Isolation of Phlorin-Dipyrrin Conjugates from the Acid-Catalyzed Condensation of Dipyrromethanes and Aldehydes

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The product distribution of the acid-mediated condensation of dipyrromethanes and aldehydes was studied and a novel type of macrocycle phlorin-dipyrrin conjugate was isolated and identified by X-ray analysis. The generality of its formation from sterically hindered dipyrromethanes and pentafluorophenyldipyrromethane was demonstrated. The influence of the *meso*-aryl groups on the stability of the phlorin was studied. The reported two-step synthesis of a phlorin derivative is one of the simplest routes leading to this type of molecules.

Introduction

The last few years have witnessed a large increase in the range of new pyrrole-based macrocycles and linear oligomers, obtained by changes in the reaction conditions that were originally optimized for the synthesis of porphyrins from pyrrole (or its derivatives) and aldehydes.[1–3] Phlorins are nonaromatic isomers of chlorins produced either by reduction of porphyrins at one of the *meso* positions, or by the addition of nucleophiles to the porphyrin macrocycle.[4–12] The stability of most phlorins is limited, and only in a few favorable cases (usually when stabilized by steric hindrance) could these compounds be isolated in a pure state.[5,6,11] The main decomposition process relies on a simple oxidation to the parent porphyrin, but the irreversible *meso* addition of the carbon nucleophile does not allow this reaction to proceed. Recently, such *meso*-derivatized phlorins have been isolated and characterized by Callot and coworkers.[7,9,10] Here, we wish to report the results of our study on the oxidative transformation of oligopyrroles leading to the novel phlorin-dipyrrin conjugate.

Results and Discussion

During our studies towards the synthesis of *trans*-A_2B-corroles from dipyrromethanes and aldehydes[13–16] we observed additional, colored side-products. We were particularly intrigued by dark green species that were slightly more polar than the respective corroles, and that invariably formed when sterically hindered dipyrromethanes were employed. The reaction between mesityldipyrromethane **1** and pentafluorobenzaldehyde **2**, using standard conditions (TFA catalysis, followed by oxidation with DDQ or *p*-chloranil), was chosen as a model system for the investigation of the formation and structure of the corroles. From the crude reaction mixture,[15] we were able to isolate corrole **3** (27% yield) and a substance that exhibited molecular mass 1140 (16% yield), which corresponds to a compound formed from three molecules of mesityldipyrromethane **1** and two molecules of pentafluorobenzaldehyde **2** (Scheme 1). Given that the ratio of the substrates used (2:1) did not correspond to the ratio of both of the moieties in the structure (3:2), an optimization study was undertaken. Applying the stoichiometric ratio (**1**:**2** = 3:2) under virtually the same reaction conditions surprisingly gave a lower yield of **4** (4.5%) and, as the main products, 5,15-dimesityl-10,20-bis(pentafluorophenyl)porphyrin and 5,15,25-trimesityl-10,20,30-tris(pentafluorophenyl)hexaphyrin(1.1.1.1.1.1). The use of *p*-chloranil instead of DDQ in the second step resulted in a decrease in the yield of **4**. Furthermore, the increase in the concentration of TFA[15] also caused a drop in the yield (12%). Reaction of dipyrromethane **1** with pentafluorobenzaldehyde performed under conditions optimized for the formation of *trans*-A_2B_2-porphyrins (**1**:**2** = 1:1, [TFA] = 17.8 mM)[17] only gave traces of compound **4**. Thus, although formation of **4** is rather general, isolable quantities are formed only when the ratio is 2:1 (or close) and a relatively low concentration of TFA is used.

