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Convenient synthetic route of versatile 21-monothiatetraphenylporphyrins of the A_4 and AB_3 type

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Abstract—A novel convenient synthetic route for poly-functional 21-monothiatetraphenylporphyrins of the type A_4 und AB_3 having base labile substituents in meso position was developed. Using this method a series of symmetric and asymmetric 21-thiaporphyrins containing different functional groups at the meso position is reported. The new products were characterized by NMR, UV–Vis and mass spectroscopy.

1. Introduction

Core-modified porphyrins show new interesting properties in metal-complexation, acid–base behaviour, redox-potentials, photochemistry and medicine in comparison with the well-known N_4 porphyrin system that may lead to useful applications.[1–6] 21-Monothiatetraphenylporphyrins represent such a promising type; asymmetric substituted AB_2C and AB_3 monothiatetraphenylporphyrins were previously reported, although the synthesis of reactive functional groups at the phenyl substituents has been difficult to achieve.[7,8] Groups such as carboxylic, amino, bromo, and hydroxy are needed as building blocks for the construction of large porphyrin arrays or for the dendritic encapsulation of the units. Such large and defined supramolecular structures and their metal complexes open up new application possibilities in medicine, optoelectronics and catalysis.[9–12]

2. Results and discussion

2.1. Modified synthesis of symmetric thiophene diols and corresponding porphyrins

The preparation of 2,5-bis-phenylhydroxymethyl substituted thiophene occurs with the classical deprotonation of the α-hydrogens on the thiophene with *n*-butyl lithium and subsequent addition of the benzaldehyde-derivative to the bislithiated dianion.[13] For base-insensitive phenyl substituents is the established reaction sequence (addition the aldehyde to the dianion) the favoured method. However, the procedure does not work when base-labile substituents on the benzaldehyde, for example, phenylcarboxylates, are used due to side reactions between the carboxylic substituents and the dianion. In order to avoid more complex protective groups or longer reaction sequences, we changed the reaction order at the addition step. The addition of the thiophene dilithiate to the base-labile benzaldehyde leads to the wanted substituted diols in good yields (Table 1). The synthesis of the desired 21-monothiatetraphenylporphyrins from the prepared diols occurred with the well established Lindsey-conditions,[14,15] which obviously gives higher yields in comparison with the method described by Adler et al.[16,17] The porphyrin condensation resulted in the mixture of three porhyrins with different core patterns: N_4, N_3S and N_2S_2. The porphyrins were separated by column chromatography, in which the desired monothiaporphyrins eluted as the second porphyrin fraction. The ether and ester cleavage was accomplished by common methods (Table 2) (Scheme 1).

Table 1. Yields of thiophene diols

Compound	**1**	**2**
Substituent R	4-COOMe	3,5-OMe
Yield [%]	40	95

2.2. Modified synthesis of asymmetric thiophene diols and corresponding porphyrins

We are also interested in synthesizing asymmetric monothiatetraphenylporphyrins of the type AB_3. The direct condensation of thiophene mono-ols to thiaporphyrins

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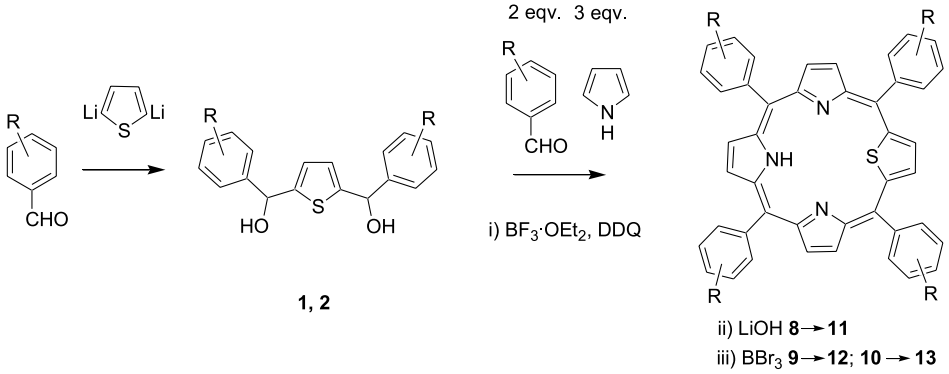
Table 2. Yields of symmetric thiaporphyrins

Compound	**8**	**9**	**10**	**11**	**12**	**13**
Substituent R	4-COOMe	3,5-OMe	4-OMe	4-COOH	3,5-OH	4-OH
Yield [%]	22	18	19	96[a]	91[a]	92[a]

[a] These yields are related to the deprotecting reaction.



