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SYNTHESIS OF 5-(4-ACETAMIDOPHENYL)-10,15,20-TRIS(4-SUBSTITUTED PHENYL) PORPHYRINS USING DIPYRROMETHANES

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Abstract. A convenient procedure for the synthesis of 5-(4-acetamidophenyl)-10,15,20-tris(4-substituted phenyl) porphyrins (**5-8**) from dipyrromethane is reported. *meso*-(4-Substituted phenyl) dipyrromethanes (**1-4**) were obtained in yields of 72-84% by the reaction of 4-substituted benzaldehyde with an excess of pyrrole. The porphyrins (**5-8**) were isolated with appreciable yields of 15-17%.

Tetrapyrrolic macrocycles are vital for life on this planet. Without light-harvesting and trapping activities of reduced porphyrins there could be no photosynthesis. The porphyrins lie at the focal point formed from divergent fields of research, including solar energy conversion, photosynthesis model, photodynamic therapy and novel electronic and optical materials. Particularly, the *meso*-tetraphenylporphyrins offer attractive features in this context and have been used in a wide variety of model studies.[1] Moreover, porphyrin moiety covalentely linked to carotenoid polyene has been usefully utilized in the design of artificial photosynthetic membrane that biomimics natural processes of solar energy

conversion.[2] Also, electroactive porphyrins could have applications in the design of molecular-scale electronic devices.[3] Therefore, the synthesis of well-defined asymmetric porphyrin derivatives is the great interest for the development of new molecular structures.

Tetraphenylporphyrin was first synthesized many years ago by Rothermund.[4] Thus, benzaldehyde and pyrrole was reacted in pyridine at 150 °C for 24 h. The yield was low and the condition so severe. Adler and co-workers used a modified method carried out the reaction for 30 min in refluxing propionic acid open to the air.[5] The mainly problem is the high level of tar produced that presents purification problems and the reproducibility of the reaction is often rather poor. A more recent approach for the synthesis of symmetric *meso*-tetraphenylporphyrins was using equilibrium conditions developed by Lindsey and co-workers.[6] The yields were 30-40% under mild reaction conditions.

For many interesting cases, asymmetric porphyrins, such as *meso*-substituted phenyl porphyrins bearing only one functional phenyl group and keeping three identical substituted phenyl groups (AB_3-porphyrin) are request.[7,8] However, a major limitation of available methods concerns the ability to place different substituents at the four *meso*-positions of the porphyrin. Thus, porphyrins bearing two different types of *meso*-substituents can be prepared by a binary mixed aldehyde condensation. This approach is statistical in nature and usually a multiple porphyrin products are obtained.[6] Often, six porphyrins are formed, the work up is no simple because the tar present. The isolate requires slowly chromatographic separation and no pure porphyrin is always possible. Moreover, when the separate can be taken out the yield is very poor.[9]

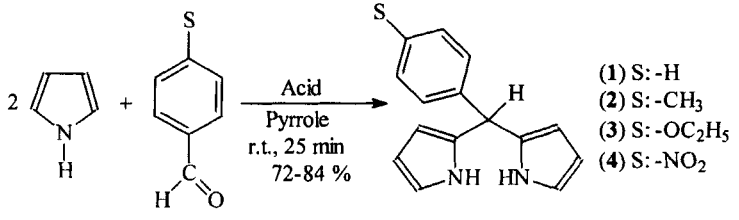
More direct approaches to *trans*-substituted porphyrins (ABAB-porphyrin) are provided by condensation of dipyrromethane with aldehyde. These porphyrins require access to *meso*-substituted dipyrromethane, which can be synthesized from the reaction of aldehyde with excess of pyrrole catalyzed by acid.[10]

Finally, porphyrins bearing four different *meso*-substitutents (ABCD-porphyrin) can be synthesized via a stepwise synthetic approach. Rational ABCD-porphyrins synthesis bearing four different aryl rings were performed from MacDonald's routes.[11] An attractive synthesis of a regioisomerically pure ABCD-porphyrin involves the synthesis of two *meso*-substituted dipyrromethanes, funtionalization of the 1- and 9- position of one of the dipyrromethanes, and a convergent MacDonald-type 2+2 condensation between both dipyrromethanes.[12,13] The ability to place four different groups around the periphery of the porphyrins should enable synthesis of sophisticates building block porphyrins. The yield in the porphyrin condensation is not high and this condensation is mainly useful for synthesis of regioisomerically pure ABCD-porphyrins.

