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Novel synthesis of *meso*-tetraarylporphyrins using CF_3SO_2Cl under aerobic oxidation

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Abstract—*meso*-Tetraarylporphyrins are synthesized from pyrrole and aryl aldehydes cleanly and efficiently in one pot at room temperature using equimolar amount of CF_3SO_2Cl in the presence of air as oxidant. By this novel method 5,10,15,20-tetraarylporphyrins can be prepared in excellent yields.

1. Introduction

The continuing progress in porphyrin chemistry in recent years has caused a growing interest for such compounds. The remarkably diverse photo-electro- and bio-chemical properties of the porphyrins continue to attract the attention of researchers even after well over a hundred years. Porphyrin research has gone from Hans Fischer's pioneering synthesis of hemin in the 1920s,[1] to their use as selective catalysts,[2–5] molecular electronic devices,[6] photodynamic therapy agents[7] and applications to materials chemistry.[8] Advances in porphyrin model systems are closely tied to methods for preparing synthetic porphyrins.

Over the past years, numerous advances in porphyrin synthetic methodology have been realized. These developments have advanced systematically through monopyrrole tetramerization,[9–13] dipyrromethene self-condensation in organic acid metals,[14] '2+2' *MacDonald* dipyrromethane syntheses[15] and '3+1' synthesis with a tripyrrane and a diformylpyrrole.[16] Most porphyrin syntheses proceed by tetramerization of monopyrrole. Tetraphenylporphyrin was first synthesized by *Rothemund*,[9] then *Adler-Longo* proposed a simplified synthesis for *meso*-tetraphenylporphyrin.[10] In this method a solution of aldehyde and pyrrole in a high-boiling acid solvent is heated at reflux 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 and a high percentage of tarry by-products are also formed.

Lindsey et al.[11] 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 mono pyrrole include the use of an oxidizing cosolvent,[17] Lewis acids,[18] and various clays as catalysts.[19] 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 CF_3SO_2Cl 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 25–67% yields.

2. Result and discussion

The conversion of aldehydes and pyrroles to porphyrins is a multi-step process involving condensation (polymerization and cyclization) followed in timed sequence by oxidation. Porphyrins are known to be easily obtained by treatment of the precursor 'porphyrinogen' with oxidizing agents such as chloranil[11,18,19] or aerobic oxidation[10,20] (Scheme 1). The existence of this intermediate has been shown by *Dolphin*,[21] who isolated β-octamethyl-*meso*-tetraphenylporphyrinogen under *Adler-Longo* conditions.

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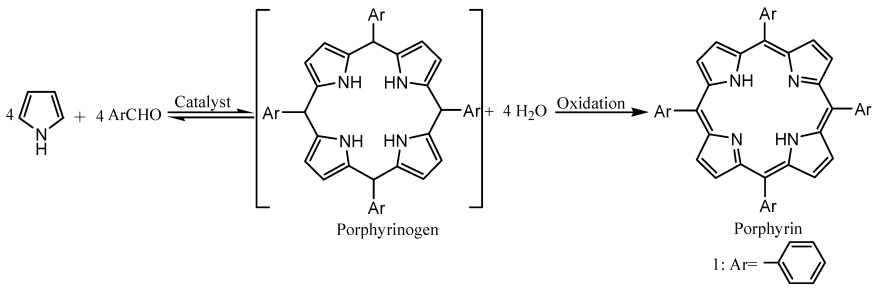


Scheme 1. For Ar, see Table 2.

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 oxidative workup.

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 CF_3SO_2Cl showed excellent activity for the condensation of pyrrole and benzaldehyde for the preparation of **1** (Table 1). In a typical trial reaction, 1 equiv. of CF_3SO_2Cl 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 °C, 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.

