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Synthesis and Electrochemical Investigation of β-Alkyloxy Substituted *meso*-Tetraphenylporphyrins

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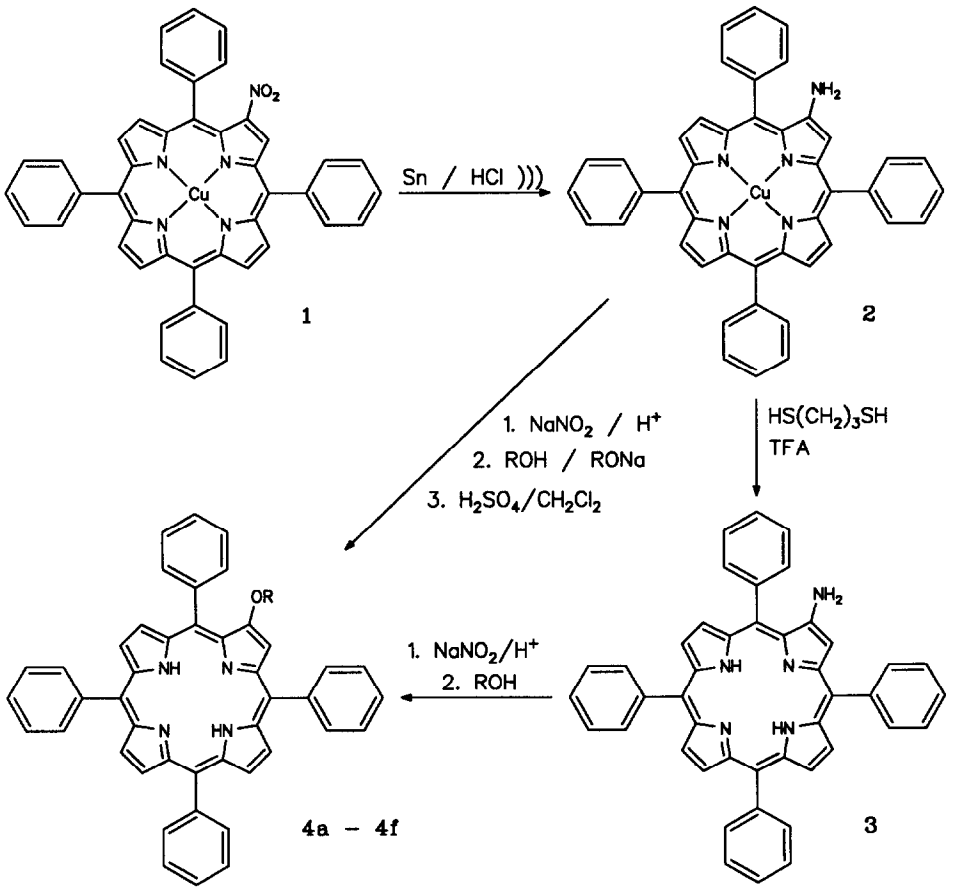
Abstract: The synthesis of β-alkyloxy substituted tetraphenylporphyrins is described. Due to interaction between the β-alkyloxy substituent and the meso-phenyl moiety the porphyrins are slightly non planar. The deviation from planarity in these compounds is investigated by cyclic voltammetry.

The synthesis of biomimetic model systems for the natural photochemical reaction center chromophores of bacteria and plants is an exciting and important field in porphyrin chemistry.[1] In these natural systems the two special pair chromophores are only different with respect to their deviation from planarity.[2] Generally non-planarity seems to be an important structural feature of many naturally occurring porphyrin and related tetrapyrrole chromophores with respect to efficiency of electron transfer processes in the ground and excited state. Examples for natural systems where ruffling is an important feature are the above mentioned photochemical reaction center chromophores,[2] vitamin B12 and B12 dependent enzymes[3] and factor F430,[4] a highly reduced porphyrin derivative found in methyl coenzyme M reductase.[5] In view of this, synthesis of non-planar porphyrins is very interesting and of great importance for the development of new model systems for natural electron transfer systems.

