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

Mireille Vonlanthen, Julio Gonzalez-Ortega, Pasquale Porcu, Andrea Ruiu, Efraín Rodríguez-Alba, Amanda Cevallos-Vallejo, Ernesto Rivera[*]

Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Circuito Exterior Ciudad Universitaria, C.P. 04510, Ciudad de México, Mexico

ARTICLE INFO

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

---

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 (CH_2), 67.3 (CH_2), 41.7 (CH_2), 33.3 (CH_2), 29.4 (CH_2), 28.4 (CH_2). 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, 16H). ^{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 (CH_2), 68.0 (CH_2), 51.7 (C), 33.5 (CH_2), 29.5 (CH_2), 28.8 (CH_2). 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).
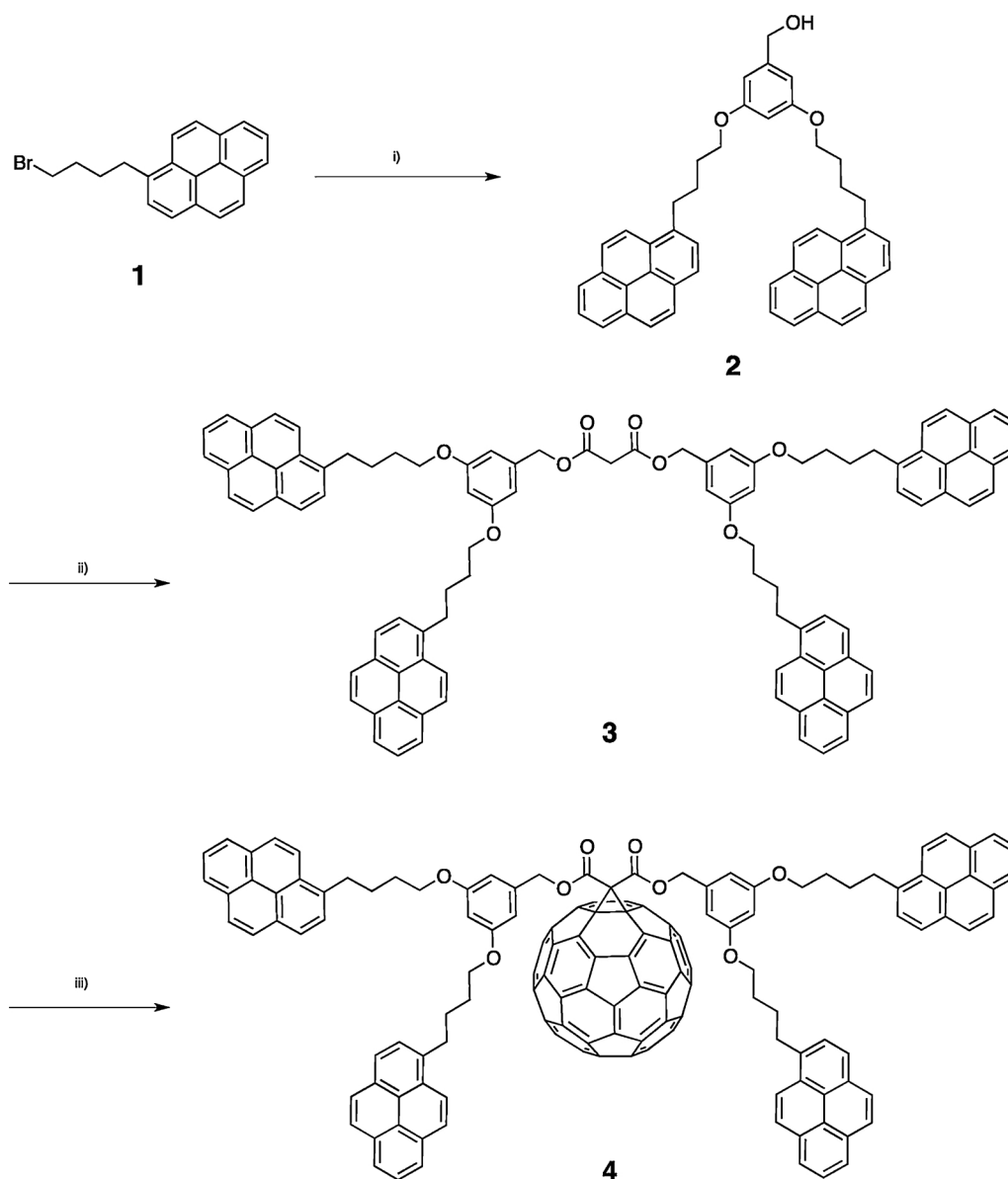
Scheme 1. Synthetic scheme of pyrene-labeled dendrimer **3** and the pyrene-fullerene C$_{60}$ dyad **4**. Reaction conditions: i) 3,5-dihydroxybenzylalcohol, K$_2$CO$_3$, 18-C-6, Acetone, reflux, 72 h, 72% ii) Meldrum's acid, 130 °C, 5 h, 34% iii) fullerene C$_{60}$, I$_2$, DBU, Toluene, rt, 24 h, 41%.

