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Review

Core-modified porphyrin based assemblies

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Contents

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ABSTRACT

Core-modified porphyrins, resulting from the replacement of one or two pyrrolic nitrogens with other hetero atoms such as O, S, Se, and Te possess very interesting and distinct properties compared to tetrapyrrolic porphyrins. Specially, the singlet state energy levels can be fine tuned with suitable modification of porphyrin core by substituting pyrrolic "N" with hetero atoms such as "O" and "S". In this review, we discuss the synthesis of various core-modified porphyrin building blocks containing one, two, three and four functional groups by following various synthetic methodologies developed in the past decade and the use of these core-modified porphyrin building blocks in the construction of several covalently and non-covalently linked hetero porphyrin dyads, triads, tetrads and pentads containing one or more different types of porphyrin sub-units. The photophysical studies are also described to show the possibility of singlet–singlet energy transfer from one porphyrin sub-unit to another in these hetero porphyrin arrays.

1. Introduction

The photosynthetic proteins in green plants and photosynthetic bacteria provided the inspiration for developing synthetic architectures to explore the energy and electron transfer functions of these natural solar energy conversion systems [1–5]. The basic conversion and storage processes of solar energy in these systems involves, first the collection of sunlight by a light-harvesting antenna system followed by an energy funnel to the reaction center through rapid and efficient transfer processes among chromophores. In the reaction center, an electron-transfer process starts from a primary electron donor constituted by two bacteriochlorophylls held in close proximity (the so-called "special pair") and then the electron is transferred along an energy gradient to the final acceptor with the formation of a charge-separated state [6–8]. Detailed information of all factors influencing these processes has yet to be explored and many issues are still ambiguous. Spectroscopic and theoretical studies of the photosynthetic processes are difficult to attain directly on natural systems because of their complexity and a useful approach could be the development of simpler synthetic models. The synthetic models provide the advantage to mimic natural processes without the complex structure of the protein scaffolding [9,10]. Porphyrin dimers or oligomers are good photosynthetic models, in that the geometry, distance, and/or angle between the porphyrin moieties strongly influence the efficiency of the photophysical processes [9,11]. Irradiation of a porphyrin dimer can be followed by two different processes between the subunits: an energy transfer, an electron transfer, or a combination of both processes [12,13]. The specific mechanism will depend on the type of dimer, and the type of interaction between the two moieties of the dimeric unit. A charge separation between chromophores is not observed in the light-harvesting antenna system

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of bacteria and green plants which provides energy to the special pair in the reaction center, and it was therefore of interest to synthesize porphyrin dyads in which energy transfer but not electron transfer would occur between the two sub-units immediately after irradiation [11]. A knowledge of the deactivation mechanism and the direction of energy transfer following irradiation of such compounds should provide information to the nature of the chromophores and their role in the photochemical properties of natural antenna systems.

Several covalently [14–18] and non-covalently [19–22] linked porphyrin arrays have been synthesized as model compounds for photosynthetic processes in natural systems and for their use in broad range of applications including medicine [23], catalysis [24] and optical devices [25,26]. However, porphyrin oligomers reported in the literature generally possess two identical macrocycles which neither allow for a selective excitation nor an elucidation of the energy transfer pathway upon irradiation. The direction of photoinduced energy transfer has been generally induced in porphyrin arrays by selective metallation of one of the porphyrin sub-unit and keeping the other porphyrin unit in metal free state. Several such systems have been synthesized and demonstrated as an efficient singlet–singlet energy transfer from one porphyrin unit to another [27–32]. However, in these porphyrin arrays, the absorption and emission bands of metallated porphyrin overlaps with the free base porphyrin leading sometimes to confusion in the correct estimation of energy transfer in these systems. The selective excitation of the porphyrin unit to induce electron or energy transfer in a particular direction can be achieved easily if the tetrapyrrolic macrocycles in the array are not identical (hetero). Several covalently linked hetero macrocyclic arrays such as porphyrin-chlorin [33–41], porphyrin-corrole [41–53], porphyrin-pheophorbide [54] and porphyrin-phthalocyanine [55–63] containing two different macrocyclic units in the array have been synthesized to study the photosynthesis process. A common feature of all these hetero macrocyclic arrays is that they all have similar pyrrole nitrogens as donor atoms. The hetero porphyrin arrays containing two dissimilar cores having different donor atoms are expected to possess interesting structural and electronic properties.

