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Fluorescent properties of novel dendrimer dyes based on thiazole orange

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ABSTRACT

In this paper, polyamidoamine (PAMAM) dendrimers with active amino group of some generations ($G=0.5$–2) were prepared from commercial aminoacetaldehyde diethyl acetal by the divergent method. After that, thiazole orange (TO) with –COOH was incorporated with dendrimers of $G=1$ and 2 to afford novel dendrimer-TO dyes. The fluorescent properties studies showed that the fluorescent intensity of the same concentration of dendrimer-TO ($G=2$) was higher than that of the dendrimer-TO ($G=1$), and both of them were much stronger than free TO with –COOH. There was a fluorescent enhancement of the dendrimer dyes compared with free dye. The dendrimer dyes were of well-defined chemical structure,with little aggregation and self-quenching as well as good fluorescence properties of good stability, high intensity and sensitivity, which could be used in labeling cancer cells and further in diagnosis and detection of early-stage tumors.

1. Introduction

Many scientific efforts have gone into the design and synthesis of dendrimers over the past decades. Dendrimers have attracted much attention in the fields of conjugates, medical applications, diagnostics, host–guest chemistry, dendritic catalysts and so on because of their multifunctional properties, such as well-defined chemical structure, good solubility, low viscosity, well-defined structure and abundant functional groups [1]. In this area, the photoisomerization of dendrimers with photoresponsive cores – such as stilbene [2,3], azobenzene [4,5], diarylethene [6,7] and so on [8] has been extensively investigated.

As various advanced contrast agents in cancer diagnosis and cancer therapies, dendrimers are being applied to target cancer cells specifically or to improve the safety and effectiveness of many therapeutics [9–11]. Diagnosis and detection of early-stage tumors are regarded as one of the current challenges in the biomedical sciences. With the advantage of low-price, safety and accuracy, biological molecular marker has attracted more and more attention in the early-stage diagnosis in medical science. As one of the widely used fluorescent labeling compounds (fluorescence dye probe), organic fluorescent dyes may have fluorescence in dilute solution, but a decrease in the solid state or an aggregation in solution occurs because of the interaction between molecules and the formation of nonfluorescent dye dimers. If the dye–dye distances can be controlled to suppress the dimer formation, the fluorescence may increase [12,13]. Therefore an ideal fluorescent probe should bear a large but also distinct number of chromophores as well as biologically active groups.

Introduction of small molecules into the nucleus of dendrimers can avoid aggregation to decrease the interaction between small molecules and afford a stable and homogeneous tiny condition [14–17].

Adjusting the generation of dendrimers, rules of characters of functional small molecules can be observed. The synthesis of a polyphenylene dendrimer carrying three perylene monoimide dyes as well as one biotin group was presented by Minard-Basquin [18]. Due to the hydrophobic polyphenylene scaffold, this dendrimer was insoluble in water thus preventing investigations in aqueous media.

Winnik et al. [19,20] obtained hyperbranched polymer of pyrene chromophores and studied the interaction of the pyrene-labeled polymer with sodium dodecyl sulfate in aqueous solution. Frank et al. [21] found that the branched samples had reduced quenching rate constants, and the fraction of accessible chromophores decreased for higher generation polymers.

Novel and well-defined pyrene-containing eight-arm star-shaped dendrimer-like copolymers were successfully achieved by Yuan et al. [22]. Fluorescence analysis indicated that $(\mathrm{PSt\text{-}b\text{-}(PCL\text{-}pyrene)_2})_4$ presented slightly stronger fluorescence intensity than 1-pyrenebutyric acid when their pyrene concentration of them was the same.

Some other studies on dendrimer nanocomposites [23,24], dendrimers bearing rhodamine derivatives [25], dendrimers binding the fluorescent probe 8-anilino-l-naphthalene-sulfonic acid [26] and so on have also been reported. Russo reported a

