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One-pot general synthesis of metalloporphyrins

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Abstract—A new general one-pot method for the synthesis of various metalloporphyrins has been developed from pyrrole and substituted aldehydes using transition metal salts. This method allows higher working concentrations than those previously reported. Along with the reported metalloporphyrins, some new metalloporphyrins were synthesized in good yield.

The diverse photo-electro and biochemical properties of porphyrins and metalloporphyrins continue to attract the attention of researchers. Porphyrin research has progressed from its pioneering synthesis by Fischer[1] in 1920s to their use as selective catalysts,[2–5] in molecular electronic devices,[6] as photodynamic therapy agents[7] and other varied applications in materials chemistry.[8] Despite such interest, the reported protocols for the preparation of sterically hindered porphyrins result only in low yields even using drastic reaction conditions.[9,10] Though substituted benzaldehydes bearing multiple functionalities in the *meta* and *para* positions are easily converted into the corresponding porphyrins, *ortho* substituted aldehydes react poorly. Numerous advances in porphyrin synthetic methodology have been made through monopyrrole tetramerisation,[11–15] dipyrromethene self-condensation in organic acid,[16] 2+2 McDonald dipyrromethane synthesis,[17] and 3+1 synthesis with a tripyrrane and a diformylpyrrole.[18] Most porphyrin syntheses proceed by tetramerisation of a monopyrrole. Rothemund[11] first synthesized tetraphenylporphyrin, and subsequently Alder–Longo[12] reported a simplified synthesis of *meso*-tetraphenylporphyrin. This method has advantages but provided low yields of sensitive porphyrins, reflecting the rather vigorous conditions, and difficult purification problems from the by-products. Recent methods used in the synthesis of tetraarylporphyrins via tetramerization of pyrroles include the use of an oxidizing cosolvent,[19] Lewis acids,[20] clays,[21] ionic liquids,[22] hydrogen peroxide in acetic acid,[14] microwave assisted synthesis of porphyrin,[23] mixtures of xylenes and chloroacetic acid,[24] vapor phase synthesis without the use of solvents or catalysts,[25] and micro-wave assisted synthesis.[26] In all these methods there are intrinsic disadvantages and most importantly the reaction fails completely with substituents in the *ortho* position. To date, there is no report available in the literature for the synthesis of metalloporphyrins directly via a condensation reaction.

In this Letter, we report a one-pot synthesis[27] of metalloporphyrins with various aldehydes, which can be used with a large variety of substituted benzaldehydes including *ortho* substituted and using different transition metals (Scheme 1). All the porphyrins and metalloporphyrins were characterized by ^1H, ^{13}C NMR, and UV–visible spectroscopy.[33] Spectroscopic data for known compounds were comparable with reported data. The present reaction conditions were optimized with respect to solvent, temperature, amount of hydrochloric acid, time of the reaction, use of different metal salts, and on the concentration of reactants used. In solvents such as ethanol, methanol, dichloromethane, and chloroform, a precipitate formed just after the addition of HCl and further addition of metal salts, followed by refluxing, yielded only trace amounts of porphyrins/metalloporphyrins. Finally, dimethylformamide was identified as the best solvent to keep the reaction mixture homogeneous. It was also observed that addition of acid prior to the pyrrole and aldehyde in DMF