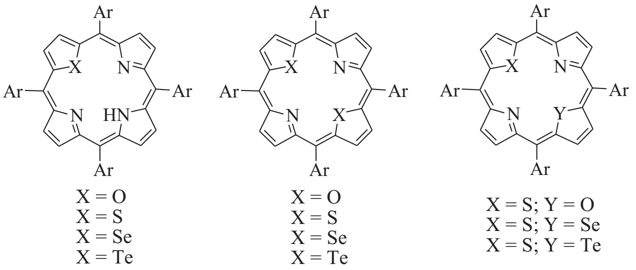
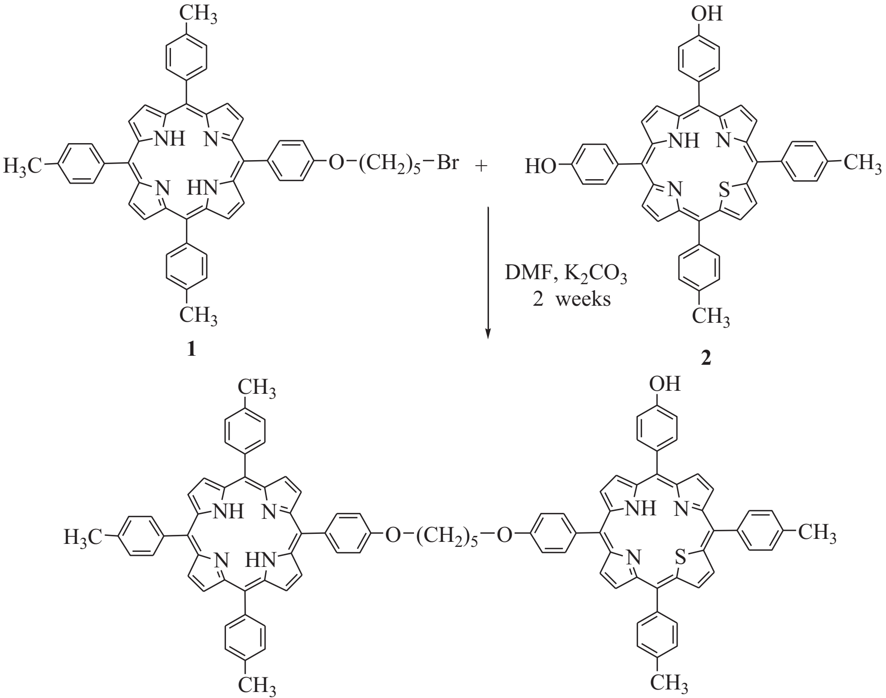
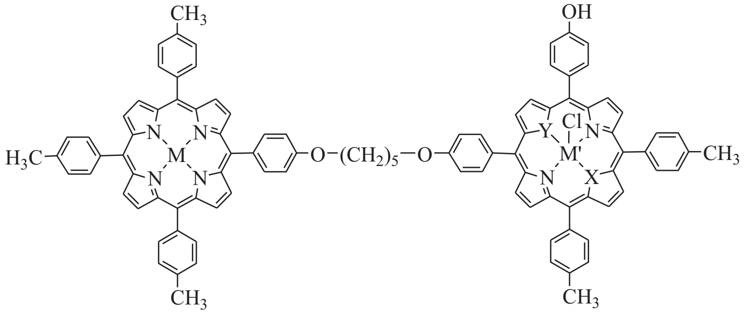


Chart 1. Molecular structure of core-modified porphyrins.

The replacement of one or two inner pyrrole nitrogens of porphyrin by heteroatoms such as O, S, Se and Te gives new macrocyclic systems called heteroatom-substituted porphyrins or core-modified porphyrins [64,65] (Chart 1), which possess quite different properties from normal porphyrins (N_4 core) in terms of both aromatic character and their ability to stabilize metals in unusual oxidation states [64]. For example, core-modified porphyrins stabilize copper and nickel in the +1 oxidation state which it is not possible to attain with regular porphyrins [66,67]. The assembly of such a heteroatom-substituted porphyrin (N_3S, N_3O, N_2S_2, N_2O_2, N_2SO, etc.) with normal porphyrin (N_4 core) or an assembly of two different heteroatom-substituted porphyrins would offer unique arrays which are expected to have unusual electronic structure and interesting properties. In the recent past, considerable work has been reported in the field of hetero porphyrin arrays containing different porphyrin sub-units and in this review, we discuss the synthetic advances of covalent and non-covalent hetero porphyrin arrays containing different types of porphyrin sub-units and also at relevant places, the photophysical properties are discussed to show that the energy transfer from one porphyrin sub-unit to another is possible in these hetero porphyrin arrays.

