

Sensing of Nitroaromatic Compounds by Naphthodithiophene Derivative

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Abstract:

Nitroaromatic compounds, e.g. 2, 4, 6-trinitrotoluene (TNT), are primary components of explosives which can adversely affect environment and communities where wars once were made. Detecting the remnant of these toxic compounds, therefore, is necessary for environmental management of former conflict areas and their surroundings. The fluorescence-based detection is an alternative method having gained more attention recently for the explosive detection because of its high sensitivity, easy visualization, and short response time for detection. Herein, the dithiophene-based fluorogenic compound diPy26NDT was designed and successfully synthesized. The compound showed good photo-luminescence efficiency and it could be used as visual fluorescence sensors for the TNT detection based on fluorescence quenching mechanism.

1. Introduction Explosives, e.g. land-mines, are a kind of destructive weapons widely used in wars. Although the fights have ended for years, there may be plenty of land-mines still buried in the conflict areas and can pose serious dangers to community in the region[1]. However, even if the inert bombs cannot cause further destruction, their primary components of explosives which are nitroaromatic compounds (NACs) such as 2,4,6-trinitrotoluene (TNT), dinitrotoluene (DNT), and 1,3,5-trinitrobenzene (TNB), can still contaminate the surroundings and intoxicate living organisms around the areas as in surface soil, groundwater or seawater[2]. The toxicity of TNT may cause skin irritation, damage liver and haematological system[3].

Several techniques have been used for nitroaromatic explosive detection such as chromatographic and spectrometric methods, electrochemical sensors, mass sensors, and optical sensors[4]. Each of these techniques, however, has specific limitations for on-field applications due to high cost, inconvenience or very slow response[5]. The fluorescence-based detection is an alternative method recently gained greater attention to detect the explosives because of its high sensitivity, easy visualization, and short response time for detection[6]. This method can potentially become one of the most powerful techniques in the explosive investigation.

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In general, fluorescence-based sensing of nitro-aromatic compounds involved the fluorescence quenching mechanism. The process depends upon the electron-transfer efficiency between electron rich fluorophore and electron deficient nitroaromatic materials.[7] Due to their high electron deficient characteristic, nitroaromatic compounds readily accept electrons from the electron rich fluorescent probes to form a complex with decreased fluorescence intensity [8].

Thiophene-fused aromatic compounds have been proved to be a useful precursor for the preparation of materials with promising applications in the field of organic electronics such as organic field-effect transistors (OFETs)[9], organic solar cells (OSCs)[10] and organic light-emitting diodes (OLEDs)[11]. It was proposed that the choice of end-capping group of thiophene could influence the properties of the materials to suit the desired applications.

Pyrene is one of the most studied end-capping units since it can emit light with high quantum efficiency and it is sensitive to the change of environment which is useful for sensor applications. Pyrene derivative has also been used in the application for TNT sensing. For example, Shanmugaraju et al.[12] synthesized the π -electron rich pyrene derivative 1 that fluoresced at 442 nm and its photoluminescence was shown to be quenched by TNT in solution.

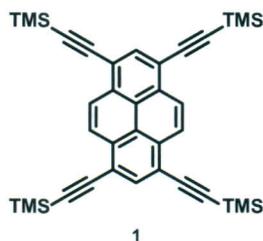


Fig.1 Structures of pyrene based fluorophore 1.

Naphthodithiophene-based fluorophores (Figure 2) were first synthesized by Rungtaweevoranit et al.[13] This structure consists of naphthodithiophene in the core which provide the possibility to modify their electronic properties as well as to attach end-capping group. Pyrene group was then used as fluorescence capping unit and t-butyl group was placed at the periphery to improve the solubility. Because of its electron-rich nature and good fluorescence property in solution, herein the naphtho-dithiophene derivative diPy26NDT10 was synthesized and used as a fluorogenic sensing material for the TNT detection based on the fluorescence quenching mechanism. The visual efficiency of this sensor would also be investigated.

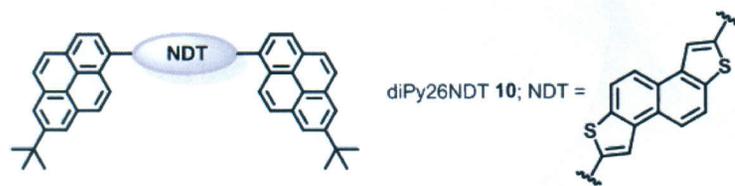


Fig.2 Structure of the designed fluorogenic sensing materials diPy26NDT 10.

