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A facile synthetic access to porphyrin fullerene dyads and their optical properties

Michael Wedel and Franz-Peter Montforts*

Institut für Organische Chemie, FB 2, Universität Bremen, Leobener Str. NW2
28359 Bremen, Germany

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Abstract: Porphyrin fullerene dyads **5** and **6** can be derived by Bingel reaction from a deuteroporphyrin derivative **3** with an attached macrocyclic bislactone moiety. The porphyrin bislactone **3** on the other hand is easily formed in an esterification reaction between malonic acid and a deuteroporphyrin bisalcohol **2**. Missing fluorescence in the dyads **5** and **6** indicates a light induced intramolecular electron transfer from the porphyrin to the fullerene part. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Porphyrins and analogues; fullerenes; cyclopropanation; light induced electron transfer

A great variety of dyads and more complex molecular arrangements of donor and acceptor subunits have been designed to investigate photoinduced energy and electron transfer and to mimic natural photosynthesis. Since the discovery[1] and availability[2] of the fullerenes, especially fullerene C_{60} was used as a subunit for the construction of molecular dyads which undergo light induced electron transfer from a porphinoid donor to the fullerene acceptor.[3] A possible advantage of fullerenes over quinones, which are used as acceptors by nature[4] and in the majority of artificial photosynthetic systems,[5] is the ability of C_{60} to accept up to six electrons.

We represent here a facile synthetic access to porphyrin fullerene dyads with a porphyrin moiety derived from the naturally occuring red blood pigment heme which is available in almost any amount from slaughterhouse wastes.

Deuteroporphyrin IX dimethylester **1** directly obtained from heme by demetalation and devinylation[6] was reduced with $LiAlH_4$[7] and metalated with zinc(II)-acetylacetonate to yield the porphyrin dialcohol **2**. Metalation protects the inner nitrogens during the following acylation of the diol with malonic acid. For the acylation malonic acid is activated by propyl phosphonic acid anhydride and then reacted with the porphyrin dialcohol **2** giving porphyrin **3**.

The formation of the 16-membered bislactone structure of **3** proceeds very easily and with good yield, most likely due to conformational restrictions caused by the rigidity of the porphyrin macrocycle. Both, zinc porphyrin **3** and its metal-free derivative **4** obtained by acid induced demetalation react in a modified Bingel

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* Corresponding author. e-mail: mont@chemie.uni-bremen.de

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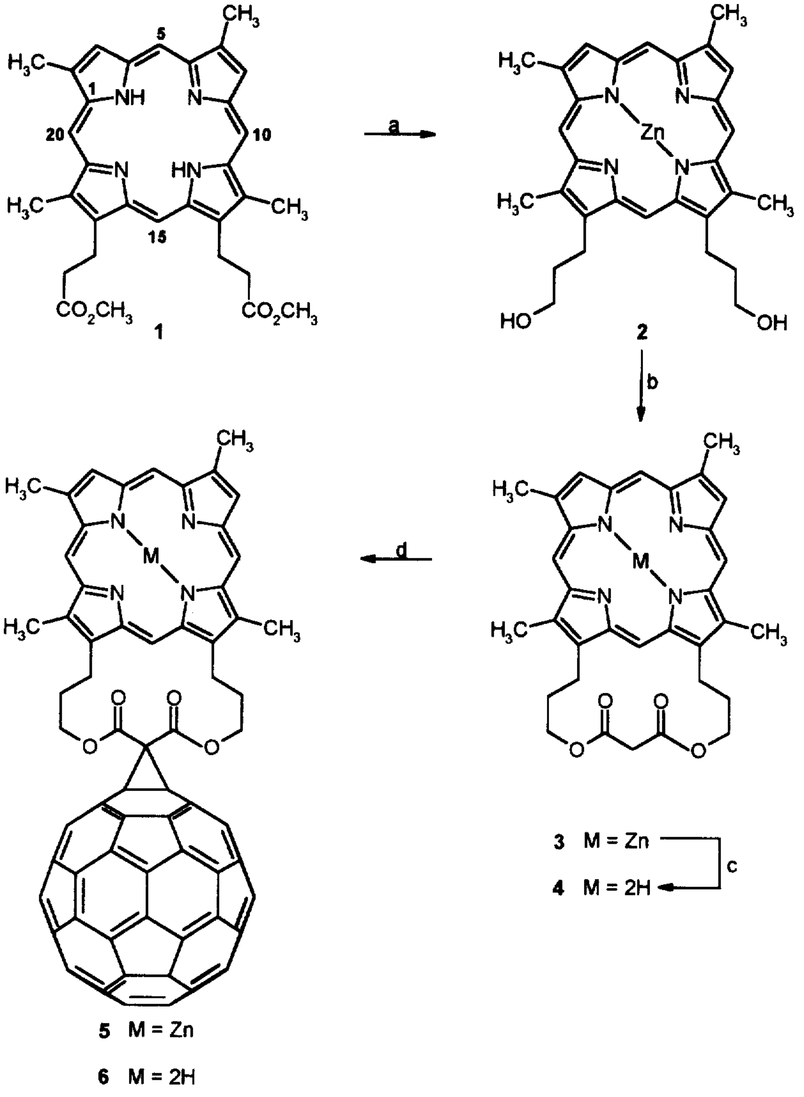
reaction[8, 9] with fullerene C_{60} to yield the porphyrin fullerene dyads **5** and **6**.[10]



