

# A new fluorosensor based on bis-1,8-naphthalimide for metal cations and protons

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## Abstract

The paper reports on the synthesis and spectral characteristics of a new fluorescent bis-1,8-disubstituted naphthalimide linked by a diethylenetriamine bridge (NI2TEA). The ability of the new compound to detect cations has been evaluated by monitoring spectrophotometrically the changes in the fluorescence intensity performed on its *N,N*-dimethylformamide (DMF) solution. The behaviour of the new compound has been tested in the presence of different metal cations: Fe<sup>3+</sup>, Cr<sup>3+</sup>, Mn<sup>2+</sup>, Sr<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, Cu<sup>2+</sup> and Co<sup>2+</sup>. The results show clearly that only Fe<sup>3+</sup> and Cr<sup>3+</sup> cations are effectively detected. Besides, in *N,N*-di-methylformamide solution the NI2TEA can be used as a naked eye sensor for hydroxyl anions. © 2007 Published by Elsevier B.V.

**Keywords:** Naphthalimides; Sensors; Photophysics; Fluorescence; PET; Metal cations

## 1. Introduction

In the last decade, much attention has been paid to supramolecular fluorescent systems for the sensing and reporting of analytes which may be of importance for chemical, biological and environmental sciences. Variations of the fluorescence intensity of such devices can be used for evidencing and quantitatively measuring the concentrations of ions or molecules with high sensitivity [1–3]. Many of these fluorescent chemosensors are based on a photoinduced electron transfer (PET) process occurring under certain conditions. The multicomponent sensor is designed, as far as possible, in such a way that the electron transfer process originates, in the excited state, from an electron donating receptor separated from the electron acceptor by a short spacer. In this situation, the fluorescence of the signalling fluorescent unit will be quenched while guests (metal ions or protons) capable of binding with the receptor of the molecule when available in the medium, will cut off PET process and switch on the fluorescence of the system. The 1,8-naphthalimide derivatives, comprising a substituent with electron donating receptor

have proved to be good PET sensors for metal cations and protons [4–14].

Based on our previous research on the PET systems, a new bis-1,8-naphthalimide derivative (NI2TEA) has been synthesized. Its two 1,8-naphthalimides are substituted with a *N,N*-dimethylaminoethylamino group as receptor while a triethyleneamine linker is used to connect the two chromophores. The basic photophysical properties were investigated in organic solvents of different polarity and the influence of metal cations on the fluorescence intensity is reported.

## 2. Experimental

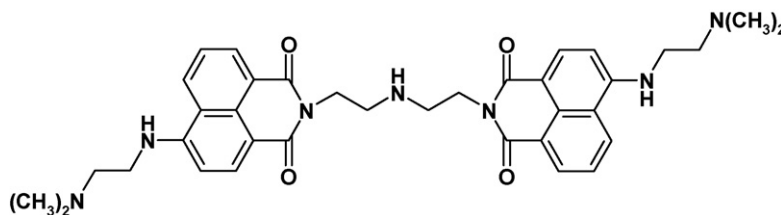
The synthesis of the nitro precursor of the NI2TEA derivative was already described [15]. The structure of NI2TEA is presented in Scheme 1.

### 2.1. Synthesis of NI2TEA

Bis-4-nitro-1,8-naphthalimide (0.01 M) was reacted with 0.006 M of *N,N*-dimethylethylenediamine in 50 ml of *N,N*-dimethylformamide (DMF) for 24 h at room temperature. After that 500 ml of water were added to the solution. The precipitate was filtered off, washed with water and then dried under

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Scheme 1. Chemical structure of NI2TEA.

vacuum at 40 °C. Yield: 80%. FT-IR (KBr)  $\text{cm}^{-1}$ : 3103, 2950, 2825, 1665, 1645, 1581, 1530, 1348, 1243, 779, 759;  $^1\text{H}$  NMR ( $\text{CDCl}_3$  (ppm), 250 MHz): 8.37 (dd,  $J=1.0$ , 8.2 Hz, 2 H), 8.36 (dd,  $J=1.0$ , 7.3 Hz, 2 H), 8.25 (d,  $J=1.1$ , 8.3 Hz, 2 H), 7.48 (m 4H), 6.35 (1 H, NH), 6.56 (2 H, NH);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm): 164.8, 164.2, 149.5, 132.5, 130.9, 129.6, 128.7, 126.7, 1143, 104.2, 56.6, 47.5, 44.9, 39.4; analysis:  $\text{C}_{36}\text{H}_{41}\text{O}_4\text{N}_7$  (635.2); Calcd (%): C 68.01, H 6.45, N 15.45; found (%): C 68.12, H 6.59, N 15.76.