We now report here the synthesis and investigation of β-alkyloxy substituted *meso*-tetraphenylporphyrins, where the interaction of the β-substituent and the meso-aryl moiety leads to a small deviation from planarity of the porphyrin macrocycle. This ruffling of the porphyrin chromophore was already mentioned by Smith[6] and Hombrecher.[7] It was shown, that ruffling of the chromophore influences especially the absorption[7,8] and NMR-spectra[6,9] as well as Raman spectra[10] of the porphyrins. Changes due to ruffling were also



4	R
a	$-CH_3$
b	$-CH_2CH_3$
c	$-CH_2CH_2CH_3$
d	$-CH(CH_3)_2$
e	$-C_6H_{11}$
f	$-CH_2-C(CH_3)_3$

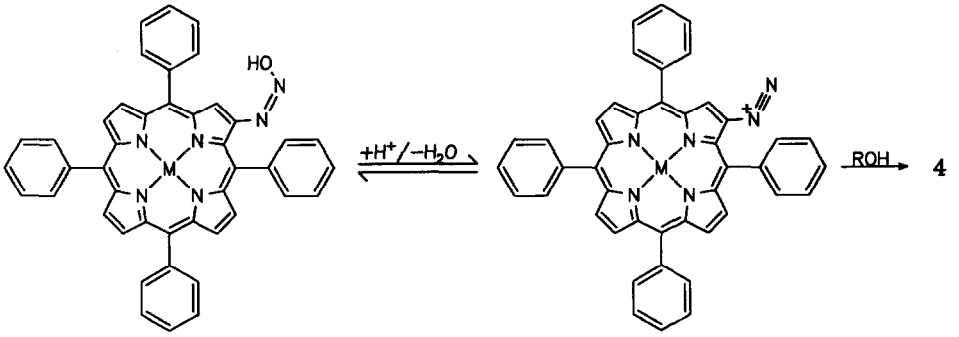
Scheme 1

detected in the electrochemical behaviour of porphyrinic systems.[11] Though the deviation from planarity in our systems is very small, it can be detected by electrochemical measurement of the oxidation and reduction potential of the synthesized systems.

The synthesis of the β-alkyloxy derivatives is outlined in scheme 1. TPP (*meso*-tetraphenylporphyrin)

is nitrated with $Cu(NO_3)_2$ in acetic anhydride.[12] The nitro compound is isolated in the yield of 86% and purified by column chromatography. Reduction of the nitro derivative is done with Sn/HCl in a ultrasonic bath in 80% yield or, alternatively, with $NaBH_4$/LiCl in THF or NH_4OOCH-Pd/C or $NaBH_4$/Pd/C/CH_3OH. Nevertheless, we found it much more convenient to carry out the reduction via the Sn/HCl-ultrasound procedure. Demetallation of the copper porphyrin **2** is performed using propanedithiol[13] and TFA (trifluoroacetic acid) in a yield of 90%. The metall free amino compound **3** is purified by flash chromatography on a silica gel column. This compound is unstable and decomposes within 5 days.[14] Diazotization by reaction with H_2SO_4 and $NaNO_2$[15] and in situ reaction with alcohol leads to the formation of the β-alkyloxy derivatives (method A). Alternatively the reaction can be carried out with the copper complex and sodium methoxide (method B). Depending upon the nature of the substituent the yield varies from 62% (methoxy) to only 2% (neopentyloxy). This is mainly due to the increasing reductive capability of the higher alcohols thus leading to the formation of TPP. This reduction of diazonium ions by alcohols to the hydrocarbons is a well known reaction.[16] Metall complexes were preapared by standard procedures[17] and purified by chromatography.

We also tried to isolate the porphyrin diazonium ion by reacting **2** with sodium nitrite and sulfuric acid. in THF/methanol. After a standard work up procedure we obtained a green compound in 54% yield with m/e = 719 and a strong IR absorption at 2200 and 1670 cm^{-1} to which we assign structure **5a**. Demetallation was performed using H_2SO_4/CH_2Cl_2 in 80% yield. This diazohydroxide can be transferred to the diazonium ion by the well known pH-dependent diazohydroxide - diazonium equilibrium (scheme 2).[18] Thus reacting the isolated



5a,b 6a,b

a: M = Cu
b: M = H_2

Scheme 2

diazo hydroxide with H_2SO_4 in the presence of methanol we isolated the methoxy substituted derivative **4a** in a yield of 95% (method C). To the best of our knowledge, this is the first reported isolation of a β-porphyrinyl diazoniumion/diazohydroxide. In our opinion the synthesis of **5** offers a new attractive route to porphyrin derivatives substituted in the β-position via the various well known diazoniumion reactions.

