J. prakt. Chem. 338 (1996) 257–263

Journal für praktische Chemie
Chemiker-Zeitung

Synthesis and Electrochemical Investigation of Azobenzene-Substituted Porphyrins

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Recveived August 30th, 1995

Abstract. The synthesis of azobenzene-substituted porphyrins (**3a-g**) is described. With respect to possible applications as model systems for photochemical reaction centers the spectroscopic and electrochemical properties of the synthesized compounds were investigated. For compound **3e** the obtained spectroscopic and electrochemical data confirm that a light driven electron transfer from a porphyrin to the azobenzene moiety is possible.

Since some years much porphyrin compounds bearing electron donor and electron acceptor groups were synthesized. These systems were often used to study light induced electron transfer processes and designed as model compounds for the photochemical reaction center chromophores of bacteria and plants [1]. Much information about influence of distance, acceptor strength and chromophore orientation on the electron transfer efficiency is known [2]. Nearly all systems synthesized for these investigations have quinone groups as electron acceptor groups and only a few other acceptor groups were reported [3]. Though the azo group is known to be an electron withdrawing substituent and an electron acceptor, there are no reports in the literature describing the use of azo substituted porphyrins for application in photoinduced electron transfer processes. This might be due to the more negative reduction potential of these acceptor groups compared to quinone moieties thus making electron transfer processes thermodynamically less favourable. On the other side the azo group is known to be an optical switch, which upon irradiation undergoes *E/Z* isomerization [4]. This isomerization offers the possibility to change the porphyrin-acceptor distance in a controlled way thus leading to different spectroscopic and photophysical properties of the two isomers. During our studies directed towards the synthesis of model compounds for photochemical reaction center chromophores, we became interested in the synthesis of azo substituted porphyrins and diporphyrins, especially in the electrochemical and spectroscopic properties of these compounds because these properties are of great importance for a light driven electron transfer process.

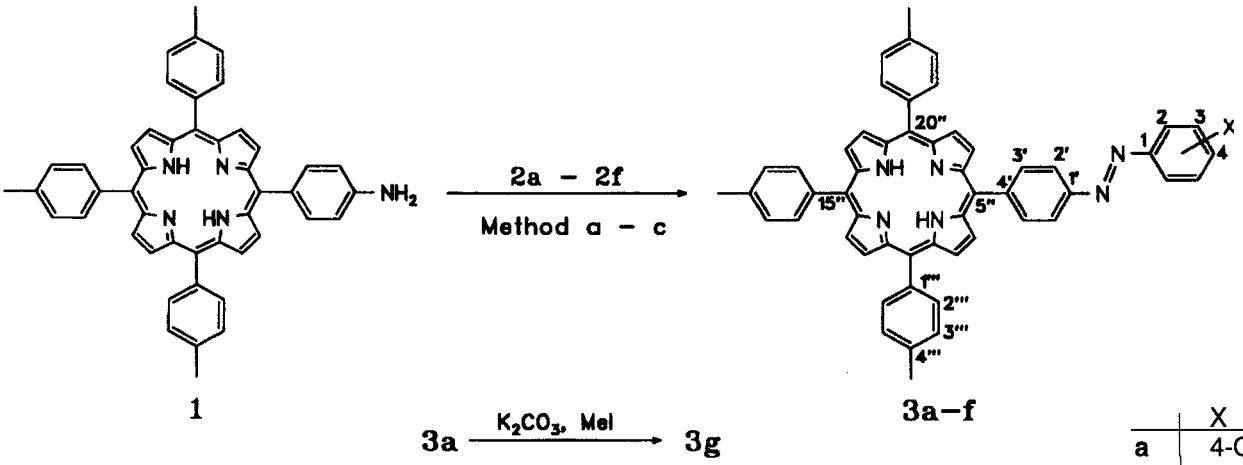
The synthesis of the new compounds is outlined in scheme 1. Three methods, all starting from aminoporphyrin **1**, were used depending upon the reactivity of the aryl compounds **2**. For reactive compounds like **2a**, **2b** and **2c** the diazotization reaction was carried out in a two-phase system under phase transfer catalysis. Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (TFPB) was used as phase transfer catalyst [5].

Although compound **3a** was already synthesized by Semeikin et al. [6] we found, that **3b** and **3c** were only formed in low yield (8–10%) using the method reported. Furthermore, the authors published no detailed spectroscopic data.

Electron deficient aromatic compounds like **2d** and **2e** were treated with the aminoporphyrin **1** in an oxidative coupling reaction with activated MnO_2. Although this method gives fair yields, diporphyrinic systems formed by self coupling of **1** were obtained as side products [7]. Diazo compound **3f** was synthesized by a Mills-reaction [8] of **1** with nitrosobenzene in acetic acid. Azoporphyrin **3g** was easily synthesized from **3a** by a standard alkylation procedure with CH_3I/K_2CO_3 in THF.

