

Synthesis and photostability of cyclooctatetrane-substituted free base porphyrins

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Syntheses

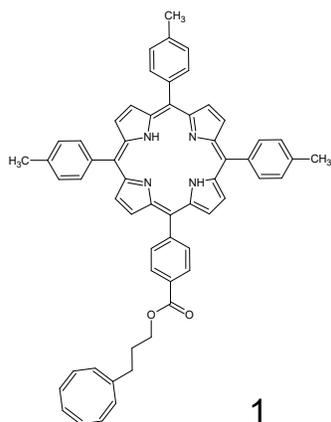
5-(4-Methoxycarbonylphenyl)-10,15,20-tri(*p*-tolyl)porphyrin **6**¹, 5,15-bis(4-methylesterphenyl)-10,20-bis(mesityl)porphyrin **7**², 5-(*p*-acetamidophenyl)-10,15,20-tris(*p*-tolyl)porphyrin **8**³, 5-(4-carboxyphenyl)-10,15,20-tri(*p*-tolyl)porphyrin **9**⁴, 1,3,5,7-cyclooctatetraene-1-propanol COT-OH **10**⁵, 5-(4-(hydroxymethyl)phenyl)-10,15,20-tritolylporphyrin **11**¹, 5-(*p*-aminophenyl)-10,15,20-tris(*p*-tolyl)-porphyrin **12**³, 5,15-bis[4-(hydroxymethyl)phenyl]-10,20-dimesitylporphyrin **13**², tetrakis(4-carboxyphenyl)porphyrin **14**⁶ were synthesized following previously published procedures.

General procedure A

To a stirred solution of porphyrin (1 eq, 0,144 mmol), COT-OH **10**⁵ (2 eq, 0,288 mmol for one carboxyl group) and 4-DMAP (2 eq, 0,288 mmol for one carboxyl group) in anhydrous THF (15 mL) was added EDCI.Cl (2 eq, 0,288 mmol for one carboxyl group) and the solution was stirred overnight at room temperature. THF was evaporated under reduced pressure and the residue was diluted with H₂O (15 mL) and extracted with CH₂Cl₂ (3 x 50 ml). The combined organic layers were washed with H₂O and brine and dried over anhydrous Na₂SO₄. The filtrated solution was evaporated under reduced pressure and the resulting solid was subjected to further purification.

General procedure B

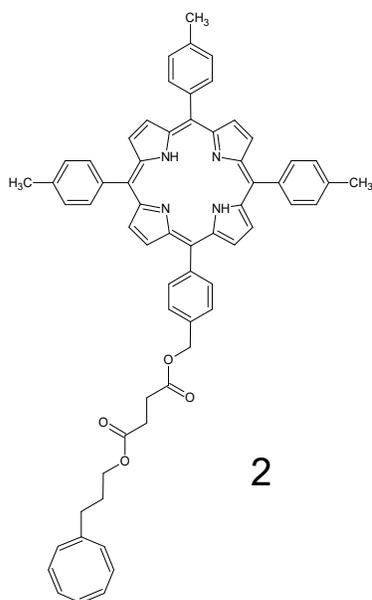
To a stirred solution of porphyrin (1 eq; 0,217 mmol) in anhydrous DCM (15 mL) was added one drop of Et₃N and a solution of succinic anhydride (2 eq; 0,434 mmol) in DCM (4mL) was added slowly over 30 min. After 16 h the solution was concentrated and the resulting residue was passed through a short plug of silica gel using 97:3 DCM/MeOH to provide the crude acid, which was used without further purification in order to avoid aggregation.



5-{4-[3-(1,3,5,7-cyclooctatetraenyl)]-propoxy}carbonylphenyl}-10,15,20-tri-*p*-tolylporphyrin **1**.

Porphyrin **1** was synthesized according to general procedure A from porphyrin **9**⁴ as a starting material. The desired product was precipitated with methanol, filtrated and washed with fresh portion of methanol. Compound **1** was obtained as a purple powder with 49% yield.

