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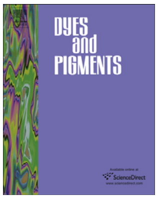

Perylene derivatives as a fluorescent probe for sensing of amines in solution

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ABSTRACT

Amines play an important role in many physiological processes in living organisms. The present study explores the use of perylene diimide (**PDI**) and perylene monoimide (**PMI**) for the detection of common amines in solution. A systematic investigation using primary, secondary and tertiary amines as electron donors and perylene derivatives as electron acceptors is carried out in solution to understand the molecular interactions. Results from steady-state luminescence spectroscopy suggested that the **PDI** and **PMI** interact with the amine derivatives in the excited state, which led to photoinduced electron transfer and fluorescence quenching. Stern-Volmer plots were used to understand the quenching behavior of perylene derivatives in presence of various amines. The bimolecular rate constants of the dynamic quenching have been deduced for **PDI**, the values are in the range of 1.8×10^9 $M^{-1}s^{-1}$ for primary amines, 8×10^9 $M^{-1}s^{-1}$ for tertiary amines and 2.2×10^{10} $M^{-1}s^{-1}$ for aniline. Similar quenching rate constants for primary, secondary and tertiary amines were also observed for **PMI**. **PDI** showed higher selectivity for bulky hydrophobic amines over linear primary amines in solution. Such interactions could be investigated further to understand the response of perylene based sensors for amines.

1. Introduction

Detection of amines is important for monitoring industrial and environmental pollution, checking the quality of food products and medical diagnosis of certain diseases [1]. Moreover, aliphatic amines are found in waste water effluents from pharmaceutical industries, agriculture, and food processing units [2–4]. Biogenic amines are biomarkers for certain type of diseases such as lung cancer (aniline), uremia (dimethylamine and trimethylamine) [1,5] and ammonia for several diseases [6].

Several methods have been developed for detection of amines in the vapor phase using different techniques [7] Majority of the sensors are based on oxidation of amines on anode materials which lead to an output signal proportional to the concentration of amines [8]. Biosensors are also developed for amines with immobilized aminooxidase or aminodehydrogenase enzymes [9–11]. Piezoelectric quartz crystal microbalance and ion-channel sensors are other forms of amine sensors based on host-guest interactions [12–14]. Most methods have certain limitations such as need for reference electrodes, low sensitivity, low selectivity and short lifetime. Chemical sensors based on optical transduction method are designed for sensing ammonia and organic amines [15] using indicator dyes which are prone to photobleaching [16,17].

Among widely used sensors such as ion selective electrodes, electrochemical devices and chemical sensors, fluorescent sensors based on organic materials are promising owing to high sensitivity, selectivity and fast response [18,19]. Perylene diimide (**PDI**) derivatives with excellent photostability and electron deficient nature have been used for the detection of amines [22]. Recently, perylene diimide incorporated nanofibers were prepared and used as fluorescent sensors for organic amine vapors [20–23]. But little is known about the interactions of **PDI** with amines in solution. Here we explore the fluorescence quenching behavior of perylene derivatives in presence of various organic amines in solution and understand the selectivity of interaction among primary (1°), secondary (2°) and tertiary (3°) amines (Fig. 1). In addition, amine induced fluorescence quenching of perylene monoimide (**PMI**) is also investigated and compared with perylene diimide (**PDI**) – amine interactions in solution.

2. Experimental section

2.1. Measurements

All solvents and reagents (analytical grade or spectroscopic

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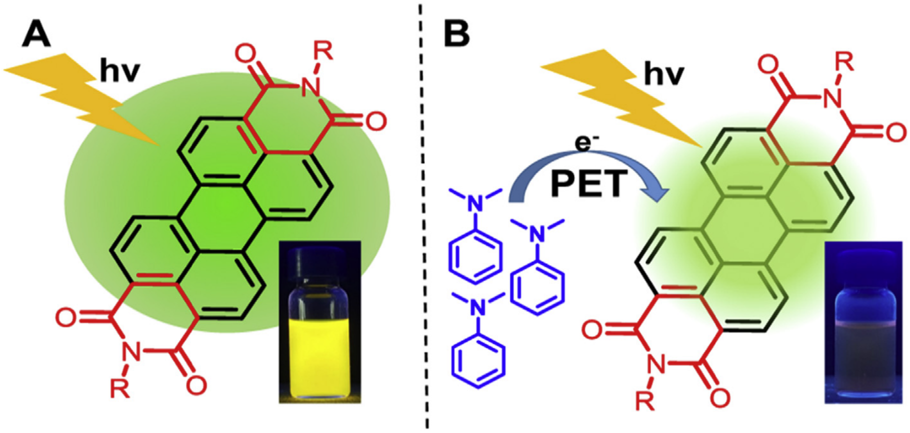

Fig. 1. Emission (**A**) and fluorescence quenching (**B**) of **PDI** molecules by the amines through photoinduced electron transfer in solution.

grade) were obtained from commercial sources and used as received. ^{1}H nuclear magnetic resonance (NMR) spectra were recorded on Bruker Avance AV300 (300 MHz) NMR instrument using $CDCl_3$ as the solvent. Absorption and emission spectra were measured on a UV-1601PC Shimadzu spectrophotometer and RF-5301PC Shimadzu spectrofluorophotometer. Bruker ALPHA FT-IR Spectrophotometer was used for the Fourier transform infrared (FT-IR) spectroscopy analysis.