Spectroscopic Properties

The absorption spectroscopic properties of the synthesized arylazo-substituted porphyrins are comparable for all compounds. The Soret absorption appears among 418 and 420 nm; the Q_{X00}-absorption appears at 647–



	X
a	4-OH
b	2,4,6-OMe
c	4-NMe_2
d	4-Br
e	4-NO_2
f	H
g	4-OMe

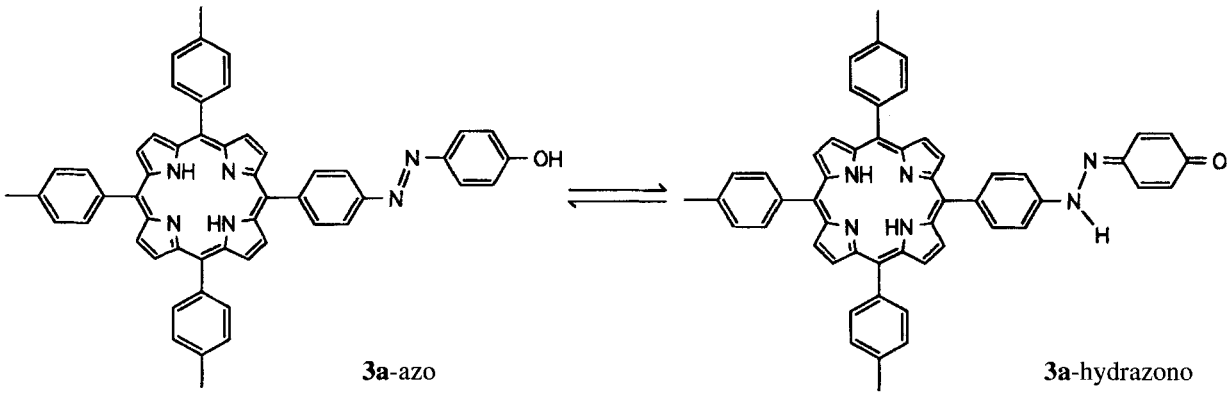
2a: phenol; **2b**: 2,4,6-trimethoxybenzene; **2c**: N,N-dimethylaniline
2d: 4-bromoaniline; **2e**: 4-nitrobenzene; **2f**: nitrosobenzene
Method a: **2a–2c**, CH_2Cl_2, TBFP, $NaNO_2$, Δ
Method b: **2d–2e**, MnO_2, CH_2Cl_2, Δ
Method c: acetic acid, **2f**, Δ

Scheme 1

648 nm. The Soret absorption band is significantly broadened compared to other Tetraphenylporphyrin (TPP) derivatives [9]. This broadening indicates some degree of ground state interaction between the porphyrin and the azobenzene chromophore [10]. Furthermore a small but significant bathochromic shift of either the Soret absorption and the Q-bands compared to TPP is observed. This observation can also be attributed to the interaction between the azobenzene and the porphyrin chromophore. Besides the porphyrinic absorption bands the spectra of all compounds exhibit an absorption band in the azobenzene $\pi \rightarrow \pi^*$ region among 320 and 360 nm. For **3c** a somewhat different behaviour is observed. For this compound the $\pi \rightarrow \pi^*$ absorption of the azobenzene unit appears at the red edge of the Soret absorption. The observed bathochromic shift of the $\pi \rightarrow \pi^*$ absorption of **3c** may be due to the higher polarisation of this compound due to the strong electron donating amino substituent. Taking into consideration that the porphyrin chromophore is an electron withdrawing substituent, the behaviour observed is similar to that observed for other azobenzene systems substituted with electron donating and withdrawing substituents [11]. Nevertheless, the spectroscopic properties of the synthesized porphyrins do not differ substantially from those of other TPP derivatives. This leads to the conclusion that the porphyrin moiety and the azobenzene moiety are independent chromophores and that there are only weak interactions in the ground state. This obviously is a result of the perpendicular orientation of the porphyrinic macrocycle and the phenyl moieties. Furthermore it has to be stressed, that it is not possible to differentiate between the *E*- and *Z*-configuration of the azogroup on the basis of the absorption spectra due to the overlap of the strong Soret absorption with azobenzene absorptions. Therefore an $\pi \rightarrow \pi^*$ absorption of a possible *Z*-isomer can not be detected.

The fluorescence spectra of the synthesized compounds are characterised by the two Q^*-emission bands. For all synthesized compounds the Q^*_{X00}-emission appears at 654 – 658 nm, the Q^*_{X01}-emission at 717–719 nm. The fluorescence intensity is comparable for all compounds. Only for compound **3e** the fluorescence intensity is reduced by a factor of > 30. Furthermore, the relative intensity of the two Q^* emission bands is different for **3e**.