We also studied the electrochemical behaviour of the synthesized compounds. The oxidation and reduction potentials of the synthesized compounds were estimated by cyclic voltammetry. The observed voltammetric waves are reversible, as indicated by the peak-separation of approximately 60 - 65 mV. The electrochemical data are summarized in table 1. As can be seen, the first oxidation potential (formation of the radical cation) is decreasing linearly with respect to the σ^+ value. The second oxidation potential (formation of the dication) is independent of the σ^+ value for the methoxy, ethoxy and propoxy derivative. With increasing bulkyness of the substituent, the second oxidation potential is decreasing. In contrast to the first oxidation potential the first and second reduction potentials show no dependency upon the σ^+-value. The electrochemical behaviour can be explained as follows. The alkyloxy substituent is an electron donating substituent thus leading to an increased electron density in the macrocycle and therefore to a decreased oxidation potential. This effect is mainly operative for the first oxidation step as can be seen from the dependency of the corresponding potential on σ^+. Interaction of beta and meso substituents leads to a deviation from planarity of the porphyrin chromophore. This will result in a decreased delocalisation of π-electrons thus leading to a destabilized HOMO. A destabilized HOMO corresponds to a decreased oxidation potential. This effect is especially important for the second oxidation step. The HOMO of the radical cation must be very sensitive to ruffling, because here a positive charge has to be stabilized. In the copper complexes this dependency is not found. Complexation leads to a more planar system and differences in planarity diminish or become very small. Thus the oxidation potentials are almost identical in this series for the second oxidation step. Nevertheless, the dependency of the first oxidation potential on the σ^+-value is still given. Interestingly, the difference between the first and the second oxidation potential in the free base porphyrins is only 190 mV, whereas in the copper complexes this difference is 330 - 350 mV. This behaviour is in contrast to TPP where the difference between the first and second oxidation potential in the copper-complex (260 mV) is smaller then for the free base (330 mV).[19] This is indicating that especially the second oxidation potential of the free base porphyrin is influenced by the β-alkyloxy substituent.

As can be seen from table 1, the σ^+-values of the neopentyloxy group and the cyclohexyloxy group are not known. Comparing the estimated potentials of the first oxidation step for these compounds with the other data, one can estimate a σ^+-value of -0.83 for the neopentyloxy substituent and -0.86 for the cyclohexyloxy substituent.

Though the structural changes in our systems induced by the alkyloxy moieties are very small, we were able to show, that cyclic voltammetry is a very sensitive tool for studying the non-planarity of porphyrin macrocycles.

Table 1: Electrochemical data of the synthesized porphyrins.

Compound	$E_{1/2}$ (ox1)[a]	$E_{1/2}$ (ox2)[a]	$E_{1/2}$ (red1)[a]	$E_{1/2}$ (red 2)	σ^+
4a	0.440	0.630	-1.765	-2.070	-0.78
Cu-4a	0.445	0.770	-1.885	-	-0.78
4b	0.430	0.630	-1.770	-2.080	-0.81
Cu-4b	0.435	0.775	-1.885	-	-0.81
4c	0.425	0.630	-1.765	-2.070	-0.83
Cu-4c	0.435	0.770	-1.875	-	-0.83
4d	0.420	0.620	-1.770	-2.070	-0.85
Cu-4d	0.420	0.770	-1.875	-	-0.85
4e	0.415	0.610	-1.770	-2.070	-
4f	0.425	0.610	-1.765	-2.080	-

[a] Data estimated by cyclic voltammetry scan-rate 100 mV/s. Solvent CH_2Cl_2 0.1 M Tetrabutylammonium tetrafluoroborate. Temperature 20°C. All potentials given with respect to ferrocene. Ox1 = 1st oxidation potential, ox2 = 2nd oxidation potential, red1 = 1st reduction potential, red2 = 2nd reduction potential.

Furthermore we were able to synthesize the very interesting diazonium hydroxide **5a** in very good yield. This compound offers new attractive ways for synthesis of various porphyrin derivatives via diazoniumion reactions. Work making use of this compound for the synthesis of porphyrin β-derivatives is in progress.