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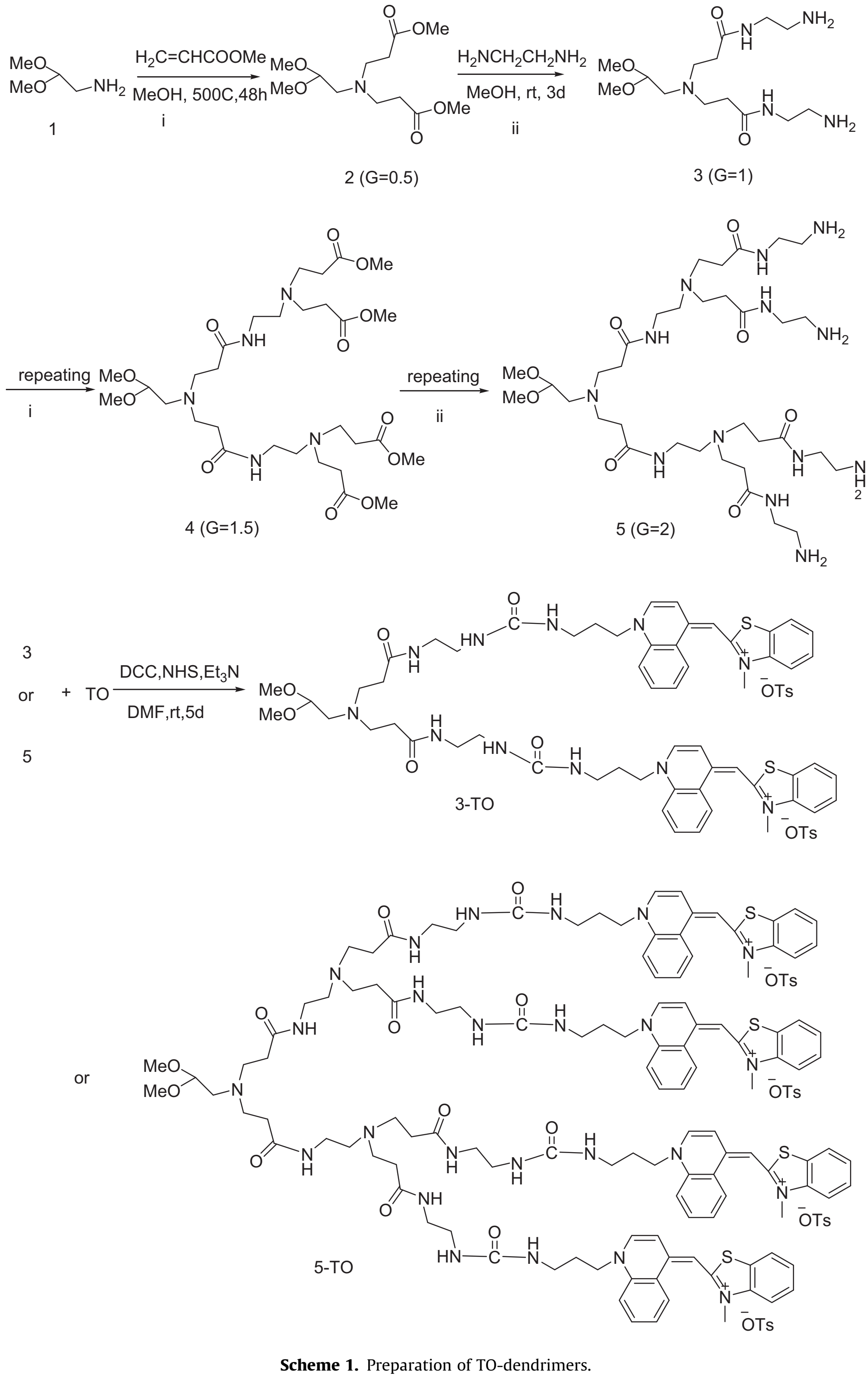
dendrimer equipped with a covalently coupled fluorescent label [27]. But the dendrimer bearing embedded probe has not been reported.

Thiazole orange (TO), a benzothiazole ring covalently linked to a quinoline through a monomethine bridge, has been widely used as an embedded cyanine dye for labeling nucleic acids, allowing the detection of DNA and RNA in gels by flow cytometry or microscopy. Although the fluorescence of free TO is extremely low in aqueous solution, when bound to nucleic acids the viscosity of the dye's local environment would be markedly increased [28–32]. The large difference in fluorescence between free dye and nucleic acid-bound dye provides an excellent way to image, label and detect cancer cells [33–36].

In order to load more dye molecules onto a certain group of cells and enhance the fluorescent signals while suppressing aggregation, the authors designed and synthesized a kind of novel embedded dendrimer probe. This probe used dendrimer molecule as a scaffold with dye molecules at its end group to increase the number of dye



Scheme 1. Preparation of TO-dendrimers.