Phosphorus Pentachloride (PCl_5) Mediated Synthesis of Tetraarylporphyrins

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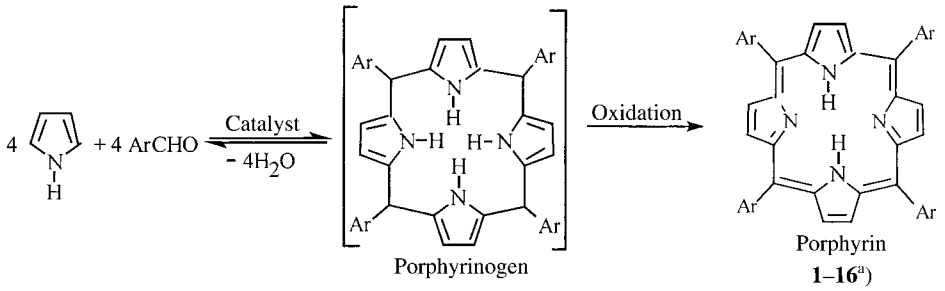
A new synthesis of porphyrins from pyrrole and substituted benzaldehydes is described, with PCl_5 as catalyst. Aromatic aldehydes condense irreversibly with pyrrole in the presence of this catalyst, and aerobic oxidation of porphyrinogen provides functionalized porphyrins in yields of 20–65%.

Introduction. – Porphyrins and their metal complexes have been the subject of many studies because of their potential application as selective catalysts [1–5], as photosensitisers [6], and in solar-energy conversion [7]. Over the past years, numerous advances in porphyrin synthetic methodology have been realized. These developments have advanced systematically through monopyrrole tetramerization [8–10], dipyrromethene self-condensation in organic acid metals [11], '2 + 2' *MacDonald* dipyrromethane syntheses [12], and '3 + 1' synthesis with a tripyrrane and a diformylpyrrole [13]. Most porphyrin syntheses proceed by tetramerization of monopyrrole. In the classical *Adler–Longo* porphyrin synthesis [9], a solution of aldehyde and pyrrole in a high-boiling acid solvent is refluxed in air so that condensation and oxidation occur simultaneously. This method gives low yields of sensitive porphyrins, reflecting rather vigorous conditions, and intractable purification problems arise for porphyrins, which do not readily crystallize or precipitate from the tar-laden propionic acid. *Lindsey et al.* [10] published results on studies of improved methods of some *meso*-tetraarylporphyrins and discussed a mechanistic interpretation of the reaction. Recent methods in the synthesis of tetraphenylporphyrins from tetramerization of monopyrrole include the use of an oxidizing cosolvent [14], *Lewis* acids [15], and various clays as catalysts [16]. In these methods, there are intrinsic disadvantages in the requirement for the expensive high-potential quinone oxidant and in elaborate, costly purification procedures needed to isolate the porphyrin, and/or high-thermal conditions, so that the reaction fails completely with benzaldehydes bearing substituents in *ortho* positions and sensitive functional groups.

In this paper, we report a method for preparing porphyrins under mild conditions at room temperature. Pyrrole and benzaldehyde in the presence of PCl_5 react to form tetraphenylporphyrin in one pot without the need of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) as oxidant. The reaction conditions were optimized for benzaldehyde. Under these reaction conditions, tetraarylporphyrins are formed in 20–65% yields.

Results and Discussion. – The success of the room-temperature porphyrin synthesis has relied in part on finding effective catalytic conditions for the pyrrole–aldehyde condensation. Porphyrins are known to be easily obtained by treatment of the precursor 'porphyrinogen' with oxidizing agents such as chloranil [10][15][16] or aerobic oxidation [9][17] (*Scheme 1*). Therefore, the preparation of porphyrinogen by the pyrrole–aldehyde condensation is the important step in this synthesis. To synthesize *meso*-tetraarylporphyrins efficiently, it is necessary to select the specific conditions for the generation of the corresponding porphyrinogen, followed by appropriate oxidation workup.

Scheme 1



a) For Ar, see *Table 2*.