Scheme 1. General synthetic scheme of symmetric thiaporphyrins.

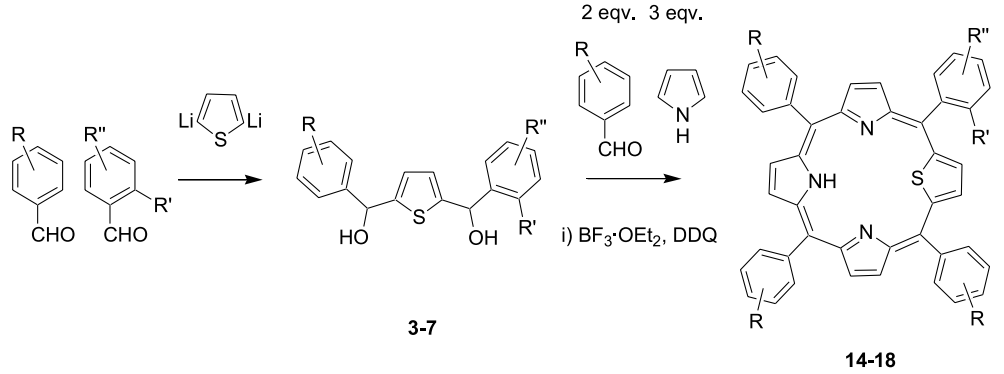
Table 3. Yields of asymmetric thiophene diols

Compound	**3**	**4**	**5**	**6**	**7**
Substituent R	4-Br	4-Br	4-Br	3,5-OMe	4-COOMe
Substituent R′	OMe	OAllyl	OMe	OAllyl	OAllyl
Substituent R″	H	5-Br	5-Br	3-OMe	H
Yield [%]	36	21	38	18	11

appears due to the lower yields rather unfavourable, thus the preparation of unsymmetrical thiophene diols is necessary. This can be effected, such as already described, with a stepwise procedure[8] or like in our case in one concerted step as described above, with the main difference of using two differently substituted aldehydes (Table 3). This reaction yields more side-products, but saves one reaction step, and is necessary for substituents that are unstable under the drastic lithiation condition. The chromatographic separation of the desired diol was achieved without any problems. Standard porphyrin synthesis resulted in asymmetric monothiaporphyrins with different core patterns: N_4, N_3S and N_2S_2. The porphyrins were separated by column chromatography, in which the desired

Table 4. Yields of asymmetric thiaporphyrins

Compound	**14**	**15**	**16**	**17**	**18**
Substituent R	4-Br	4-Br	4-Br	3,5-OMe	4-COOMe
Substituent R′	OMe	OAllyl	OMe	OAllyl	OAllyl
Substituent R″	H	5-Br	5-Br	3-OMe	H
Yield [%]	3	15	9	4	7



Scheme 2. General synthetic scheme of asymmetric thiaporphyrins.

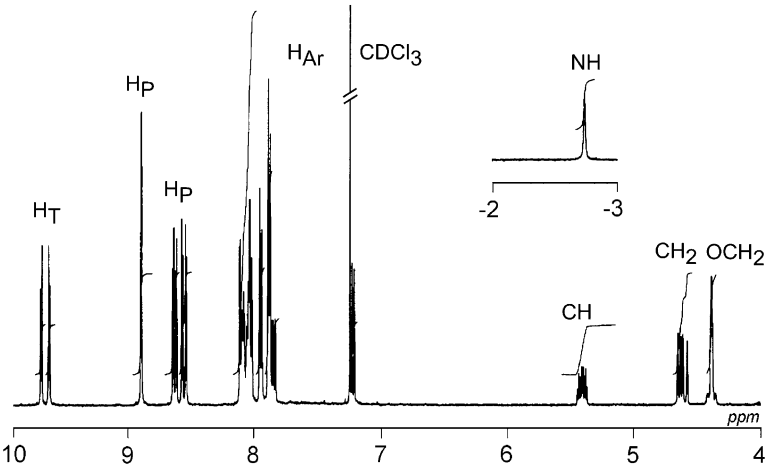


Figure 1. ^{1}H NMR spectrum of **15** recorded in $CDCl_3$. Resonance assignments: H_T, thiophene H; H_P, pyrrole H; H_{Ar}, H of the phenyl rings. The showed spectrum corresponds with the accomplished 2D NMR measurements.

monothiaporphyrins eluted as the second porphyrin fraction (Table 4) (Scheme 2).