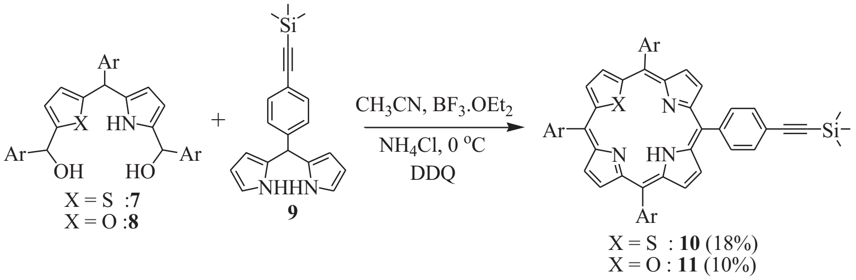


Scheme 1. Synthesis of covalently linked hetero porphyrin dyad **3** with flexible linker.



X = S; Y = NH; M = 2H : **3**
X = S; Y = NH; M = Zn^{+2} : **4**
X = S; Y = NH; M = Ni^{+2}; M' = Ni^{+2} : **5**
X = S; Y = NH; M = Zn^{+2}; M' = Cu^{+2} : **6**

Chart 2. Flexible ether bridged covalent hetero porphyrin dyads **3**–**6**.

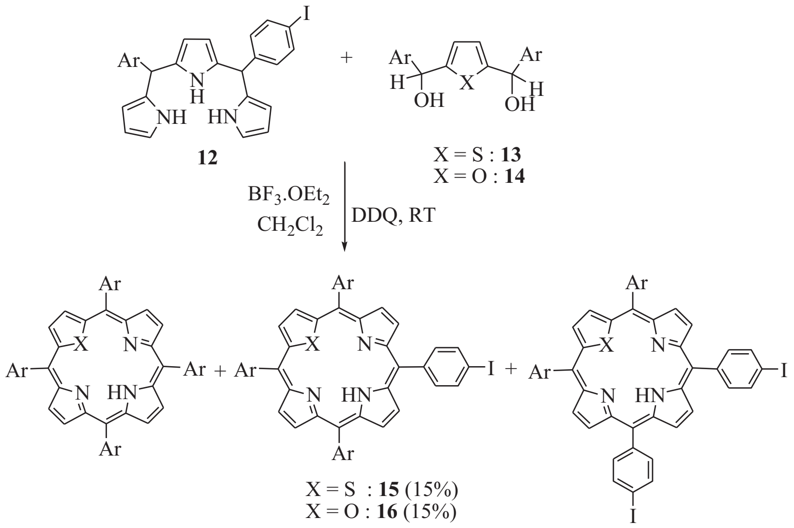


Scheme 2. Lindsey and co-workers method for the synthesis of mono-functionalized 21-heteroatom substituted porphyrins **10** and **11**.

2. Covalently linked hetero porphyrin arrays

2.1. Covalently linked hetero porphyrin dyads

The first covalently linked hetero porphyrin dyad **3** containing normal porphyrin (N_4 core) and thiaporphyrin (N_3S core) sub-units was synthesized in 1994 by Pandian and Chandrashekar [68]. A *cis*-difunctionalized thiaporphyrin building block, 5,20-bis(*p*-tolyl)-10,15-(*p*-hydroxyphenyl)-21-thiaporphyrin **2** was used instead of mono-functionalized thiaporphyrin building block which was not accessible at that time. The thiaporphyrin building block **2** was synthesized by following Ulman's methodology [69] and condensed with 5-[4-(5-bromo-1-pentoxy)phenyl]-10,15,20-tri(*p*-tolyl)porphyrin [70] **1** in DMF in the presence of K_2CO_3 for 2 weeks at room temperature (Scheme 1). The reaction proceeded very slowly and the dyad **3** was isolated in 27% yield. Surprisingly, the triad formation was not noticed in this reaction although *cis*-difunctionalized thiaporphyrin building block was used. The homo and hetero bis-metal derivatives such as dinickel porphyrin dyad **5** and copper–zinc porphyrin dyad **6** were synthesized by subjecting dyad **3** under standard metallation conditions [69]. The NMR, absorption, and electrochemical studies of dyads **3** and **4** indicated that the porphyrin and core-modified porphyrin sub-units in these dyads interact very weakly and retain most of their individ-