Table 1. Reaction of pyrrole (10^{-2} M) and benzaldehyde (10^{-2} M) in the presence of 1 equiv. of various catalysts, at room temperature with DDQ as oxidant

Entry	Catalyst	Solvent	Time (h)	Yield (%) of **1**
1	—	CH_2Cl_2	6	0
2	Al_2O_3 (pH=7)[a]	CH_2Cl_2	3	5
3	Al_2O_3 (pH=4.5)[a]	CH_2Cl_2	3	12
4	CH_3SO_3H	CH_2Cl_2	3	10
5	Al_2O_3/CH_3SO_3H[b]	CH_2Cl_2	3	11
6	$MgSO_4$	CH_2Cl_2	4	9
7	CsCl	CH_2Cl_2	4	5
8	$Al(O_2CCH_3)_3$	CH_2Cl_2	3	8
9	$Al(O_2CCF_3)_3$	CH_2Cl_2	3	18
10	$AlCl_3$	CH_2Cl_2	3	20
11	$CaCl_2$	CH_2Cl_2	4	15
12	CaO	CH_2Cl_2	4	13
13	MgO	CH_2Cl_2	4	11
14	$(CF_3CO)_2O$	CH_2Cl_2	4	19
15	TsCl	CH_2Cl_2	3	25
16	$SOCl_2$	CH_2Cl_2	3	22
17	CH_3SO_2Cl	CH_2Cl_2	2.5	49
18	CF_3SO_2Cl	CH_2Cl_2	2	62
19	CF_3SO_2Cl	$CHCl_3$	3	58
20	CF_3SO_2Cl	CH_3CN	4	18
21	CF_3SO_2Cl	THF	5	7
22	CF_3SO_2Cl	CH_3COCH_3	5	Trace
23	CF_3SO_2Cl	C_6H_6	4	30
24	CF_3SO_2Cl	Et_2O	4	23

[a] 1 g for 1 mmol of reactants.
[b] Three drops of CH_3SO_3H was added to 1 g of Al_2O_3 for 1 mmol of reactants.

The results from Table 1 (entries 2–18) show the influence of the nature of catalyst on porphyrin synthesis and clearly indicate that CF_3SO_2Cl is the best catalyst for this condensation reaction. Several metal salts have been used as catalyst but metal insertion does not occur under these reaction conditions (Table 1 entries 6–11). The reactions were carried out in CH_2Cl_2, $CHCl_3$, CH_3CN, THF, CH_3COCH_3, C_6H_6 and Et_2O. As shown in Table 1 (entry 18), 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 Figure 1. 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. 1). The yield declines markedly at concentrations 10-fold higher and 10-fold lower. This relies on the fact that pyrrole and benzaldehyde under acid catalysis will stabilise a balance with tetraphenylporphyrinogen. The dilution conditions are important to optimize formation of the porphyrinogen at the expense of open chain polypyrrylmethanes.

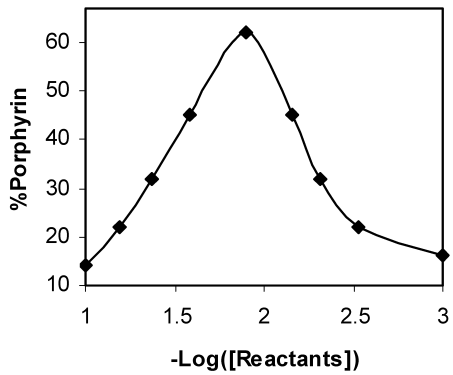


Figure 1. Dependence of porphyrin formation on concentration of reactants.

A milder and slower oxidant gave the best results for porphyrinogen oxidation.[17] Molecular oxygen is the oxidant in the *Adler*[10] and *Drain*[20] reactions. The specially 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 4 h, porphyrinogen, under aerobic oxidation, was converted to porphyrin, and DDQ or *para*-chloranil was