2.2.7. Synthesis of porphyrin 7

Porphyrin **6** (100 mg, 0.088 mmol) and potassium hydroxide (49 mg, 0.881 mmol) were dissolved in a mixture THF/ethanol: 3/1. The reaction mixture was stirred at reflux for 2 h. The solvent was concentrated under vacuum and the residue was taken in water. An aqueous solution of HCl (1 N) was added until pH 5 was reached. The aqueous phase was extracted with THF:CH$_2$Cl$_2$ 1:1 and the organic phase was dried over MgSO$_4$ and concentrated under vacuum. The obtained solid was purified by recrystallization from methanol to give the desired product **7** as a purple solid (70 mg, 78%).

^{1}H NMR (δ ppm, 400 MHz, DMSO-d$_6$): 12.26 (s, br, 4 H), 8.85 (s, 8 H), 8.10 (d, 8H, J = 8.3), 7.35 (d, 8H, J = 8.4), 4.28 (t, 8H, J = 6.2), 2.56 (t, 8H, J = 7.4), 2.19 − 2.10 (m, 8H), −2.9 (s, 2 H).

2.2.8. Synthesis of porphyrin 8

Porphyrin **7** (40 mg, 0.039 mmol) and dendron of the first generation **2** (102 mg, 0.156 mmol) were dissolved in DMF (10 mL). DCC (65 mg, 0.313 mmol) and DPTS (46 mg, 0.156 mmol) were added and the reaction mixture was stirred at room temperature for 5 days. The organic phase was washed with water. The organic phase was dried

over MgSO$_4$ and concentrated under vacuum. The crude product was purified by column chromatography (CH$_2$Cl$_2$, CH$_2$Cl$_2$:MeOH 99:1) to give the desired dendrimer **8** as a purple solid (42 mg, 30%).

^{1}H NMR (δ ppm, 400 MHz, CDCl$_3$): 8.80 (s, 8H), 8.15 (d, 8H, J = 9.3), 8.06 − 8.00 (m, 24 H), 7.97 − 7.92 (m, 16 H), 7.89 − 7.84 (m, 24 H), 7.74 (d, 8H, J = 7.8), 7.14 (d, 8H, J = 8.8), 6.53 (d, 8H, J = 2.2), 6.39 (t, 4H, J = 2.2), 5.10 (s, 8H), 4.17 (t, 8H, J = 6.1), 3.95 (t, 16H, J = 6.1), 3.29 (t, 16H, J = 7.5), 2.69 (t, 8H, J = 7.4), 2.26 (quint, 8H, J = 6.8), 1.98 − 1.83 (m, 32 H), −2.76 (s, 2 H). ^{13}C NMR (δ ppm, 100 MHz, CDCl$_3$): 173.2 (por, C), 160.5 (C), 158.7 (por, C), 138.2 (C), 136.5 (C) 135.7 (por, CH), 134.8 (por, C), 131.4 (C), 130.9 (C), 129.8 (C), 128.6 (C), 127.5 (CH), 127.3 (CH), 126.6 (CH), 125.8 (CH), 125.1 (C), 125.0 (C), 124.9 (CH), 124.8 (CH), 124.7 (CH), 119.8 (por C), 112.8 (por, CH), 106.7 (CH), 101.2 (CH), 67.9 (CH2), 67.0 (por, CH2), 66.5 (CH2), 33.2 (CH2), 31.1 (por CH2), 29.3 (CH2), 28.3 (CH2) 25.0 (por, CH2). MALDI-TOF: m/z calculated for C$_{248}$H$_{206}$N$_4$O$_{20}$ [M]$^+$: 3562.30 g/mol, found [M]$^+$: 3562.579 g/mol. Anal. Calcd for C$_{248}$H$_{206}$N$_4$O$_{20}$: C, 83.62; H, 5.83; N, 1.57. Found: C, 83.23 ; H, 5.99 ; N, 1.55.

2.2.9. Synthesis of porphyrin 9

Porphyrin **8** (20 mg, 0.006 mmol) was dissolved in CHCl$_3$/MeOH and zinc chloride was added. The reaction mixture was stirred at room temperature for 4 h. The reaction mixture was concentrated under vacuum. The crude product was purified by column chromatography (CH$_2$Cl$_2$, CH$_2$Cl$_2$:MeOH 99:1) to give the desired dendrimer **9** as a purple solid (16 mg, 80%)

^{1}H NMR (δ ppm, 400 MHz, CDCl$_3$): 8.85 (s, 8 H), 8.09 (d, 8 H), 7.96 − 7.77 (m, 64 H), 7.69 (d, 8 H), 7.15 (d, 8 H), 6.54 (d, 8 H), 6.40 (t, 4 H), 5.11 (s, 8 H), 4.19 (t, 8 H), 3.96 (t, 16 H), 3.25 (t, 16 H), 2.71 (t, 8 H), 2.27 (m, 8 H), 1.98 − 1.84 (m, 32 H). MALDI–TOF: *m/z* calculated for C$_{248}$H$_{204}$N$_4$O$_{20}$Zn [M]$^+$: 3625.3 g/mol, found [M]$^+$: 3625.02 g/mol. Anal. Calcd for C$_{248}$H$_{204}$N$_4$O$_{20}$Zn: C, 83.62; H, 5.83; N, 1.57. Found: C, 82.56 ; H, 5.59 ; N, 1.57.