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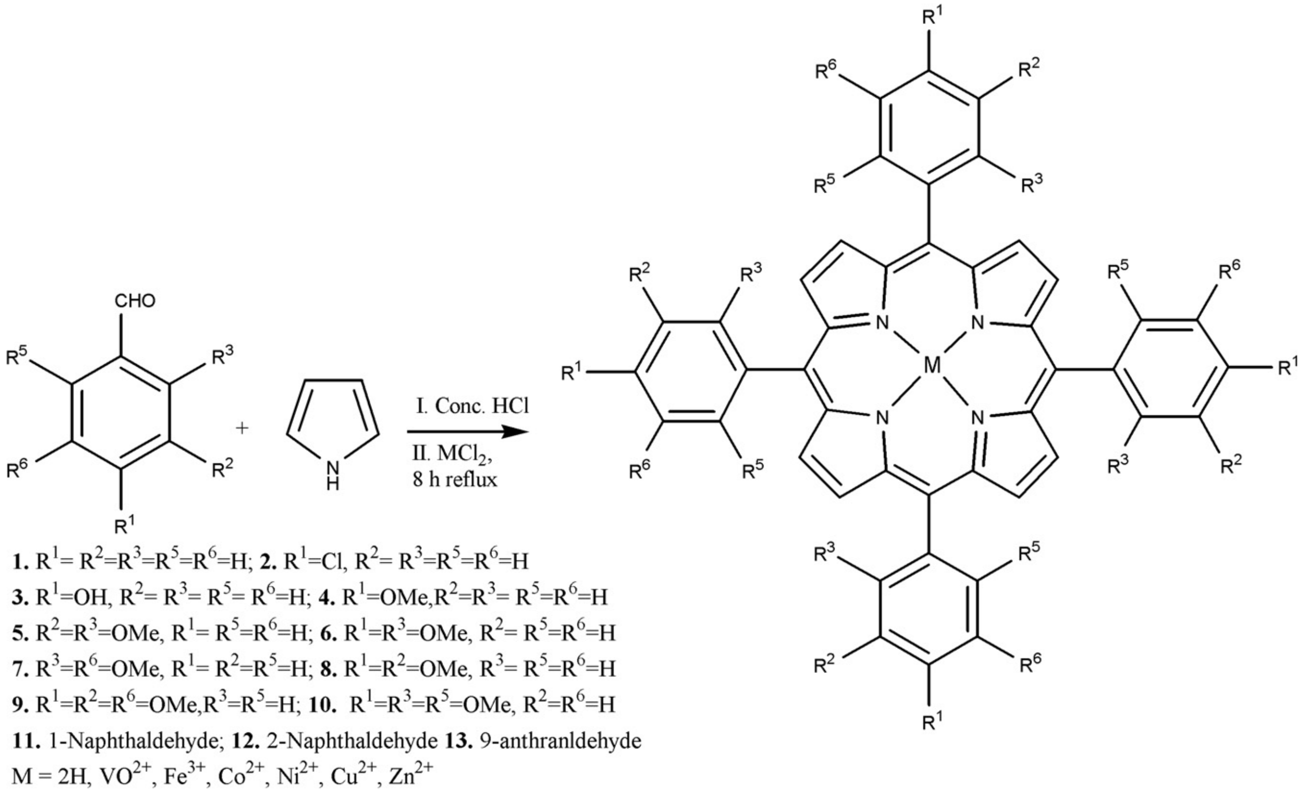

1. R^1= R^2=R^3=R^5=R^6=H; **2.** R^1=Cl, R^2= R^3=R^5=R^6=H
3. R^1=OH, R^2= R^3= R^5= R^6=H; **4.** R^1=OMe,R^2=R^3= R^5=R^6=H
5. R^2=R^3=OMe, R^1= R^5=R^6=H; **6.** R^1=R^3=OMe, R^2= R^5=R^6=H
7. R^3=R^6=OMe, R^1= R^2=R^5=H; **8.** R^1=R^2=OMe, R^3= R^5=R^6=H
9. R^1=R^2=R^6=OMe,R^3=R^5=H; **10.** R^1=R^3=R^5=OMe, R^2=R^6=H
11. 1-Naphthaldehyde; **12.** 2-Naphthaldehyde **13.** 9-anthranldehyde
M = 2H, VO^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}

Scheme 1. Reaction scheme.

resulted in lower yields than if the acid was added after the aldehyde and followed by pyrrole. Metalloporphyrin yields were lower at room temperature even on long standing.

Benzaldehyde and cupric sulfate were used to optimize the reaction conditions. In a typical reaction freshly distilled benzaldehyde (1.0 ml, 9.8 mmol) was dissolved in 50 ml of argon-purged dimethylformamide. HCl (0.5 ml, concentrated) was added followed by dropwise addition of freshly distilled pyrrole (0.68 ml, 9.8 mmol). The mixture was stirred under argon for 1 h and then ~2.5 equiv of MCl_2 (or MSO_4)[†] ($M = Cu^{2+}$, Ni^{2+}, Zn^{2+}, VO^{2+}, Co^{2+}, Fe^{2+}) were added. The final reaction mixture was refluxed for 8 h in air. The solvent was removed using a vacuum pump and the crude product was washed several times with acidic water[††] and dried. The product was dissolved in chloroform and purified by flash chromatography over silica gel using chloroform as eluent.[§] The yields of various metalloporphyrins obtained are shown in Table 1.

The best yields of metalloporphyrins were obtained with cupric sulfate and vanadyl sulfate. Using this method, we have synthesized a variety of metalloporphyrins including complexes with sterically encumbered porphyirns such as 9-anthracenylporphyrin, *meso*-tetrakis(2,3-dimethoxyphenyl)porphyrin, and *meso*-tetrakis(2,4,6-trimethoxyphenyl)porphyrin in good yields. These porphyrins fail to respond to the Adler-Longo[12] procedure, and using the Lindsey[13] methodology, the product was isolated in very low yield.

