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A dendritic fullerene–porphyrin dyad

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We describe the synthesis, characterization and photophysical properties of a fullerene derivative whose structure includes a Zn-porphyrin and a second generation liquid-crystalline (LC) dendrimer. The size of the fullerene and porphyrin units with respect to the size of the LC dendrimer prevents the formation of liquid-crystalline phases. However, this system gives interesting photoinduced electron transfer phenomena. Compound **1** has been investigated by steady state and time resolved fluorescence as well as transient absorption spectroscopy in polar and apolar solvents. We demonstrate that the fluorescence of the porphyrin unit in **1** is quenched compared to the Zn-tetraphenylporphyrin used as reference. Femto- and picosecond transient absorption permit to identify the formation of a radical ion pair while nanosecond experiments allowed the determination of the charge recombination lifetimes.

Introduction

Fullerene-based photoactive materials have been extensively studied for photovoltaic[1–5] and light emitting diode[6] applications. Various donors as tetrathiafulvalene (TTF),[7,8] conjugated oligomers,[2,3,9–15] porphyrins[16–19] and ferrocenes[20–22] have been associated to C_{60} to obtain efficient intramolecular electron and/or energy transfer.

We previously demonstrated that addition of liquid-crystalline addends *via* the Bingel[23] or 1,3-dipolar cycloaddition[24–26] reactions on C_{60} leads to mesomorphic materials.[27–29] In most cases, the liquid-crystalline properties of the addend (malonate or aldehyde) are transferred to the fullerene without notable change in the mesomorphism.

This synthetic strategy was also applied for the preparation of liquid-crystalline C_{60} derivatives containing electron donor moieties (ferrocene,[30–32] oligophenylenevinylene[12] and TTF[33]). This approach is of particular interest since such materials spontaneously form ordered assemblies that could be oriented to give high-performance thin films.

Porphyrins are the molecules chosen by Nature to transform light into chemical energy and so due to their exceptional optical and electronic properties they have been extensively used as electron donor associated with fullerene.[16–19]

We report, herein, the synthesis and photophysical behavior of the fulleropyrrolidine **1** containing a Zn-porphyrin (ZnP) and a second-generation liquid-crystalline dendrimer (Fig. 1).

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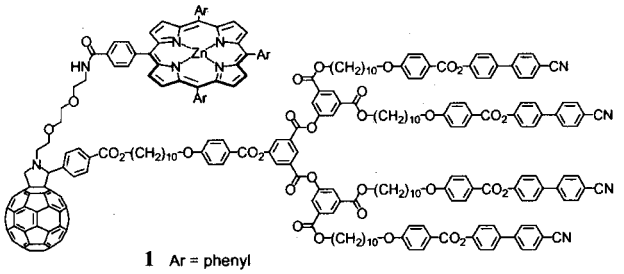
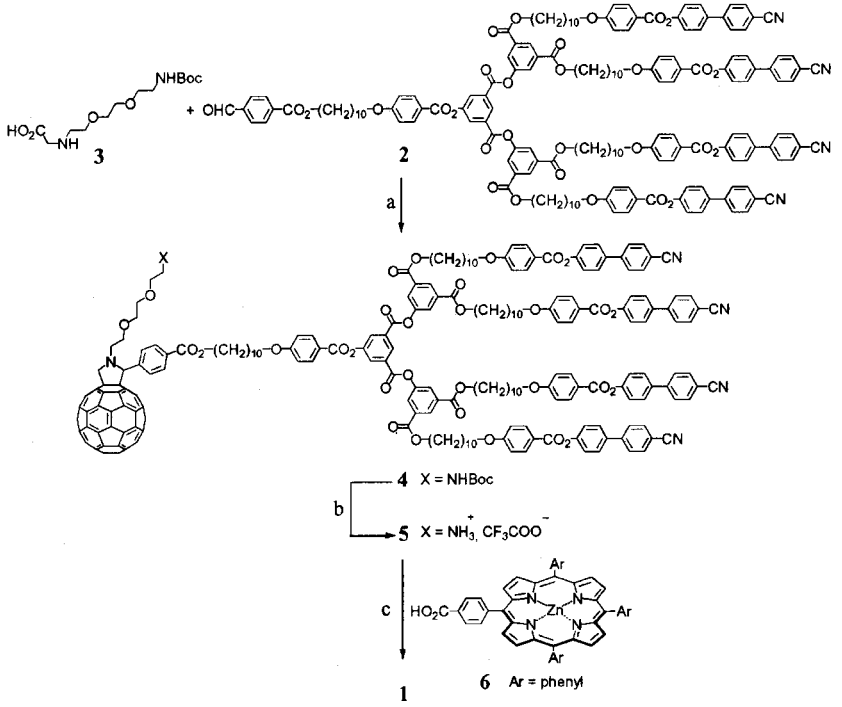


Fig. 1 The structure of the fulleropyrrolidine **1** containing a Zn-porphyrin (ZnP) and a second-generation liquid-crystalline dendrimer.

