Efficient Synthesis of 5,10,15-Triarylcorroles using Amberlyst 15 Under Solvent-Free Conditions

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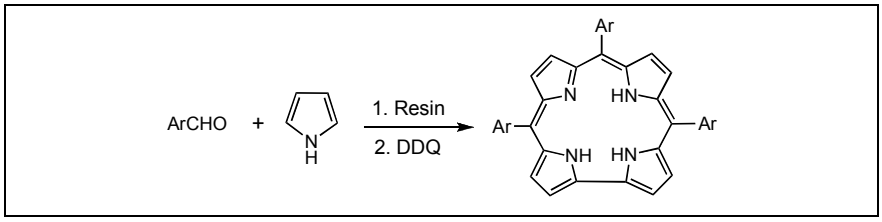

An efficient and convenient synthesis of 5,10,15-triarylcorroles by the condensation of aryl aldehydes with pyrrole catalyzed by Amberlyst 15 followed by oxidative cyclization with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) at room temperature has been reported. Amberlyst 15 is more efficient catalyst under solvent free conditions and DDQ is more suitable oxidant in dichloromethane than those of other catalysts and oxidants, respectively, for the synthesis of corroles at room temperature.

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INTRODUCTION

Corroles are tetrapyrrolic macrocyclic analogues of porphyrins which contain 18-π electrons aromatic core with a direct link between two pyrrole rings similar to vitamin B_{12} [1]. Corroles are attractive systems due to their distinct applications in catalysis [2,3], sensors [4], photodyanamic therapy [5], coordination chemistry [6], photophysics [7] and electrochemistry [8]. Many practical methods have been developed for the synthesis of 5,10,15-triarylcorroles which generally employ corrosive acids such as hydrochloric acid [9], acetic acid [10,11] and trifluoroacetic acid [12] for the condensation of aldehydes with pyrrole. Moreover, the above methods lead to formation of many by-products and the separation and purification of corroles is the most tedious problem. Thus, the search for more mild and efficient methods to synthesize corroles has become more enviable.

Owing to present environmental awareness, attempts are being made towards the evolution of environmentally benign processes. Recently, Amberlyst 15, a macro-reticular sulfonic acid based polystyrene cation exchange resin, has been used as a mild and excellent acidic catalyst in a number of organic reactions such as carbonyl regeneration [13], esterification of carboxylic acids [14], alkylation of phenol [15], oligomerization of isobutene, [16] etherification [17] and in the synthesis of porphyrins [18]. We have also reported the green synthesis of 5,10,15,20-tetraarylporphyrins using clay [19] and under microwave condition [20]. In continuation of our ongoing research into the application and synthesis of porphyrins [19-21], herein we report an efficient and simple synthesis of 5,10,15-triarylcorroles, tetraarylporphyrin analogues, using Amberlyst 15 as a catalyst in solvent-free condensation of aromatic aldehydes with pyrrole followed by oxidative macrocyclization with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) at room temperature under different reaction conditions.