Table 2 compares yields of various copper porphyrins formed by the methods of Adler and Lindsey and those in the present study. For some of the free bases synthesized by the Adler or Lindsey method the corresponding copper complex was not known and therefore an optimistic 90% yield of a copper complex from such a base

Table 1. Yields of porphyrins with or without metal ions

Aldehyde	2H	VO^{2+}	Fe^{3+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
1	32	44	38	28	28	44	38
2	38	40[a]	32	28	28	46	42
3	18	22[a]	5	5	14	22[a]	20
4	24	33	27	24	25	34	30
5	25	32[a]	18	15[a]	20[a]	38[a]	25[a]
6	15	20[a]	15[a]	10[a]	15[a]	20[a]	17[a]
7	20	21[a]	12	12	17	24[a]	22[a]
8	25	37[a]	18	18	20	29	25
9	18	27[a]	17	17	19	19	17
10	11	11[a]	11	12	10	14	12
11	36	44[a]	32	32	35	44	39
12	32	40[a]	22[a]	28	30	44	22[a]
13	1.8	2.5[a]	2	—	2	2.5[a]	2.5[a]

[a] New metalloporphyrins.

[†] $CoCl_2{\cdot}6H_2O$, $NiCl_2{\cdot}6H_2O$, $CuSO_4{\cdot}5H_2O$, and $ZnCl_2$ were used in the synthesis of CoP, NiP, CuP, and ZnP, respectively, and in the case of VOP and FePCl, $VOSO_4{\cdot}5H_2O$ and $FeCl_2{\cdot}4H_2O$ were used, respectively. In the case of free base porphyrin, no metal salt was used.

[††] In the case of free base, only hot water was used.

[§] 0.5% Methanol–chloroform mixture was used in case of FePCl and methoxy and hydroxy group substituted porphyrins.

Table 2. Comparative yields (%) of representative copper porphyrins from the Adler, Lindsey methods and this work

Aldehydes	Adler method[12]	Lindsey method[13]	This work
1	17[28]	25[28]	44
2	14[28]	14[28]	46
3	4.9[29]	4.9[29]	22
4	14[28]	25[28]	34
5	—[a]	—[a]	38
6	18[b]	—[a]	20
7	4.5[b]	—[a]	24
8	16[b]	—[a]	29
9	12[b]	—[a]	19
10	1.8[30]	1.8[30]	14
11	18[31]	—[a]	44
12	23[32]	—[a]	44
13	0.8	—[a]	2.5

[a] Data not available.

[b] Computed value based on 90% yield from the free base.

is used for comparison. From Table 2 it is apparent that the present method produces better yields of all these porphyrin systems.

In this method, the intermediate porphyrinogen is directly metallated in the presence of a metal ion to yield metalloporphyrins under aerobic conditions. The advantage of our method is the general nature of the reaction which is valid for any type of substituted aldehyde. The yield of the metalloporphyrin was reasonably good and the reaction time was shorter than in other methods. Also, higher concentrations of reagents (0.38 M) can be employed.

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33. *Selected spectral data*: ^{1}H and ^{13}C NMR spectra were measured in CDCl$_3$ at 400 MHz and 100 MHz and UV–visible spectra were recorded in chloroform. Compound **2b**: $\lambda_{\max}$ (logε) 425 (6.2), 548 (5.0), 586 (4.1). FAB-MS: *m*/*z* 817, IR (KBr pellet, cm^{-1}): 3062 (ν Cp–H), 3062 (ν C–H Bz), 1577 (ν C=C Bz), 1449 (ν Cp–Cp), 1446 (ν Cp–N), 1357 (ν Cp–Cp), 1182 (δ Cp–H), 1089 (δ CCN), C H N (%): Calcd: C, 64.65; H, 2.96; N, 6.85. Found: C, 64.53; H, 2.88; N, 6.82.

    Compound **3b**: $\lambda_{\max}$ (logε) 427 (5.54), 552 (4.36), 609 (4.04). FAB-MS: *m*/*z* 744, IR (KBr pellet, cm^{-1}) 3510 (ν O–H), 3012 (ν Cp–H), 2920 (ν C–H Bz), 1589 (ν C–C Bz), 1481 (ν Cp–Cp), 1442 (ν Cp–N). C H N (%): Calcd: C, 71.06; H, 3.8; N, 7.53. Found: C, 71.01; H, 3.68; N, 7.49.

