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A ratiometric rhodamine–naphthalimide pH selective probe built on the basis of a PAMAM light-harvesting architecture

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ABSTRACT

PAMAM light harvesting antenna of second generation was synthesized and investigated. Novel compound was configured as a wavelength-shifting bichromophoric molecule where the system surface is labeled with yellow-green emitting 4-(*N*,*N*-dimethylamino)ethylamino-1,8-naphthalimide “donor” units capable of absorbing light and efficiently transferring the energy to a focal Rhodamine 6G “acceptor”. Furthermore, the 1,8-naphthalimide periphery of the system was designed on the “fluorophore-spacer-receptor” format, capable of acting as a molecular fluorescence photoinduced electron transfer based probe. Due to the both effects, photoinduced electron transfer in the periphery of the system and pH dependent rhodamine core absorption, novel antenna is able to act as a selective ratiometric pH fluorescence probe in aqueous medium. Thus, the distinguishing features of light-harvesting systems (fluorescence resonance energy transfer) were successfully combined with the properties of classical ring-opening sensor systems, which may be beneficial for monitoring pH variations in complex samples.

1. Introduction

Solar light is steadily becoming one of the main sources of energy for human kind. Therefore, the utilization of solar energy has attracted much attention by the scientific community and is the most enormous scientific challenge in the next half-century [1]. The phenomenon of sunlight harvesting by natural complexes and its utilization served as an inspiration for research in various disciplines. As a result, artificial antenna systems were developed and new attractive materials for application to photoactive devices were produced [2].

The monitoring of the various chemical analytes has become a mandatory task in many applications related to the management of minimum standards of foods, environment, agriculture sciences, medicine and health sciences [3–7]. Because of the high sensitivity, high speed and cheap instrumentation, particularly the fluorescence sensors and switches have been actively investigated [8–10]. They are designed on three basic approaches: intramolecular charge transfer (ICT), photoinduced electron transfer (PET) and energy transfer [11–15]. As the emission intensity change of fluorescent probes upon binding to species of interest is the only detection signal, factors such as instrumental efficiency, environmental conditions, and the probe concentration can interfere with the signal output. To eliminate these effects, a ratiometric fluorescent measurement is desirable.

The ratiometric fluorescent probes emit fluorescence at two wavelengths that enable a built-in correction for the undesired environmental effects. They operate via dual output signaling of the ICT [16–18], excited-state intramolecular proton transfer (ESIPT) [19] or bichromophoric systems [20,21]. Among the ratiometric fluorescent probes, we were interested in developing new fluorescence sensing bichromophores, based on fluorescence resonance energy transfer (FRET). FRET is a distance-dependent interaction between the electronic excited states of two dye molecules in which excitation is transferred from a donor molecule to an acceptor molecule without emission of a photon [22,23]. The pseudo-Stokes shifts of FRET based probes are larger than the Stokes shifts of either the donor or acceptor dyes; thus, the possible self-quenching as well as fluorescence detection errors due to backscattering effects from the excitation source will be efficiently avoided [24].

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Development of artificial light-harvesting systems is attractive for application to ratiometric fluorescent probes. One of the most attractive artificial light-harvesting systems is the dendritic assemblies because of their unique structures and reminiscent of the architecture of natural light-harvesting complexes [25–28]. The globular shape of dendritic architectures provides a large surface area that can be decorated with chromophores, resulting a large absorption cross section and efficient capture of photons. Furthermore, because of their proximity, the various functional groups of dendritic systems may easily interact with one another to give high efficiency energy transfer [29]. The polyamidoamines (PAMAM) are a well known class of commercial dendrimers. The use of flexible aliphatic PAMAM bone as a scaffold for light-harvesting antennae could give new systems with high efficiency of energy transfer [29–32].

Recently, our group has synthesized FRET based wavelength-shifting bichromophoric systems using 1,8-naphthalimide donor fluorophores and Rhodamine 6G acceptor dye [33–36]. Apart the high chemosensing potential of the synthesized wavelength-shifting bichromophores these systems exhibited lower ability to capturing photons by donating periphery in comparison with the acceptor rhodamine core due to the lower extinction coefficient of the 1,8-naphthalimide units. This encouraged our efforts towards the synthesis of light-harvesting system of higher generation, containing a greater number of 1,8-naphthalimide donor fluorophores around a single Rhodamine 6G unit. Here we report on the design, synthesis and photophysical properties of a novel ratiometric fluorescence “off–on” light-harvesting antenna of second generation based on a core and peripherally functionalized PAMAM dendron (Scheme 1). Also, the peripheral 1,8-naphthalimides were designed on a “fluorophore-spacer-receptor” format thus providing PET based sensing properties of the novel light harvesting antenna.

