MINI REVIEW

Porphyrins with Five-Membered Ring Substituents on *meso*-Position and their Derivatives

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Tetrapyrrolic porphyrins are the molecules of choice for nature where light absorption and metal based chemistry plays an important role in biological systems. Constant efforts are directed at modifying the porphyrin skeletal structure to result in porphyrins with fine-tuned physical properties. This review focusses on the chemistry of porphyrins with five-membered aromatic rings such as furan, pyrrole and thiophene as substituents at the *meso* position of porphyrins. Substitution with these five-membered rings at the *meso*-position of porphyrins brings about significant modulation of HOMO-LUMO gap, which reflects in shifts in the absorption and fluorescence spectra and in their electrochemical properties compared to the conventional porphyrins with six-membered aryl substituents. The synthetic modification of these five-membered rings by introdcution of various functional groups were also discussed.

Keywords: Porphyrin, Pyrrole, Furan, Thiophene, Extended conjugation.

INTRODUCTION

Tetrapyrrolic macrocycles play a number of critical biological roles such as molecular binding [1], reaction catalysis [2], energy and electron transfer [3], light harvesting, *etc*. Porphyrins have been regarded as one of the most versatile molecules in molecular recognition research [4], due to their unique features like (a) a conjugated framework to which various functional groups can be attached, (b) high susceptibility for the spectroscopic methods to probe the intermolecular interactions, (c) aromatic framework, which is a potentially efficient counterpart for van der Waals and charge-transfer interactions, and (d) number of metals incorporated with varying Lewis acidity.

The controlled modification of porphyrins to create required structural and electronic properties has emerged as an important research topic. A large variety of methods have been employed to synthetically modify porphyrins to introduce changes in their properties, which is important to develop molecular materials with desired features. Porphyrin macrocycles are highly flexible and by introducing substituents selectively at the β- or *meso*-positions, the properties can be tuned at will for many applications.

Porphyrins with modified electronic properties have been developed by introducing electron withdrawing or electron donating groups either at β-pyrrole and/or on the aryl substituents at the *meso*-positions of porphyrin skeleton. Electronic properties are also altered in a big way by introducing changes in the porphyrin ring, which causes changes in the planarity of the molecule. One such way is the synthesis of highly-substituted porphyrins where a large number of substituents like phenyl groups are introduced at the β-pyrrole and *meso*-positions. This causes a change in planarity of the molecule due to steric effects and the subsequent change in electronic properties. However, most of the modification methods for tuning the electronic properties of porphyrins have utilized *meso*-tetra aryl porphyrins owing to their ease of synthesis and facile functionalization. Most of the large functional multi-component molecular systems which include one or more porphyrins in the molecular architecture make use of *meso*-aryl substituted porphyrins. It has been shown that the electronic properties can be fine-tuned by replacing six membered aryl groups with five membered heterocycles such as pyrrole, thiophene, furan, *etc*. and some relevant literature is discussed below.

Osuka and coworkers [5] reported the first synthesis of porphyrins with four pyrroles in the *meso*-positions. These

Scheme-I: Synthesis of pyrrolyl porphyrins
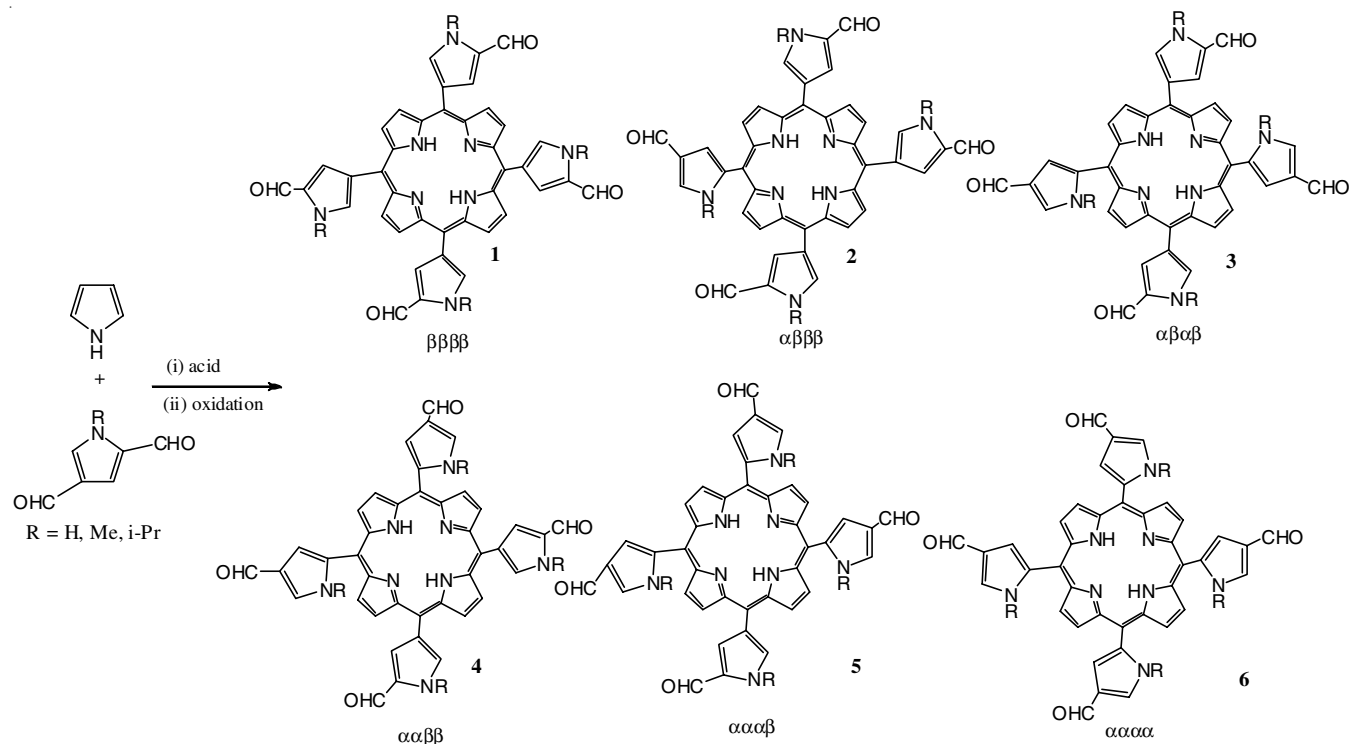
tetrapyrrolyl porphyrins resulted during their attempts to synthe-size doubly *N*-confused porphyrins by acid-catalyzed reaction of pyrrole with 2,4-diformyl pyrrole. They found out that under acetic acid catalyzed conditions (**Scheme-I**), it was possible to isolate a mixture of six isomers differing from each other by the position of attachment of the pyrrole (α- or β-position) to the *meso*-position of porphyrin.

Grazynski and co-workers [6] were able to isolate pyrrole appended derivatives of O-confused oxaporphyrin **7** when they attempted to synthesize O-confused oxaporphyrin by the acid catalyzed condensation between a furan-diol, pyrrole and aldehyde in high yields. It was noticed that condensation did not stop at the porphyrin stage but always proceeded to the appending the pyrrole group to furyl moiety in the O-confused porphyrin (**Scheme-II**).

Gross and co-workers [7] were able to isolate a pyrrole substituted porphyrin while attempting to devise a rational

Scheme-II: Synthesis of O-confused oxaporphyrin **7**
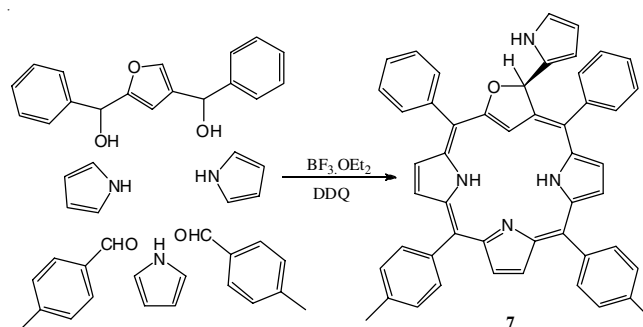
method for the synthesis of corroles. Werner *et al*. [8] synthesi-zed a series of pyrazole substituted porphyrins (**8,9**) with different pyrazolyl aldehydes and found that tetrapyrazolyl porphyrins always existed as a mixture of atropisomers (**Scheme-III**).