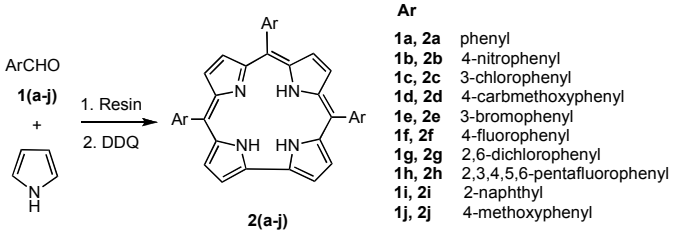
RESULTS AND DISCUSSION

The condensation reaction of benzaldehyde (**1a**) with pyrrole at 1:1 **1a**/pyrrole molar ratio catalyzed by Amberlyst 15 and subsequent oxidation with DDQ (1 equiv. *vs* **1a**) gave 5,10,15-triphenylcorrole (**2a**) in 4% yield (Scheme 1, Table 1, entry 1). The formation of **2a** in the reaction was confirmed by different spectroscopic analysis. The UV-visible spectrum of **2a**, similar to porphyrins showed a Soret-like band at 414 nm and three broad Q-bands in 570-650 nm regions. In IR spectrum of **2a**, a band at 3421 cm^{-1} was assigned to NH stretching and the appearance of a broad peak at -2.90 ppm in ^1H NMR spectrum indicated the presence of highly shielded internal NH protons in aromatic macrocycle of **2a**. Unlike porphyrins, the β-pyrrolic protons resonances appeared in a broader range from 8.83 ppm to 8.50 ppm due to its reduced symmetry from D_{4h} in the case of the unsubstituted porphyrins to C_{2v} for the corroles (assuming N-H tautomerism is fast). Further, ESI-MS spectrum of **2a** showed a peak at m/z 527.52 corresponding to $[M+H]^+$, supporting the formation of **2a** in the reaction.

The influence of aldehyde/pyrrole molar ratio on the yield of corroles was investigated under different reaction conditions (Table 1). It was observed that a change in **1a**/pyrrole molar ratio from 1:1 to 1:2 improved the yield of **2a** to 15%, but the yield significantly decreased to 9% on further increasing **1a**/pyrrole ratio to 1:3 (Table 1, entries 2 and 3). Similarly, the reaction of **1b** at 1:1

1b/pyrrole ratio gave **2b** in poor yield (5%) and the best yield of **2b** was obtained at 1:2 **1b**/pyrrole molar ratio (Table 1, entries 4-6). The reactions of other aldehydes with pyrrole at different **1**/pyrrole ratio are given in Table 1.

Scheme 1



Ar	
1a, 2a	phenyl
1b, 2b	4-nitrophenyl
1c, 2c	3-chlorophenyl
1d, 2d	4-carbmethoxyphenyl
1e, 2e	3-bromophenyl
1f, 2f	4-fluorophenyl
1g, 2g	2,6-dichlorophenyl
1h, 2h	2,3,4,5,6-pentafluorophenyl
1i, 2i	2-naphthyl
1j, 2j	4-methoxyphenyl

Table 1

Synthesis of corroles (**2a-2j**) by the reaction of aldehyde with pyrrole catalyzed by Amberlyst 15 followed by oxidation with DDQ

Entry	Ald.	Corrole	1/pyrrole	Oxidant[a] (equiv *vs.* 1)	% Yield of 2[b]
1	1a	2a	**1:1**	**1**	**4**
2	1a	2a	**1:2**	**1**	**15**
3	1a	2a	**1:3**	**1**	**9**
4	1b	2b	**1:1**	**1**	**5**
5	1b	2b	**1:2**	**1**	**27**
6	1b	2b	**1:3**	**1**	**21**
7	1b	2b	**1:2**	**0.5**	**19**
8	1c	2c	**1:2**	**0.5**	**16**
9	1c	2c	**1:2**	**1**	**22**
10	1c	2c	**1:2**	**2**	**0**
11	1c	2c	**1:2**	**0.5**[c]	**21**
12	1c	2c	**1:2**	**2**[d]	**trace**
13	1c	2c	**1:2**	**2**[e]	**0**
14	1c	2c	**1:2**	**1**	**21**[f]
15	1c	2c	**1:2**	**1**	**0**[g]
16	1d	2d	**1:2**	**1**	**3**
17	1d	2d	**1:2**	**1**	**13**[h]
18	1e	2e	**1:2**	**1**	**19**
19	1f	2f	**1:2**	**1**	**25**
20	1g	2g	**1:2**	**0.5**	**12**
21	1h	2h	**1:1**	**0.5**	**23**
22	1h	2h	**1:2**	**1**	**30**
23	1i	2i	**1:2**	**0.5**	**12**
24	1j	2j	**1:2**	**1**	**13**
25	1j	2j	**1:3**	**1**	**8**

[a] Oxidant used: DDQ. Time for second step: 15 min; [b] Isolated yields. [c] Oxidant used: Chloranil. Time for second step: 12 hr; [d] Oxidant used: $FeCl_3$. Time for second step: 15 min; [e] Oxidant used: $K_3[Fe(CN)_6]$. Time for second step: 24 hr; [f] Dilution with CH_2Cl_2 (20 equiv *vs* **1**) in condensation step; [g] Dilution with CH_2Cl_2 (300 equiv *vs* **1**) in condensation step;[h] In the presence of 10 equiv NH_4Cl in oxidation step.

