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Facile synthesis of *meso*-substituted dipyrromethanes and porphyrins using cation exchange resins

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Abstract—The macroporosity and acidity of cation exchange resins play a crucial role in the synthesis of dipyrromethanes and porphyrins; for the first time, cation exchange resins have been used as heterogeneous solid acid catalysts to produce dipyrromethanes and porphyrins in good yields. The reaction, at room temperature, of substituted aromatic aldehydes with pyrrole catalysed by cation exchange resin afforded the corresponding *meso*-substituted dipyrromethane in yields ranging from 70 to 80%, indicating the broad scope of the reaction. Further, the condensation of *meso*-substituted dipyrromethane with similar or different substituted aromatic aldehydes, using cation exchange resins furnished *meso*-tetrakis-symmetrical and mixed porphyrins, respectively. One-pot synthesis of porphyrins can also be carried out directly from the aldehydes and pyrrole under the above conditions. Acidolysis of the dipyrromethane is negligible under the conditions of the porphyrin-forming reaction.

1. Introduction

A multitude of structurally diverse porphyrins have been synthesized as mimics for heme-dependent proteins during the past three decades. The great majority of these are embellished derivatives of the basic tetraphenylporphyrin framework. Tetraphenylporphyrins have been widely exploited in the development of porphyrin model systems.[1]

meso or 5-substituted dipyrromethanes are important precursors for the synthesis of *meso*-substituted porphyrins, expanded porphyrins and porphyrin analogues.[2] These are used as key building blocks in the synthesis of linear porphyrin arrays. Several methods have been reported for the synthesis of 5-substituted dipyrromethanes by the condensation of an aldehyde and pyrrole using various combinations of acids and solvents.[3] All these reports claim moderate yields of *meso*-substituted dipyrromethanes. Thus, aldehydes and pyrrole readily undergo condensation using homogeneous acid catalysts such as BF_3·etherate, trifluoroacetic acid (TFA), propionic acid, etc., at room temperature to yield *meso*-substituted dipyrromethanes along with oligomeric by-products. The yields are reduced due to the formation of oligomers and this calls for stringent purification methods to remove the by-products.

Cyclocondensation of aryl aldehydes with pyrrole in propionic acid is one of the most common methods for the synthesis of symmetrical 5,10,15,20-tetraaryl porphyrins[4] in low yields. Porphyrins in which the phenyl rings bear sterically hindered or electron withdrawing groups have been prepared by using BF_3–etherate as the acid catalyst, along with DDQ as oxidant in moderate yields.[5] There have been recent advances to improve the synthesis of 5,10,15,20-tetraaryl porphyrins, including solid state and other modifications.[6] However, these syntheses suffer from purification problems and lead to low yields of the products. One of the major disadvantages of the above methods is the requirement of large amounts of corrosive, acidic and environmentally harmful chlorinated solvents.

In connection with our interest in the synthesis of porphyrins we describe here for the first time, a facile efficient synthetic strategy for preparing 5-substituted dipyrromethanes in excellent yields using cation exchange resins as heterogeneous acid catalysts (Scheme 1). These dipyrromethanes are subsequently transformed to symmetrical and mixed porphyrins. We are also reporting here a simple, convenient one-pot synthesis of symmetrical porphyrins by condensing pyrrole with substituted aldehydes in the presence of cation exchange resins as acid catalysts.

These resins are the functional resins with a styrene divinylbenzene copolymer matrix having sulfonic acid groups. Macroporous (or macroreticular) functional resins (present on the market mostly as polystyrene crosslinked with divinylbenzene) are isotropic materials formed by chemically interconnected polymer chains, normally insoluble in any conceivable solvent. Each resin particle can be viewed as a mini reactor (vide infra) filled with a solution of functional polymer chains with pendant arms bearing sulfonic acid groups.[7] Functional synthetic cation exchange resins serve as efficient industrial heterogeneous catalysts, potentially useful in the area of fine chemical

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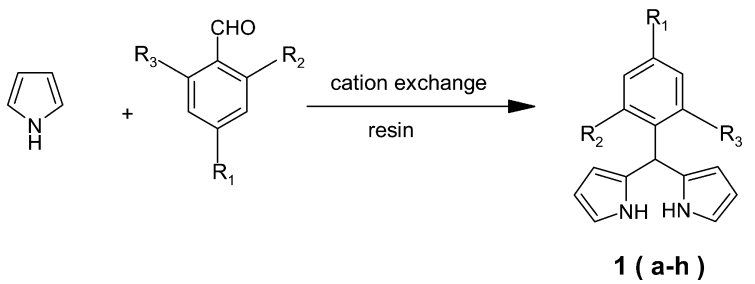


Scheme 1.

synthesis. They offer an environment for the catalytic reaction quite different from that of a free solution or the surface of conventional heterogeneous catalysts based on inorganic supports. The mechanism of ion exchanger catalysed reaction in a non-aqueous environment is similar to that operating for conventional heterogeneous catalysts (adsorption–surface reaction–desorption). An important consequence of the catalysis being a multiplet of sulfonic acid groups is that it shows more than a proportional dependence of the reaction rate on the concentration of acidic centres. In this connection, the environment of a catalytic site embedded in the polymer network can almost be considered as a micro reactor.[8]

2. Results and discussion

2.1. Synthesis of *meso*-substituted dipyrromethanes

The condensation of pyrrole with benzaldehyde in the presence of various cation exchange resins afforded very good yields of *meso*-phenyldipyrromethane (Scheme 1, Table 1). Among the different polymeric cation exchange resins used, T-63 and Indion-130 resins were found to be more suitable with respect to the product yields, batch-to-batch consistency and clean work-up. These resins are of macroreticular type, having a styrene divinylbenzene co-polymer matrix (15–17% crosslinking) and the exchange capacity is in the range of 4.5–4.7 mequiv./g.

Dipyrromethanes (**1a**–**h**) were prepared by condensation of substituted aromatic aldehydes in neat excess pyrrole (1:20) (Scheme 1, Table 2). Most of the dipyrromethanes were readily crystallized after removal of pyrrole. The identity of the products was confirmed by comparing melting points and NMR spectra with that of the reported compounds.

