

## Synthesis and Photophysical Properties of Tripodal Pyrene Derived Luminescent Probe<sup>†</sup>

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**Abstract:** We report a tripodal pyrene compound **1**, via two step simple synthetic procedure. It has been characterized by FT-IR, <sup>1</sup>H & <sup>13</sup>C NMR and ESI-HRMS spectroscopy. The detailed photophysical (UV-vis, Fluorescence) studies on **1** has been done and found of special interest. The quantum yield ( $\Phi_F$ ) for **1** has been determined to be 0.11. The fluorescent cation detection abilities of **1** has been investigated and found it responsive for most of the heavy metal ions. The basics of sensing phenomenon affirms that the probe must be selective towards a particular analyte therefore fluorescence detection studies for cations have been omitted.

**Keywords:** Schiff base; pyrene; fluorescence.

### 1. Introduction

The development of emissive molecules has paid immense attention for last few decades to study the luminescence behavior of the molecule.<sup>1</sup> Synthesizing fluorescent molecule whose emissive properties can be tuned by variation of temperature, light, potential, pH etc. holds great promise for targeted biological applications.<sup>2</sup> To achieve expected fluorescence from organic molecules are generally incorporated to the receptor site or central part of the molecule.<sup>3</sup>

Pyrene is definitely one of the most investigated fluorophore due to its well-defined emission characteristics.<sup>4</sup> It shows structured fluorescence, high fluorescence quantum yields, has long excited-state fluorescence lifetimes, and demonstrates distinctive monomer and excimer emissions.<sup>5</sup> Formation of low-energy inter- or intra-molecular excimers (i.e., excited dimers) is a feature specific to pyrene being the most distinguished one.<sup>6</sup> A variety of pyrene-appended systems capable of switching the monomer/excimer emissions by external inputs (e.g., temperature, metal ions, pH, among others) have been anticipated so far. Many such pyrene-appended systems have been reported to be capable of showing metal-

induced excimer fluorescence changes.<sup>7</sup> With these objectives, we have designed and successfully synthesized a highly fluorescent molecular system **1** by incorporating three pyrene fluorophores with tripodal N,N,N type chelator. This molecule seems to be star shaped and therefore excimer formation in the excited state is anticipated. Furthermore, the presence of tetra-nitrogen chelating site offers metal recognition ability of **1**. It is anticipated that the pyrene present in the **1** would be extremely sensitive to interaction with metal ions, which might enable selective sensing of metal ions. These studies are in progress.

## 2. Experimental

Fluorescence spectra were recorded on a Varian Luminescence Cary eclipsed and electronic spectra were recorded on a Perkin-Elmer-Lambda 20 UV-vis spectrometer with a 10 mm quartz cell at room temperature. Melting points were measured using a JSGW melting point apparatus and are uncorrected. <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained in CDCl<sub>3</sub> solutions on a JEOL-DELTA2 500 model spectrometer operating at 500 MHz and 125 MHz, respectively. The chemical shifts are referenced with respect to TMS. ESI-HRMS mass spectra were recorded on a MICROMASS QUATTRO II triple quadrupole mass spectrometer. The ESI capillary was set at 3.5 kV and the cone voltage was 40V. 1-Pyrenenlycarboxaldehyde and Tris(2-aminoethyl)amine was purchased from Sigma-Aldrich. Solvents were purchased from Merck Chemicals (India) and they were purified prior to use. Fluorescence quantum yields in each case were determined by comparing the emission intensity of the sample with that of a fluorescence standard as anthracene ( $\Phi_F = 0.27 \pm 0.03$ ).<sup>9</sup>

$$\Phi_U = \Phi_R (A_U/A_R) (n_U^2/n_R^2)$$

where  $A_U$  and  $A_R$  are the integrated area under the corrected fluorescence spectra for the sample and reference,  $n_U$  and  $n_R$  are the refractive indexes of the sample and reference, respectively.