The displayed NMR (Fig. 1) and absorption (Fig. 2) spectras of the monothiatetraphenylporhyrin **15** indicate the asymmetric structure and the typical absorption behaviour.

3. Conclusion

We report a modified synthetic method to generate novel monothiatetraphenylporphyrins having carboxyphenylic substituents at the meso position. The marginal additional preparative expense of our method results in better yields and smaller amounts of side products. We also describe an alternative way to obtain AB_3-type 21-thiaporphyrins with acceptable yields based on the one step synthesis of the asymmetrical thiophene diol precursor. The preparation and characterization of transition metal complexes with these heteroporphyrins are now underway in our group.

4. Experimental

4.1. General

^{1}H and ^{13}C NMR spectra were obtained on a Bruker DRX-500 at 500 and 126 MHz, respectively. UV/Vis spectra were recorded on a Perkin Elmer Lambda 2. The mass spectra were measured on a Esquire Hewlett & Packard and a Shimadzu Kratos Kompact MALDI II mass spectrometer. Column chromatography was carried out with silica gel 60 (0.040–0.063 mm Merck). Fine chemicals were supplied by Fluka and solvents were dried by standard procedures before use.

4.2. Data for compounds

The preparation of 5,10,15,20-(4-methoxyphenyl)-21-thiaporphyrin **10** and 5,10,15,20-(4-bromophenyl)-21-thiaporphyrin were described earlier but we used our modified approach.[18]

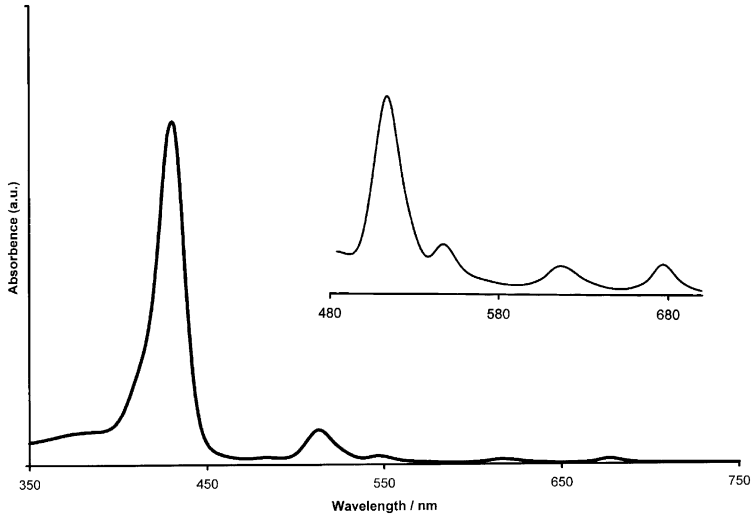


Figure 2. Absorption spectrum of **15** recorded in toluene. The concentrations used were 5×10^{-6} and 5×10^{-5} M, respectively. Enlarged Q-Bands are shown in the inset.

4.2.1. 2,5-Bis[(4-carboxymethyl)phenyl(hydroxy)-methyl]-thiophene 1. In a three neck flask equipped with rubber septum, gas inlet tube and reflux condenser dry *n*-hexane (25 ml) was taken. TMEDA (16 mmol, 1.86 ml) and *n*-butyl lithium (20 ml of a 1.6 M solution) were added into the stirred solution. Destilled thiophene (8 mmol, 317 μl) was added and the reaction mixture was refluxed for 1 h under slow argon purging.

After this time, the dilithiated thiophene mixture was cooled to 0 °C and transferred into the ice cold solution of methyl 4-formylbenzoate (16 mmol, 2.63 g) in dry THF (30 ml). The mixture was stirred for 10 min and saturated NH_4Cl added to quench the reaction. The organic layer was extracted with ethyl acetate and dried over Na_2SO_4. The crude product was purified by silica gel column chromatography (ethyl acetate/*n*-heptane 1:1) and the desired diol **1** was obtained besides small amounts of unreacted aldehyde and mono-ol as the third fraction (1.32 g, 40%).

^{1}H NMR ($CDCl_3$, δ in ppm) 2.65 (bs, 2H, OH), 3.9 (s, 6H, OMe), 6.0 (s, 2H, CH), 6.7 (s, 2H, β-thiophene), 7.5 (d, 4H, meta-H), 8.0 (d, 4H, ortho-H).