Results and discussion

Synthesis

The synthesis of the C_{60}–ZnP conjugate **1** is depicted in Scheme 1. A reaction between the cyanobiphenyl based dendrimer **2**[28] and amino acid **3**[34] in the presence of C_{60} led to the amino-protected derivative **4**. The isolated yield of 79% for **4** is unusually high for the synthesis of a monoadduct of C_{60}. In fact, most cycloadditions to C_{60} start producing multiple adducts, making it not profitable to prolong the reaction times after the monoadduct has reached 20–40% yields. In the present case, the size of the cyanobiphenyl-based dendrimer probably inhibits the formation of higher adducts, thus leading to impressive yields of the monoadduct **4**. The amino group in **4** was quantitatively deprotected with trifluoroacetic acid (TFA) to give **5**. Finally, reaction between the ammonium salt **5** and the zinc porphyrin **6** in the presence of 1-hydroxybenzotriazole (HOBT), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC) and triethyl amine led to **1**. ZnP **6** was prepared, using a slightly modified Adler's procedure,[35] by a mixed condensation reaction of benzaldehyde, methyl terephthalaldehyde, and pyrrole in the presence of $Zn(OAc)_2$ under reflux in propionic acid, followed by chromatographic separation and hydrolysis of the ester group.



Scheme 1 (a) C_{60}, toluene, reflux, 1 h, 79%. (b) Trifluoroacetic acid (TFA), CH_2Cl_2, rt, 1 h, 95%. (c) Et_3N, HOBt, EDC, CH_2Cl_2, rt, 24 h, 25%.

Liquid-crystalline properties

The thermal and liquid-crystalline properties of **1** and **2** were investigated by polarized optical microscopy (POM) and differential scanning calorimetry (DSC). The phase transition temperatures and enthalpies are reported in Table 1.

The dendrimer **2** showed a smectic A phase which was identified by POM from the observation of focal-conic and homeotropic textures. Compound **1** was found to be non-mesomorphic.

The fact that **1** does not exhibit liquid-crystalline properties can be explained by the bulkiness of the porphyrin and C_{60} moieties. We demonstrated before that the dendrimer of second generation could camouflage efficiently the fullerene moiety and even the couple fullerene–ferrocene led to mesomorphic materials.[28,31,36] This is not possible with the tetraphenylporphyrin.

Photophysical properties

First we tested the ZnP fluorescence of the C_{60}–ZnP derivative **1** relative to that shown by a ZnP reference (*i.e.*, zinc tetraphenylporphyrin) in a variety of solvents by either photoexciting into the ZnP Soret- or Q-band. Initially, we probed them in toluene, THF, benzonitrile and DMF. While the reference showed nearly constant fluorescence quantum yields (0.040 ± 0.005) for the two emission peaks at 600 and 650 nm, the corresponding yields in **1** were an order of magnitude lower, that is, 10^{-3}. Interestingly, despite the polarity change, when going, from toluene (2.38) and THF (7.6) to benzonitrile (24.8), the fluorescence quantum yields revealed only minor changes—see Fig. 2 and Table 2. Similar results came from fluorescence lifetime measurements.[37] For ZnP the corresponding fluorescent decays yielded invariant lifetimes of approximately 2.1 ± 0.1 ns.

Table 1 Phase transition temperatures[a] and enthalpies of **2** and **1**

Compound	Tg/°C	Transition	T/°C	ΔH/kJ mol^{-1}
2[28]	35	$S_A \rightarrow I$	185	12.8
1	.....	$Cr \rightarrow I$	169	12.9

[a] Tg = glass transition temperature, S_A = smectic A phase, Cr = semicrystalline solid, I = isotropic liquid. Temperatures are given as the onset of the peak obtained during the second heating run. Tgs are determined during the first cooling run.

