

New green fluorescent polymer sensors for metal cations and protons

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Abstract

A new 4-(*N*-methylpiperazine)-*N*-allyl-1,8-naphthalimide with intense yellow-green fluorescence has been synthesized. Then it has been copolymerized with styrene and methylmetacrylate. The photophysical characteristics of the fluorescent dye and its copolymers (poly(St-co-NI) and poly(MAA-co-NI)) have been determined viewing their sensor properties for protons and transition metal cations (Cu^{2+} , Fe^{3+} and Zn^{2+}). Fluorescence enhancement is the photophysical response of the 4-(*N*-methylpiperazine)-*N*-allyl-1,8-naphthalimide to the presence of metal cations and protons, while fluorescence quenching is observed for both copolymers.

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1. Introduction

As the environmental pollution is one of the major concerns of the contemporary society, much effort has been focused on the design of highly selective and sensitive sensory materials. With this regard, fluorescent chemosensors have been of particular interest, as fluorescence spectroscopy has turned to be one of the most effective and reliable analytical methods. Most of the research in this scope is focused on conjugated polymers with fluorescent units in the main chain or as pendant groups

[1–11]. Less attention has been paid to non-conjugated polymer sensors. The incorporation of fluorescent units into the polymer matrix is expected to improve their performance and efficiency. Major advantages of the copolymers comprising sensor units are: (i) the sensor is obtained simultaneously with the synthesis of the copolymers without any further steps; (ii) the sensing units comprised by the copolymers are firmly bonded to the main chain which eliminates any migration from the matrix; (iii) no crystallization processes occur during their exploitation. Thus, one can produce reusable sensors for monitoring pollution in water sources.

In our previous papers we have discussed the selectivity and sensitivity of polymer sensors based on 1,8-naphthalimide derivatives [12–15]. We have

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found that the monomeric sensor and its copolymer respond differently to the presence of metal cations in the microenvironment. Depending on the rigidity of the polymer main chain, as well as on the nature of the cations, one can observe fluorescence quenching or enhancement. We should note that the investigated 1,8-naphthalimide derivative consists of a *N,N*-dimethylamino group as receptor fragment, an ethylene spacer and a 1,8-naphthalimide chromophore responsible for the recognition event. The chemosensors employ the photoinduced electron transfer process that is quenched upon cation complexation and the fluorescence is switched-on i.e. this is an 'OFF–ON' sensor type. If the complexation with the receptor unit is somehow perturbed, the interaction can take place at another chelating site and may result in fluorescence quenching i.e. the sensor is of an 'ON–OFF' type.

This paper presents the synthesis and photophysical properties of a chemosensor based on 4-(*N*-methylpiperazine)-*N*-allyl-1,8-naphthalimide and its copolymer with styrene and methylmetacrylate. Their response to the presence of different transition metal cations has been investigated as well.

2. Experimental part

2.1. Materials

4-Nitro-*N*-allyl-1,8-naphthalimide was synthesized by condensation reaction between 4-nitro-1,8-naphthalic anhydride and allylamine and the synthesis is described in [16]. *N*-Methylpiperazine (Aldrich) was used as obtained. Commercial, styrene (St) and methylmetacrylate (MMA) were used after purification by distillation under reduced pressure. Dibenzoyl peroxide (DBP) (Fluka), recrystallized from chloroform and methanol, and was used as initiator for free radical copolymerization. $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ were investigated as sources for metal cations as obtained from Aldrich.

2.1.1. Synthesis of 4-(*N*-methylpiperazine)-*N*-allyl-1,8-naphthalimide

4-Nitro-*N*-allyl-1,8-naphthalimide (0.6 g (0.002 M)) was reacted with 1 ml *N*-methylpiperazine in 5 ml *N,N*-dimethylformamide for 48 h, at room temperature. The reaction was followed by TLC. The product was precipitated by pouring the reaction mixture into 100 ml water. Next, the precipitate was filtered

off, washed with water and dried under vacuum at 40 °C. Yield: 65%; m.p. 147–149 °C.

FTIR(KBr), cm^{-1} : 3095, 3007, 2963, 2842, 1692, 1656, 1589, 1512, 1453, 1380, 1245, 1078, 981, 881, 784.

^1H NMR(CDCl_3 , δ , ppm): 2.45 (s, 3H), 2.78 (d, $J = 4.5$ Hz, 4H), 3.32 (t, $J = 4.6, 4.7$ Hz, 4H), 4.82 (d, $J = 8.3$ Hz, 2H), 5.33 (dd, $J = 13.2, 10.2$ Hz, 2H), 6.07 (m, 1H), 7.26 (d, $J = 12.6$ Hz, 2H), 7.72 (t, $J = 8.6, 7.4$ Hz, 1H), 8.40 (d, $J = 9.6$ Hz, 1H), 8.61 (dd, $J = 7.3, 8.1$ Hz, 2H).

Elemental analysis: $\text{C}_{20}\text{H}_{21}\text{N}_3\text{O}_2$ (335.1 g mol^{-1}):
Calc. (%): C-71.62, H 6.26, N 12.53.

Found (%): C-71.36, H 6.19, N 12.59.

2.1.2. Copolymerization

Free radical copolymerization of styrene and methylmetacrylate with 4-(*N*-methylpiperazine)-*N*-allyl-1,8-naphthalimide was carried out in bulk [17].

2.1.2.1. Styrene monomer. Styrene (9.2 g), 0.6 g of the monomeric dye and 0.05 g, DBP were mixed in an ampoule flushed with pure dry nitrogen. The ampoule was sealed and heated at 80 °C in a thermostat for 24 h.

2.1.2.2. Methylmetacrylate monomer. Methylmetacrylate (10 g), 0.6 g of the monomeric dye and 0.05 g DBP were mixed in an ampoule flushed with pure nitrogen. The ampoule was sealed and heated at 80 °C in a thermostat for 24 h.

The modified copolymers were dissolved in chloroform and precipitated several times with ethanol in order to remove the unreacted monomer and the low-molecular weight oligomers. The precipitated copolymers were dried under vacuum at 40 °C to a constant weight.

Thin polymeric films for all spectral measurements were obtained from 10% solutions of the respective copolymers in chloroform.

2.2. Analysis

All UV–Vis spectrophotometric investigations were performed on a UVIKON 930 spectrophotometer (KONTRON instruments). Fluorescence quantum yields of the monomeric dye have been determined from the absorption and fluorescence spectra. NaOH solution (0.1 N) of fluorescein was used as a reference ($\Phi_0 = 0.86$). For all the absorption and fluorescence measurements, the dye concentrations in the solution were $10^{-5} \text{ mol l}^{-1}$. For

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