It is well known, that 2-, and 4-hydroxy azobenzene compounds exist in two tautomeric forms [12]. The hydroxy-azo/hydrazone equilibrium depends strongly upon solvent, temperature and the substitution pattern of the compounds. Thus the azo/hydrazone tautomerism has to be taken into consideration for porphyrin **3a** (scheme 2). The results of NMR-spectroscopy indicate that in neutral solution ($CDCl_3$) the azo tautomer is dominant. The NMR-signals of the p-phenylene system bearing the azo moiety and the porphyrinyl moiety appear for all investigated compounds in the region between $\delta = 8.2$ and 8.4 ppm as an AB-system. The same chemical shift values were obtained for **3a**. Furthermore the ^1H-resonances of the phenylene ring substituted with an OH and an azo-group appear at $\delta = 6.95$ and 8.02 ($J = 8.80$ Hz). These values agree with calculated values obtained from increments. These data are only consistent with an hydroxy-azo tautomer. No resonances at-



Scheme 2

tributable to a quinoid like structure were detected. Nevertheless, the possibility of an hydrazone tautomer becomes important in the electrochemical investigations.

Electrochemical Investigations

The electrochemical properties of the azobenzene substituted porphyrins were investigated by pulse voltammetry and cyclic voltammetry. The obtained electrochemical data are summarised in table 1. The cyclic voltammograms of compounds **3b-3g**, cp. Fig. 1, exhibit two reversible waves in the anodic region corresponding to the formation of the porphyrinyl radical cation and dication, respectively. Three electrochemical processes corresponding to the reduction of the azobenzene subunit and the reduction of the porphyrin system to the radical anion and dianion, respectively, were observed for **3b–3g** in the cathodic region. Compound **3a** shows a different behaviour. Only two one-electron reduction processes at –1.70 V and –2.05 V *vs.* the ferrocene–ferrocinium system can be detected according to the reduction of the porphyrin ring to the radical anion $\mathbf{3a}^{\cdot-}$ and dianion $\mathbf{3a}^{2-}$, respectively. The existence of only two one-electron voltammetric waves is only consistent with a compound bearing no azobenzene group. Thus under the experimental conditions (THF, 0.1 M TBAHFP) of the electrochemical measurements the hydrazone tautomer seems to be dominant. Furthermore, **3a** exhibits only one irreversible anodic voltammetric wave at 0.47 V. The existence of only one electrochemical oxidation process can also be attributed to the existence of an hydrazone tautomer. Oxidation of **3a** leads to the formation of a porphyrinyl radical cation $\mathbf{3a}^{\cdot+}$. Electron transfer from the hydrazone moiety and subsequent deprotonation and formation of an azobenzene radical system seems to be possible.

The oxidation potentials of all other compounds (**3b–3g**) appear between 0.470 and 0.520 volts *vs.* the ferrocene–ferrocinium system for the formation of the porphyrinyl radical cation. Dication formation is observed at 0.700 to 0.750 V *vs* the ferrocene–ferrocinium system. No linear dependency of the first and the second oxidation potential from the substituent constant σ^+ is observed. Furthermore, no dependency upon the substituent's electronic nature is found for the reduction potentials corresponding to the porphyrin radical anion and dianion, respectively, for compounds **3b–3g**. These findings indicate, that the oxidation and reduction potentials of the porphyrin ring system are not influenced by the substituents at the terminal phenyl group. This is in accordance with the spectroscopic data which show

Table 1 Electrochemical data of synthesized porphyrins. All potentials given in volts *vs.* ferrocene–ferrocinium system. Reduction potentials measured in THF, oxidation potentials measured in CH_2Cl_2, concentration 10^{-3} M. TBAHFP (0.1 M) was used as supporting electrolye.

	$E_{1/2}$(ox1)	$E_{1/2}$(ox2)	$E_{1/2}$(red1)	$E_{1/2}$(red2)	$E_{1/2}$(azo)	σ^+
3a	0.470	—	–1.700	–2.050	—	–0.92
3b	0.485	0.730	–1.710	–2.100	–1.985	–1.16
3c	0.480	0.750	–1.690	–2.090	–1.960	–1.70
3d	0.530	0.730	–1.730	–2.075	–1.660	0.15
3e	0.520	0.725	–1.685	–2.070	–1.285	0.79
3f	0.520	0.730	–1.675	–2.080	–1.800	0.00
3g	0.470	0.700	–1.690	–2.065	–1.880	–0.78

that the porphyrin chromophore and the azo chromophore behave as independent moieties. In contrast to this, the reduction potential of the azobenzene subunit of **3b–3g** stongly depends upon the substituents nature.