EXPERIMENTAL SECTION

NMR Spectra were obtained in $CDCl_3$ and recorded with a Varian XL 200 spectrometer or a Bruker AMX 300 spectrometer. Chemical shift values were given in ppm relative to TMS. Coupling constants were given in Hertz. Mass spectra were obtained with a VG-Analytical instruments (VG70:250 E, AutoSpec Q and VG 7070E). Electronic spectra were recorded on a Kontron Uvikon 860 or on a Shimadzu UV-160 A instument. IR spectra were recorded on a Shimadzu IR-435 spectrometer. Melting points were measured on a Büchi 510 apparatus or on a hot-stage Reichert Thermovar apparatus. Melting points are uncorrected. Column chromatography was carried out with Merck silica gel mesh size 0.06 - 0.2 mm. TLC chromatography was carried out using Merck PSC 5745 2 mm silica plates (no fluorescence indicator!). Electrochemical measurements were carried out with a Tacussel PJT-24 potentiostat connected to a Tacussel IMT1-interface and a IBM personal computer and a Siemens Oscillar D 1015 oscilloscope. Ohmic drop compensation was done by positive feedback. A three electrode cell was used for all measurements. A Ag/AgCl electrode was used as reference electrode and a Pt electrode was used either for the working and the auxiliary electrode. All potentials

were given with respect to ferrocene. All measurements were carried out in the temperature range of 20 - 21°C. The scan rate was varied from 50 mV/s to 5000 mV/s. All reported oxidation and reduction values are averaged values of at least 5 independent measurements. The data were checked for outliers by a Nalimov test. A plot of the measured peak currents for all peaks vs the square root of the scan rate is linear in the range of 50 mV/s to 5000 mV/s thus indicating a diffusion controlled process. Tetrabutylammonium tetrafluoroborate (0.1 M) was used as supporting electrolyte and CH_2Cl_2 was used as solvent and dried over CaH_2 prior to use. All measurements were carried out under nitrogen.

Synthesis of porphyrins

Synthesis of (2-nitro-5,10,15,20-tetraphenylporphyrinato)copper-II (1)

In a 1 l round bottom flask 1.0 g (1.6 mmol) tetraphenylporphyrin is dissolved in 750 ml $CHCl_3$. Then 1.13 g (5 mmol) $Cu(NO_3)_2 \cdot 3H_2O$ and 72 ml acetic anhydride were added. The mixture is stirred for 48 h at room temperature. Then 50 ml 0.1 M NaOH solution were added, the organic layer separated and washed with water and dried ($MgSO_4$). The solvent is evaporated and the residue chromatographed on a silica gel column (9 x 20 cm) with $CHCl_3/C_6H_{14}$ (3:2) as eluent. Yield: 1.00 g (86%).- UV-Vis ($CHCl_3$): λ = 421, 547, 589 nm.- MS (FAB): m/e = 721 (M^+ + 1), 676 (M^+ - 47).- IR (KBr): 1595, 1470 cm^{-1}.

Synthesis of (2-amino-5,10,15,20-tetraphenylporphyrinato)copper-II (2)

In a 100 ml round bottom flask 200 mg (0.28 mmol) **1** was dissolved in 20 ml $CHCl_3$. Then 2.8 g tin-powder and 9 ml concentrated HCl were added. The reaction mixture was sonicated in a ultrasonic bath for 1 h. The mixture was filtered, the residue extracted with CH_2Cl_2 and the combined organic layers washed with water and dried ($MgSO_4$). The solvent was evaporated and the residue chromatographed on a silica gel column (9 x 20 cm) with $CHCl_3$ as eluent. Yield: 0.152 g (80%).- UV-Vis ($CHCl_3$): λ = 412, 540, 593 nm.- MS (FAB): m/e = 691 (M^+ + 1), 673 (M^+ - 18).- IR (KBr): 1609, 1503 cm^{-1}.

Synthesis of 2-amino-5,10,15,20-tetraphenylporphyrin (3)

In a 100 ml round bottom flask 75 mg (0.108 mmol) **2** was dissolved in 20 ml TFA. Then 0.2 ml propanedithiol and 10 ml $CHCl_3$ were added. The reaction mixture was stirred for 1 h at room temperature. Then 20 ml 1 M NaOH solution were added, the organic layer was separated and dried (Na_2SO_4). The solvent was evaporated and the residue chromatographed on a silica gel column (2 x 20 cm) with $CHCl_3$ as eluent. Yield: 0.068 g (94%).- ^{1}H-NMR ($CDCl_3$): δ = -2.02 (br s, 2 H, NH), 4.42 (br s, 2 H, NH_2), 7.69 - 7.82 (m, 13 H, H_m, H_p H-3), 7.88 - 7.93 (m, 2 H, $H_{o'}$), 8.10 - 8.22 (m, 6 H, H_o), 8.57 (s, 2 H, H-12,13), 8.50 - 8.78 (m, 4 H, $H_{pyrrole}$).- MS (FAB): m/e = 630 (M^+ + 1).- UV-Vis ($CHCl_3$): λ = 404, 522, 556, 594, 650 nm.

