A macrocyclic [60]fullerene–porphyrin dyad involving π–π stacking interactions

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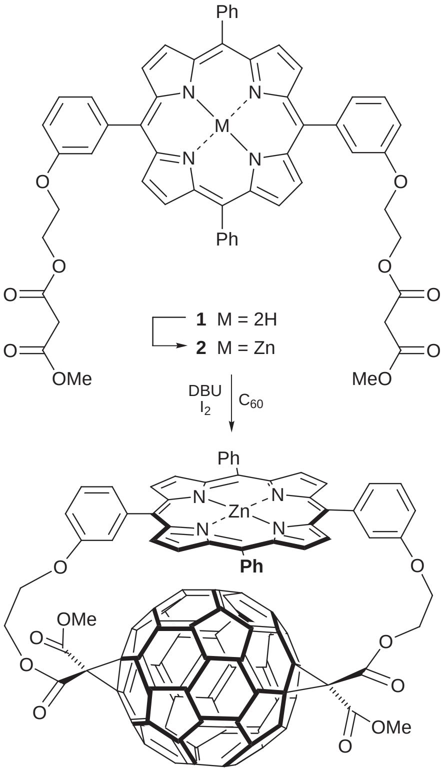
The very regioselective twofold cyclopropanation of C_{60} with a porphyrin bismalonate leads to a C_2 symmetrical [60]fullerene–porphyrin dyad with pronounced electronic interactions between the two π–π stacked chromophores.

In a project aimed at the synthesis of stereochemically defined architectures involving fullerene and porphyrin building blocks[1] we became interested in the development of a model compound with a face-to-face arrangement of the two π-systems and an electronic interaction between the two chromophores. In order to achieve this goal, we decided to restrict the conformational freedom within a dyad by introducing two covalent linkages *via* a tether controlled synthesis[2] with the porphyrin itself being an integral part of the tether.

For this purpose we synthesized the bifunctionalized porphyrin **1** using a mixed aldehyde approach (Scheme 1).[3] Benzaldehyde, 3-[2-(methoxymalonyloxy)ethoxy]benzaldehyde and pyrrole were stirred with $BF_3{\cdot}Et_2O$ as catalyst and Ph_4PCl in CH_2Cl_2 for one hour. After the addition of chloranil the mixture was refluxed for another hour. Separation of **1** from other reaction products required repeated purification with column chromatography (silica gel, CH_2Cl_2–ethyl acetate 20 : 1). The free base porphyrin was converted into the metallated compound **2**† by stirring with $ZnCl_2$ in refluxing acetone. **2** was attached to C_{60} *via* a twofold cyclopropanation achieved by the action of iodine and DBU.[4] This bisaddition proceeds with outstanding regioselectivity, since next to uncharacterized oligomeric material, bisadduct **3** with a *trans*-2 addition pattern (out–out isomer[2]) was formed as the only regioisomer (HPLC) and isolated in 41% yield by flash chromatography (silica gel, toluene–ethyl acetate 9 : 1).



3

Scheme 1

The dyad **3** was completely characterized‡ allowing for an unambiguous structure assignment. The symmetry of **3** is C_2. This is clearly reflected by the splitting of the porphyrin signals to a doublet, for example four signals instead of two observed in **2** for the β-pyrrole C atoms at 131.74, 131.79, 132.03 and 132.08 ppm. Moreover, the C_2 symmetric binding of the tether is revealed by only one signal for the equivalent methoxy protons at 53.87 ppm, two signals for the two different carbonyl groups at 163.49 and 163.53 ppm, two signals for the two different sp^3-C atoms at 70.06 and 70.72 ppm and 26 resolved signals for the 28 different sp^2-C atoms of the fullerene core. Next to the *cis*-**3** and *trans*-**3** adducts (with in–in or out–out bridging and C_2 symmetry) the depicted structure of **3** is the only one consistent with the NMR spectra. The correct structure assignment of **3** as the *trans*-**2** out–out isomer was provided by a combination of molecular mechanics calculations and UV/VIS spectroscopy: (1) the other C_2 symmetric isomers are inaccessible for this tether (MM+ force field), since their strain energy is considerably higher; (2) each addition pattern gives rise to a characteristic electronic absorption spectrum in both the visible and the UV part.[5] The latter is not covered by the absorptions of the porphyrin moiety and therefore the presence of a *trans*-2 addition pattern within **3** is unambiguously revealed by the comparison with the UV/VIS spectra of a variety of series of corresponding bisadducts.[5]