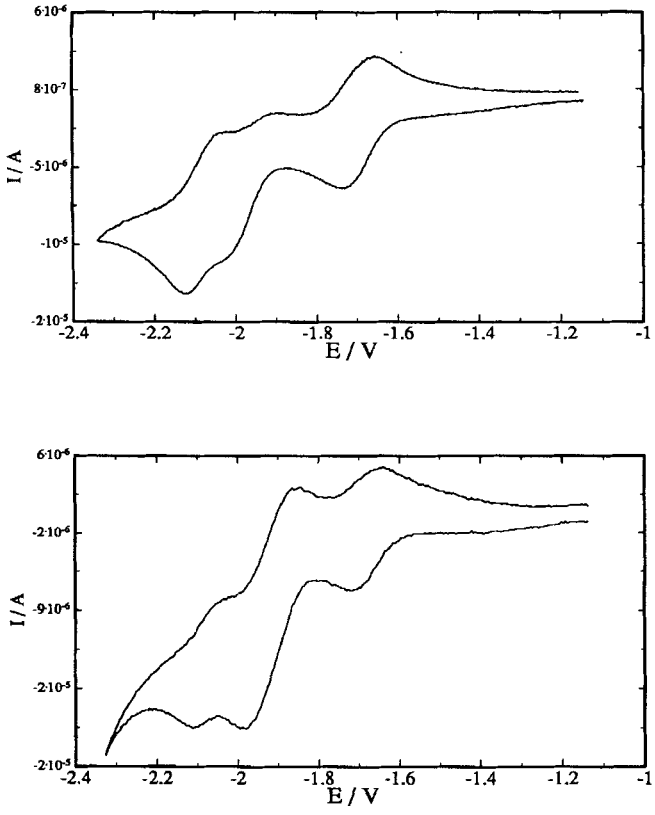


Fig. 1 Cyclic voltammogram of porphyrin **3b** (upper curve) and **3c** (lower curve). 10^{-3} M. in THF (0.1 M TBAHFP). Scan rate 0.10.1 V/s. Measured at a platinum working electrode against SCE, reverenced *vs.* ferrocen–ferrocinium

From the slope of a Hammett plot of $E_{1/2}$ *vs.* σ^+ we calculated an electrochemical reaction constant ρ of 0.28 volts. For compounds **3b** and **3d–3g** three one-electron transfer reduction processes were observed.

Interestingly, the amino compound **3c** exhibits two one-electron transfer processes and one two-electron transfer process (figure 2). Porphyrins are always reduced in two one-electron transfer processes to the porphyrinyl radical anion and the porphyrin dianion, respectively. These two reduction potentials are separated approximately by 0.35 V for TPP derivatives [13]. Therefore it is obvious, that the two-electron transfer process is due to the reduction of the azobenzene moiety. Furthermore, this reduction process is observed at a much more anodic potential than expected from the dependency of the potentials upon the electronic nature of the substituents observed for compounds **3b** and **3d–3g**. Taking also into consideration, that a *Z*-azobenzene compound is much easier to reduce than an *E*-azobenzene system [14] and that the reduction of a *Z*-azobenzene system is a two-electron process, the observation leads to the conclusion, that compound **3c** has the *Z*-configuration. The reason for the increased stability of this configuration might be the strong polarisation of the compound bearing a strong electron donating amino substituent and an electron withdrawing porphyrinyl moiety. It is commonly assumed, that *Z*-azobenzene systems isomerize to the *E*-configuration via a rotational mechanism or an inversion process [15]. For push-pull substituted azobenzenes it is under discussion that a rotational isomerization process is more likely [16]. Due to the big porphyrinyl substituent such an isomerization process might be much more difficult and requires a higher activation energy than azobenzene systems bearing small substituents. Nevertheless, more detailed investigations are necessary to clarify the behaviour of compound **3c**.

The feasibility of a light induced electron transfer within a donor-acceptor system can be assessed by the well-known Weller equation [17].

$$\Delta G_{ET} = E_{ox} - E_{red} - E_{00} - E_{coul}$$

Neglecting any electrostatic interactions, we calculated the thermodynamic driving force ΔG_{ET} for an photoinduced electron transfer from the porphyrin moiety to the azobenzene subunit. For E_{ox} the first oxidation potential of the porphyrin, for E_{red} the reduction potential of the azobenzene unit was used. From the spectroscopic data a zero-zero excitation energy E_{oo} of 1.904–1.907 eV was calculated. From the calculations we obtained positive ΔG_{ET} values (0.21–0.57 eV) for compounds **3b–3d** and **3f–3g**. Therefore, an electron transfer process is not possible in these systems. Nevertheless, for nitro compound **3e**, a ΔG_{ET} value of –0.11 eV was calculated. Thus, a photoinduced electron transfer from the excited porphyrin donor to the azobenzene should be possible in this system. Although the obtained driving force is small, introduction of a second nitrogroup should increase the driving force substantially. It was already reported, that an electron transfer induced isomerization of azo-compounds is possible [18]. Our findings now offer the possibility to design new systems which absorb at long wavelengths and lead to isomerization *via* an electron transfer process. This is of considerable interest for the design of new information storage devices based on isomerization processes [14]. In this context it is of importance, that neither the oxidation potentials nor the zero-zero excitation energies of porphyrin ring systems are affected by variation of the substitution pattern of the azobenzene moiety.