Scheme-III: Synthesis of pyrazolyl porphyrins
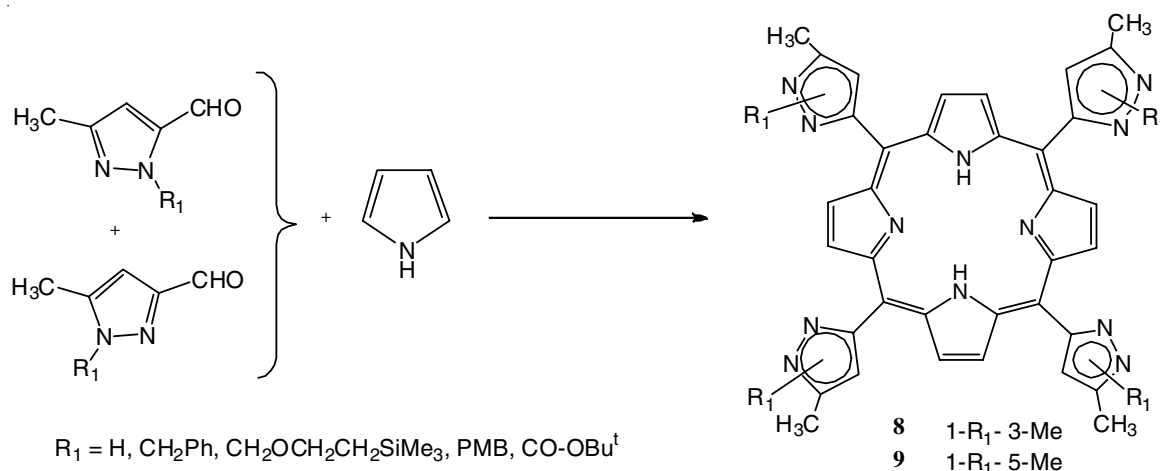
Milgrom *et al*. [9] synthesized a series of *tetrakis-N*-protected imidazolyl and benzimidazolyl porphyrins and studied their atropisomerism. Kobuke and Miyaji [10] have synthesized imidazolyl porphyrins and studied their ability to organize in a supramolecular fashion in solution to form slipped cofacial dimer **10** (Fig. 1), which could be *mimics* of the photosynthetic center.
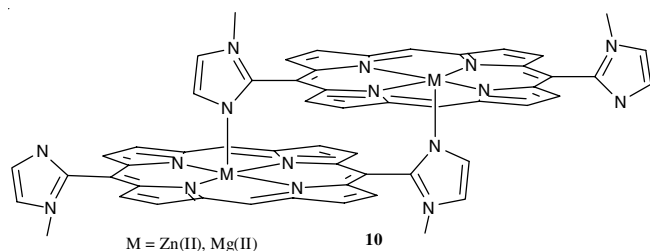

Fig. 1. Slipped cofacial dimer **10**

The same author also constructed ferrocene-bridged trisporphyrin (**11**) with imidazolyl groups at the *meso*-positions (Fig. 2) and studied the self-assembling behaviour based on the complementary coordination motif of imidazolylporphyrinatozinc(II). They were able to separate, using gel permeation chromatography, giant macrocycles (**12**) even upto decamer with 30 porphyrin sub-units [11].

Osuka and Kurotobi [12] have synthesized a series of azulene substituted porphyrins, where azulene was attached to porphyrin *meso*-position in four different positions, two of them being attached at the five membered ring of azulene (**Scheme-IV**). They noticed that these porphyrins exhibited red shifts in absorption and fluorescence spectra.

Among the five membered heterocyclic rings, thiophene is the mostly utilized and studied system, though the number of reports are few compared to porphyrin systems with six-
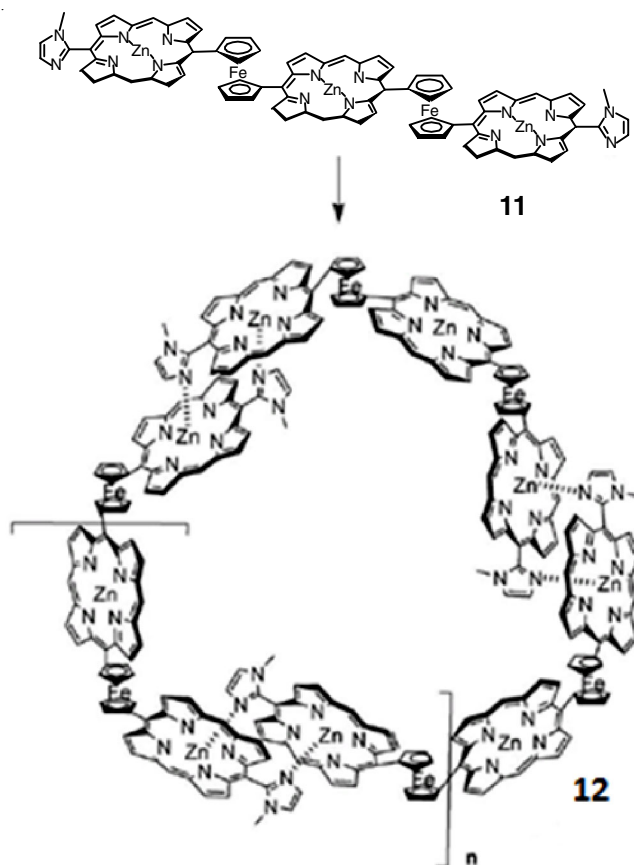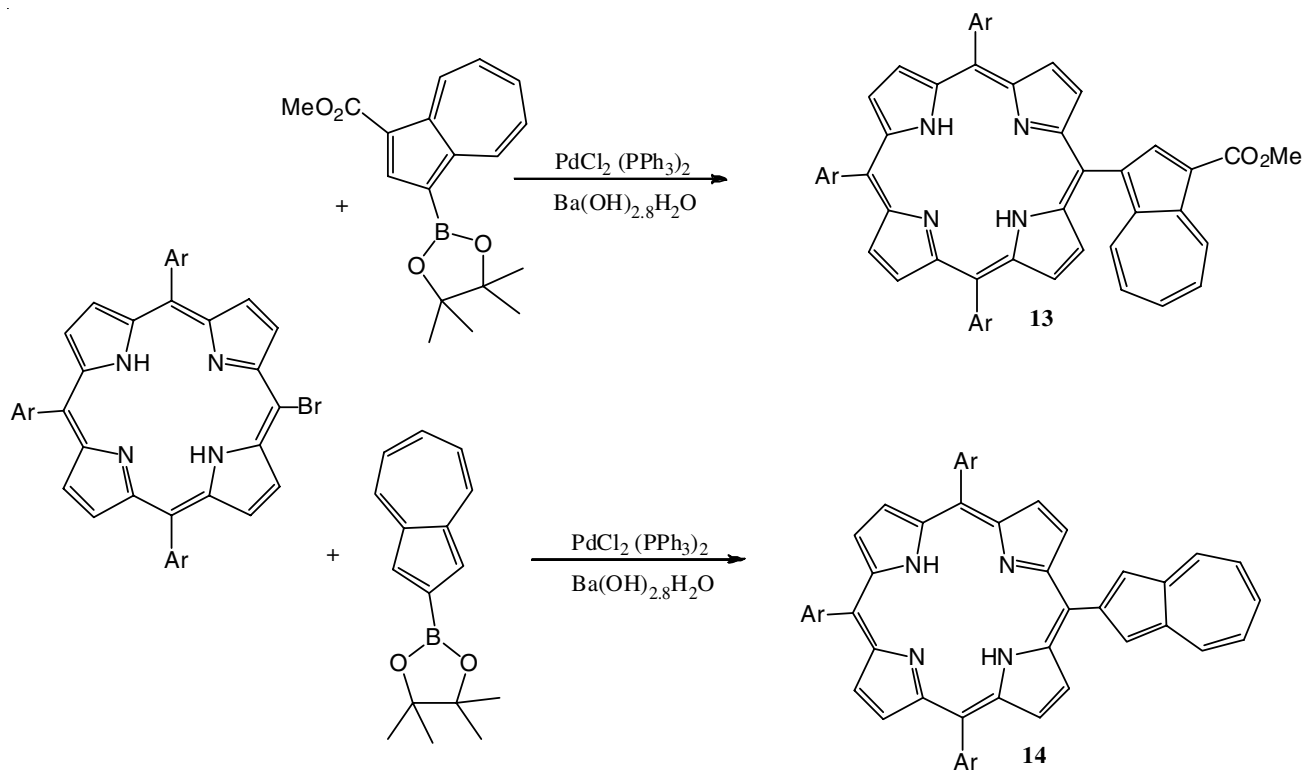

Fig. 2. Ferrocene-bridged trisporphyrin **11** and giant macrocycle **12**

membered aryl groups. Oligothiophenes, due to their conducting properties, have attracted many groups to investigate several donor-acceptor-bridged systems (DABS) have been

Scheme-IV: Synthesis of azulene appended porphyrins **XIII** and **XIV**

synthesized, where oligothiophenes been have utilized as the molecular bridge for electronic communication.