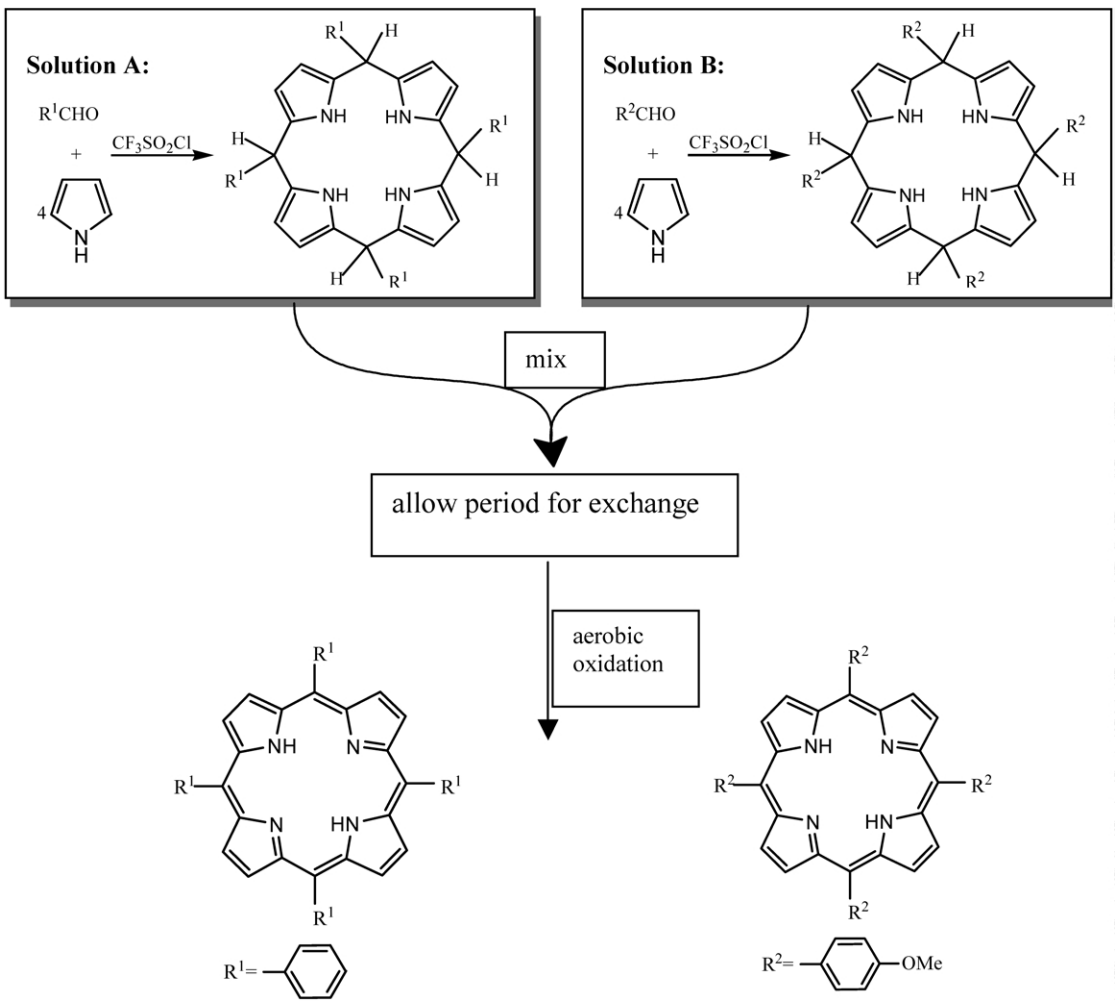
Table 2. Synthesis of *meso*-tetraarylporphyrins from pyrrole and aryl aldehydes in the presence of CF_3SO_2Cl, at room temperature with air as oxidant

Entry	Ar	Product	Reaction time (h)	Yield (%)
1	Ph	**1**	3	62
2	*p*-MeC_6H_4	**2**	3	60
3	*p*-$MeOC_6H_4$	**3**	3	67
4	*p*-ClC_6H_4	**4**	3	56
5	*p*-BrC_6H_4	**5**	3	64
6	*p*-CNC_6H_4	**6**	3.5	40
7	*p*-$NO_2C_6H_4$	**7**	4	34
8	*p*-IsopropylC_6H_4	**8**	3	60
9	*m*-MeC_6H_4	**9**	3	57
10	*m*-$MeOC_6H_4$	**10**	3	40
11	*m*-ClC_6H_4	**11**	3.5	41
12	*m*-$NO_2C_6H_4$	**12**	4	40
13	*o*-MeC_6H_4	**13**	3	40
14	*o*-ClC_6H_4	**14**	3	35
15	*o*-$NO_2C_6H_4$	**15**	4	27
16	Mesityl	**16**	4	25

not required. This avoids the requirement for expensive quinones, and simplifies workup.

