

Bispyrenylalkane Chemosensor for the Naked-eye Detection of Nitro-explosives

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Abstract

Pyrene-based compounds have a great potential as fluorescent chemosensors for various analytes including common nitro-explosives, such as 2,4,6-trinitrotoluene (TNT). Compounds having two pyrene units in one molecule, such as bispyrenylalkanes, are able to form stable, bright emissive in a visual wavelength region excimers both in non-polar and polar environments. In this work we wish to report that in non-polar solvents the excimer has poor chemosensing properties while in aqueous solutions it provides significant “turn-off” fluorescence response to TNT in the sub-nanomolar concentrations.

Keywords

detection of explosives
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chemical sensors
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fluorescence quenching

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1. Introduction

Due to an increased terrorism threats, the remote detection of TNT and DNT as main components of explosive blends [1] has become an actual task. Visual detection of explosives [2–5] is one of the oldest analytical techniques offering vast possibilities for the on-site, real-time analysis with a very fast response time. Among the visual methods, fluorescence [6–9] “turn-off” [10–15] detection is the most convenient due to high sensitivity and fast response time; in the last two decades, various fluorescent sensors for many analytes, including (nitro)explosives, have been reported. Among many fluorescent chemosensors [16], those based on polycyclic aromatic hydrocarbons (PAH-based) have gained wide attention owing to their unique fluorescent properties, such as long-wavelength excimer emission [17] either in a solution [18] or in a solid state. And pyrene-based chemosensors can be ideal candidates to use in PAH-based chemosensors because of the well-known pyrene intense emission with long lifetime values [19–28], tendency to form excimers [29] and high sensitivity to electron-deficient molecules (e.g., nitroaromatics) [30,31].

In this manuscript we wish to report our study of the ability of the simple bispyrenylalkane chemosensor to ef-

fectively detect a common nitro-explosive, such as 2,4,6-trinitrotoluene (TNT).

2. Experimental

Starting materials are commercially available. UV-Vis absorption spectra were measured on the spectrophotometer Shimadzu UV-1600 (Japan). Emission and excitation spectra were measured on the Horiba FluoroMax-4 (USA). The emission spectra were normalized automatically using the “Normalize columns” option in the OriginPro 2015 software (64-bit) b9.2.196. Fluorescence titration experiments were carried out by using the Horiba-Fluoromax-4 spectrofluorometer (USA). Photos were taken with the Canon D3000 Kit camera.

3. Results and Discussion

Chemosensor **1** was prepared as reported earlier [32,33] by using the condensation reaction between the 1-pyrenecarboxaldehyde and acetone with the following reduction of the obtained condensation product (Fig. 1).

Next, the photophysical properties of compound **1** in the absence and in the presence of TNT were studied. Previously, the intensive excimer emission of 10^{-5} M solutions of compound **1** in methylcyclohexane was reported [32].

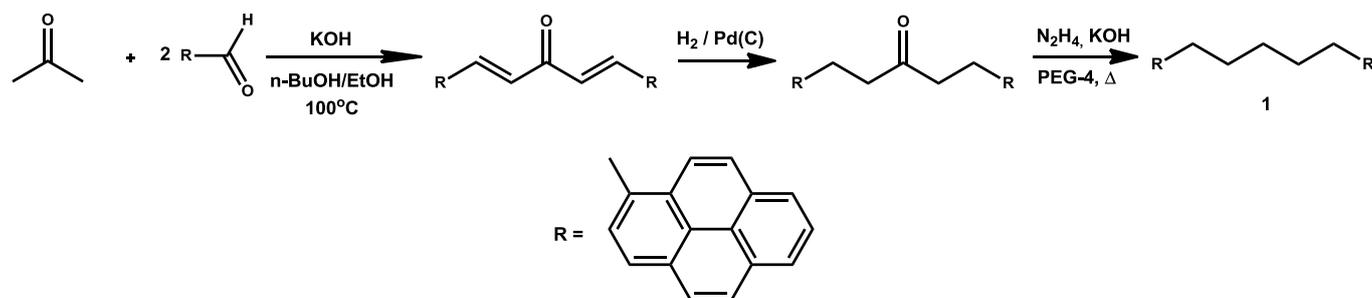


Fig. 1 Synthetic scheme for sensor 1

However, in our experiments only a feeble response through the excimer fluorescence quenching with poor linearity in the Stern-Volmer plot was observed in cyclohexane.