Odobel *et al*. [13] have reported a series of porphyrin dimers (**15-18**) connected to each other through four different kinds of oligothiophene based spacers and studied the modulation of electronic communication based on the length, extent of conjugation and the rigidity of oligothiophene spacers (Fig. 3).

Effenberger *et al*. [14] synthesized anthryl oligo thienyl porphyrins (**19**) containing the anthracene donor, porphyrin acceptor and a conjugated oligothiophene bridge (Fig. 4). This system showed an efficient energy transfer from anthracene to porphyrin unit mediated by the oligothiophene π-bridge. The oligomeric thienyl porphyrins also showed film forming and efficient conductivity behaviour.

In their effort to utilize aryl-substituted pyrroles to synthesize dodeca aryl substituted porphyrins, Ono *et al*. [15] found that the dodecaporphryins with thienyl substituents (**20**) showed significant shifts in the electronic properties as reflected in their absorption spectrum and electrochemistry. The most interesting

aspect is that the HOMO-LUMO gap for copper derivatives decreased from 2.34 V for tetraphenyl porphyrin to 1.48 V for dodeca-(2-thienyl)porphyrin (Fig. 5) as reflected in the difference between the first oxidation and first reduction potential.

Bhyrappa *et al*. [16,17] have reported on the synthesis, optical, redox and axial ligation properties of *meso*-tetrathienyl porphyrin and reported that simple substitution of six-membered aryl at the four *meso*-positions with thienyl groups affected the electronic properties as compared to that of tetraaryl porphyrins.

Ravikanth *et al*. [18-21] have reported the synthesis of *meso*- furyl and *meso*-thienyl porphyrins with different cores such as N_4, N_3S, N_3O and N_2S_2 and found that the replacement of four six-membered aryl groups with five-membered furyl groups at *meso*-positions alter the electronic properties drastically, suggesting that *meso*-furyl porphyrins can be tested in place of *meso*-aryl porphyrins for various applications (Fig. 6). Such a drastic change in the electronic properties has not been witn-essed in case of tetrathienyl porphyrins (Table-1).
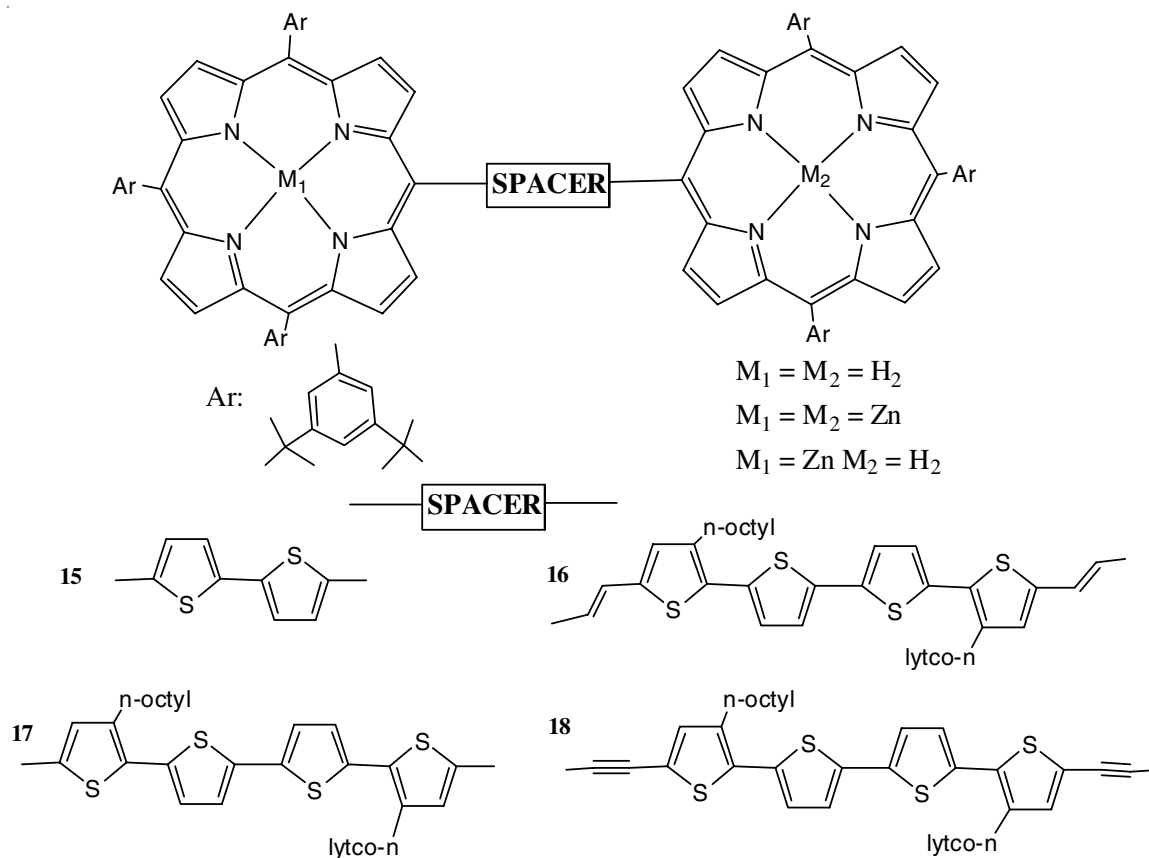

Fig. 3. Porphyrin dimers with oligothiophene spacers **XV-XVIII**

TABLE-1
COMPARISON OF UV-VIS ABSORPTION, STEADY STATE FLUORESCENCE AND ^{1}H NMR
DATA OF *meso*-ARYL PORPHYRINS WITH *meso*-FURYL PORPHYRINS