We are interesting in the synthesis of porphyrins bearing three identical *meso*-phenyl substituents and one different. However, for AB_3-porphyrins the stepwise method described above requires many steps (i.e. about 8 starting from pyrrole and aldeydes). Therefore, this paper reports a convenient procedure for the synthesis of 5-(4-acetamidophenyl)-10,15,20-tris(4-substituted phenyl) porphyrins from dipyrromethanes. In this way, four *meso*-(4-substituted phenyl) dipyrromethanes were synthesized, two new dipyrromethanes (**3**) and (**4**) bearing -

OC_2H_5 and $-NO_2$ groups respectively were formed in similar condition than for ones with -H (**1**) and $-CH_3$ (**2**), showing that this reaction is feasible with benzaldehydes substituted by either electron-donor or electron-withdrawing groups. The reaction of dipyrromethane (**1-4**) with a mixture of two appropriate substituted benzaldehydes affords a mixture of three *meso*-substituted porphyrins, which can be easily separate by flash chromatography. Thus, the desired *meso*-substituted porphyrins (**5-8**), bearing one 4-acetamidophenyl group and three identical peripheral functional groups have been prepared with appreciable yields (15-17%) on two-step one-flask reaction.

Dipyrromethane formation. Aldehyde and pyrrole undergo acid-catalyzed condensation at room temperature. The condensation of substituted benzylaldehyde with a large excess of pyrrole (1:45 aldehyde/pyrrole mol ratio) catalyzed by $BF_3{\cdot}O(Et)_2$ affords *meso*-(4-substituted phenyl) dipyrromethane (**1-4**). The reaction mixture was stirred for 25 min at room temperature resulting in complete consumption of the aldehyde. Under this reaction condition, pyrrole serves as the reactant in excess and as the solvent for the reaction, giving direct formation of dipyrromethane (Scheme 1).



Scheme 1

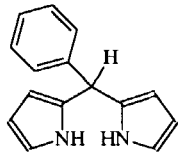
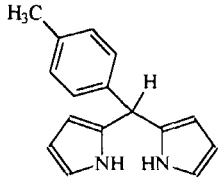
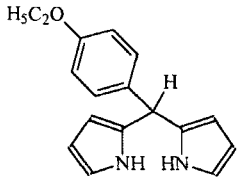
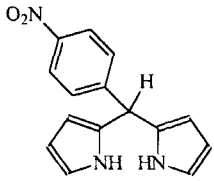
The brown crude solution was washed with dilute aqueous NaOH. The dipyrromethanes were isolated 72-84 % by flash chromatography on silica gel in a mildly basic medium, using n-hexane/ethyl acetate/triethylamine (80/20/1) as eluent. The use the neutral organic solvent leads to decomposition of the dipyrromethane on silica. Thus, triethylamine (≅1%) was added to prevent decomposition of the dipyrromethane on silica column, which is slightly acidic. Dipyrromethanes (**1-4**) are stable in the purified form upon storage at 0°C in nitrogen atmosphere and absence of light.

Dipyrromethane yields are shown in Table 1. Dipyrromethanes (**1**) and (**2**) have been synthesized before under similar conditions.[10] However, 45/1 molar excess of pyrrole showed that the condensation reaction gives better yield. Also, two new dipyrromethanes (**3**) and (**4**) bearing a *p*-ethoxy and *p*-nitro groups were prepared in this way. Thus, the reaction is compatible with aromatic aldehydes bearing electron-donor ($-OC_2H_5$) or electron-withdrawing ($-NO_2$)groups indicating the broad scope of these reactions. Consequently, dipyrromethanes can be easily performed with high purity witch is essential for its application in the synthesis of asymmetric *meso*-substituid porphyrin.

Synthesis of porphyrin. The 5-(4-acetamidophenyl)-10,15,20-tris(4-substituted phenyl) porphyrin (**5-8**) was synthesized by the acid-catalyzed condensation of dipyrromethane (**1-4**) and the correspondent 4-substituted benzaldehydes in chloroform at room temperature (Scheme 2).