Scheme 1. a) (i) $LiAlH_4$, Ar, THF, reflux, (ii) $Zn(acac)_2$, Ar, THF, reflux (57 %); b) propyl phosphonic acid anhydride, DMAP, NEt_3, malonic acid, Ar, THF, room temperature (48 %); c) 10 % TFA, CH_2Cl_2, room temperature (100 %); d) I_2, DBU, C_{60}, Ar, toluene, room temperature (**5**: 34 %, **6**: 38 %).

The UV/Vis spectra of the dyads consist simply of a superposition of the electronic absorption spectra of the fullerene and porphyrin subunits thus indicating independence of both chromophores. However, the luminescence spectra of the dyads **5** and **6** compared to those of porphyrins **3** and **4** show a striking difference. Whereas with **3** and **4** a strong luminescence could be observed luminescence of **5** and **6** is almost completely quenched. Quenching which did not show any dependence on concentration indicates intramolecular light induced electron transfer from the porphyrin to the fullerene. Further photophysical studies to determine rates of formation and lifetimes of transients are under investigation.

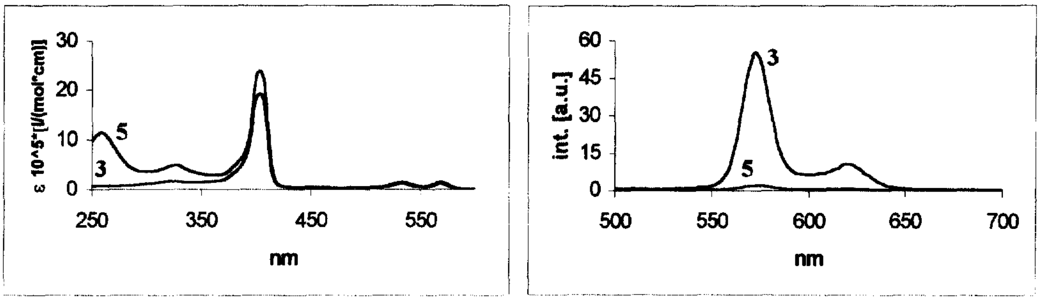


Figure 1. Electronic absorption spectra of **3** and **5** in $CHCl_3$ (10^{-5} M) and luminescence spectra of **3** (10^{-7} M) and **5** (10^{-5} M) in $CHCl_3$. The soret band was chosen as the excitation wavelength.