Porphyrin	Absorption data		Fluorescence			^{1}H NMR chemical shift (δ ppm)	
	Soret (nm)	Q_1 (nm)	λ_{em} (nm)	φ_f	Lifetime (ns)	β-Pyrrole	Inner NH
H_2TPP	417	647	652	0.1100	9.32	8.72	-2.79
H_2TFP 21	433	670	697	0.0110	5.77	9.16	-2.59
STPPH	428	675	678	0.0170	1.77	8.88, 8.72, 8.61	-2.66
STFPH 22	448	7.5	729	0.0021	1.06	9.22, 9.01, 8.85	-2.41
S_2TPP	435	696	706	0.0076	1.34	8.67	–
S_2TFP 23	458	740	773	0.0017	1.20	8.97	–
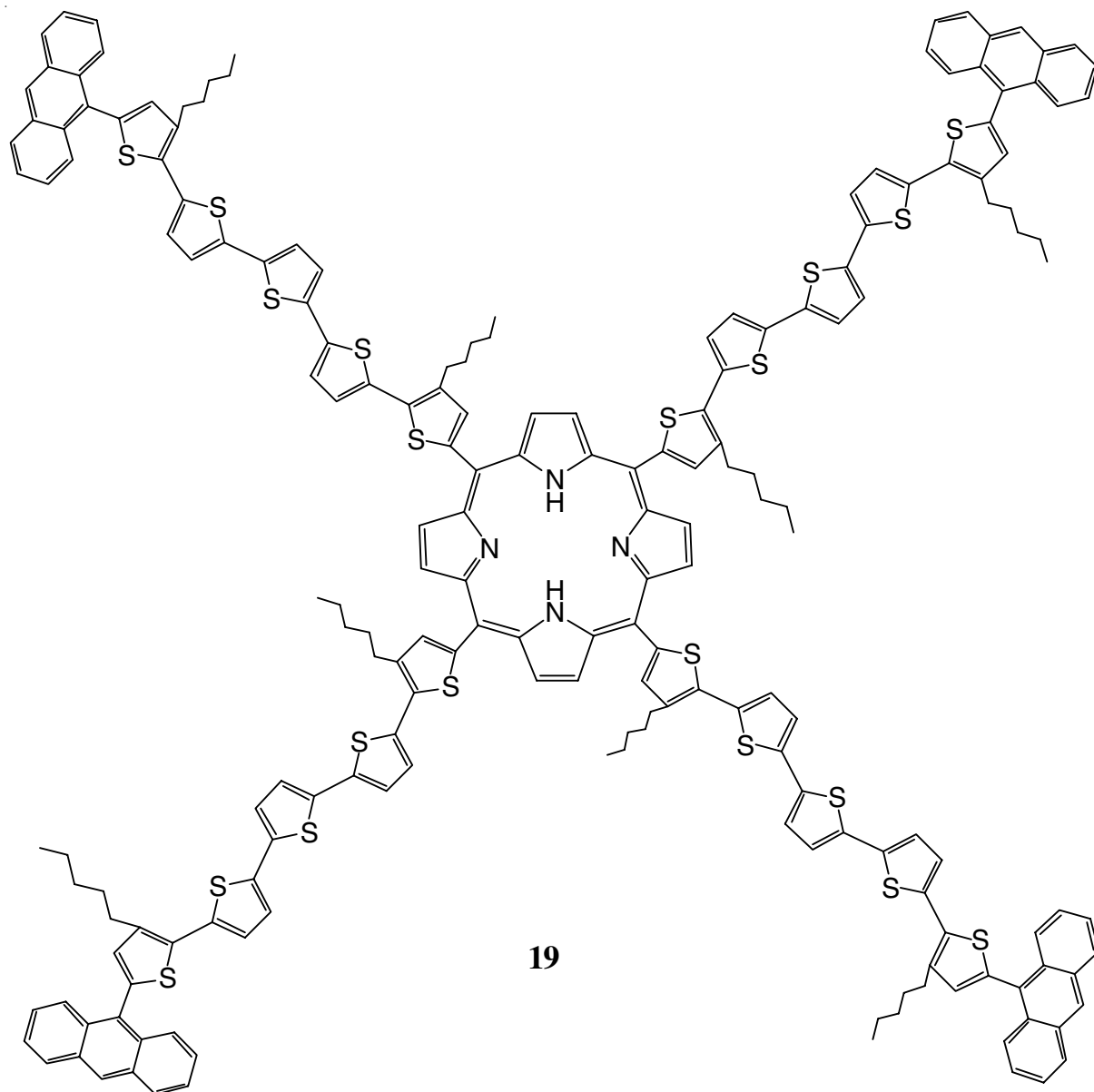
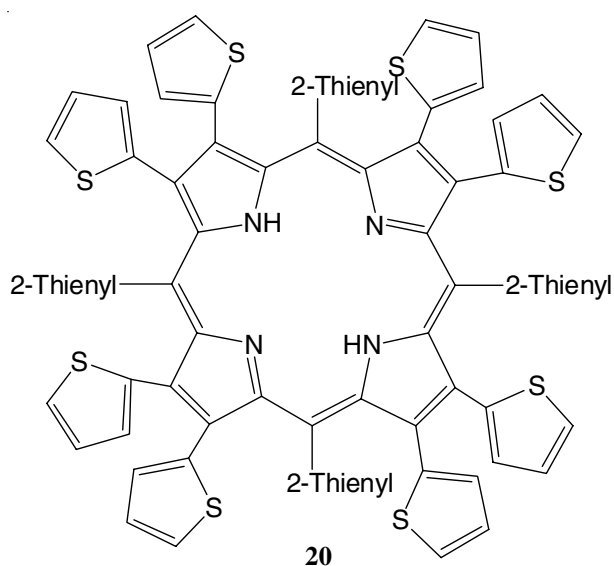Fig. 4. Anthryl oligo thienyl porphyrin (**19**)

20

Fig. 5. Structure of dodeca-(2-thienyl)porphyrin (**20**)

As shown in Table-1, the introduction of furyl groups at *meso*-positions in place of six membered aryl groups shifts the Q1 and Soret band of porphyrin by 20-40 nm bathochromically, indicating that *meso*-furyl porphyrins were energetically low as compared to *meso*-aryl porphyrins. Thus connecting *meso*-furyl porphyrins, when linked to chromophores of higher energy, lead to fluorescence energy transfer systems. This property has been exploited for the synthesis of a series of covalently linked porphyrin dyads containing *meso*-arylporphyrin and *meso*-furylporphyrin sub-units (Fig. 7) and the demonstration of an efficient energy transfer from *meso*-arylporphyrin to *meso*-furylporphyrin on selective excitation of *meso*-aryl porphyrin subunit [22].

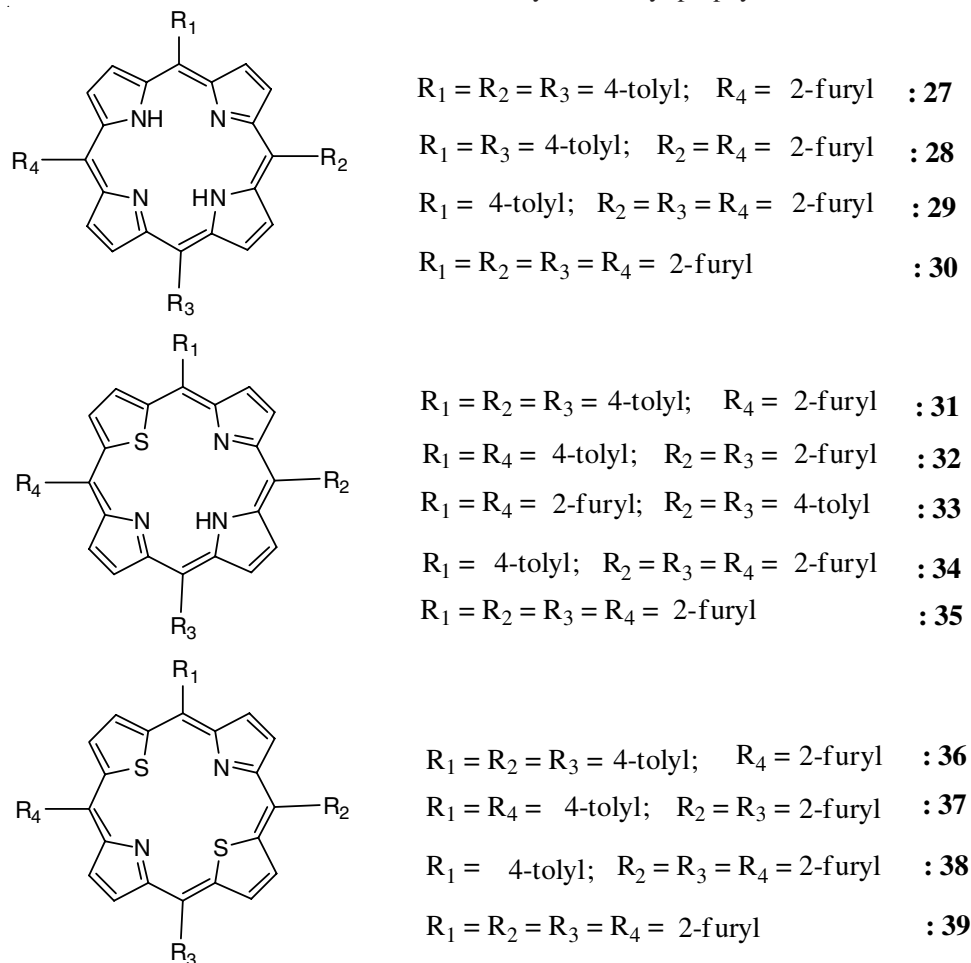Ravikanth *et al*. [23] have synthesized porphyrins having one, two, three and four *meso*-furyl groups with three different porphyrins cores such as N_4 (**27-30**), N_3S (**30-34**), N_2S_2 (**35-39**) and compared the spectral properties with their corresponding *meso*-tetraaryl porphyrins (Fig. 8). The spectral studies clearly indicate that with the replacement of one to four *meso*-aryl