Synthesis of 2-diazo-((5,10,15,20-tetraphenylporphyrinato)copper-II) hydroxide (5a)

In a round bottom flask 57 mg (0.082 mmol) **2** were added to a mixture of 5 ml THF and 1 ml methanol. Then 40 mg $NaNO_2$ and 0.1 ml H_2SO_4 (99%) were added and the reaction mixture stirred overnight. The mixture was poured into water and extracted 3 times with $CHCl_3$. The combined organic extracts were washed with dilute aqueous sodium hydrogen carbonate and water, and then dried (Na_2SO_4). The solvent was

evaporated and the residue chromatographed on a silica gel plate (Merck 2 mm) using CH_2Cl_2 as eluent. The green major fraction was extracted with CH_2Cl_2. The solvent was evaporated giving 32 mg (54%) of **5a**. MS (FAB): m/e = 719 (M^+), 691 (M^+ - 28).- UV-Vis ($CHCl_3$): λ = 430, 580, 609 nm.- IR (KBr): 3400 (br), 2100 (s), 1670 (s) cm^{-1}.

Synthesis of 2-diazo-(5,10,15,20-tetraphenylporphyrin) hydroxide (5b)

Compound **5a** (32 mg, 0.044 mmol) was added to a mixture of conc. H_2SO_4 and CH_2Cl_2 (1:10) and stirred for 0.5 h. The mixture was carefully neutralized with sodium hydrogen carbonate solution. Then the organic layer was separated, washed with brine and water and dried (Na_2SO_4). The solvent was evaporated and the residue crystallized from methanol/CH_2Cl_2. Yield: 15 mg (52%).- ^{1}H-NMR ($CDCl_3$): δ = -2.40 (br s, 1 H, NH), -2.22 (br s, 1 H, NH), 7.69 - 7.88 (m, 13 H, H_m, H_p, H-3), 7.92 - 7.95 (m, 2 H, H_o, phenyl at C-20), 8.10 - 8.19 (m, 6 H, H_o), 8.58 (d, 1 H, J = 3.7 Hz, H-12,13), 8.64 (d, 1 H, J = 3.7 Hz, H-12,13), 8.65 (d, 1 H, J = 3.4 Hz, H-17,18), 8.67 (d, 1 H, J = 3.4 Hz, H-7,8), 8.76 (d, 1 H, J = 3.4 Hz, H-17,18), 8.83 (d, 1 H, J = 3.4 Hz, H-7,8).- MS (FAB): m/e = 657 (M^+).- UV-Vis ($CHCl_3$): λ = 429 (5.51), 525 (4.34), 560 (4.06), 598 (3.99), 653 (3.88) nm.- IR (KBr): 3395 (br), 2083 (s), 1670 (s) cm^{-1}.

Synthesis of 2-methoxy-5,10,15,20-tetraphenylporphyrin (4a)

Method A: 100 mg (0.16 mmol) of amino compound **3** was dissolved in 20 ml of $CHCl_3$ and cooled to 0 - 5°C. Then 100 mg $NaNO_2$ and 5 drops of H_2SO_4 (conc.) were added. The reaction mixture was stirred for 2 h. Then 0.5 ml methanol was added and the reaction mixture stirred for 1 h. Sodium carbonate and 10 ml of water was added, the organic layer separated, the water layer extracted with $CHCl_3$ (20 ml) and the combined organic layers dried ($MgSO_4$). The solvent was evaporated and the residue chromatographed on a silica gel column (2 x 20 cm) with $CHCl_3$ as eluent. The first porphyrinic fraction collected was TPP, the second fraction was the expected product. Yield: 32 mg (31 %).- ^{1}H-NMR ($CDCl_3$); δ = -2.84 (br s, 2 H, NH), 3.98 (s, 3 H, -OMe), 7.63 - 7.80 (m, 13 H, H_m, H_p, H-3), 7.99 - 8.04 (m, 2 H, H_o, phenyl at C-20), 8.16 - 8.23 (m, 6 H, H_o), 8.68 (d, 1 H, J = 4.9 Hz, H-17,18), 8.74 (d, 1 H, J = 4.9 Hz, H-7,8), 8.76 (s, 2 H, H-12,13), 8.81 (d, 1 H, J = 4.9 Hz, H-17,18), 8.85 (s, 1 H, J = 4.9 Hz, H-7,8).- MS (FAB): m/e = 645 (M^+ + 1).- UV-Vis ($CHCl_3$): λ (log ε) = 419 (5.29), 516 (4.02), 549 (3.61), 591 (3.58), 644 (3.40) nm.- Anal. Calc. for $C_{45}H_{32}N_4O \cdot 1/2H_2O$ (662.99): C 82.67 H 5.09 N 8.57. Found: C 82.93 H 4.92 N 8.55.- M.p. > 300°C.