Based on the earlier reports [34,35], we suggested that the polarity of a solvent can be the driving force for the geometry changes in the molecule of **1**, which are highly soluble in non-polar solvents. In polar solvent media, this lipophilic molecule could act as a surfactant and the hydrophobic interactions would make molecule **1** to bend over the pentane linker. In this case, the proximity effect between two pyrene moieties will result in excimer emission, while the monomeric emission of **1** will be suppressed. In addition, the lipophilic nature of the interior of the cavity formed by molecule **1** would provide a driving force for the transport of TNT molecules from the polar solvent media inside the non-polar micellar chemosensor to cause the dramatic excimer fluorescence quenching.

To prove that, the photophysical studies of compounds **1** (10^{-6} M) in different solvent systems were carried out. The selected solvents were arranged in the order of their increasing polarity: cyclohexane, THF (tetrahydrofuran), DMSO (dimethyl sulfoxide), and various solutions of DMSO in water. As it was expected, upon the increasing the polarity of solvents, a gradual decrease in the absolute intensity of the monomer emission was observed (Fig. 2), along with an increase in the intensity of the excimer emission. The highest excimer emission was observed for the 50% aqueous solution of DMSO, and this solvent was selected for our experiments.

The visual detection experiments were carried out for the solution of sensor **1** by using common borosilicate glass vials (10 mL), and the picture is presented below (Fig. 3). Thus, depending on the concentration of TNT (10^{-4} M solution of in acetonitrile) added to the 10^{-6} M solution of sensor **1** in DMSO/H₂O (1:1), different degree of fluorescence quenching was observed ($\lambda_{\text{ex}} = 365$ nm).

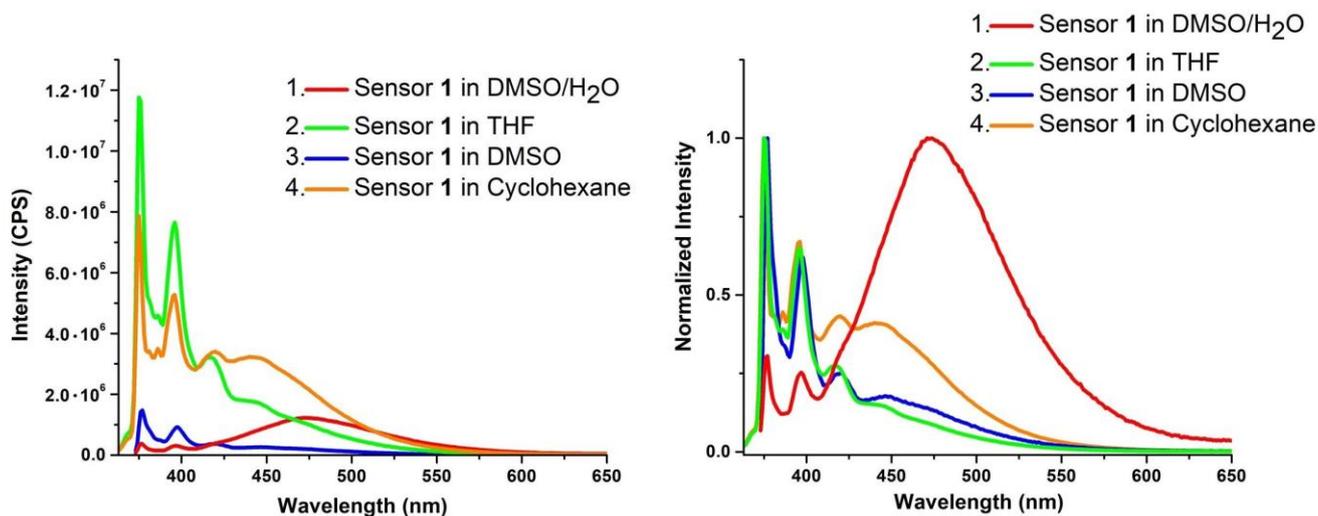


Fig. 2 Emission spectra (left) and normalized emission spectra (right) of sensor **1** (10^{-6} M) in the solvents of different polarity