2.2. Preparation of N,N′-bis (2-ethylhexyl) perylene-3,4,9,10-tetracarboxylic diimide (PDI)

N,N′-Bis (2-ethylhexyl) perylene-3,4,9,10-tetracarboxylic diimide was synthesized based on a literature report [24]. 2-Ethyl hexylamine (3.3 g, 25.4 mmol) was added to a solution of perylene-3,4,9,10-tetracarboxydianhydride (2.3 g, 5.2 mmol) in a mixture of dimethylacetamide (30 mL) and dioxane (30 mL). The mixture was refluxed at 120 °C for 4 h, filtered, the residue was washed with water (2 × 30 mL) and dried at 60 °C to yield a red solid product (2.2 g, 70%). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 8.71 (d, $J = 8.0$ Hz, 4H), 8.65 (d, $J = 8.0$ Hz, 4H), 4.2 (4H, m), 1.93 (2H, m), 1.34 (16H, m), 0.98 (12H, m); FT-IR stretching (cm^{-1}): 2958-2858 (C—H stretching of alkyl chains), 1695-1651 (imide C═O stretching), 1594 (aromatic C—C stretching), 1441 (C—N stretching from perylene diimide). MS (APCI-TOF): calculated for $C_{40}H_{42}N_2O_4$: 614.3150, found: 614.3137.

2.3. Preparation of N-(2-ethylhexyl)perylene-3,4-anhydride-9,10-imide (PMI)

N-(2-Ethylhexyl)perylene-3,4-anhydride-9,10-imide was synthesized according to a published procedure [25]. Perylene dianhydride (1.0 g, 2.3 mmol) and 2-ethylhexylamine (1.5 g, 11.5 mmol) were mixed in ethanol - water mixture (70 mL, volume ratio 4:1) and refluxed at 90 °C for 6 h. The reaction mixture was cooled and stirred overnight by adding conc. HCl (40 mL, 12 M) and water (40 mL). The crude product obtained was treated with hot aqueous KOH solution (10%, 200 mL) for 3 h. Dark pink filtrate was collected by washing the precipitate to remove all **PMI** salts. Aqueous solution of KCl (2%) was added to precipitate the dipotassium salt of **PMI**, centrifuged and washed again with aqueous KCl solution. The residue was dispersed in hot water and centrifuged to remove the remaining diimides. To the supernatant solution, aqueous HCl (10%) was added and stirred overnight to form **PMI** product. Reddish brown solid obtained was filtered and washed with water until pH of the washings was neutral. Yield: 300 mg, 30%. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 8.76—8.67 (8H, m), 4.2 (2H, m), 1.93 (1H, m), 1.34 (8H, m), 0.98 (6H, m); FT-IR stretching (cm^{-1}): 2958-2858 (C—H stretching of alkyl chains), 1762-1720 (anhydride C═O stretching), 1695-1651 (imide C═O stretching), 1595 (aromatic C—C stretching), 1465 (C—N stretching from perylene diimide). MS (APCI-TOF): calculated for $C_{32}H_{25}NO_5$: 503.1738, found: 503.1714.

2.4. Spectroscopic studies of perylene derivatives in presence of amines

All photophysical studies were done using solution of the compounds in tetrahydrofuran (THF). Stock solutions of **PDI**, **PMI** (0.1 mM) and amines at a concentration range of 0.1—1.0 M were prepared in THF. In order to investigate the amine induced fluorescence quenching, 1 mL of **PDI** stock solution (0.1 M) and 1.5 mL of amine solution at various concentrations (0.1—1.0 M) were mixed and the corresponding quenching of fluorescence intensities were recorded. Percentage quenching efficiency and Stern - Volmer constant (K_{sv}) were determined from the fluorescence data and quenching efficiency was calculated using equation (1).

$$\text{Quenching efficiency (\%)} = \left(\frac{I_o - I}{I_o}\right) \times 100 \tag{1}$$

where, I_o and I are the fluorescence intensities of **PDI** or **PMI** in the absence and presence of amines, respectively. Recovery of fluorescence of perylene derivatives were carried out by adding a few drops of concentrated hydrochloric acid to the solution, mixing it thoroughly and recording the spectrum.

3. Results and discussion

Perylene monoimide (**PMI**) and perylene diimide (**PDI**) are n-type semiconductors with high photostability, which is an essential requirement in optical applications (Fig. 2). Full details on the synthesis and characterization of both molecules are given in the experimental section. The perylene molecules are easy to synthesize, characterize and accessible in large quantities.

Absorption and emission spectra of **PDI** were measured in THF solution (Fig. 3). **PDI** showed three characteristic vibronic peaks for the S_0—S_1 transitions at 455, 485 and 520 nm in the absorption spectrum (Fig. 3a). Emission spectrum showed maxima at 540, 568 and 614 nm for **PDI** (Fig. 3b). **PMI** also showed absorption spectra similar to **PDI** with three absorption maxima around 452, 480 and 516 nm and emission spectrum also had three maxima at 533, 566