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A fluorescent probe for TNP detection in aqueous solution based on joint properties of intramolecular charge transfer and aggregation-induced enhanced emission

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ABSTRACT

A donor–acceptor (D–A) fluorescent molecule, Nph-An composed of anthracene and 1,8-Naphthalimide units, was designed and synthesized. It presented typical intramolecular charge transfer (ICT) emission from 1,8-Nphthalimide units to anthracene units, and this emission was enhanced obviously in aqueous solution, which was attributed to aggregation-induced enhanced emission (AIEE). Further, Nph-An was used as a fluorescent probe to detect 2,4,6-trinitrophenol (TNP) in aqueous solution. The proton transfer from TNP to Nph-An could efficiently block the ICT emission of Nph-An, and cause the fluorescence remarkably to be quenched. The calculated limit detection is 4.7×10^{-7} M.

1. Introduction

Due to the extremely danger of the nitroaromatics explosives in public security, human health and environment, many efforts have been devoted to detecting explosives [1]. Among the nitroaromatics explosives, 2,4,6-trinitrotoluene (TNT) and 2,4,6-trinitrophenol (TNP) are the most widely used in dyes, explosives, fireworks, matches, and pharmaceutical industries and their residues often cause much damages [2]. In particular, TNP has higher solubility in water than TNT, which is easily absorbed by human and animals and causes serious diseases [3]. Thus, the detection of TNP in water is of more importance. However, less attention has been paid to TNP than other explosives [4]. Thereby, it is necessary to develop a rapid, sensitive and portable method to detect TNP, especially in aqueous solution.

Up to now, some materials have been employed to detect TNP, including graphitic carbon nitride nanosheets [5], polydiacetylene microtube [6], metal complex [7], electron-rich polymer [8], and metal-organic framework [9]. Among them, fluorescent materials received more and more attentions, due to their sensitive, simple and low-cost properties [10]. The mechanism of TNP fluorescent detection is mainly ascribed to the photo-induced electron transfer (PET). Though many good results have been achieved for the fluorescent detection of TNP, in our opinion, it still remains a challenge to develop a facile way to fabricate fluorescent probe in aqueous solution.

As we known, the conventional fluorescent materials are commonly aggregated in aqueous solution, and the fluorescence is often weakened or quenched due to the strong intermolecular π–π interactions. The phenomenon is usually called "aggregation-caused quenching" (ACQ) [11,12]. But some fluorescent materials present opposite properties, which have strong emission in high concentration or solid state [13]. It is called aggregation-induced emission or enhanced emission (AIE/AIEE) [14], which offers the opportunity for fluorescent detection in aqueous solution. On the other hand, some donor–acceptor molecules with highly efficient Intramolecular charge transfer (ICT) emission have been reported [15,16]. The ICT emission can easily be blocked by TNP, causing the emission remarkably decreased [17], which could afford the possibility to detect TNP. Up to date, the reports combining AIEE and ICT to detect TNP in aqueous solution are rare.

In this work, we report a molecule, Nph-An. Its molecular structure is shown in Fig. 1a. Nph-An presents strong fluorescence emission in aqueous solution. Moreover, Nph-An is a donor (D)–acceptor (A) type molecule, composed of 1,8-Naphthalimide units as the acceptor and anthracene units as the donor, respectively. Its emission is attributed to the intramolecular charge transfer (ICT) from 1,8-Naphthalimide units to anthracene units.

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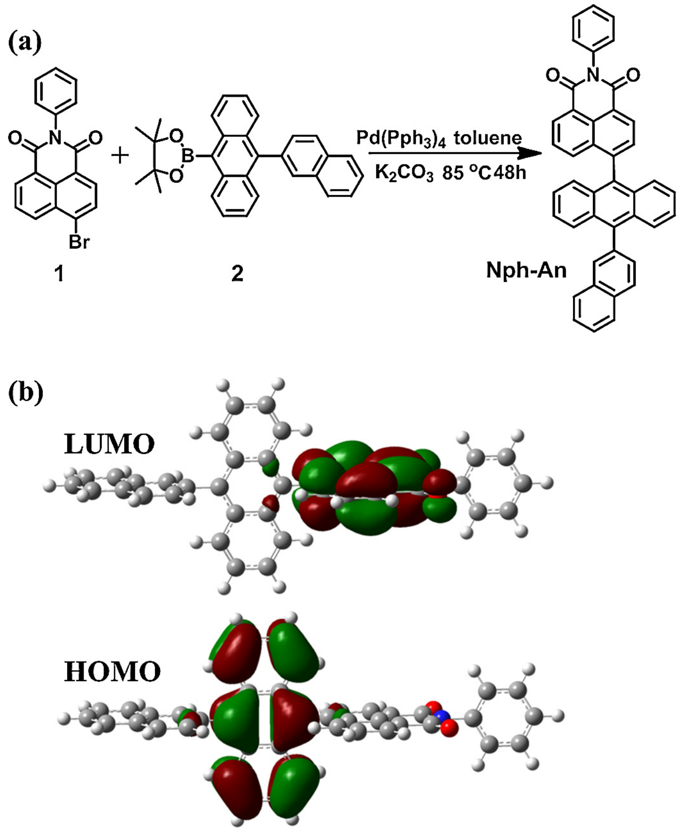

Fig. 1. (a) Synthetic route of Nph-An; (b) distribution of HOMO and LUMO of Nph-An calculated by TD-DFT.