Our efforts in this area have been largely directed toward the systematic investigation of best conditions for porphyrin synthesis. We have investigated the effects of numerous reaction parameters on the yield of tetraphenylporphyrin (**1**) obtained in a one-flask, room-temperature synthesis. Initially, a systematic study was undertaken with various catalysts, and it was found that PCl_5 showed excellent activity for the condensation of pyrrole and benzaldehyde for the preparation of **1** (*Table 1*). In a typical trial reaction, 0.2 equiv. of PCl_5 was added to a solution of benzaldehyde and pyrrole (1:1) in CH_2Cl_2 (10^{-2} M) under N_2 gas. After 1 h, the stoichiometric amount of DDQ (39°, 1 h) was then added to oxidize the porphyrinogen to porphyrin. The general workup involves concentration of the crude reaction mixture, followed by passing over a short chromatography column. The porphyrin product obtained in this manner is relatively pure.

The results from *Table 1* (*Entries 1–6*) show the influence of the nature of catalyst on porphyrin synthesis and clearly indicate that PCl_5 is the best catalyst for this condensation reaction. The reactions were carried out in $CHCl_2$, $CHCl_3$, MeCN, Et_2O, EtOH, THF, and benzene. As shown in *Entry 1*, CH_2Cl_2 is the best solvent for porphyrin synthesis under these reaction conditions.

Porphyrin (**1**) yields as a function of reactant concentration are shown in the *Figure*. The concentrations of benzaldehyde and pyrrole are critical determinants of the ultimate yield of porphyrin. The maximum yield of **1** is observed, when an equimolar amount of benzaldehyde and pyrrole concentrations of 10^{-2} M are used (*Fig.*) The yield declines markedly at concentrations 10-fold higher and 10-fold lower.

Table 1. *Reaction of Pyrrole* (10^{-2} M) and Benzaldehyde (10^{-2} M) in the Presence of Various Catalysts

Entry	Catalyst (equiv.)	Solvent	Time [h]	Yield [%] of **1**
1	PCl_5 (0.2)	CH_2Cl_2	2	56
2	$POCl_3$ (0.3)	CH_2Cl_2	3	38
3	PCl_3 (0.3)	CH_2Cl_2	4	trace
4	H_3PO_4 (0.2)	CH_2Cl_2	3	12
5	P_2O_5 (1.0)	CH_2Cl_2	4	10
6	PPA[a])	CH_2Cl_2	4	5
7	PCl_5 (0.2)	$CHCl_3$	2	50
8	PCl_5 (0.2)	MeCN	4	20
9	PCl_5 (0.2)	Et_2O	4	15
10	PCl_5 (0.2)	EtOH	4	trace
11	PCl_5 (0.2)	THF	4	5
12	PCl_5 (0.2)	Benzene	4	5

[a]) Poly(phosphoric acid) (0.2 g for 1 mmol of reactants).

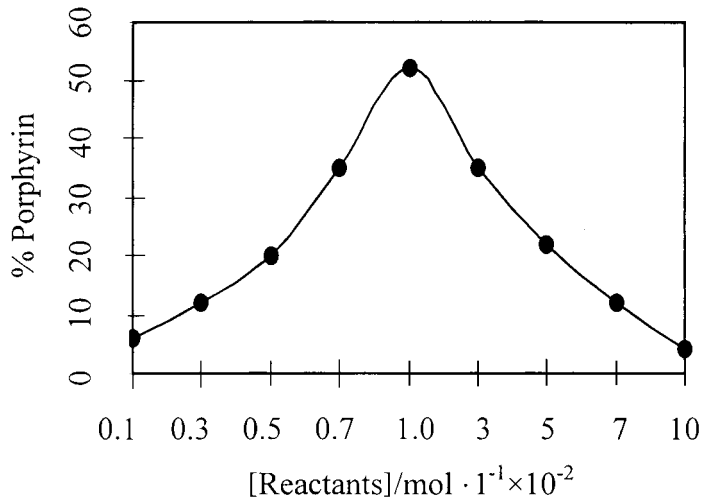


Figure. *Dependence of porphyrin formation on concentration of reactants*

A milder and slower oxidant gave the best results for porphyrinogen oxidation [14]. Molecular oxygen is the oxidant in the *Adler* [9] and *Drain* [17] reactions. However, the harsh reaction conditions result in complete failure with benzaldehydes bearing sensitive functional groups. The especially demanding conditions for the oxidation of the *meso*-tetraarylporphyrinogens led us to check their behavior in aerobic oxidations. We found that, when the reaction time extended to 6 h, porphyrinogen, under aerobic oxidation, was converted to porphyrin, and DDQ or *para*-chloranil was not required. This avoids the requirement for expensive highly potential quinones, and simplifies workup.