### 2.1 Synthesis of A:

1-Pyrenenlycarboxaldehyde (0.690 g, 3.0 mmol) was dissolved in hot methanol (20 mL) and to it a methanolic solution of tris(2-aminoethyl)amine (0.146 mg, 1.0 mmol) was added dropwise and then the solution was stirred at 50 °C for 4 hours. A yellow precipitate obtained was filtered, washed with hot methanol, and recrystallized from

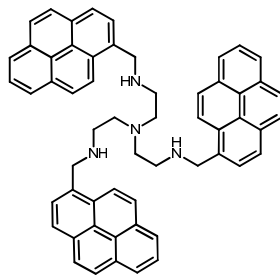
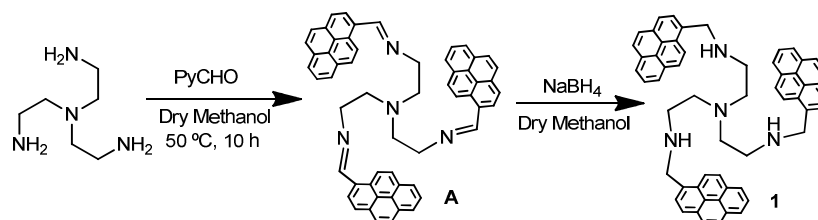
CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane at 0°C to get pure **A** (0.610 g, 78.0%) Mp 158°C. FT-IR (KBr) (v/cm<sup>-1</sup>); 3423b, 2922s, 2852s, 1677s, 1595s, 1507s, 1383s, 1239s, 1201s, 876s, 711s. <sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>, 25°C, TMS) δ(ppm) = 3.18 (t, 6H, CH<sub>2</sub>-N-); 3.96 (t, 6H, CH<sub>2</sub>-N=C); 9.25 (s, 6H, -CH=N-), 8.36-7.52 (m, 27H, Pyrene H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 25°C, TMS) δ (ppm) = 65.05, 78.64, 121.43, 122.07, 123.50, 125.45, 126.71, 127.06, 127.85, 127.95, 128.68, 131.66, 131.88, 161.99. ESI-HRMS: C<sub>57</sub>H<sub>43</sub>N<sub>4</sub> [M+H]<sup>+</sup>: 783.3488 (calculated), 783.3480 (found).

## 2.2 Synthesis of **1**

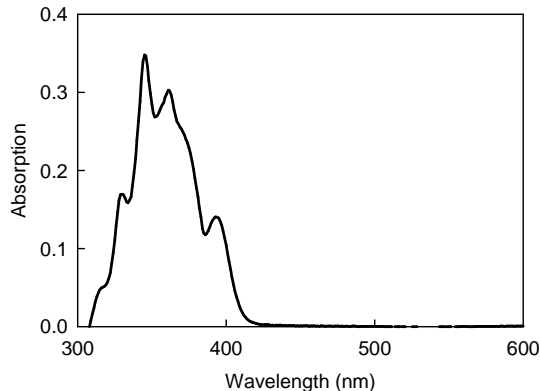
Compound **A** (0.390 g, 0.5 mmol) was dissolved in methanol (20 mL) and to it a methanolic solution of sodium borohydride (0.74 mg, 2.0 mmol) was added dropwise and then the solution was stirred at room temperature for 5 hours. A yellow precipitate obtained was filtered, washed with hot methanol, and recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane at 0°C to get pure **1** (0.32 g, 82.0%) Mp 165°C. FT-IR (KBr) (v/cm<sup>-1</sup>); 3359b, 3039s, 2951s, 1662s, 1601s, 1432s, 1383s, 1350s, 1283s, 842s, 708s. <sup>1</sup>H NMR: (500 MHz, DMSO-d<sub>6</sub>, 25°C, TMS) δ(ppm) = 1.72 (broad, 6H, -NH-); 3.24 (t, 6H, C-CH<sub>2</sub>-N-); 4.03 (t, 6H, -N-CH<sub>2</sub>-C); 4.18 (s, 6H, CH<sub>2</sub>-Py), 8.47-7.25 (m, 27H, Pyrene H). <sup>13</sup>C NMR (500 MHz, DMSO-d<sub>6</sub>, 25°C, TMS) δ (ppm) = 65.23, 77.86, 78.45, 123.58, 124.13, 124.67, 125.20, 126.12, 126.76, 126.91, 127.16, 127.50, 128.63, 131.91, 132.14, 132.88. ESI-HRMS: C<sub>57</sub>H<sub>43</sub>N<sub>4</sub> [M+H]<sup>+</sup>: 789.3957 (calculated), 789.3947 (found).

