

Zinc(II)-driven Fluorescence Quenching of a Pyrene-labelled Bis-2,2'-bipyridine Ligand†

Jean-Ernest Sohna Sohna, Pascale Jaumier and Frédéric Fages*

Laboratoire de Chimie Organique et Organométallique, UMR 5802 CNRS, Université Bordeaux I, 33405 Talence Cedex, France

The title compound has been synthesized and its fluorescence emission is quenched upon complexation of the Zn^{2+} in methanol solution.

The development of selective fluorescent chemosensors for metal ions remains an active search of research.¹ Two-component supramolecular systems² in which a fluorescent chromophore and a metal cation complexing site are covalently linked have thus emerged as a very promising family of photosensitive compounds for the detection and quantification of trace metal analytes in solution. Recent efforts have been devoted to the production of such systems designed to detect Zn^{II} , an extremely important biological cation.³ In that connection, a variety of zinc fluorosensors have been reported that allowed the signalling of Zn^{II} -ligand interaction through fluorescence intensity enhancement^{3–6} or ratiometric methods.^{7,8} Although the d^{10} Zn^{2+} cation is a non-quenching metal ion, several systems that function according to a Zn^{II} -driven chelation-enhanced quenching (CHEQ) effect were also envisaged.^{9,10} They were designed to undergo profound conformational changes upon Zn^{2+} chelation, the effect of which is to decrease the distance between a donor and an acceptor and, thereby, to permit intramolecular photoinduced electron transfer (PET) fluorescence quenching. In line with our investigations on receptors for transition-metal ions that incorporate the pyrene chromophore,¹¹ we wish to report here the synthesis of the bis-2,2'-bipyridine ligand **1** and its nonfluorescent analogue **2** (Scheme 1). Although 2,2'-bipyridine (bpy) is among the most studied bidentate ligands in coordination chemistry, its utilization as chelating site in chemosensors

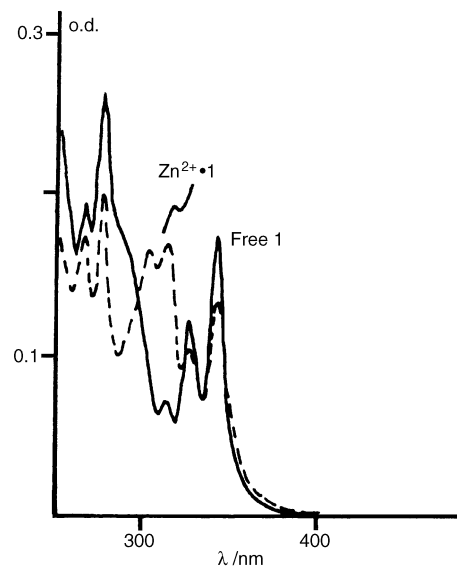
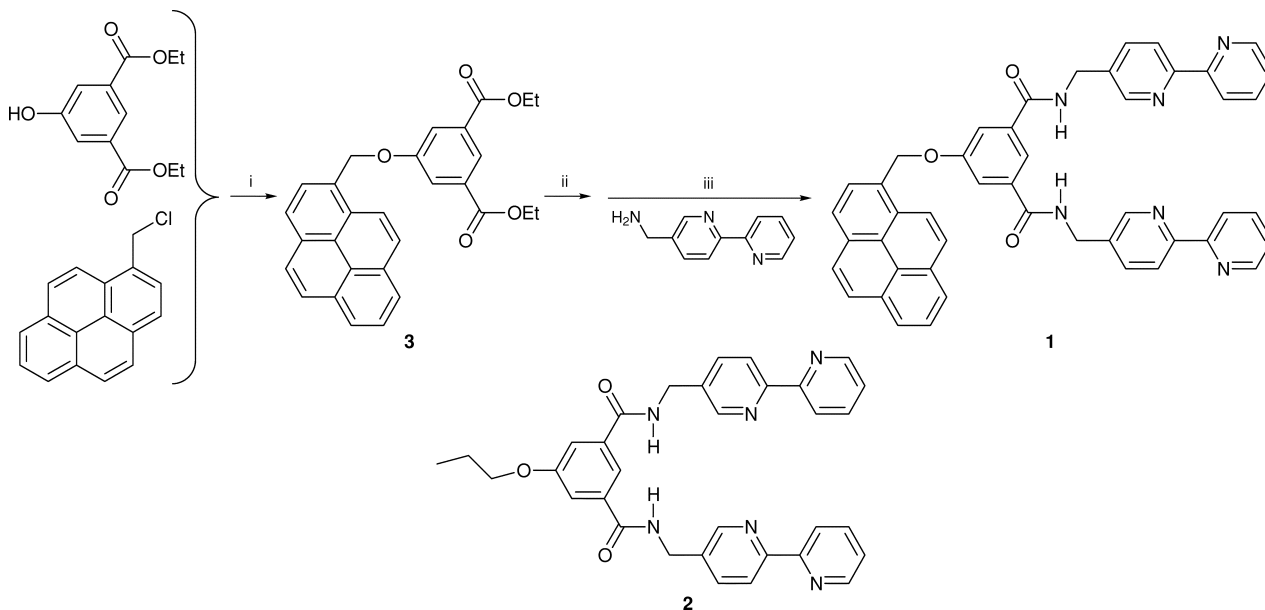


Fig. 1 Electronic absorption spectra, at room temperature, in methanol, of ligand **1** and its Zn^{2+} complex (10^{-5} M)

structures has not been frequently reported so far.^{9,12} Complexation of divalent zinc was found to quench the fluorescence emission of **1**, which was quite unexpected as



Scheme 1 Reagents and conditions: i, NaH, DMF, 90 °C, 10 h; ii, NaOH, ethanol, reflux, 6 h; iii, HOSu, DCC, DMF, room temp., 96 h

*To receive any correspondence.