This synthetic procedure can be used for the synthesis of a large number of tetraarylporphyrins, with pyrrole and aryl aldehydes (*Table 2*). The results show that 5,10,15,20-tetraarylporphyrins can be prepared in good yield by this procedure. Both aldehydes containing electron-donating and electron-withdrawing substituents can be

Table 2. *Synthesis of* meso-*Tetraarylporphyrins from Pyrrole and Aryl Aldehydes in the Presence of PCl_5, at Room Temperature with Air as Oxidant*

Entry	Ar	Product	Raction time [h]	Yield [%]
1	Ph	**1**	5	56
2	4-MeC_6H_4	**2**	5	65
3	4-$MeOC_6H_4$	**3**	5	51
4	4-CNC_6H_4	**4**	5	50
5	4-BrC_6H_4	**5**	5	50
6	4-ClC_6H_4	**6**	5	48
7	4-(i-Pr)C_6H_4	**7**	5	57
8	4-$NO_2C_6H_4$	**8**	5.5	45
9	3-MeC_6H_4	**9**	5	50
10	3-$MeOC_6H_4$	**10**	5	38
11	3-ClC_6H_4	**11**	5	56
12	3-$NO_2C_6H_4$	**12**	6	30
13	2-MeC_6H_4	**13**	5	40
14	2-ClC_6H_4	**14**	5	37
15	2-$NO_2C_6H_4$	**15**	6	35
16	2,4,6-$Me_3C_6H_2$	**16**	6	18

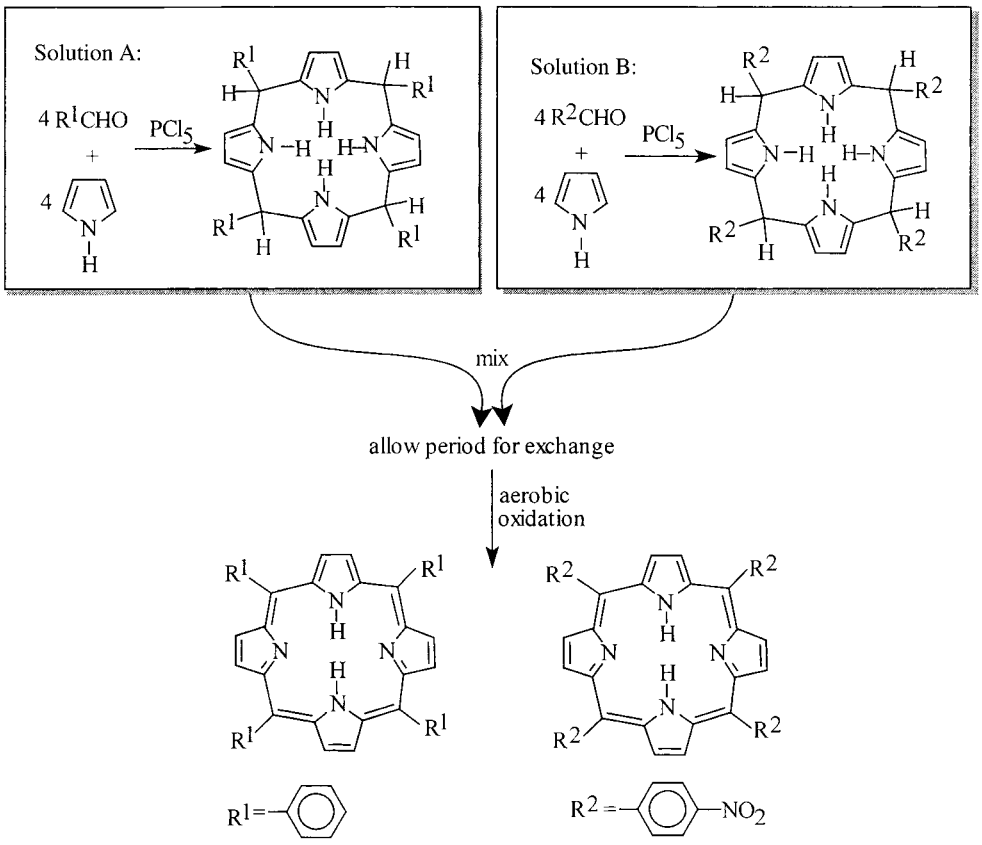
used under these reaction conditions. All reactions were run under standard conditions: 10^{-2} M aldehyde and 10^{-2} M pyrrole with 2×10^{-3} M PCl_5 in CH_2Cl_2. The yields given in *Table 2* reflect the ease with which pure material (one spot in TLC) could be obtained from a single chromatographic step. The porphyrins were identified by comparison with authentic samples prepared according to literature procedures [10][16][19].