Table 1. Synthesis of *meso*- phenyldipyrromethane (**1a**) using various resins

Entry[a]	Resin	Time (h)	Yield (%)
1	Amberlyst-15	12	90
2	IR-120	15	71
3	Tulsion T-40	17	69
4	Tulsion T-42	15	72
5	Tulsion T-63	10	91
6	Indion-130	11	89
7	Amberlyte IR-100	20	65
8	Zeocarb 225	20	58

[a] Entries 1–8 are strongly acidic cation exchange resins (H^+ form) having a matrix structure with a styrene divinylbenzene copolymer functionalised with sulfonic acid groups.

Table 2. Synthesis of *meso*-substituted dipyrromethanes

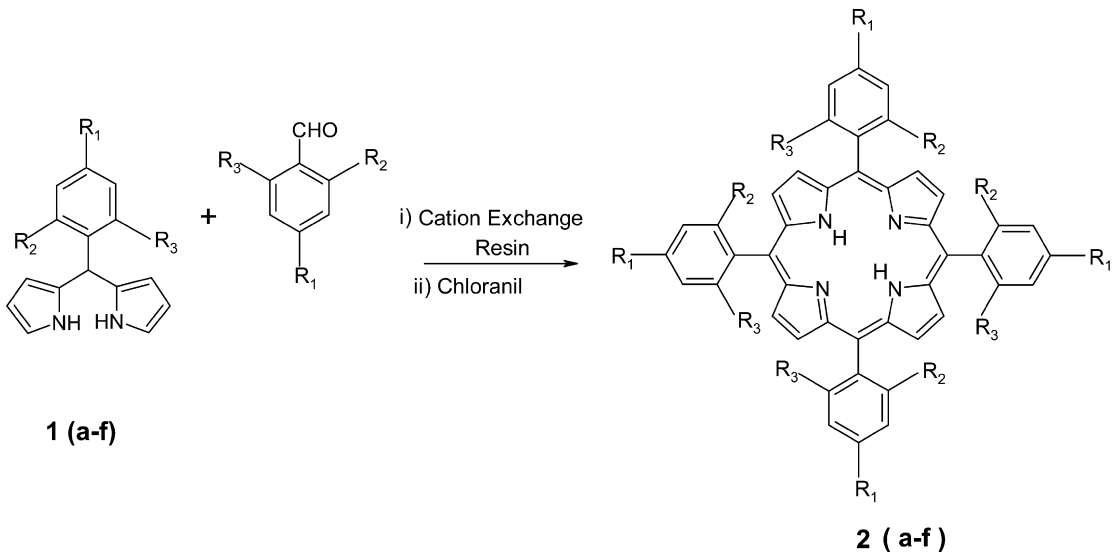
Compound number	R_1	R_2	R_3	Resin	Time (h)	Yield (%)
1a	H	H	H	In-130	12	80
1b	OCH_3	H	H	In-130	15	65
				T-63	10	72
1c	H	Cl	Cl	In-130	15	66
				T-63	10	71
1d	Cl	H	H	In-130	15	75
				T-63	10	77
1e	H	NO_2	H	T-63	10	73
1f	F	H	H	T-63	10	77
1g	CH_3	H	H	T-63	10	71
1h	NO_2	H	H	T-63	10	61

Most of the dipyrromethanes are stable for more than 2 months in the purified form, upon storage at 0°C in the absence of light.

The use of macroporous cation exchange resins has the advantages of controlled acidity due to site isolation of sulphonic acid groups, high selectivity and purity of the product due to trace side reactions and easy work-up procedures, which was evidently proven by the reduction of oligomer formation and the production of excellent yields of *meso*-substituted dipyrromethanes (70–80% yield) in pure forms. This refined process enabled the straightforward preparation of multi-gram batches of 5-substituted dipyrromethanes. The yields of dipyrromethanes obtained in our method are also much better than those in the existing methods where homogeneous acid catalysts have been employed.

2.2. Formation of symmetrical *meso*-substituted porphyrins and mixed porphyrins

The '2+2 synthesis' using dipyrromethanes as intermediates, forms the backbone of the building block approach towards the synthesis of porphyrins. We have further extended our strategy of using cation exchange resins as acid catalysts in the preparation of symmetrical and mixed porphyrins incorporating various functional groups from aryldipyrromethanes. One of our objectives has been to develop a set of porphyrin building blocks that can be combined in a rational manner to form multi-porphyrin arrays and related porphyrin model systems. The cation exchange resin-catalysed condensation of the aryl dipyrromethanes (**1a**–**h**) with aromatic aldehydes give rise to porphyrinogens, which subsequently get oxidized to the corresponding *meso*-substituted porphyrins (**2**) by means of *p*-chloranil. With aromatic aldehydes having the substituents as in (**1**), dipyrromethane give symmetrical



Scheme 2.

Table 3. Synthesis of 5,10,15,20-tetraarylporphyrins

Compound number	R_1	R_2	R_3	Time (h)	Yield (%)
2a	H	H	H	16	24
2b	OMe	H	H	17	46
2c	H	Cl	Cl	17	19
2d	Cl	H	H	17	21
2e	F	H	H	17	19
2f	CH_3	H	H	16	30

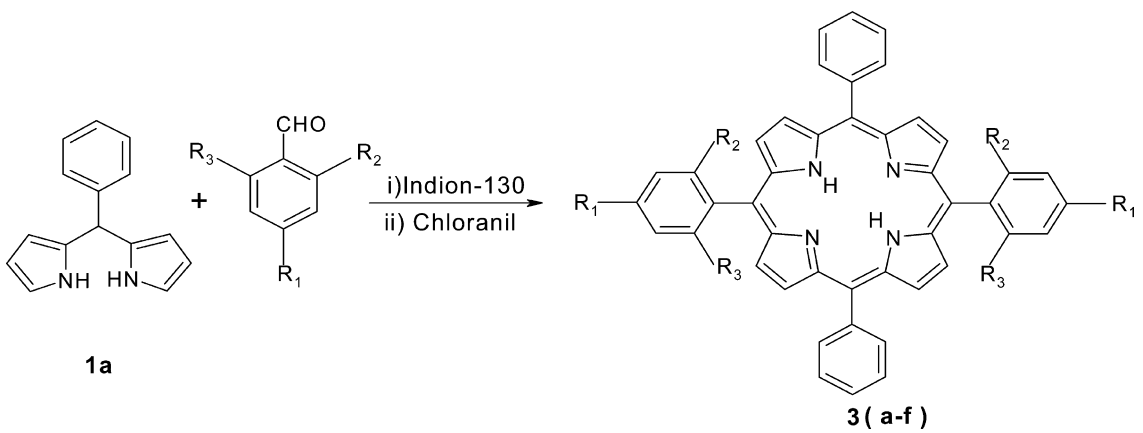
Cation exchange resin used is Indion-130.

meso-porphyrins (Scheme 2, Table 3) and with different aromatic aldehydes (mixed condensation) it furnishes trans substituted mixed porphyrins (**3**) (Scheme 3, Table 4).