It was clear that the final product was the result of the transformation of the initially formed linear oligocondensate ("hexapyrromethane"). The appealing assumption that the green macrocycle was hexaphyrin(1.1.1.1.1.0) was ruled out by analysis of the ^{1}H NMR spectra. The number of signals is not in agreement with the C_2-symmetrical structure. Furthermore, the data were typical of a nonaromatic

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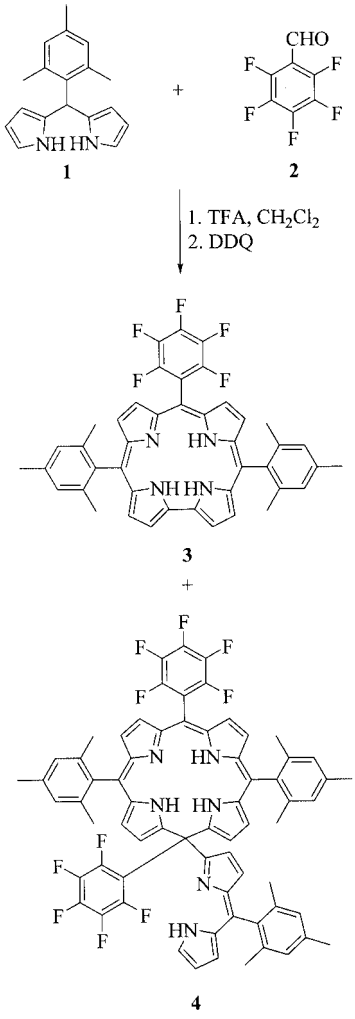

Scheme 1.

conjugated system with pyrrolic signals in the δ = 6.6–7.1 range. Two broad signals were observed at ca. 3.6 and 11.7 and were assigned to NH protons.

With the reason that it might be possible that electron-withdrawing groups could stabilize the molecule (as it is the case for corroles) we tried to obtain an analogous macrocycle from 5-pentafluorphenyldipyrromethane and 4-cyanobenzaldehyde. Under the conditions used for the synthesis of compound **4**, only traces of compound **5** (Figure 1) were detected. However, after a short optimization, we were able to isolate **5** in 9% yield. This compound was far more stable than **4** and formed crystals, but they were not suitable for X-ray analysis. Subsequently, nitro groups were introduced on the periphery of the macrocycle in order to improve crystal-forming properties of the molecule. Macrocycle **6** was prepared in 6% yield under the conditions optimized for the synthesis of **5** (Figure 1).

Subsequent 2D experiments (COSY, HMQC, HMBC etc.) (Figure 2) suggested a more complex structure, and X-ray analysis was thought to be the only way to elucidate the structure unambiguously. We found that compound **4**, like corrole **3**, was stable as a solid, but decomposed in solution to polar products, particularly in the presence of dioxygen

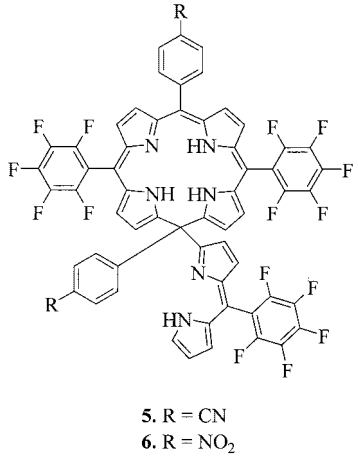

Figure 1. Structures of phlorins **5** and **6**.

under illumination. Additionally, its very high solubility in all commonly used solvents excluded the chance to obtain diffraction grade crystals.

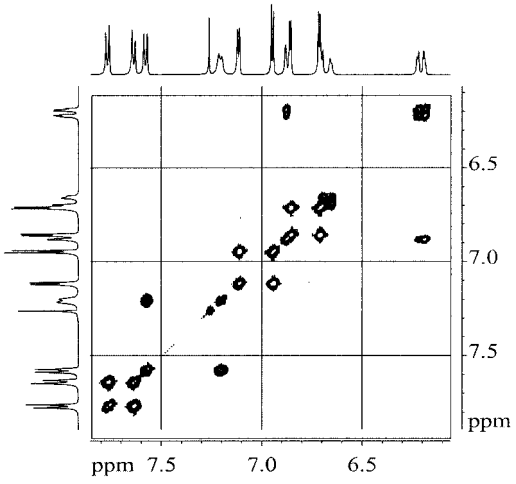

Figure 2. COSY spectrum of phlorin-dipyrrin **5** (aromatic region).