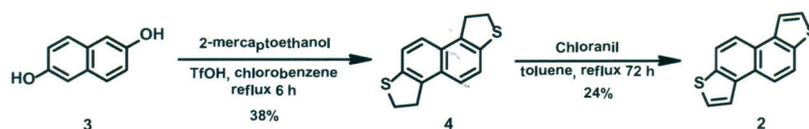
2. Materials and Methods

2.1 Materials

2,6-dihydroxynaphthalene(3), tetrakis(triphenyl-phosphine)palladium(0)(Pd(PPh₃)₄), chloranil were purchased from TCI chemicals. Trifluoromethane-sulfonic acid (TfOH), 2-Mercaptoethanol, N-bromosuccinimide (NBS), pyrene, t-butyl chloride, anhydrous aluminium trichloride (AlCl₃), n-butyl-lithium (n-BuLi), triisopropyl borate (B(OPr-i)₃), hydrochloric acid (HCl) were purchased from Sigma-Aldrich. Anhydrous sodium sulfate (Na₂SO₄) and potassium carbonate (K₂CO₃) were purchased from Fisher Scientific. Bromine solution (Br₂) was purchased from Panreac Sintesis. Carbontetrachloride (CCl₄) was purchased from Merck (German). Toluene, dichloromethane (CH₂Cl₂), chloroform (CHCl₃), ethanol (EtOH), tetrahydro-furan (THF) were purchased from ACL Labscan.

2.2 Synthesis of Naphthodithiophene (NDT) 2

Naphthodithiophene 2 could be prepared by a modified method[14] (scheme 1). Reaction of 2,6-dihydroxynaphthalene 3 with 2-mercaptoethanol in the presence of TfOH form dihydrothiophene 4. Subsequently, oxidation of 4 with chloranil in refluxing toluene provided the desired naphthodithiophene 2.



Scheme 1. The synthesis of NDT 2.

2.3 Synthesis of 2,6-diBrNDT5

A solution of Br₂ (1.95 M; 0.46 mL, 0.90 mmol) was added to the stirred solution NDT2 (0.10 g, 0.42 mmol) in CCl₄ (10 mL) at 0 °C and stirred for 30 min. Then the reaction was allowed to warm up to room temperature and left stirred overnight. The reaction was later quenched with H₂O (20 mL), and extracted with CH₂Cl₂ (2x30 mL). The combined organic layers were dried over anhydrous Na₂SO₄, filtered, and evaporated to dryness. Precipitation of the crude product with CH₂Cl₂ and MeOH afforded compound 5 in 46% yield (0.074 g).

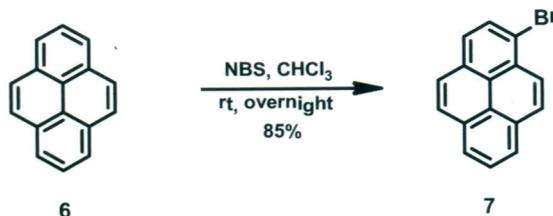


Scheme 2. The synthesis of 2,6-diBrNDT5.

2.4 Synthesis of pyrene derivatives

2.4.1 Bromination of pyrene

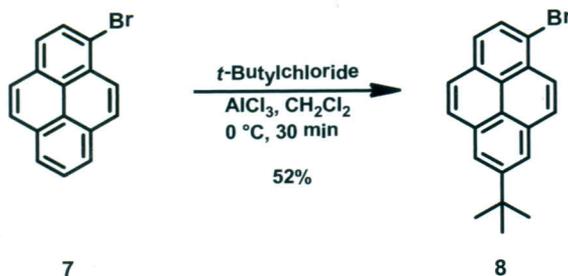
NBS (1.94 g, 10.9 mmol) was added to the stirred solution of pyrene 6 (2.0 g, 10.4 mmol) in CHCl_3 (80 mL). The reaction was stirred overnight at room temperature and then quenched with H_2O (40 mL), and extracted with CH_2Cl_2 (3x40 mL). The combined organic extracts were dried over anhydrous Na_2SO_4 , filtered, and evaporated to dryness. The crude product was precipitated from the solution of CH_2Cl_2 and MeOH to obtain 1-bromopyrene 7 in 85% yield (4.86 g).



Scheme 3. The synthesis of 1-bromopyrene 7.

2.4.2 Synthesis of t-butyl bromopyrene 8

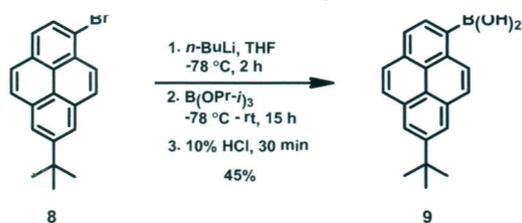
t-Butylchloride (1.60 mL, 14.2 mmol) was added to the stirred solution of 1-bromopyrene 7 (2.00 g, 7.10 mmol) in CH_2Cl_2 (30 mL) at $0\text{ }^\circ\text{C}$, followed by anhydrous AlCl_3 (1.14 g, 8.52 mmol). The reaction was allowed to stir at that temperature for 30 min. Then it was quenched with ice water and extracted with CH_2Cl_2 (3x30 mL). The organic layer was then washed with brine (50 mL), dried over anhydrous Na_2SO_4 , filtered, and evaporated to dryness. Precipitation of the crude product with CH_2Cl_2 and MeOH gave compound 8 (1.13 g, 52% yield).