4.2.2. 2,5-Bis[(3,5-methoxy)phenyl(hydroxy)methyl]-thiophene 2. Compound **2** was prepared following the same method given for **1** by using dry *n*-hexane (10 ml), TMEDA (10 mmol, 1.5 ml), *n*-butyl lithium (6.25 ml of 1.6 M solution) and thiophene (5 mmol, 397 μl) for the dilithiated thiophene, which was added at 0 °C to a precooled solution of 3,5-methoxybenzaldehyde (10 mmol, 1.66 g) in dry THF (10 ml). The crude product was purified by silica gel column chromatography in ethyl acetate/*n*-heptane (4:6). Compound **2** was obtained as a white solid (1.98 g, 95%).

^{1}H NMR ($CDCl_3$, δ in ppm) 2.9 (bs, 2H, OH); 3.75 (s, 12H, OMe); 5.85 (d, 2H, CH); 6.45 (t, 2H, para-H); 6.6 (d, 4H, ortho-H); 6.7 (s, 2H, β-thiophene).

4.2.3. 2-[(4-Bromo)phenylhydroxymethyl]-5-[(2-methoxy-phenyl)hydroxymethyl]-thiophene 3. Compound **3** was synthesized in the same way as **1** by using dry *n*-hexane (25 ml), TMEDA (19 mmol, 2.87 ml), *n*-butyl lithium (23.9 ml of 1.6 M solution) and thiophene (9.6 mmol, 766 μl) for the dilithiated thiophene. This mixture was added at 0 °C to a precooled 1:1 mixture of 4-bromobenz-aldehyde (9.6 mmol, 1.77 g) and 2-methoxybenzaldehyde (9.6 mmol, 1.30 g) in dry THF (30 ml). The crude product was purified by silica gel column chromatography (ethyl acetate/*n*-heptane 1:1). **2** was obtained as a yellow solid (1.39 g, 36%).

^{1}H NMR ($CDCl_3$, δ in ppm): 2.4 (bs, 1H, OH); 3.25 (bs, 1H, OH); 3.8 (s, 3H, OMe); 5.9 (s, 1H, CH); 6.1 (s, 1H, CH); 6.7 (m, 2H, thiophene); 6.85 (d, 1H, H-Ar); 6.95 (t, 1H, H-Ar); 7.3 (t, 2H, ortho-H); 7.35 (d, 1H, H-Ar) 7.4 (d, 2H, metha-H).

4.2.4. 2-[(4-Bromo)phenylhydroxymethyl]-5-[(2-allyl-oxy-5-bromophenyl)hydroxymethyl]-thiophene 4. Preparation of **4** was done following the same method given for **1** by using dry *n*-hexane (30 ml), TMEDA (19 mmol, 2.97 ml), *n*-butyl lithium (38 ml of 1.6 M solution) and thiophene (9.5 mmol, 750 μl) for the dilithiated thiophene, which was added at 0 °C to a precooled 1:1 mixture of 4-bromobenzaldehyde (9.5 mmol, 1.76 g) and 2-allyloxy-5-bromobenzaldeyhde (9.5 mmol, 2.285 g) in dry THF (30 ml). The crude product was purified by silica gel column chromatography (ethyl acetate/*n*-heptane 3:7) and obtained as yellow solid (1.0 g, 21%).

^{1}H NMR ($CDCl_3$, δ in ppm) 2.3 (bs, 1H, OH); 3.0 (m, 1H, OH); 4.5 (m, 2H, OCH_2); 5.25 (dd, 2H, CH_2); 5.9 (dq, 1H, CH); 5.95 (d, 1H, CH); 6.15 (d, 1H, CH); 6.65 (d, 2H, β-thiophene); 6.7 (d, 1H, meta-H); 7.3 (d, 2H, ortho-H); 7.35 (dd, 1H, para-H); 7.45 (d, 2H, meta-H); 7.5 (d, 1H, ortho-H).

4.2.5. 2-[(4-Bromo)phenylhydroxymethyl]-5-[(2-meth-oxy-5-bromophenyl)hydroxymethyl]-thiophene 5. Compound **5** was prepared following the same method given for **1** by using dry *n*-hexane (20 ml), TMEDA (10.8 mmol, 1.62 ml), *n*-butyl lithium (13.5 ml of 1.6 M solution) and thiophene (5.4 mmol, 430 μl) for the dilithiated thiophene. The mixture was cooled to 0 °C and transferred into a precooled 1:1 mixture of 4-bromobenzaldehyde (5.4 mmol, 1.0 g) and 2-methoxy-5-bromobenzaldehyde (5.4 mmol, 1.16 g) in dry THF (30 ml). The crude product was purified by silica gel column chromatography (ethyl acetate/*n*-heptane 3:7). Compound **5** was obtained as a colorless solid (0.992 g, 38%).

