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Imidazolylmethylpyrene sensor for dual optical detection of explosive chemical: 2,4,6-Trinitrophenol

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ABSTRACT

Fluorescence and colorimetric sensor with simplistic synthesis method based on 1-imidazolylmethylpyrene (**IMPY**) was found to be a specific recognition for an explosive chemical: 2,4,6-trinitrophenol or picric acid (**PA**). The sensor did not only provide highly sensitive OFF–ON fluorescence enhancement toward **PA** in acetonitrile, but also offered ON–OFF fluorescence quenching upon **PA** binding in toluene solution. In addition, the sensor **IMPY** provided high selectivity to 2,4,6-trinitrophenol and was shown to discriminate various phenolic compounds such as *p*-iodophenol, *p*-bromophenol, *m*-hydroxybenzaldehyde, *o*-nitrophenol, *m*-nitrophenol, *p*-nitrophenol and 2,4-dinitrophenol. Upon binding to **PA**, the fluorogenic change of the sensor were observed and accompanied by the noticeable chromogenic change from colorless to yellow, therefore the sensor could also serve as a "naked-eye" indicator. Finally, two different types of crystal structures of **IMPY**·**PA** complexes were successfully recrystallized and characterized, which confirmed highly interactive affinity of the host-guest molecules.

1. Introduction

Nowadays, terrorists-attacks occur in countries around the world with an extensive use of explosive chemicals. Therefore, the detection of those explosives in a trace amount becomes great interests and necessary for social safety [1]. 2,4,6-Trinitrophenol or picric acid (**PA**) is one of the highly reactive compounds and its explosive power is almost similar to other nitroaromatic compounds (NACs) such as trinitrotoluene (TNT), and dinitrotoluene (DNT) [2]. Moreover, **PA** is widely used in many industries as a composition of the products such as firework, matches, leather, and dyes [3–5]. Currently, **PA** determination can be detected by gas chromatography, Raman spectroscopy, and fluorescence spectroscopy [6,7]. However, fluorescence detection of **PA** presents many promising approaches because it allows high sensitivity, rapid response and real-time monitoring [8,9]. In addition, fluorescent sensor for **PA** can allow the on-site preliminary screening which will greatly benefit prevention of the explosion and social security.

The continuous developments of probes for **PA** detection have been provided through the compounds with electron deficient phenyl ring and/or the acidic hydroxyl group [9–17]. Anthracene and pyrene were found to be potential fluorophores to detect NACs, due to the strong binding of the electron deficient phenyl ring of the nitro groups on the NACs to the polyaromatic hydrocarbon (PAHs) through π-π interaction [18,19]. In particularly, pyrene and their derivatives have been one of the most intensive-used fluorophores for **PA** fluorescent sensors due to their high fluorescent emission. Commonly, developed pyrene structures for **PA** sensor were based on several hydrogen bonding and π-π interactions. However, most of the reported **PA** fluorescent chemosensors operated

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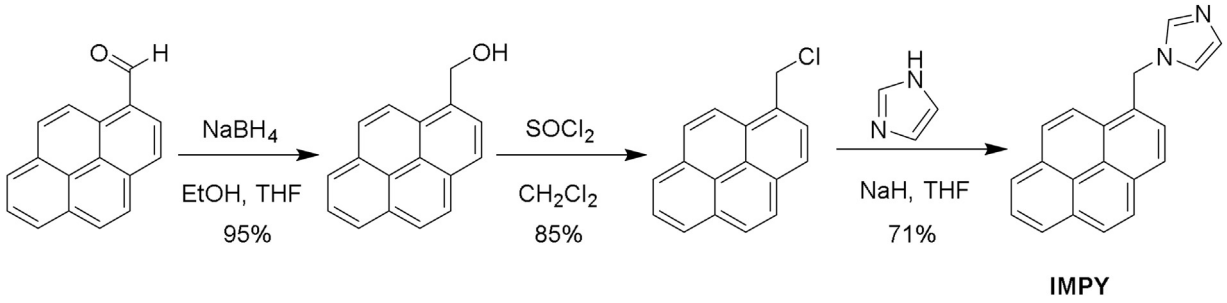

Scheme 1. Synthetic approach to prepare 1-imidazolylmethylpyrene (**IMPY**).