Previous workers have demonstrated that porphyrinogen formation is a reversible process, when aryl aldehydes are condensed with pyrrole [10]. We examined the porphyrinogen exchange according to *Lindsey*'s procedure. Two pairs of aryl aldehydes were chosen, which reacted at similar rates and gave similar yields of porphyrin. Two aldehydes were condensed separately with pyrrole, and, when the porphyrinogen concentrations had reached a maximum (t_{max} 1 h), the solutions were mixed (*Scheme 2*). At a common time, 5 h after mixing, the distribution of products was analyzed. We only obtained two porphyrins, and scrambling was not detected.

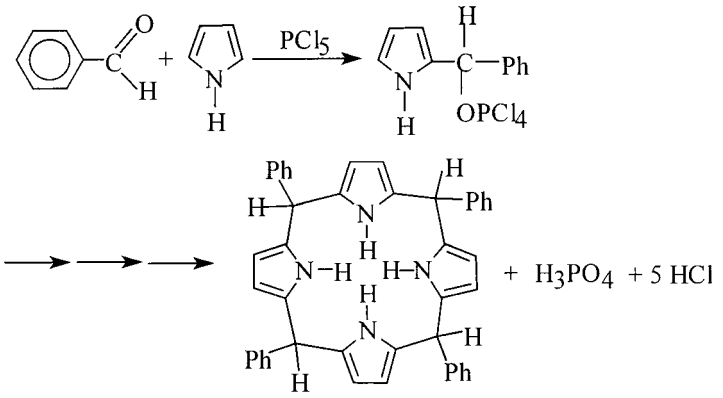
These results indicate that under these conditions the condensation of monomers and cyclization of tetrapyrrolic oligomers are irreversible. The proposed mechanism for irreversible condensation of pyrrole and aldehyde is shown in *Scheme 3*.

In conclusion, we first presented a survey of the effects of different catalysts in the reaction of pyrrole and benzaldehyde, focusing primarily on reactions at 0.01M. Second, we examined the effects of aerobic oxidation, solvent, and the reversibility of the pyrrole–aldehyde condensation under these conditions. Third, we reported the application of the best reaction conditions identified, for a variety of aldehydes. By this method, porphyrinogen, under aerobic oxidation, was converted to porphyrin, and this oxidation system avoids application of organic oxidants. This procedure currently allows the preparation of a large variety of porphyrins in good-to-excellent yields from the corresponding aldehydes. The advantages of our method are high yield of

Scheme 2



Scheme 3



porphyrins without need of man-made oxidant, ease of isolation and purification of the porphyrins obtained, and mild conditions for aldehydes bearing sensitive substituents.

Experimental Part

General. CH_2Cl_2 and $CHCl_3$ (*Merck*) were distilled from K_2CO_3. Pyrrole was distilled from CaH_2, and stored samples were rejected when discoloration occurred. Benzaldehyde was distilled under reduced pressure. Substituted benzaldehydes and other chemical materials were purchased from *Fluka* and *Merck* in high purity. Elemental analyses were performed at the *National Oil Co.* of Iran, Tehran Research Center.