^{1}H NMR ($CDCl_3$, δ in ppm) 2.45 (m, 1H, OH); 3.05 (m, 1H, OH); 3.75 (d, 3H, OMe); 5.9 (d, 1H, CH); 6.1 (d, 1H, CH); 6.15 (2d, 2H, β-thiophene); 6.25 (dd, 1H, meta-H); 7.3 (d, 2H, ortho-H); 7.35 (dd, 1H, para-H); 7.45 (d, 2H, meta-H); 7.5 (d, 1H, ortho-H).

4.2.6. 2-[(3,5-Methoxy)phenylhydroxymethyl]-5-[(2-allyl-oxy-3-methoxyphenyl)hydroxymethyl]-thiophene 6. Compound **6** was synthesized in the same way as **1** by using dry *n*-hexane (25 ml), TMEDA (15.6 mmol, 2.34 ml), *n*-butyl lithium (19.5 ml of 1.6 M solution) and thiophene (7.8 mmol, 660 μl). The mixture of the dilithiated thiophene was cooled to 0 °C and transferred into a cold solution of 3,5-dimethoxybenzaldehyde (7.8 mmol, 1.29 g) and 2-allyloxy-3-methoxybenzaldehyde (7.8 mmol, 1.5 g) in dry THF (30 ml). Purification of the product was done by silica gel column chromatography (ethyl acetate/*n*-heptane 1:1). Compound **6** was isolated as a yellow solid (0.61 g, 18%).

^{1}H NMR ($CDCl_3$, δ in ppm) 2.3 (bs, 1H, OH); 3.2 (dd, 1H, OH); 3.75 (s, 6H, OMe); 3.85 (s, 3H, OMe); 4.35 (m, 2H, OCH_2); 5.2 (m, 2H, CH_2); 5.85 (m, 1H, CH); 5.9 (d, 1H, CH); 6.1 (t, 1H, CH); 6.35 (t, 2H, β-thiophene); 6.55 (s, 2H, ortho-H); 6.65 (t, 1H, para-H); 6.85 (dd, 1H, H-Ar); 7.0 (dt, 1H, H-Ar); 7.05 (dd, 1H, H-Ar).

4.2.7. 2-[(4-Carboxymethyl)phenylhydroxymethyl]-5-[(2-allyloxyphenyl)hydroxymethyl]-thiophene 7. The synthesis of **7** followed the same manner as given for **1** by using dry *n*-hexane (10 ml), TMEDA (26 mmol, 3.9 ml), *n*-butyl lithium (32.5 ml of 1.6 M solution) and thiophene (13 mmol, 1.03 ml). After cooling to 0 °C, the mixture of the

dilithiated thiophene was cooled added to a cold solution of methyl 4-formylbenzoate (13 mmol, 2.17 g) and 2-allyloxybenzaldehyde (13 mmol, 2.14 g) in dry THF (15 ml). After separating by silica gel column chromatography (ethyl acetate/*n*-heptane 1:1), **7** was isolated as a yellow solid (0.59 g, 11%).

^{1}H NMR ($CDCl_3$, δ in ppm) 2.4 (bs, 1H, OH); 3.3 (m, 1H, OH); 3.9 (s, 3H, OMe); 4.5 (bs, 2H, OCH_2); 5.2 (m, 2H, CH_2); 5.9 (dqi, 1H, CH); 6.0 (d, 1H, CH); 6.15 (t, 1H, CH); 6.7 (m, 2H, β-thiophene); 6.85 (d, 1H, H-Ar); 6.95 (t, 1H, H-Ar); 7.3 (t, 1H, H-Ar); 7.4 (d, 1H, H-Ar); 7.5 (d, 2H, ortho-H); 8.0 (d, 2H, metha-H).