All the *meso*-substituted and mixed porphyrins have been purified by column chromatography and characterized by ^{1}H NMR, UV–vis and mass spectra.

2.3. One-pot synthesis of *meso*-substituted porphyrins

One flask synthesis of porphyrins has also been carried out



Scheme 3.

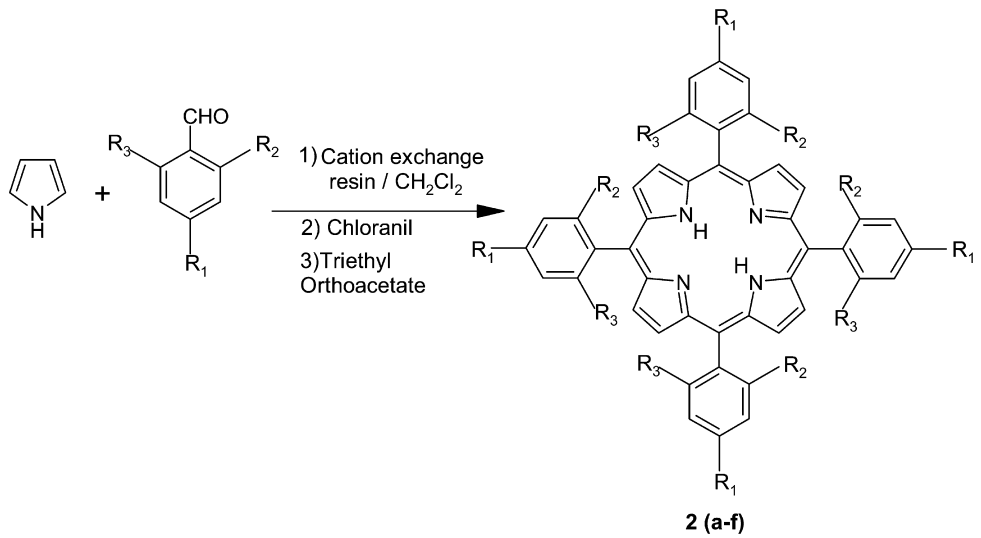
Table 4. 5,15 Diaryl-10,20 diphenylporphyrins

Compound number	R_1	R_2	R_3	Time (h)	Yield[a] (%)
3a	OCH_3	H	H	17	22
3b	H	Cl	Cl	20	20
3c	Cl	H	H	18	22
3d	F	H	H	20	16
3e	CH_3	H	H	17	23
3f	NO_2	H	H	16	21

Cation exchange resin used is Indion-130.
[a] Isolated yields.

without isolation of the dipyrromethane intermediate. Reaction of pyrrole with substituted aromatic aldehydes using cation exchange resin, in dichloromethane with triethyl-orthoacetate gives *meso*-substituted porphyrins in good yields (Scheme 4, Table 5). The procedure is mild, clean and convenient.

It has been observed that when the aldehyde contains an electron donating substituent such as methoxy or methyl, higher yields of porphyrins are obtained. However, the reactions with aldehydes containing electron withdrawing groups viz. 4-fluoro benzaldehyde, 2,6-dichloro



Scheme 4.

Table 5. Synthesis of *meso*-tetrakis porphyrins (one-pot synthesis)

Compound number	R_1	R_2	R_3	Time (h)	Conc. (mmol)	Yield[a] (%)
2a	H	H	H	16	6	33
				16	10	64
2b	OCH_3	H	H	17	6	46
				17	10	60
2c	H	Cl	Cl	17	10	22
2d	Cl	H	H	17	6	18
				17	10	23
2e	F	H	H	17	10	20
2f	CH_3	H	H	16	10	68

Cation exchange resin used is Indion-130.
[a] Isolated yields.

benzaldehyde etc. result in lower yields of the product. Similarly, as reported earlier,[5b] maximum yields are obtained in one-pot condensation when the reactions are carried out on a 10 mmol scale. The workup is just mere filtration, removal of the solvent and flash chromatography using silica gel.

It should be noted that the use of cation exchange resins as heterogeneous catalysts is found to be superior to using conventional, homogeneous acid catalysts in terms of purity of the product, reduction in the amount of unwanted polymeric by-products and ease of work-up.

3. Conclusion

Taking advantage of its macroporosity and acidity, a versatile, novel, eco-friendly and simple protocol for the synthesis of dipyrromethanes and porphyrins have been achieved for the first time, using macroporous cation exchange resins as catalysts.

4. Experimental

4.1. General

All melting points are uncorrected. All chemicals used were of analytical grade. Proton NMR spectra were recorded at a frequency of AC 200 MHz with a Bruker instrument. Mass spectra were obtained using a Finnigan Mat, 1020 Automated GC/MS with solid probe facility. For compounds with higher molecular weights (800 and above), LSIMS (FAB) spectra were obtained. Absorption spectra were obtained using UV-1601 Shimadzu. Infra-red were obtained using Shimadzu FTIR 8400 spectrophotometer. For Flash Column Chromatography, SISCO silica gel (230–400 mesh) was used. TLC was performed with pre-coated aluminium sheets with silica gel 60 F_{254}. Cation-exchange resins were procured from Thermax (India) Ltd., Pune and Ion-Exchange India Ltd., Mumbai. The identities of all known products were confirmed by comparison with their physical and spectral data. Pyrrole was distilled at atmospheric pressure from CaH_2. CH_2Cl_2/$CHCl_3$ were distilled from K_2CO_3. The dipyrromethanes are easily visualized upon exposure of thin layer chromatography plates to Br_2 vapour.