In an effort to evaluate the range of applicability of our method, we also examined some other benzaldehydes having a wide variety of *ortho*, *meta* and *para* substituted, both electron-donating and withdrawing. The reaction conditions for benzaldehyde were applied to a set of sixteen aldehydes (Table 2). This synthetic procedure can be used for the synthesis of a large number of tetraarylporphyrins, with pyrrole and aryl aldehydes. Sterically hindered aldehydes such as 2,4,6-trimethylbenzaldehyde and 2-nitrobenzaldehyde can also be employed in the reaction (Table 2, entries 15, 16). A comparison of the reaction of aldehydes with pyrrole in the presence of CF_3SO_2Cl indicates that an increase in steric hindrance and the presence of electron withdrawing groups at the benzaldehyde results in a general decrease in the yield of porphyrin formation (for example, compare Table 2, entry *1* with entry *15*). All reactions were run under standard conditions: 10^{-2} M aldehyde and 10^{-2} M pyrrole with equimolar amount of CF_3SO_2Cl 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.[11,12,19,20,22–24] The advantage of this method is that it allows the formation of porphyrins from sensitive aldehydes, in higher yields, with more facile purification.

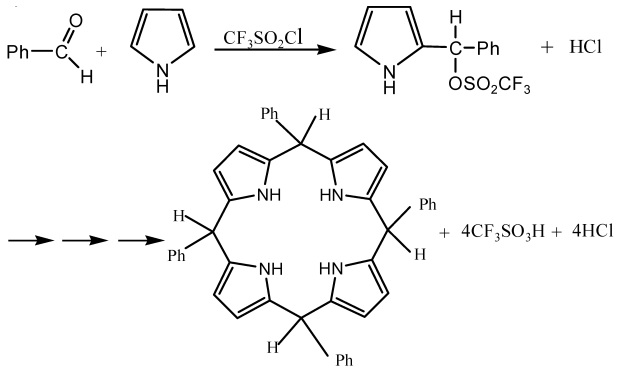
Previous workers have demonstrated that porphyrinogen formation is a reversible process, when aryl aldehydes are



Scheme 2. Porphyrinogen exchange experiment.

condensed with pyrrole.[11,22] We examined the porphyrinogen exchange according to Lindsey's procedure.[11b] The procedure is illustrated for one pair of aldehydes, benzaldehyde and *p*-methoxybenzaldehyde (two pairs of aryl aldehydes which reacted at similar rates and gave similar yields of porphyrin). Two solutions (**A** and **B**) were prepared and two aldehydes were condensed separately with pyrrole by addition of CF_3SO_2Cl under N_2 gas. 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.

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



Scheme 3.

In this paper, we first present a survey of the effects of different catalysts in the reaction of pyrrole and benzaldehyde, focusing primarily on reactions at 0.01 M. Second, we examined the effects of solvent, reactant concentration, aerobic oxidation, 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 porphyrins without need of man-made oxidant, ease of isolation and purification of the porphyrins obtained, and mild conditions for aldehydes bearing sensitive substituents.

3. Experimental

Dichloromethane and chloroform (Merck) were distilled from K_2CO_3. Pyrrole was distilled from calcium hydride, and stored samples were rejected when discoloration occurred. Benzaldehyde was distilled under reduced pressure. Substituted benzaldehydes and other chemical materials obtained from commercial sources (Aldrich, Fluka) were used as received. Elemental analyses were performed at the National Oil Co. of Iran, Tehran Research Center. IR spectra were recorded on Perkin–Elmer spectrometer. Proton NMR spectra were recorded on a Bruker Advance DPX FT 250 MHz instrument. UV/Vis. Spectra was obtained with an Ultrospec 3000 UV/Visible spectrometer.