4.2.8. 5,10,15,20-(4-Carboxymethyl)phenyl-21-thiaporphyrin 8. Diol **1** (3.2 mmol, 1.32 g), methyl 4-formylbenzoate (6.4 mmol, 1.05 g) and pyrrole (9.6 mmol, 665 µl) were dissolved in dry CH_2Cl_2 (350 ml) under argon purging (degassing) in a one-neck flask. $BF_3 \cdot OEt_2$ (0.32 mmol, 40 µl) was added to start the cyclocondensation and the reaction mixture was stirred for 2 h under argon atmosphere in the dark at room temperature. DDQ (96 mmol, 2.18 g) was added and the solution was stirred on air for additional 3 h. The solvent was removed under reduced pressure and the compound was isolated by silica gel column chromatography (chloroform/methanol 99:1) as eluent to acquire the purple solid in the second yellow-brown fraction (0.61 g, 22%).

^{1}H NMR ($CDCl_3$, δ in ppm) −2.75 (s, 1H, NH), 4.1 (s, 9H, COOMe), 8.28 (d, 4H, H_{aryl}), 8.33 (d, 4H, H_{aryl}), 8.45 (d, 4H, H_{aryl}), 8.5 (d, 4H, H_{aryl}), 8.6 (d, 4H, β-pyrrole), 8.9 (s, 2H, β-pyrrole), 9.7 (s, 2H, β-thiophene). ESI-MS (+75 V) obsd mass 864, calcd mass 863.95.

4.2.9. 5,10,15,20-(3,5-Methoxy)phenyl-21-thiaporphyrin 9. Compound **9** was synthesized in the same procedure like **8**, using dry CH_2Cl_2 (200 ml), diol **2** (2.6 mmol, 1.1 g), 3,5-methoxybenzaldehyde (5.3 mmol, 0.88 g) and pyrrole (7.9 mmol, 547 µl). $BF_3 \cdot OEt_2$ (0.3 mmol, 37.5 µl) was added to start the reaction. After stirring for 1 h, DDQ (5.3 mmol, 1.2 g) was added. The crude product was purified by silica gel column chromatography (chloroform) and isolated as a purple, crystalline solid (0.40 g, 18%).

^{1}H NMR ($CDCl_3$, δ in ppm) −2.75 (bs, 1H, NH); 3.9 (d, 24H, OMe); 6.9 (t, 4H, para-H); 7.4 (dd, 8H, ortho-H); 8.7 (dd, 4H, β-pyrrole); 9.0 (d, 2H, β-pyrrole); 9.8 (s, 2H, β-thiophene). ESI-MS (+75 V) obsd mass 872, calcd mass 872.02.

4.2.10. 5,10,15,20-(4-Methoxy)phenyl-21-thiaporphyrin 10. Compound **10** was synthesized in the same manner like **8**, using dry CH_2Cl_2 (250 ml), 2,5-Bis[(4-methoxy)-phenyl(hydroxy)methyl]-thiophene (3.9 mmol, 1.4 g), 4-methoxybenzaldehyde (7.8 mmol, 0.95 ml) and pyrrole (11.8 mmol, 814 µl). $BF_3 \cdot OEt_2$ (0.4 mmol, 49 µl) was added to start the reaction. After stirring for 3 h, DDQ (5.3 mmol, 1.2 g) was added. The crude product was purified by silica gel column chromatography (chloroform/methanol 99:1) and isolated as a purple, crystalline solid (0.56 g, 19%).

^{1}H NMR ($CDCl_3$, δ in ppm) −2.7 (bs, 1H, NH); 4.1 (s, 12H, OMe); 7.3 (dd, 8H, meta-H); 8.1 (dd, 8H, ortho-H); 8.65 (dd, 4H, β-pyrrole); 8.95 (d, 2H, β-pyrrole); 9.75 (s, 2H, β-thiophene). MALDI-MS obsd mass 753, calcd mass 751.9.

4.2.11. 5,10,15,20-(4-Carboxy)phenyl-21-thiaporphyrin 11. Compound **8** (0.17 mmol, 150 mg) was dissolved in THF (20 ml) and water (10 ml) and LiOH (30 mmol, 750 mg) was added. The mixture was refluxed for 5 h, THF was removed and the pH value was set to 4 (1 N HCl), so the porphyrin **10** precipitated. After centrifugation the water was removed and the product was washed with cold ethyl acetate and water (0.134 g, 96%).

^{1}H NMR (DMSO-d_6, δ in ppm) −2.8 (s, 1H, NH); 8.37 (d, 8H, ortho-H); 8.39 (d, 8H, metha-H); 8.6 (dd, 4H, β-pyrrole); 9.0 (d, 2H, β-pyrrole); 9.8 (s, 2H, β-thiophene); 11.1 (bs, 4H, COOH). ESI-MS (+75 V) obsd mass 808, calcd mass 807.95.