Finally, we were able to obtain crystals of **6** suitable for single-crystal X-ray diffraction analysis (Figure 3). This analysis reveals that compound **6** comprises two units: a tetrapyrrole non-conjugated macrocycle (phlorin) and a dipyrromethene linked by a quaternary carbon atom. Such products are novel but they very closely resemble the phlorins obtained by Lee and coworkers from pentapyrranes by reaction with DDQ.[18] The only difference is that the pyrrole linked to the quaternary carbon atom is replaced in our structures by the dipyrrin unit. Both types of phlorins form under analogous conditions (reaction of DDQ with oligopyrranes). According to expectations, the structure is substantially distorted from planarity. Subsequent dihedral angles between pyrrole rings are: 14.1(4), 13.9(4), 119.4(3) and 37.3(3)°; the largest bending occurs between the pyrrole units directly attached to the sp^3 carbon. Also, an acetone molecule is strongly bound to the phlorin moiety by two hydrogen bonds (Figure 3).

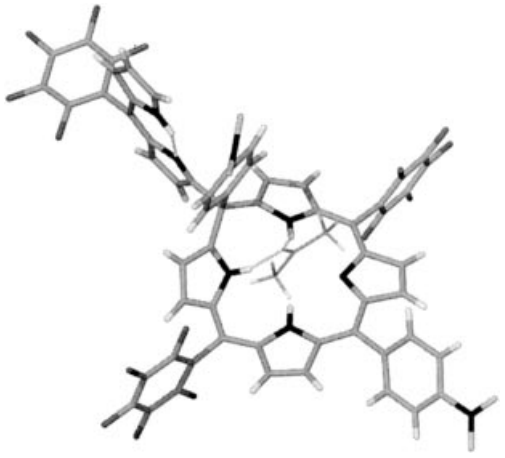

Figure 3. X-ray structure of phlorin-dipyrrin **6**.

Presumably, phlorin-dipyrrin conjugates **4**–**6** were formed by the DDQ-mediated oxidative macrocyclization of "hexapyrranes" in analogy to the formation of phlorins from pentapyrranes.[18] Due to the fact that aldehydes react faster with dipyrromethanes than with pyrrole, oligomer formation is inevitable in the acid-catalyzed condensation of aldehydes with pyrrole.[2,19] Bearing this in mind, one should not be surprised that once formed, tetrapyrranes react with subsequent molecules of aldehydes and dipyrromethanes to form hexapyrranes, octapyrranes etc. Judging from the formation of conjugates **4**–**6**, this is an important side reaction, although the yields of the respective hexapyrranes are difficult to estimate due to the unknown efficiency of macrocyclization. The DDQ-mediated macrocyclization step is thought to proceed first by oxidation of the hexapyrranes and then macrocyclization. The formation of the macrocycle containing four pyrrole units is preferred, which is in agreement with the result of the oxidative transformation of pentapyrranes.[18]

Phlorin-dipyrrin conjugates were detected in substantial amounts (based on ESI-MS and TLC) in reactions of mesityldipyrromethane and 5-(2,6-dichlorophenyl)phenyldipyrromethane with other aromatic aldehydes (2,6-difluorobenzaldehyde, 2,3,6-trifluorobenzaldehyde, 2,4-difluorobenzaldehyde, 4-cyanobenzaldehyde, 4-nitrobenzaldehyde, 3,4,5-trimethoxybenzaldehyde, 2-hydroxy-3-methoxybenzaldehyde and pyridine-4-carboxyaldehyde). On the other hand, they were detected only in miniscule amounts in reactions of phenyldipyrromethane and 5-(4-methoxyphenyl)dipyrromethane with the analogous set of aldehydes.

