

Short Note

$\hbox{$2$-((Pyren-1-ylmethylamino)methyl) quinolin-8-ol}\\$

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Abstract: A new fluorescent compound **L1** derived from 1-pyrenemethylamine hydrochloride (**A**) has been synthesized by classical Schiff-base reaction between (**A**) and 8-hydroxyquinoline-2-carbaldehyde (**B**) followed by a chemical reduction with NaBH₄. The chemical structure was confirmed by elemental analysis, FAB-MS spectrometry and by IR, UV-vis and ¹H-NMR spectroscopy. The photophysical characterization was achieved by UV-vis and emission spectroscopy and lifetime measurements. Compound **L1** was explored as pH fluorescent chemosensor in water-acetonitrile (95.5/0.5 v:v) solutions.

Keywords: imines; amines; luminescent probes; pyrene; quinoline

1. Introduction

The development of compounds that selectively respond to specific metal ions and thus can be used as ion sensors is an area of growing interest [1,2]. Particular attention has been paid to fluorescence chemosensors, since fluorescence modulation allows the detection of the target ions at very low concentrations [3]. Moreover, fluorescent sensors offer several distinct advantages such as selectivity, time response, and spatial resolution.

8-Hydroxyquinoline (8-HQ) and derived compounds are known to be the best chelating agents after EDTA and its derivatives, due to their guest-modulated chromogenic and fluorescent behavior. Accordingly, they have been used in chromatography [4], for the detection of metal ions [5], in the preparation of organic light emitting diode devices [6], in electrochemiluminiscence [7], *etc*.

On the other hand, pyrene reveals to be one of the most commonly used fluorophores due to its peculiar fluorescent properties: intense fluorescence signals, vibronic band dependence with the media

Molbank **2010** M698 (Page 2)

[8], long lifetime values [9], and excimer formation [10]. Due to these particular properties and because of its chemical stability, it is also employed as a probe for solid-state studies [11], polymer association [12], polymer–polymer interactions, polymer–surfactant interactions, micelle critical concentration determinations, *etc* [13]. In continuation of our group's research line on development and study of new fluorescent and colorimetric chemosensors, we here report the synthesis of a new asymmetric bis-chromophoric compound bearing one 8-hydroxyquinoline moiety as chelating unit, and one pyrene emissive unit.

2. Experimental

A solution of 8-hydroxyquinoline-2-carbaldehyde (0.090 g, 0.52 mmol) in absolute ethanol (10 mL) was added dropwise to a refluxing solution of 1-pyrenemethylamine hydrochloride and triethylamine in the same solvent (30 mL). The resulting solution was gently refluxed with magnetic stirring for ca. 4 h. The colour changed from yellow to orange. After that time, the mixture was allowed to cool to room temperature and then concentrated in the rotary evaporator. The resulting brown oil was stirred with cold diethyl ether. A brown powder precipitate was formed, which was filtered off and dried under vacuum. This compound was characterized as **L**. NaBH₄ was added in excess (20%) to a solution of **L** (0.123 g, 0.2 mmol) in absolute ethanol at room temperature. The resulting solutions were gently refluxed with magnetic stirring for 4 h; within that time, the colour changed slowly from brown to orange. The mixtures were filtered and evaporated to dryness. The residues were then extracted with water—chloroform. The organic extract was dried over anhydrous Na₂SO₄ and evaporated to yield an orange oil that was stirred with diethyl ether. The orange powder formed was separated by centrifugation and dried under vacuum. This compound was characterized as **L1**.

Yield: 190 mg (**L**) (96%), 60.0 mg (**L1**) (30%).

FAB-MS: m/z (rel. int%): 387.1 (100) ([L+H]⁺; 389.1 (90) ([L1+H]⁺.

¹H NMR (CDCl₃) (**L**): δ = 8.6 (s, 2H, N=C-H); 8.4–7.1 (m, C-H, Ar); 5.8 (s, 1H, OH); 5.7 (s, 2H, CH₂) ppm. ¹H NMR (CDCl₃) (**L1**): δ = 8.4–7.1 (m, C-H, Ar); 5.4 (s, 1H, OH) 4.5(s, 2H, CH₂); 4.2 (s, 2H, CH₂) ppm.

IR (cm⁻¹) (**L**): 3040 (C-H, Ar), 2911 and 2849 (C-H, Alq), 1633 (C=N, Imine), 1610, 1591, 1560 and 1503 (C=C, Ar).

IR (cm⁻¹) (**L1**): 3037 (C-H, Ar), 2936 and 2846 (C-H, Alq), 2844 (N-H, Amine), 1594, 1576 and 1503 (C=C, Ar).

Elemental analysis: Calcd for $C_{27}H_{18}N_2O$ (**L**): C, 83.92; H, 4.70; N, 7.25. Found (**L**): C, 83.80; H, 4.85; N, 6.90%. Calcd for $C_{27}H_{20}N_2O^{\circ}H_2O$ (**L1**): C, 79.77; H, 6.90; N, 5.45. Found (**L1**): C, 79.80; H, 6.85; N, 5.65%.

Uv-vis (H₂O/CH₃CN; 95.5/0.5), [**L1**] = 7.1×10^{-6} M, λ_{max} 273, 276, 329 and 343 nm.

Fluorescence Emission (H₂O/CH₃CN; 95.5/0.5); [**L1**] = 7.1 ×10⁻⁶ M): λ_{max} 375, 394 and 412 nm.

Molbank **2010** M698 (Page 3)

Fluorescent Decay time of L1 in $H_2O(\tau)$: pH 5.5, 118.6 ns; pH 10.3, 108.3 ns.

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Molbank **2010** M698 (Page 4)

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