4.2. General method for the preparation of *meso*-substituted dipyrromethanes

A solution of benzaldehyde (10 mmol) and pyrrole (200 mmol) was degassed by bubbling the mixture with argon for 10 min. Cation exchange resin T-63 (5 g) was added to this mixture. The solution was stirred at room temperature. After the time indicated in Table 2, the reaction mixture was diluted with CH_2Cl_2 (10 ml), 100 μl of triethylamine was added to prevent acidolysis of the *meso*-phenyl dipyrromethane and filtered. The filtrate was washed with water and the organic layer was dried over Na_2SO_4. The solvent was removed under reduced pressure and the unreacted pyrrole was removed by vacuum distillation (5–8 mm/30–35°C). The resulting pale yellow amorphous solid was purified by crystallization or flash chromatography using pet. ether–ethylacetate–triethylamine (85:14:1) to give dipyrromethanes as white crystals (70–80%).

4.2.1. *meso*-Phenyldipyrromethane (1a).[3e] White crystals. Yield 80%. Mp 101°C. ^{1}H NMR (200 MHz, $CDCl_3$): δ=5.49 (s, 1H, *meso*H), 5.92 (s, 2H), 6.18 (m, 2H), 6.72

(m, 2H), 7.18–7.35 (m, 5H, ArH), 7.93 (brs, 2H, NH). MS *m/z* (%): 222 (M^+, 97), 194 (6), 179 (2), 165 (5), 154 (33), 145 ($M^+-C_6H_5$, 100) 127 (14), 102 (7), 91 (19), 77 (20), 67 (15), 57 (25). R_f=0.71 (0.5% MeOH in DCM).

4.2.2. *meso*-(4-Methoxy)dipyrromethane (1b).[3e] Brownish-white crystals. Yield 65%. Mp 98–99°C. ^{1}H NMR (200 MHz, $CDCl_3$): δ=3.78 (s, 3H, OCH_3), 5.43 (s, 1H, *meso*H), 5.92 (m, 2H), 6.16 (dd, *J*=2.9, 2.9 Hz, 2H), 6.69 (m, 2H), 6.86 (AA′BB′, m, 2H), 7.13 (AA′BB′, m, 2H), 7.92 (brs, 2H). MS *m/z* (%): 252 (M^+, 94), 263 (7), 219 (6), 208 (10), 196 (7), 185 (14), 170 (38), 154 (19), 145 ($M^+-C_7H_7O$, 100), 126 (17), 117 (30), 97 (23), 91 (46), 77 (36), 71 (55), 57 (100). R_f=0.63 (0.5%MeOH in DCM).

4.2.3. *meso*-(2,6-Dichloro)dipyrromethane (1c).[3e] Yellowish solid. Yield 66%. Mp 102–103°C. ^{1}H NMR (200 MHz, $CDCl_3$): δ=6.06 (s, 1H, *meso*H); 6.18 (dd, *J*=3.0, 3.0 Hz, 2H); 6.47 (s, 1H); 6.72–6.74 (m, 2H), 7.12 (t, *J*=7.9 Hz, 2H), 7.32 (d, *J*=7.9 Hz, 2H), 8.28 (bs, 2H, NH). MS *m/z* (%): 290 (M^+, 48), 264 (6), 253 (9), 238 (6), 224 (12), 188 (24), 174 (41), 159 (10), 145 ($M^+-C_6H_2Cl_2$, 100), 126 (15), 108 (23), 91 (12), 83 (65), 77 (32), 67 (45), 57 (30). R_f=0.83 (0.5%MeOH in DCM).

4.2.4. *meso*-(4-Chloro)dipyrromethane (1d).[3m] Pale-yellow solid. Yield 77%. Mp 112°C. ^{1}H NMR (200 MHz, $CDCl_3$): δ=5.46 (s, 1H, *meso*H), 5.88 (m, 2H), 6.24 (m, 2H), 6.83 (m, 2H), 7.30 (m, 4H), 7.97 (brs, 2H, NH). MS *m/z* (%): 256 (M^+, 43), 190 (30), 145 ($M^+-C_6H_4Cl$, 100), 91 (7), 71 (20). R_f=0.85 (0.5% MeOH in DCM).

4.2.5. *meso*-(2-Nitro)dipyrromethane (1e).[3m] Yellow coloured liquid. Yield 73%. ^{1}H NMR (200 MHz, $CDCl_3$): δ=5.86 (s, 1H, *meso*H), 6.10–6.20 (m, 4H), 6.68–6.71 (m, 2H), 7.26–7.56 (m, 3H), 7.86–7.90 (m, 1H), 8.17 (brs, 2H, NH). MS *m/z* (%): 267 (M^+, 100), 251 (2), 236 (4), 220 (15), 201 (25), 191 (10), 163 (4), 154 (32), 145 ($M^+-C_6H_4NO_2$, 80), 127 (12), 117 (22), 104 (6), 89 (10), 75 (18), 67 (39). R_f=0.67 (0.5% MeOH in DCM).

4.2.6. *meso*-(4-Fluoro)dipyrromethane (1f).[3e] White crystals. Yield 77%. Mp 81–82°C. ^{1}H NMR (200 MHz, $CDCl_3$): δ=5.49 (s, 1H, *meso*H), 5.93 (m, 2H), 6.20 (dd, *J*=2.8, 2.8 Hz, 2H), 6.74 (m, 2H), 7.04 (m, 2H), 7.94 (m, 2H), 8.18 (brs, 2H, NH). MS *m/z* (%): 240 (M^+, 100), 212 (6), 197 (1), 174 (70), 159 (80), 145 ($M^+-C_6H_4F$, 45), 130 (5), 117 (10), 108 (4), 91 (24), 86 (12), 77 (6), 67 (10). R_f=0.75 (0.5% MeOH in DCM).

4.2.7. *meso*-(4-Methyl)dipyrromethane (1g).[3e] Buff coloured solid. Yield 71%. Mp 110–111°C. ^{1}H NMR (200 MHz, $CDCl_3$): δ=2.32 (s, 3H, Ar–CH_3), 5.44 (s, 1H, *meso*H), 5.91 (m, 2H), 6.15 (m, 2H), 6.68 (m, 2H), 7.11 (m, 4H), 7.91 (brs, 2H, NH). MS *m/z* (%): 236 (M^+, 15), 221 (M^+-CH_3, 3), 208 (3), 181 (3), 170 (24), 155 (20), 136 (5), 119 (34), 105 (7), 91 (51), 77 (19), 65 (32), 56 (100). R_f=0.71 (0.5% MeOH in DCM).