To understand the course of reaction and confirm the intermediate involved in the formation of corrole, the reaction of **1d** with pyrrole (1:2 ratio) catalyzed by Amberlyst 15 was quenched with aqueous sodium hydroxide solution before DDQ addition and 5-(4-carbomethoxyphenyl)dipyrromethane (**3d**), 5,10-bis(4-carbomethoxyphenyl)tripyrrane (**4d**) and 5,10,15-tris(4-carbomethoxyphenyl)tetrapyrrane (**5d**) were isolated in 16%, 12% and 14% yields, respectively [22]. Their structures were identified by different spectroscopic data that concur with published data [23]. The intermediate **5d** was cyclized to **2d** by oxidation with DDQ as reported in literature [24]. It justifies the involvement of tetrapyrrane (bilane) intermediate in the synthesis of corrole using Amberlyst 15 under solvent-free condition. Further, the reaction of **1d** at 1:10 **1d**/pyrrole ratio afforded **5d** in only 2% yield and **3d** and **4d** were isolated in 36% and 7% yields, respectively. Thereby, optimal formation of corroles using Amberlyst 15 could be attributed to maximum tetrapyrrane formation at 1:2 **1**/pyrrole molar ratio. This is in accordance with the influence of aldehydes/pyrrole ratio on relative yields of different oligomeric species [25].

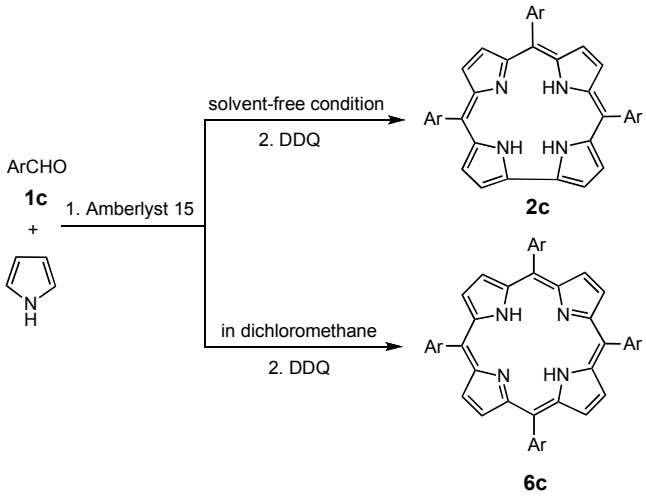
As the formation of corrole by oxidative macrocyclization of tetrapyrrane depends on its concentration [9], the reaction mixture was diluted with dichloromethane before oxidation with DDQ and other conditions for the oxidation step were optimized. The use of 0.5 equiv of DDQ in the reaction of **1c** with pyrrole (1:2 ratio) decreased the yield of **2c** from 22% (with 1 equiv of DDQ) to 16% and no **2c** was isolated when 2 equiv of DDQ was used in the reaction (Table 1, entries 8-10). Similar results were obtained with other aldehydes under the given condition (Table 1). Hence, an optimal amount of DDQ is required to furnish corrole in maximum yield.

The effect of other oxidants such as *p*-chloranil [9], ferric chloride [26] and potassium ferricyanide [27] on the yield of corrole was also investigated in Amberlyst 15 catalyzed condensation of **1c** with pyrrole (1:2 ratio) (Table 1). Chloranil showed more selectivity but less reactivity than DDQ as **2c** was obtained in higher yield and longer reaction time using chloranil as compared to DDQ (Table 1, entries 8 and 11). This could be explained by interference by DDQ in corrole synthesis [28]. Further, the broadening of Soret band at 416 nm with a great absorbance intensity loss and complete disappearance of Q bands was observed on addition of equimolar DDQ solution in **2c** solution, supporting the formation of a corrole-DDQ complex in the reaction. However, DDQ was favored over *p*-chloranil for the synthesis of corroles as radical oxidative coupling is fast with DDQ and *p*-chloranil afforded reaction mixtures of greater complexity due to presence of additional pigments. The use of ferric chloride as oxidant in the reaction of **1c** with pyrrole catalyzed by Amberlyst 15 afforded **2c** only in trace amount but no **2c** formation was detected using potassium ferricyanide. The inactivity of the oxidant may be attributed to its poor solubility in organic solvents.

