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Full Paper

Colorimetric Detection of Nitroaromatics Using Organic Photochromic Compounds

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An organic photochromic compound is explored as a new portable colorimetric sensor for nitroaromatics. This photochromic compound switches from colourless to pink upon exposure to ultraviolet light. In the presence of nitroaromatic explosive derivatives the photoswitching behaviour of the dithienylethene is suppressed, while a potential false positive (toluene) has little effect. The degree of photoswitching inhibition was determined by comparing the integrated visible absorption with the concentration of the analyte to give the *pseudo* Stern–Volmer constant (K_{PSV}). The K_{PSV} s measured varied from 12900 (*p*-nitrotoluene) to 236 M⁻¹ (toluene), which were directly related to the analyte absorption at the excitation wavelength.

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Introduction

The discovery of inexpensive portable devices for sensing explosives is needed because of the escalating threat towards public security. In particular, the detection of high explosives such as 2,4,6-trinitrotoluene (TNT) is in high demand because of their widespread availability. Although TNT can be detected with devices based on X-ray scanning and ion mobility spectrometry, they lack the portability required for on-the-spot sensing. Therefore, devices based on fluorescence quenching of light-emitting conjugated polymers and dendrimers have attracted much attention because they can be used in portable nitroaromatic explosive sensing devices.[1-3] The portability and cost of explosive sensors still needs to be improved to further the accessibility of this useful technology. Colorimetric detectors, such as the litmus test for acidity, are powerful sensors because they are cost-effective, portable, and permit visual detection allowing use by non-experts.^[4] Therefore, the colorimetric detection of TNT and their derivatives is of great interest.^[5–7] In this manuscript, the colorimetric detection using an organic photochromic compound is explored.

Organic photochromic compounds are a widely applicable class of molecules that undergo a reversible colour change upon irradiation with light.^[8–10] Of these photochromic molecules, diarylethenes (DAEs) have shown significant promise in terms of ease of synthesis,^[8] solid state switching, switching speed, and fatigue-resistance.^[11,12] Because of the promising photo-switching properties, DAEs have been investigated as active materials for ophthalmic lenses,^[8] carbon dioxide capture,^[13] optical data storage, and logic components where the two photoisomers can display a unique electronic^[14] or optical output.^[15] Furthermore, these photochromes have been used

in biologically relevant applications such as mimicking pyridoxal phosphate^[16] and imaging in living cells.^[17]

Regulation of the switching behaviour of DAEs has been an area of great interest for sensing applications. To that end, the chemosensing of metals,^[18] fluoride ions,^[19] and cysteine^[20] has been demonstrated. In these instances, the DAE interacted with the analyte to obtain the desired selectivity. Alternatively, if the analyte has a unique absorption spectrum, then inhibition of photoswitching could be used to detect that compound at a specific wavelength. This would be particularly applicable to nitroaromatic compounds as they have high molar absorptivities, meaning a small amount of compound could afford a large change in the photoswitching property. To that end, the inhibition of photoswitching of a dithienylethene (DTE) derivative, Scheme 1, in the presence of various nitroaromatic compounds is investigated herein.

Results

Fig. 1 depicts the photoswitching of a DTE as a function of DNB concentration. It is apparent that as the concentration of the DNB increases, the extent of photoswitching decreases.

A method to quantify, and therefore directly compare, this photoswitching inhibition of the various nitroaromatic analytes was developed, which is analogous to Stern–Volmer fluorescence quenching. In doing so, the change in the fluorescence intensity area is replaced with the absorption intensity area in the Stern–Volmer equation. This *pseudo* Stern–Volmer relationship is represented by Eqn 1:

$$\frac{A_0}{A} = 1 + K_{PSV}[An] \tag{1}$$



Scheme 1. Photoswitch inhibition of a dithienylethene using a nitroaromatic compound.



Fig. 1. Absorption spectrum of dithienylethene solutions (0.5 mM) as a function of DNB concentration after exposing each solution to 280 nm for 200 s.