H$_2$TFP (**21**)   STFPH (**22**)   S$_2$TFP (**23**)
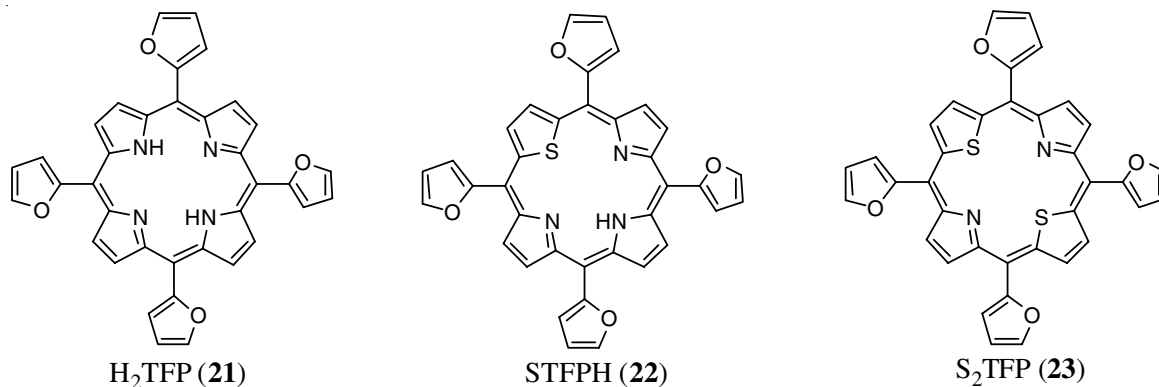
Fig. 6. Structure of tetra(2-furyl)porphyrins with N$_4$, N$_3$S and N$_2$S$_2$ cores

24 X = Y = NH
25 X = S, Y = NH
26 X = Y = S
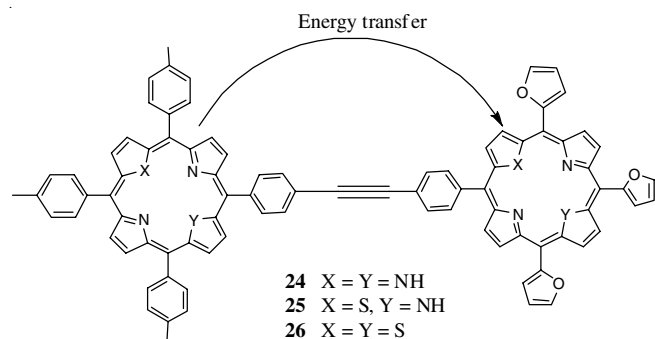
Fig. 7. Porphyrin dyads containing *meso*-aryl porphyrin and *meso*-furyl
porphyrin

groups with furyl groups, the electronic properties observed for *meso*-furyl porphyrins is quite unique. It was shown that the electrochemical and photophysical properties of porphyrin can be systematically tuned by stepwise replacement of six membered aryl groups with five membered furyl groups at the *meso*-positions of porphyrin macrocycle. Although the systematic alteration of electrochemical and photophysical properties of porphyrins has been shown previously by introducing substituents stepwise at β-positions, which are in direct conjugation with porphyrin, the variation of electronic properties *versus* the number of *meso*-substituents is not common.

Chemistry of porphyrins with *meso*-thienyl substituents: By far, thienyl porphyrins are the most studied of three type

R$_1$ = R$_2$ = R$_3$ = 4-tolyl;   R$_4$ = 2-furyl : **27**

R$_1$ = R$_3$ = 4-tolyl;   R$_2$ = R$_4$ = 2-furyl : **28**

R$_1$ = 4-tolyl;   R$_2$ = R$_3$ = R$_4$ = 2-furyl : **29**

R$_1$ = R$_2$ = R$_3$ = R$_4$ = 2-furyl : **30**

R$_1$ = R$_2$ = R$_3$ = 4-tolyl;   R$_4$ = 2-furyl : **31**

R$_1$ = R$_4$ = 4-tolyl;   R$_2$ = R$_3$ = 2-furyl : **32**

R$_1$ = R$_4$ = 2-furyl;   R$_2$ = R$_3$ = 4-tolyl : **33**

R$_1$ = 4-tolyl;   R$_2$ = R$_3$ = R$_4$ = 2-furyl : **34**

R$_1$ = R$_2$ = R$_3$ = R$_4$ = 2-furyl : **35**

R$_1$ = R$_2$ = R$_3$ = 4-tolyl;   R$_4$ = 2-furyl : **36**

R$_1$ = R$_4$ = 4-tolyl;   R$_2$ = R$_3$ = 2-furyl : **37**

R$_1$ =   4-tolyl;   R$_2$ = R$_3$ = R$_4$ = 2-furyl : **38**

R$_1$ = R$_2$ = R$_3$ = R$_4$ = 2-furyl : **39**

Fig. 8. Structures of mono, di, tri and tetra(2-furyl)porphyrins with N$_4$, N$_3$S and N$_2$S$_2$ cores

of porphyrins, due to the special properties displayed by thienyl substituents especially in molecular electronics applications.

Metallation: Metallation of the central core of porphyrin bearing five membered aromatic substituents in *meso*-positions is the easiest synthetic modification that is possible to synthetically porphyrins. Similar to the case of six-membered aryl substituted porphyrins, a large number of metals have been conveniently inserted into the porphyrin cores. The metals include Zn^{2+}, Cu^{2+}, Co^{2+}, Mg^{2+} and Sn^{4+}. Ravikanth *et al*. [25] synthesized tin metallated *meso*-furyl **40** and *meso*-thienyl porphyrins **41** (Fig. 9) using a modified chemical synthetic protocol and found that the spectral and electrochemical properties were sensitive to *meso*-substituents present.

tion spectra and fluorescence spectra. Electrochemical studies and density functional theory based calculations corroborated these results whereby the HOMO-LUMO gap was narrowed on moving from tetra aryl Mg porphyrin to tetrathienyl Mg porphyrin to tetrafuryl Mg porphyrin.

Liu *et al*. [27] synthesized tetrathienyl porphyrin and tetra-*kis*(3-methyl-2-thienyl)porphyrins and synthesized Zn^{2+}, Cu^{2+} and Co^{2+} metal complexes (Fig. 10). They found out that Zn(II) complex showed enhanced fluorescence, whereas Cu(II) and Co(II) complexes did not show any fluorescence.

44	R = H; M = Cu	**47**	R = CH₃; M = Cu

44 R = H; M = Cu   **47** R = CH_3; M = Cu
45 R = H; M = Co   **48** R = CH_3; M = Co
46 R = H; M = Zn   **49** R = CH_3; M = Zn

Fig. 10. Structure of Cu(II), Co(II) and Zn(II) complexes of unsubstituted and substituted thienyl porphyrins

40 X = O
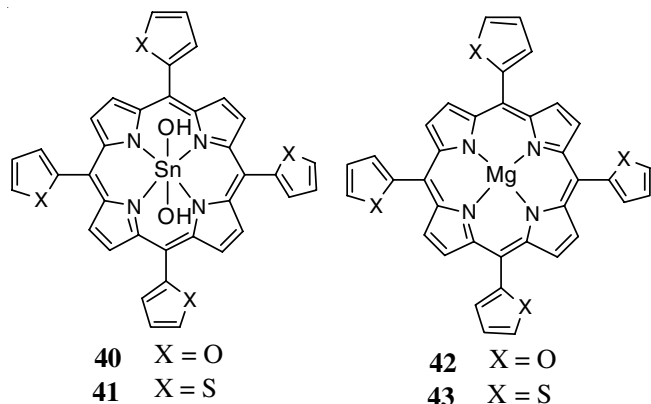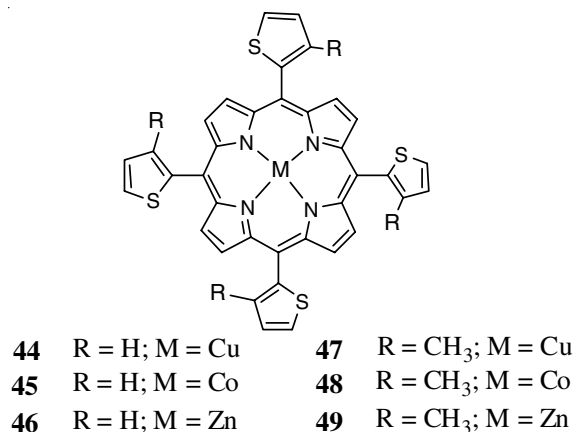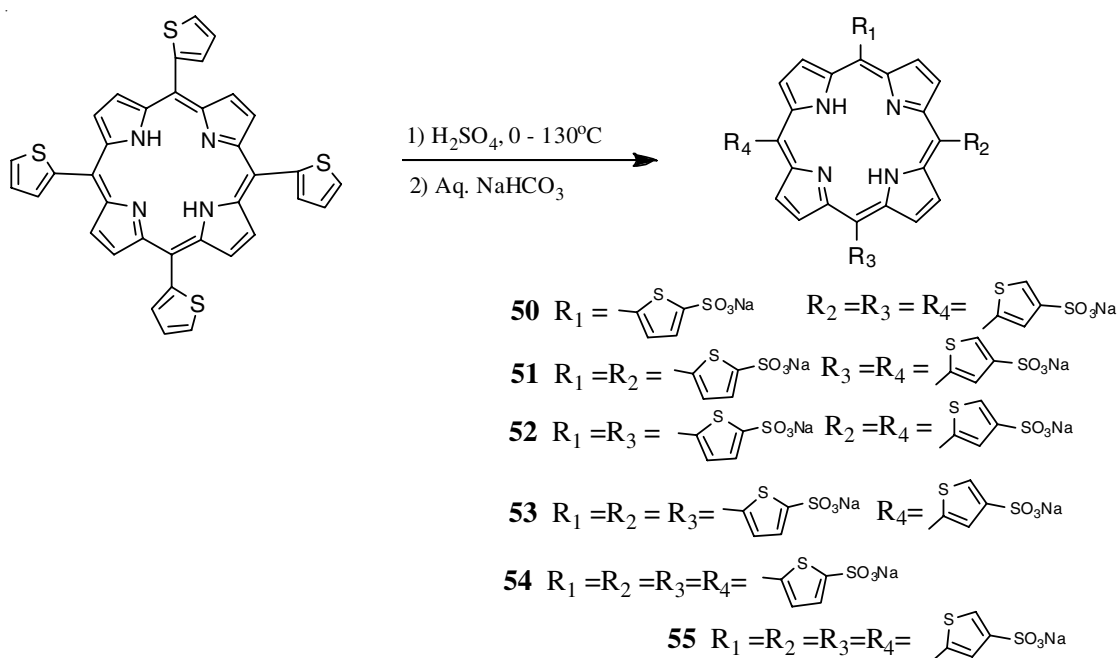**41** X = S