3.1. General procedure for synthesis of *meso*-tetraarylporphyrins

A 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 solution, with nitrogen flow rates maintained at about 2 ml per min. The flask was charged with 100 ml of distilled CH_2Cl_2, benzaldehyde (0.1 ml, 1 mmol, 10^{-2} M), and pyrrole (0.07 ml, 1 mmol, 10^{-2} M). The resulting solution was magnetically stirred at room temperature. After stirring the solution for 5–10 min, an appropriate amount of CF_3SO_2Cl (0.1 ml, 1 mmol) was added via syringe. 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 °C). During this time, the mixture became dark purple, and porphyrinogen under aerobic oxidation was converted to porphyrin. The solution was concentrated by rotary evaporation and chromatographed (silica gel; with CH_2Cl_2/petroleum ether 1:1) to give **1** in 62% yield.

3.1.1. 5,10,15,20-Tetraphenylporphyrin (1). Purple crystal; mp >300 °C; yield=62%; [Found: C, 85.72; H, 5.01; N, 8.93. $C_{44}H_{30}N_4$ requires C, 85.90; H, 4.92; N, 9.12%]; λ_{max} (benzene; log ε): 418 nm (5.68), 483 (3.53), 517 (4.27), 549 (3.91), 591 (3.72), 647 (3.57). δ_H (250 MHz, $CDCl_3$): −2.76 (br. *s* 2NH); 7.73 (*m*, 12 arom. H); 8.21 (*d*, 8H_o); 8.80 (*s*, 8H (pyrrole)). δ_C (62.9 MHz; $CDCl_3$) 120.5 (C(5), C(10), C(15), C(20)), 127.1, 128.1 (C(β) (pyrrole)); 134.9, 139.2, 142.6.

3.1.2. 5,10,15,20-Tetrakis(*p*-methylphenyl)porphyrin (2). Purple crystal; mp >300 °C; yield=60%; spectroscopic data identical to that reported in the literature.[19b]

3.1.3. 5,10,15,20-Tetrakis(*p*-methoxyphenyl)porphyrin (3). Purple crystal; mp >300 °C; yield=67%; spectroscopic data identical to that reported in the literature.[12]

3.1.4. 5,10,15,20-Tetrakis(*p*-chlorophenyl)porphyrin (4). Purple crystal; mp >300 °C; yield=56%; spectroscopic data identical to that reported in the literature.[19b]

3.1.5. 5,10,15,20-Tetrakis(*p*-bromophenyl)porphyrin (5). Purple crystal; mp >300 °C; yield=64%; [Found: C, 56.75; H, 2.78; N, 6.11. $C_{44}H_{26}Br_4N_4$ requires C, 56.80; H 2.81; N, 6.02%]; λ_{max} (benzene; log ε): 421 nm (5.71), 518 (4.40), 550 (3.99), 591 (3.76), 649 (3.54). δ_H (250 MHz, $CDCl_3$): −2.94 (br. *s* 2NH); 7.81 (*d*, 8H_m); 8.01 (*d*, 8H_o); 8.76 (*s*, 8H (pyrrole)). δ_C (62.9 MHz; $CDCl_3$): 118.1 (C(5), C(10), C(15), C(20)); 127.5, 131.6 (C(β) (pyrrole)); 133.9, 136.9, 139.9.

