

Loading a Porphyrin with Fullerene Units

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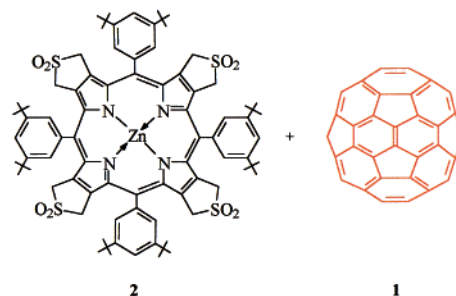
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The porphyrinoids, the “pigments of life”,¹ enrich nature in a multitude of elementary processes.² The role of the chlorophylls in photosynthesis is particularly fascinating.^{3,4} Several strategies were developed for the preparation of complex porphyrinoid systems, to mimic the redox- and photoreactions, that drive photosynthesis.^{5,6}

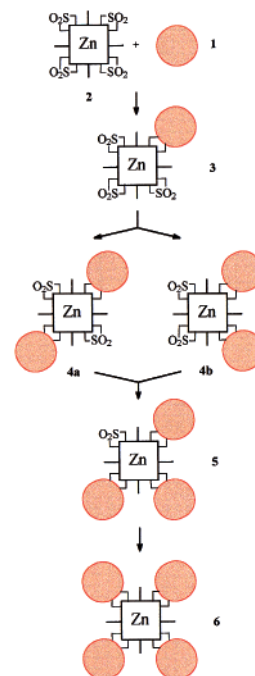
The assembly of artificial “reaction centers”⁵ and other porphyrinoid “electronic” devices⁷ may be achieved by non-covalent⁶ or covalent^{5,8} arrangement of redox- and photoactive units. Covalent bonding with limited flexibility typically results from [4 + 2]-cycloadditions.^{5,9–11} The Gunter group⁹ recently prepared functionalized porphyrins from a monosulfoleno-porphyrin. Montforts and co-workers synthesized a fullerene-chlorin from a novel monosulfoleno-tetrapyrrole.¹⁰ The zinc-tetrasulfoleno-porphyrinate **2** was designed as a reactive building block for the preparation of functionalized porphyrinoid assemblies.¹¹ Here, we report on the resulting new approach toward fullereno-porphyrins, by successive attachment of up to four [60]-fullerenes (**1**) to reactive porphyrinoids, generated in situ via thermolysis of **2**.

Heating of a solution of tetrakis-(3,5-di-*tert*-butylphenyl)-zinc-tetrasulfoleno-porphyrinate **2** (Scheme 1)¹¹ and of 10 equiv of **1** in 1,2-dichlorobenzene to 140 °C resulted in the stepwise transformation of **2** into fullereno-porphyrates (see Scheme 2): After an overnight reaction the complex **2** was decomposed completely, to give (besides traces of **5**) about 60% of the meso-tetrakis-(3,5-di-*tert*-butylphenyl)-zinc-tetrafullereno-porphyrinate **6**.¹² The porphyrinate **6** could be isolated by size exclusion chromatography. A reaction time of 2.5 h gave 24% of the bis-adduct **4a**¹¹ and 35% of the trisfullereno-porphyrinate **5**. Heating for 1 h converted about 72% of **2** into the monofullereno-porphyrinate **3** (31%)¹¹ and the bisfullereno-porphyrinates **4a** (21%) and **4b** (13%).

Scheme 1



Scheme 2



The increasing number of fullerene units in **3**, **4a** and **4b**, **5**, and **6** correlated with the intensity of the absorbance near 710 nm, characteristic for (6,6)-cycloadducts of [60]-fullerene.¹³ It also caused an increasing bathochromic shift of the visible and Soret bands,^{14a} typical for highly substituted, non-planar porphyrins.¹⁵ The number of fullerenes attached in the zinc-fullereno-porphyrinates **3–6** was deducible from the FAB-mass spectra,^{14b} for example, from a group of signals in the range of *m/z* 4119–4109 for the pseudomolecular ion of **6**. The sites of attachment of fullerene units were deduced from the ¹H NMR spectra.^{14c} The 500 MHz ¹H NMR spectrum of the tetraadduct **6** exhibited only five signals, due to five sets of symmetry equivalent protons (see Figure 1). The ¹H NMR spectra of **5** and **6**, recorded at room temperature, indicated an effectively diastereotopic nature of the geminal β'-methylene protons. The inequivalence of the methylene protons reflects the folding of the cyclohexene units connecting the fullerene and porphyrin moieties and of the remaining sulfoleno units.¹³ In contrast, in the room temperature ¹H NMR spectra of the monoadduct **3** and the diagonal bis-adduct **4a** the signals of the methylene protons next to the fullerene units give broad singlets,¹¹ due to rapid equilibration. However, the ¹H NMR spectra of **3**, **4a**, and **4b** are strongly temperature-dependent near