General Procedure for Synthesis of meso-*Tetraarylporphyrins.* Standard reaction was performed in a 150-ml, three-necked, round-bottomed flask fitted with a septum port, a reflux condenser, and a gas-inlet port. The inlet port consisted of a glass disk immersed in the soln., with N_2 flow rates maintained at *ca.* 2 ml per min. The flask was charged with 100 ml of distilled benzaldehyde in CH_2Cl_2 (0.1 ml, 1 mmol, 10^{-2} M) and pyrrole (0.07 ml, 1 mmol, 10^{-2} M). The resulting soln. was magnetically stirred at r.t. After stirring the soln. for 10–15 min, an appropriate amount of PCl_5 (0.04 g, 0.2 mmol) was added. After 1 h, the yield of porphyrinogen was maximum. Then, the gas-inlet line was switched to filtered house air, and the mixture was aerated for 4 h (39°). During this time, the mixture became dark purple, and porphyrinogen under aerobic oxidation was converted to porphyrin. The soln. was concentrated by rotary evaporation and chromatographed (silica gel; CH_2Cl_2/petroleum ether 1:1) to give *tetraphenylporphyrin* (**1**) in 56% yield. M.p. >300°. UV (Benzene): λ_{max} 418 (478), 483 (3.4), 517 (18.8), 549 (8.1), 591 (5.3), 647 (3.4). ^{1}H-NMR ($CDCl_3$, 250 MHz): −2.76 (br. *s*, 2 NH); 7.73 (*m*, 12 arom. H), 8.21 (*d*, 8 H_o); 8.80 (*s*, 8 H (pyrrole)). ^{13}C-NMR ($CDCl_3$, 62.9 MHz) 120.5 (C(5), C(10), C(15), C(20)), 127.1; 128.1 (C(β) (pyrrole)); 134.9; 139.2; 142.6. Anal. calc. for $C_{44}H_{30}N_4$: C 85.90, H 4.92, N 9.12; found: C 85.72, H 5.1, N 8.93.

5,10,15,20-Tetrakis(4-methylphenyl)porphyrin (**2**): UV (Benzene): 422 (495), 488 (4.3), 518 (170), 560 (11.9), 595 (5.5), 655 (14.5). ^{1}H-NMR ($CDCl_3$, 250 MHz): −2.77 (br. *s*, 2 NH); 2.06 (*s*, 4 Me); 7.75 (*d*, 8 H_m), 8.11 (*d*, 8 H_o); 8.85 (*s*, 8 H (pyrrole)). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): 22.0; 120.2 (C(5), C(10), C(15), C(20)); 129.7; 137.3; 139.1; 141.4; 146.4. Anal. calc. for $C_{48}H_{38}N_4$: C 85.97, H 5.67, N 8.36; found: C 85.7, H 5.7, N 8.22.

5,10,15,20-Tetrakis(4-methoxyphenyl)porphyrin (**3**): UV (Benzene): 424 (485), 519 (17.0), 555 (11.9), 595 (5.5), 670 (23). ^{1}H-NMR ($CDCl_3$, 250 MHz): −2.77 (br. *s*, 2 NH); 4.2 (*s*, 4 MeO); 7.30 (*d*, 8 H_m); 8.11 (*d*, 8 H_o), 8.81 (*s*, 8 H (pyrrole)). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): 56.1; 119.9 (C(5), C(10), C(15), C(20)); 128.5; 133.6 (C(β) (pyrrole)); 134.9; 137.0; 140.4. Anal. calc. for $C_{48}H_{38}N_4O_4$: C 78.45, H 5.21, N 7.62; found: C 78.43, H 5.19, N 7.60.

5,10,15,20-Tetrakis(4-cyanophenyl)porphyrin (**4**): UV (Benzene): 419 (546), 515 (8.6), 545 (4.0), 590 (3.7), 650 (3.8). ^{1}H-NMR ($CDCl_3$, 250 MHz): −2.95 (br. *s*, 2 NH); 8.15 (*d*, 8 H_m); 8.28 (*d*, 8 H_o); 8.73 (*s*, 8 H (pyrrole)). Anal. calc. for $C_{48}H_{26}N_8$: C 80.66, H 3.66, N 15.68; found: C 80.42, H 3.71, N 15.47.