Acknowledgements: Support of this work from the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie,

Siemens AG and IBM-Deutschland GmbH is gratefully acknowledged.

Experimental

NMR-spectra were obtained in $CDCl_3$ with a Varian XL 200 spectrometer. Chemical shift values are given in ppm relative to TMS. Coupling constants are given in Hertz. Mass spectra were measured with a VG-Analytical VG70:250 E instrument. Electronic spectra were recorded on a Kontron Uvikon 860 instrument. Fluorescence spectra were recorded on a Perkin Elmer Luminescence spectrometer LS 50. Melting points were determined with a Büchi 510 apparatus and are uncorrected. Cyclic voltammetry and pulse voltammetry were carried out with a Tacussel Potentiostat PJT 24-1 equipped with an IMT-1 Interface, connected to an IBM-AT computer and a Siemens Oscillar D 1015 100 MHz oscilloscope. Ohmic drop compensation was performed electronically by positive feed back. Cyclic voltammetry and pulse voltammetry experiments were carried out in an oven-dried electrochemical cell at 20 °C under nitrogen using freshly distilled and degassed solvents. All voltammetric experiments were performed using a standard three-electrode configuration with a platinum working electrode, a platinum wire counter electrode and a Saturated Calomel Electrode (SCE) as the reference electrode. Ferrocene was added as internal standard after the last measurement. All solvents used for electrochemical measurements were carefully dried and cleaned. Tetrabutyl ammonium hexafluorophosphate (Merck) was used as supporting electrolyte. Column chromatography was carried out with Merck silica gel mesh size 0.06–0.2 mm.

Compound **1** was prepared from 5-(p-acetamidophenyl)-10,15,20-tri(methylphenyl)porphyrin according to a recently published procedure [7]. Activated MnO_2 was prepared according to the procedure given by Attenburrow [19].

4-Hydroxy-4'-[10'',15'',20''-tris(4'''-methylphenyl)-5''-porphyrinyl]azobenzene (**3a**)

170 mg (0.250 mmol) **1** were dissolved in 25 ml CH_2Cl_2. Then 62 mg (0.890 mmol) $NaNO_2$ and 2 mg Tetrakis[3,5-bis(trifluormethyl)phenyl]borate (TFPB) were added. To the stirred solution 25 ml 0.5 M H_2SO_4 were added. After 15 min. at 30 °C 140 mg (1.490 mmol) **2a** were added. After 6 h the reaction mixture was neutralized carefully with 10% KOH solution. The aqueous layer was separated and extracted 3 times with CH_2Cl_2. The combined organic layers were dried (Na_2SO_4), the solvent evaporated and the residue chromatographed on a silica gel column (5 × 25 cm) using CH_2Cl_2 as eluent. Yield: 75 mg (38%). Fp. > 250 °C. – ^{1}H-NMR ($CDCl_3$): δ = –2.70 (br, 2 H, NH), 2.71 (s, 9 H, CH_3), 6.95 (d, J = 9.4 Hz, 2 H, 3-H), 7.57 (d, J = 7.8 Hz, 6 H, 3'''-H), 8.02 (d, J = 8.8 Hz, 2 H, 4-H), 8.10 (d, J = 8.4 Hz, 6 H, 2'''-H), 8.26 (d, J = 8.8 Hz, 2 H, 2'-H), 8.36 (d, J = 8.8 Hz, 2 H, 3'-H), 8.80 (s, 4 H, Hb), 8.82 (s, 4 H, Hb). – ^{13}C-NMR ($CDCl_3$): δ = 21.55 (q, CH3-4'''), 115.92 (d, C-3), 118.95, 119.24, 120.44 (3 × s, C-5'', C-10''', C-15'', C-20''), 120.88 (d, C-2'), 125.50 (d, C-2), 127.50 (d, C-3'''), 130.98 (d, Cb), 134.60 (d, C-2'''), 135.46 (d, C-3'), 137.51 (s, C-4'''), 139.08 (s, C-1'''), 144.39 (s, C-4'), 147.00 (br s, Ca), 147.32 (s, C-1), 152.18 (s, C-1'), 158.65 (s, C-4). – UV-Vis (CH_2Cl_2): λ (log ε) = 340.0 (4.191), 420.0 (5.488), 516.7 (4.112), 553.6 (3.905), 591.6 (3.413), 647.1 (3.368). – Fluorescence (CH_2Cl_2): λ = 653, 719 nm (excited at 419 nm). – IR (KBr): ν = 3400, 3310, 3020, 2900, 1598, 1500, 1470, 1340, 1270, 1210, 1180, 1130, 960, 800, 730 cm^{-1}. – FAB-MS: m/e = 777 (M^+ + 1).

$C_{53}H_{40}N_6O$ (776.94): Calc.: C 81.93 H 5.19 N 10.82.y
Found: C 81.37 H 5.22 N 10.97.