3.1.6. 5,10,15,20-Tetrakis(*p*-cyanophenyl)porphyrin (6). Purple crystal; mp >300 °C; yield=40%; spectroscopic data identical to that reported in the literature.[11b]

3.1.7. 5,10,15,20-Tetrakis(*p*-nitrophenyl)porphyrin (7). Purple crystal; mp >300 °C; yield=34%; spectroscopic data identical to that reported in the literature.[23]

3.1.8. 5,10,15,20-Tetrakis(*p*-isopropylphenyl)porphyrin (8). Purple crystal; mp >300 °C; yield=60%; [Found: C, 85.78; H, 6.61; N, 7.43. $C_{56}H_{54}N_4$ requires C, 85.93; H, 6.90; N, 7.16%]; λ_{max} (benzene; log ε): 420 nm (5.72), 489 (3.32), 518 (4.23), 520 (4.04), 599 (3.95), 652 (4.32). δ_H (250 MHz, $CDCl_3$): −2.74 (br. *s* 2NH); 1.40 (*d*, 24H, *J*=4.4 Hz, 8Me); 3.2 (*m*, 4CH); 7.55 (*d*, $8H_m$); 8.02 (*d*, $8H_o$); 8.83 (*s*, 8H (pyrrole)).

3.1.9. 5,10,15,20-Tetrakis(*m*-methylphenyl)porphyrin (9). Purple crystal; mp >300 °C; yield=57%; spectroscopic data identical to that reported in the literature.[23]

3.1.10. 5,10,15,20-Tetrakis(*m*-methoxyphenyl)porphyrin (10). Purple crystal; mp >300 °C; yield=40%; [Found: C, 78.37; H, 5.24; N, 7.65. $C_{48}H_{38}N_4O_4$ requires C, 78.45; H, 5.21; N, 7.62%]; λ_{max} (benzene; log ε): 418 (5.73), 518 (4.09), 550 (3.95), 589 (3.91), 650 (3.90). δ_H (250 MHz, $CDCl_3$): −2.79 (br. *s* 2NH); 3.97 (s, 12H, 4MeO); 7.33–7.77 (*m*, 16 arm. H); 8.46 (*s*, 8H (pyrrole)).

3.1.11. 5,10,15,20-Tetrakis(*m*-chlorophenyl)porphyrin (11). Purple crystal; mp >300 °C; yield=41%; spectroscopic data identical to that reported in the literature.[12]

3.1.12. 5,10,15,20-Tetrakis(*m*-nitrophenyl)porphyrin (12). Purple crystal; mp >300 °C; yield=40%; [Found: C, 66.38; H, 3.27; N, 14.22. $C_{44}H_{26}N_8O_8$ requires C, 66.50; H, 3.27; N, 14.10%]; λ_{max} (benzene; log ε): 418 nm (5.72), 480 (3.08), 515 (4.33), 550 (4.04), 591 (4.02), 646 (3.63). δ_H (250 MHz, $CDCl_3$): −2.96 (br. *s* 2NH); 8.13–8.70 (*m*, 16 arom. H); 8.93 (*s*, 8H (pyrrole)).

3.1.13. 5,10,15,20-Tetrakis(*o*-methylphenyl)porphyrin (13). Purple crystal; mp >300 °C; yield=40%; spectroscopic data identical to that reported in the literature.[19b]

3.1.14. 5,10,15,20-Tetrakis(*o*-chlorophenyl)porphyrin (14). Purple crystal; mp >300 °C; yield=35%; spectroscopic data identical to that reported in the literature.[19b]

3.1.15. 5,10,15,20-Tetrakis(*o*-nitrophenyl)porphyrin (15). Purple crystal; mp >300 °C; yield=27%; [Found: C, 66.53; H, 3.41; N, 14.06. $C_{44}H_{26}N_8O_8$ requires C, 66.50; H, 3.27; N, 14.10%]; λ_{max} (benzene; log ε): 422 nm (5.72), 518 (3.99), 550 (3.85), 588 (3.66), 650 (3.36). δ_H (250 MHz, $CDCl_3$): −2.95 (br. *s* 2NH); 7.54–8.27 (*m*, 16 arom. H); 8.64 (*s*, 8H (pyrrole)).

3.1.16. 5,10,15,20-Tetramesitylporphyrin (16). Purple crystal; mp >300 °C; yield=25%; spectroscopic data identical to that reported in the literature.[11c]

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