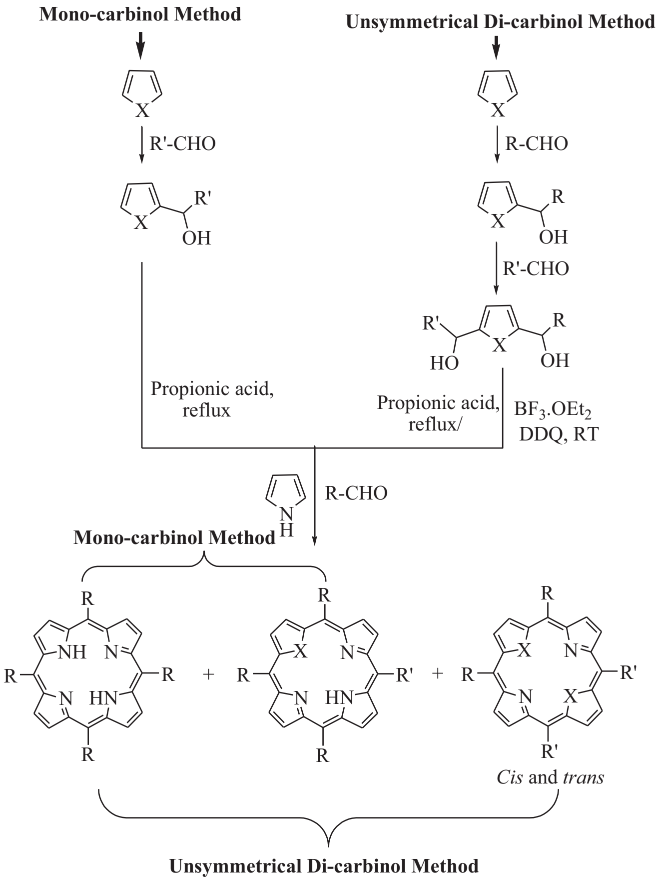
Scheme 3. Lee and co-workers method for the synthesis of mono-functionalized 21-heteroatom substituted porphyrins **15** and **16**.

ual characteristic features. However, in homo and hetero bis-metal derivatives **5** and **6** (Chart 2), they observed substantial interaction between the two sub-units which was attributed to the structural change caused by the introduction of metal in two different porphyrin cores.

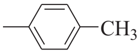
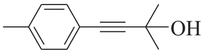
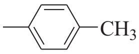
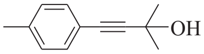
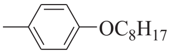
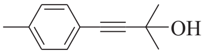
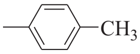
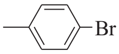
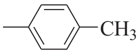
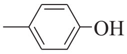
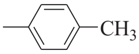
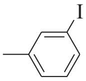
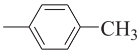
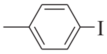
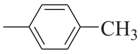
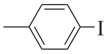
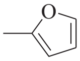
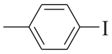
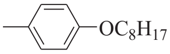
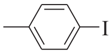
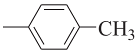
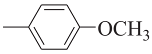
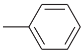
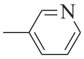
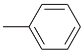
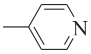
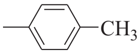
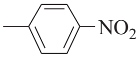
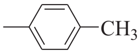
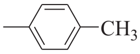
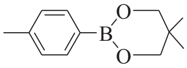
Electrochemical studies on bis metal derivatives **5** and **6** indicated that the thiaporphyrin unit stabilizes metals like Cu and Ni in the +1 oxidation state whereas the normal porphyrin unit stabilizes these metals in the +2 oxidation state. Thus, these novel hetero porphyrin dyads have the same metal existing in two different oxidation states. The photophysical studies in various solvents indicated that the dyads **3** and **4** exist in folded and unfolded conformations and indicated the possibility of energy transfer at singlet state from N_4/ZnN_4 porphyrin sub-unit to N_3S porphyrin sub-unit [71].

