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Toward carboxylate group functionalized A_4, A_2B_2, A_3B oxaporphyrins and zinc complex of oxaporphyrins

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ABSTRACT

Series of new oxaporphyrins were isolated from the reaction of furan-1,4-diol, pyrrole, and an aldehyde under Lindsey's conditions, which gives easy access to ester group functionalized oxaporphyrins. The ester substituents can be readily hydrolyzed to terminal carboxylic acid in the presence of KOH. The Zn(II) oxaporphyrins have been synthesized from the reaction of free base with $ZnCl_2$ and fully characterized by variable temperature NMR, 2D NMR, and single crystal X-ray diffraction studies.

1. Introduction

Porphyrins and their derivatives are one of the most important classes of heterocycles attracting interdisciplinary research and having broad range of application. Porphyrins play key roles in the field of photodynamic therapy (PDT),[1] DNA photocleavage,[2] organic light emitting diodes (OLED),[3] dye sensitized solar cells (DSSC),[4] organocatalysis,[5] and asymmetric catalysis.[6] In additional to the studies using regular N_4-porphyrins, replacement of pyrrolic nitrogen with a heteroatom to provide new physicochemical properties is an attractive aspect of study. Alternation of pyrrolic nitrogen with various heteroatoms, such as oxygen, sulfur, selenium, or phosphorus explores the notable changes in terms of electronic structure, physicochemical, spectroscopic, and metal binding properties.[7] Newly developed water soluble thiaporphyrin and selenaporphyrins found competitive candidates for photodynamic therapy (PDT).[1h] Heteroporphyrins with one or more functional groups on *meso* position is one of the important building blocks in synthesis of hybrid porphyrin diad, triad, tetrad, pentad, nonad or arrays.[8] Synthesis, characterization, and various properties of thiaporphyrins have been extensively studied by Ravikanth[8,9a–f] and other researchers.[1h,9g,h] Moreover, Matano and co-workers reported synthesis, structure, reactivity, optical, and redox properties of new phosphaporphyrins.[8a,b,10] Although there are several articles focusing on synthesis and characterization of heteroporphyrins,[11] reports on their metal complexes are still limited. Latos-Grażyński and co-workers explored the most promising and pioneering study on metal binding properties of Ni(II) thiaporphyrin,[12] Cu(II) thiaporphyrin,[13] Fe(II) thiaporphyrin,[12d] Pd(II) thiaporphyrin,[14] Fe(II) oxaporphyrin,[15,16a] Ni(II) oxaporphyrin,[16] Ni(II) dioxaporphyrin,[16b] and Ni(II) selenaporphyrin.[17] Our group has reported the exclusive metal complex of dithiaporphyrin, $[Ru(S_2TTP)Cl_2]$.[18] Metal binding properties of Cu(II) with oxaporphyrin, dioxaporphyrin, and oxathiaporphyrin were reported by Chandrashekhar and co-workers.[19] Arnold and co-workers synthesized and characterized lithium 21-thiaporphyrin complex.[20] To the best of our knowledge, there is only one report on Zn(II) oxaporphyrin with incomplete characterizations.[21] Herein we report the synthesis and characterization of newly designed oxaporphyrins with terminal carboxylic acid functional groups and their Zn(II) oxaporphyrin complexes as a step toward applying oxaporphyrins and their metal complexes to energy related research areas.

2. Results and discussion

Condensation of 1 equiv of 2,5-bis(arylhydroxymethyl)furan with 2 equiv of aryl aldehyde and 3 equiv of pyrrole under regular porphyrin forming conditions followed by separation of reaction products by column chromatography resulted in symmetrical A_4 and A_2B_2 ester functionalized oxaporphyrins while the A_3B oxaporphyrin with a lower symmetry can be prepared using α-aryl-2,5-furandimethanol as the starting diol.[10h] Hydrolysis of ester

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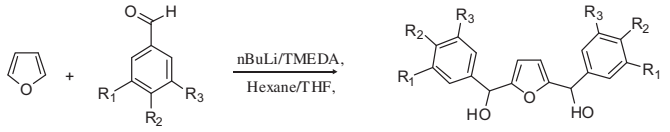
functionalized oxaporphyrins to free-base carboxylic acid oxaporphyrins can be easily achieved by using aqueous KOH.[22] The zinc metalation of these oxaporphyrins can be readily obtained from reaction with molar excess of $ZnCl_2$ by using literature methods.[23]

2.1. Synthesis of 2,5-bis(arylhydroxymethyl)furan

The symmetrical diols **1**, **2**, and, **3** were synthesized with slight modification of the literature method.[10h] Condensation of 1 equiv of 2,5-dilithiated furan with 2.5 equiv of corresponding aryl carboxaldehyde in THF at 0 °C yields required diols after usual work-up and separation methods. The structures of studied aldehydes and products with respective yields are cited in Table 1. TLC analysis of the reaction mixture showed the exclusive formation of symmetrical diol with some unreacted aldehyde. The reaction mixtures were purified by silica gel column chromatography using ethyl acetate/hexane (30:70) as eluent to afford diols **1**, **2**, and **3** in 78%, 37%, and 35% yield, respectively. All the three diols were characterized by ^{1}H NMR, ^{13}C NMR, IR, and mass spectrometry.

Table 1
Synthesis of 2,5-bis(arylhydroxymethyl)furan[a]



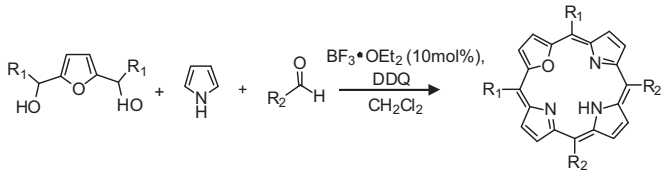
Product	R_1	R_2	R_3	Yield (%)[b]
1	–H	$-CH_3$	–H	78
2	$-OCH_3$	$-OCH_3$	$-OCH_3$	37
3	–H	$-COOCH_3$	–H	35

[a] Reactions conditions: (i) 37 mmol ^{n}BuLi (2.5 M solution in hexane), 37 mmol tetramethylethylenediamine (TMEDA), 50 mL hexane, 15 mmol furan, rt, 1 h; (ii) 37 mmol aldehyde, 30 mL hexane, 0 °C, 1 h.
[b] Yield of analytically pure product.

2.2. Synthesis of A_4 and A_2B_2 oxaporphyrins

The usual condensation of symmetrical diol with aromatic aldehyde and pyrrole in the presence of catalytic amount of $BF_3 \cdot OEt_2$, followed by oxidation with DDQ gives oxaporphyrins as represented in Table 2. The oxaporphyrins **4**–**9** were prepared by condensing 1 equiv of respective diols **1**–**3**, 2 equiv of corresponding aldehyde and 3 equiv of pyrrole in CH_2Cl_2 in the presence of catalytic amount of $BF_3 \cdot OEt_2$ followed by oxidation with DDQ. TLC as well as mass spectrum analysis of the crude reaction mixture showed the formation of only two porphyrins, the desired oxaporphyrin and N_4-porphyrin. Formation of the dioxaporphyrin was not observed, which is in agreement with the previous reports.[10h] All six oxaporphyrins, **4**–**9**, are achieved in reasonable yields and were characterized by ^{1}H NMR, IR, absorption, and mass spectroscopy.

Table 2
Synthesis of oxaporphyrin[a]



Product	R_1	R_2	Yield (%)[b]
4	4-MeC_6H_4	4-MeC_6H_4	10
5	3,4,5-$MeOC_6H_2$	3,4,5-$MeOC_6H_2$	10
6	4-$MeO_2CC_6H_4$	4-$MeO_2CC_6H_4$	7
7	4-MeC_6H_4	4-$MeO_2CC_6H_4$	9
8	4-$MeO_2CC_6H_4$	4-MeC_6H_4	9
9	4-$MeO_2CC_6H_4$	3,5-^{t}BuC_6H_3	14

[a] Reaction conditions: (i) 1 mmol diol, 3 mmol pyrrole, 2 mmol aldehyde, 10 mol % $BF_3 \cdot OEt_2$ (48%), 100 mL CH_2Cl_2, 1 h (ii) 1 mmol DDQ, 1 h.
[b] Yield of analytically pure product.