3. Results and discussion

3.1. Synthesis of the pyrene-fullerene C$_{60}$ dyad

The dendron of the first generation **2** was synthesized according to a procedure previously reported by our group [15,32]. The benzylic alcohol of the dendron of the first generation **2** was then converted into the malonate dimer **3** by reaction with Meldrum'acid, melting at 130 °C for 5 h. Pyrene-fullerene C$_{60}$ dyad **4** was prepared using the Bingel-Hirsch cyclopropanation reaction between the malonate **3** and fullerene C$_{60}$. The reaction was carried out at room temperature in toluene in the presence of I$_2$ and DBU (Scheme 1).

### 3.2. Synthesis of the pyrene-labeled dendronized porphyrins

The synthesis of the dendrimers containing a porphyrin at the core was performed according to Schemes 2 and 3. The porphyrin core was first synthesized according to a typical Lindsey procedure starting from previously synthesized aldehyde **5** and pyrrole, using benzyltributyl ammonium chloride salt as catalyst to improve the yield [35,36]. The obtained porphyrin ester **6** was hydrolyzed using potassium hydroxide, and a THF-ethanol mixture in the proportion 1–3 as solvent to give the porphyrin acid **7**. The dendrimer **8** was formed by esterification between the porphyrin **7** and the corresponding alcohol of the first generation dendron **2** using DCC and DPTS in DMF. A zinc complex **9** was

formed from porphyrin **8** using zinc acetate in a mixture of chloroform and methanol.

3.3. Characterization of the new dendrimers

All obtained dendrimers were fully characterized by ^{1}H and ^{13}C NMR spectroscopies and the structures were confirmed by MALDI–TOF mass spectrometry. In the ^{1}H NMR spectrum of compound **3**, the singlet at 3.44 ppm corresponds to the protons of the malonate. The integration that account for 2 protons was the indication that both substitutions had occurred. In the ^{13}C NMR of compound **3** a signal was observed at 41.7 ppm corresponding to the malonate. The absence of the malonate signal in the ^{1}H NMR of the fullerene C$_{60}$ derivative **4** indicated that the reaction had taken place. It was proved by the ^{13}C NMR spectrum where various signals accounting for quaternary carbon of the fullerene C$_{60}$ could be observed between 144 and 138 ppm. Additionally, the signal of the malonate at 41.7 ppm disappeared and two new quaternary carbon signals appeared at 71.2 and 51.7 ppm. The structure of compound **4** was further confirmed by MALDI–TOF mass spectrometry; the molecular ion peak was observed at *m/z* = 2093.161 g/mol. This value was very close to the calculated molecular weight for compound **4** (2093.31 g/mol).