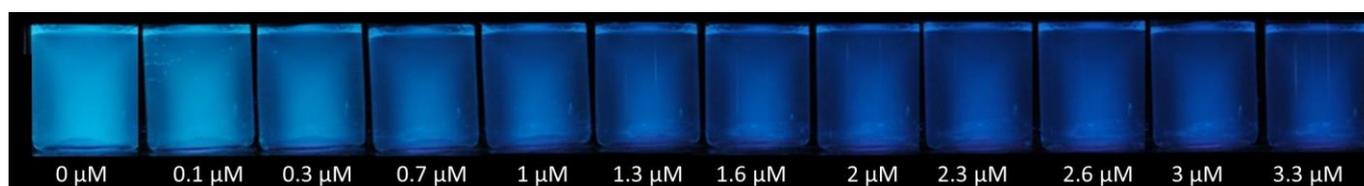


Fig. 3 The visual detection experiment for chemosensor **1** in DMSO/H₂O (1:1): pictures of sensor **1** under UV light ($\lambda = 365$ nm) after stepwise addition of nitro explosive (TNT)

Next, the fluorescence quenching titration was carried out. The fluorescence response of the chemosensor towards the nitro-analyte was quantitatively calculated using the Stern-Volmer static quenching model according to Eq. (1):

$$\frac{I_0}{I} = 1 + K_{sv}[Q]. \quad (1)$$

The calculated Stern-Volmer constant value for TNT was determined to be as high as $K_{sv} = 4.67 \cdot 10^5 \text{ M}^{-1}$ for the static quenching model (Fig. 4). At low concentration of TNT quencher the close to linear behavior of Stern-Volmer plots was observed, which suggests the prevalence of only one quenching mechanism, such as static quenching.

The calculated limit of detection (LOD) of 143 $\mu\text{g/L}$ (136 ppb) for the sensor 1 was estimated as reported earlier [36].

4. Conclusions

In summary, we described a tunable bispyrenylalkane chemosensor, which provides a simple, fast and convenient way for the detection of common nitroaromatic explosive (2,4,6-TNT) in aqueous solutions. Its sensory response is visible enough to be detected even by the naked eye. The value of the Stern-Volmer constant of the fluorescence quenching for 2,4,6-trinitrotoluene was found to be high and equal to $4.67 \cdot 10^5 \text{ M}^{-1}$.

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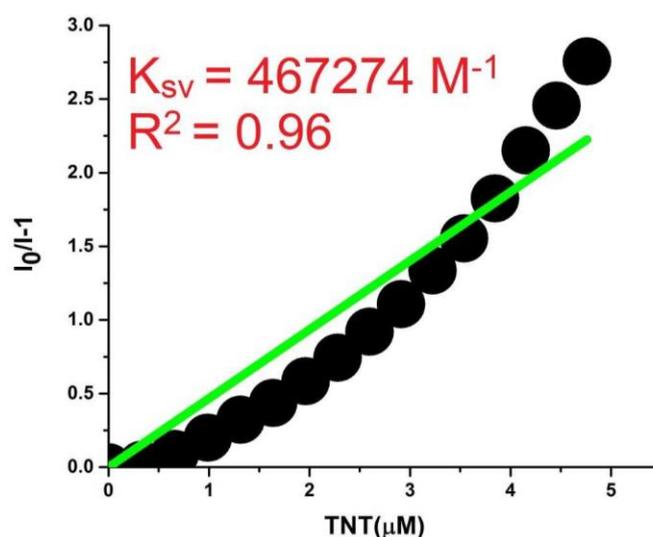


Fig. 4 Stern-Volmer plot of emission quenching for sensors 1: points – experimental data, line – linear fit

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