Method B: The copper complex **2** (42 mg, 0.061 mmol) in 3 ml of dry THF and 1 ml dry methanol was stirred with 70 mg $NaNO_2$ and 0.1 ml conc. H_2SO_4 until the color changed from brown to green. Then 160 mg sodium methoxide was added and the reaction mixture refluxed for 4 h. After the mixture has been allowed to cool it was poured in water and extracted with $CHCl_3$. The organic extract was washed with water, dried (Na_2SO_4) and the solvent evaporated. The residue was chromatographed by preparative TLC on silica gel plates using CH_2Cl_2/petrol ether (20%) as eluent. Yield: 26 mg (62%) of the copper complex. Demetallation was performed as described for compound **3**.

Method C: In a round bottom flask 30 mg (0.04 mmol) **5a** were refluxed for 2 h in a mixture of 0.5 ml methanol, 2 ml $CHCl_3$ and 0.1 ml concentrated H_2SO_4. After the reaction mixture was cooled to room

temperature, water (20 ml) was added, the organic layer separated and washed with a saturated solution of sodium carbonate and water. The organic layer was separated and dried (Na_2SO_4). The solvent was evaporated and the residue chromatographed on a silica gel plate using $CHCl_3$/hexane (1:0.05) as eluent. Yield: 25 mg (93%) of the copper free compound **4a**.

Synthesis of 2-ethoxy-5,10,15,20-tetraphenylporphyrin (4b)

Method A: Yield: 23%.- ^{1}H-NMR ($CDCl_3$): δ = -2.83 (br s, 2 H, NH), 1.14 (t, 3 H, J = 6.8 Hz, CH_3-), 4.23 (q, 2 H, J = 6.8 Hz, -OCH_2-), 7.61 - 7.75 (m, 13 H, H_p, H_m, H-3), 8.03 (m, 2 H, H_o, phenyl at C-20), 8.15 - 8.23 (m, 6 H, H_o), 8.72 (d, 1 H, J = 5.1 Hz, H-17,18), 8.75 (d, 1 H, J = 4.9 Hz, H-7,8) 8.76 (s, 2 H, H-12,13), 8.81 (d, 1 H, J = 5.1 Hz, H-17,18), 8.85 (d, 1 H, J = 4.9 Hz, H-7,8).- MS (FAB): m/e = 659 (M^+ + 1).- UV-Vis ($CHCl_3$): λ (log ε) = 419 (5.29), 516 (4.02), 549 (3.61), 591 (3.58), 644 (3.40).- Anal. Calc. for $C_{46}H_{34}N_4O \cdot 1/2H_2O$ (676.82): C 82.73 H 5.28 N 8.39. Found: C 82.81 H 5.01 N 8.22.- M.p. > 300°C.

Synthesis of 2-propoxy-5,10,15,20-tetraphenylporphyrin (4c)