For the porphyrin derivatives, the characteristic signal of the NH proton signal of the porphyrin were observed at −2.7 ppm for compound **6** and at −2.9 for the acid **7**. The dendrimer **8** is presenting a well-resolved ^{1}H NMR spectrum. All the signals of the dendron as well as those of the porphyrin moiety were identified with small chemical shift modification. The integration confirms that the obtained compound was fully substituted. The signal at 8.8 ppm appears as a singlet, indicating that only one symmetric porphyrin species was present. The structure of compound **8** was further confirmed by MALDI–TOF mass spectrometry; the molecular ion peak was observed at *m/z* = 3562.579 g/mol. This value was very close to the calculated molecular weight for compound **8** (3562.30 g/mol). The structure of zinc complex **9** was confirmed as well by MALDI–TOF mass spectrometry. The obtained molecular ion peak was observed at 3625.02 g/mol that was very close to the calculated value (3625.3 g/mol).
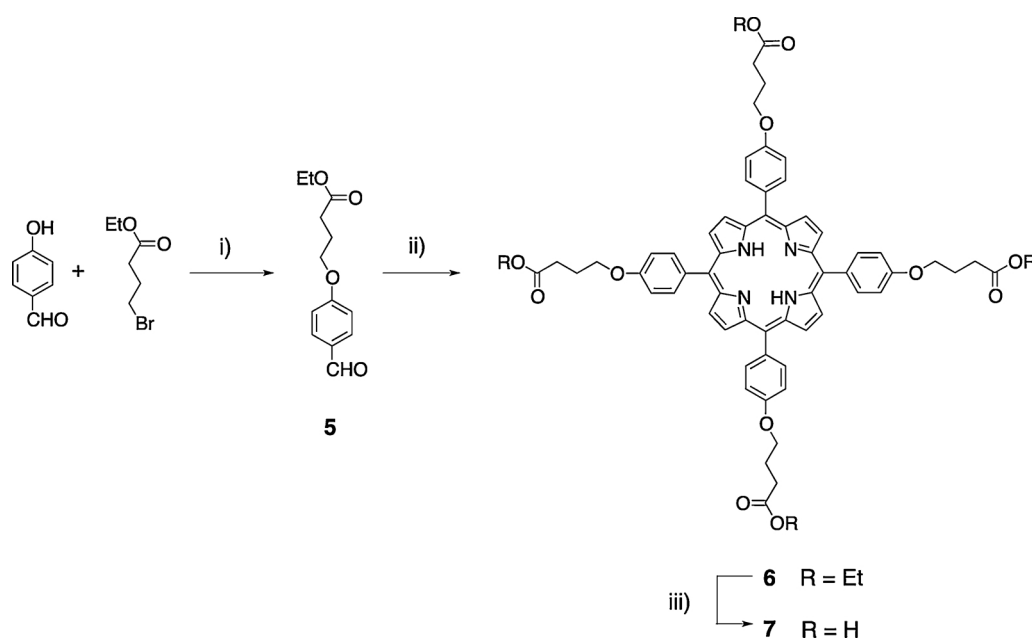
Scheme 2. Synthetic scheme of the porphyrin core **7**. Reaction conditions: i) K$_2$CO$_3$, DMF, 100 °C, 2 h, 73% ii) 1. Pyrrol, benzyltributylammonium chloride, CH$_2$Cl$_2$, rt, 10 min; 2. BF$_3$·OEt, rt, 10 min; 3. DDQ, rt, 2 h, 47% iii) KOH, THF/EtOH 3/1, reflux, 2 h, 78%.
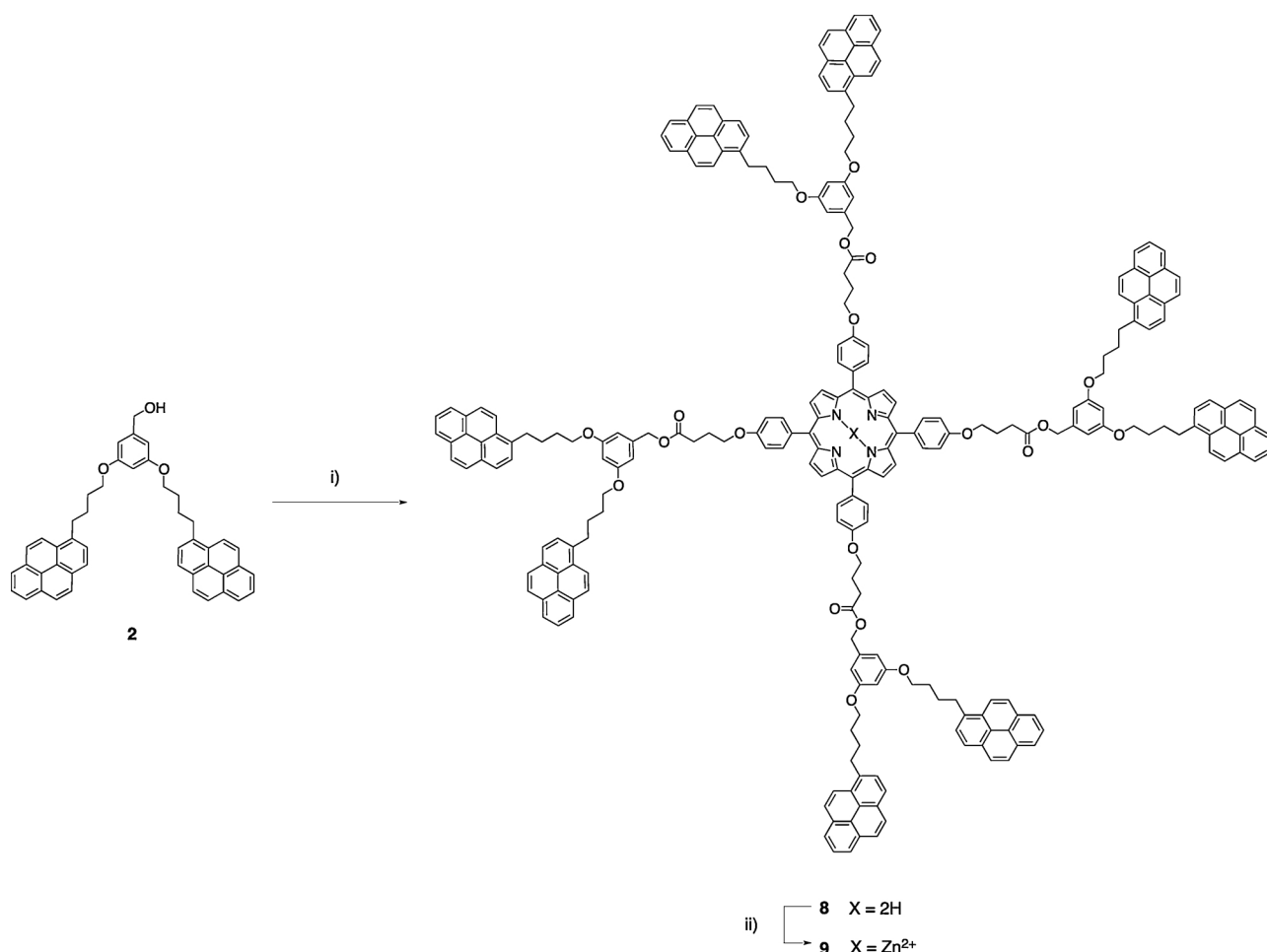
Scheme 3. Synthetic scheme of the porphyrin dendrimer **8** and metalloporphyrin dendrimer **9**. Reaction conditions i) **7**, DCC, DPTS, DMF, rt, 5d, 30% ii) Zn (OAc)$_2$·H$_2$O, CHCl$_3$/MeOH 1/1, rt, 4 h, 80%.