2. Experimental

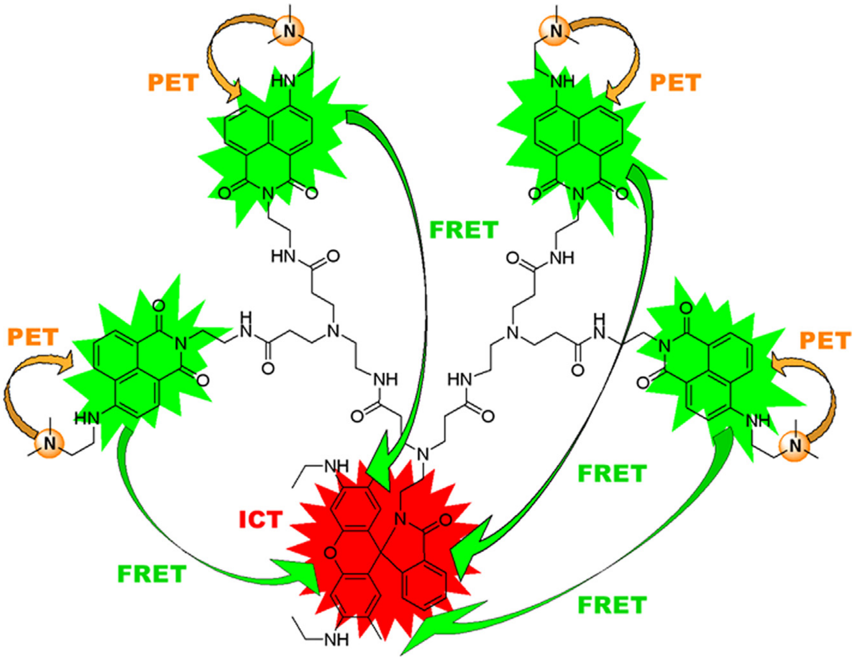
2.1. Materials

Commercially available Rhodamine 6G **1**, methyl acrylate, ethylenediamine and *N*,*N*-dimethylethylenediamine (Aldrich, Merck) were used without purification. The intermediate dendron **6** and 4-nitro-1,8-naphthalic anhydride **7** were prepared according to the reported procedures [36,37]. All solvents (Fluka, Merck) were pure for analysis or of spectroscopy grade. NaOH and HCl were supplied by Merck (Germany). HEPES buffer solution (pH 7.3, Aldrich), metal stock solutions (1×10^{-3} M) of $Zn(NO_3)_2$, $Cu(NO_3)_2$, $Ni(NO_3)_2$, $Co(NO_3)_2$, $Pb(NO_3)_2$, $Fe(NO_3)_3$, $Cd(NO_3)_2$, $AgNO_3$, $Cr(NO_3)_3$, $AlCl_3$ and $Hg(NO_3)_2$ in water (all Aldrich salts at p.a. grade) and working dye solutions (1×10^{-5} M) were prepared daily.

2.2. Methods

FT-IR spectra were recorded on a Varian Scimitar 1000 spectrometer. The ^{1}H NMR spectra (chemical shifts are given as δ in ppm) were recorded on a Bruker DRX-250 spectrometer, operating at 250.13 MHz. Absorption spectra were recorded on a Hewlett Packard 8452A spectrophotometer. Fluorescent spectra were recorded on a Scinco FS-2 fluorescence spectrophotometer. The excitation source was a 150 W Xenon lamp. Excitation and emission slits width were 5 nm. Fluorescence measurement was carried out in right angle sample geometry. A 1×1 cm^2 quartz cuvette was used for the spectroscopic analysis. Relative fluorescence quantum yields (Φ_F) were measured using Rhodamine 6G (Φ_F=0.95 in ethanol [38]) or Coumarin 6 (Φ_F=0.78 in ethanol [39]) as standards. All experiments were performed at room temperature. The spectral data were collected using FluoroMaster Plus 1.3 and further processed by OrginPro 6.1 software. A pH meter Metrohm 704 coupled with combined pH electrode was used for pH measurements. The commercial standard buffers for pH 2, 7 and 10 (Aldrich) were used for calibration. TLC was performed on silica gel, Fluka F60 254, 20×20 cm^2, 0.2 mm. The melting points were determined by means of a Kofler melting point microscope.

The absorption and fluorescence properties were studied as a function of pH by multiple additions of NaOH and HCl aqueous solutions to 400 mL 1×10^{-5} M solution of examined compounds in water/DMF (4:1, v/v). The addition was limited to 1 mL so that dilution remains insignificant. The solution pH, absorption and fluorescence spectra were recorded at each addition. The effect of the metal cations was examined by adding 10 μL of the metal stock



Scheme 1. PAMAM light-harvesting antenna **9**, core and peripherally functionalized with Rhodamine 6G and 4-(*N*,*N*-dimethylamino)ethylamino-1,8-naphthalimides.