5,10,15,20-Tetrakis(4-bromophenyl)porphyrin (**5**): UV (Benzene): 421 (517), 518 (25), 550 (9.9), 591 (5.7), 649 (3.5) ^{1}H-NMR ($CDCl_3$, 250 MHz): −2.94 (br. *s*, 2 NH); 7.81 (*d*, 8 H_m); 8.01 (*d*, 8 H_o), 8.76 (*s*, 8 H (pyrrole)). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): 118.1 C(5), C(10), C(15), C(20)); 127.5; 131.6 (C(β) (pyrrole)); 133.9; 136.9; 139.9. Anal. calc. for $C_{44}H_{26}Br_4N_4$: C 56.80, H 2.81, N 6.02; found: C 56.75, H 2.78, N 6.11.

5,10,15,20-Tetrakis(4-chlorophenyl)porphyrin (**6**): UV (Benzene): 418 (515), 483 (2.0), 517 (21.0), 549 (9.0), 593 (6.0), 649 (4.0). ^{1}H-NMR ($CDCl_3$, 250 MHz): −2.81 (br. *s*, 2 NH); 7.79 (*d*, 8 H_m); 8.15 (*d*, 8 H_o); 8.87 (*s*, 8 H (pyrrole)). ^{13}C-NMR ($CDCl_3$, 62.9 MHz): 119.1 (C(5), C(10), C(15), C(20)); 127.2, 131.4 (C(β) (pyrrole)); 134.6; 137.7; 140.0. Anal. calc. for $C_{44}H_{26}Cl_4N_4$: C 70.23, H 3.48, N 7.44; found: C 70.2, H 3.6, N 7.45.

5,10,15,20-Tetrakis[4-(1-methylethyl)phenyl]porphyrin (**7**): UV (Benzene): 420 (521), 489 (2.1), 518 (17.0), 52 (11.1), 599 (9.0), 652 (21.1). ^{1}H-NMR ($CDCl_3$, 250 MHz): −2.74 (br. *s*, 2 NH); 1.4 (*d*, 8 Me); 3.2 (*m*, 4 CH); 7.55 (*d*, 8 H_m); 8.02 (*d*, 8 H_o); 8.83 (*s*, 8 H (pyrrole)). Anal. calc. for $C_{53}H_{48}N_4$: C 85.91, H 6.53, N 7.56; found: C 85.78, H 6.61, N 7.43.

5,10,15,20-Tetrakis(4-nitrophenyl)porphyrin (**8**): UV (Benzene): 422 (475), 480 (2.0), 517 (19.1), 548 (6.7), 590 (5.9), 650 (4.3), 676 (2.4). ^{1}H-NMR ($CDCl_3$, 250 MHz): 2.95 (br. *s*, 2 NH); 7.80 (*d*, 8 H_m); 8.30 (*d*, 8 H_o); 8.87 (*s*, 8 H (pyrrole)). Anal. calc. for $C_{44}H_{26}N_8O_4$: C 66.49, H 3.30, N 14.10; found: C 66.45, H 3.38, N 14.

5,10,15,20-Tetrakis(3-methylphenyl)porphyrin (**9**): UV (Benzene): 418 (523), 484 (2.1), 517 (16.1), 542 (8.0), 591 (6.2), 649 (7.8). ^{1}H-NMR ($CDCl_3$, 250 MHz): −2.73 (br. *s*, 2 NH); 2.6 (*s*, 4 Me); 7.28 (*t*, 4 H_m); 7.67 (*d*, 4 H_o, 4 H_p); 8.07 (*s*, 4 H_o); 8.88 (*s*, 8 H (pyrrole)). Anal. calc. for $C_{48}H_{38}N_4$: C 85.97, H 5.67, N 8.36; found: C 85.81, H 5.68, N 8.19.

