 nm for TCAC are observed. The big red-shifts of TCAC might be attributed to the π - π interaction between the carbazole groups and the rigid backbone of TCAC. This significantly small red-shift of TCA films suggests TCA films have much looser microstructure, which could provide efficient pathway for the diffusion of the explosives vapor.

Figure 1

Figure 1. PL spectra of TCAC and TCA in solution and as films. The inset: enlarged view of PL spectra.

Further, TCAC and TCA films were used as the fluorescent sensors for explosives. As we know that the false signals often come from similar explosives in the sensing field, and the false signals are related to the lack of selectivity. Therefore, some common explosives were tested firstly shown as Figure 2, including DNT, TNT, Octahydro-1, 3, 5, 7-tetranitro-1, 3, 5, 7-tetrazocine (HMX), Pentaerythritoltetranitrate (PETN), 2, 4, 6-Trinitrophenylmethylnitramine (Tetryl) and 1, 3, 5-Trinitro-1, 3, 5-triazacyclohexane

(RDX). As can be seen, TCA presents better sensitivity for explosives than TCAC. And among the testing explosives, TCA shows higher selectivity to DNT vapor than other explosives. The main reason might be attributed to two factors, one is the microstructures of the fluorescent films, the other is the explosives molecular structure and their saturated vapor pressure. The aromatic nitro explosives, such as TNT, DNT and Tetryl could form π - π stacking with rigid backbone easily compared to PETN, HMX and RDX [12, 30]. Meanwhile, the saturated vapor pressure of DNT (411 ppb) is much higher than TNT (9.15 ppb), PETN (0.0107 ppb), HMX (0.0000000237 ppb), Tetryl (0.00741 ppb) and RDX (0.00485 ppb) [31]. Moreover, TCA has much looser microstructure than TCAC, which benefit the diffusion of explosives. Thus, these synergistic effects of DNT molecular structure and its saturated vapor pressure resulted in the TCA films are more sensitive to DNT vapor than other explosives vapor.

Figure 2

Figure 2. Fluorescence quenching efficiency of TCA and TCAC exposed to DNT and TNT, HMX, PETN, Tetryl and RDX vapor.

Figure 3a demonstrates the fluorescence quenching efficiency of TCA exposed to TNT and DNT vapor as a function of exposed time. The TCA films are more sensitive to DNT vapor, after the TCA films upon exposure to DNT vapor for 30 s, the fluorescence quenching efficiency could be about 90 %. However, the fluorescence quenching efficiency of TCA to TNT is only 13 % after 30 s, and 47 % after 300 s. It should be noted that the response of TCA to DNT was rather rapid. As can be seen from the inset pictures (I) of Figure 3a, exposing TCA films to DNT for 5 s, the fluorescence was

quenched obviously. After 30 s, the fluorescence was nearly quenched completely. While for TNT, there was nearly no fluorescence quenching could be observed by naked eyes. Such rapid and selective detection of TCA to DNT vapor has reached the high standard for real-time field detection. Moreover, the TCA films can be used repetitively shown in Figure 3b. After being exposed to DNT vapor for 30 s, the TCA films exhibit the same fluorescence quenching efficiency after each cycle, and the fluorescence intensity could be recovered when the DNT vapor was removed. For comparison, some fluorescence quenching data for DNT from different literatures are summarized in the Table 1.

Figure 3

Figure 3. (a) Fluorescence quenching efficiency of TCA exposed to TNT and DNT vapor as a function of exposed time. The inset: photos of TCA films exposed to DNT vapor in 0 s, 5 s, 10 s, 30 s; photos of TCA films exposed to TNT vapor in 0 s, 30 s. (b) Fluorescent recovery cycles of TCA films: the blue solid arrows represent the quenching process and the green dot arrows represent the recovery process. The solid black squares (■) correspond to the initial fluorescence intensity of TCA films or the recovery fluorescence intensity of quenched TCA films washed by methanol. The solid red circles (●) correspond to the fluorescence intensity of TCA films exposed to DNT vapor.

Table 1 Fluorescence quenching data for DNT vapor from different literature.

Table 1

We further performed the detection of DNT residual products using the filter paper, because workers inevitably contact with DNT in actual production, such as preparation and packaging of explosive devices, the leakage of explosives will adsorb on human clothes and skins [41]. So the real-time field detection is very necessary. Figure 4a shows a common filter paper was immersed in TCA solution and dried under vacuum. This filter paper exhibits a blue emission under the UV light at 365 nm (Figure 4b). Then a gloved finger was rubbed with DNT, visible DNT particles were all brushed off, and the gloved finger pressed on the filter paper for 10 s. As we can see from Figure 4c, the finger print of the gloved finger could be observed under the UV light at 365 nm by the naked eye. These images illustrate the utility of the fluorescent filter paper for real-time field and visualized detection of trace DNT residual products.

Figure 4

Figure 4. (a) Image of filter paper after immersed in TCA solution (10^{-5} M) under daylight; (b) Image of TCA filter paper under UV light at 365 nm; (c) Image of TCA filter paper contacted with human thumb, which rubbed with DNT.

4. Conclusion

In conclusion, we designed and synthesized two fluorescent small molecules, TCAC and TCA, which have same rigid backbone and different sidechains. Their spin-coated films exhibit blue emission and were used as the fluorescent sensor for explosives vapor detection. In particular, TCA films display not only rapid response but also high selectivity and sensitivity to DNT vapor and the films can be used repetitively. Moreover, we illustrate the utility of the TCA filter paper for real-time field and visualized detection of trace DNT residual products.

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Table 1 Fluorescence quenching data for DNT vapor from different literature .

Sensing material (different explosives)	Fluorescence Quenching efficiency (exposure time)		Reference
TCA	60 % (5 s)	90 % (30 s)	This work
MSNF film	62 % (10 s)	74 % (30 s)	[17]
F4	52 % (30 s)	79 % (90 s)	[32]
Gel-P(DNT)	60 % (50 s)	100 % (300 s)	[33]
Si-QDs(DNT)	70 % (30 s)	~	[34]
PEO/MePyCz (DNT)	24 % (300 s)	73.2 % (7200 s)	[35]
oligomer 1(DNT)	48 % (60 s)	77 % (600 s)	[36]
PVP/pyrene/APTS/r GO nanonets (DNT)	~	89 % (540 s)	[37]
F2 films (DNT)	39.2 % (30 s)	88.2 % (300 s)	[38]
P1 (DNT)	48 % (10 s)	97 % (300 s)	[39]
3 (DNT)	~	~69 % (600 s)	[40]

(a)

(b)

(c)