



Design and synthesis of a new fluorescent tripod for chemosensor applications



Mohammad S.I. Makki^a, Desislava Staneva^b, Tariq R. Sobahi^a, Paula Bosch^c,
Reda M. Abdel-Rahman^a, Ivo Grabchev^{a,d,*}

^aChemistry Department, Faculty of Science, King Abdulaziz University, Jeddah 21589, Saudi Arabia

^bUniversity of Chemical Technology and Metallurgy, 1756 Sofia, Bulgaria

^cInstitute of Science and Technology of Polymers, CSIC, Juan de la Cierva 3, 28006 Madrid, Spain

^dSofia University "St. Kliment Ohridski", Faculty of Medicine, 1407 Sofia, Bulgaria

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ABSTRACT

A new yellow-green fluorescent tripod based 1,8-naphthalimide has been synthesized and characterised. Its photophysical properties have been investigated in organic solvents of different polarity. The effect that the metal ions (Cd^{2+} , Co^{2+} , Zn^{2+} , Mn^{2+} , Mg^{2+} , Ni^{2+} , Pb^{2+} , Cu^{2+} , Ba^{2+} , Fe^{3+} and Ag^{+}) produce upon the fluorescent intensity of acetonitrile solutions of the tripod has been discussed viewing its potential applications as a detector for metal cations. The influence of protons on the fluorescence intensity of the tripod in DMF and methanol–water (1:4 v/v) solutions has also been investigated.

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1. Introduction

In recent years the fluorescent compounds capable of changing their photophysical characteristics have been investigated intensively due to their use in medicine, biology, chemistry and environmental protection. One of the advanced applications is their implementation as fluorescent chemosensors for detection of metal cations and protons in the environment or in living cells.^{1–3} Detection is based on photoinduced electron transfer (PET) occurring in multifunctional systems comprised of a fluorophore unit as a signalling fragment and a receptor, most often an amine possessing a free electron pair, which can interact and form a dative bond with the metal ions. Sensing systems, which increase their fluorescence upon complex formation are called 'OFF-ON' sensors, while those, which quench their fluorescence are 'ON-OFF' ones.^{4–6} Recently, special attention has been devoted to tailored 1,8-naphthalimide systems and the potential of these fluorophores to act as sensors for metal cations and protons.⁷ In that aspect dendritic and branched molecules are of great interest because of their properties deriving from the well-defined, tridimensional structure. In our previous studies the photophysical properties of

PAMAM and PPA type dendrimers and dendrons having 1,8-naphthalimide fluorescent units have been investigated with regard to their sensor application for detection of metal ions and protons.^{8–18}

In this paper, we report on the synthesis of a new fluorescent tripod comprising tree 4-*N,N*-dimethylaminoethylamino-1,8-naphthalimide fluorescent units, bonded to the central aromatic nucleus. The photophysical characteristics of the new compound have been determined in organic solvents of different polarity. The influence of metal cations and protons on the fluorescence intensity has been studied in acetonitrile and methanol–water (1:4 v/v) solutions.

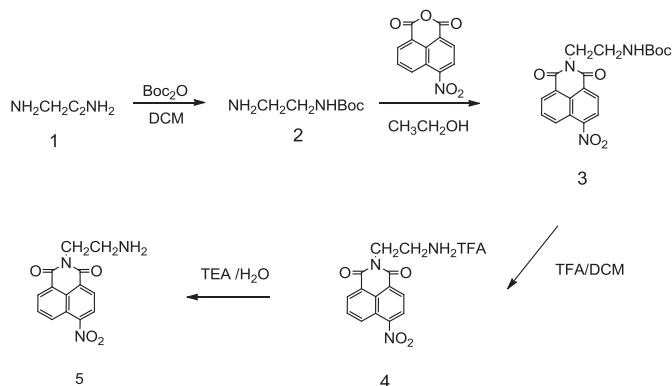
2. Results and discussion

2.1. Synthesis of tripod 7

The synthesis of the tripod **7** began by firstly carrying out the synthesis of the 1,8-naphthalimide having a primary amino group – **5** (Scheme 1). This was undertaken by the mono-BOC protection of ethylenediamine, and then via its reaction with 4-nitro-1,8-naphthalic anhydride, compound **3** has been obtained. After **3** was dissolved in dichloromethane (DCM) and trifluoroacetic acid

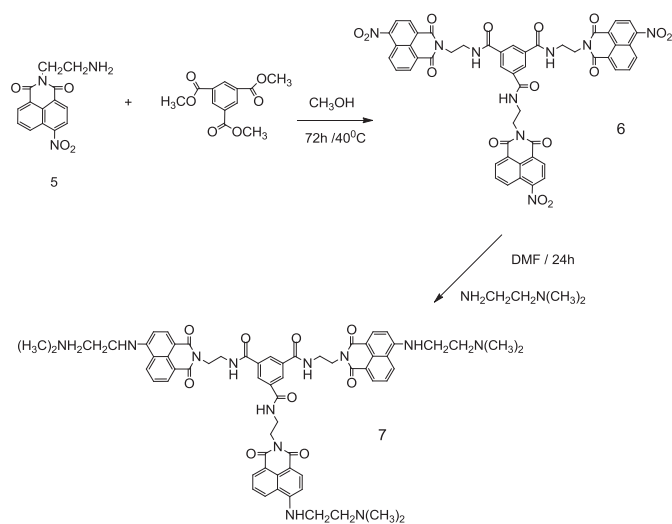
* Corresponding author. Tel.: +359 2 8161319; e-mail address: i.grabchev@chem.uni-sofia.bg (I. Grabchev).