42 X = O
43 X = S

Fig. 9. Structure of furyl and thienyl porphyrins metallated with Sn and Mg

Magnesium metallated tetrafuryl and tetrathienyl porphyrins **42** and **43** were also reported by Ravikanth *et al*. [26]. The crystal structure of tetrafuryl derivative revealed that the furyl rings were coplanar with the porphyrin plane compared with that of tetrathienyl and tetraaryl derivatives. This coplanarity enabled stronger resonance between the furyl rings and the porphyrin ring resulting in bathochromic shifts in the absorp-

Sulphonation of thienyl moiety: Arai *et al*. [28] studied the aromatic electrophilic sulphonation reaction of tetra(2-thienyl)porphyrin in the presence of concentrated sulphuric acid (**Scheme-V**). They observed the regioselective products of the reaction were formed depending on the reaction conditions. Thus, it was observed that predominantly sulphonation occurred at 5-poisiton of thienyl when the temperature of reaction mixture was maintained between 0 and 20 ºC and thus was kinetically

1) H_2SO_4, 0 - 130ºC
2) Aq. $NaHCO_3$

50 R₁ = [thienyl]-SO₃Na   R₂ =R₃ = R₄= [thienyl]-SO₃Na

51 R₁ =R₂ = [thienyl]-SO₃Na R₃ =R₄ = [thienyl]-SO₃Na

52 R₁ =R₃ = [thienyl]-SO₃Na R₂ =R₄ = [thienyl]-SO₃Na

53 R₁ =R₂ = R₃= [thienyl]-SO₃Na R₄= [thienyl]-SO₃Na

54 R₁ =R₂ =R₃=R₄= [thienyl]-SO₃Na

55 R₁ =R₂ =R₃=R₄= [thienyl]-SO₃Na

Scheme-V: Sulphonation of tetrathienyl porphyrin [Ref. 23]

controlled whereas thermodynamically controlled 4-sulphonation of thienyl moieties was observed, when the reaction was performed at 130 ºC. The sulphonated products were highly soluble in water and also found to be highly aggregated.

Formylation of thienyl moeity: de Olievera *et al.* [29] had studied the Vilsmeiyer Haack reaction conditions on tetra(2-thienyl)porphyrin using POCl₃ and DMF. The reaction resulted in mono-, di-, tri- and tetra-formylated products (Fig. 11) with

the exclusive α-formylation on thienyl moieties. The group envisaged that these formylated thienyl porphyrins would be useful intermediates for synthesizing extended conjugated derivatives.

Tan *et al.* [30] converted a mono-formylated thineyl porphyrin with various other alkyl substituents on the thienyl substituents to derivatives (Fig. 12) with an appended 2-cyanoacrylic acid electron acceptor. These derivatives were then studied for
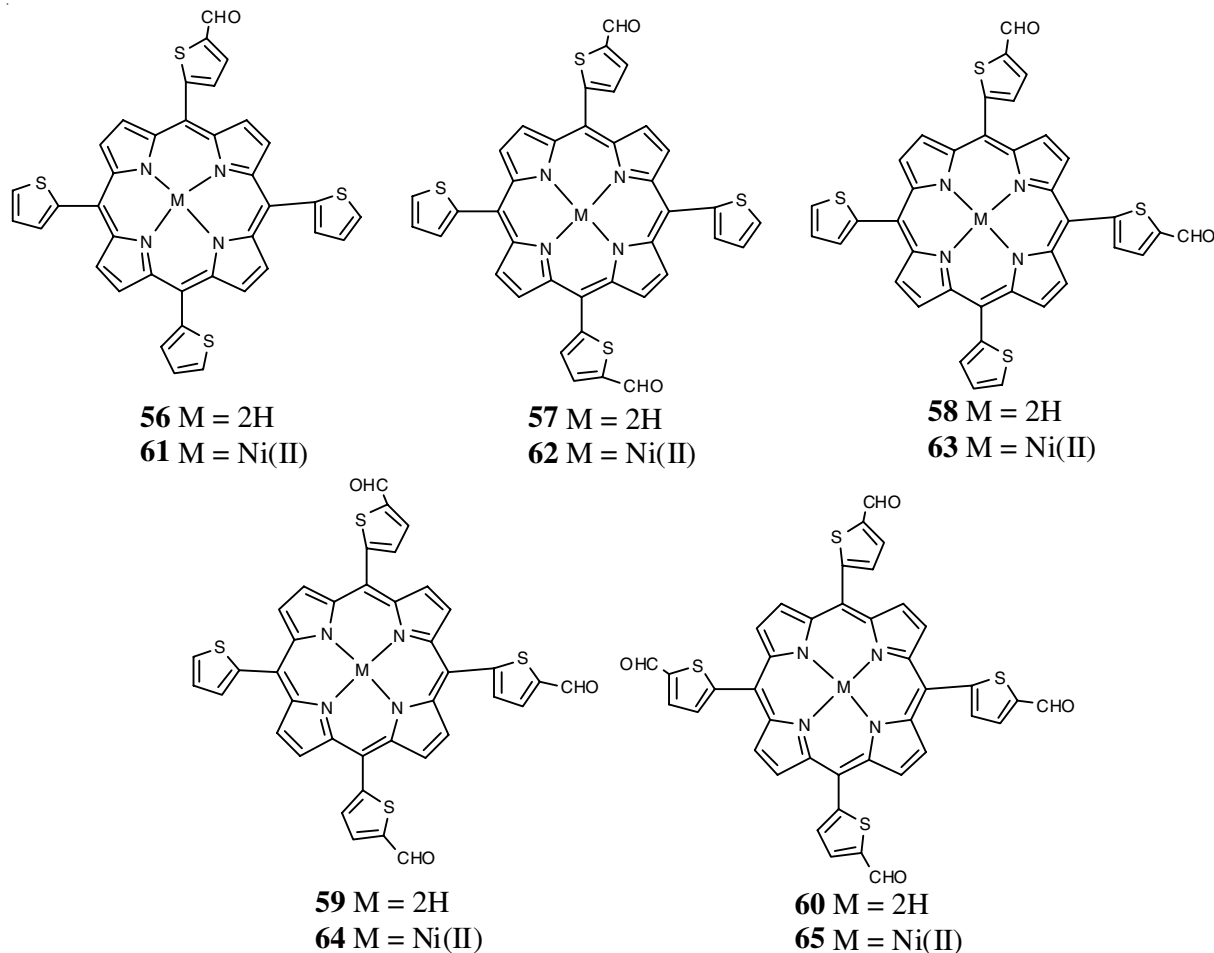