Scheme 4. The synthesis of pyrene 8.

2.4.3 Synthesis of pyreneboronic acid 9

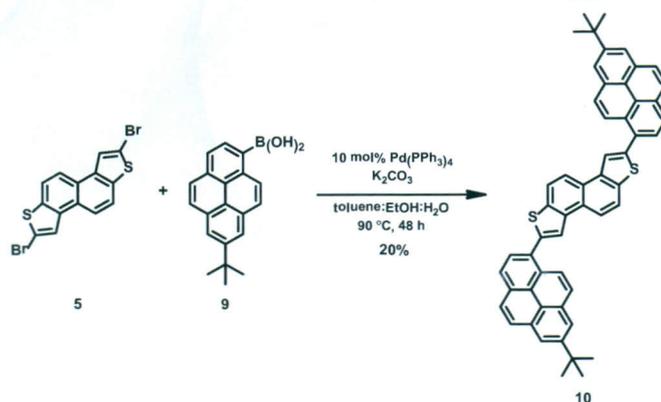
To a stirred solution of pyrene 8 (1.50g, 4.90 mmol) in dry THF (18 mL) under nitrogen atmosphere at -78°C , was added slowly a solution of *n*-BuLi in hexane (1.02 N; 8.65 mL, 8.82 mmol). The reaction mixture was stirred for 30 min. Then $\text{B}(\text{OPr-}i\text{)}_3$ (5.13 mL, 22.2 mmol) was added and the reaction was slowly allowed to warm up to room temperature and it was stirred overnight. Then 10% aqueous HCl (25 mL) was added to the reaction and the mixture was stirred for 30 min. H_2O was then added and the mixture was extracted with CH_2Cl_2 (3x20 mL). The organic layer was washed with brine (40 mL), dried over anhydrous Na_2SO_4 , filtered, and evaporated to dryness. The crude product was precipitated with CH_2Cl_2 /hexanes to yield compound 9 (0.675 g, 45% yield).



Scheme 5. The synthesis of pyrene 9.

2.5 Synthesis of diPy26NDT 10

To a mixture of 2,6-diBrNDT 5 (0.050 g, 0.14 mmol) with pyrene boronic acid 9 (0.16 g, 0.53 mmol), K_2CO_3 (0.13 g, 0.95 mmol) and tetrakis(triphenylphosphine)palladium ($\text{Pd}(\text{PPh}_3)_4$) (0.23 g, 0.033 mmol) under nitrogen atmosphere, was added a degassed solution of toluene (10 mL), EtOH (10 mL) and H_2O (2.5 mL) through syringe at room temperature. The reaction mixture was heated and left stirred at 90°C for 48 h with protection from light exposure. Then the reaction was cooled to room temperature where 10% aqueous HCl (25 mL) was added. The mixture was then extracted with CH_2Cl_2 (3x20 mL) and the combined organic layers was washed with H_2O and dried over anhydrous Na_2SO_4 , filtered, and evaporated to dryness. Column chromatography on silica gel using hexanes and CH_2Cl_2 (hexanes: CH_2Cl_2 , 9 : 1 v/v), followed by precipitation of the resulting product with CH_2Cl_2 /MeOH gave the desired diPy26NDT 10 (0.021 g, 20% yield).



Scheme 6. The synthesis of diPy26NDT10.

2.6 Visual detection of TNT

To demonstrate the ability of diPy26NDT10 for the TNT visual detection, fluorescence quenching titration method between diPy26NDT and trinitrotoluene (TNT) in solution was investigated. TNT (0, 50, 100, 200, 300, 400, 500 and 1000 ppm) in chloroform was added to a 5 μ M, 0.5 μ M and 0.05 μ M solution of diPy26NDT in the final volume of 6 mL. The solution was then transferred to separate glass cuvette and the visual colour change would be observed under UV light (at 366 nm) at room temperature.

