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Design and synthesis of novel fluorescence sensing perylene diimides based on photoinduced electron transfer

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ABSTRACT

Two novel tetraester- and PAMAM-branched perylene diimides were synthesized and configured as “fluorophore-spacer-receptor” systems based on photoinduced electron transfer. Due to their long alkylester and alkylamine terminal groups the examined compounds were well soluble in organic solvents. Photophysical characteristics of the dyes were investigated in DMF and water/DMF (1:1, v/v) solution. The ability of the synthesized perylene diimides to detect cations was evaluated by the changes in their fluorescence intensity in the presence of metal ions (Zn^{2+}, Co^{2+}, Cu^{2+}, Fe^{3+}, Pb^{2+}, Hg^{2+}, Ag^{+} and Ni^{2+}) and protons. The dyes under study displayed “off–on” switching in its fluorescence as a function of pH, which is attributed to disallowing photoinduced electron transfer from the receptor moiety to the fluorophore. PAMAM-branched dye displayed a good pH sensor activity (FE = 6.4), however the pH sensing ability of tetraester was substantially higher (FE = 184). In the presence of Cu^{2+} and Pb^{2+} ions tetraester quenched its fluorescence intensity (FQ = 22 and 12 respectively), while PAMAM-branched dye enhanced its fluorescence intensity with pronounced selectivity to Cu^{2+} and Fe^{3+} (FE = 3.2 and 4.9, respectively). The results obtained indicate the potential of the novel compounds as fluorescent detectors for metal ions with pronounced selectivity towards Cu^{2+}, Pb^{2+} and Fe^{3+} ions and highly efficient “*off–on*” pH switches, especially a tetraester-branched perylene diimide.

1. Introduction

Perylene-3,4,9,10-tetracarboxylic diimides exhibit a unique combination of electrooptical and redox properties. They are highly stable and widely used n-type materials for organic electronic devices such as solar cells [1–3], field-effect transistors [4–6], light-emitting diodes [7–9], in liquid crystal displays [10,11], as chemosensing materials [12–14], light-harvesting materials [15,16] and as dyes in photodynamic therapy [17]. However, most of the synthesised dyes possess low solubility in organic solvents; this is a serious drawback for their processing and material science applications [18,19]. Usually the solubility is improved with the long-tail or swallow-tail conformation that is obtained by long alkyl substitutions in *N*-position of the dye [20–22].

Dendrimers are well defined macromolecules exhibiting a three-dimensional structure that is roughly spherical or globular. A characteristic of dendritic macromolecules is the presence of numerous peripheral chain ends that all surround a single core [23,24]. The usage of perylene diimides as dendrimer core would increase their solubility in organic solvents due to the dendritic swallow-tail conformation [25,26]. The polyamidoamine (PAMAM) is a class of commercial dendrimers. Considerable interest in polyamidoamine (PAMAM) dendritic macromolecules has arisen because of their novel structural properties and wide range of potential applications [27–31]. Constructing a PAMAM dendrimer around a luminescent group could profitably alter the luminescence signals in the macromolecular structure and amplify the signals for sensing purposes [32–36].

Development of new sensors with improved characteristics (selectivity, sensitivity etc.) is a challenging and necessary task in the 21st century, marked by the technological booms consequences [37–41]. Because of the high sensitivity, high speed, and safety the fluorescent chemosensors and switches have been actively investigated in the recent years. The photoinduced electron transfer (PET) using the “*fluorophore-spacer-receptor*” format is the most commonly exploited approach for the design of the fluorescent sensors and switchers [42]. The components are chosen so that PET from the receptor (usually an amino group) to the fluorophore quenches the fluorescence of the system. However, in the presence of a guest, PET communication between the receptor and the fluorophore gets cut off

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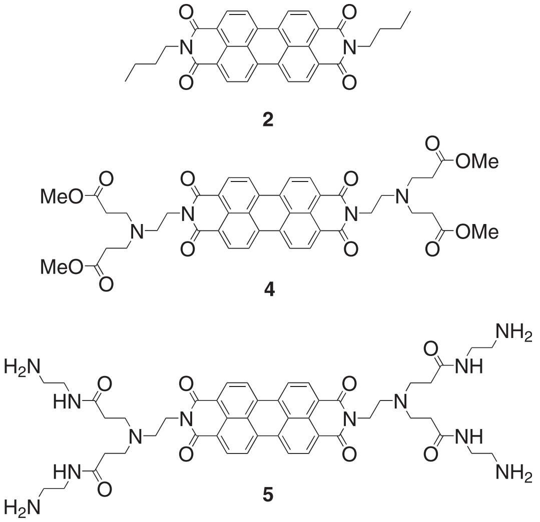


Scheme 1.

and the fluorescence of the system is recovered. In other words, the presence of a guest is signaled by fluorescence enhancement of the system [43–46].

In this work we were focused on the divergent construction of a novel perylene diimide core functionalized PAMAM dendrimer **5** and tetraester **4** together with their photophysical and fluorescence chemosensing properties. Hence, compounds **4** and **5** (Scheme 1) were synthesized and investigated by electronic absorption and emission spectroscopy as potential PET sensors for protons and transition metal ions.