The acid catalyzed cyclocondensation of aldehyde with pyrrole in organic medium followed by oxidation with DDQ is the most common method for the synthesis of 5,10,15,20-tetraarylporphyrins [29]. Solvent-free conden-

sation of **1c** with pyrrole (1:2 ratio) catalyzed by Amberlyst 15 and subsequent oxidation with DDQ (1 equiv) gave **2c** in 22% yield and no 5,10,15,20-tetrakis(4-chlorophenyl)porphyrin (**6c**) formation was detected in the reaction (Scheme 2). Dilution of the reaction mixture with dichloromethane (20 equiv *vs* **1c**) in Amberlyst 15 catalyzed condensation step of **1c** with pyrrole showed a slight decline in the yield of **2c** (21%) along with the formation of **6c** in trace amount (Table 1, entry 14). No corrole (**2c**) was formed at 300 fold dilution of reaction mixture with dichloromethane and **6c** was isolated in 20% yield (Table 1, entry 15). As high dilution condition is more favorable for porphyrinogen formation than long oligomers [30,31], solvent free condition is ideal for the synthesis of corroles and dilution leads to formation of porphyrins under the condition of experiment.

Scheme 2



The solvent-free condensation reaction of aldehyde with pyrrole catalyzed by Amberlyst 15 is greatly influenced by the nature of substituents on phenyl ring. Aldehydes bearing electron-withdrawing group condensed rapidly with pyrrole in the presence of Amberlyst 15 as compared to other aldehydes. The presence of electron-withdrawing groups on benzaldehyde favored the formation of corroles under the condition of experiment as 5,10,15-tris(pentafluorophenyl)corrole (**2h**) was isolated in maximum yield (30%) (Table 1, entry 22). Similarly, the reaction of **1d** with pyrrole catalyzed by Amberlyst 15 and subsequent oxidation with DDQ gave **2d** in 3% yield. The presence of ammonium chloride (inorganic additive), known to raise the corrole yield during oxidative coupling of tetrapyrrane [24], substantially improved the yield of **2d** to 13% (Table 1, entry 17). The method was also employed successfully for aldehyde bearing electron donating group (**1j**) (Table 1, entry 24).

The catalytic potential of other cation exchange resins was also examined for the synthesis of corroles. The reaction of **1c** and pyrrole catalyzed by Amberlite IR-120 followed by oxidative coupling by DDQ gave **2c** in 3 % yield, whereas in Dowex MR-3, Amberlyte IRC-50 and Zerolit-225 catalyzed reactions the formation of corrole (**2c**) was not observed. The reaction remained unaffected on prolonging the reaction time from 2 hr to 10 hr. Lower acidic character of these cation exchange resins than Amberlyst 15 is believed to be responsible for inactivity.

The reusability of Amberlyst 15 was examined in the reaction of **1c** with pyrrole by conducting two runs. After the reaction, Amberlyst 15 was filtered and then refluxed with methanol: chloroform mixture (1:1, v/v) for 30 min to remove any adsorbed materials from the catalyst surface and pores and dried at 110°C after every use. In second run, Amberlyst 15 catalyzed condensation of **1c** with pyrrole (1:2 ratio) and subsequent oxidation by DDQ (1 equiv) afforded **2c** in 15% yield which deceased to 9 % in third run.

In conclusion, the condensation of aldehydes with pyrrole catalyzed by Amberlyst 15 followed by oxidative cyclization with DDQ at room temperature is a simple and efficient method for the synthesis of corroles. The method offers various advantages such as mild reaction condition, less by-products, high yields of products, a simple experimental procedure and reusability of the heterogeneous catalyst. Thus, Amberlyst 15 catalyzed reactions open an avenue to the synthesis of a broad range of corroles bearing various substituents in good yield under mild conditions.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on Brucker 300 MHz spectrometer using TMS as internal standard and $CDCl_3$ as solvent and the chemical shifts were expressed in ppm. IR spectra were recorded on Perkin Elmer Spectrum 2000 infrared and ν_{max} were expressed in cm^{-1}. UV-visible spectra Perkin Elmer Lambda 35 UV/VIS Spectrophotometer and absorption maxima have been expressed in nm and ESI-MS spectra were recorded on Micromass LCT KC 455 using electrospray positive ion mass spectra. Elemental analyses were obtained on GmbH Vario EL-III elemental analyzing system.