The benchmark compound oxaporphyrin **4** has been reported by Lindsey[10b] and Lee[10c] in more than four steps from starting material. In our current protocol oxaporphyrin **4** was achieved in only two steps with reasonable yield. The characterization data of the oxaporphyrin **4** is in agreement with the literature reports.[10b]

The ^{1}H NMR spectra of the oxaporphyrins **4**–**9** recorded in $CDCl_3$ show a C_2-axis embedded porphyrinic pattern with some minor differences depending upon the substituents. As expected β-furan protons appears as singlet in the most downfield region, followed by β-pyrrolic protons opposite to furan ring and β-pyrrolic protons adjacent to furan ring. In oxaporphyrin **6** and **8**, β-pyrrolic protons adjacent to furan ring give sharp doublets with a coupling constant of 4.5 Hz and 4.8 Hz, respectively (see Supplementary data). The δ values of the protons on aromatic rings vary in a range of 7–8.5 ppm, whereas the aliphatic protons are observed in the range of 1.5–4.5 ppm depending on the substituents. As reported in literature the inner NH signal was not observed on ^{1}H NMR spectra when commercially supplied $CDCl_3$ was used as the solvent due to the more basic nature of oxaporphyrins in comparison with N_4-porphyrin.[10b,e]

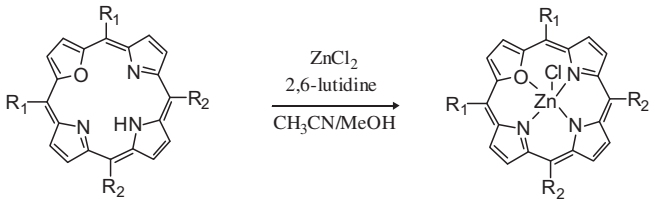
The IR spectra of oxaporphyrin **6**–**9** show stretching frequency at around 1723 cm^{-1} supporting the presence of carbonyl group. The UV–vis absorption spectra of oxaporphyrin **4**–**9** in CH_2Cl_2 displayed one *Soret* band and four indistinct *Q* bands. The $Q_x(0,0)$ band at ~672 nm is red-shifted significantly in comparison with ~649 nm for N_4-porphyrins. The *Soret* band for oxaporphyrin **5** (426 nm) with its electron donating groups experiences the highest degree of red-shift in comparison to all oxaporphyrins. The oxaporphyrin **4** (421 nm) shows comparable *Soret* band with its N_4-porphyrin (~419 nm).[24] Based on these observations, the oxaporphyrins bearing identical substituents exhibit red-shifts absorption bands compared with the parent N_4-porphyrins. This is in consistent with the literature report that, although not as significant as dioxaporphyrins or thiaporphyrins, the slight stabilization of the LUMO and destabilization of HOMO results red shift on the absorption spectra of oxaporphyrin.[25]

2.3. Synthesis and spectral characterization of Zn(II) complexes

Insertion of zinc ion has been readily achieved[22] with high yields by reacting the free base oxaporphyrins **4**–**9** with molar excess zinc chloride in the presence of 2,6-lutidine as listed in Table 3. This method is broadly applied for the metalation of regular N_4-porphyrins but has never been applied for the preparation of zinc(II) oxaporphyrins.[8a,b,10] Monitoring on reaction progress showed rapid change in solution color, which accompanied by splitting of *Soret* band and red-shifting in *Q* bands on absorption spectra.[26] After work-up, the formation of Zn(II) complex was confirmed by the observation of mass spectra with m/z corresponding to $[M-Cl]^+$ of Zn(II) oxaporphyrin **10**–**14**, or **15**.

The NMR spectra of Zn(II) complexes show significant changes, compared to those of free base oxaporphyrins. The furan, pyrrole, and aromatic protons shift downfield, whereas pyrrole and aromatic protons show increased number of resonances resulted from less symmetrical square-pyramidal coordination geometry. Interestingly, except complex **12**, the NMR spectra of Zn(II) oxaporphyrins

Table 3
Synthesis of zinc(II) complexes[a]



Product	R_1	R_2	Yield(%)[b]
10	4-MeC_6H_4	4-MeC_6H_4	80
11	3,4,5-$MeOC_6H_2$	3,4,5-$MeOC_6H_2$	90
12	4-$MeO_2CC_6H_4$	4-$MeO_2CC_6H_4$	96
13	4-MeC_6H_4	4-$MeO_2CC_6H_4$	80
14	4-$MeO_2CC_6H_4$	4-MeC_6H_4	78
15	4-$MeO_2CC_6H_4$	3,5-$^tBuC_6H_3$	99

[a] Reaction conditions: 25 mg oxaporphyrin, molar excess $ZnCl_2$, 2,6-lutidine, 20 mL CH_3CN/MeOH (3:1), 1 h.
[b] Yield of analytically pure product.

demonstrate broadened signals for the resonances on *meso* phenyl protons at room temperature suggesting that the tolyl groups are under dynamic process. For the Zn(II) oxaporphyrin **10**, the eight doublets from four tolyl *meso*-substituents can be classified into two groups with significantly different half-widths. The temperature-dependent ^{1}H NMR study on Zn(II) oxaporphyrin **10** was performed and the results are overlaid in Fig. 1 to demonstrate that the tolyl resonances at 8.25, 7.93, 7.58, and 7.52 ppm completely coalesce at 60 °C, while, at the same temperature, resonances from another set of tolyl groups are still visible. All resonances are sharpened when the temperature is decreased and, at −60 °C, two of the most downfield phenyl resonances merge into a triplet resonance at 8.215 ppm. Similar dynamic behavior on NMR signals of *meso* tolyl rings in ruthenium dithiaporphyrin complex has been reported as a result of the reduced steric constrain between tolyl *ortho*-protons and β pyrrolic protons from a highly twisted core.[18] However, it is unanticipated to observe a dramatic difference on rotational energy barriers for the tolyl groups adjacent to furan group in comparison with those adjacent to the pyrrole ring.

The absorption spectra show distinctively different pattern for free base oxaporphyrins and their metal complexes.[25] A split *Soret* band with λ_{max} at 426 and 442 nm is observed for zinc oxaporphyrin **12** as shown in Fig. 2, which is in consistent with the breaking of orbital degeneracy because of the formation of a less symmetrical five coordinated zinc oxaporphyrin complex. Similar split *Soret* band has been observed in the iron(II) and copper(II) complex of oxaporphyrin. Noticeably, significant red-shifted with an *oxorhodo*-type pattern are observed in the *Q* bands region of **12**. Near identical *Soret* and *Q* band patterns are observed among zinc oxaporphyrins with an either A_4 or A_2B_2 *meso*-substituents.

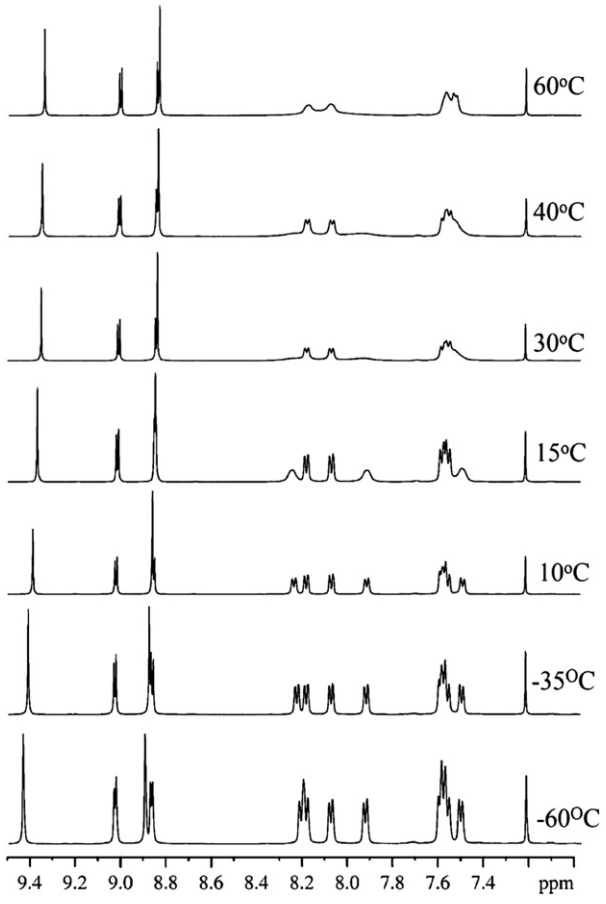


Fig. 1. Variable temperature NMR spectra of Zn(II) oxaporphyrin **10**.

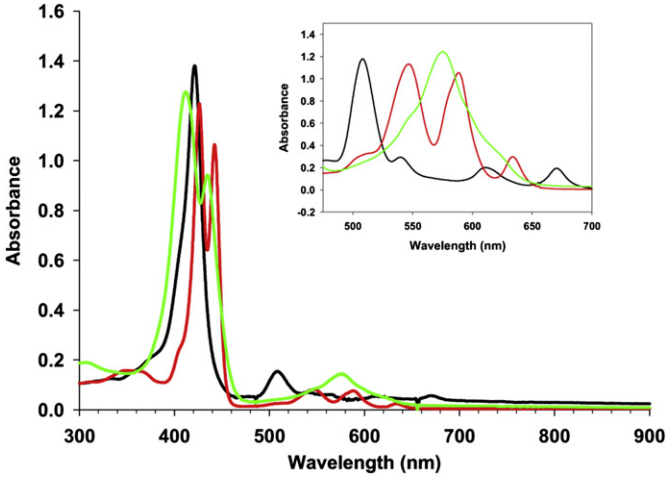


Fig. 2. Absorption spectra of oxaporphyrin **6** (—), Zn(II) oxaporphyrin **12** (—), and oxaporphyrin **16** (—). The inset depicts the spectra in the *Q* band region under higher concentration.