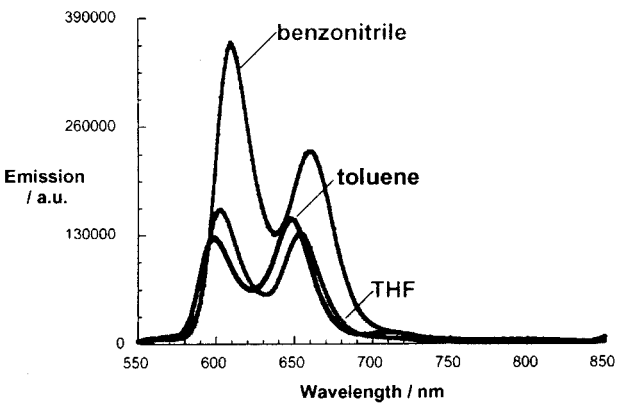


Fig. 2 Steady-state fluorescence spectra of **1** in toluene, THF and benzonitrile solution with matching optical absorption (*i.e.*, 0.2) at the 425 nm excitation wavelength.

Compound **1**, on the other hand, gave rise to much shorter ZnP radiative decays, which are about 0.38 ± 0.1 ns. Note

Table 2 Summary of the photophysical data[a] of **1** in room temperature solutions

Solvent	Φ_F	τ_F/ns	τ_S[b]/ns	Φ_R	τ_R/ns
Toluene	1.6×10^{-3}	0.41	0.46		
THF	2.2×10^{-3}	0.36	0.34	0.21	330
Benzonitrile	2.2×10^{-3}	0.38	0.36	0.15	290
DMF				0.12	240

[a] Φ_F = Fluorescence quantum yields, τ_F = fluorescence decay, τ_S = singlet decay, Φ_R = radical pair quantum yield, τ_R = radical pair decay. [b] Derived from picosecond transient absorption measurements.

the lack of evidence for an intramolecular transduction of singlet excited energy between the ZnP and C_{60} components in THF, benzonitrile and DMF. This conclusion is based on the absence of C_{60} fluorescence that is known to maximize around 720 nm.

Next we started to complement the fluorescence experiments with transient absorption measurements. ZnP and **1** were photoexcited with short (*i.e.*, 150 fs or 20 ps) and long (*i.e.*, 8 ns) laser pulses at 532 nm. Regardless of the solvent, in the ZnP reference the characteristic singlet–singlet features evolve, including bleaching of the Q-band around 550 nm and a broad maximum that tails out into the 800 nm range. These singlet features decay rather rapidly through intersystem crossing to populate the corresponding triplet manifold.[38] Singlet decays and triplet growths are concomitant to give rise to an intersystem crossing rate constant of 2.3 ± 0.5 ns. Transient characteristic of the oxygen sensitive ZnP triplet excited state (*i.e.*, reacts with nearly diffusion controlled dynamics with molecular oxygen to produce singlet oxygen) is a maximum at 840 nm. During the picosecond experiments, compound **1** showed initially the same singlet excited state features, which confirm the successful photoexcitation of the ZnP component in **1**. However, instead of showing the typical spectroscopic and kinetic features associated with an intersystem crossing process, the singlet–singlet transitions decayed rather quickly within the first few hundred picoseconds. The analysis of the transient absorption changes at several wavelengths led to kinetics that are virtually identical to those derived from the fluorescence decay measurements.[39] In other words, both experimental approaches gave corroborating results. The two major products might be either a fullerene singlet excited state or a charge separated radical ion pair state as a consequence of an intramolecular energy or electron transfer event, respectively.[40] Considering that the photoproduct reveals all the characteristics of a ZnP radical cation (*i.e.*, broad absorption between 600 and 750 nm, Fig. 3) and of a fullerene radical anion (*i.e.*, absorption at 1000 nm) the electron transfer route seems to occur.[41]

Since on the time scale of our femto- or picosecond experiments no appreciable decay of the charge separated radical ion pair state is registered, we turned to nanosecond experiments. Not only this technique allowed determining the charge recombination dynamics with lifetimes on the order of several hundred nanoseconds (Fig. 4), moreover, the true quantum yields of charge separation were established through the comparative method (*i.e.*, using the known quantum yields and extinction coefficient of the fullerene triplet excited state as a standard) and are on the order of about 20% (see Table 2).