4.2.8. *meso*-(4-Nitro) dipyrromethane (1h).[3e] Yellowish-white solid. Yield 61%. Mp 160°C. ^{1}H NMR (200 MHz, $CDCl_3$): δ=5.57 (s, 1H, *meso*H), 5.86 (m, 2H), 6.17 (m, 2H), 6.74 (m, 2H), 7.35 (m, 2H), 8.03 (brs, 2H, NH), 8.13 (m, 2H). MS *m/z* (%): 267 (M^+, 100), 251 (2), 236 (4), 220 (15), 201 (25), 191 (10), 163 (4), 154 (32), 145 ($M^+-C_6H_4NO_2$, 80), 127 (12), 117 (22), 104 (6), 89 (10), 75 (18), 67 (39). R_f=0.62 (0.5% MeOH in DCM).

4.3. General method for the synthesis of porphyrins 2a–f and 3a–f

A mixture of *meso*-phenyl dipyrromethane (2 mmol) and aldehyde (2 mmol) was stirred under a nitrogen atmosphere in CH_2Cl_2 (50 ml) in presence of cation exchange resin (1 g) at 25°C for the corresponding time as mentioned in Tables 2 and 3. Chloranil (2 mmol) was then added and the reaction mixture was further refluxed for 3 h, cooled and filtered. The filtrate was concentrated and the crude product was subjected to soxhlet purification using methanol. The methanol insoluble product was then purified by flash chromatography on silica gel to afford pink crystals of porphyrins.

4.3.1. 5,10,15,20-Tetraphenylporphyrin (2a).[6k] Purple crystals. Yield 24%. Mp >300°C. UV–vis (CH_2Cl_2) λ_{max} (nm) (ε): 412 (90.0), 478 (8.1), 514 (42.2), 588 (12.9), 645 (10.7). ^{1}H NMR (200 MHz, $CDCl_3$): δ=-2.17 (s, 2H, NH), 7.74 (m, 12H, *p*- and *m*-Ph); 8.20 (d, *J*=8.9 Hz, 8H, *o*-Ph); 8.84 (s, 8H, pyrrole-H). MS *m/z* (%): 614 (M^+, 100), 538 (4), 458 (1), 308 ($M^+-C_{24}H_{18}$, 11), 277 (3), 204 (1), 180 (6), 121 (12), 91 (19), 77 (14). R_f=0.92 (0.5% MeOH in DCM).

4.3.2. 5,10,15,20-(4-Methoxy) tetraphenylporphyrin (2b).[6k] Purple crystals. Yield 46%. Mp >300°C. UV–vis (CH_2Cl_2) λ_{max} (nm) (ε): 420 (78.6), 454 (7.6), 518 (6.0), 554 (4.7), 592 (2.3), 648 (2.6). ^{1}H NMR (200 MHz, $CDCl_3$): δ=−2.47 (brs, 2H, NH); 4.15 (s, 12H, OCH_3); 7.31 (d, *J*=8.3 Hz, 8H, *m*-Ph), 8.11 (m, 8H, *o*-Ph), 8.51 (m, 8H, pyrrole-H). MS *m/z* (%): 735 (M^+, 36), 551 (20), 523 (14), 460 (76), 443 (18), 307 ($M^+-C_{28}H_{28}O_4$, 47), 289 (20), 154 (84), 137 (100), 120 (18), 107 (26), 91 (15), 77 (28), 55 (11). R_f=0.82 (0.5%MeOH in DCM).

4.3.3. 5,10,15,20-(2,6-Dichloro) tetraphenylporphyrin (2c).[9a] Purple crystals. Yield 19%. Mp>300°C. UV–vis (CH_2Cl_2) λ_{max} (nm) (ε): 423 (525.2), 489 (18.8), 519 (67.7), 557 (45.8), 593 (22.2), 650 (22.6). ^{1}H NMR (200 MHz, $CDCl_3$): δ=−2.57 (s, 2H, NH), 7.72–7.87 (m, 12H), 8.71 (m, 8H, pyrrole-H). MS *m/z* (%): 890 (M^+, 5), 735 (62), 551 (32), 523 (22), 460 (72), 443 (14), 307 ($M^+-C_{24}H_{11}Cl_8$, 44), 289 (20), 155 (100), 137 (98), 120 (18), 107 (24), 91 (16), 77 (30), 55 (13). R_f=0.79 (0.5% MeOH in DCM).

4.3.4. 5,10,15,20-(4-Chloro) tetraphenylporphyrin (2d).[6k] Purple crystals. Yield 21%. Mp >300°C. UV–vis (CH_2Cl_2) λ_{max} (nm) (ε): 485 (19.9), 515 (106.6), 550 (44.8). ^{1}H NMR (200 MHz, $CDCl_3$): δ=−2.16 (brs, 2H, NH); 7.76 (d, *J*=8.2 Hz, 8H, *m*-Ph); 8.14 (d, *J*=8.2 Hz, 8H, *o*-Ph); 8.83 (s, 8H, pyrrole-H). MS *m/z* (%): 752 (M^+, 44), 717 (M^+-Cl, 8), 664 (9), 647 (7), 604 ($M^+-C_6H_5Cl_2$, 32), 577 (27), 551 (14), 524 (6), 495 (7), 467 (8), 439 (10), 339 (14), 327 (4), 313 (10), 289 (6), 281 (13), 263 (11), 243 (6), 219 (10), 207 (16), 185 (8), 176 (12), 165 (19). R_f=0.90 (0.5% MeOH in DCM).