Structure of oxaporphyrin zinc(II) complex **12** has been confirmed by the single crystal X-ray diffraction study. The molecular structure with thermal ellipsoids is shown in Fig. 3. The zinc center adopted a five coordinated square-pyramidal geometry with chloride sit in the apical position. The bond distance of 2.2078(16) Å is in the normal

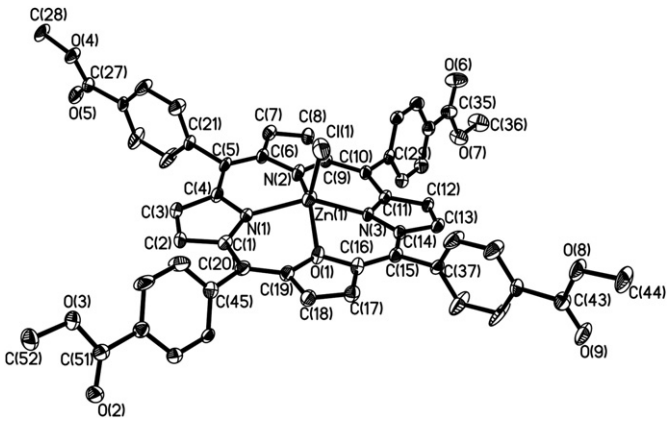


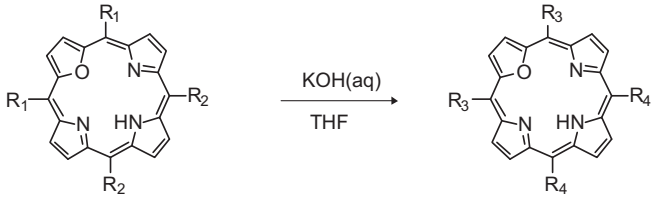
Fig. 3. The X-ray crystal structure of Zn(II) oxaporphyrin **12**.

range for Zn–Cl bond. The zinc metal ion deviates 0.59 Å from the four-atom-mean-plane defined by three inner core nitrogens and the oxygen atom on the furan moiety. According to the thermal parameters, the oxygen atom of furan moiety has been assigned to disorder with its *trans* pyrrolic nitrogen with 50% occupancy on each site. The disordering precludes a precise comparison on the Zn–O and Zn–N bond distances. The porphyrin core in the structure of **12** adopts a significant S_4 ruffling distortion with an average atomic deviation of 0.153 Å from the 24-atom-mean-plane on the oxaporphyrin core. Noticeably, limited reports are available on the crystal structures of metallooxaporphyrins[15,16b] and compound **12** is the first structurally characterized zinc oxaporphyrin complex.

2.4. Base hydrolysis to the carboxylic acid functionalized oxaporphyrin

The free base oxaporphyrins **16**–**18**, and **19**, all with two carboxylic acid functional groups, can be achieved in quantitative yields by hydrolysis of their corresponding oxaporphyrin **6**–**8**, and **9** using aqueous KOH as represented in Table 4.[21] The obtained product was characterized by ^{1}H NMR, IR, absorption, and mass spectroscopy. As per the expectations, ^{1}H NMR spectrum shows significant downfield shifts of all signals comparing to its starting oxaporphyrin. For example in the case of oxaporphyrin **19** the furan protons downshifted 0.26 ppm in comparison to its starting oxaporphyrin **9** supporting the presence of carboxylic acid groups (see Supplementary data). Dramatic changes observed in absorption spectroscopy are shown in Fig. 2. Dicarboxylic acid oxaporphyrin **16** experiences blue shift accompanied by splitting in *Soret* band, whereas *Q* bands becomes broad and indefinite in comparison with its oxaporphyrin **6** and zinc complex **12**. The broadening of absorption bands presumably is a result of molecular aggregation through intermolecular hydrogen bonding interactions and/or porphyrin π–π interactions.

Table 4
Hydrolysis of oxaporphyrin[a]

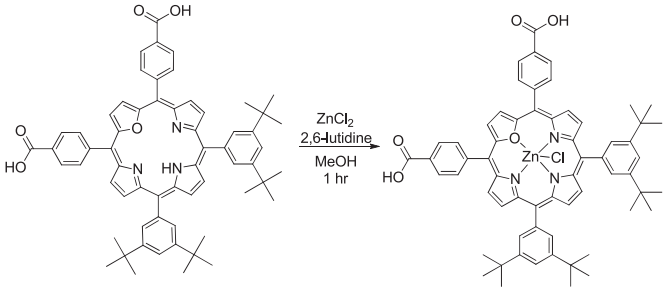


Product	R1	R2	R3	R4	Yield(%)[b]
16	4-$MeO_2CC_6H_4$	4-$MeO_2CC_6H_4$	4-$HO_2CC_6H_4$	4-$HO_2CC_6H_4$	99
17	4-MeC_6H_4	4-$MeO_2CC_6H_4$	4-MeC_6H_4	4-$HO_2CC_6H_4$	97
18	4-$MeO_2CC_6H_4$	4-MeC_6H_4	4-$HO_2CC_6H_4$	4-MeC_6H_4	99
19	4-$MeO_2CC_6H_4$	3,5-^{t}BuC_6H_3	4-$HO_2CC_6H_4$	3,5-^{t}BuC_6H_3	98

[a] Reaction conditions: 25 mg oxaporphyrin, 500 mg aqueous KOH, 50 mL THF, reflux, 10 h.
[b] Yield of analytically pure product.

2.5. Synthesis of zinc(II) oxaporphyrin dicarboxylic acid complexes

The conversion of free base oxaporphyrin **19** to zinc(II) oxaporphyrin **20** is represented in Scheme 1. Treatment of the free base oxaporphyrin **19** in MeOH with excess $ZnCl_2$ and drops of 2,6-lutidine gives zinc(II) oxaporphyrin **20**. However, the Zn(II) metalation on oxaporphyrin **16**, **17**, and **18** turned into highly insoluble precipitation in all common organic solvents and no further characterization was attempted. The Zn(II) oxaporphyrin complex **20** was characterized by ^{1}H NMR, IR, and mass spectroscopy. The absorption spectrum of Zn(II) oxaporphyrin complex **20** (421 nm) shows marked red-shift in *Soret* band compared to free base dicarboxylic acid oxaporphyrin **19** (417 nm). (see Supplementary data).



Scheme 1. Synthesis of zinc(II) oxaporphyrin **20**. Reaction conditions: 20 mg oxaporphyrin, molar excess $ZnCl_2$, 2,6-lutidine, 20 mL MeOH 1 h. Analytically pure product obtained in quantitative yield.

2.6. Synthesis of A_3B type zinc(II) oxaporphyrin monocarboxylic acid complexes

The A_3B type zinc oxaporphyrion **26** was prepared as represented in Scheme 2. Furan-2-carbaldehyde was reduced to furan-2-methanol **21** using $NaBH_4$ in 94% yield. Furan-2-methanol on treatment with 3,4,5-trimethoxybenzaldehyde in presence of ^{n}BuLi and tetramethylethylenediamine (TMEDA) gives α-(3,4,5-trimethoxyphenyl)-2,5-furandimethanol **22**, which undergoes regular porphyrin forming condensation with 3 equiv of pyrrole and 2 equiv of 3,4,5-trimethoxybenzaldehyde gives A_3B type *meso*-unsubstituted oxaporphyrin **23**. Oxaporphyrin **23** on reaction with NBS in CH_2Cl_2 gives *meso* brominated oxaporphyrin **24**. The metalation of oxaporphyrin **24** using $ZnCl_2$ gives Zn(II) oxaporphyrin **25**. Zn(II) oxaporphyrin **25** was characterized by ^{1}H NMR, IR, Mass, absorption spectroscopy, and single crystal X-ray crystallography. Zn(II) oxaporphyrin **25** undergoes Sonogashira coupling with 4-ethynylbenzoic acid under reported reaction conditions gives A_3B type zinc(II) oxaporphyrin monocarboxylic acid complexes **26** in 31% yield, which is successfully characterized by ^{1}H NMR, IR, Mass, and absorption spectroscopies. A noticeable difference between the spectroscopic properties of oxaporphyrin **25** and ethynyl group appended oxaporphyrin **26** is the significant red shift on the Soret band from 434 to 451 nm and the Q band from 449 to 461 nm. The presence of ν(C≡C) stretching band at 2130 cm^{-1} further signifies the presence of ethynyl moiety.