2,4,6-Trimethoxy-4'-[10'',15'',20''-tris(4'''-methylphenyl)-5''-porphyrinyl]azobenzene (**3b**)

102 mg (0.150 mmol) **1** and 72 mg (0.600 mmol) **2b** were treated as described for the synthesis of **3a**. Yield: 68 mg (53%). Fp. 248–255 °C. – ^{1}H-NMR ($CDCl_3$): δ = –3.00 (br s, 2 H, NH), 2.70 (s, 9 H, CH_3), 3.90 (s, 3 H, 4-OCH_3), 3.97 (s, 6 H, 2-OCH_3), 6.28 (s, 2 H, 3-H), 7.56 (d, J = 7.8 Hz, 6 H, 3'''-H), 8.10 (d, J = 7.8 Hz, 6 H, 2'''-H), 8.20 (d, J = 8.6 Hz, 2 H, 2'-H), 8.32 (d, J = 8.6 Hz, 2 H, 3'-H), 8.78 (s, 4 H, $H_β$), 8.81 (s, 4 H, $H_β$). – ^{13}C-NMR ($CDCl_3$): δ = 20.51 (q, CH_3), 54.59 (q, OCH_3-4), 55.60 (q, OCH_3-2,6), 90.47 (d, C-3), 118.08, 119.28 (s, C-5'', C-10'', C-15'', C-20''), 119.48 (d, C-2'), 126.24 (d, C-3'), 129.84 (d, Cβ), 130.29 (s, C-1), 133.49 (d, C-2'''), 134.30 (d, C-3'), 136.38 (s, C-1'''), 138.13 (d, C-4'''), 142.90 (s, C-4'), 145.31 (br, s, $C_α$), 152.16 (s, C-1'), 154.45 (d, C-2), 161.67 (s, C-4). – UV-Vis (CH_2Cl_2): λ (log ε) = 340.5 (4.177), 419.5 (5.485), 516.2 (4.162), 553.0 (3.955), 589.2 (3.629), 646.8 (3.545). – Fluorescence (CH_2Cl_2): λ = 653, 719 nm (excited at 419 nm). – IR (KBr): ν = 3310, 3020, 2910, 1598, 1460, 1410, 1335, 1275, 1200, 1180, 1145, 1120, 965, 800, 730, 615 cm^{-1}. – FAB-MS: *m/e* = 851 (M^+–1).

$C_{56}H_{47}N_6O_3$ (852.03): Calcd.: C 78.94 H 5.56 N 9.86.
Found: C 78.83 H 5.52 N 9.86.

4-(N,N-Dimethyl)amino-4'-[10'',15'',20''-tris(4'''-methylphenyl)-5''-porphyrinyl]azobenzene (**3c**)

55 mg (0.082 mmol) **1** and 40 mg (0.330 mmol) **2c** were treated as described for the synthesis of **3a**. Yield: 28 mg (42%).Fp. 246–255 °C. – ^{1}H-NMR ($CDCl_3$): δ = –2.73 (br s, 2 H, NH), 2.70 (s, 9 H, CH_3), 3.13 (s, 6 H, 4-$N(CH_3)_2$), 6.81 (d, J = 9.2 Hz, 2 H, 3-H), 7.55 (d, J = 8.0 Hz, 6 H, 3'''-H), 8.04 (d, J = 9.2 Hz, 2-H), 8.10 (d, J = 7.8 Hz, 6 H, 2''-H), 8.22 (d, J = 8.6 Hz, 2 H, 2'-H), 8.33 (d, J = 8.4 Hz, 2 H, 3'-H), 8.86 (s, 4 H, Hβ), 8.90 (s, 4 H, $H_β$). – ^{13}C-NMR ($CDCl_3$): δ = 21.57 (q, CH_3-4'''), 40.38 (q, $N(CH_3)_2$-4), 111.59 (d, C-3), 119.31, 120.31 (s, C-5'', C-10'', C-15'', C-20''), 120.49 (d, C-2'), 125.26 (d, C-2), 127.47 (d, C-3'''), 131.10 (d, $C_β$), 134.56 (d, C-2'''), 135.42 (d, C-3'), 137.41 (d, C-4'''), 139.21 (s, C-1'''), 143.32 (s, C-1), 143.93 (C-4'), 146.80 (br s, $C_α$), 152.59 (s, C-1'), 152.72 (s, C-4). – UV-Vis (CH_2Cl_2): λ (log ε) = 420.0 (5.430), 460.7 (4.804), 516.5 (4.263), 554.3 (4.076), 591.8 (3.549), 647.4 (3.540). – Fluorescence (CH_2Cl_2): λ = 654, 720 nm (excited at 419 nm). – IR (KBr): ν = 3310, 3010, 2900, 1598, 1510, 1470, 1445, 1360, 1310, 1135, 1110, 965, 800, 730 cm^{-1}. – FAB-MS: *m/e* = 805 (M^+ + 1),

$C_{55}H_{45}N_7 \cdot H_2O$ (822.04): Calcd.: C 80.36, H 5.76 N 11.93.
Found: C 81.31 H 5.73 N 11.11.