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9 Experimental procedure for the Bingel reaction: 22.1 mg (0.04 mmol) **3** was dissolved together with 28.8 mg (0.04 mmol, 1.0 eq.) C_{60} und 10.1 mg (0.04 mmol, 1.0 eq.) iodine in 40 ml toluene under argon. 24 µl (0.16 mmol, 4.0 eq.) DBU were added and the mixture was stirred for four hours at room temperature. The mixture was poured on a column (diameter: 3 cm) filled with 120 ml SiO_2. Unreacted C_{60} was first eluated with toluene and the product was eluated with dichloromethane.

10 All compounds show correct spectroscopic and analytical data. Selected spectroscopic and analytical data: **3**: m.p. 304-306 °C; TLC (SiO_2, CH_2Cl_2/EtOAc (19+1)): $R_f = 0.59$; IR (KBr): $\tilde{\nu}$ = 2951 cm^{-1} (w, CH), 2919 (m, CH), 2854 (w, CH), 1749 (s, C=O), 1686 (m), 1646 (m), 1632 (m), 1455 (m), 1380 (w, $\delta(CH_3)$), 1331 (m), 1260 (m), 1237 (m), 1136 (m), 1100 (w), 1034 (m), 1016 (m), 953 (w), 842 (w), 754 (w); UV/Vis ($CHCl_3$): λ_{max} (ε) = 318 nm (23300), 401 (187864), 531 (16310), 567 (16504); Fluorescence ($CHCl_3$, c = $0.99 \cdot 10^{-7}$ M): λ_{max} (I) = 620 nm (10.3), 572 (68.3); ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 2.51 (m, 4H, propyl), 3.48, 3.53 (2 s, each 3H, methyl), 3.65 (d, 3H, ^4J = 0.74 Hz, methyl), 3.69 (d, 3H, ^4J = 0.93 Hz, methyl), 3.90 (s, 2H, malonic acid), 3.97 (m, 4H, propyl), 4.67 (m, 4H, propyl), 8.93 (d, 1H, ^4J = 1.11 Hz, 3-/8-H), 8.98 (d, 1H, ^4J = 0.93 Hz, 3-/8-H), 9.60, 9.75, 9.78, 9.82 (4 s, each 1H, 5-, 10-, 15-, 20-H); MS (EI, 70 eV): 612 (100 %) [M^+]; HR-MS: $C_{33}H_{34}N_4O_4$: calcd. 612.17151, found 612.17085.

5: m.p. >350 °C; TLC (SiO_2, CH_2Cl_2): $R_f = 0.76$; IR (KBr): 2917 cm^{-1} (s, CH), 2849 (m, CH), 1733 (m, C=O), 1646 (s, C=C), 1454 (m), 1433 (m), 1374 (m, $\delta(CH_3)$), 1320 (w), 1228 (s), 1131 (m), 1032 (s), 1018 (s), 892 (w), 845 (m), 749 (m), 525 (m); UV/Vis ($CHCl_3$): λ_{max} (ε) = 258 nm (119900), 326 (56535), 401 (232376), 532 (19900), 568 (19801); Fluorescence ($CHCl_3$, c = $1.01 \cdot 10^{-5}$ M): λ_{max} (I) = 572 nm (3.2); ^{1}H-NMR (200 MHz, $CDCl_3$ + 10 µl pyridine-d_5): δ = 2.78 (m, 4H, propyl), 3.65, 3.69 (2 s, each 3H, methyl), 3.74 (d, 3H, ^4J = 0.88 Hz, methyl), 3.78 (d, 3H, ^4J = 0.88 Hz, methyl), 4.36 (m, 4H, propyl), 5.06 (m, 4H, propyl), 9.09 (d, 1H, ^4J = 1.03 Hz, 3-/8-H), 9.12 (d, 1H, ^4J = 1.17 Hz, 3-/8-H), 10.01, 10.04, 10.15, 10.28 (4 s, each 1H, 5-, 10-, 15-, 20-H); MS (MALDI-TOF, pos., matrix: dctb): 1332.6 [M^+].