3.4. Optical and photophysical properties of the dendrimers

The malonate pyrene-labeled dendrimer **3** and the pyrene-fullerene C$_{60}$ dyad **4** were dissolved in toluene for the photophysical measurements while solutions of the dendronized porphyrin **8** and **9** were prepared in THF. The absorption spectra are presented in Figs. 1 and 2. Since all the compounds are based on pyrene chromophore, the main characteristic of all spectra is the appearance of a band at 344 nm corresponding to the S$_0$→S$_2$ transition. The absorption spectrum of the malonate **3** shows exclusively the typical absorption bands of pyrene and is very similar to the spectra of the model compound 1-pyrenbutanol. For the fullerene C$_{60}$ derivative **4**, the absorption spectrum is compared to the sum of the two individual components, fullerene C$_{60}$ and dendrimer **3** (See Supporting information Figs. S1 and S2). The overlap is not complete for the higher energy wavelengths of the spectra indicating that the pyrene unit slightly interacts with the fullerene C$_{60}$ unit in the ground state. The absorption band at 330 nm is more intense than for the parent malonate **3** due to the intense absorption of fullerene C$_{60}$ in this region. Moreover, the extended absorption in the visible region is attributed to the fullerene cage. The excitation spectrum of the fullerene derivative **4** was recorded in toluene at 376 nm. The resulting spectrum does not overlap exactly its absorption spectrum confirming that the two chromophores are slightly interacting in the ground state (See Supporting information Fig. S3).

In the case of the porphyrin derivatives **8** and **9**, the typical Soret absorption band of a porphyrin moiety was present at 420 nm. The typical Q bands of the porphyrin were observed at 518, 555, 598 and 652 nm for the free porphyrin **8,** and at 560 and 599 nm for the
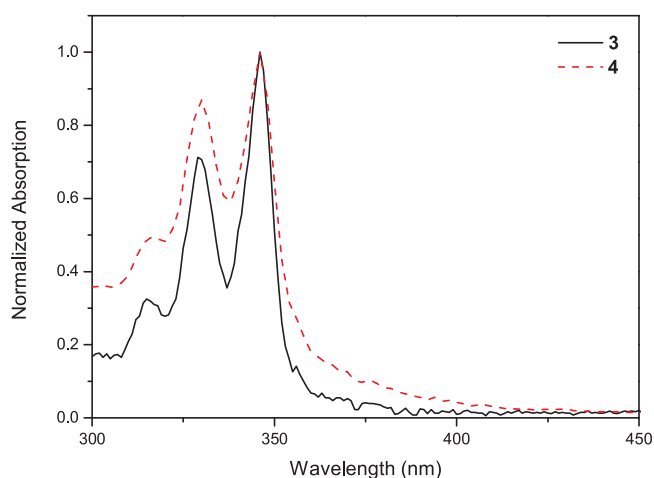

Fig. 1. Normalized absorption spectra of pyrene-labeled dendrimer **3** (black) and fullerene C$_{60}$ adduct **4** (red), recorded in toluene. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

metallated porphyrin **9**, indicating a successful metallation reaction. The absorption spectra of compounds **8** and **9** are corresponding to the sum of the spectra of their respective components. Moreover their excitation spectra were measured at 720 and 600 nm, respectively. The obtained excitation spectra were superposed with their respective
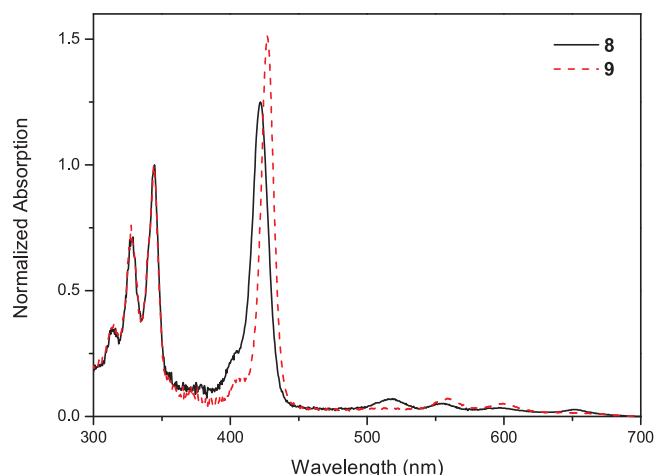
Fig. 2. Normalized absorption spectra of the pyrene-dendronized porphyrins **8** (black) and **9** (red) in THF. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
Extinction coefficients, quantum yields and FRET efficiencies for compounds **3**, **4**, **8** and **9**.