Mixed-benzaldehyde dipyrromethane condensations were performed using about [2.2:1.4:1] molar relation of dipyrromethane, 4-acetamidabenzaldehyde and

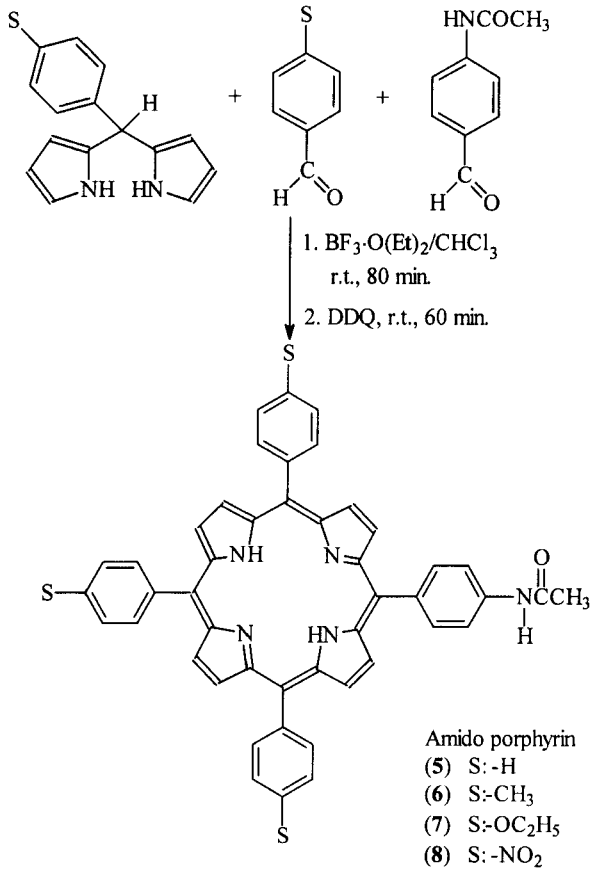
Table 1. Synthesis of *meso*-(4-substituted phenyl) dipyrromethanes from the appropriate benzaldehyde and excess of pyrrole.

	Dipyrromethane	Yield %
1		81
2		82
3		84
4		72

Reaction time 25 min at r.t.

4-substituted benzaldehyde. These amount of reactants allows better yield of selected porphyrins (**5-8**). The results are shown in Table 2.

The reaction was performed using catalytic among of $BF_3{\cdot}O(Et)_2$ and chloroform as solvent, at room temperature. The reaction mixture was subject to



Scheme 2

oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). Thus, this mixed condensation affords a mixture of three porphyrins, the 5,10,15,20-tetra(4-substituted phenyl) porphyrin, the 5-(4-acetamidophenyl)-10,15,20-tris(4-substituted phenyl) porphyrin (**5-8**) and the 5,15-bis(4-acetamidophenyl)-10,20-bis(4-substituted phenyl) porphyrin.

Table 2. Synthesis of 5-(4-acetamidophenyl)-10,15,20-tris(4-substituted phenyl) porphyrins from dipyrromethanes. Values between square bracket mean the molar relation of reactant mixed in the condensation.

Porphyrin	Dipyrromethane	4-Acetamido benzaldehyde	4-Substituted benzaldehyde	Yield %
5	**1** [2.2]	[1.4]	-H [1]	15
6	**2** [2.2]	[1.4]	$-CH_3$ [1]	16 [b]
7	**3** [2.0]	[1.3]	$-OC_2H_5$ [1]	17 [c]
8	**4** [2.3]	[1.5]	$-NO_2$ [1]	16

Reaction time 80 min at r.t. [b] 3.6% from Ref. 9, [c] 3.0 % using a modified Adler method where the reaction was carried out in propionic acid at 90 °C (see experimental section).

The three porphyrins were easily separated by flash chromatography with high purity using dichloromethane/methanol or acetone gradient. In all these cases, the first purple band corresponds to *meso*-tetra porphyrin, the second is the desired mono-amide porphyrin (**5-8**) and the third more polar band belongs to bis-amido porphyrin.

Another way to prepare these porphyrins, bearing two different types of *meso*-substituents, could be by a binary mixed aldehyde condensation. Usually, multiple porphyrin products are obtained using this procedure. Thus, porphyrin (**7**) was synthesized using this procedure by heat a mixture of 4-acetamidobenzaldehyde, 4-ethoxybenzaldehyde and pyrrole (1:3:4 molar relation)

in propionic acid at 90 °C for 1 h. The reaction work up was no simple because the difficulty to remove propionic acid and the tar present. The isolation requires a slowly chromatographic column separation and the yield is very poor (3.0 %). Moreover, porphyrin (**6**) was prepared under similar condition using a mixture of 4-acetamidobenzaldehyde, 4-methylbenzaldehyde and pyrrole yielding after a long procedure of purification about 3.6 %.[9] Thus, these results show that dipyrromethane method presents advantage still for the synthesis of AB_3-porphyrins, mainly for both easier work up and higher yield.