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(12) C₆₀ (**1**) (134 mg, 186 μmol), zinc-tetrasulfoleno-porphyrinate **2** (30 mg, 19 μmol) and 4-(dimethylamino)-pyridine (6.8 mg, 56 μmol) in 1,2-dichlorobenzene (58 mL) were heated at 140 °C (20 h). Tetrafullereno-porphyrin **6** was purified by column chromatography (silica gel 60) and eluted with CS₂ as a mixture with **1**. Pure **6** (44 mg, 58%) was obtained from this mixture by gel filtration (Sephadex LH-20, CS₂/CH₂Cl₂ 3: 7) and precipitation with *n*-hexane from a solution in CS₂ (40 mg, black powder, 52%). A reaction time of 2.5 h gave **4a** (24%) and **5** (35%), eluted from silica gel column with CS₂/CH₂Cl₂ (1:4) and (3:2). A reaction time of 1 h converted 72% of **2** and gave **4b** (13%), **4a** (21%), and **3** (31%), which were eluted with CS₂/CH₂Cl₂ (1:3), (1:4), and (1:6), respectively.

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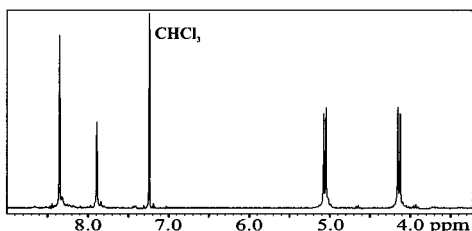


Figure 1. Section of 500 MHz ^1H NMR spectrum of **6** (1.4 mM in $\text{CDCl}_3/\text{CS}_2$ 1:1).

and below room temperature, and lowering of the temperature yields more complex spectra. Preliminary experiments indicate a coalescence temperature for the methylene signals near -35°C for **3**, near 0°C for the diagonal bis-adduct **4a** and near room temperature for the lateral bis-adduct **4b**.

The ^1H NMR spectra are consistent with a non-planar nature not only of the six-membered ring connecting the fullerene and porphyrin moieties of the five fullerene-porphyrinates **3**, **4a**, **4b**, **5**, and **6**, but also of their porphyrinoid macrocycles, for which a common mode of a “saddle” deformation¹⁶ is deducible. Highly substituted porphyrins typically contain non-planar porphyrinoid macrocycles^{15–17} with temperature-dependent NMR spectra.¹⁷ The room-temperature NMR spectra of **3** are compatible with an effective C_{2v} -symmetric structure and of an effective D_{2h} symmetry for the “diagonal” bis-adduct **4a**. The spectra of the “lateral”

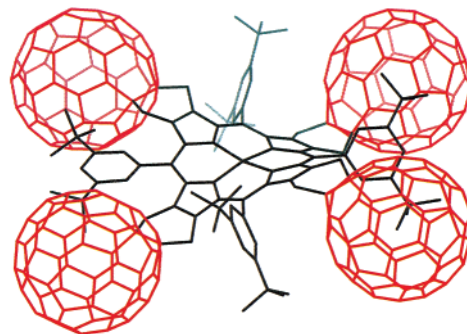


Figure 2. Three-dimensional model of zinc-tetrafullereno-porphyrinate **6**.

bis-adduct **4b** at 50°C suggested an effective C_{2v} symmetry. In contrast, the spectra indicate only C_s symmetry for the tris-adduct **5** and an effective D_{2d} symmetry for the tetraadduct **6** (see Figure 2).