General procedure for the synthesis of 5,10,15-triarylcorroles using ion-exchange resins. A sample of aryl aldehyde (2 mmol) was dissolved in pyrrole (2 mmol, 4 mmol or 6 mmol) at room temperature and activated ion exchange resin (200 mg) was added. The above reaction mixture was stirred for 1-3 hr at room temperature. The viscous reaction mixture was dissolved in dichloromethane (10 mL). Resin was filtered off and washed with dichloromethane (3 × 5 mL). The dichloromethane solution was collected in a round bottom flask (and 20 mmol NH_4Cl was added in one case with **1d**) and a solution of DDQ (1 or 2 mmol) in tetrahydrofuran (5 mL) was added with stirring. The reaction mixture was stirred for additional 15 min at room temperature. The solvent was removed under reduced pressure and the

residue was chromatographed on neutral alumina. The elution of column with chloroform/pertroleum ether (varying ratio) gave the corresponding corrole as a green-violet solid. The used Amberlyst 15 was washed thoroughly with methanol: chloroform mixture (1:1, v/v) followed by refluxing for 30 min. Amberlyst 15 was reactivated and reused for catalyzing other condensation reactions.

Selected characterization data 5,10,15-triphenylcorrole (2a) [11]. UV-vis (CH_2Cl_2): λ_{max} (log ε) = 414 (4.73), 575 (3.95), 615 (3.88), 646 nm (3.79). IR (KBr): 3421, 1685, 1595, 1577, 1550, 1491, 1377, 1330, 1269, 1222, 1039, 1010, 960, 794, 752, 699 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.83 (br s, 4H), 8.50 (br s, 4H), 8.33 (d, J = 5 Hz, 4H), 8.15 (d, J = 5 Hz, 2H), 7.85-7.70 (m, 9H), -2.90 (s, 3H). MS (ESI): m/z = Calculated ($C_{37}H_{26}N_4$), 526.63; Observed (M + H^+), 527.59. *Anal*. Calc for $C_{37}H_{26}N_4$: C, 84.38; H, 4.98; N, 10.64. Found: C, 84.26; H, 4.94; N, 10.59.

5,10,15-Tris(4-nitrophenyl)corrole (2b) [11]. UV-vis ($CHCl_3$): λ_{max} (log ε) = 426 (4.22), 592 nm (3.64). IR (KBr): 3427, 1654, 1594, 1517, 1343, 1059, 1028, 846, 792, 719 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 9.11 (d, J = 4 Hz, 2H), 8.88 (d, J = 4 Hz, 2H), 8.82 (s, 1H), 8.71 (d, J = 8 Hz, 4H), 8.65 (m, 2H), 8.57-8.54 (m, 6H), 8.37 (t, J = 9 Hz, 3H), -2.82 (s, 3H). MS (ESI): m/z = Calculated ($C_{37}H_{23}N_7O_6$), 661.62; Observed (M + H^+), 662.34. *Anal*. Calc for $C_{37}H_{23}N_7O_6$: C, 67.17; H, 3.50; N, 14.82. Found: C, 67.12; H, 3.42; N, 14.52.

5,10,15-Tris(4-chlorophenyl)corrole (2c). UV-vis (CH_2Cl_2): λ_{max} (log ε) = 416 (4.65), 577 (3.77), 616 (3.68), 648 nm (3.61). IR (KBr): 3318, 1586, 1487, 1395, 1222, 1174, 1091, 1012, 963, 845, 796, 722 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.97 (br s, 2H), 8.83 (br s, 2H), 8.54 (m, 4H), 8.26 (m, 4H), 8.11 (br s, 2H), 7.75 (m, 6H), -2.82 (s, 3H). MS (ESI): m/z = Calculated ($C_{37}H_{23}Cl_3N_4$), 629.97; Observed (M + H^+), 630.97. *Anal*. Calc for $C_{37}H_{23}Cl_3N_4$: C, 70.54; H, 3.68; N, 8.89. Found: C, 70.42; H, 3.54; N, 8.80.