In order to receive a more complete comparative picture for the influence of the polyamidoamine backbone to the perylene diimide fluorophore, perylene diimide **2**, not containing tertiary amine in its molecule, was involved in the present study (Scheme 1).

2. Experimental

2.1. Material

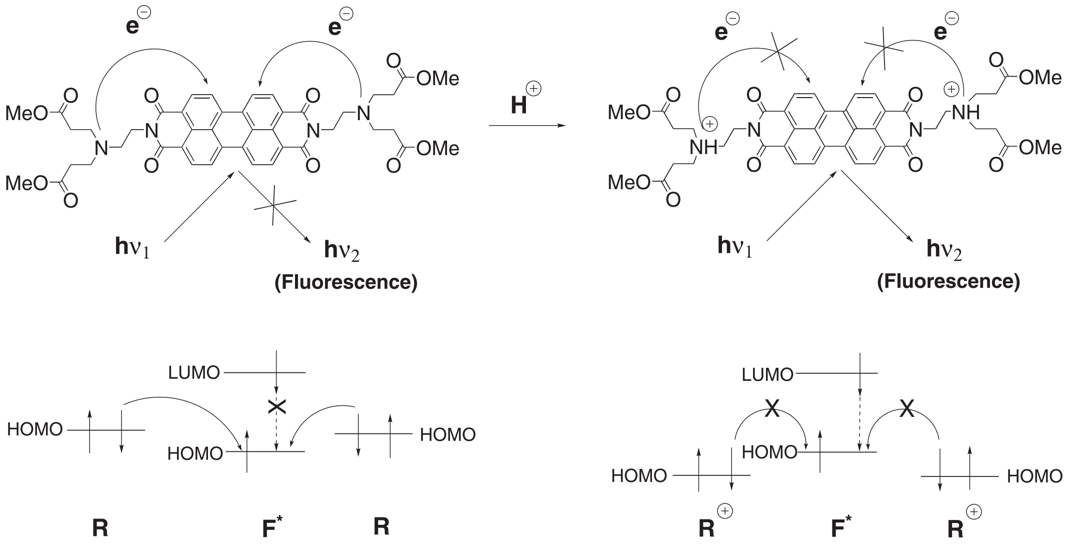
Reference perylene-3,4,9,10-tetracarboxylic diimide **2** was synthesized according to the procedure described before [47]. Ethylenediamine, methyl acrylate and perylene-3,4,9,10-tetracarboxylic acid dianhydride **1** (Aldrich), p.a. grade, were used without purification. All solvents (Fluka, Merck) were pure or of spectroscopy grade. $Zn(NO_3)_2$, $Cu(NO_3)_2$, $Ni(NO_3)_2$, $Co(NO_3)_2$, $Pb(NO_3)_2$, $Fe(NO_3)_3$, $Hg(NO_3)_2$ and $AgNO_3$ salts were the sources for metal cations.

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. TLC was performed on silica-gel, Fluka F60 254, 20 × 20, 0.2 mm. The melting points were determined by means of a Kofler melting point microscope. The UV–VIS absorption spectra were recorded on a spectrophotometer Hewlett Packard 8452A. The corrected fluorescence spectra were taken on a Scinco FS-2 spectrofluorimeter at room temperature (25 °C). To adjust the pH values very small volumes of hydrochloric acid and sodium hydroxide solution were used. The pH was determined with a pH meter Metrohm 704, which was standardized with Aldrich buffers. The effect of the metal cations and protons upon the fluorescence intensity was examined by adding 30 μl portions of the metal cations stock solution (2.0×10^{-6} mol L^{-1}) to a known volume of the fluorophore solution (3 ml).

2.3. Synthesis of amino functionalized perylene-3,4,9,10-tetracarboxylic diimide (3)

To a suspension of 2 g (5 mmol) perylene-3,4,9,10-tetracarboxylic acid dianhydride in 25 ml of benzene, 6 ml ethylenediamine (90 mmol) was added and the resulting mixture was heated under reflux for 5 h. After cooling to room temperature the precipitate was collected by filtration, washed with benzene and dried. Then the crude solid was treated with 50 ml of 5% aqueous sodium hydroxide to give after filtration, washing with water and drying 2.04 g (84%) of pure diimide **3** (m.p. > 250 °C). IR (KBr) cm^{-1}: 3368 (νNH_2); 1684 (ν^{as}N-$\underline{C}$=$\underline{O}$); 1658 (ν^{s}N-$\underline{C}$=$\underline{O}$). ^{1}H NMR (CF_3COOD-*d*, 250.13 MHz) ppm: 8.41 (m, 8H, perylene H); 4.39 (m, 4H, 2 × $\underline{CH_2}N(CO)_2$); 3.41 (m, 4H, 2 × $\underline{CH_2}NH_2$). Elemental analysis: Calculated for $C_{28}H_{20}N_4O_4$ (MW 476,5) C 70.58, H 4.23, N 11.76%; Found C 70.49, H 4.36, N 11.55%.



Scheme 2.