Method A: Yield: 5%. *Method B*: Yield: 20%.- ^{1}H-NMR ($CDCl_3$): δ = -2.81 (br s, 2 H, NH), 0.85 (t, 3 H, J = 7.0 Hz, -CH_3), 1.50 (tq, 2 H, J = 6.5 Hz, J_q = 7.0 Hz, -CH_2-CH_3), 4.17 (t, 2 H, J = 6.5 Hz, -O-CH_2-), 7.64 - 7.79 (m, 13 H, H_m, H_p, H-3), 8.01 - 8.04 (m, 2 H, H_o, phenyl at C-20), 8.17 - 8.22 (m, 6 H, H_o), 8.67 (d, 1 H, J = 4.9 Hz, H-17,18), 8.75 (d, 1 H, J = 5.1 Hz, H-7,8), 8.76 (s, 2 H, H-12,13), 8.80 (d, 1 H, J = 4.9 Hz, H-17,18), 8.85 (d, 1 H, J = 5.1 Hz, H-7,8).- MS (FAB): m/e = 673 (M^+ + 1).- UV-Vis ($CHCl_3$): λ (log ε) = 419 (5.30), 516 (3.99), 548 (3.44), 589 (3.49), 643 (3.16).- Anal. Calc. for $C_{47}H_{36}N_4O \cdot 1/2H_2O$ (690.85): C 82.79 H 5.47 N 8.22. Found: C 83.30 H 5.44 N 8.19.- M.p. > 300°C.

Synthesis of 2-isopropoxy-5,10,15,20-tetraphenylporphyrin (4d)

Method A: Yield: 5%.- ^{1}H-NMR ($CDCl_3$): δ = -2.83 (br s, 2 H, NH), 1.22 (d, 6 H, J = 6.1 Hz, -$CH(C\underline{H}_3)_2$), 4.68 - 4.78 (sept., 1 H, J = 6.1 Hz, -O-$C\underline{H}(CH_3)_2$), 7.61 - 7.79 (m, 13 H, H_m, H_p, H-3), 7.98 - 8.01 (m, 2 H, H_o, phenyl at C-20), 8.17 - 8.22 (m, 6 H, H_o), 8.71 (d, 1 H, J = 4.9 Hz, H-17,18), 8.75 (d, 1 H, J = 4.9 Hz, H-7,8), 8.76 (s, 2 H, H-12,13), 8.80 (d, 1 H, J = 4.9 Hz, H-17,18), 8.84 (d, 1 H, J = 4.9 Hz, H-7,8).- MS (FAB): Accurate Mass: 673.29566. Calculated for $C_{47}H_{37}N_4O$ (M^+ + 1): 673.29674.- UV-Vis ($CHCl_3$): λ (log ε) = 419 (4.65), 516 (3.72), 548 (3.00), 590 (3.06), 645 (2.77).- M.p. > 300°C.

Synthesis of 2-cyclohexyloxy-5,10,15,20-tetraphenylporphyrin (4e)

Method A: Yield: 2%.- ^{1}H-NMR ($CDCl_3$): δ = -2.89 (br s, 2 H, NH), 2.50 - 2.75 (m, 10 H, -CH_2-), 4.26 (m, 1 H, -O-CH), 7.64 - 7.84 (m, 13 H, H_m, H_p, H-3), 8.01 - 8.10 (m, 2 H, H_o,), 8.18 - 8.30 (m, 6 H, H_o), 8.66 - 8.92 (m, 4 H, $H_{pyrrole}$), 8.79 (s, 2 H, H-12,13).- UV-Vis ($CHCl_3$): λ = 419, 516, 547, 589, 643 nm .- Anal. Calc. for $C_{50}H_{41}N_4O$ (713.90): C 84.12 H 5.79 N 7.85. Found: C 84.01 H 5.70 N 7.77.- M.p. > 300°C.

Synthesis of 2-neopentyloxy-5,10,15,20-tetraphenylporphyrin (4f)

Method A: Yield: 2%. *Method B*: Yield: 2%.- ^{1}H-NMR ($CDCl_3$): δ = -2.83 (br s, 2 H, NH), 0.84 (s, 9 H, -CH_3), 3.94 (s, 2 H, -O-CH_2-), 7.66 - 7.79 (m, 13 H, H_m, H_p, H-3), 8.05 - 8.10 (m, 2 H, H_o, phenyl at C-20), 8.17 - 8.23 (m, 6 H, H_o), 8.49 (d, 1 H, J = 4.9 Hz, H-17,18), 8.73 (d, 1 H, J = 4.2 Hz, H-7,8), 8.75 (s, 2

H, H-12,13), 8.76 (d, 1 H, J = 4.9 Hz, H-17,18), 8.84 (d, 1 H, J = 4.2 Hz, H-7,8).- MS (FAB): Accurate mass: 701.33078. Calculated for $C_{49}H_{41}N_4O$ (M^+ + 1): 701.32804.- UV-Vis ($CHCl_3$): λ (log ε) = 419 (471), 516 (3.52), 548 (2.97), 590 (3.02), 643 (2.71).- M.p. > 300°C.

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