Fig. 2. Photoswitching inhibition of the dithienylethene as a function of DNB concentration and excitation wavelength.

where A_0 is the integrated absorption intensity in the absence of analyte, A is the integrated absorption intensity after the analyte addition, [An] is the concentration of the analyte, and K_{PSV} is the *pseudo* Stern–Volmer constant. An additional advantage of this quantification method is that it enables the responsiveness of this colorimetric detection to be directly compared with traditional fluorescence quenching technologies (Stern–Volmer constant, K_{SV}) for explosives detection. In doing so, Fig. 2 illustrates a linear relationship between the decrease in the absorption area between 425 and 600 nm and the concentration of the DNB (•) at various excitation wavelengths. Upon exposure at 280 nm, the K_{PSV} was $8200 \pm 520 \text{ M}^{-1}$. Importantly, the corrected K_{SV} of fluorescent polymers, dendrimers, and small molecules are generally in the tens or hundreds, and rarely in the thousands M^{-1} .^[1–3] The K_{PSV} s were found to be excitation wavelength dependent, where K_{PSV} varied from 4000 to 4900 M⁻¹ when excited at 300 and 320 nm.

A key characteristic of an explosives sensor is its selectivity to avoid false positives. To determine the photoswitching inhibition selectivity of the DTE, the photoswitching inhibition of *p*-nitrotoluene (pNT), 2,4-dinitrotoluene (DNT), 1,4-dinitrobenzene (DNB), benzophenone (BP), and toluene were investigated (Fig. 3a). The K_{PSV} was $12900 \pm 745 \text{ M}^{-1}$ for pNT, $9650 \pm 650 \text{ M}^{-1}$ for DNT, $6030 \pm 310 \text{ M}^{-1}$ for the nonexplosive BP and only $236 \pm 38 \,\mathrm{M}^{-1}$ for toluene at 280 nm excitation. The different response to the analytes was correlated with the molar absorptivity (ε) of the analyte at the excitation wavelength (280 nm). To that end, Fig. 3b illustrates the absorption traces of all the analytes in dichloromethane. It is clear the greater the analyte's molar absorptivity at 280 nm, the greater the photoswitching inhibition. For instance, pNT has the highest molar absorptivity $(11700 \text{ cm}^{-1} \text{ M}^{-1})$ at 280 nm and gives the greatest photoswitching inhibition $(K_{PSV} =$ 9650 M^{-1}), while the non-explosive toluene has the lowest molar absorptivity (<10 cm⁻¹ M⁻¹) and has the lowest photoswitching inhibition ($K_{PSV} = 236 \text{ M}^{-1}$). The comparison of the K_{PSV} of all the analytes with respect to their molar absorptivity is given in Fig. 3c. It is clear that the analyte absorption at 280 nm is directly correlated with the photoswitching inhibition, meaning that the photoswitching inhibition is primarily attributed to competing absorption of the photochrome and the analyte at the given excitation wavelength. That is, as the analyte concentration increases, the analyte absorbs more light, which increases photoswitching inhibition. To further demonstrate this difference in selectivity, Fig. 3a inset depicts the response after UV-irradiation in the absence of an analyte (DTE), in the presence of pNT (DTE + pNT) and in the presence of toluene (DTE + toluene). This demonstrates that the photoswitching is inhibited in the presence of pNT while virtually unaffected in the presence of toluene. Therefore, given the excitation wavelength dependence (Fig. 2) and the absorption profile of any analyte, the selective detection at a particular excitation wavelength can be predicted.

Experimental

Materials

n-Butyl lithium, 2,5-dimethylthiophene, *N*-bromosuccinimide, DNB, PNT, DNT, BP, and toluene were obtained from



Fig. 3. (a) Photoswitching inhibition as a function of *p*-nitrotoluene (\blacklozenge), 2,4-dinitrotoluene (\square), 1,4-dinitrobenzene (\blacklozenge), benzophenone (\times), and toluene (\triangle) at 280 nm excitation. Inset: DTE, DTE with pNT (1.8 mg, 5.2 mM), and DTE with toluene (3.0 mg, 13.0 mM) solution depicting photoswitching inhibition after irradiating with UV light for 30 s. (b) the molar absorptivity (L mol⁻¹ cm⁻¹) of the analytes in dichloromethane as a function of wavelength. (c) Comparison of the analyte absorption at 280 nm and their *pseudo* Stern–Volmer constants.