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this compound was not designed to contain a pre-programmed quenching process. The mechanism of quenching is discussed.

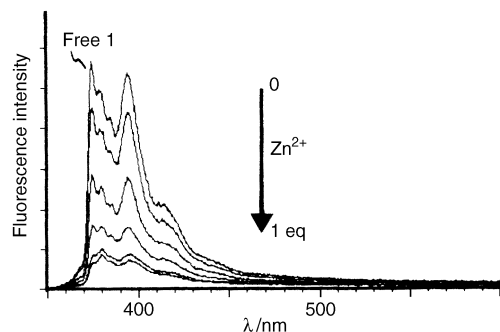


Fig. 2 Corrected fluorescence spectra, at room temperature, in methanol, of **1** (10^{-6} M), in the absence and in the presence of increasing amounts of ZnCl_2

The synthesis of the title compound, **1** is outlined in Scheme 1. The nonfluorescent model **2** was obtained similarly by using 1-bromopropane in the first alkylation step. The electronic absorption spectrum of **1** in methanol (Fig. 1) consists of the additive superimposition of the absorption bands of the 2,2'-bipyridine and pyrene chromophores as recorded from the corresponding reference compounds **2** and **3**, respectively. The addition of one molar equivalent of ZnCl_2 to a methanolic solution of **1** caused a strong modification of the position and shape of the $\pi\pi^*$ transition bands of the bpy units (Fig. 1)¹³ This effect, also detected for ligand **2**, enabled us to determine spectrophotometrically the stoichiometry of the Zn^{II} complex of **1** by the method of continuous variations (Job plot).¹⁴ A characteristic triangular plot with linear segments indicated the occurrence of a single, strong complex, the apex being located at a mole fraction value of 0.5. The formation in methanol of a 1:1 Zn^{2+} ligand **1** complex was also confirmed by a titration experiment. Moreover, treatment of **1** (30 mmol) with one molar equivalent of ZnCl_2 in DMF (5 ml) followed by precipitation with diethyl ether afforded the mononuclear complex $\text{Zn}^{2+}\cdot\mathbf{1}$ as a beige amorphous solid. The FAB mass spectrum showed the molecular ion with high intensity and the absence of any stoichiometries other than 1:1. ^1H NMR spectroscopy showed the participation of both bpy units of **1** in the coordination of the metal.

The fluorescence spectrum of **1** in non-degassed methanol (Fig. 2) was found to be typical of 1-alkyl pyrene derivatives¹¹ and of similar intensity (fluorescence quantum yield $\Phi_{\text{f}}=0.02$). Amazingly, titration with Zn^{II} of a methanolic solution of **1** produced an efficient quenching of the fluorescence emission to reach a plateau value at 1 equivalent (Fig. 2). At room temperature, in the methanol-ethanol (1:4 v:v) solvent system, the isolated mononuclear complex (*vide supra*) displayed a very low fluorescence quantum yield ($\Phi < 0.001$). Freezing of the solution at 77 K led to the total revival of the pyrene fluorescence, which suggested¹⁵ a significant contribution of a PET process to the quenching of the photoexcited pyrene nucleus by the zinc(II)-containing moiety. Moreover, addition of an excess of trifluoroacetic acid to a methanol solution of **1** was also followed by the extensive quenching of fluorescence.

The latter observation can be related to the protonation-induced fluorescence quenching of the anthracene chromophore bound to pyridyl-containing ligands.^{2,4,10,16} The ability of the 2,2'- or 4,4'-bipyridinium cation to promote an electron-transfer reaction from the excited state of organic or inorganic chromophores is also well documented.¹⁷ Similarly, complexation of the hard Lewis acid zinc(II) cation is expected to increase the reduction potential of the bpy fragments, as reported recently,^{18a} so that the latter could then play the role of electron acceptor, the excited

pyrene being the donor, which is consistent with our previous work.^{18b} In contrast to the case of other fluorosensors pre-programmed to display Zn^{II} -induced fluorescence quenching,^{9,10} the deactivation of the pyrene singlet state within **1** would result from a direct photophysical interaction between the excited aromatic part and the metallic centre. Finally, the Zn^{2+} cation, well known for its photophysical inertness towards fluorescent receptors based on nitrogen-containing ligand units other than bpy moieties, would affect the photophysical properties of **1**, as do open-shell transition metal ions.² Compound **1**, incorporating a fluorescent chromophore tethered to bpy ligand units, thus belongs to a new family of photosensitive ligands that could find potential applications in the field of metal sensing and molecular electronics.

Experimental

General methods as published elsewhere.¹¹

Ligand **1** had δ_{H} (ppm) (CDCl_3) 4.60 (4 H, d), 5.90 (2 H, s), 7.4–8.7 (26 H, m), 9.50 (2 H, t) (Found: C, 76.1; H, 4.75; N, 11.0. $\text{C}_{47}\text{H}_{35}\text{N}_6\text{O}_3 \cdot 0.5\text{H}_2\text{O}$ requires C, 76.2; H, 4.9; N, 11.3%).

Ligand **2** had δ_{H} ($[\text{D}_6]\text{acetone}$) 0.91 (3 H, t), 1.80 (2 H, m), 3.92 (2 H, t), 4.68 (4 H, s), 7.3–8.7 (17 H, m) (Found: C, 68.4; H, 5.5; N, 15.0. $\text{C}_{33}\text{H}_{30}\text{N}_6\text{O} \cdot \text{H}_2\text{O}$ requires C, 68.7; H, 5.6; N, 14.6%).

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