5,10,15-Tris(4-carbomethoxyphenyl)corrole (2d) [9]. UV-vis (CH_2Cl_2): λ_{max} (log ε) = 420 (5.09), 515 (3.93), 584 (4.14), 619 (4.00), 652 nm (3.89). IR (KBr): 3435, 1723, 1654, 1607, 1459, 1437, 1278, 1113, 1074, 794, 794, 767, 733 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 9.01 (br s, 2H), 8.87 (br s, 2H), 8.82 (s, 1H), 8.58 (m, 4H), 8.43 (m, 8H), 8.29 (m, 3H), 4.10 (s, 9H). *Anal*. Calc for $C_{43}H_{32}N_4O_6$: C, 73.70; H, 4.60; N, 8.00. Found: C, 73.60; H, 4.53; N, 7.92.

5,10,15-Tris(3-bromophenyl)corrole (2e) [11]. UV-vis (CH_2Cl_2): λ_{max} (log ε) = 417 (4.78), 515 (3.47), 578 (3.85), 614 (3.69), 648 nm (3.62). IR (KBr): 3408, 1653, 1588, 1557, 1468, 1404, 1336, 1291, 1057, 1026, 782, 691 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 9.04, 8.88, 8.62, 8.56 (each d, J = 4 Hz, 2H), 8.51 (s, 2H), 8.35 (d, J = 8 Hz, 2H), 8.28 (d, J = 8 Hz, 2H), 8.15 (m, 4H), 7.87 (m, 2H), -2.82 (s, 3H). MS (ESI): m/z = Calculated ($C_{37}H_{23}Br_3N_4$), 763.32; Observed (M + H^+), 764.03. *Anal*. Calc for $C_{37}H_{23}Br_3N_4$: C, 58.22; H, 3.04; N, 7.34. Found: C, 58.05; H, 3.00; N, 7.50.

5,10,15-Tris(4-fluorophenyl)corrole (2f) [32]. UV-vis (CH_2Cl_2): λ_{max} (log ε) = 415 (4.55), 573 (3.58), 613 (3.49), 646 nm (3.43). IR (KBr): 3421, 1656, 1599, 1505, 1305, 1227, 1157, 1055, 1028, 805, 728 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8. 96 (d, J = 4.1Hz, 2H), 8.82 (d, J = 4.6 Hz, 2H), 8.54 (d, J = 4.1 Hz, 2H), 8.51 (d, J = 4.7 Hz, 2H), 8.30 (m, 4H), 8.22 (d, J = 2.8 Hz, 2H), 7.44 (m, 6H), -2.81 (s, 3H). MS (ESI): m/z = Calculated ($C_{37}H_{23}F_3N_4$), 580.61; Observed (M + H^+), 581.43. *Anal*. Calc for $C_{37}H_{23}F_3N_4$: C, 76.54; H, 3.99; N, 9.65. Found: C, 76.34; H, 4.22; N, 9.82.

5,10,15-Tris(2,6-dichlorophenyl)corrole (2g) [33]. UV-vis (CH_2Cl_2): λ_{max} (log ε) = 409 (4.78), 423 (4.69), 566 (3.97), 604 (3.74), 632 nm (3.17). IR (KBr): 3391, 1557, 1428, 1279, 1253, 1189, 1031, 957, 797, 777, 713 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.91 (d, J = 4 Hz, 2H), 8.49 (d, J = 4.7 Hz, 2H), 8.35 (m, 4H), 7.72 (m, 6H), 7.33(m, 3H), -1.70 (s, 3H). MS (ESI): m/z = Calculated ($C_{37}H_{20}Cl_6N_4$), 733.30; Observed (M + H^+), 734.34. *Anal*. Calc for $C_{37}H_{20}Cl_6N_4$: C, 60.60; H, 2.75; N, 7.64. Found: C, 60.45; H, 2.67; N, 7.58.