4-Bromo-4'-[10'',15'',20''-tris(4'''-methylphenyl)-5''-porphyrinyl]azobenzene (**3d**)

To a solution of 50 mg (0.074 mmol) **1** and 52 mg 4-bromoaniline (**2d**) in 15 ml $CHCl_3$ 900 mg MnO_2 were added. The reaction mixture was refluxed for 2 h. MnO_2 was removed by filtration. The solvent was removed and the residue chromatographed on a silica gel column (5 x 20 cm) using CH_2Cl_2 as eluent. The crude porphyrinic fraction was chromatographed on a small silica gel column using CH_2Cl_2/hexane (1:1) as eluent. Yield: 22 mg (35%). Fp. 225–231 °C. – ^{1}H-NMR ($CDCl_3$): δ = –2.75 (br s, 2 H, NH), 2.70 (s, 9 H, CH_3), 7.55 (d, J = 7.8 Hz, 6 H, 3'''-H), 7.73 (d, J = 8.8 Hz, 2 H, 2-H), 7.96 (d, J = 8.8 Hz, 2 H, 3-H), 8.10 (d, J = 7.8 Hz, 6 H, 2'''-H), 8.29 (d, J = 8.2 Hz, 2 H, 3'-H), 8.37 (d, J = 8.6 Hz, 2 H, 2'-H), 8.87 (s, 4 H, H_β), 8.88 (AB, J = 3.5 Hz, H_β). – ^{13}C-NMR ($CDCl_3$): δ = 21.53 (q, CH3-4'''), 118.43, 120.54 (s, C-5'', C-10'', C-15'', C-20''), 120.35 (d, C-2'), 121.14 (d, C-2), 124.52 (d, C-4), 127.42 (d, C-3'''), 131.11 (d, C_β), 132.47 (d, C-3), 134.49 (d, C-2'''), 135.44 (d, C-3'), 137.13 (s, C-4'), 139.13 (s, C-1'''), 145.53 (s, C-4'), 146.50 (br, C_α), 150.90 (s, C-1), 151.78 (s, C-1'). – UV-Vis (CH_2Cl_2): λ (log ε) = 354.5 (4.367), 419.5 (5.467), 516.6 (4.177), 553.1 (3.994), 591.9 (3.655) nm. – Fluorescence: λ = 655, 717 nm (excited at 419 nm). – IR (KBr): ν = 3310, 3005, 2920, 1598, 1500, 1470, 1400, 1350, 1220, 1180, 1060, 965, 800, 730 cm^{-1}. – FAB-MS: *m/z* = 839 (M^+ + 1).
$C_{53}H_{39}N_7Br$ (839.85): Calcd.: C 75.80 H 4.68 N 7.20.
Found: C 75.88 H 4.86 N 7.40.

4-Nitro-4'-[10'',15'',20''-tris(4'''-methylphenyl)-5''-porphyrinyl]azobenzene (**3e**)

To a solution of 100 mg (0.149 mmol) **1** and 250 mg (0.302 mmol) nitro aniline (**2e**) in 25 ml $CHCl_3$ 1.9 g MnO_2 were added. The reaction mixture was refluxed for 6 h. The same work up procedure as described for the synthesis of **3e** was used. Yield: 22 mg (18%). Fp. 250 °C. – ^{1}H-NMR ($CDCl_3$): δ = –2.76 (br, 2 H, NH), 2.71 (s, 9 H, CH_3), 7.58 (d, J = 7.8 Hz, 6 H, 3'''-H), 8.11 (d, J = 8.2 Hz, 6 H, 2'''-H), 8.17 (d, J = 6.0 Hz, 2 H, 2-H), 8.40 (d, J = 8.0 Hz, 2 H, 3-H), 8.47 (d, J = 8.0 Hz, 2 H, 3'-H), 8.49 (d, J = 8.0 Hz, 2 H, 2'-H), 8.87 (s, 4 H, Hβ), 8.93 (AB, J = 3.5 Hz, 4 H, H_b). – ^{13}C-NMR ($CDCl_3$): δ = 20.51 (q, CH3-4'''), 119.40, 119.71 (s, C-5'', C-10'', C-15'', C-20''), 120.66 (d, C-2'), 122.58 (d, C-2), 123.85 (d, C-3), 126.40 (d, C-3'''), 129.98 (d, C_β), 133.47 (d, C-2'''), 134.51 (d, C-3'), 136.40 (s, C-4'''), 138.04 (s, C-1'''), 145.00 (br, C_α), 145.74 (s, C-4'), 147.76 (s, C-1'), 150.75 (s, C-4), 154.83 (s, C-1). – UV-Vis (CH_2Cl_2): λ (log ε) = 362.5 (3.950), 418.5 (5.158), 516.1 (3.963), 555.5 (3.777), 591.8 (3.423), 648.3 (3.400) nm. – Fluorescence (CH_2Cl_2): λ = 655, 718 nm (excited at 419 nm). – FAB-MS: *m/z* = 807 (M^+ + 1).
$C_{53}H_{39}N_7O_2$ (805.95): Calcd.: C 78.99 H 4.88 N 12.17
Found: C 78.66 H 4.48 N 12.38