Contrary to phlorins obtained by Callot et al. (both by nucleophilic addition[7,9,10] and by reduction of *N*-phenylporphyrins[7,8,10,11]) which are only moderately stable, especially in solution,[20] phlorins **5** and **6** are very stable both in solid state and in solution (see Experimental Section). Phlorins obtained by the addition of organolithium reagents to tetraphenylporphyrin (TPP), as well as phlorin obtained from tetraphenyl pentapyrrane,[18,21] are unstable in solution in spite of the fact that one of the *meso* positions is "locked". Our results show that the process of decomposition can be inhibited by placing only electron-withdrawing substituents on the *meso*-positions. Based on the decomposition products reported by Callot et al.[12] (biladienones), we can assume that oxygen attack is the first step of this process, the same as that suggested for the decomposition of corroles.[22] Given that electron-withdrawing groups, which certainly increase the oxidation potential, stabilize corroles,[16] the mechanism of stabilization of phlorins might be analogous.

It is worth noting that the *para* fluorine atom in the C_6F_5 group present in phlorins **5** and **6** is reactive and easy to transform into other chemical handles by nucleophilic aromatic substitution.

The UV/Vis spectra of compounds **4**–**6** are characteristic of a phlorin chromophore (broadened UV and visible bands in the range 300–400, 400–500 and 600–700 nm, with considerably reduced extinction coefficients relative to porphyrins) and are approximately the sum of the spectra of the constituent components (Figure 4).[23]

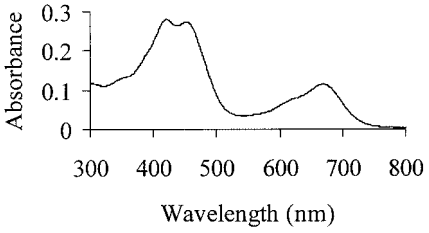

Figure 4. Absorption spectrum of phlorin-dipyrrin **5**.

In summary, phlorin-dipyrrin conjugates can be added to the list of products [porphyrins, corroles, and [24]hexaphyrins(1.1.1.1.1.1)[24]] which are easy to obtain by the reaction of dipyrromethanes with aldehydes. Although phlorin-dipyrrin conjugates are formed from a variety of dipyrromethanes, they can be isolated in reasonable yields only when sterically hindered dipyrromethanes as well as 5-(pentafluorophenyl)dipyrromethane are used as substrates. It was found that the incorporation of electron-withdrawing groups at the perimeter of phlorins greatly increases their stability (molecules **5** and **6** represent one of the most stable phlorins known). These results are of theoretical significance since they provide new insights into the factors influencing the course of the reaction of pyrrole derivatives with aldehydes leading to macrocyclic structures. Given the increasing interest in the application of dipyrrines used as BF_3 complexes[25] and also more recently as metal complexes,[26] phlorin-dipyrrin conjugates also offer possibilities for supramolecular chemistry.

Experimental Section

All chemicals were used as received unless otherwise noted. Reagent grade solvents (CH_2Cl_2, hexane, cyclohexane) were distilled prior to use. All reported NMR spectra were recorded on Bruker AM 500 MHz. UV/Vis spectra were recorded in toluene (Cary). Chromatography was performed on silica (Kieselgel 60, 200–400 mesh), or dry column vacuum chromatography[27] was performed on preparative thin layer chromatography silica (Merck 107747).

Mass spectra were obtained by electrospray MS (ESI-MS). The purity of all new compounds was established from their ^{1}H NMR and ^{13}C NMR spectra, as well as ESI-MS spectra and elemental analysis. All dipyrromethanes were prepared as described in the literature.[28]

General Procedure for the Synthesis of Phlorins from Sterically Hindered Dipyrromethanes: A sample of a dipyrromethane (0.40 mmol) and an aldehyde (0.20 mmol) were dissolved in a pre-prepared solution (3 mL) of TFA (10 μL, 0.13 mmol) in CH_2Cl_2 (100 mL). The reaction mixture was stirred at room temperature for 5 h. Then, the reaction mixture was diluted to 5 mL with CH_2Cl_2 and added to vigorously stirred CH_2Cl_2 (20 mL) simultaneously with the solution of DDQ (118 mg, 0.52 mmol) in THF (10 mL) over 10 min. Subsequently the reaction mixture was stirred at room temperature for a further 15 min and purified in each case as follows.