4.3.5. 5,10,15,20-(4-Fluoro) tetraphenylporphyrin (2e). Purple crystals. Yield 19%. Mp >300°C. UV–vis (CH_2Cl_2) λ_{max} (nm) (ε): 416 (194.3), 428 (1.7), 513 (7.7), 548 (3.1), 589 (2.4), 644 (1.5). FT-IR ν_{max} (cm^{-1}): 3303 (ν_{NH}), 2964 (ν_{CH}), 2850, 1600 (ν_{C-C}), 1502, 1377 (ν_{C-C})methine bridge, 1126 (δ_{CH}), 1074 (δ_{CH}), 979 (δ_{NH}), 702 (γ_{NH}). ^1H NMR (200 MHz, $CDCl_3$): δ=−2.70 (brs, 2H, NH), 7.85 (d, J=8.2 Hz, 8H), 8.17 (d, J=8.2 Hz, 8H), 8.83 (s, 8H, pyrrole-H). MS m/z (%): 687 (M^+, 49), 551 (15), 524 (18), 495 (34), 468 (48), 440 (66), 419 (26), 411 (39), 383 (40), 355 (14), 307 ($M^+-C_{24}H_{16}F_4$, 100), 289 (63), 272 (13), 257 (22), 242 (13), 229 (15), 197 (12), 183 (30), 166 (34). Anal. calcd for $C_{44}H_{26}N_4F_4$: C, 76.96; H, 3.79; N, 8.16. Found C, 76.75; H, 3.93; N, 8.21. R_f=0.91 (0.5% MeOH in DCM).

4.3.6. 5,10,15,20-(4-Methyl) tetraphenylporphyrin (2f).[5e] Purple crystals. Yield 30%. Mp >300°C. UV–vis (CH_2Cl_2) λ_{max} (nm) (ε): 419 (86.8), 485 (4.2), 517 (11.0), 553 (6.4), 592 (4.1), 648 (3.2). ^1H NMR (200 MHz, $CDCl_3$): δ=−2.17 (brs, 2H, NH), 2.70 (s, 12H, CH_3), 7.54 (m, 8H), 8.08 (m, 8H), 8.84 (s, 8H, pyrrole-H). MS m/z (%): 670 (M^+, 24), 551 (18), 460 (18), 418 (11), 391 (13), 353 (11), 333 (14), 307 ($M^+-C_{28}H_{27}$, 100), 289 (71), 278 (14), 259 (16), 241 (17), 228 (22), 218 (17), 204 (16), 194 (21), 180 (29), 167 (37). R_f=0.90 (0.5% MeOH in DCM).

4.3.7. 5,15-Bis(4-methoxyphenyl)-10,20-diphenylporphyrin (3a).[9b] Purple crystals. Yield 22%. Mp >300°C. UV–vis (CH_2Cl_2) λ_{max} (nm) (ε): 420 (112.9), 452 (17.8), 516 (6.7), 552 (3.8), 590 (2.1); ^1H NMR (200 MHz, $CDCl_3$): δ=−2.59 (s, 2H, NH), 4.16 (s, 6H, OCH3), 7.25 (m, 4H), 7.51–7.55 (m, 6H), 7.97 (m, 8H); 8.58 (s, 8H, pyrrole-H). MS m/z (%): 674 (M^+, 78), 307 ($M^+-C_{26}H_{23}O_2$, 33), 243 (6), 154 (100), 107 (26), 89 (25), 83 (10), 77 (28), 69 (17), 55 (24). R_f=0.79 (0.5% MeOH in DCM).

4.3.8. 5,15-Bis(2,6-dichlorophenyl)-10,20-diphenylporphyrin (3b).[9c] Purple crystals. Yield 20%. Mp >300°C. UV–vis (CH_2Cl_2) λ_{max} (nm) (ε): 218 (4.3), 375 (7.7), 484 (1.0), 515 (5.9), 550 (2.0), 591 (1.7), 646 (1.0). ^1H NMR (200 MHz, $CDCl_3$): δ=−2.16 (brs, 2H, NH), 7.73–7.78 (m, 12H, *p*- and *m*-Ph), 8.20 (m, 4H, *o*-Ph), 8.85 (s, 8H, pyrrole-H). MS m/z (%): 752 (M^+, 14), 683 (M^+-2Cl, 100), 615 (76), 566 (6), 492 (3), 444 (3), 380 (9), 342 (44), 306 ($M^+-C_{24}H_{16}Cl_2$, 21), 256 (11), 210 (14), 154 (17), 77 (34). R_f=0.80 (0.5% MeOH in DCM).

4.3.9. 5,15-Bis(4-chlorodiphenyl)-10,20-diphenylporphyrin (3c). Purple crystals. Yield 21%. Mp >300°C. UV–vis (CH_2Cl_2) λ_{max} (nm) (ε): 215 (11.6), 591 (4.1), 550 (5.7), 576 (13.5), 487 (2.7). FT-IR: ν_{max} (cm^{-1}): 3319 (ν_{NH}), 3018 (ν_{CH}), 2927, 2399, 1596 (ν_{C-C}), 1350 (ν_{C-C})methine bridge, 1180 (δ_{CH}), 1089 (δ_{CH}), 966 (δ_{NH}), 700 (γ_{NH}). ^1H NMR (200 MHz, $CDCl_3$): δ=−2.55 (brs, 2H, NH), 7.72–7.76 (m, 6H, *m*- and *p*-Ph), 7.97–8.01 (m, 4H, *o*-Ph), 8.12–8.23 (m, 4H), 8.59 (m, 4H), 8.85 (s, 8H, pyrrole-H). MS m/z (%): 684 (M^+, 23), 649 (M^+-Cl, 36), 495 (7), 460 (10), 329 (6), 307 ($M^+-C_{24}H_{18}Cl_2$, 24), 289 (13), 259 (8), 217 (94), 154 (100), 136 (75), 107 (27), 90 (26), 77 (28), 53 (8). Anal. calcd for $C_{44}H_{28}N_4Cl_2$: C, 77.31; H, 4.10; N, 8.20. Found C, 77.24; H, 4.36; N, 8.05. R_f=0.83 (0.5%MeOH in DCM).