    Compound **5b**: $\lambda_{\max}$ (logε) 429 (5.52), 464 (4.42), 550 (4.32). FAB-MS: *m*/*z* 921, IR (KBr pellet, cm^{-1}) 2926 (ν C–H, OCH$_3$), 1605 (ν C=C Bz), 1505 (ν Cp–Cp), 1245 (ν C=O). C H N (%): Calcd: C, 67.90; H, 4.82; N, 6.09. Found: C, 67.97; H, 4.75; N, 6.01.

    Compound **5d**: $\lambda_{\max}$ (logε) 410 (5.7), 432 (4.34), 535 (3.6). FAB-MS: *m*/*z* 913, IR (KBr pellet, cm^{-1}) 2926 (ν C–H, OCH$_3$), 1605 (ν C=C Bz), 1505 (ν Cp–Cp), 1245 (ν C–O). C H N (%): Calcd: C, 68.49; H, 4.86; N, 6.14. Found: C, 68.37; H, 4.75; N, 6.07.

    Compound **5e**: ^{1}H δ 3.94–4.01 (m, 12H x, *o*-OCH$_3$), 7.11–7.36 (m, 8H, phenyl), 7.53–7.74 (m, 4H, phenyl), 8.60–8.63 (s, 8H, pyrrole); ^{13}C δ 55.9 (*o*-OCH$_3$), 60.7, 60.8, 60.9 (*m*-OCH$_3$), 122.06, 127.06, 127.28, 127.67 (*meso*-C), 135.16 (β-C, pyrrole), 149.02 (α-C, pyrrole), 149.16, 152.3, 112.3, 114.5, 131.8, 142.5, 142.63, 142.67; $\lambda_{\max}$ (logε) 414 (5.39), 527 (4.30), 559 (3.84). FAB-MS: *m*/*z* 921, C H N (%): Calcd: C, 67.90; H, 4.82; N, 6.09. Found: C, 67.97; H, 4.88; N, 6.01.

    Compound **5f**: $\lambda_{\max}$ (logε) 416 (5.68), 538 (4.34), 573 (3.60). IR (KBr pellet, cm^{-1}) 2959, 2851 (ν C–H, OCH$_3$), 1600 (ν C=C Bz), 1505 (ν Cp–Cp), 1260 (ν C–O). C H N (%): Calcd: C, 68.15; H, 4.84; N, 6.11. Found: C, 67.97; H, 4.75; N, 6.83.

    Compound **6b**: $\lambda_{\max}$ (logε) 429 (5.52), 464 (4.42), 550 (4.32). IR (KBr pellet, cm^{-1}) 2948 (ν C–H, OCH$_3$), 1600 (ν C=C Bz), 1515 (ν Cp–Cp), 1256 (ν C–O). C H N (%): Calcd: C, 67.90; H, 4.82; N, 6.09. Found: C, 67.97; H, 4.75; N, 6.01.

    Compound **6c**: $\lambda_{\max}$ (logε) 381 (4.5), 422 (4.7), 510 (4.0), 582 (3.6), 690 (3.44). IR (KBr pellet, cm^{-1}) 2936 (ν C–H, OCH$_3$), 1605 (ν C=C Bz), 1245 (ν C–O) C H N (%): Calcd: C, 66.14; H, 4.70; N, 5.93. Found: C, 66.07; H, 4.65; N, 5.87.

    Compound **6d**: $\lambda_{\max}$ (logε) 412 (5.7), 432 (4.34), 535 (3.6).

    Compound **6e**: ^{1}H δ 3.38–3.56 (m, 12H, *o*-OCH$_3$), 3.77–3.98 (m, 12H, *p*-OCH$_3$), 6.68–6.75 (m, 8H, phenyl), 7.14–7.84 (m, 4H, phenyl), 8.58 (s, 8H, pyrrole); ^{13}C δ 55.5 (*o*-CH$_3$), 103.3 (*meso*-C), 142.94 (α-C, pyrrole), 131.56 (β-C, pyrrole), 160.9; $\lambda_{\max}$ (logε) 418 (5.12), 530 (4.00). IR (KBr pellet, cm^{-1}) 2956 (ν C–H, OCH$_3$), 1600 (ν C=C Bz), 1248 (ν C–O). C H N (%): Calcd: C, 68.51; H, 4.86; N, 6.15. Found: C, 68.47; H, 4.75; N, 6.11.