In conclusion, the following two basic steps were used sequentially in the synthesis: 1) *meso*-(4-substituted phenyl) dipyrromethane was formed from correspondent benzaldehyde derivative and pyrrole catalyzed by acid, 2) condensation of dipyrromethane with appropriate benzaldehydes yields a mixture of three porphyrins which can be easily isolated by flash chromatography. Thus, the desired porphyrins (**5-8**), bearing one 4-acetamidophenyl group and three identical peripheral functional groups, were obtained with appreciable yields of 15-17%. This approach has a relatively simple reaction work up and higher yield than modified Alder method. Also, it involves only two-reaction flask, while that the stepwise method[11,12] that allow obtaining a pure selected porphyrin would request many steps. Thus, this present strategy may be used for preparation of other similar porphyrin derivatives bearing only one different peripheral phenyl substituent. The resultant amido porphyrins (**5-8**) can be hydrolyzed to amine porphyrin by heat in tetrahydrofuran/methanol/KOH medium. Therefore, these acetamidophenyl porphyrins are interesting starting material in the devise of

porphyrin derivatives and supramolecules bearing porphyrin moiety linked by amide bound.[2,3b,9]

Experimental Section

General. Absorption spectra were recorded on a Shimadzu UV-2401PC. NMR spectra were recorded on a Varian Gemini spectrometer at 300 MHz. Mass spectra were taken with a Varian Matt 312 opering in EI mode at 70 eV. TLC Uniplate Silica gel GHLF, 250 microns, thin layer chromatography plates, from Analtech and silica gel 230-400 mesh for column chromatography from Aldrich were used.

Starting materials. Benzaldehyde, 4-methylbenzaldehyde, 4-ethoxybenzaldehyde, 4-nitrobenzaldehyde, 4-acetamidophenylbenzaldehyde, pyrrole, boron trifluoride diethyl etherate ($BF_3{\cdot}O(Et)_2$), trifluoroacetic acid and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) from Aldrich were used without further purification. Dichloromethane and chloroform (GR grade) from Merck were distilled and storage over 4Å molecule sieves.

Synthesis of dipyrromethanes

***meso*-Phenyldipyrrometane (1).** A solution of benzaldehyde (849 mg, 8 mmol) and pyrrole (24.17 g, 360 mmol) was degassed by bubbling with argon for 15 min, then trifluoroacetic acid (154 μL, 2 mmol) was added. The solution was stirred for 25 min at room temperature, at which point no starting aldehyde was shown by TLC analysis (cyclohexane/ethyl acetate/triethylamine; 80:20:1). The mixture was diluted with dichloromethane (100 mL), washed with aqueous 0.1 M NaOH and then washed with water. The organic phase was dried with Na_2SO_4,

filtered and the solvent was removed under reduced pressure. The unreacted pyrrole was removed by vacuum distillation at room temperature. The product was purified by flash chromatography (silica gel, cyclohexane/ethyl acetate/triethylamine; 80:20:1) yielded 1.44 g (81%) of the pure *meso*-phenyldipyrrometane (**1**). MS [m/z] 222.1 (M^+). Spectroscopy data agree with those previously reported.[10]

***meso*-(4-Methylphenyl)dipyrrometane (2).** A sample of 4-methybenzaldehyde (960 mg, 8 mmol) was processed as described for dipyrromethane (**1**), affording 1.55 g (82%) of the pure *meso*-(4-methylphenyl)dipyrrometane (**2**). MS [m/z] 236.1 (M^+). Spectroscopy data agree with those previously reported.[10,11]

***meso*-(4-Ethoxylphenyl)dipyrrometane (3).** A sample of 4-ethoxybenzaldehyde (1.20 g, 8 mmol) was processed as described for dipyrromethane (**1**), affording 1.79 g (84%) of the pure *meso*-(4-ethoxylphenyl)dipyrrometane (**3**). ^{1}HNMR ($CDCl_3$, TMS) δ 1.21 (t, 3H, J=7.2Hz); 4.01 (q, 2H, J=7.2Hz); 5.42 (s, 1H, *meso*-H); 5.90 (m, 2H, pyrrole-H); 6.16 (q, 2H, pyrrole-H); 6.70 (m, 2H, pyrrole-H); 6.90 (d, 2H, J=8.7Hz); 7.45 (d, 2H, J=8.7Hz); 7.90 (s, brs, 2H, pyrrole NH). MS [m/z] 266.1 (M^+). Anal. Calcd. for $C_{17}H_{18}N_2O_1$: C 76.66, H 6.81, N 10.52; found C 76.57 H 6.91, N 10.43.