¹H NMR (500 MHz, CDCl₃) δ = 8.9-8.82 (m, 6H, H_β pyrrole), 8.77 (d, J = 4.5 Hz, 2H, H_β pyrrole), 8.44 (d, J = 8.0 Hz, 2H, H aryl), 8.30 (d, J = 8.0 Hz, 2H, H aryl), 8.08 (d, J = 8.0 Hz, 6H, H aryl), 7.53 (d, J = 8.0 Hz, 6H, H aryl), 5.95 - 5.76 (m, 6H, COT), 5.76 - 5.67 (m, 1H, COT), 4.56 (t, J = 6.5 Hz, 2H, CH₂CH₂CH₂), 2.69 (s, 9H, PhCH₃), 2.33 (bs, 2H, CH₂CH₂CH₂), 2.03 (bs, 2H, CH₂CH₂CH₂); ¹³C NMR (500 MHz, CDCl₃) δ = 166.87, 147.15, 143.15, 139.21, 139.16, 137.43, 134.58, 134.51, 133.94, 132.24, 132.16, 131.82, 131.2, 129.80, 127.87, 127.46, 127.26, 120.41, 118.29, 64.69, 34.14, 27.71, 21.52; MS (ESI) m/z calcd for C₅₉H₄₈N₄O₂ : 845.3856; found 845.3843 [M + H]⁺.

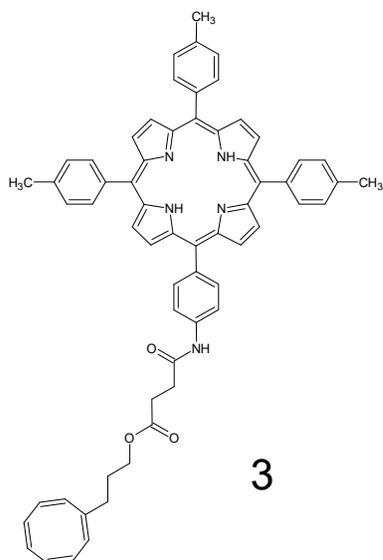


3-(1,3,5,7-cyclooctatetraenyl)prop-1-yl-*p*-(10,15,20-tri-*p*-tolylporphyrin-5-yl)benzyl 1,4-butanedioate **2**.

Porphyrin **11**¹ in reaction with succinic anhydride according to general procedure B provided easily porphyrin with the prolonged chain (estimated 48% yield of crude acid), which was used without further purification. Directly after drying, crude acid was taken to react with COT-OH **10**⁵ according to procedure A, giving the desired compound **2**. The product was purified by column chromatography (silica gel, hexane/ethyl acetate 4:1) to afford porphyrin **2** as a purple powder in 55% yield.

¹H NMR (500 MHz, CDCl₃) δ = 8.88-8.83 (m, 6H, H_β pyrrole), 8.82 (d, J = 4.5 Hz, 2H, H_β pyrrole), 8.21 (d, J = 8.0 Hz, 2H, H aryl), 8.09 (d, J = 7.5 Hz, 2H, H aryl), 7.72 (d, J = 8.0 Hz, 6H, H aryl), 7.55 (d, J = 7.5 Hz, 6H, H aryl), 5.85 - 5.66 (m, 6H, COT), 5.62 - 5.55 (m, 1H, COT), 5.50 (s, 2H, PhCH₂O), 4.21 (t, J = 6.5 Hz, 2H, CH₂CH₂CH₂), 2.89 - 2.84 (m, 2H, CH₂CH₂), 2.81 - 2.76 (m, 2H, CH₂CH₂), 2.70 (s, 9H, PhCH₃), 2.17 - 2.10 (m, 2H, CH₂CH₂CH₂), 1.83 - 1.73 (m, 2H, CH₂CH₂CH₂); ¹³C NMR (500 MHz, CDCl₃) s = 172.38, 172.30, 143.0, 142.30, 139.23, 137.35, 135.22, 134.7, 134.51, 133.82, 132.14, 132.04, 131.07,

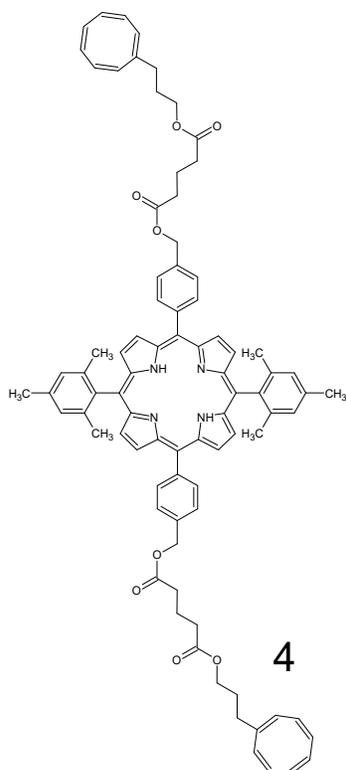
131.1, 127.4, 126.38, 120.3, 120.2, 119.12, 66.54, 64.26, 33.88, 29.7, 29.4, 29.3, 27.4, 21.5.
MS (ESI) m/z calcd for C₆₃H₅₄N₄O₄ : 931.4223; found 931.4232 [M + H]⁺.