    Compound **6g**: ^{1}H δ 3.74–3.80 (m, 12H, *o*-OCH$_3$), 3.9–4.01 (m, 12H, *p*-OCH$_3$), 6.76–6.80 (m, 8H, phenyl), 7.69–7.81 (m, 4H, phenyl), 8.76 (s, 8H, pyrrole); ^{13}C δ 55.5 (*o*-OCH$_3$), 55.8 (*p*-OCH$_3$), 103.15, 116.1, 124.5 (*meso*-C), 135.86 (β-C, pyrrole), 150.5 (α-C, pyrrole), 105.6, 130.74, 131.3, 160.15, 160.98; $\lambda_{\max}$ (logε) 422 (5.66), 549 (4.36), 589 (4.55). FAB-MS: *m*/*z* 856, IR (KBr pellet, cm^{-1}): 2945 (ν C–H, OCH$_3$), 1605 (ν C=C Bz), 1248 (ν C–O). C H N (%): Calcd: C, 73.05; H, 5.42; N, 6.55. Found: C, 72.97; H, 5.35; N, 6.39.

    Compound **7b**: $\lambda_{\max}$ (logε) 427 (5.41), 460 (4.52), 548 (4.25), 660 (3.74). FAB-MS: *m*/*z* 921, IR (KBr pellet, cm^{-1}): 2926 (ν C–H, OCH$_3$), 1605 (ν C=C Bz), 1245 (ν C–O). C H N (%): Calcd: C, 67.90; H, 4.82; N, 6.09. Found: C, 67.97; H, 4.75; N, 6.01.

    Compound **8b**: $\lambda_{\max}$ (logε) 430 (5.78), 508 (3.92), 547 (4.61), 586 (3.90). FAB-MS: *m*/*z* 921, IR (KBr pellet, cm^{-1}) 2932 (ν C–H, OCH$_3$), 1582 (ν C=C Bz), 1259 (ν C–O). C H N (%): Calcd: C, 67.90; H, 4.82; N, 6.09. Found: C, 67.97; H, 4.75; N, 6.01.

    Compound **9b**: $\lambda_{\max}$ (logε) 429 (6.05), 550 (4.89), 592 (4.17). FAB-MS: *m*/*z* 1041, IR (KBr pellet, cm^{-1}) 2935 (ν C–H, OCH$_3$), 1578 (ν C=C Bz), 1234 (ν C–O). C H N (%): Calcd: C, 64.67; H, 5.04; N, 5.39. Found: C, 64.57; H, 4.95; N, 5.27.

    Compound **10b**: $\lambda_{\max}$ (logε) 429 (5.97), 550 (4.77), 587 (3.95). FAB-MS: *m*/*z* 1041, IR (KBr pellet, cm^{-1}) 2939 (ν C–H, OCH$_3$), 1607 (ν C=C Bz), 1203 (ν C–O). C H N (%): Calcd: C, 64.67; H, 5.04; N, 5.39. Found: C, 64.57; H, 4.95; N, 5.27.

    Compound **11b**: $\lambda_{\max}$ (logε) 429 (4.36), 549 (3.0), 583 (2.0). FAB-MS: *m*/*z* 881, IR (KBr pellet, cm^{-1}) 3048 (ν Cp–H), 3026 (ν C–H, Bz), 1578 (ν C=C Bz). C H N (%): Calcd: C, 81.90; H, 4.12; N, 6.37. Found: C, 81.81; H, 4.10; N, 6.31.

    Compound **12b**: $\lambda_{\max}$ (logε) 430 (5.7), 551 (4.4), 588 (3.6). FAB-MS: *m*/*z* 881, IR (KBr pellet, cm^{-1}) 3057 (ν Cp–H), 3026 (ν C–H, Bz), 1578 (ν C=C Bz). C H N (%): Calcd: C, 81.90; H, 4.12; N, 6.37. Found: C, 81.81; H, 4.10; N, 6.31.

    Compound **12c**: $\lambda_{\max}$ (logε) 380 (4.6), 424 (4.9), 512 (41), 583 (3.53), 665 (3.53).

    Compound **13b**: $\lambda_{\max}$ (logε) 428 (6.0), 551 (4.94), 584 (3.74), 642 (3.32). IR (KBr pellet, cm^{-1}) 3062(ν Cp–H), 3021 (ν C–H, Bz), 1572 (ν C=C Bz). C H N (%): Calcd: C, 84.41; H, 4.11; N, 5.19. Found; C 84.49, H 4.09, N 5.14.

    Compound **13f**: $\lambda_{\max}$ (logε) 425 (5.55), 543 (4.63), 579 (4.11). IR (KBr pellet, cm^{-1}) 3048 (ν Cp–H), 3016 (ν C–H, Bz), 1578 (ν C=C Bz). C H N (%): Calcd: C, 84.78; H, 4.12; N, 5.20. Found: C, 84.73; H, 4.09; N, 5.15.