4'-[10'',15'',20''-Tris(4'''-Methylphenyl)-5''-porphyrinyl)-azobenzene (**3f**)

In a 5 ml round bottom flask 140 mg (0.208 mmol) **1** were dissolved in 3 ml acetic acid and warmed to 40 °C. Then 35 mg (0.330 mmol) nitroso benzene (**2f**) were added and the reaction mixture was warmed to 70 °C for 2 h. The mixture was cooled to room temperature. The acetic acid was removed in vacuum and the residue dissolved in CH_2Cl_2 and chromatographed on a silica gel column (5×30 cm) using CH_2Cl_2 as eluent. Yield: 97 mg (61%). Fp: 236 °C. – ^{1}H-NMR ($CDCl_3$): δ = –2.74 (br, 2 H, NH), 2.69 (s, 9 H, CH_3), 7.54 (d, J = 7.8 Hz, 6 H, 3'''-H), 7.55 (m, 3 H, 3-H, 4-H), 8.01 (d, J = 7.8 Hz, 2 H, 2-H), 8.10 (d, J = 7.8 Hz, 6 H, 2'''-H), 8.30 (d, J = 8.4 Hz, 2 H, 2'-H), 8.38 (d, J = 8.8 Hz, 2 H, 3'-H), 8.80 (s, 4 H, H_β), 8.83 (s, 4 H, H_β). – ^{13}C-NMR ($CDCl_3$): δ = 21.55 (q, CH_3-4'''), 120.34, 120.53 (s, C-5'', C-10'', C-15'', C-20''), 121.10 (d, C-2'), 123.06 (d, C-2), 127.44 (d, C-3'''), 129.24 (d, C-3), 131.15 (d, C_β), 134.51 (d, C-2'''), 135.39 (d, C-3'), 137.38 (s, C-4'''), 139.15 (s, C-1'''), 145.17 (s, C-4'), 147.00 (br, C_α), 152.02 (s, C-1), 152.18 (s, C-1'), 158.65 (s, C-4). – UV-Vis (CH_2Cl_2): λ (log ε) = 340.0 (4.191), 419.8 (5.522), 516.6 (4.182), 553.4 (3.978), 591.4 (6.604), 647.2 (3.589) nm. – Fluorescence (CH_2Cl_2): λ = 654, 720 nm (excited at 419 nm). – IR (KBr): ν = 3310, 3005, 2910, 1598, 1500, 1470, 1398, 1350, 1215, 1180, 1150, 965, 800, 730, 680 cm^{-1}. – FAB-MS: *m/z* = 761 (M^+ + 1).
$C_{53}H_{40}N_6$ (760.95): Calcd.: C 83.66 H 5.30 N 11.04
Found: C 83.55 H 5.29 N 10.86

4-Methoxy-4'-[10'',15'',20''-tris(4'''methylphenyl)-5'-porphyrinyl]azobenzene (**3g**)

To a solution of 15 mg (0.019 mmol) **3a** in 2 ml CH_2Cl_2 50 mg K_2CO_3 were added. The mixture was stirred for 14 h at room temperature. Then 10 ml CH_2Cl_2 were added and the solution was washed with water. The solvent was evaporated and the residue chromatographed on a silica gel column (2 x 20 cm) using CH_2Cl_2 as eluent. Yield: 13 mg (85%). Fp: 250 °C. – ^{1}H-NMR $CDCl_3$): δ = –2.80 (br, 2 H, NH), 2.70 (s, 9 H, CH3), 3.88 (s, 3 H, OCH_3), 7.05 (d, J = 8.8 Hz, 2 H, 3-H), 7.48 (d, J = 8.2 Hz, 6 H, 3'''-H), 8.02 (d, J = 8.2 Hz, 6 H, 2'''-H), 8.03 (d, J = 8.8 Hz, 2 H, 2-H), 8.18 (d, J = 8.1 Hz, 4 H, 2'-H), 8.28 (d, J = 8.1 Hz, 2 H, 3'-H), 8.80 (s, 4 H, H_β), 8.85 (s, 4 H, H_β). – UV-VIS (CH_2Cl_2): λ = 419.0, 516.0, 552.5, 590.5, 646.6 nm. – IR (KBr): ν = 3310, 3010, 2900, 1598, 1500, 1470, 1350, 1245, 1180, 1130, 960, 800, 730 cm^{-1}. FAB-MS: *m/e* = 791 (M^+ + 1).
$C_{54}H_{42}N_6O \cdot H_2O$ (808.99): Calcd.: C 80.17 H 5.48 N 10.39
Found: C 80.41 H 5.77 N 9.60.

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