4.2.12. 5,10,15,20-(3,5-Hydroxy)phenyl-21-thiaporphyrin 12. BBr_3 (6.02 mmol, 580 µl) was transferred into a solution of **9** (0.40 g, 0.46 mmol) in 25 ml of dry CH_2Cl_2 and stirred for 24 h at room temperature under dry conditions. The reaction was quenched with water, the pH value was set to 7 (1 N NaOH) and the phases were separated. The aqueous phase was extracted with ethyl acetate. The organic layers were dried over Na_2SO_4 and the solvent was evaporated. Purification was done by silica gel column chromatography (ethyl acetate). After removing solvent the product affords as dark purple solid (0.32 g, 91%).

^{1}H NMR (acetone-d_6, δ in ppm) −2.7 (s, 1H, NH); 6.9 (t, 4H, para-H); 7.3 (d, 8H, ortho-H); 8.75 (2 s, 8H, OH); 8.8 (d, 4H, β-pyrrole); 9.2 (d, 2H, β-pyrrole); 9.95 (s, 2H, β-thiophene). ESI-MS (+75 V) obsd mass 760, 821 [M+HAc], calcd mass 759.8.

4.2.13. 5,10,15,20-(4-Hydroxy)phenyl-21-thiaporphyrin 13. Compound **13** was synthesized like porphyrin **11**, dissolving **12a** (0.114 mmol, 0.086 g) in CH_2Cl_2 (8 ml) and adding BBr_3 (1.14 mmol, 110 µl). The product (73 mg, 92%) was isolated by silica gel column chromatography (ethyl acetate).

^{1}H NMR (acetone-d_6, δ in ppm) −2.5 (s, 1H, NH); 7.4 (dd, 8H, meta-H); 8.1 (dd, 8H, ortho-H); 8.7 (d, 2H, β-pyrrole); 8.9 (2 s, 4H, OH); 9.1 (s, 2H, β-pyrrole); 9.9 (s, 2H, β-thiophene). MALDI-MS obsd mass 697, calcd mass 695.8.

4.2.14. 5-(2-Methoxy)phenyl-10,15,20-(4-bromo)phenyl-21-thiaporphyrin 14. Compound **14** was prepared following the method given for **8**, using dry CH_2Cl_2 (250 ml), **3** (3.5 mmol, 1.35 g), 4-bromobenzaldehyde (7 mmol, 1.29 g) and pyrrole (10.5 mmol, 724 µl). $BF_3 \cdot OEt_2$ (0.35 mmol, 44 µl) was added and the mixture was stirred for 3 h before DDQ (5.2 mmol, 1.19 g) was added. The crude product was purified by silica gel column chromatography (chloroform) and isolated as a purple, crystalline solid (100 mg, 3%).

^{1}H NMR ($CDCl_3$, δ in ppm) −2.75 (bs, 1H, NH); 3.6 (s, 3H,

OMe); 7.4 (m, 2H, ortho-H); 7.8–8.1 (m, 14H, H-Ar); 8.6 (2d, 4H, β-pyrrole); 8.9 (s, 2H, β-pyrrole); 9.5 (dd, 2H, β-thiophene). ESI-MS (+75 V) obsd mass 898, calcd mass 898.52.

4.2.15. 5-(2-Allyloxy-5-bromo)phenyl-10,15,20-(4-bromo)phenyl-21-thiaporphyrin 15. Preparation of **15** followed the same steps like the preparation of **8**, using dry CH_2Cl_2 (250 ml), **4** (1.96 mmol, 1 g), 4-bromobenzaldehyde (3.92 mmol, 0.72 g) and pyrrole (5.88 mmol, 410 µl). After $BF_3 \cdot OEt_2$ (0.2 mmol, 25 µl) was added, the mixture was stirred for 3 h before DDQ (3.92 mmol, 0.89 g) was added. The crude product was purified by silica gel column chromatography (chloroform). After another silica gel column chromatography (*n*-heptane/chloroform 1:2) **15** was isolated as a purple, crystalline solid (300 mg, 15%).

^{1}H NMR ($CDCl_3$, δ in ppm) −2.75 (bs, 1H, NH); 4.4 (m, 2H, OCH_2); 4.6 (dd, 2H, CH_2); 5.4 (dq, 1H, CH); 7.2 (dd, 1H, H-Ar); 7.8 (dd, 1H, H-Ar); 7.85–8.1 (12H, H-Ar); 8.15 (d, 1H, H-Ar); 8.6 (2 d, 4H, β-pyrrole); 8.9 (s, 2H, β-pyrrole); 9.65 (dd, 2H, β-thiophene). ESI-MS (+75 V) obsd mass 1003, 962 [M−allyl], calcd mass 1003.45.