### 3. Materials and methods

All organic solvents were of spectroscopy grade and used without special treatment.  $\text{Zn}(\text{ClO}_4)_2$ ,  $\text{Cu}(\text{ClO}_4)_2$ ,  $\text{Mn}(\text{ClO}_4)_2$ ,  $\text{Sr}(\text{ClO}_4)_2$ ,  $\text{Ni}(\text{ClO}_4)_2$ ,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ , salts were the sources for metal cations. Sulphuric acid was used as a source of protons.

UV–vis spectrophotometric investigations were performed on a Varian Cary-50 instrument and the fluorescence spectra on a Varian Cary Eclipse at  $10^{-5} \text{ M l}^{-1}$ . Fluorescence quantum yield was determined by comparison with Rhodamine 101 used as a reference ( $\Phi_F = 1.00$ ). The NMR spectra were obtained on a Bruker DRX-250 spectrometer, operating at 250.13 and 62.90 MHz for  $^1\text{H}$  and  $^{13}\text{C}$ , respectively, using a dual 5 mm probe head. The measurements were carried out in  $\text{CDCl}_3$  solution at ambient temperature. The chemical shifts were referenced to a tetramethylsilane standard. Experiments with  $30^\circ$  pulses, 1 s relaxation delays, 16 K time domain points, zero-filled to 64 K for protons and 32 K for carbons were performed. The distortion less enhancement by polarisation transfer (DEPT) spectra were recorded under the conditions used for the  $^{13}\text{C}$  NMR spectra at  $\tau = (2 \ ^1J_{\text{CH}})^{-1} = 3.45 \ \mu\text{s}$ . The 2D  $^1\text{H}/^1\text{H}$  correlated spectra (COSY) were performed with spectral width 2200 Hz, relaxation delay 2 s, number of increments 512, and

size  $1\text{K} \times 1\text{K}$ . The 2D  $^1\text{H}/^{13}\text{C}$  heteronuclear multiple quantum coherence (HMQC) experiments were carried out with a spectral width of 2200 Hz for  $^1\text{H}$  and 9000 Hz for  $^{13}\text{C}$ , relaxation delay 1.5 s, FT size  $1\text{K} \times 256 \text{ W}$ . The effect of the metal cations and protons upon the fluorescence intensity was examined by adding a few  $\mu\text{l}$  of stock solution of the metal cations to a known volume of the dendrimer solution (3 ml). The addition was limited to 0.08 ml so that dilution remains insignificant [16].

### 4. Results and discussion

It is well known that the light absorption properties of the 1,8-naphthalimide derivatives are basically related to the polarization of the chromophoric system. Light absorption in this molecule generates a charge transfer (CT) interaction between the substituents at C-4 position and the imide functionality. This interaction strongly depends on the medium, especially, on the polarity of organic solvents. Organic solvents with different dielectric constants were used to investigate this effect on the photophysical properties of NI2TEA. Table 1 summarizes the spectral characteristics of the NI2TEA in the organic solvents used: the absorption ( $\lambda_A$ ) and fluorescence ( $\lambda_F$ ) maxima, the extinction coefficient ( $\log \epsilon$ ), Stokes shift ( $\nu_A - \nu_F$ ) and quantum yield of fluorescence ( $\Phi_F$ ).

The NI2TEA compound has yellow-green colour with absorption maxima at 422–435 nm and fluorescence emission maxima at 509–526 nm in all organic solvents under study at room temperature.

Fig. 1 presents the normalized absorption and fluorescence spectra of NI2TEA in *N,N*-di-methylformamide solution as an example. In the long-wavelength region, the fluorescence spectrum is the mirror image of the absorption one. This is indicative for the preserved planarity of the molecular structure of the NI2TEA in the excited state. The overlap of the absorption and flu-

Table 1  
Photophysical properties of NI2TEA in organic solvents of different polarity

	$\lambda_A$ (nm)	$\epsilon$ ( $\text{l mol}^{-1} \text{ cm}^{-1}$ )	$\lambda_F$ (nm)	$\nu_A - \nu_F$ ( $\text{cm}^{-1}$ )	$\Phi_F$
Toluene	423	20,600	509	3974	0.313
Chloroform	429	21,400	510	3702	0.280
Ethyl acetate	422	20,600	510	4008	0.196
Tetrahydrofuran	424	22,400	511	4015	0.106
Di-chloromethane	428	22,200	513	3871	0.094
Acetone	426	22,700	520	4243	0.022
Ethanol	433	22,300	526	4083	0.013
Methanol	433	23,800	528	4155	0.010
<i>N,N</i> -di-methylformamide	435	21,000	526	3977	0.014
Acetonitrile	428	21,300	522	4207	0.012

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