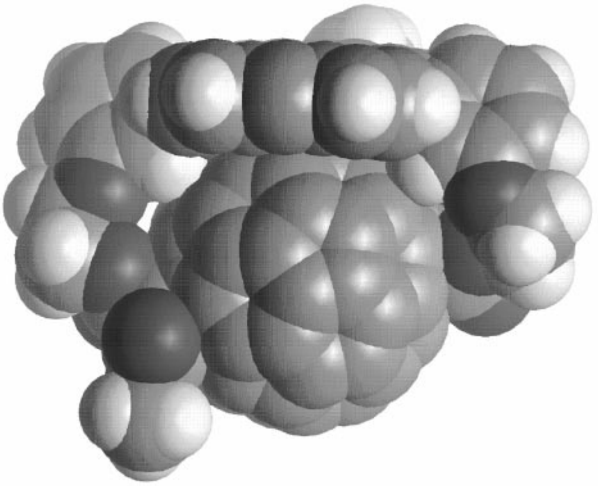


Fig. 1 Space-filling model of the PM3 (Spartan 4.1) calculated structure of **3**. The *meso*-phenyl ring in the front is omitted for clarity.

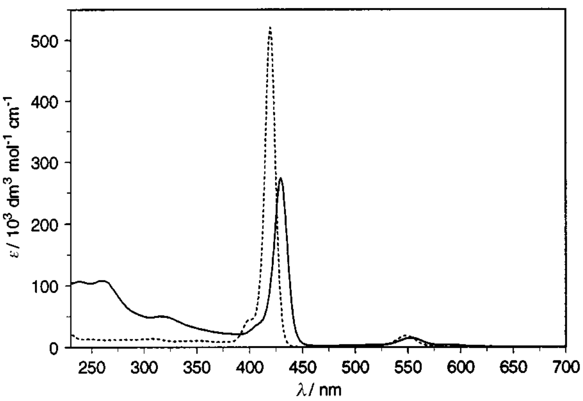
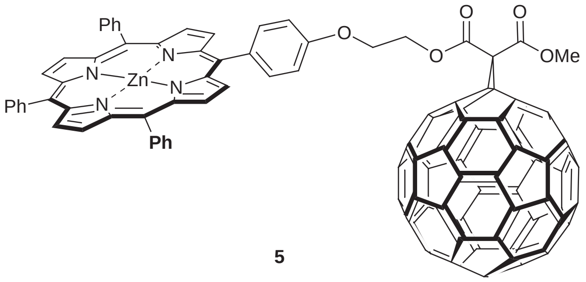


Fig. 2 Electronic absorption spectra of **2** (dashed line) and **3** in CH_2Cl_2 at $c = 3.5 \times 10^{-6}$ mol dm^{-3}.

In the MM+ minimized structure of **3** (Fig. 1) the average distance between the four pyrrole N atoms and the Zn atom of the macrocycle and their nearest neighbours on the fullerene moiety is 3.4 Å. The shortest distance between the Zn atom and a fullerene C atom is only 3.0 Å and therefore even shorter than the interplanar distance in graphite.

Electroanalytical investigations on **3** using cyclic voltammetry and differential pulse voltammetry reveal two oxidative and six reductive electron transfer processes which are also present in either the parent porphyrin **2** or the *trans*-2-bis(diethylmalonate) **4**.[5] Only slight shifts, for example of 16 mV, to a more negative potential for the first porphyrin oxidation are detected.§ Compared with **2** the Soret- and Q-bands of **3** show a bathochromic shift and decrease of the molar absorption coefficients indicating a considerable photoinduced interaction between the two chromophores (Fig. 2). Also photophysical analyses of **3** reflect the close proximity and stacking interaction between the corresponding π-systems. Time-dependent luminescence measurements reveal a complete quenching of the typical porphyrin fluorescence with a maximum at about 500 nm which is present in the monoadduct dyad **5**.[1] However, a new luminescence band at 850 nm was found. The luminescence intensity increases with decreasing temperature. The luminescence decay can be fitted double exponentially with the decay times $\tau_1 = 2.84$ ns and $\tau_2 = 0.42$ ns. The relative amplitudes of the decay times were calculated to be 2.12 : 1. This, together with a complete lack of photosensitized $^1O_2$ generation typical for porphyrins,[6] C_{60} and many of its derivatives,[7] suggests an efficient photoinduced energy transfer from the porphyrin to the fullerene.