56 M = 2H
61 M = Ni(II)

57 M = 2H
62 M = Ni(II)

58 M = 2H
63 M = Ni(II)

59 M = 2H
64 M = Ni(II)

60 M = 2H
65 M = Ni(II)

Fig. 11. Structure of formylated tetrathienyl porphyrin

66 R₁= C₆H₁₃; R₂=H
67 R₁= CH₃;   R₂= H
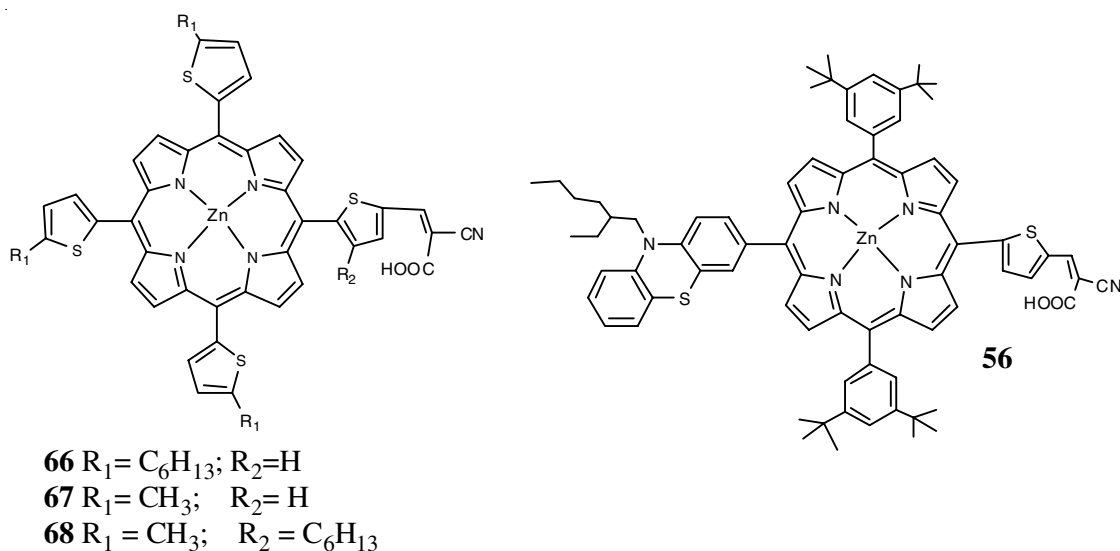**68** R₁ = CH₃;   R₂ = C₆H₁₃

56

Fig. 12. Structure of cyano acrylic acid appended thienyl porphyrins

their efficiency as dye-sensitized solar cells. Zheng *et al*. [31] also converted the formylated thienyl porphyrin into derivatives with an appended 2-cyano acrylic acid acceptor, which also featured a phenothiazine electron donor in the *trans-* position. These push-pull porphyrins were evaluated for their efficiency as dye sensitized solar cells.

Nitration of thienyl porphyrins: Bhavana *et al*. [32] had investigated the electrophilic nitration reaction of a variety of nickel(II) complexes of *meso*-tetra(2-thienyl)porphyrins with and without methyl substitution at various positions around the thienyl moiety. When mononitration was performed by reacting the porphyrin with one equivalent of cupric nitrate, they observed that porphyrin **69** with 2-thienyl *meso*-substitution underwent nitration at the 5-position of thiophene and porphyrin **70** with 5-methyl 2-thienyl *meso*-substituents underwent nitration at the 4-position of thiophene (Fig. 13). The nitration in the latter case was counterintuitive as the most preferred site (5-position of thienyl) for electrophilic substituition on the thiophene was blocked by a methyl group. They also observed that when porphyrin **71** with 3-methyl 2-thienyl *meso*-substituents was nitrated, the nitro group was introduced at the β-pyrrole position rather than the 5-position of thiophene (which is the most preseferred for the electrophilic substitution reaction). The authors also explained these counter intuitive results on the basis of conformation of thienyl ring with respect to the porphyrin ring. They reasoned that in the former case, since methyl groups on thienyl were directed away from the porphyrin ring, thienyls could adopt a coplanar conformation with the porphyrin ring and thus maximizing the extended conjugation which facilitated the nitration of thiophene ring. Whereas in the latter case, methyl groups at 3-position which were directed towards porphyrin ring made thienyls to adopt a non-coplanar conformation and thus resulting in the β-pyrrolic nitration in preference over the nitration of thiophene 5-position.

Bhavana *et al*. [33] also investigated the multi-nitration of nickel(II) complexes of unsubstituted and 5-methyl substituted (2-thienyl)porphyrins by appropriately increasing the stoichiometry of cupric nitrate being added to the reaction mixture. Accordingly, they observed that when mono, di and trinitration of tetra(2-thienyl)porphyrin was attempted, upto three 2-thienyl moieties were nitrated at 5-position respectively,

whereas tetranitration reaction resulted in the fourth nitration being directed to one of the β-pyrrolic positions instead of the 5-position of the fourth thienyl moeity. In the case of tetra(5-methyl 2-thienyl) porphyrin, mono and dinitration resulted in the expected nitration at 3-positions of thienyl group. However, trinitration resulted in a mixture of tri(3-nitro-5-methyl-2-thienyl)porphyrin as the major product with the β-nitrated di(3-nitro-5-methyl-2-thienyl) porphyrin as the minor product. When the major product was isolated and further nitration to tetra(3-nitro-5-methyl-2-thienyl) porphyrin was attempted, the reaction mixture resulted in a mixture of β-nitrated product was obtained as the major product whereas tetra(3-nitro-5-methyl- 2-thienyl)-porphyrin was obtained only as a minor product in poor yields. They also observed that in case of tetra(3-methyl-2-thienyl)-porphyrin, due to the presence of hindering methyl groups, thienyl rings were orthogonal to porphyrin ring and thus hindering extended conjugation. This resulted in the nitration being directed at the β-pyrrolic positions.

Further demonstration of how nitro thienyl substituted porphyrins can be utilized as building blocks to produce more complicated porphyrin based materials (Fig. 14). Bhavana *et al*. [34] converted mono and di(5-nitro-2-thienyl)porphyrins respectively to mono and di(5-amino-2-thienyl)porphyrins by the standard reduction reaction using Sn and HCl. Ferrocene moiety was appended to the porphyrin by condensing ferrocene carboxaldehyde with 5-amino-2-thienyl porphyrins obtained in the previous step.

In contrast to the above mentioned nitration reactions, mononitration using cupric nitrate on Cu(II) complex of *meso*-(3-thienyl)porphyrin [35] resulted only in β-nitration and no nitration happening at the thienyl residues

Halogenated thienyl porphyrin: Halogenated aryl porphyrins are important intermediates and precursors molecules for the synthesis of many porphyrin based functional materials. A few halogenated thienyl porphyrins are reported in literature. However, unlike the nitration, formylation and sulphonation reactions which were performed on the thineyl porphyrins, regioselective halogenation reaction was not done on thienyl porphyrins. Instead, halogen appended thiophene carboxaldehydes were utilized in the standard porphyrin synthesis to afford these halogenated thienyl porphyrins.
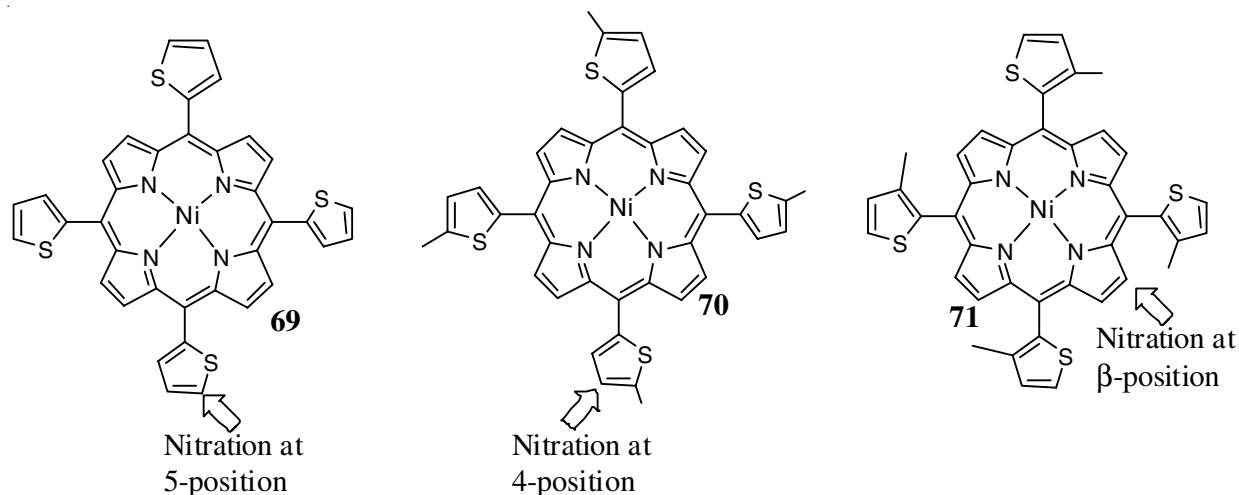