3-(cyclooctatetraenyl)propyl 4-oxo-4-[4-[(5Z,10Z,14Z,19Z)-10,15,20-tris(*p*-tolyl)-21,23-dihydroporphyrin-5-yl]anilino]butanoate **3**.

Porphyrin **12**³ in reaction with succinic anhydride according to general procedure B readily provided porphyrin with the prolonged chain (with the estimated yield of crude acid of 83%), which was used without further purification. Directly after drying crude acid was taken to react with COT-OH **10**⁵ according to procedure A, giving a desired compound **3**. The product was purified by column chromatography (silica gel, hexane/ethyl acetate from 4:1 to 2:1). The desired compound was precipitated with methanol, filtrated and washed with fresh portion of methanol to afford porphyrin **3** as a purple powder in 53% yield.

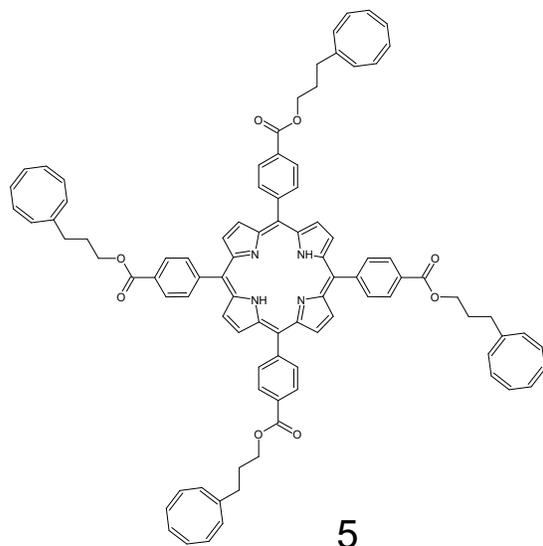
¹H NMR (500 MHz, CDCl₃) δ = 8.88-8.79 (m, 8H, H_β pyrrole), 8.21 (d, J = 8.0 Hz, 2H, H aryl), 8.09 – 8.06 (m, 6H, H aryl), 7.90 (bs, 1H, PhNH), 7.83 (d, J = 8.0 Hz, 2H, H aryl), 7.52 – 7.44 (m, 6H, H aryl), 5.87 - 5.70 (m, 6H, COT), 5.66 - 5.54 (m, 1H, COT), 4.24 (t, J = 6.5 Hz, 2H, CH₂CH₂CH₂), 2.89 – 2.82 (m, 2H, CH₂CH₂), 2.80 – 2.73 (m, 2H, CH₂CH₂), 2.70 (m, 9H, PhCH₃), 2.18 – 2.08 (m, 2H, CH₂CH₂CH₂), 1.84 – 1.73 (m, 2H, CH₂CH₂CH₂); ¹³C NMR δ = 173.38, 170.116, 142.98, 139.29, 139.26, 138.18, 137.54, 137.32, 135.07, 134.5, 133.84, 132.18, 132.10, 131.75, 131.14, 131.02, 127.41, 127.16, 120.23, 120.187, 119.24, 117.92, 64.53, 33.89, 32.44, 29.68, 27.41, 21.41; MS (ESI) calcd for C₆₂H₅₃N₅O₃ : 916.4227; found 916.4215 [M + H]⁺.



5-[[4-[(5Z,10Z,14Z,19Z)-15-[4-[[5-[3-(cyclooctatetraenyl)propoxy]-5-oxo-pentanoyl]oxymethyl]phenyl]-10,20-bis(2,4,6-trimethylphenyl)-21,23-dihydroporphyrin-5-yl]phenyl]methyl] 1-[3-(cyclooctatetraenyl)propyl] pentanedioate **4**.