Compound	λ max abs (nm) ε (M^{-1} cm^{-1})	Φ pyrene unit (λ_{ex} = 344 nm)[a]	Φ acceptor unit (λ_{ex} = 344 nm)[b]	FRET[c]
3	344/ 148'000	0.58	–	–
4	346/146'000	0.005	–	0.99
8	344/304'000 422/386'000	0.0025	0.0015	0.99
9	344/311'000 427/465'000	0.0035	0.0015	0.99

Measurements were done in toluene for compound **4** and in THF for compounds **8** and **9**.

[a] Quantum yields were determined relative to pyrene (Φ = 0.32) in cyclohexane and quinine sulfate (Φ = 0.546) in 0.05 M H$_2$SO$_4$.

[b] Quantum yield of the acceptor unit having undergone FRET from an excited pyrene.

[c] FRET efficiencies were calculated according to the following equation : FRET = 1 – (I_{DA}/I_D), where I_{DA} is the relative fluorescence intensity of the donor (pyrene) in presence of the acceptor and I_D is the relative fluorescence intensity of the donor in absence of the acceptor.

absorption spectra (See Supporting information Figs. S4 and S5) As a result, it was concluded that no interaction between the pyrene units and the porphyrin moiety are present in the ground state. Molar extinction coefficients for all relevant absorption bands are reported in Table 1.

Fluorescence measurements were performed in solution at a concentration of pyrene units of 1.25 10^{-6} M in order to keep the absorbance around 0.04 at 346 nm. The steady state emission spectrum of compound **3** is showing the typical band of pyrene "monomer" emission at 375 nm as well as a broad emission band centred at 480 nm corresponding to the excimer emission of pyrene (Fig. 3). The excitation spectra were measured at 376 nm for the monomer emission as well as at 480 nm for the excimer emission (See Supporting information Fig. S6). Since the obtained spectra are identical, we can conclude that the formation of excimer is dynamic and no preorganization is present in the ground state [10,11]. A quantum yield of 0.58 was calculated for compound **3** for the sum of the monomer and excimer emission. The ratio of the excimer emission intensity measured at 480 nm (I_E) and the monomer emission intensity measured at 376 nm (I_M), I_E/I_M is function of the number of pyrene moieties in the construct as well as of the flexibility of the backbone. For compound **3**, the obtained I_E/I_M was 3.0. The value is similar to a second generation dendrons containing 4 pyrene units previously reported by our group [32].
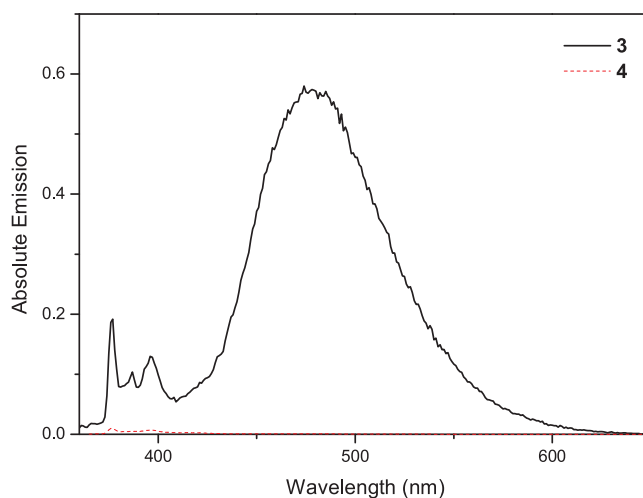

Fig. 3. Absolute emission of dendrimer **3** (black) and fullerene C60 adduct **4** (red), recorded in toluene. Excitation wavelength: 346 mn. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
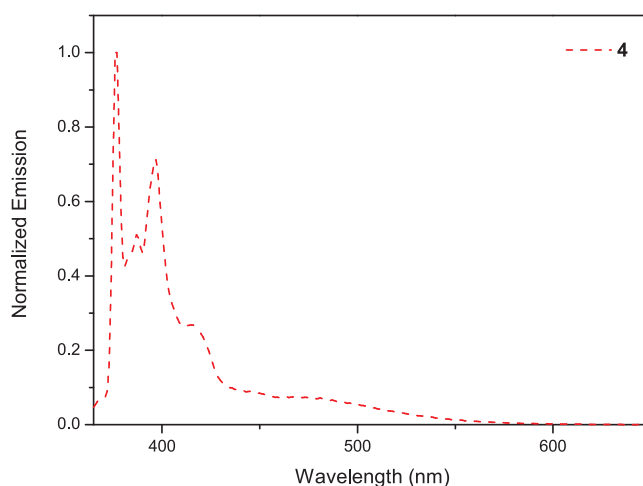

Fig. 4. Normalized emission of the fullerene C60 adduct **4** recorded in toluene. Excitation wavelength: 346 mn.