4.3.10. 5,15-Bis(4-fluorophenyl)-10,20-diphenyl porphyrin (3d). Purple crystals. Yield 16%. Mp >300°C. UV–vis (CH_2Cl_2) λ_{max} (nm) (ε): 418 (15.8), 541 (2.0), 515 (2.3), 343 (3.9). FT-IR ν_{max} (cm^{-1}): 3309 (ν_{NH}), 2923 (ν_{CH}), 2854, 1596 (ν_{C-C}), 1504, 1367 (ν_{C-C})methine bridge, 1155 (δ_{CH}), 1070 (δ_{CH}), 966 (δ_{NH}), 698 (γ_{NH}). ^1H NMR (200 MHz, $CDCl_3$): δ=−2.50 (s, 2H), 7.42 (m, 10H, *m*- and *p*-Ph), 7.77 (m, 4H), 8.20 (m, 4H), 8.85 (m, 8H, pyrrole-H). MS m/z (%): 650 (M^+, 14), 603 (13), 551 (20), 523 (14), 460 ($M^+-C_{12}H_8F_2$, 76), 443 (18), 307 ($M^+-C_{24}H_{17}F_2$, 47), 289 (20), 154 (84), 137 (100). Anal. calcd for $C_{44}H_{28}N_4F_2$: C 81.23; H, 4.31; N, 8.61. Found C, 80.96; H, 4.40; N, 8.81. R_f=0.82 (0.5%MeOH in DCM).

4.3.11. 5,15-Bis(4-methylphenyl)-10,20-diphenylporphyrin (3e).[9c] Purple crystals. Yield 23%. Mp >300°C. UV–vis (CH_2Cl_2) λ_{max} (nm) (ε): 646 (0.7) 543.0 (0.9), 542 (1.3), 517 (2.9), 419 (62.1). ^1H NMR (200 MHz, $CDCl_3$): δ=−2.80 (brs, 2H, NH), 2.70 (s, 6H, CH_3), 7.53 (4H, d, J=7.8 Hz, 5,15 Ar-3,5H), 7.76 (6H, m, 10,20 Ar-3,4,5H), 8.11 (4H, m, 10,20-Ar-2,6H), 8.21 (4H, m, 5,15-Ar-2,6H) and 8.83 (8H, m, pyrrole-H). MS m/z (%): 642 (M^+, 7), 493 (2), 434 (2), 385 (4), 311 (9), 270 (14), 231 (9), 185 (11), 148 (16), 91 ($M^+-C_{39}H_{27}N_4$, 30), 77 (28), 51 (100). R_f=0.82 (0.5% MeOH in DCM).

4.3.12. 5,15-Bis(4-nitrophenyl)-10,20-diphenyl porphyrin (3f).[9d] Purple crystals. Yield 21%. Mp >300°C. UV–vis (CH_2Cl_2) λ_{max} (nm) (ε): 416 (90.0), 514 (5.6), 548 (2.6), 590 (1.8), 648 (1.4). ^1H NMR (200 MHz, $CDCl_3$): δ=−2.56 (brs, 2H, NH), 7.76 (m, 10H), 8.19 (m, 8H), 8.84 (s, 8H, pyrrole-H). MS m/z (%): 704 (M^+, 7), 664 (11), 647 (7), 313 (4), 281 (5), 252 (5), 227 (3), 207 (8), 165 (10), 154 (28), 133 (61), 105 (32), 91 ($M^+-C_{37}H_{21}N_6O_4$, 45), 77 (60), 57 (100). R_f=0.78 (0.5% MeOH in DCM).

4.4. General method for one-pot condensation of pyrrole and aldehydes

To a degassed solution of dry DCM (400 ml) was added aldehyde (10 mmol). After stirring for 10 min under nitrogen, pyrrole (10 mmol) was added dropwise with continuous stirring followed by cation exchange resin T-63 (4.5 g) and triethylorthoacetate (10 mmol). After 16–17 h of stirring at room temperature, chloranil (10 mmol) was added and the reaction mixture refluxed for 2 h. The mixture was filtered and the filtrate concentrated. The crude product was purified by flash chromatography using silica gel to obtain purple crystals of porphyrins.

4.4.1. *meso*-Tetraphenyl porphyrin (2a).[6k] Purple crystals. Yield 33% when 6-mmol batch was performed. Purple crystals. Yield 64% when 10-mmol batch was performed.

4.4.2. *meso*-Tetrakis (4-methoxy) phenylporphyrin (2b).[6k] Purple crystals. Yield 46% when 6-mmol batch was performed. Purple crystals. Yield 60% when 10-mmol batch was performed.

4.4.3. *meso*-Tetrakis (2,6-dichloro) phenylporphyrin (2c).[9a] Purple crystals. Yield 22% when 10-mmol batch was performed.

4.4.4. *meso*-Tetrakis (4-chloro) phenylporphyrins (2d).[6k] Purple crystals. Yield 18% when 6-mmol batch was performed. Purple crystals. Yield 23% when 10-mmol batch was performed.

4.4.5. *meso*-Tetrakis (4-fluoro) phenylporphyrin (2e). Purple crystals. Yield 20% when 10-mmol batch was performed.

4.4.6. *meso*-Tetrakis (4-methyl) phenylporphyrin (2f).[5e] Purple crystals. Yield 68% when 10-mmol batch was performed.