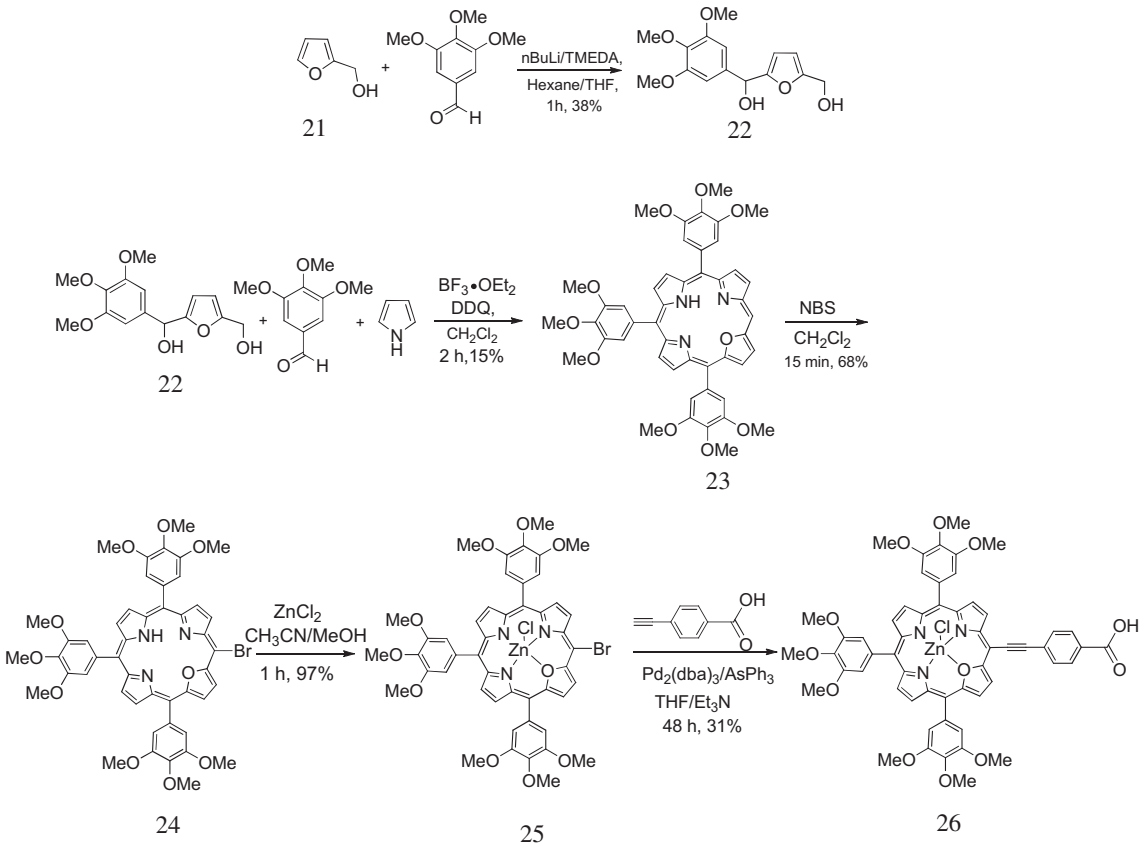
3. Conclusion

In conclusion the current article reveals facile and straight forward synthesis of A_4, A_2B_2, and A_3B oxaporphyrins with carboxylic acid as a terminal functional group. We have successfully investigated the preparation of functionalized Zn(II) oxaporphyrin complexes with fully characterizations. Free base oxaporphyrin dicarboxylic acids can be easily obtained from the hydrolysis of their corresponding ester oxaporphyrin, which provide an important functional group for exploring the potential to apply oxaporphyrins in material science or biological research areas.

4. Experimental section

4.1. General information

All chemicals were purchased from Acros Organics and Sigma Aldrich and used directly without further purification. ^{1}H NMR and



Scheme 2. Synthesis of Zn(II) oxaporphyrin **26**. See Experimental section for reaction conditions and more synthetic details. Zn(II) oxaporphyrin **25** was characterized by single crystal X-ray crystallography. Reported yields are of analytically pure products.

^{13}C NMR spectra were recorded on a Bruker 300 or 400 MHz spectrometer and performed in $CDCl_3$ (δ=7.26 ppm) and CD_3OD (δ=3.31 ppm) solutions. Chemical shifts are reported in parts per million. Coupling constants *J* are reported in hertz. The signals are described as s: singlet; d: doublet; dd: doublet of doublet; m: multiplet, and br: broad. FT-IR measurements were carried out by a Perkin–Elmer Paragon 1000 spectrophotometer. The high-resolution mass spectra and HR-FAB were conducted on a JMS-700 double focusing mass spectrometer. UV–vis spectra were recorded with an Agilent 8453 spectrophotometer. Flash chromatography was carried out by using silica gel (40–63 μm, Merck). Analytical TLC was performed on Merck silica gel plates. Melting points were recorded using an Electrothermal capillary melting point apparatus.

4.2. Single crystal X-ray diffraction data collection for 12

The measurement was performed on a Burker APEX diffractometer using Mo Kα radiation (λ=0.71073 Å) at *T*=100 K in ω scan mode with $2\theta_{max}$=52.7°. Crystals were prepared by the slow diffusion of hexane into a solution of **12** in CH_2Cl_2 to yield a brown crystal of $C_{52}H_{36}ClN_3O_9Zn$. Crystal data for **12**: triclinic space group *P*−1, *a*=11.525(2), *b*=14.575(3), *c*=16.811(3) Å, α=78.55(3), β=70.61(3), γ=76.38(3)°, *V*=2566.5(9) Å^3, ρ_{calcd}=1.226 Mg/m^3, *Z*=2; total no. of reflections collected: 34,254; no. of independent reflections: 10,090 [*R*(int)=0.0883]. An absorption correction based on a least-squares fit against $|F_c|-|F_o|$ differences was applied with μ=0.585 mm^{-1}, $T_{min.}$=0.9547, and $T_{max.}$=0.9713. The structure was solved by direct methods with SHELXTL v.6.14 and refined against [F2] using SHELXTL.[27] **1997**. The final R_1 and wR_2 indices (for $I>2\sigma(I)$) are 0.0730 and 0.1621, respectively, with max./min. residual electron density: +0.965/−0.728 e A^{-3}; H atoms were calculated from the SHELXTL program and fixed for further refinements.

4.3. Furan-2,5-diylbis(*p*-tolylmethanol) (1)

Distilled dry *n*-hexane (50 mL) was added to a 250 mL two-necked, round-bottomed flask fitted with a rubber septum and nitrogen gas inlet tube. Tetramethylethylenediamine (TMEDA, 5.6 mL, 37.5 mmol) and ^{n}BuLi (14.8 mL of 2.5 M solution in hexane, 37 mmol) were added and solution was stirred under nitrogen for 10 min. Furan (1.08 mL, 15 mmol) was then added and stirred for another 1 h at ambient temperature. As the reaction progressed, turbid solution appeared indicating the formation of the 2,5-dilithiated salt of furan. Reaction mixture was cooled to 0 °C in an ice bath; to it an ice-cold solution of *p*-tolualdehyde (4.3 mL, 37 mmol) in dry THF (30 mL) was added and stirred for 15 min. Reaction was quenched by adding an ice-cold saturated NH_4Cl aqueous solution. Organic layer was washed with water and brine solution, and dried over anhydrous $MgSO_4$. Solvent was removed on rotary evaporator to afford the crude compound. TLC analysis showed only two spots corresponding to unchanged *p*-tolualdehyde and desired diol **1**. Crude product was purified on silica gel column chromatography using 30% ethyl acetate/hexane to afford diol **1** as a yellow solid (3.60 gm, 78% yield); mp: 110–112 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ=7.27 (d, *J*=8.1 Hz, 4H), 7.14 (d, *J*=8.1 Hz, 4H), 5.89 (d, *J*=2.7 Hz, 2H), 5.89 (d, *J*=5.1 Hz, 2H), 3.29 (br s, 2H), 2.35 (s, 6H); ^{13}C NMR (300 MHz, $CDCl_3$) δ=156.07, 137.62, 129.00, 126.61, 126.57, 108.04, 69.71, 21.11; IR (KBr, cm^{-1}): 3312, 3016, 2919, 1613, 1411, 1014, 856, 797, 767; HRMS-ESI calcd for $C_{20}H_{20}O_3Na$ ([M+Na]$^+$): 331.1310, found 331.1308.

4.4. Furan-2,5-diylbis((3,4,5-trimethoxyphenyl)methanol) (2)

The 2,5-dilithiofuran was prepared by treating furan (1.08 mL, 15 mmol) with ^{n}BuLi (14.8 mL of 2.5 M solution in hexane, 37 mmol) in the presence of tetramethylethylenediamine (TMEDA, 5.6 mL, 37.5 mmol) in *n*-hexane (50 mL). The condensation of 2,5-dilithiofuran with 3,4,5-trimethoxybenzaldehyde (7.35 gm, 37.5 mmol) under the same experimental conditions and purification procedures as mentioned for diol **1**, afford the diol **2** as a sticky yellow solid (2.55 gm, 37% yield); mp 41–43 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ=6.59 (d, *J*=4.5 Hz, 4H), 5.96 (d, *J*=3.0 Hz, 2H), 5.65 (s, 2H), 3.78 (s, 6H), 3.74 (s, 12H), 3.56 (br s, 2H); ^{13}C NMR (300 MHz, $CDCl_3$) δ=155.81, 153.05, 137.40, 136.27, 108.04, 103.57, 69.90, 60.73, 55.97; IR (KBr, cm^{-1}): 3430, 2940, 2839, 1594, 1506, 1462, 1419, 1331, 1232, 1124, 1006, 84, 772, 796; HRMS-ESI calcd for $C_{24}H_{28}O_9Na$ ($[M+Na]^+$): 483.1631, found 483.1632.