In the case of compound **4**, it was observed that the fluorescence emission of the pyrene unit is almost completely quenched by the presence of the fullerene C$_{60}$ moiety (Figs. 3 and 4). This quenching is an indication that the fluorescence deactivation occurs through fast energy transfer from the excited pyrene to the fullerene C$_{60}$ core. The Förster radius was calculated to be 29 Å (see Supporting Information). This distance has been shown to be almost equal to the expected distance in the extended conformation for a similar type of dendrimers, which was estimated to be about 30 Å [32]. Moreover, it is expected that those compounds in solutions are not found in an extended conformation, $\pi-\pi$ interactions between the pyrene moiety and the fullerene C$_{60}$ core are allowed inside the dendrimer, thereby reducing the distance between the donor and the acceptor. Therefore an energy transfer is feasible in compound **4**. The energy transfer is faster than the formation of excimers since almost no residual emission of the excimer could be observed. However, since the intrinsic emission of fullerene C$_{60}$ is very weak, no emission could be seen [27,37].

The fluorescence emission study of dendronized porphyrin **8** and **9** was performed in THF following the same methodology as for compound **3** and **4** (Fig. 5). The emission of the pyrene units was almost completely quenched and typical emission of the porphyrin moiety was observed at 658 nm with a quantum yield of 0.0015 (Table 1). The
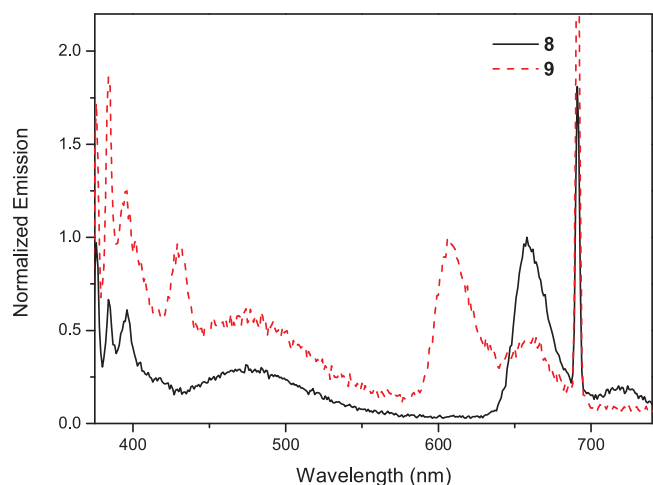
Fig. 5. Emission spectra of the pyrene-dendronized porphyrins **8** (black) and **9** (red) in THF. Excitation wavelength: 344 mn. The sharp peak at 688 nm corresponds to the harmonic (double the excitation wavelength). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

quantum yield of the pyrene units was reduced to a value of 0.0025 (Φ (pyrenebutanol) = 0.52). The observed decrease in the intensity of the emission of the pyrene units is due to a highly efficient FRET process occurring from the pyrene to the porphyrin moiety. The calculated efficiency of the FRET process was of 99%. A Förster radius of 52 Å for the FRET process between pyrene and porphyrin has been reported previously. This distance has been shown to be larger than the expected distance in the extended conformation for similar type of dendrimers [32]. As for the fullerene C_{60} derivatives, it is not expected that those compounds are found in a folded conformation when placed in solution, thereby reducing the effective distance between the chromophores. Similar emission spectrum was obtained for the zinc-coordinated porphyrin **9**. The emission of the pyrene units was almost completely quenched and typical emission of the zinc-porphyrin moiety was observed at 606 nm. As for the metal free porphyrin derivative, efficient energy transfer was observed.

4. Conclusion

Pyrene-labeled dendrons were synthesized and used to form new dendrimers containing a fullerene C_{60} or a porphyrin moiety at the core. The characterization was performed through NMR spectroscopy, MALDI-TOF spectrometry and their optical and photophysical properties were studied. In the ground state, no interaction between the pyrene units and the porphyrin was observed whereas a slight interaction was observed between pyrene units and fullerene C_{60}. An important decrease of the fluorescence intensity of the pyrene unit was observed in the presence of the fullerene C_{60} or porphyrin acceptor. Therefore efficient FRET process from pyrene to fullerene C_{60}, as well as from pyrene to porphyrin, was observed. The obtained compounds are acting as efficient light harvesting antennas.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi: https://doi.org/10.1016/j.synthmet.2018.09.001.