***meso*-(4-Nitrophenyl)dipyrrometane (4).** A sample of 4-nitrobenzaldehyde (2.50 g, 16.6 mmol) and pyrrole (67.09 g, 1 mol) was processed as described for dipyrromethane (**1**), adding slowly $BF_3{\cdot}O(Et)_2$ (0.61 mL, 5 mmol) to yield 3.19 g (72%) of the pure *meso*-(4-nitrophenyl)dipyrrometane (**4**). ^{1}HNMR ($CDCl_3$, TMS) δ 5.58 (s, 1H, *meso*-H); 5.86 (m, 2H, pyrrole-H); 6.17 (q, 2H, pyrrole-H); 6.74 (m,

2H, pyrrole-H); 7.37 (d, 2H, J=9.0Hz); 8.01 (s, brs, 2H, pyrrole NH); 8.16 (d, 2H, J=9.0Hz). MS [m/z] 267.1 (M^+). Anal. Calcd. for $C_{15}H_{13}N_3O_2$: C 67.39, H 4.91, N 15.73; found C 67.29 H 4.97, N 15.62.

Synthesis of *meso*-substituted porphyrins

5-(4-Acetaminophenyl)-10,15,20-tris(phenyl) porphyrin (5). A solution of benzaldehyde (156 μL, 1.55 mmol), 4-acetamidobenzaldehyde (350 mg, 2.15 mmol) and *meso*-phenyldipyrrometane (**1**) (766 mg, 3.45 mmol) in 250 mL of chloroform was purged with argon for 15 min. Then $BF_3{\cdot}O(Et)_2$ (1.05 mmol, 0.42 mL of 2.5 M stock solution in chloroform) was added. The solution was stirred for 80 min at room temperature. Then, DDQ (510 mg, 2.25 mmol) was added and the mixture was stirred for an additional 1 h at room temperature. TLC analysis of the reaction mixture showed a mixture of three porphyrins with R_f 0.89, 0.47 (dichloromethane/methanol 3%) and 0.30 (dichloromethane/methanol 6%). The solvent was removed under reduced pressure and flash column chromatography (silica gel, dichloromethane/methanol 1%, gradient) give 156 mg (15%) of the pure desired porphyrin (**5**) as second moving band. UV-visible λ_{max} (dichloromethane) [nm] 418, 514, 550, 587 and 645. ^{1}HNMR ($CDCl_3$, TMS) δ - 2.78 (s, 2H, brs, pyrrole N-H); 7.22 (m, 9H, 10,15,20-Ar); 7.41 (d, 6H, J=7.8Hz, 10,15,20-Ar); 7.47 (brs, 1H, Ar-NHCO); 7.87 (d, 2H, J=8.0Hz, 5-Ar and 3-H, 5-H); 8.17 (d, 2H, J=8.0Hz, 5-Ar, 2-H and 6-H); 8.79-8.90 (m, 8H, pyrrole-H). MS [m/z] 671.3 (M^+). Anal. Calcd. for $C_{46}H_{33}N_5O_1$: C 82.24, H 4.95, N 10.42; found C 82.35, H 4.87, N 10.51.

5-(4-Acetaminophenyl)-10,15,20-tris(4-methylphenyl) porphyrin (6). A sample of 4-methylbenzaldehyde (186 mg, 1.55 mmol), 4-acetamidobenzaldehyde (350 mg, 2.15 mmol) and *meso*-(4-methylphenyl)dipyrrometane (**2**) (814 mg, 3.45 mmol) was processed as described for porphyrin (**5**). TLC analysis showed three porphyrins with R_f 0.87, 0.45 (dichloromethane/methanol 3%) and 0.28 (dichloromethane/methanol 6%). Flash chromatography yielded 177 mg (16%) of the pure selected porphyrin (**6**) as second moving band. MS [m/z] 713.3 (M^+). Porphyrin (**6**) was previously reported.[9]