4.5. Methyl 4-[hydroxyl(5-{hydroxyl[3-(methoxycarbonyl) phe-yl]methyl}furan-2-yl)methyl]benzoate (3)

The 2,5-dilithiofuran was prepared by treating furan (1.08 mL, 15 mmol) with ^{n}BuLi (14.8 mL of 2.5 M solution in hexane, 37 mmol) in the presence of tetramethylethylenediamine (TMEDA, 5.6 mL, 37.5 mmol) in *n*-hexane (50 mL). The condensation of 2,5-dilithiofuran with methyl 4-formylbenzoate (6.19 gm, 37.5 mmol) under the same experimental conditions and purification procedures as mentioned for diol **1**, afforded the diol **3** as a yellow solid (2.1 gm, 35% yield). Mp 112–114 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ=7.96 (d, 8.4 Hz, 4H), 7.42 (d, 8.4 Hz, 4H), 5.90 (d, 2.1 Hz, 2H), 5.77 (d, 3.9 Hz, 2H), 3.89 (s, 6H), 3.47 (br s, 2H); ^{13}C NMR (300 MHz, $CDCl_3$) δ=166.86, 155.33, 145.49, 129.48, 126.42, 126.37, 108.44, 69.14, 52.06; IR (KBr, cm^{-1}): 3286, 2953, 1719, 1609, 1432, 1278, 1181, 1018, 814, 738; HRMS-ESI calcd for $C_{22}H_{20}O_7Na$ ($[M+Na]^+$): 419.1107, found 419.1111.

4.6. Oxaporphyrin (4)

In a 250-mL round-bottom flask CH_2Cl_2 (100 mL) was added and purged with nitrogen for 15 min. In this flask furan-2,5-diylbis(*p*-tolylmethanol) **1** (308 mg,1 mmol), *p*-touladehyde (236 μL, 2 mmol), and pyrrole (206 μL, 3 mmol) were dissolved. $BF_3\cdot Et_2$ (48%) (30 μL, 0.1 mmol) was added and the reaction mixture was stirred at room temperature for 1 h. DDQ (227 mg, 1 mmol) was added and stirred for an additional 1 h in air. TLC analysis indicated the formation of the desired oxaporphyrin **4** and N_4-porphyrin. Solvent was evaporated on rotary evaporator and crude compound was passed through a short neutral alumina column using 10% acetone/CH_2Cl_2 as eluent. The obtained material was separated by silica gel column chromatography using 20% acetone/CH_2Cl_2 as eluent gives oxaporphyrin **4** as a solid product (67 mg, 10% yield). Mp>300 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ=9.21 (s, 2H), 8.90 (s, 2H), 8.66 (d, *J*=3.4 Hz, 2H) 8.59 (d, *J*=4.5 Hz, 2H), 8.09 (d, *J*=7.5 Hz, 8H), 7.57 (d, *J*=7.5 Hz, 8H), 2.72 (s, 6H), 2.71 (s, 6H); IR (KBr, cm^{-1}): 3455, 3236, 3021, 2911, 1510, 1181, 964, 810, 770; λ_{max} (CH_2Cl_2) [nm (log ε)]: 421 (5.14), 509 (3.92), 576 (3.8), 604 (3.60), 672 (2.48); HRMS-ESI calcd for $C_{48}H_{37}N_3O$ ($[M+H]^+$): 672.3015, found 672.3000.

4.7. Oxaporphyrin (5)

The diol, furan-2,5-diylbis((3,4,5-trimethoxyphenyl)methanol) (**2**, 461 mg, 1 mmol), 3,4,5-trimethoxybenzaldehyde (392 mg, 2 mmol), and pyrrole (206 μL, 3 mmol) were dissolved in CH_2Cl_2 (100 mL) under nitrogen. $BF_3\cdot Et_2$ (48%) (30 μL 0.1 mmol) was added and the reaction mixture was stirred at room temperature for 1 h, followed by oxidation with DDQ (227 mg, 1 mmol) in air for an additional 1 h resulting in a mixture of two porphyrins, desired oxaporphyrin **5** and N_4-porphyrin. Chromatographic separation of the crude mixture in the same way as that of oxaporphyrin **4** gives oxaporphyrin **5** as a solid product (97 mg, 10% yield). Mp>300 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ=9.31 (s, 2H), 8.99 (s, 2H), 8.73 (d, *J*=3.72 Hz, 2H), 8.67 (d, *J*=4.2 Hz, 2H), 7.43 (d, *J*=6 Hz, 8H), 4.18 (s, 6H), 4.17 (s, 6H), 3.99 (s, 12H), 3.96 (s, 12H); IR (KBr, cm^{-1}): 3451, 2932, 2827, 1578, 1502, 1409, 1234, 1126, 1004, 915, 816, 721; λ_{max} (CH_2Cl_2) [nm (log ε)]: 426 (5.25), 510 (4.30), 582 (3.95), 611 (3.92), 672 (3.83); HRMS-ESI calcd for $C_{56}H_{53}N_3O_{13}$ ($[M+H]^+$): 976.3657, found 976.3660.

4.8. Oxaporphyrin (6)

Methyl 4-[hydroxyl(5-{hydroxyl[3-(methoxycarbonyl)phenyl] methyl}furan-2-yl)methyl]benzoate (**3**, 396 mg, 1 mmol), methyl 4-formylbenzoate (328 mg, 2 mmol), and pyrrole (206 μL, 3 mmol) were dissolved in CH_2Cl_2 (100 mL) under nitrogen. $BF_3\cdot Et_2$ (48%) (30 μL 0.1 mmol) was added and the reaction mixture stirred at room temperature for 1 h, followed by oxidation with DDQ (227 mg, 1 mmol) in air for an additional 1 h resulting in a mixture of two porphyrins, desired oxaporphyrin **6** and N_4-porphyrin. Chromatographic separation of the crude mixture in a same way as that of oxaporphyrin **4** gives oxaporphyrin **6** as a solid product (66 mg, 7% yield). Mp>300 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ=9.17 (s, 2H), 8.86 (s, 2H), 8.58 (d, *J*=4.8 Hz, 2H), 8.51 (d, *J*=4.8 Hz, 2H), 8.48–8.42 (m, 8H), 8.28–8.24 (m, 8H) 4.11 (s, 12H); IR (KBr, cm^{-1}): 3438, 2924, 2852, 1723, 1607, 1434, 1278, 1112, 1018, 810; λ_{max} (CH_2Cl_2) [nm (log ε)]: 421 (5.50), 509 (4.63), 541 (4.51), 620 (4.36), 669 (4.40); HRMS-ESI calcd for $C_{52}H_{37}N_3O_9$ ($[M+H]^+$): 848.2608, found 848.2584.

4.9. Oxaporphyrin (7)

Furan-2,5-diylbis(*p*-tolylmethanol) (**1**, 308 mg, 1 mmol), methyl 4-formylbenzoate (328 mg, 2 mmol), and pyrrole (206 μL, 3.0 mmol) were dissolved in CH_2Cl_2 (100 mL) under nitrogen. $BF_3\cdot Et_2$ (48%) (30 μL, 0.1 mmol) was added and the reaction mixture stirred at room temperature for 1 h, followed by oxidation with DDQ (227 mg, 1 mmol) in air for an additional 1 h resulting in a mixture of two porphyrins, desired oxaporphyrin **7** and N_4-porphyrin. Chromatographic separation of the crude mixture in a same way as that of oxaporphyrion **4** gives oxaporphyrin **7** as a solid product (68 mg, 9% yield). Mp>300 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ=9.28 (s, 2H), 8.84 (s, 2H), 8.64 (d, *J*=4.5 Hz, 2H), 8.60 (d, *J*=4.2 Hz 2H), 8.46 (d, *J*=8.1 Hz, 4H), 8.30 (d, *J*=7.8 Hz, 4H), 8.10 (d, *J*=7.2 Hz, 4H), 7.59 (d, *J*=7.8 Hz, 4H), 4.13 (s, 6H), 2.73 (s, 6H); IR (KBr, cm^{-1}): 3438, 2924, 2852, 1723, 1607, 1434, 1275, 1109, 1021, 964, 804, 708; λ_{max} (CH_2Cl_2) [nm (log ε)]: 421 (5.48), 508 (4.47), 541 (4.08), 592 (3.86), 674 (4.00); HRMS-ESI calcd for $C_{50}H_{37}N_3O_5$ ($[M+H]^+$): 760.2811, found 760.2838.