Lee, Lindsey and co-workers [72] developed a [2 + 2] route to synthesize the first examples of mono-functionalized N_3S and N_3O porphyrin building blocks **10** and **11** which are the key precursors required for the synthesis of variety of hetero porphyrin dyads. Condensation of dipyrromethane having trimethylsilylethynylphenyl functional group at *meso*-position **9** with thienylpyrromethane di-carbinol **7** or furylpyrromethane di-carbinol **8** in acetonitrile at 0 °C catalyzed by BF_3OEt_2 in the presence of ammonium chloride yielded the mono-functionalized 21-thiaporphyrin **10** or 21-oxaporphyrin **11** in 8–10% yields (Scheme 2). Lee et al. [73] have used [3 + 1] condensation approach to synthesize the mono-functionalized core-modified porphyrin building blocks **15** and **16** by condensing *meso*-iodophenyl functionalized unsymmetrical tripyrrane **12** with symmetrical thiophene di-carbinol **13** and furan di-carbinol **14** respectively under mild porphyrin forming conditions (Scheme 3). However, interestingly, the authors have not used these mono-functionalized N_3O and N_3S porphyrin building blocks for the synthesis of any hetero porphyrin dyads containing core-modified porphyrin sub-units.

Ravikanth and co-workers developed two simple synthetic methods such as “mono-carbinol” [74,75] and “unsymmetrical di-carbinol” [76] methods to synthesize the mono-functionalized core-modified porphyrin building blocks. In mono-carbinol method, two equivalents of the functionalized thiophene or furan mono-carbinol were condensed with two equivalents of aryl aldehyde and three equivalents of pyrrole under Adler’s conditions [77] which resulted in the formation of mixture of two porphyrins (Scheme 4). The desired mono-functionalized core-modified porphyrins **17**–**32** were separated by column chromatography and isolated in 2–6% yields. Although the mono-carbinol method was very simple, the yields of mono-functionalized core-modified porphyrins were quite low and the method was useful only for the synthesis of the mono-functionalized 21-thia (N_3S core) and 21-oxaporphryins (N_3O core). Hence, an unsymmetrical di-carbinol method [76] was developed, which was useful to synthesize any desired mono-functionalized core-modified porphyrin with variety of porphyrin cores such as N_3O, N_3S, N_2SO, N_2S_2, etc. In the unsymmetrical di-carbinol method [76] the functionalized unsymmetrical thiophene/furan di-carbinol was condensed with aryl aldehyde and pyrrole under porphyrin forming conditions (Scheme 4) and led to mono-functionalized N_3S or N_3O porphyrins in 10–12% yields. Similarly, the mono-functionalized di-hetero atoms substituted porphyrins **33**–**47** were synthesized by condensing one equivalent of functionalized unsymmetrical thiophene/furan di-carbinol with one equivalent of suitable tripyrrane under Adler’s [77] or Lindsey’s [78] porphyrin forming conditions (Scheme 5). Ravikanth and co-workers were also synthesized mono *meso*-functionalized



Scheme 4. Synthesis of mono-functionalized 21-heteroatom substituted porphyrins using mono-carbinol and dicarbinol methods.

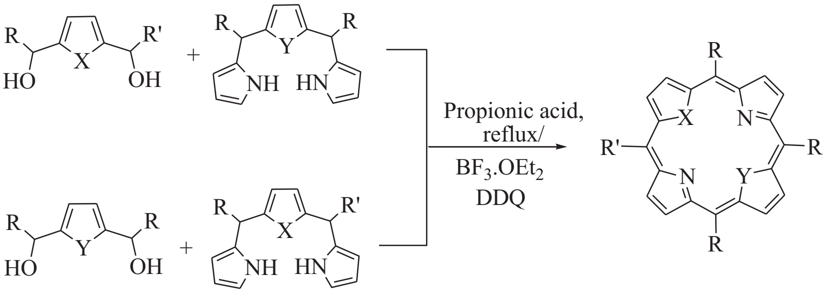
C. No.	X	R	R'	Mono-carbinol Method (Yield)	Di-carbinol Method (Yield)
17	S			-	9%
18	O			4%	-
19	S			6%	-
20	S			6%	10%
21	S			6%	-
22	S			2%	-
23	S			-	6%
24	O			2%	-
25	S			-	8%
26	O			3%	-
27	S			-	11%
28	S			7%	-
29	S			6%	-
30	S			-	12%
31	S		−H	-	6%
32	S			-	12%