Condensation of 5-Mesityldipyrromethane with Pentafluorobenzaldehyde: The reaction mixture was passed through a chromatography column (silica, CH_2Cl_2/hexane, 1:4) to obtain two main fractions. The first fraction contained pure 5,15-dimesityl-10-(pentafluorophenyl)corrole (**3**, 37 mg, 26%, spectral and published properties concur with published data).[14]

The second fraction, containing contaminated **4** was re-chromatographed (silica, hexane/toluene, 100:1, then 97:3, 93:7, 90:1, 85:5) to afford pure compound (18 mg, 16%): R_f = 0.34 (silica, CH_2Cl_2:hexane, 1:3). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 1.91 (s, 6 H, CH_3, mesityl), 2.10 (s, 6 H, CH_3, mesityl), 2.13 (s, 6 H, CH_3, mesityl), 2.36 (s, 3 H, CH_3, mesityl), 2.40 (s, 6 H, CH_3, mesityl), 3.2–4.0 (br. s, 3 H, pyrrole NH), 6.10–6.20 (m, 2 H, dipyrrin), 6.68 (s, 4 H, Ar-H, mesityl), 6.72–6.76 (m, 3 H, dipyrrin and 2 β-pyrrole), 6.85 (m, 1 H, dipyrrin), 6.93 (s, 2 H, Ar-H, mesityl), 6.92–7.00 (m, 3 H, dipyrrin and 2 β-pyrrole), 7.02 (s, 2 H, β-pyrrole), 7.03 (d, J = 5.0 Hz, 2 H, β-pyrrole), 11.69 (br. s, 1 H, dipyrrin NH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 20.0, 20.1, 20.3, 21.1, 21.2, 111.8, 112.1, 120.6, 121.4, 122.9, 123.2, 124.7, 125.7, 127.8, 127.9, 128.1, 128.2, 128.4, 129.0, 132.4, 132.5, 132.7, 132.9, 133.4, 133.9, 135.3, 136.7, 137.5, 137.7, 137.9, 138.2, 138.7, 141.8, 143.7, 144.8, 144.9, 146.4, 147.0, 155.3, 166.8 ppm. LRMS(ESI): m/z = 1141.4 [M + H$^+$]. HRMS(ESI): calcd. for $C_{68}H_{51}F_{10}N_6$ [M + H$^+$] 1141.3976; found 1141.4010. UV/Vis (toluene): λ_{max} ($\varepsilon \times 10^{-3}$) = 385 (24.0), 409 (47.1), 438 (49.9), 641 (16.5), 786 nm (3.3).

General Procedure for the Synthesis of Phlorins from 5-(Pentafluorophenyl)dipyrromethane: A sample of a 5-(pentafluorophenyl)dipyrromethane (625 mg, 2.00 mmol) and aldehyde (1.00 mmol) were dissolved in CH_2Cl_2 (15 mL). Then TFA (15 μL, 0.20 mmol) was added, and the reaction mixture was left to stir at room temperature. After 20 min, DDQ (590 mg, 2.60 mmol) in THF (5 mL) was added. Subsequently, the reaction was stirred at room temperature for further 15 min and purified in each case as follows.

Condensation of 5-Pentafluorophenyldipyrromethane with 4-Cyanobenzaldehyde: The reaction mixture was passed through a chromatography column (silica, acetone/hexane, 1:9). The first fraction containing 5,15-bis(pentafluorophenyl)-10-(4-cyanophenyl) corrole was evaporated. The dark residue was dissolved in hot hexanes, and cooled in the freezer. After filtration, the remaining crystals were washed with hexane to obtain corrole (73 mg, 10%). For 5,15-bis(pentafluorophenyl)-10-(4-cyanophenyl)corrole, spectral and published properties concur with published data.[14]

