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Pyrene-labeled dendrimers functionalized with fullerene C_{60} or porphyrin core as light harvesting antennas

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ABSTRACT

Pyrene-labeled dendrimers linked to a fullerene C_{60} or a porphyrin core were designed and synthesized through a convergent synthetic pathway. The energy transfer process that is occuring inside the obtained dendrimers was studied by measuring and analysing their absorbance and fluorescence emission properties. All absorption spectra are showing the typical absorption band of pyrene. No ground state interaction was detected between pyrene and porphyrin whereas a slight interaction was observed between pyrene and fullerene C_{60}. An almost quantitative quenching of the pyrene fluorescence emission was observed when coupled with fullerene C_{60} as well as with porphyrin, indicating effective energy transfer. In the case of fullerene C_{60}, no emission could be seen due its weak intrinsic emission. When the acceptor was a porphyrin moiety, fluorescence emission was observed from the free porphyrin as well as from the Zn complex analogue.

1. Introduction

In the field of dendrimer chemistry, dendrimers bearing photoactive units leading to light harvesting properties are presenting a special interest [1–3]. They are constructed with a large number of the same chromophore at the periphery increasing their absorption coefficient and another type of chromophore at the core, which acts as a trap of the excitation energy. The main processes that are occurring in photoactive dendrimers are resonance energy transfer (RET), charge transfer (CT) and electron transfer (ET). The obtained compounds are mimicking natural light harvesting systems and could lead to numerous applications in optoelectronic devices, solar energy conversion, catalysis, sensing and medicinal photonics [1,4–8].

Among the available chromophores, pyrene is an attractive building block for photoactive dendrimers. The peculiar photophysical properties of pyrene have been reviewed [9–11], and pyrene has been used to label fluorescent macromolecules due to its ability of forming excimers and its long fluorescence lifetime [12]. Moreover, pyrene has been used for optoelectronic applications among others [13]. The use of the fullerene C_{60} moiety has many advantages such as a large size (about 9 Å), a rigid framework, a high symmetry and high stability. Moreover, it presents moderate electron accepting properties and when it is coupled with electron donors, the photoinduced electron transfer (PET) process yields to a charge separated state with a slow charge recombination rate [14–16]. Fullerene C_{60} is therefore a good candidate as charge separating agent, which eventually lead to creation of photocurrent. Another chromophore that is presenting a particular interest is the porphyrin. This is due to the similarity of this type of compounds with the natural chlorins, which are involved in the first steps of photosynthesis [17–21].

Photoactive dendrimers are studied for their capacity to form molecular antennae that are able to harvest light from the periphery to the core [3]. The increase in the generation number allows the addition of several donors to only one acceptor in the same molecules. Thereby, the molar absorption is raised in a predictable way and the amount of energy transferred is augmented. Moreover, the dendritic wedges are serving as an insulator for the choromophore situated at the core, reducing the negative self-quenching effect of chromophores aggregation and improving solubility. Dendrimers containing pyrene, fullerene or porphyrin units in their scaffold have been studied [22]. Fréchet has reported the first dendrimers covalently linked with fullerene moieties [23]. Later, a large variety of dendrimers including a fullerene moiety at the core have been studied for mesomorphic materials [24], and organic photovoltaic devices [13,25,26]. The dendritic wedges are encapsulating the fullerene C_{60} core improving its solubility. The study of the lifetime of the triplet state of fullerene C_{60} is a good indication of the contact of the core with the external environment [27]. Several dendrimers based on porphyrin has been reported and such compounds

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are showing promising application in material science [28–30]. In our group, we have reported pyrene-labeled dendrimers with a fullerene C_{60} core as well as pyrene-labeled dendrimers with a porphyrin core [31–33]. Pyrene has a large spectral overlap with porphyrin and a smaller spectral overlap with fullerene C_{60} but we are expecting an efficient resonance energy transfer in both cases. In this work, we are presenting the synthesis and the photophysical properties of new pyrene-labeled dendrimers linked to porphyrin and to fullerene C_{60} cores.

2. Experimental section

2.1. General conditions

All the reagents used in the synthesis were purchased from Aldrich and used as received. The solvents employed in the reactions were purified by distillation in the presence of a drying agent (metallic sodium for THF or $MgSO_4$ for acetone). Glass column were used to pack silica gel for the purification by column chromatography. Thin-layer chromatography (TLC) was performed before the column chromatography in order to determine the composition of the eluting solvent.