(TFA) was added. The mixture was allowed to stir at room temperature. The reaction was followed by TLC and upon the complete disappearance of the starting material **3** the dichloromethane and trifluoroacetic acid were removed under reduced pressure to give **4**. To an aqueous solution of **4**, triethylamine (TEA) was added to give compound **5**.



Scheme 1. Synthesis of 4-nitro-*N*-(2-aminoethyl)-1,8-naphthalimide.

The next step was reacting 1,8-naphthalimide derivative to obtain the aromatic aryl core of the tripod **7** (Scheme 2). Firstly the reaction of **5** with trimethyl-1,3,5-benzenetricarboxylate was carried out in methanol solution at room temperature. The solid precipitate was filtered and washed with cold methanol to give tripod **6**.



Scheme 2. Synthesis of tripod **7**

This compound was then stirred overnight in DMF with *N,N*-dimethylaminoethylendiamine to obtain tripod **7**. In this case, the electron accepting carbonyl group of 1,8-naphthalimide molecule favours the reactions of nucleophilic substitution wherein the nitro group is being replaced by the aliphatic *N,N*-dimethylaminoethylendiamino group. It is well known that *N,N*-dimethylaminoethylendiamino substituent is often used in the design of molecular sensor devices, which are able to coordinate with transition or heavy metal ions and protons.^{19–22}

2.2. Spectral characteristics of tripod **7**

As seen from Scheme 2 the three 4-*N,N*-dimethylaminoethylendiamino-1,8-naphthalimide fragments are covalently bonded to

the benzene core through an ethylenediamino spacer. It is well known that the basic spectral characteristics of 1,8-naphthalimides depend mainly on the polarization of the chromophoric system due to the electron-donor-acceptor interaction occurring between the substituents at position C-4 and the carbonyl groups from the imide moiety. In the case of tripod **7** the ethylenediamino group may also interact with the carbonyl groups from the imide group of the chromophoric system. On the other hand, it may be a result of the environmental effect upon the interaction. It is clear that the absorption and emission bands of 1,8-naphthalimide derivatives depend largely on the electron donating nature of the substituents at the C-4 position. The whole structure gives the possibility of obtaining a coloured photostable branched molecule emitting intense yellow-green fluorescence, which is able to produce PET. The functional properties of compound **7** have been investigated with regard to its application as a PET sensor for metal cations and protons.

4-Nitro-1,8-naphthalimide-labelled tripod **6** absorbs in the near UV region at $\lambda_A=328$ nm (in DMF) due to the electron-accepting nature of the nitro group. The replacement of the nitro groups by an electron-donating *N,N*-dimethylaminoethylendiamine one leads to a bathochromic shift in the absorption maxima with 103 nm. In all organic solvents under study the new tripod **7** is yellow-green in colour and emits a green fluorescence. Table 1 presents the basic photophysical characteristics of tripod **7** determined in organic solvents of different polarity: absorption (λ_A) and fluorescence (λ_F) maxima, the extinction coefficient (ϵ), Stokes shift ($\nu_A-\nu_F$), and quantum yield of fluorescence (Φ_F). The absorption maxima λ_A in all organic solvents under study are in the visible region at 426–435 nm corresponding to a $S_0 \rightarrow S_1$ transition without a vibrational structure. The respective fluorescence maxima are in the 505–529 nm region. As seen from Table 1, the molar extinction coefficients ϵ are in the 30,100–34,800 mol⁻¹ dm³ cm⁻¹ region. These values are approximately three-fold higher than those of the monomeric 1,8-naphthalimide derivatives with the same substituents at C-4 position.¹⁹ That allows the suggestion of no ground state interaction occurring between the 1,8-naphthalimide chromophoric units.²³

Table 1
Photophysical characteristics of tripod **7** in organic solvents of different polarity

	λ_A nm	λ_F nm	ϵ mol dm ³ cm ⁻¹	$\nu_A-\nu_F$ cm ⁻¹	Φ_F
Tetrahydrofuran	426	505	31,500	3672	0.601
Chloroform	429	507	34,800	3586	0.580
Dichloromethane	430	511	32,300	3686	0.543
DMF	431	518	30,500	3686	0.104
Acetonitrile	431	528	32,300	3670	0.016
2-Propanol	435	525	32,900	3940	0.011
Butanol	433	528	30,300	4083	0.012
Ethanol	435	529	30,100	4085	0.010

The absorption ($\lambda_A=435$ nm) and fluorescence ($\lambda_F=529$ nm) spectra of tripod **7** in ethanol are plotted in Fig. 1 as an example. As seen, the fluorescence curve appears as an approximate mirror image of the absorption, which indicates that the 1,8-naphthalimide molecular structure is maintained in the excited state and the fluorescence emission prevails. Moreover, the overlap between absorption and fluorescence spectra is small indicating the prevailing fluorescence emission and no changes in molecular structure of 1,8-naphthalimide fluorophore in the excited state.

The Stokes shift is a parameter, which indicates the difference in the properties and structure of the dyes between the ground state S_0 and the first excited state S_1 . The calculated values for the Stokes shift are in the range of 3586–4085 cm⁻¹. The highest values are observed in protic solvents (Table 1). Similar values have also been

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