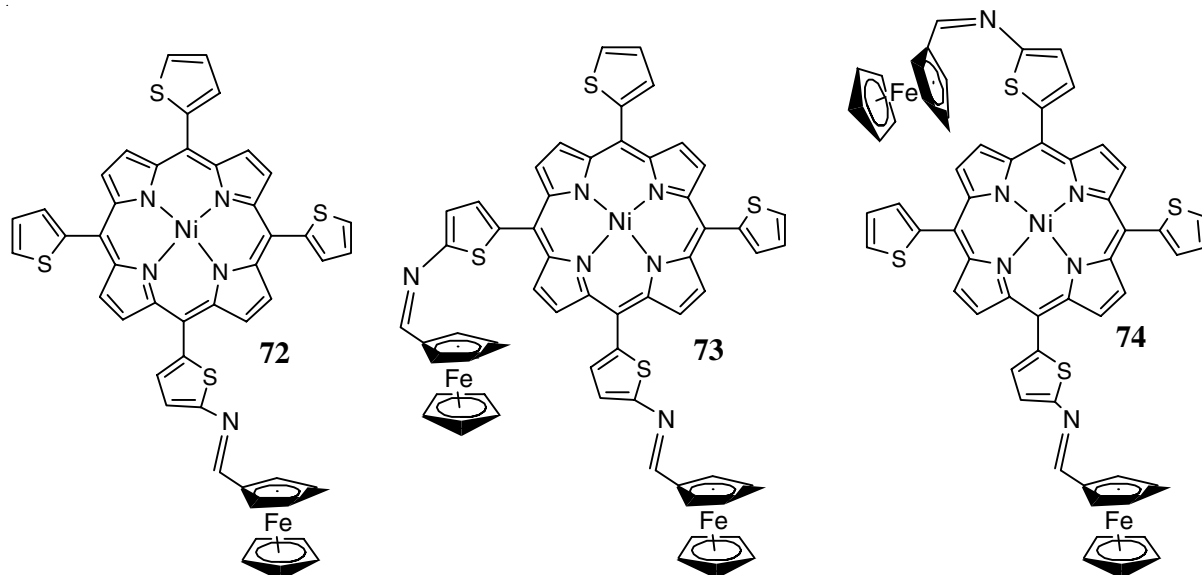Fig. 13. Nitration of substituted and unsubstituted thienyl porphyrins

Fig. 14. Structure of ferrocene appended thienyl porphyrins

Pryce *et al.* [36] have synthesized porphyrins bearing mono, di, tri and tetra(5-bromo-2-thienyl)porphyrins from 5-bromo thiophene-2-carboxaldehyde and converted them to CCTMS appended derivatives (Fig. 15) by performing standard Sonogashira reaction using palladium catalysts. The TMS protecting groups were then deprotected in these derivatives and Zn(II) metallated. The electrochemical and photophysical properties of all these derivatives were thouroughly compared and studied.

Several (2-thienyl)porphyrins bearing chloro and bromo substituents at the 5-position of thiophene were also synthesized and nitrated at the β-pyrrolic position by Bhavana *et al.* [37] and the photophysical and electrochemical properties were comparatively studied.

Utilizing 5-iodo thiophene-2-carboxaldehyde, de Oliveira *et al.* [38] synthesized tetra(5-iodo-2-thienyl)porphyrin (**79**). To establish its synthetic utility as building blocks and further functionalization, they coupled two different kinds of acrylate
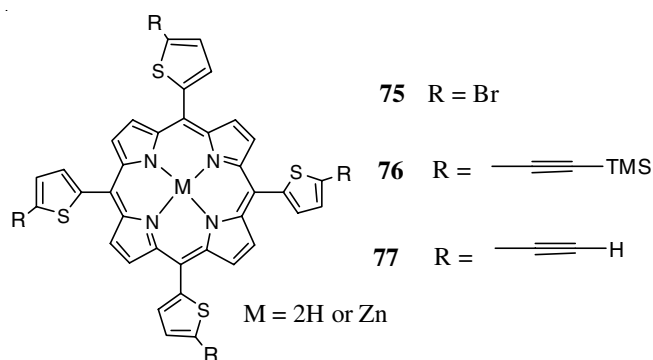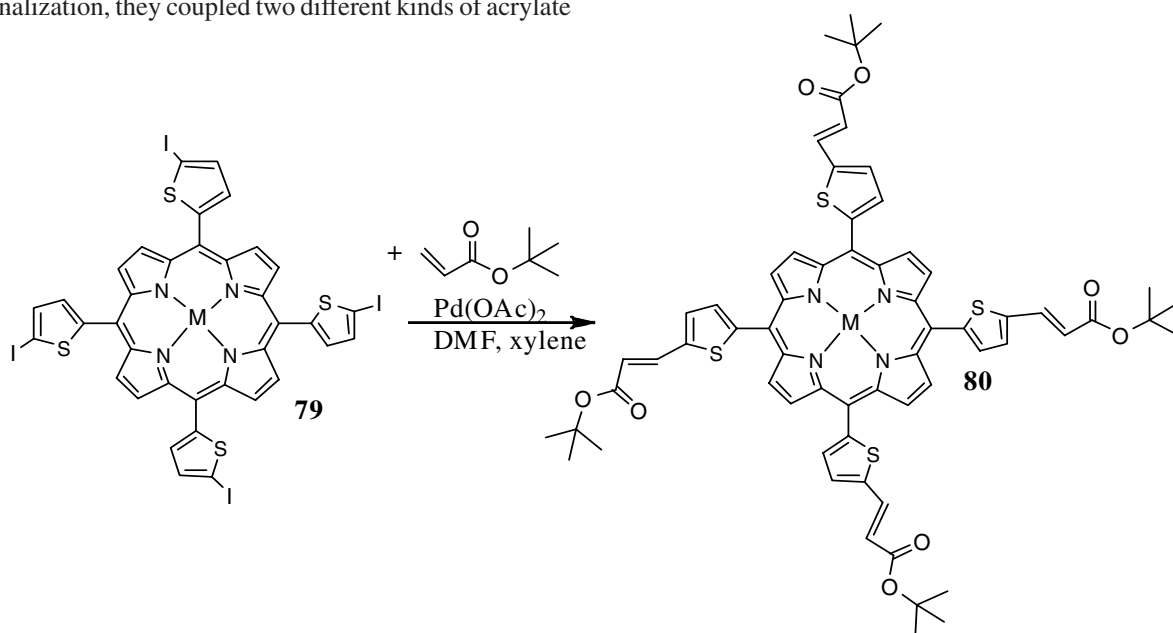

Fig. 15. Structures of thienyl porphyrin derivatives [Ref. 36]

esters using sequential one-pot Heck-Mizoroki cross-coupling reactions to afford mono, di, tri and tetra derivatized porphyrins. (**Scheme-VI**). These highly conjugated porphyrins were then demonstrated to be suitable dyes in solar cell applications.

Scheme-VI: Heck-Mizoroki cross-coupling reaction of tetra(5-iodo-2-thienyl)porphyrin

Conclusion

In conclusion, this review provides an overview of the development of chemistry of porphyins with five-membered *meso*-substituents instead of the conventional six-memberd aryl groups. Thus the introduction of thienyl, furyl and pyrolyl moieties into the *meso*-position of porphyrins paved the way to systematically alter and fine tune the electronic properties of porphyins by suitable synthesis. Further, the reactivity of thienyl porphyrins towards various reaction conditions were explored resulting in further functionalization of the thienyl substituents. Some of these substituents such as sulphonyl groups render the porphyrins water soluble, which may be highly useful in exploring their biological properties, whereas other functional groups such as formyl, amino, iodo or bromo groups can make these porphyrins suitable synthetically useful platforms for higher and complex functional materials.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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