3. Results and Discussion

The synthesis of diPy26NDT could be achieved from the Suzuki cross-coupling between 2,6-diBrNDT 5 and pyreneboronic acid 9. The chloroform solution of diPy26NDT was then prepared in 3 concentrations (5 μ M, 0.5 μ M and 0.05 μ M). Upon radiation under UV light, diPy26NDT itself emitted blue light and its fluorescence intensity was dependent on its concentration. To investigate the ability of diPy26NDT in visual detection of TNT solutions under UV light, diPy26NDT at each concentration was titrated with TNT at 0, 50, 100, 200, 300, 400, 500 and 1000 ppm. The result showed that, with naked eyes, the fluorescence intensity of the sensor started to drop when the concentration of TNT reached 100 ppm. In this study, the appropriate concentrations of the sensor were 5 μ M and 0.5 μ M since the change in fluorescence at these concentrations can obviously be observed. It was proposed that the reduction of the fluorescence sensor was from the charge-transfer complex formation between π -electron rich fluorophore and electron-deficient TNT.

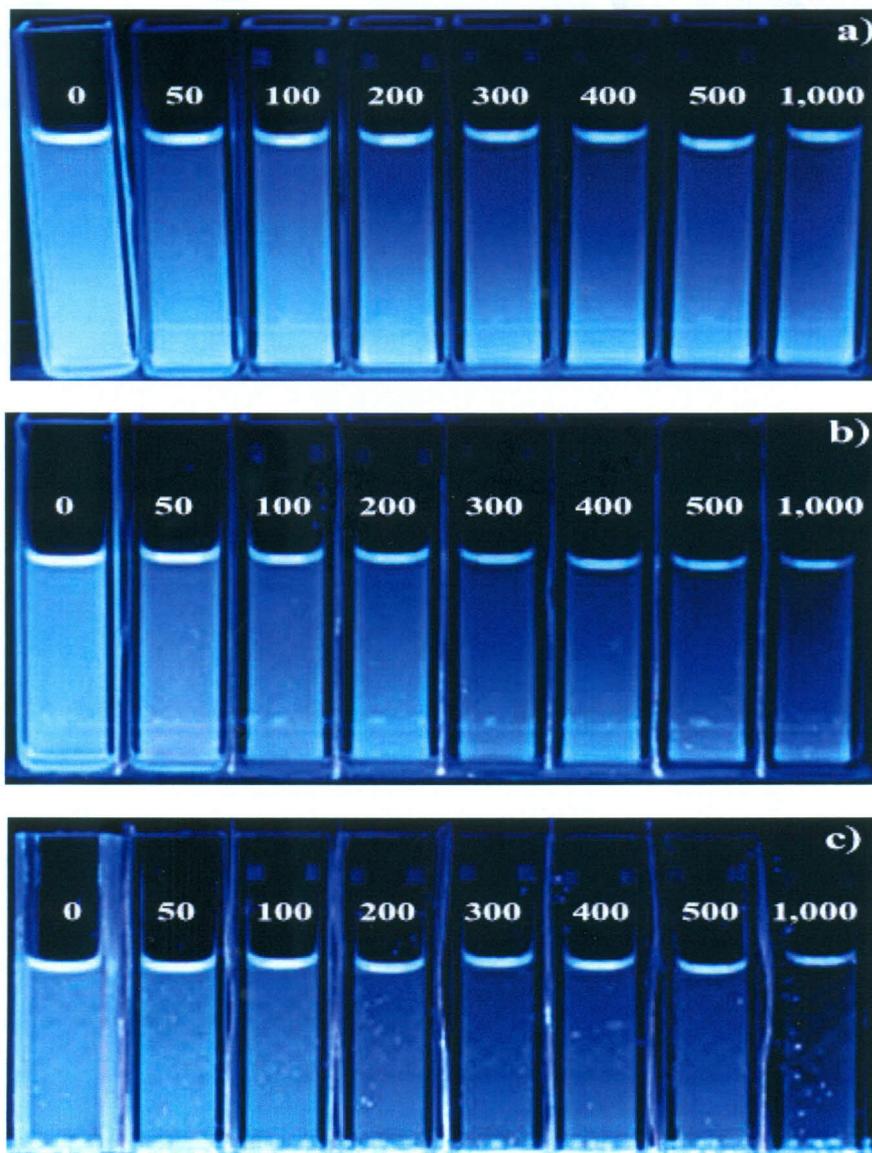


Fig. 3 Visual color changes upon titration of a) 5 μM , b) 0.5 μM and c) 0.05 μM solution of diPy26NDT in chloroform with increasing amount of TNT in chloroform (from left to right, 0, 50, 100, 200, 300, 400, 500 and 1000 ppm) under UV light

4. Conclusions

The designed naphthodithiophene-based fluorogenic compound diPy26NDT was successfully synthesized. The compound showed excellent photoluminescence efficiency under UV light. The solution of diPy26NDT could be quenched by TNT and the change in fluorescence could be visually observed at 100 ppm. Further investigation to apply DiPy26NDT as a sensor for TNT detection is under investigation.

Acknowledgements

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