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References

1. (a) *The Porphyrins*; Dolphin, D., Ed.; Academic: New York, 1978; Vols. 1–6. (b) Wijesekera, T. P.; Dolphin, D. In *Metalloporphyrins in Catalytic Oxidations*; Sheldon, R. A., Ed.; Marcel Dekker: New York, 1994; pp 193–231.
2. (a) Lindsey, J. S. *Metalloporphyrins Catalyzed Oxidations*; Kluwer: The Netherlands, 1994; pp 49–86. (b) Jasat, A.; Dolphin, D. *Chem. Rev.* **1997**, 2267–2340.
3. (a) Nagarkatti, J. P.; Ashley, K. R. *Synthesis* **1974**, 186–187. (b) Casiraghi, G.; Cornia, M.; Rassu, G.; Del Sante, C.; Spanu, P. *Tetrahedron* **1992**, *48*, 5619–5628. (c) Hammel, D.; Erk, P.; Schuler, B.; Heinze, J.; Müllen, K. *Adv. Mater.* **1992**, *4*, 737–739. (d) Brückner, C.; Posakony, J. J.; Johnson, C. K.; Boyle, R. W.; James, B. R.; Dolphin, D. J. *Porphyrins Phthalocyanines* **1998**, *2*, 455–465. (e) Littler, B. J.; Miller, M. A.; Hung, C.; Wagner, R. W.; O'Shea, D. F.; Boyle, P. D.; Lindsey, J. S. *J. Org. Chem.* **1999**, *64*, 1391–1396. (f) Jackson, A. H.; Pandey, R. K. *J. Chem. Soc., Perkin Trans. 1* **1987**, 299–305. (g) Jackson, A. H.; Lertwanawatana, W.; Pandey, R. K.; Rao, K. R. N. *J. Chem. Soc., Perkin Trans. 1* **1988**, 374–375. (h) Boyle, R. W.; Xie, L. Y.; Dolphin, D. *Tetrahedron Lett.* **1994**, *35*, 5377–5380. (i) Casiraghi, G.; Cornia, M.; Zanardi, F.; Rassu, G.; Ragg, E.; Bortolini, R. *J. Org. Chem.* **1994**, *59*, 1801–1808. (j) Lee, C.-H.; Lindsey, J. S. *Tetrahedron* **1994**, *50*, 11427–11440. (k) Mizutani, T.; Ema, T.; Tomita, T.; Kuroda, Y.; Ogoshi, H. *J. Am. Chem. Soc.* **1994**, *116*, 4240–4250. (l) Staab, H. A.; Carell, T.; Döhling, A. *Chem. Ber.* **1994**, *127*, 223–229. (m) Vigmond, S. J.; Chang, M. C.; Kallury, K. M. R.; Thompson, M. *Tetrahedron Lett.* **1994**, *35*, 2455–2458. (n) Nishino, N.; Wagner, R. W.; Lindsey, J. S. *J. Org. Chem.* **1996**, *61*, 7534–7544. (o) Wijesekera, T. P. *Can. J. Chem.* **1996**, *74*, 1868–1871. (p) Setsune, J.; Hashimoto, M.; Shiozawa, K.; Hayakawa, J.; Ochi, T.; Masuda, R. *Tetrahedron* **1998**, *54*, 1407–1424.
4. (a) Adler, A. D.; Longo, F. R.; Shergalis, W. D. *J. Am. Chem. Soc.* **1964**, *86*, 3145–3149. (b) Adler, A. D.; Longo, F. R.; Finarelli, J. D.; Goldnacher, J.; Assour, J.; Korsakoff, L. *J. Org. Chem.* **1967**, *32*, 476. (c) Adler, A. D.; Saklar, L.; Longo, F. R.; Finarelli, J. D.; Finurelli, G. M. *J. Heterocycl. Chem.* **1968**, *5*, 669–678. (d) Kim, J. B.; Adler, A. D.; Longo, F. R. *J. Am. Chem. Soc.* **1972**, *94*, 3986–3992.
5. (a) Lindsey, J. S.; Schreiman, I. C.; Hsu, H. C.; Kearney, P. C.; Marguerettaz, A. M. *J. Org. Chem.* **1987**, *52*, 827–836. (b) Lindsey, J. S.; Schreiman, I. C. *Tetrahedron Lett.* **1986**, *27*, 4969–4970. (c) Lindsey, J. S.; Wagner, R. W. *J. Org. Chem.* **1989**, *54*, 828–836. (d) Swanson, K. L.; Snow, K. M.; Jeyakumar, D.; Smith, K. M. *Tetrahedron* **1991**, *47*, 685–696. (e) Rocha Gonsalves, A. M. A.; Varejo, M. T. B.; Pereira, M. M. *J. Heterocycl. Chem.* **1991**, *28*, 685–695. (f) Drain, C. M.; Gong, X. J. *Chem. Commun.* **1997**, 2117–2118.
6. (a) Wallace, D. M.; Smith, K. M. *Tetrahedron Lett.* **1990**, *31*, 7265–7268. (b) Wallace, D. M.; Leung, S. H.; Senge, M. O.; Smith, K. M. *J. Org. Chem.* **1993**, *58*, 7245–7257. (c) Lee, C.-H.; Li, F.; Iwamoto, K.; Dadok, J.; Bothner-By, A. A.; Lindsey, J. S. *Tetrahedron* **1995**, *51*, 11645–11672. (d) Rao, P. D.; Dhanalekshmi, S.; Littler, B. J.; Lindsey, J. S. *J. Org. Chem.* **2000**, *65*, 7323–7344. (e) Vaz, B.; Alvarez, R.; Nieto, M.; Paniello, A. I.; De Lera, A. R. *Tetrahedron Lett.* **2001**, *42*, 7409–7412. (f) Shanmugathasan, S.; Edwards, C.; Boyle, R. W. *Tetrahedron* **2000**, *56*, 1025–1046. (g) Li, F.; Yang, K.; Tyhonas, J. S.; MacCrum, K. A.; Lindsey, J. S. *Tetrahedron* **1997**, *53*, 12339–12360. (h) Gradillas, A.; DelCampo, C.; Sinisterra, J. V.; Llama, E. F. *J. Chem. Soc., Perkin Trans. 1* **1995**, 2611–2613. (i) Onaka, M.; Shinoda, T.; Izumi, Y.; Nolen, E. *Chem. Lett.* **1993**, 117–120. (j) Rose, E.; Quelquejeu, M.; Pochet, C.; Julien, N.; Kossanyi, A.; Hamon, L. J. *J. Org. Chem.* **1993**, *58*, 5030–5031. (k) Chauhan, S. M. S.; Sahoo, B. B.; Srinivas, K. A. *Synth. Commun.* **2001**, *31*, 33–37.
7. Corain, B.; Kralik, M. *J. Mol. Catal.* **2000**, *159*, 153–162.
8. Corain, B.; Zecca, M.; Jerabek, K. *J. Mol. Catal.* **2000**, *177*, 3–20.
9. (a) Chorghade, M. S.; Dolphin, D.; Dupre, D.; Hill, D. R.; Lee, E. C.; Wijesekera, T. P. *Synthesis* **1996**, 1320–1324. (b) Shi, B.; Boyle, R. W. *J. Chem. Soc., Perkin Trans. 1* **2002**, 1397–1400. (c) Litter, B. J.; Ciringh, Y.; Lindsey, J. S. *J. Org. Chem.* **1999**, *64*, 2864–2872. (d) Nelca, G.; Turgut, G.; Mustafa, H. *Talanta* **1999**, *48*, 71–79.