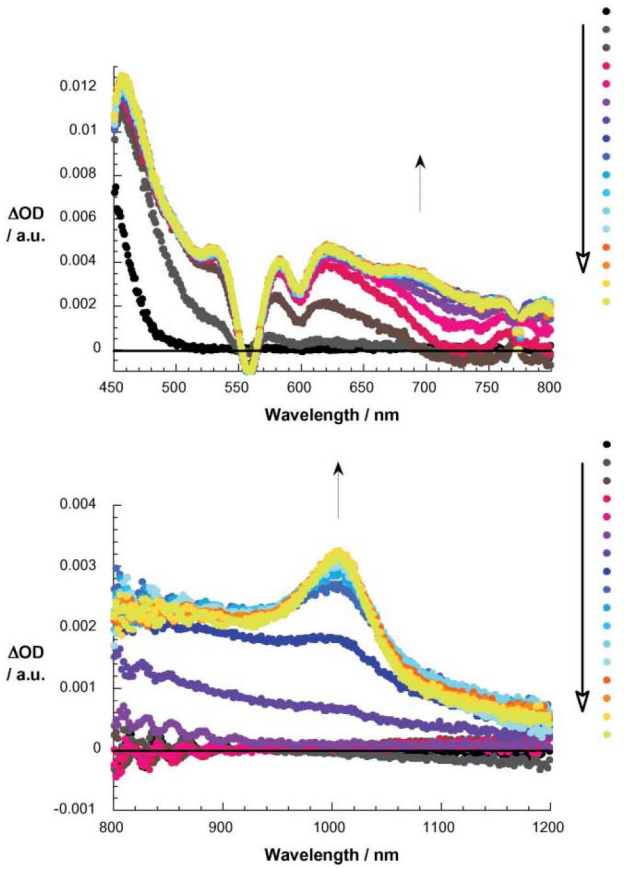


Fig. 3 Femtosecond transient absorption spectra (visible—upper part and near-infrared region—lower part) obtained upon laser flash photolysis (387 nm) of **1** (*ca.* 1.0×10^{-5} M) in deoxygenated THF with several time delays between 0 and 1500 ps at room temperature, indicating the formation of the ZnP π-radical cation and the C_{60} π-radical anion absorption.

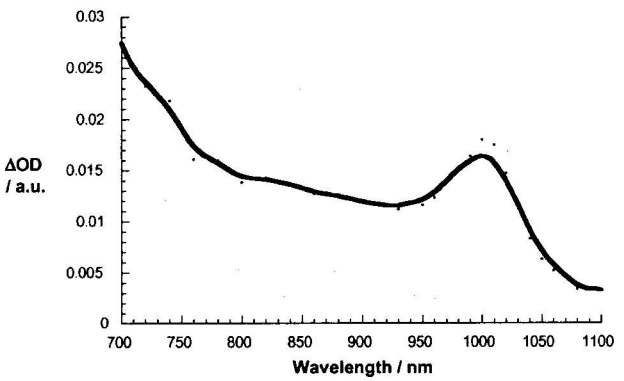


Fig. 4 Nanosecond transient absorption spectra (near-infrared region) obtained upon laser flash photolysis (387 nm) of **1** (*ca.* 1.0×10^{-5} M) in deoxygenated benzonitrile with 50 ns time delay at room temperature, indicating the C_{60} π-radical anion absorption.

Conclusions

We have described the synthesis, characterization and photophysical properties of a fulleropyrrolidine bearing a Zn-porphyrin and a liquid-crystalline dendrimer of second generation. The

fullerene derivative **1** did not exhibit mesomorphic properties probably because of the bulkiness of the fullerene and porphyrin moieties with respect to the size of the dendrimer. Probably, a third generation LC-dendrimer will be more efficient in obtaining LC phases. However, this system show very interesting photoinduced electron transfer phenomena. Compound **1** was investigated by steady state and time resolved fluorescence as well as transient absorption spectroscopy in polar and apolar solvents. We demonstrated that the fluorescence of the porphyrin unit in **1** is quenched compared to the Zn-tetraphenylporphyrin used as reference. Femto- and picosecond transient absorption permitted to identify the formation of a radical ion pair while nanosecond experiments allowed the determination of the charge recombination lifetimes.

Experimental

Materials

[60]Fullerene was purchased from BuckyUSA, (99.5%), and all other reagents and solvents were used as purchased from Fluka, Aldrich, J. T. Baker and Cambridge Isotope Laboratories. The silica gel NM Kieselgel 60 (70–230 mesh ASTM) was obtained from Macherey–Nagel and was used as the support for any column chromatographies. Coumpounds **2**,[28] **3**,[34] **4**,[31] and **5**[31] were prepared as reported in the literature.