Sigma-Aldrich and perfluorocyclopentene was obtained from SynQuest Laboratories. All chemicals were used as received.

Characterisation

¹H NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer. Gas chromatography–mass spectrometry (GCMS) chromatograms were recorded on a Hewlett Packard 5971A gas chromatograph–mass spectrometer. Fourier transform infrared (FT-IR) spectra were recorded as a powder using a Nicolet 6700 FT-IR equipped with a smart iTR attenuated total reflectance crystal.

The photochrome solutions were prepared (~ 0.5 mM) and that solution was used to prepare the analyte solutions to avoid changes in the photochrome concentration after the addition of the analyte. The photostationary state is primarily in the open state. The *pseudo* Stern–Volmer constants were calculated by comparing the integrated absorption area from 425 to 600 nm, and dividing by the total volume of the solution. The K_{PSV} coefficients and errors reported were based on an average of five measurements. Absorption spectra were recorded on a Varian Cary 5000 UV-vis–NIR spectrophotometer using freshly distilled dichloromethane as the solvent. A Horiba Jobin-Yvon Fluoromax 4 spectrometer was used as a light source for photoswitching the photochrome solutions with a 5 nm excitation slit width for 200 s at the specified wavelength.

Synthesis

3-Bromo-2,5-dimethylthiophene^[21]

A 500 mL round bottom flask was charged with 2,5-dimethyl thiophene (5.1 mL, 44.6 mmol) in glacial acetic acid (220 mL) and *N*-bromosuccinimide (7.94 g, 44.6 mmol) was added slowly portion wise at room temperature with stirring. The solution was allowed to stir for 3 h at this temperature. The reaction was quenched with a mixture of ice and water (300 mL) followed by extraction with dichloromethane (3×100 mL). The combined organic fractions were washed with 2 M Na₂CO₃ (5×100 mL), water (2×100 cm³), and dried over MgSO₄. The mixture was filtered and the solvent was removed under reduced pressure. The crude product was purified by column chromatography over silica (500 mL) using hexanes as the eluent to afford the title compound as a colourless oil (6.63 g, 77 %). $\delta_{\rm H}$ (CDCl₃) 2.32 (3H, s), 2.39 (3H, s), 6.55 (1H, m). *m/z* (GCMS): 192 (M⁺).

3,3' - (Perfluorocyclopent-1-ene-1,2-diyl)bis(2,5-dimethylthiophene), DTE^[22]

A 100 mL round bottom flask was charged with 3-bromo-2,5-dimethylthiophene (3.66 g, 19.4 mmol) in dry THF (30 mL) and cooled to -78° C. *n*-Butyl lithium (19.4 mmol) was added dropwise allowed to stir at -78°C for 1 h before perfluorocyclopentene (1.19 mL, 9.23 mmol) was added. The solution was warmed slowly to room temperature under stirring. The reaction was quenched with 3 M hydrochloric acid (5 mL) and allowed to stir for 30 min, followed by extraction with diethyl ether $(3 \times 15 \text{ mL})$. The combined organic fractions were dried over anhydrous MgSO₄, filtered, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography over silica using hexanes as the eluent and followed by recrystallisation from hexanes to afford the title compound as a white-pink crystalline solid (0.80 g, 21 %). $v_{\rm max}$ $(neat)/cm^{-1}$ 2960, 2924, 1622, 1497, 1436, 1333, 1262, 1208, 1185, 1145, 1125, 1085, 1043, 980, 888, 822, 731. $\delta_{\rm H}$ (CDCl₃) 1.81 (3H, s), 2.41 (3H, s), 6.70 (1H, s).

Conclusion

We have demonstrated a simple approach for the visible detection of nitroaromatics using a DTE photochrome. It was found that DTE is highly sensitive and selective towards nitroaromatics because of the high molar absorptivity of the nitroaromatics and the good absorption overlap of the analyte with the DTE. This technology would be useful for the production of cost-effective and portable explosive sensors.

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