4.10. Oxaporphyrin (8)

Methyl 4-[hydroxyl(5-{hydroxyl[3-(methoxycarbonyl)phenyl] methyl}furan-2-yl)methyl]benzoate (**3**, 396 mg, 1 mmol), *p*-tolualdehyde (236 mg, 2 mmol), and pyrrole (206 μL, 3.0 mmol) were dissolved in CH_2Cl_2 (100 mL) under nitrogen. $BF_3\cdot Et_2$ (48%) (30 μL, 0.1 mmol) was added and the reaction mixture stirred at room temperature for 1 h, followed by oxidation with DDQ (227 mg, 1 mmol) in air for an additional 1 h resulting in a mixture of two porphyrins, desired oxaporphyrin **8** and N_4-porphyrin. Chromatographic separation of the crude mixture in a same way as that of oxaporphyrion **4** gives oxaporphyrin **8** as a solid product (68 mg, 9% yield). Mp>300 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ=9.15 (s, 2H), 8.92 (s, 2H), 8.68 (d, *J*=4.5 Hz, 2H), 8.49 (d, 4.5 Hz, 2H), 8.45 (d, 8.7 Hz, 4H), 8.29 (d, *J*=8.7 Hz, 4H), 8.08 (d, *J*=7.8 Hz, 4H), 7.57 (d, *J*=7.8 Hz,

4H), 4.12 (s, 6H), 2.71 (s, 6H); IR (KBr, cm^{-1}): 3403, 2924, 2852, 1723, 1605, 1434, 1272, 1118, 1016, 962, 789, 708; λ_{max} (CH_2Cl_2) [nm (log ε)]: 422 (4.79), 511 (4.06), 559 (4.96), 642 (3.90), 668 (3.92); HRMS-ESI calcd for $C_{50}H_{37}N_3O_5$ ($[M+H]^+$): 760.2811, found 760.2810.

4.11. Oxaporphyrin (9)

Methyl 4-[hydroxyl(5-{hydroxyl[3-(methoxycarbonyl)phenyl] methyl}furan-2-yl)methyl]benzoate (**3**, 396 mg, 1 mmol), 3,5-Di-*tert*-butylbenzaldehyde (436 mg, 2 mmol), and pyrrole (206 μL, 3.0 mmol) were dissolved in CH_2Cl_2 (100 mL) under nitrogen. $BF_3 \cdot Et_2$ (48%) (30 μL, 0.1 mmol) was added and the reaction mixture stirred at room temperature for 1 h, followed by oxidation with DDQ (227 mg, 1 mmol) in air for an additional 1 h resulting in a mixture of two porphyrins, desired oxaporphyrin **9** and N_4-porphyrin. Chromatographic separation of the crude mixture in a same way as that of oxaporphyrion **4** gives oxaporphyrin **9** as a solid product (14% yield, 133 mg). Mp>300 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ=9.12 (s, 2H), 8.94 (s, 2H), 8.67 (d, *J*=4.5 Hz, 2H), 8.48 (d, *J*=4.5 Hz, 2H), 8.44 (d, *J*=7.8 Hz, 4H), 8.28 (d, *J*=7.8 Hz, 4H), 8.00 (s, 4H), 7.79 (s, 2H), 4.11 (s, 6H), 1.52 (s, 36H); IR (KBr, cm^{-1}): 3434, 2957, 1724, 1605, 1592, 1478, 1386, 1274, 1113, 974, 819, 710; λ_{max} (CH_2Cl_2) [nm (log ε)]: 424 (5.36), 515 (4.74), 546 (4.60), 559 (4.60) 674 (4.67); HRMS-ESI calcd for $C_{64}H_{65}N_3O_5$ ($[M+H]^+$): 956.5002, found 956.4991.

4.12. General procedure of Zn(II) insertion (10–14, or 15)

25 mg of the respective oxaporphyrin (**4**–**8**, or **9**) was dissolved in 20 mL CH_3CN/MeOH (3:1). To this solution molar anhydrous excess zinc chloride (20 equiv) and a drop of 2,6-lutidine were added. Reaction progress was monitored by TLC and UV–vis spectroscopy. The solvent was removed under reduced pressure after 1 h. Dried residue was dissolved in CH_2Cl_2 added water and extracted with dichloromethane, organic layer was collected and dried with anhydrous $MgSO_4$ and evaporated to dryness. The residue contains practically pure Zn(II) oxaporphyrin complexes (**10**–**14**, or **15**).

*4.12.1. Zn(II) oxaporphyrin (**10**).* Mp>300 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ=9.37 (s, 2H), 9.03 (s 1H), 9.01 (s, 1H), 8.87 (s, 2H), 8.85 (s, 2H), 8.25 (br s, 2H) 8.20 (d, *J*=7.5 Hz, 2H), 8.10 (d, *J*=7.5 Hz, 2H), 7.95 (br s, 2H), 7.62–7.58 (m, 8H), 2.72 (s, 6H), 2.71 (s, 6H); IR (KBr, cm^{-1}): 2918, 1262, 1178, 1013, 993, 800; λ_{max} (CH_2Cl_2) [nm (log ε)]: 426 (4.82), 443 (4.76), 538 (4.19), 551 (4.22), 661 (4.15); HRMS-ESI calcd for $C_{48}H_{36}N_3OZn$ ($[M-Cl]^+$): 734.2150, found 734.2142.

*4.12.2. Zn(II) oxaporphyrin (**11**).* Mp>300 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ=9.49 (s, 2H), 9.10 (d, *J*=5.1 Hz, 2H), 8.96 (s, 2H), 8.95 (d, *J*=4.5 Hz, 2H), 7.61 (br s, 2H), 7.55 (br s, 2H), 7.47 (br s, 2H), 7.33 (br s, 2H), 4.19 (s, 6H), 4.00 (s, 6H), 3.97–3.93 (m, 24H); IR (KBr, cm-^{1}): 2932, 2831, 1582, 1504, 1410, 1235, 1126, 1002, 943, 799, 723; λ_{max} (CH_2Cl_2) [nm (log ε)]: 443 (4.95), 446 (4.96), 550 (3.91), 590 (3.93), 635 (3.64); HRMS-ESI calcd for $C_{56}H_{52}N_3O_{13}Zn$ ($[M-Cl]^+$): 1038.2792, found 1038.2782.

*4.12.3. Zn(II) oxaporphyrin (**12**).* Mp>300 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ=9.38 (s, 2H), 8.98 (d, *J*=4.8 Hz, 2H), 8.84 (s, 2H), 8.83 (s, 2H), 8.52–8.32 (m. 14H), 8.14 (br d, *J*=7.2 Hz, 2H), 4.13 (s, 6H), 4.12 (s, 6H); IR (KBr, cm^{-1}): 2945, 1723, 1607, 1434, 1276, 1118, 1021, 867, 763, 719; λ_{max} (CH_2Cl_2) [nm (log ε)]: 426 (5.24), 442 (5.18), 547 (4.04), 588 (4.02), 656 (4.12); HRMS (FAB) calcd for $C_{52}H_{36}ClN_3O_9Zn$ ($[M]^+$): 945.1432, found 945.1429.

*4.12.4. Zn(II) oxaporphyrin (**13**).* Mp>300 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ=9.45 (s, 2H), 8.96 (d, *J*=5.1 Hz, 2H), 8.93 (d, *J*=5.1 Hz, 2H), 8.83 (s, 2H), 8.49–8.42 (m, 6H), 8.22–8.10 (m, 6H), 7.62 (m, 4H), 4.12 (s, 6H), 2.73 (s, 6H); IR (KBr, cm^{-1}): 2995, 2919, 1722, 1607, 1434, 1275, 1180, 1275, 1112, 1012, 993, 798; λ_{max} (CH_2Cl_2) [nm (log ε)]: 426 (5.11), 442 (5.04), 545 (4.06), 588 (4.03), 636 (3.82); HRMS (FAB) calcd for $C_{50}H_{36}ClN_3O_5Zn$ ($[M]^+$): 857.1635, found 857.1633.

*4.12.5. Zn(II) oxaporphyrin (**14**).* Mp>300 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ=9.32 (s, 2H), 9.06 (d, *J*=4.8 Hz, 2H), 8.88 (s, 2H), 8.78 (d, *J*=4.8 Hz, 2H), 8.51 (s, 2H), 8.48 (s, 2H), 8.42–8.31 (m, 4H), 8.25 (br s, 2H), 7.94 (br s, 2H), 7,56 (br s, 4H), 4.13 (s, 6H), 2.71 (s, 6H); IR (KBr, cm^{-1}): 2919, 1722, 1607, 1434, 1275, 1181, 1111, 1012, 993, 798, 757; λ_{max} (CH_2Cl_2) nm (log ε): 427 (5.56), 444 (5.47), 548 (4.45), 589 (4.44), 634 (4.10); HRMS (FAB) calcd for $C_{50}H_{36}ClN_3O_5Zn$ ($[M]^+$): 857.1635, found 857.1633.