Based on the features of AIEE and ICT emission, Nph-An was used in the fluorescent detection of TNP in aqueous solution with high sensitivity. There exists strong electrostatic interaction between Nph-An and TNP, due to the protonation of Nph-An caused by TNP molecule in aqueous solution [18,19]. The electrostatic interaction could efficiently block the ICT emission from 1,8-Naphthalimide to anthracene moieties of Nph-An inducing the strong fluorescent quenching.

2. Experimental

2.1. Materials and methods

All other chemicals and solvents were purchased from commercial sources and used as received except where noted. Reactions were all conducted under argon atmosphere. ^{1}H NMR spectra were recorded on a Bruker AVANCZ 500/600 spectrometer at 500/600 MHz, using $CDCl_3$/DMSO 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. Energy level was calculated by DFT/B3LYP/6-31g (d, p).

2.2. Synthesis of Nph-An

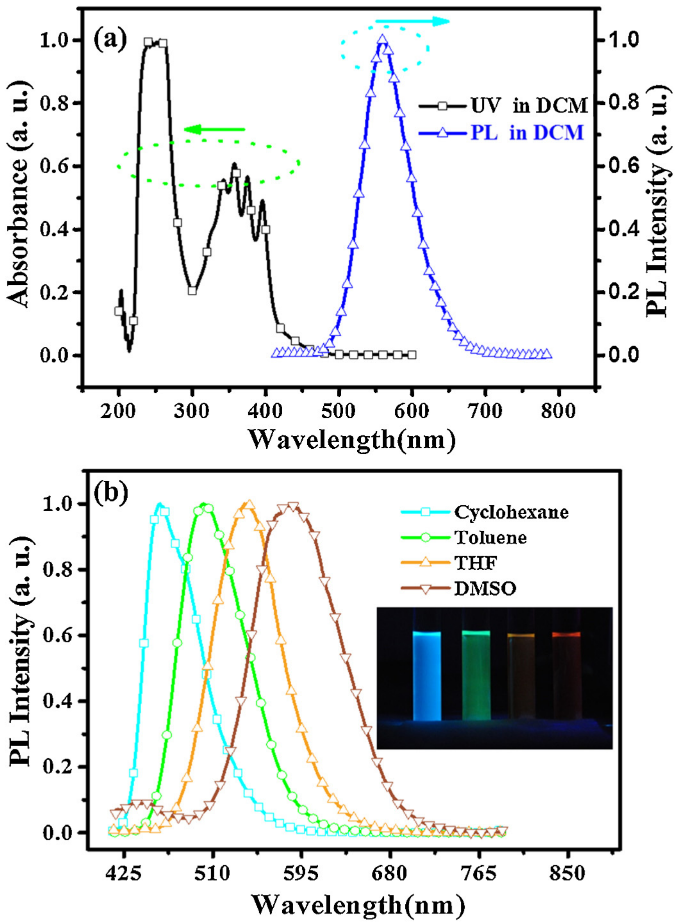

Fig. 2. (a) Absorption and PL spectra of Nph-An in DCM; (b) PL spectra of Nph-An recorded in cyclohexane, toluene, THF and DMSO, respectively. Inset: the pictures of Nph-An are in different solvents under UV light at 365 nm.

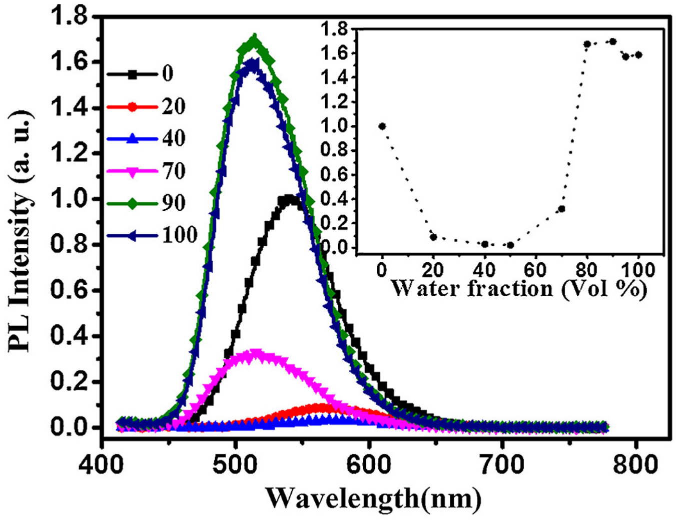

Fig. 3. The PL spectra of Nph-An recorded in water/THF mixture solvent with different f_w. The inset: the change of emission with different f_w.

Compound 1: a mixture of 4-bromo-*N*-phenyl-1,8-naphthalimide (1 mmol), aniline (2 mmol), added into acetic acid (10 mL). The mixture was refluxed for 12 h, then the mixture was poured into ice water and filtered. The crude product was recrystallized with ethanol to obtain light gray solid. The yield was 85.3%, 281.74 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.74 (d, *J* = 7.3 Hz, 1H), 8.68 (d, *J* = 8.5 Hz, 1H), 8.50 (d, *J* = 7.8 Hz, 1H), 8.12 (d, *J* = 7.8 Hz, 1H), 7.93 (t, *J* = 7.9 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 2H), 7.52 (dd, *J* = 14.8, 7.4 Hz, 1H), 7.34 (dd, *J* = 13.2, 5.9 Hz, 2H). MALDI-TOF-MS: 351.87.

Compound 2: a mixture of 9-bromo-10-(naphthalen-2-yl) anthracene (383.28 mg, 1 mmol), bis(pinacolato) diboron (380.91 mg, 1.5 mmol), [1,1′-bis(diphenyl-phosphino) ferrocene]