5,10,15-Tris(2,3,4,5,6-pentafluorophenyl)corrole (2h) [33]. UV-vis (CH_2Cl_2): λ_{max} (log ε) = 408 (4.61), 563 (3.89), 604 nm (3.67). IR (KBr): 3417, 1651, 1521, 1495, 1436, 1380, 1274, 1056, 986, 928, 795, 766 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 9.10 (d, J = 4.4 Hz, 2H), 8.75 (d, J = 4.4 Hz, 2H), 8.57 (d, J = 4.4 Hz, 4H) -2.25 (s, 3H).MS (ESI): m/z = Calculated ($C_{37}H_{11}F_{15}N_4$), 796.48; Observed (M + H^+), 797.50. *Anal*. Calc for $C_{37}H_{11}F_{15}N_4$: C, 55.79; H, 1.39; N, 7.03. Found: C, 55.66; H, 1.42; N, 7.12.

5,10,15-Tris(2-naphthyl)corrole (2i). UV-vis (CH_2Cl_2): λ_{max} (log ε) = 424 (5.06), 584 (4.29), 623 (4.26), 657 nm (4.22). IR (Film): 3391, 3198, 3118, 3054, 1693, 1596, 1502, 1357, 1272, 1051, 970, 946, 901, 802, 746 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.90-8.80 (m, 4H), 8.85 (m, 4H), 8.54 (m, 4H), 8.16 (m, 8H), 7.90-7.71 (m, 16H), -2.10 (s, 3H). MS (ESI): m/z = Calculated ($C_{44}H_{32}N_4$), 676.81; Observed (M + H^+), 677.81. *Anal*. Calc for $C_{44}H_{32}N_4$: C, 86.96; H, 4.77; N, 8.28. Found: C, 86.75; H, 4.80; N, 8.34.

5,10,15-Tris(4-methoxyphenyl)corrole (2j) [9]. UV-vis (CH_2Cl_2): λ_{max} (log ε) = 419 (4.69), 523 (3.77), 566 (3.88), 621 (3.84), 652 nm (3.78). IR (KBr): 3401, 1676, 1601, 1509, 1459, 1247, 1173, 1031, 786 cm^{-1}. MS (ESI): m/z = Calculated ($C_{40}H_{32}N_4O_3$), 616.71; Observed (M + H^+), 617.82. *Anal*. Calc for $C_{40}H_{32}N_4O_3$: C, 77.90; H, 5.23; N, 9.08. Found: C, 78.21; H, 5.32; N, 8.92.

Amberlyst 15 catalyzed condensation of 4-chlorobenzaldehyde (1c) and pyrrole under different dilution condition. The 4-chlorobenzaldehyde (**1c**) (2 mmol) and pyrrole (4 mmol) were dissolved in dichloromethane (20, 100 or 300 equiv *vs*. **1c**) at room temperature and activated Amberlyst 15 (200 mg) was added. The above reaction mixture was stirred for 1 hr at room temperature. Resin was filtered off after diluting the reaction mixture with 10 mL dichloromethane and washed with dichloromethane (3 × 5 mL). The dichloromethane solutions was collected and a solution of DDQ (2 mmol) in tetrahydrofuran (5 mL) was added with stirring. The reaction mixture was stirred for additional 15 min at room temperature. The solvent was removed under reduced pressure and the residue was chromatographed on neutral alumina. The elution of column with chloroform/petroleum ether (20: 80, v/v) gave 5,10,15-tris(4-chlorophenyl)corrole (**2c**) and 5,10,15,20-tetrakis(4-chlorophenyl)porphyrin (**6c**) in different yields.

5,10,15,20-Tetrakis(4-chlorophenyl)porphyrin (6c) [20]. UV-vis (CH_2Cl_2): λ_{max} (log ε) = 418 (5.55), 515 (4.14), 549 (3.74), 590 (3.58), 648 nm (3.56). IR (KBr): 3312, 1714, 1594, 1557, 1488, 1236, 1090, 1015, 966, 798 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.83 (s, 8H, β-pyrrolic-H), 8.14 (d, J= 8.2 Hz, 8H, *o*-Ph), 7.76 (d, J= 8.2 Hz, 8H, *m*-Ph), -2.16 (s, 2H, internal NH). MS (ESI): m/z = Calculated ($C_{44}H_{26}Cl_4N_4$), 752.52; Observed (M + H^+), 753.44.

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