*4.12.6. Zn(II) oxaporphyrin (**15**).* Mp>300 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ=9.31 (s, 2H), 9.07 (d, *J*=4.5 Hz, 2H), 8.89 (s, 2H), 8.79 (d, *J*=4.8 Hz, 2H), 8.51 (br s, 2H), 8.48 (br, s 2H), 8.41–8.33 (m 4H) 8.22 (br s, 2H), 7.91 (br s, 2H), 7.83 (br s, 2H), 4.12 (s, 6H), 1.55 (s, 18H), 1.50 (s, 18H); IR (KBr, cm^{-1}): 2957, 1724, 1609, 1274, 1194, 1113, 1021, 970, 818, 710; λ_{max} (CH_2Cl_2) [nm (log ε)]: 428 (5.18), 445 (5.10), 549 (4.12), 588 (5.11), 632 (3.83); HRMS (FAB) calcd for $C_{64}H_{64}ClN_3O_5Zn$ ($[M]^+$): 1051.3826, found 1051.3833.

4.13. General procedure of hydrolysis of free base oxaporphyrin (16–18, or 19)

25 mg of the respective oxaporphyrin (**6**–**8**, or **9**) was dissolved in 50 mL of THF, and 500 mg KOH in 2 mL water was added to it and refluxed for 10 h. After cooling, the reaction mixture was treated with 1 N HCl. The precipitation formed were filtered off and washed with distilled water. The residue remained is dissolved in methanol and dried in vacuum to yield practically pure free-base oxaporphyrin dicarboxylic acid or tetracarboxylic acid (**16**–**18**, or **19**) in quantitative yield.

*4.13.1. Oxaporphyrin (**16**).* Mp>300 °C; ^{1}H NMR (300 MHz, CD_3OD) δ=9.89 (s, 2H), 9.26 (d, *J*=5.1 Hz, 2H), 9.15 (d, *J*=5.7 Hz, 2H), 8.91 (s, 2H), 8.63–8.56 (m, 8H), 8.55–8.46 (m, 8H); IR (KBr, cm^{-1}): 3430, 3130, 1710, 1609, 1502, 1223, 1113, 1016, 981, 789, 717; λ_{max} (MeOH) [nm (log ε)]: 410 (4.53), 435 (4.32), 574 (3.53); HRMS-ESI calcd for $C_{48}H_{29}N_3O_9$ ($[M+H]^+$): 792.1982, found 792.1979.

*4.13.2. Oxaporphyrin (**17**).* Mp>300 °C; ^{1}H NMR (300 MHz, CD_3OD) δ=9.87 (s, 2H), 9.14 (d, *J*=5.1 Hz, 2H), 9.02 (d, *J*=4.8 Hz, 2H), 8.85 (s, 2H), 8.59 (m, 8H), 8.37 (d, *J*=8.1 Hz, 4H), 7.85 (d, *J*=7.8 Hz, 4H), 2.79 (s, 6H); IR (KBr, cm^{-1}): 3400, 2917, 1707, 1606, 1277, 1186, 1017, 822, 714; λ_{max} (MeOH) [nm (log ε)]: 412 (4.67), 435 (4.50), 575 (5.42); HRMS-ESI calcd for $C_{48}H_{33}N_3O_5$ ($[M+H]^+$): 732.2498, found 732. 249.

*4.13.3. Oxaporphyrin (**18**).* Mp>300 °C; ^{1}H NMR (300 MHz, CD_3OD) δ=9.85 (s, 2H), 9.53 (d, *J*=3 Hz, 2H), 8.91 (s, 2H), 8.80 (s, 2H), 8.69 (d, *J*=8.1 Hz, 4H) 8.63 (d, *J*=8.1 Hz, 4H), 8.50 (d, *J*=7.5 Hz, 4H), 7.94 (d, *J*=7.5 Hz, 4H), 2.82 (s, 6H); IR (KBr, cm^{-1}): 3436, 2918, 2851, 1717, 1606, 1223, 1112, 807, 720; λ_{max} (MeOH) [nm (log ε)]: 415 (5.21), 437 (5.04), 577 (4.22); HRMS-ESI calcd for $C_{48}H_{33}N_3O_5$ ($[M+H]^+$): 732.2498, found 732.2494.

*4.13.4. Oxaporphyrin (**19**).* Mp>300 °C; ^{1}H NMR (300 MHz, CD_3OD) δ=9.38 (s, 2H), 8.95 (s, 2H), 8.63 (br s, 2H), 8.61 (br s, 2H), 8.41 (d, *J*=7.8 Hz, 4H), 8.26 (d, *J*=7.8 Hz, 4H), 8.10 (br s, 4H), 7.92 (br s, 2H), 1.55 (s, 36H); IR (KBr, cm^{-1}): 3395, 2961, 2868, 1591, 1544, 1384,1284, 975, 818, 715; λ_{max} (MeOH) [nm (log ε)]: 417 (4.56), 439

(4.36), 577 (3.55); HRMS-ESI calcd for $C_{62}H_{61}N_3O_5$ ($[M+H]^+$): 928.4689, found 928.4681.

4.14. Synthesis of Zn(II) oxaporphyrin (20)

Free base oxaporphyrin **19** (20 mg) was dissolved in 20 mL MeOH. To this solution molar excess anhydrous zinc chloride (20 equiv) and a drop of 2,6-lutidine were added and stirred for 1 h. Excess MeOH was removed under reduced pressure. Reaction mixture was then treated with distilled water. The crystals formed were filtered off and washed with distilled water. The residue remained is dissolved in methanol and dried to vacuum to yield practically pure Zn(II) oxaporphyrin **20** in quantitative yield. Mp>300 °C; ^{1}H NMR (400 MHz, CD_3OD) δ=9.61 (s, 2H), 9.10 (d, J=4.8 Hz, 2H), 8.93 (m, 4H), 8.52 (d, J=8.0 Hz, 4H), 8.39 (d, J=8.0 Hz, 4H), 8.11 (d, J=1.5 Hz, 4H), 7.98 (m, 2H), 1.55 (s, 36H); IR (KBr, cm^{-1}): 3561, 2957, 2869, 1609, 1248, 1044, 1012, 907, 801, 721; λ_{max} (MeOH) [nm (log ε)]: 421 (3.80), 437 (3.74), 546 (2.19), 587 (2.77), 675 (2.62); HRMS (FAB) calcd for $C_{64}H_{64}N_3O_5Zn$ ($[M-Cl]^+$): 990.3824, found 990.3813.

4.15. Furan-2-methanol (21)

2-Furancarboxaldehyde (9.6 mL, 100 mmol) was added to 100 mL methanol in a 250 mL round-bottom flask under N_2 atmosphere. $NaBH_4$ (5.70 g, 150 mmol) was added to it dropwisely and stirred for 1 h. Product formation was checked by TLC. The reaction was quenched by adding 50 mL of water and extracted with ethyl acetate. The collected organic layer was dried over $MgSO_4$ and concentrated, and the crude product was purified by silica gel column chromatography using 20% ethyl acetate/hexane as eluent. The furan-2-methanol **21** was collected as a yellow oily compound (7.30 gm, 74% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ=7.38 (d, J=1.5 Hz, 1H), 6.32 (dd, J=1.8 Hz, 1H), 6.27 (d, J=2.7 Hz, 1H), 4.27 (d, J=5.7 Hz, 2H), 2.29 (br s, 1H); ^{13}C NMR (300 MHz, $CDCl_3$) δ=153.96, 142.52, 110.31, 107.70, 57.35; IR (KBr, cm^{-1}): 3435, 2926, 1638, 1570, 1262, 1017, 914, 800, 735; HRMS-ESI calcd for $C_5H_6O_2Na$ ($[M+Na]^+$): 98.0368, found 98.3453.