Techniques

Transition temperatures (onset point) and enthalpies were determined with a differential scanning Mettler DSC 822 calorimeter, under N_2/He, at a rate of 10 °C min^{-1}. Optical studies were conducted using a Zeiss-Axioscope polarizing microscope equipped with a Linkam-THMS-600 variable-temperature stage under N_2. Steady-state emission and excitation spectra were recorded with a SLM 8100 spectrofluorometer. Time-resolved emission fluorescence lifetimes were measured with a laser strobe fluorescence lifetime spectrometer (Photon Technology International) with 337 nm laser pulses from a nitrogen laser fiber-coupled to a lens-based T-formal sample compartment equipped with a stroboscopic detector. Details of the laser strobe systems are described on the manufactures web site, http://www.pti-nj.com. Fluorescence spectra were measured at room temperature. Femtosecond transient absorption studies were performed with 387 nm laser pulses (1 kHz, 150 fs pulse width) from an amplified Ti:Sapphire laser system. Picosecond laser flash photolysis experiments were carried out with 355 nm laser pulses from a mode-locked, Q-switched Quantel YG-501 DP Nd:YAG laser system (pulse width 18 ps, 2–3 mJ $pulse^{-1}$). Nanosecond laser flash photolysis experiments were performed with laser pulses from a Molectron UV-400 nitrogen laser system (337.1 nm, 8 ns pulse width, 1 mJ $pulse^{-1}$). FT-IR spectra were recorded on Jasco spectrophotometer FT/IR-200 using KBr powder (DRIFT system). UV spectra were recorded on a Varian Cary5000 spectrophotometer. ^1H and ^{13}C spectra were recorded on a Varian Gemini-200 spectrometer at 200 and 50 MHz, respectively, with TMS as internal standard. Chemical shifts are given in ppm relative to that of tetramethylsilane. Abbreviations: column chromatography = CC; 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride = EDC; 1-hydroxybenzotriazole = HOBT.

Synthesis of compound 1

A solution of ZnP carboxylic acid **6** (5.6 mg, 7.8 μmol), EDC (3.0 mg, 15.6 μmol) and HOBT (2.1 mg, 15.6 μmol) in CH_2Cl_2 (2 mL) was stirred at rt for 15 min, and then added dropwise to a suspension of **5** (35 mg, 9.4 μmol) and Et_3N (3.0 μL, 18.7 μmol) in CH_2Cl_2 (2 mL). The mixture was stirred at room temperature for 24 h. The product was purified by CC (toluene–ethyl acetate 85 : 15), precipitated from CH_2Cl_2 solution using hexane, and then washed with Et_2O. Yield: 25% (10.2 mg). ^1H NMR ($CDCl_3$): δ = 8.93–8.78 (m, 9H), 8.57 (t, J = 1.4 Hz, 2H), 8.40 (d, J = 7.8 Hz, 2H), 8.29 (d, J = 1.4 Hz, 2H), 8.23 (d, J = 7.8 Hz, 2H), 8.17–7.97 (m, 22H), 7.84 (d, J = 8.1 Hz, 2H), 7.78–7.54 (m, 33H), 7.33–7.20 (m, 8H), 6.98–6.86 (m, 8H), 4.80 (d, J = 9.3 Hz, 1H), 4.59 (s, 1H), 4.37–4.22 (m, 10H), 4.12 (t, J = 5.6 Hz, 2H), 4.40–4.20 (m, 13H), 4.18 (s, 5H), 4.06–3.71 (m, 19H), 3.37–3.22 (m, 1H), 2.84–2.67 (m, 1H), 1.87–1.60 (m, 20H), 1.55–1.08 (m, 60H). ^{13}C ($CDCl_3$): δ = 164.83, 163.66, 151.55, 150.48, 150.35, 150.10, 149.45, 145.20, 144.85, 144.20, 142.83, 136.70, 134.31, 132.68, 132.56, 132.37, 131.08, 130.93, 129.80, 129.11, 128.84, 128.37, 127.71, 127.03, 126.62, 125.43, 122.59, 121.21, 118.93, 114.38, 111.02, 68.41, 68.25, 65.95, 31.10, 30.49, 29.85, 29.57, 29.47, 29.37, 29.21, 29.06, 28.76, 26.11. IR-DRIFT (KBr): ν (cm^{-1}) 3606, 2922, 2855, 2226, 1729, 1603, 1252, 1169, 1064, 999, 755, 526. UV-Vis (λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}), CH_2Cl_2): 271 (229150), 427 (209770), 515 (4300), 552 (13140), 590 (4280), 700 (1380).

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