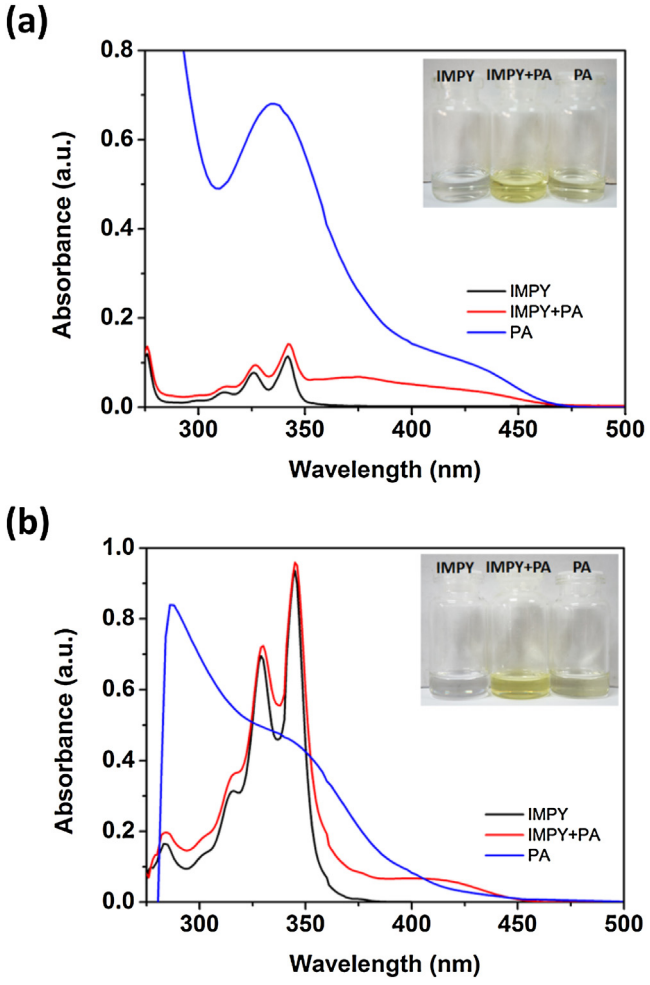

Fig. 1. Absorption spectra of **IMPY** in the presence and absence of **PA** in (a) toluene and (b) acetonitrile.

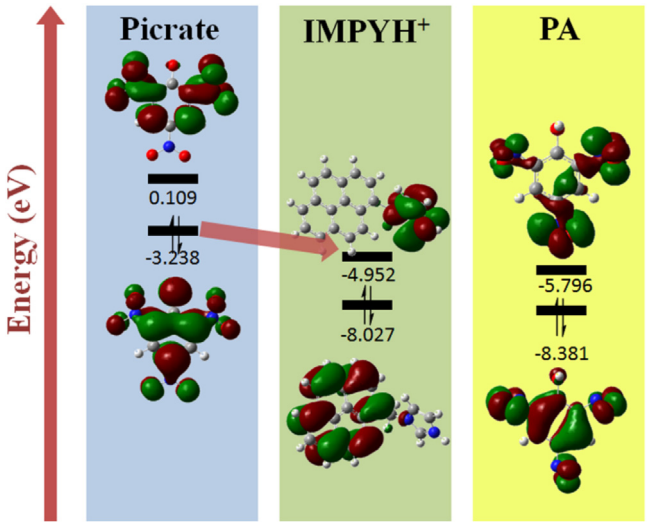

Fig. 2. Calculated energy level diagram of picrate anion, protonated **IMPY**, and picric acid (**PA**) [17].

via an ON–OFF fluorescent quenching mechanism without chromogenic change [17,20–22]. Therefore, the development of high sensitive and selective **PA** fluorescent sensor that could be operated *via* both OFF–ON and ON–OFF responses, which also exhibited the chromogenic change will be a great challenge, and could benefit on-site detection of **PA** due to the versatility to use the sensor.

Herein, we found that the designed sensor of 1-imidazolylmethylpyrene (**IMPY**) could be used as a **PA** fluorescent chemosensor and could be operated through both enhancement and quenching of fluorescence by simply switching the solvent systems. Importantly, the sensor exhibited high selectivity and sensitivity to **PA** and also exhibited chromogenic change from colorless to yellow in the presence of **PA**. Therefore, the developed sensor could also serve as a "naked-eye" indicator.

2. Experimental section

2.1. Materials and instruments

1-Pyrenecarboxaldehyde (purity, 99.0%), sodium borohydride (powder, ≥98.0%), imidazole (purity, ≥99.0%) and sodium hydride (60% dispersion in mineral oil) were purchased from Sigma-Aldrich. Thionyl chloride (purity, ≥99.0%) was purchased from Merck millipore. Precoated silica gel 60 F_{254} plates and silica gel (No. 60) used for chromatography were purchased from Merck & Co., Inc. Acetonitrile, toluene, tetrahydrofuran, and ethanol were purchased from Honeywell Burdick & Jackson® without further distillation, while the commercial grade of methanol and methylene chloride were further distilled at atmospheric pressure.

NMR spectra were obtained in $CDCl_3$ and DMSO-d_6 solutions using the known chemical shift of the residual ^1H solvent signal as the reference: $CDCl_3$ = 7.26 and DMSO-d_6 = 2.54 ppm by a Bruker-AV 400 of high-resolution magnetic resonance spectrometer for ^1H (400 MHz) nuclei. The mass spectrum of the **IMPY** product was acquired using a micro-TOF mass spectrometer of VQ-TOF 2. UV–Vis spectra were obtained on a UV–Vis spectrophotometer of JASCO Model V-530. Absorption spectra were collected in toluene and acetonitrile for molar concentrations used in **IMPY** (3 μM) and all phenolic compounds (1.2×10^{-4} M). Fluorescence spectra were obtained on a spectrofluorometer of JASCO FP-6200 using a 1 cm path length of quartz cell. In a fluorescence titration study