All fractions containing contaminated phlorin **5** were combined, and the solvents evaporated. Subsequent dry column vacuum chromatography (silica, toluene/hexane, 1:1, then 2:1) afforded pure compound (52 mg, 9%) which was crystallized from acetone/hexane to give dark green crystals: R_f = 0.43 (silica, CH_2Cl_2:hexane, 2:3). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 4.35 (br. s, 3 H, pyrrole NH), 6.15–6.25 (m, 2 H, dipyrrin), 6.60–6.70 (m, 2 H, dipyrrin), 6.71 (d, J = 4.0 Hz, 2 H, β-pyrrole), 6.85 (d, J = 4.0 Hz, 2 H, β-pyrrole), 6.88 (br. s, 1 H, dipyrrin), 6.94 (d, J = 5.0 Hz, 2 H, β-pyrrole), 7.11 (d, J = 5.0 Hz, 2 H, β-pyrrole), 7.20, 7.57 (AA′BB′, J = 9.0 Hz, 2×2 H, Ar-H), 7.64, 7.77 (AA′BB′, J = 8.0 Hz, 2×2 H, Ar-H), 11.30 (br. s, 1 H, dipyrrin NH). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 106.4, 108.7, 11.4, 111.8, 112.8, 113.6, 113.9, 118.1, 118.6, 120.4, 121.8, 124.1, 124.8, 126.3, 129.3, 130.1, 130.8, 131.2, 131.3, 131.8, 131.9, 132.7, 132.9, 133.2, 136.5, 138.6, 140.6, 142.6, 143.8, 144.3, 144.5, 145.4, 145.7, 146.5, 146.7, 156.1, 171.4, 206.9 ppm. LRMS(ESI): m/z 1155.2 [M + H$^+$]. HRMS(ESI): calcd. for $C_{61}H_{26}F_{15}N_8$ [M + H$^+$] 1155.2068; found 1155.2035. $C_{61}H_{25}F_{15}N_8 \times H_2O$ (1172.21): calcd. C 62.47, H 2.32, N 9.55; found C 62.75, H 2.28, N 9.33. UV/Vis (toluene): λ_{max} ($\varepsilon \times 10^{-3}$) = 300 (22.2), 350 (24.6), 420 (52.6), 450 (51.3), 669 nm (21.6).

Condensation of 5-Pentafluorophenyldipyrromethane with 4-Nitrobenzaldehyde: The reaction mixture was passed through a chromatography column (silica, CH_2Cl_2/hexane, 1:3, then 2:3). The first fraction containing 5,15-bis(pentafluorophenyl)-10-(4-nitrophenyl)corrole was evaporated. The remaining dark residue was dissolved in hot hexanes, and cooled in the freezer. After filtration, the remaining crystals were washed with hexane to obtain corrole (42 mg, 9%): R_f = 0.61 (silica, CH_2Cl_2:hexane, 2:3). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = –2.55 (br. s, 3 H, pyrrole NH), 8.36 (1/2 AA′BB′, J = 8.0 Hz, 2 H, Ar-H), 8.55–8.68 (m, 6 H, Ar-H and 4 β-pyrrole), 8.75 (d, J = 4.5 Hz, 2 H, β-pyrrole), 9.13 (d, J = 4.0 Hz, 2 H, β-pyrrole). HRMS(ESI): calcd. for $C_{37}H_{16}F_{10}N_5O_2$ [M + H$^+$] 752.1139; found 752.1162. $C_{37}H_{15}F_{10}N_5O_2$ (751.11): calcd. C 59.13, H 2.01, N 9.32; found C 59.25, H 1.98, N 9.20. UV/Vis (toluene): λ_{max} ($\varepsilon \times 10^{-3}$) = 423 (87.3), 569 (17.7), 613 (9.7), 639 nm (5.3).