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Detailed comparative investigations on electron and energy transfer processes of **3** and related systems including those with different central metals and additional addends like electron acceptors and dendrimers are currently under way.

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Notes and references

† Detailed procedures for the synthesis and spectroscopic data of **1** and **2** will be reported elsewhere.

‡ *Spectroscopic data* for **3**: ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 8.82–8.75 (8 H, m), 8.27 (2 H, d), 8.19 (2 H, d), 7.93 (2 H, d), 7.80–7.64 (10 H, m), 7.37 (2 H, d), 5.15 (2 H, dt), 4.77 (2 H, dt), 4.49 (4 H, t), 3.93 (6 H, s); ^{13}C NMR (100.5 MHz, $CDCl_3$, 25 °C) δ 163.53, 163.49, 156.57, 150.19, 150.08, 150.04, 147.91, 145.07, 144.98, 144.67, 144.60, 144.03, 143.47, 143.43, 142.81, 142.74, 142.63, 142.33, 142.08, 142.00, 141.82, 141.62, 141.51, 141.44, 141.38, 141.33, 141.16, 140.85, 140.74, 139.96, 139.59, 138.44, 138.41, 138.00, 137.95, 137.91, 134.40, 134.15, 132.08, 132.03, 131.79, 131.74, 127.72, 127.41, 126.77, 126.55, 126.42, 125.27, 121.40, 120.43, 115.17, 70.72, 70.06, 67.30, 65.11, 53.87, 49.16; UV/VIS $\lambda_{max}(CH_2Cl_2)$/nm (ε/dm^3 mol^{-1} cm^{-1}) 240 (109000), 260 (110200), 315 (50900), 407 (sh, 38400), 429 (273900), 552 (26200); FT-IR (KBr) ν/cm^{-1} 3053, 3021, 2950, 2922, 2867, 1750, 1596, 1576, 1480, 1433, 1237, 1108, 1069, 1003, 796, 702, 527; FAB-MS *m*/*z* 1714 (M$^+$).

§ Formal potentials ($E°$/V): **2** $E_{ox}{}^1 = 0.273$, $E_{ox}{}^2 = 0.712$, $E_{red}{}^1 = -1.898$, $E_{red}{}^2 = -2.234$; **3** $E_{ox}{}^1 = 0.257$, $E_{ox}{}^2 = 0.712$, $E_{red}{}^1 = -1.156$, $E_{red}{}^2 = -1.487$, $E_{red}{}^3 = -1.741$, $E_{red}{}^4 = -1.898$, $E_{red}{}^5 = -2.085$, $E_{red}{}^6 = -2.300$; **4** $E_{red}{}^1 = -1.102$, $E_{red}{}^2 = -1.467$, $E_{red}{}^3 = -1.910$, $E_{red}{}^4 = -1.987$, $E_{red}{}^5 = -2.325$. The redox potentials $E°$ were determined from cyclic voltammograms (mean value of corresponding $E_p{}^r$ and $E_p{}^o$) and differential pulse voltammograms in 0.22 mmolar solutions of **3** in CH_2Cl_2–NBu_4PF_6 (0.1 M) at Pt/Ir using a Ag–$AgClO_4$ (0.01 M)/NBu_4PF_6 (0.01 M)/acetonitrile reference electrode and were recalculated against internal Fc/Fc$^+$ ($\Delta V = 0.21$ V).

Note added in proof. A macrocyclic *trans*-1 fullerene–porphyrin conjugate was recently obtained by F. Diederich (personal communication).

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