Porphyrin **13**² in reaction with glutaric anhydride according to general procedure B provided readily porphyrin with the prolonged chain at two positions (with the estimated yield of crude acid of 92%). It was not necessary to filtrate it through silica gel. The product was precipitated with mixture of Et₂O/CH₂Cl₂/MeOH and was used without further purification. Directly after drying, crude diacid was taken to react with COT-OH **10**,⁵ according to procedure A, giving the desired compound **4**. The product was purified by column chromatography (silica gel, hexane/ethyl acetate 4:1). The title compound was precipitated with CH₂Cl₂/MeOH, to afford porphyrin **4** as a purple powder in 28 % yield.

¹H NMR (500 MHz, CDCl₃) δ = 8.78 (d, J = 4.5 Hz, 4H, H_β pyrrole), 8.68 (d, J = 4.5 Hz, 4H, H_β pyrrole), 8.21 (d, J = 7.7 Hz, 4H, H aryl), 7.72 (d, J = 7.7 Hz, 4H, H aryl), 7.28 (s, 4H, H-mesityl), 6.65 - 5.85 (m, 12H, COT), 5.61 - 5.52 (m, 2H, COT), 5.48 (s, 4H, PhCH₂O), 4.17 (t, J = 6.5 Hz, 4H, CH₂CH₂CH₂), 2.65 - 2.58 (m, 10H, 6H CH₃-*p*-mesityl, 4H CH₂CH₂CH₂), 2.48 (t, 4H, J = 7.3 Hz, CH₂CH₂CH₂), 1.84 (s, 12H, CH₃-*o*-mesityl), 1.78 -1.70 (m, 4H, CH₂CH₂CH₂), -2.61 (s, 2H, NH pyrrole); ¹³C NMR (500 MHz, CDCl₃) δ = 172.96, 172.94, 142.99, 141.96, 139.37, 138.39, 137.75, 135.39, 134.65, 133.79, 132.09, 132.02, 131.68, 131.07, 127.76, 127.05, 126.4, 118.4, 66.25, 63.91, 33.88, 33.49, 33.40, 29.68, 27.44, 21.60, 21.45, 20.32. MS (ESI) m/z calcd for C₈₄H₈₂N₄O₈: 1275.6211; found 1275.6206 [M + H]⁺.



5,10,15,20-tetra-*p*-{[3-(1,3,5,7-cyclooctatetraenyl)propoxy]carbonylphenyl}porphyrin **5**.

Porphyrin **5** was synthesized according to general procedure A from porphyrin **14**⁶ as a starting material. The desired product was purified by column chromatography (silica gel, hexane/ethyl acetate 4:1). Compound **5** was obtained as a purple powder with the yield of 6%.

¹H NMR (500 MHz, CDCl₃) δ = 8.82 (s, 8H, H_β pyrrole), 8.84 (m, 8H, H aryl), 8.29 (m, 8H, H aryl), 5.95 - 5.76 (m, 24H, COT), 5.73 - 5.66 (m, 4H, COT), 4.17 (t, J = 6.5 Hz, 8H, CH₂CH₂CH₂), 2.38 - 2.29 (m, 8H, CH₂CH₂CH₂), 2.08 - 1.96 (m, 8H, CH₂CH₂CH₂); ¹³C NMR (500 MHz, CDCl₃) δ = 166.71, 146.56, 143.07, 134.50, 133.89, 132.2, 132.15, 131.79, 131.2, 130.07, 128.0, 127.25, 119.42, 64.74, 34.119, 27.68; MS (ESI) m/z calcd for C₉₂H₇₈N₄O₈ : 1367.5898; found 1367.5917 [M + H]⁺.

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Determination of the photobleaching quantum yield

Room temperature solutions of porphyrins in toluene have been irradiated in quartz cells (1 cm pathlength) for equally spaced time periods. The solutions were stirred during irradiation. After each time interval, absorption spectra were recorded to determine the decrease of the chromophore concentration. Two light sources (Thorlabs LEDs) were used for irradiation, emitting at 420 nm (63 mW) and at 409 nm (432 mW). After recording the spectral profile of each diode ($D(\lambda)$), it was multiplied by a constant factor ($I_0(\lambda) = c \times D(\lambda)$), selected so that the integral of $I_0(\lambda)$ over λ gives the number of photons emitted per second.