Intermediates and products involved in the synthesis were characterized by ^1H and ^{13}C NMR spectroscopy and by MALDI-TOF mass spectrometry. An instrument Bruker Advance of 400 MHz on proton and 100 MHz on carbon 13 was used for the NMR analysis. ^1H NMR chemical shifts are reported in parts per million. Multiplicity is given as s (singlet), d (doublet), t (triplet) or m (multiplet). Coupling constants (*J*) are given in Hertz. For the determination of the molecular weight of the obtained compounds through MALDI-TOF, an instrument Bruker Daltonics Flex Analysis was used and the samples were prepared with dithranol as matrix. Elemental analyses were done on an Elementar Vario Micro Cube instrument. THF and toluene used as solvents for the photophysical measurements were purchased as spectrophotometric grade. The cuvettes were quartz cells with a dimension of 1 cm A Unicam UV300 spectrophotometer was used to record absorption spectra and a Fluorolog3 Horiba spectrofluorometer with Xenon lamp for the emission spectra. The slits widths were set to 1 nm on excitation and 1 nm on emission.

2.2. Synthetic procedures

2.2.1. 1-(4-Bromobutyl)pyrene (1)

Compound **1** was synthesized as previously reported [32]. The product was obtained as a white solid (2.190 g, 90%).

^1H NMR (δ ppm, 300 MHz, $CDCl_3$): 8.27 − 7.86 (m, 9H, CH Ar_{py}), 3.44 (t, 2H, ^3J = 6.3, CH_2), 3.38 (t, 2H, ^3J = 7.2, CH_2), 2.13 − 1.94 (m, 4H, CH_2). ^{13}C NMR (δ ppm, 100 MHz, $CDCl_3$): 136.3, 131.6, 131.1, 130.1, 128.8, 127.7, 127.6, 127.4, 126.9, 126.1, 125.3, 125.22, 125.15, 125.0, 124.9, 123.45, 33.8, 32.84, 32.82, 30.4.

2.2.2. First generation dendron (2)

Compound **2** was synthesized as previously reported [32]. The product was obtained as a white solid (0.980 g, 72%).

^1H NMR (δ ppm, 400 MHz, $CDCl_3$): 8.29 − 7.85 (m, 18H, CH Ar_{py}), 6.48 (d, 2H, ^4J = 2.1, ArH_o), 6.36 (t, 1H, ^4J = 2.1, ArH_p), 4.58 (d, 2H, ^3J = 3.8, CH_2 benzylic), 3.97 (t, 4H, ^3J = 5.8, O-CH_2), 3.39 (t, 4H, ^3J = 7.6, Py-CH_2), 2.10 − 1.88 (m, 8H, CH_2). ^{13}C NMR (δ ppm, 100 MHz, $CDCl_3$): 160.6, 143.4, 136.8, 131.6, 131.1, 130.0, 128.9, 127.7, 127.5, 127.4, 126.8, 126.0, 125.3, 125.2, 125.1, 125.0, 124.9, 123.6, 105.3, 100.8, 68.0, 65.6, 33.4, 29.4, 28.4.

2.2.3. Compound 3

Compound **2** (200 mg, 0.31 mmol) and Meldrum's acid (22 mg, 0.15 mmol) were mixed together in a flask and heated to 130 °C for 5 h. After cooling to room temperature, the crude product was purified by column chromatography (Hexane:CH_2Cl_2 40:60) to give the desired product **3** as a white solid (73 mg, 34%).

^1H NMR (δ ppm, 400 MHz, $CDCl_3$): 8.22 (d, 4H, *J* = 9.6), 8.11 − 8.02 (m, 16 H), 7.97 − 7.91 (m, 12 H), 7.82 (d, 4H, *J* = 7.8), 6.41 (d, 4H, *J* = 2.2), 6.34 (t, 2H, *J* = 2.2), 5.05 (s, 4 H), 3.89 (t, 8H, *J* = 6.2), 3.44 (s, 2 H), 3.34 (t, 8H, *J* = 7.6), 2.01 − 1.93 (m, 8 H), 1.90-1.83 (m, 8 H). ^{13}C NMR (δ ppm, 100 MHz, $CDCl_3$): 160.5 (C), 137.5 (C), 136.7 (2, C), 131.6 (C), 131.1 (C), 130.0 (C), 128.8 (C), 127.7 (CH), 127.4 (2, CH), 126.8 (CH), 125.9 (CH), 125.3 (C), 125.2 (C), 125.0 (CH), 124.9 (CH), 124.8 (CH), 123.5 (CH), 106.5 (CH), 101.5 (CH), 68.0 (CH2), 67.3 (CH2), 41.7 (CH2), 33.3 (CH2), 29.4 (CH2), 28.4 (CH2). MALDI-TOF: *m/z* calculated for $C_{97}H_{80}O_8$ $[M]^+$: 1373.67 g/mol, found $[M]^+$: 1375.95 g/mol. Anal. Calcd for $C_{97}H_{80}O_8$: C, 84.81; H, 5.87. Found: C, 84.49; H, 5.84.