Fullerene-porphyrins^{11,18} and related porphyrinoid-fulleroid conjugates^{10,19} are objects of electrochemical and photophysical studies and may have promising properties as components of electronic devices.²⁰ The non-fluorescing zinc-tetrafullereno-porphyrinate **6** is a molecular reservoir of chemically robust electro- and photoactive units and is predicted to be chargeable with more than 20 electrons per molecule. Sequential incorporation of several fullerene units into a preformed, reactive porphyrinoid is a new and efficient approach toward fullerene-porphyrins. The complexes **3–5** are a set of reactive, porphyrinoid, and fulleroid building blocks, “programmed”²¹ to open a new perspective for the synthesis of even more complex covalent assemblies between fullerenes and porphyrins.

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(14) Selected spectroscopic data: (a) UV/vis ($\text{CHCl}_3/\text{CS}_2$ (2:1), 1.5 mequiv DMAP, λ_{max} (log ϵ): **3**: 707 (2.65), 610 (3.93), 571 (4.30), 533 (3.69), 440 (5.62); **4a**: 709 (3.05), 614 (4.05), 575 (4.35), 536 (3.89), 445 (5.62); **4b**: 707 (3.05), 620 (4.04), 577 (4.33), 535 (3.90), 446 (5.63); **5**: 711 (3.12), 627 (4.11), 581 (4.38), 538 (4.03), 451 (5.63); **6**: 712 (3.25), 632 (4.13), 586 (4.40), 545 sh (4.15), 457 (5.61). (b) FAB-MS (matrix: 2-nitrophenyl-octyl ether, positive ion, m/z (%int)): **4b**: 2803.7 (60), 2802.7 (80), 2801.7 (86), 2800.7 (99), 2799.7 (100), 2798.7 (79), 2797.7 (52), 2796.7 (26, M^+), 2735.7 (23), 2734.7 (15), 2733.7 (13, $(\text{M} + 1 - \text{SO}_2)^+$), 2672.7 (34), 2671.7 (23), 2670.7 (20), 2669.7 (14, $(\text{M} + 1 - 2\text{SO}_2)^+$); **5**: 3460.7 (68), 3459.7 (78), 3458.7 (92), 3457.7 (90), 3456.7 (100), 3455.7 (79), 3454.7 (64), 3453.7 (33, $(\text{M} + 1)^+$), 3394.7 (33), 3393.7 (34), 3392.7 (32), 3391.7 (22), 3390.7 (21), 3389.7 (12, $(\text{M} + 1 - \text{SO}_2)^+$); **6**: 4117.4 (51), 4116.4 (63), 4115.4 (90), 4114.4 (94), 4113.4 (100), 4112.4 (86), 4111.4 (59), 4110.4 (45), 4109.4 (21, $(\text{M} + 1)^+$). (c) ^1H NMR (500 MHz, δ (ppm)): **4b** (CDCl_3 , 50°C): 1.41 (s, 18H), 1.45 (bs, 36H), 1.51 (s, 18H), 4.15 (bs, 8H), 4.62 (bs, 4H), 4.69 (bs, 4H), 7.93 (bs, 6H), 8.10 (s, 4H), 8.31 (s, 2H); **5** ($\text{CDCl}_3/\text{CS}_2$ 1:3, 26°C): 1.33 (s, 18H), 1.42 (s, 18H), 1.46 (s, 18H), 1.63 (s, 18H), 3.75 (d, $J = 16$, 2H), 4.07 (d, $J = 14.5$, 2H), 4.14 (d, $J = 14.5$, 2H), 4.24 (d, $J = 14.5$, 2H), 4.32 (d, $J = 16$, 2H), 5.02 (d, $J = 14.5$, 2H), 5.04 (d, $J = 14.5$, 4H), 7.90 (s, 4H), 8.01 (s, 2H), 8.19 (s, 2H), 8.29 (s, 2H), 8.32 (s, 2H); **6** ($\text{CDCl}_3/\text{CS}_2$ 1:1, 26°C): 1.43 (s, 72H), 4.14 (d, $J = 15$, 8H), 5.06 (d, $J = 15$, 8H), 7.90 (bs, 4H), 8.35 (bs, 8H).

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