The number of photons absorbed by the irradiated sample per time unit at time t , $N_{abs}(t)$ is obtained by integrating $I_0(\lambda) \times (1 - 10^{-A(\lambda,t)})$ over the emission spectrum of the diode:

$$N_{abs}(t) = \int_{\lambda_1}^{\lambda_2} I_0(\lambda) \times (1 - 10^{-A(\lambda,t)}) d\lambda \quad (1)$$

Next, the total number of photons absorbed by the since the beginning of irradiation ($t = 0$) can be obtained from:

$$N_{total}(t) = \int_0^t N_{abs}(t) dt \quad (2)$$

The photobleaching quantum yield, Φ_{pb} , is given by the ratio of the total number of photobleached molecules ($N_{pb}(t)$) to the total number of photons absorbed by the substrate ($N_{total}(t)$) after irradiating for time t . Thus, $N_{pb}(t)$ is equal to $\Phi_{pb} \times N_{total}(t)$. The value of $N_{pb}(t)$ is experimentally determined by monitoring absorption decrease upon irradiation, at a wavelength where only the substrate absorbs:

$$N_{pb}(t) = \frac{(A_0 - A(t)) \times N_{Av} \times V}{1000 \times \epsilon \times l} \quad (3)$$

A_0 and $A(t)$ are the absorbances measured before and after irradiation over t , respectively; N_{Av} is the Avogadro number, V is the sample volume (in cm^3), ϵ is the molar absorption coefficient, and l is the optical path length.

After some simple algebraic transformations, it is possible to express Φ_{pb} as:

$$\Phi_{pb} = \frac{b \times N_{Av} \times V}{1000 \times \epsilon \times l} \quad (4)$$

where b is the slope in the equation:

$$\frac{A_0}{A(t)} = 1 + bF(t), \quad (5)$$

and $F(t)$ is defined as:

$$F(t) = \frac{N_{total}(t)}{A(t)} \quad (6)$$

Thus, the photobleaching quantum yield can be determined from eq. (4) using the value of b obtained from the plots of $A_0/A(t)$ as a function of $F(t)$.

If the monitoring wavelength corresponds exclusively to the absorption of the initial species, a linear plot is expected. Otherwise, deviations can be observed, due to the contributions from the photoproducts. Another source of error may involve partial absorption of light used for photodegradation.

Deviations from linearity were observed for two porphyrins, **4** and **7**. In these cases, only the initial points were used to estimate Φ_{pb} .

For each porphyrin, at least two series of independent experiments were performed. Use of different light sources resulted in very similar values of Φ_{pb} (maximum difference of about 20%). We estimate that the error in the reported values of photobleaching quantum yields should not exceed 30%.

Table S1. Cyclic voltammetry data. Potentials given vs. Ag quasi-reference electrode in [V]

Compound	E (0/-1)	E (-1/0)	E (0/-1) _{red onset}	E (0/+1)	E (+1/0)	E (+1/0) _{ox onset}
1	-1.16	-1.09	-1.07	1.10	1.02	0.98
2	-1.24	-1.16	-1.00	0.94	0.85	0.82
3	-1.28	-1.09	-1.00	0.92	0.81	0.80
4	-1.29	-1.19	-1.17	1.08	0.99	0.96
5	-1.46	-	-0.93	1.18	0.39	1.07
7	-1.27	-1.21	-1.06	1.04	0.96	0.93
8	-1.22	-1.14	-1.10	1.01	0.94	0.89

Table S2. Experimentally determined ionization potentials (IP), electron affinities (EA), and energy gaps (Eg). All data in [eV].

Compound	IP ^a	EA ^a	E _g
1	5.92	-3.57	2.35
2	5.73	-3.65	2.08
3	5.71	-3.65	2.06
4	5.89	-3.45	2.44
5	6.02	-3.73	2.29
7	5.86	-3.59	2.27
8	5.81	-3.53	2.28

^a experimental values of IP and EA were determined from the onsets of the corresponding anodic and cathodic peaks following the procedure recommended in ref. 7:

$$\text{IP}[\text{eV}] = |e|[1.15 \times E_{\text{ox onset}} + 4.79] [\text{eV}],$$

$$\text{EA}[\text{eV}] = e [1.18 \times E_{\text{red onset}} + 4.83] [\text{eV}].$$

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