2.2.4. Compound 4

DBU (60 mg, 0.394 mmol) was added to a mixture of malonate **3** (109 mg, 0.079 mmol), fullerene C_{60} (52 mg, 0.072 mmol), and iodine (46 mg, 0.180 mmol) in dry toluene (15 mL). The reaction mixture was stirred for 24 h at room temperature. The crude product was purified by column chromatography (toluene then hexane:CH_2Cl_2, 1:1) to give the desired product **4** as a black powder (62 mg, 41%).

^1H NMR (δ ppm, 400 MHz, $CDCl_3$): 8.16 (d, 4H, *J* = 9.2), 8.10 (m, 8 H), 8.03 − 7.92 (m, 20 H), 7.77 (d, 4H, *J* = 7.9), 6.50 (d, 4H, *J* = 2.1), 6.34 (t, 2H, *J* = 2.1), 5.37 (s, 4 H), 3.81 (t, 8H, *J* = 5.6), 3.29 (t, 8H, *J* = 7.4), 1.94 − 1.80 (m, 16 H). ^{13}C NMR (δ ppm, 100 MHz, $CDCl_3$): 163.5 (C), 160.5 (C), 144.5 (C), 144.4 (C), 144.3 (C), 144.0 (C), 143.94 (C), 143.88 (C), 143.1 (C), 142.5 (C), 142.1 (C), 141.4 (C), 141.3 (C), 140.4 (C), 138.6 (C), 136.8 (C), 136.6(C), 131.6 (C), 131.1 (C), 130.0 (C), 128.7 (C), 127.7 (CH), 127.5 (CH), 127.4 (CH), 126.8 (CH), 126.0 (CH), 125.31 (C), 125.26 (C), 125.03 (CH), 124.98 (CH), 124.8 (CH) 123.5 (CH), 107.3 (CH), 101.9 (CH), 71.2 (C), 69.0 (CH2), 68.0 (CH2), 51.7 (C), 33.5 (CH2), 29.5 (CH2), 28.8 (CH2). MALDI-TOF: *m/z* calculated for $C_{157}H_{78}O_8$ $[M+H]^+$: 2093.31 g/mol, found $[M+H]^+$: 2093.161 g/mol. Anal. Calcd for $C_{157}H_{78}O_8$: C, 90.12; H, 3.76. Found: C, 89.71; H, 3.99.

2.2.5. Ethyl 4-(4-formylphenoxy)butanoate 5

Compound **5** was synthesized as previously reported in the literature [34]. The product **5** was obtained as a pale yellow oil (1.101 g, 73%).

^1H NMR (δ ppm, 400 MHz, $CDCl_3$): 9.88 (s, 1 H), 7.83 (d, 2H, *J* = 8.7), 6.99 (d, 2H, *J* = 8.7), 4.13 (q, 2H, *J* = 7.1), 4.1 (t, 2H, *J* = 6.2), 2.53 (t, 2H, *J* = 7.2), 2.15 (quint, 2H, *J* = 6.7), 1.26 (t, 3H, *J* = 7.1). ^{13}C NMR (δ ppm, 100 MHz, $CDCl_3$): 190.9 (CHO), 173.1 (CO), 164.0 (C), 132.1 (CH), 130.1 (C), 114.8 (CH), 67.2 (CH_2), 60.6 (CH_2), 30.7 (CH_2), 24.5 (CH_2), 14.3 (CH_3).

2.2.6. Synthesis of porphyrin 6

Dichloromethane (50 mL) was placed in a flask under Ar and protected from the light. Compound **5** (267 mg, 1.130 mmol), pyrrole (75 mg, 1.130 mmol) and benzyltributyl ammonium chloride (4 mg, 0.012 mmol) were added and the reaction mixture was stirred for 10 min. Borontrifluoride diethyl etherate (16 mg, 0.113 mmol) was added and the reaction mixture was stirred for 10 min. Finally, DDQ (266 mg, 1.130 mmol) was added and the reaction mixture was stirred for 2 h. Triethylamine (1.5 mL) was added to quench the reaction. The crude product was purified by column chromatography (CH_2Cl_2, CH_2Cl_2:MeOH 99:1) to give the desired product **6** as a purple solid (150 mg, 47%) [34].

^1H NMR (δ ppm, 400 MHz, $CDCl_3$): 8.88 (s, 8 H), 8.12 (d, 8H, *J* = 8.7), 7.27 (d, 8H, *J* = 8.7), 4.29 (t, 8H, *J* = 6.2), 4.25 (q, 8H, *J* = 7.2), 2.70 (t, 8H, *J* = 7.4), 2.31 (quint, 8H, *J* = 6.8), 1.35 (t, 3H, *J* = 7.2), − 2.73 (s, 2 H). ^{13}C NMR (δ ppm, 100 MHz, $CDCl_3$): 173.5 (CO), 158.8 (C), 135.7 (CH), 134.9 (C), 131 (CH), 119.9 (C), 112.8 (CH), 67.2 (CH_2), 60.7 (CH_2), 31.2 (CH_2), 25.0 (CH_2), 14.5 (CH_3).