

Sensor activity, photodegradation and photostabilisation of a PAMAM dendrimer comprising 1,8-naphthalimide functional groups in its periphery

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Abstract

The colouristic and fluorescent characteristics of a new composite material based on a PAMAM dendrimer of second generation whose periphery is modified with 4-*N,N*-dimethylaminoethylamino-1,8-naphthalimide and polyamide-6 have been investigated. This dendrimer has been investigated with regard to its application as a heterogenic sensor capable of detecting metal cations and protons in aqueous solutions. In the presence of metal cations (Ni^{2+} , Fe^{2+} , Fe^{3+} and Co^{2+}) and protons the fluorescence intensity of the composite increases due to their coordination with dendrimer molecule. The results obtained reveal the capacity of this system to act as a sensitive sensor of environmental pollution by metal cations and protons. It has been shown that in *N,N*-dimethylformamide solution the metal cations inhibit the processes of photodegradation of the dendrimer.

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1. Introduction

The immediate detection and determination of environmental pollutants have been gaining particular importance. Fluorescent composite materials capable of detecting metal ions' pollution in the environment have been studied intensively in the recent years. Most of the known fluorescent sensors are based on the photoinduced electron transfer (PET) [1]. The PET fluorescence sensors are designed so that the electron transfer occurs between the fluorophore as a signalling unit while the receptor acts as a "switch" of the fluorescence intensity.

The potential of both low and high molecular weight fluorescent sensors to act as metal cation detectors have been studied intensively [2]. Though low molecular weight sensors are

conventional and cheaper, their main disadvantage to the polymeric ones is their lower sensitivity to pollutants. Amongst polymers, dendrimers being of tailored three-dimensional molecular structure and defined molecular weight have turned to be very promising for this purpose [3]. Another advantage of these materials is their exceptional sensibility. They detect the availability even of a single metal ion [4].

Introducing fluorophores of various nature and fluorescence emission into the core or periphery of the dendrimer allows altering the desired properties of the new materials. Very suitable are poly(amidoamine) PAMAM dendrimers containing both amide and tertiary amines groups since their peripheries are functionalized with various groups that are able to furnish desired properties [5]. The molecular weight and number of peripheral functional groups of PAMAM dendrimer increase exponentially with each generation, while the dendrimer diameter increases more or less linearly. The PAMAM dendrimers from 0 to 2 generations has an open structure. Recent investigations have demonstrated the potential of

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PAMAM dendrimer molecules to coordinate some metal cations [6].

We have already published some results on the synthesis and photophysical properties of some new luminescent PAMAM dendrimers comprising 1,8-naphthalamide units in their periphery [7]. Enhancement [7a,d] or quenching [7b,c,e–g] of the fluorescence intensity in the presence of cations dependent on the PAMAM generation has been reported. We have found that these dendrimers could act as PET chemosensors for metal cations or protons. The practical need of detectors operating successfully in various media has turned our attention to the synthesis of sensors preserving their properties in the solid state, so that they could be used repeatedly.

In this paper we describe the functional properties of a second generation PAMAM dendrimer deposited onto a polyamide matrix having the capacities of high sensitive PET sensors for metal cations and protons. The core of the dendrimer comprises amide groups and tertiary amines while its periphery is of 4-dimethylaminoethylamino-1,8-naphthalamide fluorescent units.

2. Experimental part

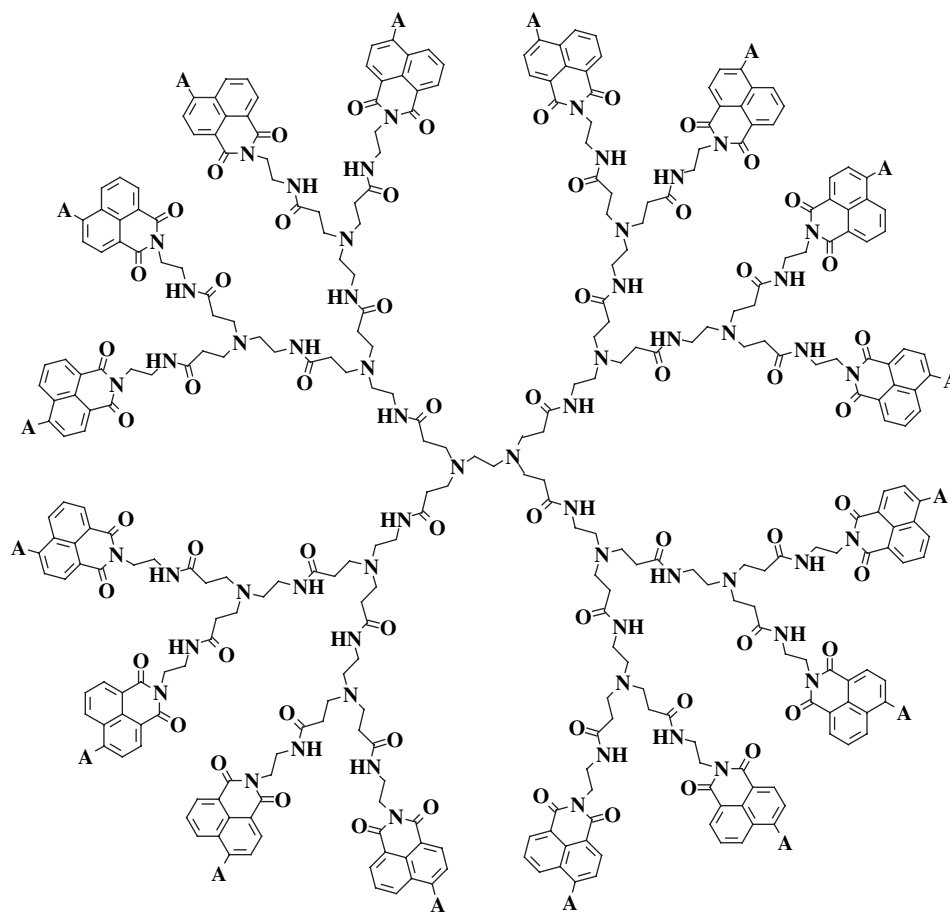
2.1. Materials and methods

Commercial polyamide-6 (PA) fibre was used as a solid polymer matrix. The dendrimer was synthesized and purified following a method described previously [7d]. The structure of the dendrimer under study is presented in Scheme 1.

Polyamide material was treated with dendrimer (0.5 wt%) according to the dispersion method in aqueous medium using deionised water [7f]. The dendrimer was evenly deposited onto the polyamide matrix. The dendrimer was fixed to the surface of the PA matrix via hydrogen bonds and Van-der Waals force.

2.2. Analysis

The fluorescence spectra were taken on a Varian Cary Eclipse spectrophotometer at 10^{-6} M l^{-1} . Fluorescence quantum yield was determined on the basis of the absorption and



Scheme 1. Structural formula of the second generation PAMAM dendrimers whose periphery is modified with 4-*N,N*-dimethylaminoethylamino-1,8-naphthalamide.

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