5,10,15,20-Tetrakis(3-methoxyphenyl)porphyrin (**10**): UV (Benzene): 418 (543), 518 (12.3), 550 (9.0), 589 (8.1), 650 (7.9). ^{1}H-NMR ($CDCl_3$, 250 MHz): −2.79 (br. *s*, 2 NH); 3.97 (*s*, 4 MeO); 7.33–7.77 (*m*, 16 arom. H); 8.46 (*s*, 8 H (pyrrole)). Anal. calc. for $C_{48}H_{38}N_4O_4$: C 78.45, H 5.21, N 7.62; found: C 78.37, H 5.24, N 7.65.

5,10,15,20-Tetrakis(3-chlorophenyl)porphyrin (**11**): UV (Benzene): 418 (505), 518 (21), 550 (9.0), 588 (7.8), 650 (3.2). ^{1}H-NMR ($CDCl_3$, 250 MHz): −2.96 (br. *s*, 2 NH); 7.40–7.82 (*m*, 12 arom. H); 8.11 (*s*, 4 H_o); 8.78 (*s*, 8 H (pyrrole)). Anal. calc. for $C_{44}H_{26}Cl_4N_4$: C 70.23, H 3.48, N 7.44; found: C 70.31, H 3.49, N 7.36.

5,10,15,20-Tetrakis(3-nitrophenyl)porphyrin (**12**): UV (Benzene): 418 (530), 480 (1.2), 515 (21.2), 550 (11.0), 591 (10.4), 646 (4.3). ^{1}H-NMR ($CDCl_3$, 250 MHz): −2.96 (br. *s*, 2 NH); 8.13–8.70 (*m*, 16 arom. H); 8.93 (*s*, 8 H (pyrrole)). Anal. calc. for $C_{44}H_{26}N_8O_4$: C 66.49, H 3.30, N 14.10; found: C 66.38, H 3.27, N 14.22.

5,10,15,20-Tetrakis(2-methylphenyl)porphyrin (**13**). UV (Benzene): 418 (5567), 514 (13.2), 545 (4.6), 591 (9.7), 646 (3.2). ^{1}H-NMR ($CDCl_3$, 250 MHz): −2.62 (br. *s*, 2 NH); 2.04 (*s*, 4 Me); 7.50–8.70 (*m*, 16 arom. H); 8.65 (*s*, 8 H (pyrrole)). Anal. calc. for $C_{48}H_{38}N_4$: C 85.97, H 5.67, N 8.36; found: C 85.92, H 5.58, N 8.23.

5,10,15,20-Tetrakis(2-chlorophenyl)porphyrin (**14**): UV (Benzene): 418 (580), 482 (2.0), 515 (12.1), 550 (4.2), 590 (7.8), 643 (1.2). ^{1}H-NMR ($CDCl_3$, 250 MHz): −2.74 (br. *s*, 2 NH), 7.55–8.01 (*m*, 16 arom. H); 8.61 (*s*, 8 H (pyrrole)). Anal. calc. for $C_{44}H_{26}Cl_4N_4$: C 70.23, H 3.48, N 7.44; found: C 70.34, H 3.38, N 7.51.

5,10,15,20-Tetrakis(2-nitrophenyl)porphyrin (**15**): UV (Benzene): 422 (529), 518 (9.7), 550 (7.1), 588 (4.6), 650 (2.3). ^{1}H-NMR ($CDCl_3$, 250 MHz): 2.95 (br. *s*, 2 NH); 7.54–8.27 (*m*, 16 arom. H); 8.64 (*s*, 8 H (pyrrole)). Anal. calc. for $C_{44}H_{26}N_8O_4$: C 66.49, H 3.30, N 14.10; found: C 66.53, H 3.41, N 14.06.

5,10,15,20-Tetrakis(2,4,6-trimethylphenyl)porphyrin (**16**): UV (Benzene): 418 (5.57), 480 (2.95), 514 (4.18), 547 (3.59), 590 (3.69), 647 (3.48), 650 (5.0). ^{1}H-NMR ($CDCl_3$, 250 MHz): −2.57 (br. *s*, 2 NH); 1.77 (*s*, 8 *o*-Me); 2.53 (4 *p*-Me); 7.18 (*s*, 4 H_m); 8.5 (*s*, 8 H (pyrrole)). Anal. calc. for $C_{56}H_{54}N_4$: C 85.90, H 7.00, N 7.20; found: C 85.82, H 7.15, N 7.3.

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