4.16. [5-(Hydroxymethyl)furan-2-yl](3,4,5-trimethoxyphenyl) methanol (22)

Distilled dry *n*-hexane (50 mL) was added into a 250-mL two-necked round-bottom flask fitted with a rubber septum and nitrogen gas inlet tube. Tetramethylethylenediamine (TMEDA) (3.48 mL, 30 mmol) and ^{n}BuLi (2.5 M solution in hexane) (12 mL, 30 mmol) were added and the solution was stirred under nitrogen for 10 min. Furan-2-methanol **21** (1.96 mL, 20 mmol) was added to the solution and stirred for 1 h at ambient temperature. The reaction mixture was cooled to 0 °C in an ice bath and then an ice-cold solution of 3,4,5-trimethoxybenzalaldehyde (5.88 gm, 30 mmol) in dry THF (30 mL) was added. The reaction mixture was stirred for another 15 min and quenched by adding an ice-cold saturated NH_4Cl solution. The organic layer was washed with water and brine solution, and dried over anhydrous $MgSO_4$. Solvent was removed on a rotary evaporator to afford the crude compound. TLC analysis showed three spots corresponding to unreacted furan-2-methanol **21**, 3,4,5-trimethoxybenzalaldehyde, and desired product. The crude product was purified by silica gel column chromatography using 20% ethyl acetate/hexane as eluent to afford [5-(hydroxymethyl)furan-2-yl](3,4,5-trimethoxyphenyl) methanol, **22**, as a yellow solid (2.23 gm, 38% yield). Mp 60–62 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ=6.64 (s, 2H), 6.17 (d, J=3 Hz, 1H), 6.00 (d, J=3 Hz, 1H), 5.69 (s, 1H), 4.52 (s, 2H), 3.82 (s, 3H), 3.81 (s, 6H), 2.46 (br s, 2H); ^{13}C NMR (300 MHz, $CDCl_3$) δ=155.86, 153.94, 153.11, 137.45, 136.29, 108.38, 108.19, 103.60, 69.92, 60.77, 57.24, 56.04; IR (KBr, cm^{-1}): 3400, 2940, 2836, 1594, 1506, 1462, 1420, 1331, 1235, 1126, 1009, 779, 703; HRMS-ESI calcd for $C_{15}H_{18}O_6Na$ ($[M+Na]^+$): 317.1001, found 317.1005.

4.17. Oxaporphyrin (23)

In a 250-mL round-bottom flask 100 mL CH_2Cl_2 was taken and purged with nitrogen for 15 min, To this [5-(hydroxymethyl)furan-2-yl](3,4,5-trimethoxyphenyl)methanol **22** (294 mg, 1.0 mmol), 3,4,5-trimethoxybenzaldehydealdehyde (392 mg, 2 mmol) and pyrrole (209 μL, 3 mmol) were dissolved. $BF_3\cdot Et_2$ (48%) (30 μL, 0.1 mmol) was added and the reaction mixture was stirred at room temperature for 1 h. DDQ (227 mg, 1 mmol) was added and the reaction mixture was stirred for an additional 1 h in air. TLC analysis of the reaction mixture showed the formation of four porphyrins. The solvent was removed on a rotary evaporator and reaction mixture was separated by silica gel column chromatography using CH_2Cl_2 as eluent to afford oxaporphyrin **23** as a solid product (121 mg, 15% yield). Mp>300 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ=10.18 (s, 1H), 9.73 (d, J=4.8 Hz, 1H), 9.47 (d, J=4.8 Hz, 1H), 9.15 (d, 4.5 Hz, 1H), 9.05–9.04 (m. 2H), 8.93 (d, J=4.5 Hz, 1H) 8.76 (d, J=4.8 Hz, 1H), 8.71 (d, J=4.5 Hz, 1H), 7.44 (d, 4.8 Hz, 4H), 7.41 (s, 2H), 4.19 (s, 6H), 4.17 (s, 3H), 4.00 (s, 6H), 3.97 (s, 12H); IR (KBr, cm^{-1}): 3439, 2928, 2849, 1580, 504, 1436, 1409, 1384, 1236, 1126, 1004, 919, 819, 817, 718; λ_{max} (CH_2Cl_2) [nm (log ε)]: 419 (4.63), 503 (3.78), 597 (3.26), 603 (3.32), 685 (2.97); HRMS-ESI calcd for $C_{47}H_{43}N_3O_{10}$ ($[M+H]^+$): 810.3027, found 810.3024.

4.18. Oxaporphyrin (24)

In a 50 mL round-bottomed flask, a solution of the oxaporphyrin **23** (24 mg, 0.030 mmol) in dichloromethane (15 mL) was treated with *N*-bromosuccinimide (7.12 mg, 0.040 mmol) at room temperature for 15 min. The progress of the reaction was monitored by TLC. After a complete consumption of the oxaporphyrin **23**, the reaction was stopped and the solvent was removed on a rotary evaporator. The crude compound was subjected to silica gel column chromatography with 30% CH_2Cl_2/hexane as eluent. Oxaporphyrin **24** was afforded as a solid product (18 mg, 68% yield). Mp>300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ=10.09 (d, J=4.8 Hz, 1H), 9.53 (d, J=4.71 Hz, 1H), 9.41 (d, J=4.98 Hz, 1H) 8.96 (s, 2H), 8.78 (d, J=4.56 Hz, 1H), 8.68 (d, 4.71 Hz, 1H), 8.61 (d, J=4.74 Hz, 1H), 7.42 (s, 2H), 7.39 (d, J=5.67 Hz, 4H), 4.19–4.17 (m, 9H), 4.00–3.97 (m, 18H); IR (KBr, cm^{-1}): 3452, 2933, 2831, 1508, 1501, 1463, 1409, 3161, 1331, 1235, 1127, 919, 816, 723; λ_{max} (CH_2Cl_2) [nm (log ε)]: 427 (5.06), 513 (4.05), 619 (3.40), 653 (3.17), 677 (3.19); HRMS-ESI calcd for $C_{47}H_{42}BrN_3O_{10}$ ($[M+H]^+$): 888.2132, found 888.2139.

4.19. Zn(II) oxaporphyrin (25)

The oxaporphyrin **24** (10 mg) was dissolved in 20 mL CH_3CN/MeOH (3:1). To this solution molar excess anhydrous zinc chloride (20 equiv) was added. Reaction progress was monitored by TLC and UV–vis spectroscopy. After 1 h stirring, the solvent was removed by rotary evaporator. Dried residue was dissolved in CH_2Cl_2 added water and extracted with dichloromethane, organic layer separated and dried over anhydrous $MgSO_4$, and evaporated to dryness to obtain pure Zn(II) oxaporphyrin **25** in quantitative yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ=10.20 (d, J=5.1 Hz, 1H), 9.83 (d, J=5.1 Hz, 1H), 9.61 (d, J=5.1 Hz, 1H), 9.19 (d, J=4.8 Hz, 1H), 9.06 (d, 4.8 Hz, 1H), 8.94–8.89 (m, 3H), 7.60 (s, 1H), 7.56–7.55 (m, 2H), 7.43 (d, J=1.5 Hz, 1H), 7.30–7.28 (m, 2H), 4.20–4.17 (m, 9H), 4.00–3.90 (m, 18H); λ_{max} (CH_2Cl_2) [nm (log ε)]: 434 (4.97), 449 (4.97), 552 (3.95), 595 (3.94), 641 (3.50); IR (KBr, cm^{-1}): 2935, 2844, 1581, 1504, 1463, 1410, 1336, 1236, 1126, 1007, 804; HRMS-ESI calcd for $C_{47}H_{41}BrN_3O_{10}Zn$ ($[M-Cl]^+$): 950.1267, found 950.1257.

4.20. Zn(II) oxaporphyrin (26)

A mixture of Zn(II) oxaporphyrin **25** (60 mg, 0.06 mmol), [$Pd_2(dba)_3$] (21.98 mg, 0.024 mmol), 4-ethenylbenzoic acid (13.15 mg, 0.09 mmol), and triphenylarsine (45.94 mg, 0.15 mmol) added in two-neck 50 mL flask and kept under vacuum for 30 min was flushed with N_2, then added THF/triethylamine (12 mL, 1:1 v/v) and stirred under N_2 for 48 h. After the complete consumption of Zn(II) oxaporphyrin **25** (as confirmed by TLC and absorption spectroscopy), the reaction was stopped and the solvent was removed under reduced pressure. The crude mixture was purified by column chromatography with 5% MeOH/CH_2Cl_2. Yield (31%), mp>300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ=10.22 (d, J=4.8 Hz, 1H), 9.85 (d, J=4.8 Hz, 1H), 9.61 (d, J=5.2 Hz, 1H), 9.21 (d, J=4.8 Hz, 1H), 9.04 (d, J=4.8 Hz, 1H), 8.90 (m, 3H), 8.12–8.00 (m, 4H), 7.62 (s, 1H), 7.58 (d, J=6 Hz, 2H), 7.33 (s, 1H), 7.28 (s, 1H), 7.28 (s, 1H), 4.21–4.17 (m, 9H), 4.02–3.92 (m, 18H); λ_{max} (CH_2Cl_2) [nm (log ε) 451 (5.2), 461 (5.3), 563 (4.2), 613 (4.3), 657 (2.0); IR (KBr, cm^{-1}): 2925, 2853, 2130, 1729, 1624, 1580, 1408, 1232, 1121, 999, 930, 800, 761, 722, 649; HRMS-ESI calcd for $C_{56}H_{46}N_3O_{12}Zn$ ([M−Cl]$^+$): 1016.2373, found 1016.2360.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC 809694. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 (0)1223 336033 or e-mail: deposit@ccdc.cam.ac.Uk).

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Supplementary data

Collections of ^{1}H and ^{13}C NMR for all compounds. Supplementary data related to this article can be found online at doi:10.1016/j.tet.2011.04.034. These data include MOL files and InChiKeys of the most important compounds described in this article.

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