4.2.16. 5-(2-Methoxy-5-bromo)phenyl-10,15,20-(4-bromo)phenyl-21-thiaporphyrin 16. Compound **16** was synthesized using the general procedure (s. **8**), with dry CH_2Cl_2 (450 ml), diol **5** (3.1 mmol, 1.49 g), 4-bromobenzaldehyde (6.2 mmol, 1.14 g), pyrrole (9.2 mmol, 640 µl), $BF_3 \cdot OEt_2$ (0.3 mmol, 37 µl) and DDQ (6.2 mmol, 1.396 g). The purification of the product was done by silica gel column chromatography (chloroform). After another silica gel column chromatography (*n*-heptane/chloroform 1:2) **16** was obtained as a purple, crystalline solid (270 mg, 9%).

^{1}H NMR ($CDCl_3$, δ in ppm) −2.75 (bs, 1H, NH); 3.55 (s, 3H, OMe); 7.2 (d, 1H, H-Ar); 7.8–8.1 (m, 14H, H-Ar); 8.55 (dd, 2H, β-pyrrole); 8,6 (dd, 2H, β-pyrrole); 8,9 (d, 2H, β-pyrrole); 9,6 (dd, 2H, β-thiophene). ESI-MS (+75 V) obsd mass 977, calcd mass 977.42.

4.2.17. 5-(2-Allyloxy-3-methoxy)phenyl-10,15,20-(3,5-methoxy)phenyl-21-thiaporphyrin 17. Compound **17** was prepared in the general procedure (s. **8**), with dry CH_2Cl_2 (100 ml), **6** (1.4 mmol, 0.61 g), 4-bromobenzaldehyde (2.8 mmol, 0.456 g) and pyrrole (4.1 mmol, 290 µl), $BF_3 \cdot OEt_2$ (0.14 mmol, 17 µl) and DDQ (2.8 mmol, 0.635 g). After two silica gel column chromatographies (chloroform) the product was isolated as a orange-purple, crystalline solid (50 mg, 4%).

^{1}H NMR ($CDCl_3$, δ in ppm) −2.75 (bs, 1H, NH); 4.0 (s, 18H, OMe); 4.1 (s, 3H, OMe); 4.1 (s, 2H, OCH_2); 4.3 (dd, 2H, CH_2); 4.9 (dq, 1H, CH); 6.9 (d, 6H, ortho-H); 7.4 (m, 8H, H-Ar); 7.65 (dd, 1H, H-Ar); 8.65 (s, 2H, β-pyrrole); 8.7 (d, 1H, β-pyrrole); 8.75 (d, 1H, β-pyrrole); 9.02 (s, 2H, β-pyrrole); 9.7 (d, 2H, β-thiophene). ESI-MS (+75 V) obsd mass 898, 857 [M−allyl], calcd mass 898.06.

4.2.18. 5-(2-Allyloxy)phenyl-10,15,20-(4-carboxymethyl)phenyl-21-thiaporphyrin 18. Preparation of **18** was prepared in analogue to **8**, using dry CH_2Cl_2 (100 ml), **7** (1.3 mmol, 0.534 g), methyl 4-formylbenzoate (2.6 mmol, 0.426 g) and pyrrole (3.9 mmol, 270 µl), $BF_3 \cdot OEt_2$ (0.13 mmol, 16 µl) and DDQ (2.6 mmol, 0.59 g). The crude product was purified by two silica gel column chromatographies (chloroform) and the product afforded as a orange-purple, crystalline solid (82 mg, 7%).

^{1}H NMR ($CDCl_3$, δ in ppm) −2.75 (bs, 1H, NH); 4.0 (s, 9H, OMe); 4.4 (s, 2H, OCH_2); 4.6 (dd, 2H, CH_2); 5.45 (dq, 1H, CH); 7.35 (d, 1H, H-Ar); 7.4 (t, 1H, H-Ar); 7.75 (dt, 1H, H-Ar); 8.0 (d, 1H, H-Ar); 8.3–8.7 (m, 16H, H-Ar, β-pyrrole); 8.9 (s, 2H, β-pyrrole); 9.5 (s, 2H, β-thiophene). ESI-MS (+75 V) obsd mass 862, 841 [M−allyl], calcd mass 861.98.

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