5-(4-Acetaminophenyl)-10,15,20-tris(4-ethoxylphenyl) porphyrin (7). A sample of 4-ethoxylbenzaldehyde (300 mg, 2.0 mmol), 4-acetamidobenzaldehyde (407 mg, 2.5 mmol) and *meso*-(4-methylphenyl)dipyrrometane (**3**) (1.06 g, 4.0 mmol) was processed as described for porphyrin (**5**). TLC (CH_2Cl_2/CH_3OH 5%) analysis showed three porphyrins with R_f 0.91, 0.55 and 0.14. Flash chromatography afforded 273 mg (17%) of the pure selected porphyrin (**7**) as second moving band. UV-visible λ_{max} (dichloromethane) [nm] 418, 516, 552, 593 and 649. ^{1}HNMR ($CDCl_3$, TMS) δ -2.76 (s, 2H, brs, pyrrole N-H); 1.20 (t, 3H, J=7.2Hz); 2.34 (s, 3H, $-COCH_3$); 4.02 (q, 2H, J=7.2Hz); 7.27 (d, 6H, J=8.6Hz, 10,15,20-Ar 3-H and 5-H); 7.45 (brs, 1H, Ar-NHCO); 7.87 (d, 2H, J=8.0Hz, 5-Ar and 3-H, 5-H); 8.10 (d, 6H, J=8.6Hz, 10,15,20-Ar, 2-H and 6-H); 8.15 (d, 2H, J=8.0Hz, 5-Ar, 2-H and 6-H); 8.80-8.85 (m, 8H, pyrrole-H). MS [m/z] 803.3 (M^+). Anal. Calcd. for $C_{52}H_{45}N_5O_4$: C 77.69, H 5.64, N 8.71; found C 77.78, H 5.54, N 8.64.

Also, porphyrin (**7**) was synthesized by a modified Alder method.[5] Thus, a solution of 4-ethoxylbenzaldehyde (1.8 g, 12 mmol) and 4-

acetamidobenzaldehyde (652 mg, 4 mmol) in propionic acid (100 mL) was stirred at 90 °C. Then, 1.9 mL of pyrrole (27 mmol) was slowly added. The resulting mixture was allowed to reflux for one hour at which time it was poured into 400 mL of water (containing 16 g of NaCl). The precipitated material (green mass) was collected by vacuum filtration. The precipitate was dried under vacuum at 60 °C for 48 hours to remove propionic acid. The resulting material was dissolved in chloroform/methanol (5%) and filtered on short column of alumina. This procedure was repeated using silica gel. The solvents were removed under reduced pressure and treated with DDQ (908 mg, 4 mmol) in 200 mL of chloroform for 2 hours. The solvent was evaporated and the residual was pulverized to a fine powder. Slow chromatography column (silica gel, chloroform/methanol gradient) afforded 98 mg (3.0%) of the pure desired porphyrin (**7**) as second moving band.

5-(4-Acetaminophenyl)-10,15,20-tris(4-nitrophenyl) porphyrin (8). A solution of 4-nitrobenzaldehyde (188 mg, 1.25 mmol), 4-acetamidobenzaldehyde (302 mg, 1.85 mmol) and *meso*-(4-nitrophenyl)dipyrrometane (**8**) (760 mg, 2.85 mmol) was processed as described for porphyrin (**5**). TLC (dichloromethane/acetone 5%) analysis showed three porphyrins with R_f 0.84, 0.41 and 0.11. Flash chromatography (silica gel, dichloromethane/acetone 3%) give 161 mg (16%) of the pure desired porphyrin (**8**) as second moving band. UV-visible λ_{max} (dichloromethane) [nm] 426, 519, 557, 590 and 650. ^{1}HNMR ($CDCl_3$, TMS) δ -2.76 (s, 2H, brs, pyrrole N-H); 2.33 (s, 3h, $COCH_3$); 7.47 (brs, 1H, Ar-NHCO); 7.88 (d, 2H, J=8.1Hz, 5-Ar 3-H and 5-H); 8.16 (d, 2H, J=8.1Hz, 5-Ar 2-H and 6-

H); 8.39 (d, 6H, J=8.4Hz, 10,15,20-Ar 2-H and 6-H); 8.65 (d, 6H, J=8.4Hz, 10,15,20-Ar 3-H and 5-H); 8.75-8.80 (m, 6H, pyrrole-H); 9.01 (d, 2H, J=5.1 Hz, pyrrole-H). MS [m/z] 806.2 (M^+). Anal. Calcd. for $C_{46}H_{30}N_8O_7$: C 68.48, H 3.75, N 13.89; found C 68.55, H 3.67, N 13.94.

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