References

[1] D.L. Andrews, J. Mater. Res. 27 (2012) 627–638.
[2] Y. Zeng, Y.-Y. Li, J. Chen, G. Yang, Y. Li, Chem. Asian J. 5 (2010) 992–1005.
[3] G.D. D'Ambruoso, D.V. McGrath, Adv. Polym. Sci. (2008) 87–147.
[4] V. Balzani, P. Ceroni, M. Maestri, V. Vicinelli, Curr. Opin. Chem. Biol. 7 (2003) 657–665.
[5] D. Astruc, E. Boisselier, C. Ornelas, Chem. Rev. 110 (2010) 1857–1959.
[6] D. Astruc, Nat Chem 4 (2012) 255–267.
[7] V. Viswanath, K. Santhakumar, J. Photochem. Photobiol. B 173 (2017) 61–83.
[8] N. Ibrayev, E. Seliverstova, N. Nuraje, A. Ishchenko, Mater. Sci. Semicond. Process. 31 (2015) 358–362.
[9] F.M. Winnik, Chem. Rev. 24 (1993) 587–614.
[10] J. Duhamel, Acc. Chem. Res. 39 (2006) 953–960.
[11] J. Duhamel, Polymers 4 (2012) 211–239.
[12] J. Yip, J. Duhamel, G.J. Bahun, A. Adronov, J. Phys. Chem. B 114 (2010) 10254–10265.
[13] T.M. Figueira-Duarte, K. Müllen, Chem. Rev. 111 (2011) 7260–7314.
[14] H. Imahori, Y. Sakata, Adv. Mater. 9 (1997) 537–546.
[15] D.M. Guldi, M. Prato, Acc. Chem. Res. 33 (2000) 695–703.
[16] R.A. Marcus, Angew. Chem. Int. Ed. 32 (1993) 1111–1121.
[17] A. Harriman, J.P. Sauvage, Chem. Soc. Rev. 25 (1996) 41–48.
[18] M.G. Walter, A.B. Rudine, C.C. Wamser, J. Porphyrins Phthalocyanines 14 (2010) 759–792.
[19] M.V. Martínez-Díaz, G. de la Torre, T. Torres, Chem. Commun. 46 (2010) 7090–7108.
[20] J.C. Bertran, F.-P. Montforts, Eur. J. Org. Chem. 2017 (2017) 1608–1617.
[21] H.L. Anderson, Chem. Commun. (1999) 2323–2330.
[22] V. Balzani, P. Ceroni, M. Maestri, C. Saudan, V. Vicinelli, Top. Curr. Chem, Springer, Berlin Heidelberg, Berlin, Heidelberg, 2003, pp. 159–191.
[23] K.L. Wooley, C.J. Hawker, J. Fréchet, F. Wudl, S. Srdanov, S. Shi, C. Li, M. Kao, J. Am. Chem. Soc. 115 (1993) 9836–9837.
[24] T. Chuard, R. Deschenaux, J. Mater. Chem. 12 (2002) 1944–1951.
[25] S.A. Backer, K. Sivula, D.F. Kavulak, J.M.J. Fréchet, Chem. Mater. 19 (2007) 2927–2929.
[26] A. Hirsch, O. Vostrowsky, Top. Curr. Chem. 217 (2001) 51–93.
[27] R.B. Martin, K. Fu, H. Li, D. Cole, Y.-P. Sun, Chem. Commun. (2003) 2368–2369.
[28] B.C. Thompson, J.M.J. Fréchet, Angew. Chem. Int. Ed. 47 (2008) 58–77.
[29] M.-S. Choi, T. Aida, T. Yamazaki, I. Yamazaki, Chem. Eur. J. 8 (2002) 2668–2678.
[30] D. Yao, X. Zhang, O. Mongin, F. Paul, C.O. Paul-Roth, Chem. Eur. J. 22 (2016) 5583–5597.
[31] G. Zaragoza-Galán, J. Ortíz-Palacios, B.X. Valderrama, A.A. Camacho-Dávila, D. Chávez-Flores, V.H. Ramos-Sánchez, E. Rivera, Molecules 19 (2014) 352–366.
[32] G. Zaragoza-Galán, M.A. Fowler, J. Duhamel, R. Rein, N. Solladié, E. Rivera, Langmuir 28 (2012) 11195–11205.
[33] G. Zaragoza-Galán, M. Fowler, R. Rein, N. Solladié, J. Duhamel, E. Rivera, J. Phys. Chem. C 118 (2014) 8280–8294.
[34] I.D. Kostas, A.G. Coutsolelos, G. Charalambidis, A. Skondra, Tetrahedron Lett. 48 (2007) 6688–6691.
[35] M.I. Sluch, I. Samuel, M.C. Petty, Chem. Phys. Lett. 280 (1997) 315–320.
[36] F. Li, K. Yang, J.S. Tyhonas, K.A. MacCrum, J.S. Lindsey, Tetrahedron 53 (2003) 12339–12360.
[37] R.B. Martin, K. Fu, Y.-P. Sun, Chem. Phys. Lett. 375 (2003) 619–624.