## 3. Results and Discussion

The synthesis of the **1** was carried out by simple condensation reaction of the 1-Pyrenenlycarboxaldehyde and tris(2-aminoethyl)amine that afforded **A** in excellent yield. Reduction of azomethine groups led to the formation of star shaped compound **1** in almost quantitative yield (Figure 1). A representative synthetic protocol is shown in Scheme 1. Compounds **1** is soluble in a wide range of organic solvents and is quite stable in solution as evidenced by the presence of strong [M+H]<sup>+</sup> peaks in their high resolution ESI-MS spectra recorded under positive ion mode. Appearance of a singlet at 9.25 ppm in <sup>1</sup>H NMR spectrum strongly suggested the formation of Schiff base **A**. Formation of **1** indicated by the disappearance of singlet at 9.25 ppm and appearance of a new singlet signal at 4.18 ppm. As well, a broad signal appeared at 1.72 ppm further authenticates the successful synthesis of **1**.

Figure 1: Chemical structure of compound **1**.Scheme 1: Synthesis of **1** (PyCHO = Pyrene-1-carboxaldehyde).

The absorption spectra of **1** were acquired in toluene/acetonitrile (1:1, v/v) in 10  $\mu\text{M}$  concentration (figure 2). Compound **1** showed absorbance values at  $\lambda_{\text{abs}}(\text{max})$ , nm ( $\epsilon$ ); 315 ( $4.891 \times 10^{-3}$ ), 328 ( $1.774 \times 10^{-3}$ ), 344 ( $3.465 \times 10^{-3}$ ), 361 ( $3.024 \times 10^{-3}$ ), 393 ( $1.405 \times 10^{-3}$ ). These spectral bands demonstrate typical feature for pyrene-containing compounds and the absorptions are due to pyrene  $\pi$ - $\pi^*$  transition.<sup>8</sup>

Figure 2: UV-Vis spectra of **1** (10 $\mu\text{M}$ ) in toluene/acetonitrile (1:1, v/v).

Compound **1** shows emission bands  $\lambda_{\text{em}}(\text{max})$ , nm at 353 nm, 364 nm and a broad structure less band at 404 nm are characterized as monomer and excimer emission, respectively of pyrene as upon excitation ( $\lambda_{\text{ex}}$ ) at 315 nm (figure 3). The quantum yield ( $\Phi_f$ ) obtained for **1** is 0.11.<sup>9</sup>

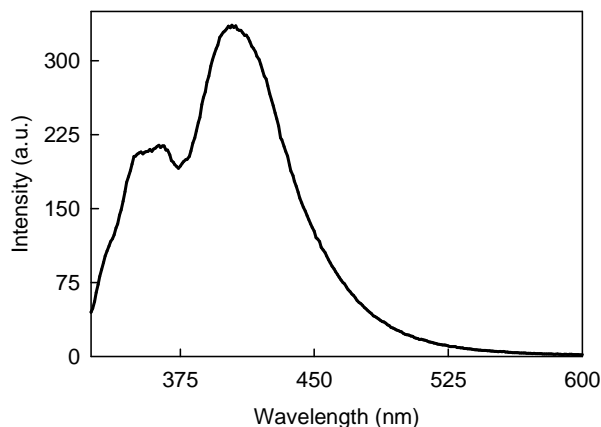


Figure 3: Fluorescence spectra of **1** in toluene/acetonitrile (1:1, v/v) (10  $\mu\text{M}$ ), with an excitation wavelength of 315 nm.

#### 4. Conclusion

In summary we report a tripodal pyrene based compound **1** which is highly fluorescent in nature and possesses a highly chelating N,N,N-core. It has been well characterized by common physicochemical techniques such as FT-IR, NMR and ESI-HRMS spectroscopy. This star shaped molecule extends possibility of formation of excimer in its excited state which has been also supported further by emission studies. It exhibits significant interaction with utmost of the cations which overrules its use as fluorescent probe for cations however it can be used as a fluorescent chelator for various metal ions.

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