All fractions containing contaminated phlorin **6** were combined, and the solvents evaporated. Subsequent dry column vacuum chromatography (silica, toluene/hexanes, 1:1 then 3:2) afforded pure compound (28 mg, 8%) which was crystallized from acetone/cyclohexane to give dark green crystals: R_f = 0.65 (silica, CH_2Cl_2/hexane, 1:1). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 3.0–4.0 (br. s, 3 H, pyrrole NH), 6.10–6.30 (m, 2 H, dipyrrin), 6.60–6.72 (m, 2 H, dipyrrin), 6.74 (d, J = 3.8 Hz, 2 H, β-pyrrole), 6.83 (br. s, 1 H, dipyrrin), 6.87 (d, J = 3.8 Hz, 2 H, β-pyrrole), 6.98 (d, J = 5.0 Hz, 2 H, β-pyrrole), 7.14 (d, J = 4.9 Hz, 2 H, β-pyrrole), 7.29, 8.13 (AA′BB′, J = 8.5 Hz, 2×2 H, Ar-H), 7.70, 8.35 (AA′BB′, J = 8.4 Hz, 2×2 H, Ar-H), 11.35 (br. s, 1 H, dipyrrin NH). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 106.5, 108.3, 112.9, 113.5, 113.8, 120.5, 121.9, 123.2, 123.3, 124.1, 125.0, 126.1, 129.3, 130.3, 130.9, 131.3, 132.7, 133.0, 133.3, 136.6, 137.1, 138.6, 140.7, 142.7, 143.7, 144.5, 145.4, 145.7, 146.3, 146.5, 146.7, 147.3, 147.4, 148.3, 156.1, 171.2. HRMS(ESI): calcd. for $C_{59}H_{26}F_{15}N_8O_4$ [M + H$^+$] 1195.1832; found 1195.1903; LRMS(ESI): m/z 1195.2 [M + H$^+$]. $C_{59}H_{25}F_{15}N_8O_4$ (1194.86): calcd. C 59.31, H 2.11, N 9.38; found C 59.34, H 2.18, N 9.40. UV/Vis (toluene): λ_{max} ($\varepsilon \times 10^{-3}$) = 363 (27.5), 382 (29.9), 461 (49.6), 675 nm (16.8).

Stability Study: The stability of phlorins **4**–**6** was measured by the following experiments. TLC as well as ESI-MS analysis of the solutions of phlorins **4**–**6** left in the open flask on the bench top in the presence of light for 10 h were performed and compared with freshly dissolved samples. These experiments showed that phlorins **5** and **6** developed only very slight starting point on TLC and that no difference between ESI-MS of the fresh and "aged" samples was

observed. On the other hand, the solution of phlorin **4** shows few spots by TLC and many different peaks on ESI-MS.

Bubbling air through the solution of phlorins **4**–**6** for half an hour gave the same difference in the rate of decomposition as in the previous experiment.

TLC spots of phlorins **4**–**6** were observed. While spots of phlorins **5** and **6** maintained the same color after many hours, phlorin **4** turned brown after a few minutes and repetitive TLC from such spot shows significant decomposition.

Crystal Data for Phlorin-Dipyrrin 6: $C_{80}H_{67}F_{15}N_8O_5$, M = 1505.42, $0.13 \times 0.10 \times 0.07$ mm^3, triclinic, space group P-1 (No. 2), a = 12.046(5), b = 15.873(7), c = 20.474(8) Å, α = 67.41(4), β = 81.73(4), γ = 80.83(4)°, V = 3553(3) Å^3, Z = 2, D_c = 1.407 g/cm^3, F_{000} = 1556, μ = 0.116 mm^{-1}, Kuma4CCD, Mo-$K\alpha$ radiation, λ = 0.71073 Å, T = 150(2) K, $2\theta_{max}$ = 57.7°, 50912 reflections collected, 17138 unique (R_{int} = 0.1566). The crystal was positioned at 65 mm from the KM4CCD camera. 1547 frames were measured at 0.6° intervals with a counting time of 50 sec. The data were corrected for Lorentz and polarization effects. No absorption correction was applied. Data reduction and analysis were carried out with the Kuma Diffraction (Wrocław) programs. The structure was solved and refined using the programs SHELXS-97[29] and SHELXL-97[30] respectively. The program X-Seed (Barbour, 1999) was used as an interface to the SHELX programs, and to prepare the figures.[31] All non-hydrogen atoms were refined anisotropically, except disordered cyclohexane molecule. All hydrogen atoms were located from a differential map and refined isotropically. Final *GooF* = 0.706, R_1 = 0.0777, wR_2 = 0.1873, R indices based on 2902 reflections with $I > 2\sigma(I)$ (refinement on F^2), 929 parameters, 132 restraints. Scattering factors were taken from Tables 6.1.1.4 and 4.2.4.2.[32]

CCDC-254742 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request.cif.

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