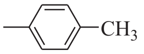
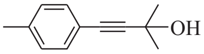
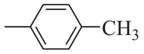
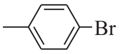
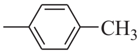
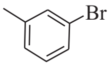
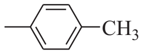
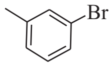
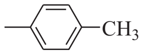
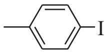
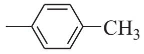
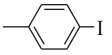
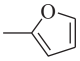
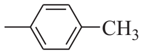
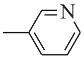
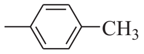
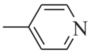
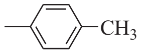
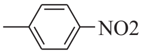
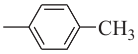
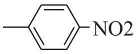
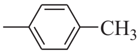
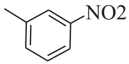
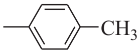
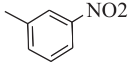
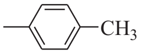
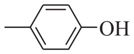
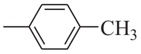
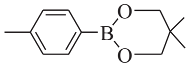
Scheme 4. (*Continued*).

core-modified porphyrin building blocks [79,80] starting from mono *meso*-unsubstituted core-modified porphyrins **48**–**51** as outlined in Scheme 6. The *meso*-bromo core-modified porphyrins [80,81] **52**–**55** were prepared by treating one equivalent of *meso*-unsubstituted core-modified porphyrins **48**–**51** respectively with one equivalent of *N*-bromo succinimide in $CHCl_3$ at room temperature (Scheme 6). The mono *meso*-ethynyl core-modified porphyrins **60**–**63** were prepared in two steps from their corresponding *meso*-bromo core-modified porphyrins **52**–**55** [79–81]. In the first step, *meso*-trimethylsilylacetyl-core-modified porphyrins **56**–**59** were prepared by treating *meso*-bromo core-modified porphyrins **52**–**55** with trimethylsilyacetylene in the presence of catalytic amount of $Pd_2(dba)_3/AsPh_3$ at 35 °C in triethylamine for 12 h. In the second step, the trimethylsilyl group was deprotected with K_2CO_3 in THF/CH_3OH and afforded the *meso*-ethynyl core-modified porphyrins **60**–**63** in decent yields (Scheme 6). In subsequent reports, Ravikanth and co-workers [74–76,82] showed the utility of mono-functionalized core-modified porphyrin building blocks for the synthesis of series of hetero porphyrin dyads **64**–**70** containing two different types of porphyrin sub-units (Chart 3).

The dyads **64**–**70** were prepared by coupling of the appropriate porphyrin building blocks having iodophenyl group at the *meso* position with the porphyrin building blocks having phenylethyne group at the *meso* position under Lindsey's copper free mild palladium(0) coupling conditions [83] as illustrated in Scheme 7 for the synthesis of diphenyl ethyne bridged hetero ZnN_4–N_2S_2 porphyrin dyad **67**. The hetero porphyrin dyad **67** was prepared by coupling of 5,10,15-tri(*p*-tolyl)-20-(4-iodophenyl)porphyrinatozinc(II) [84] **71** with 5-(4-ethynylphenyl)-10,15,20-tri(*p*-tolyl)-21,23-dithiaporphyrin [76] **72** in the presence of $Pd_2(dba)_3/AsPh_3$ at 35 °C in toluene/triethylamine for 4 h (Scheme 7). Similarly, all other hetero diphenyl ethyne bridged dyads **64**–**70** containing two different porphyrin sub-units were synthesized by coupling the appropriate porphyrin building blocks under copper free palladium(0) coupling conditions. The spectroscopic studies supported a weak interaction between the porphyrin sub-units in dyads **64**–**70**.

The photophysical studies carried out on hetero porphyrin dyads **64**–**70** indicated a possibility of efficient energy transfer from one porphyrin sub-unit to another on selective excitation of

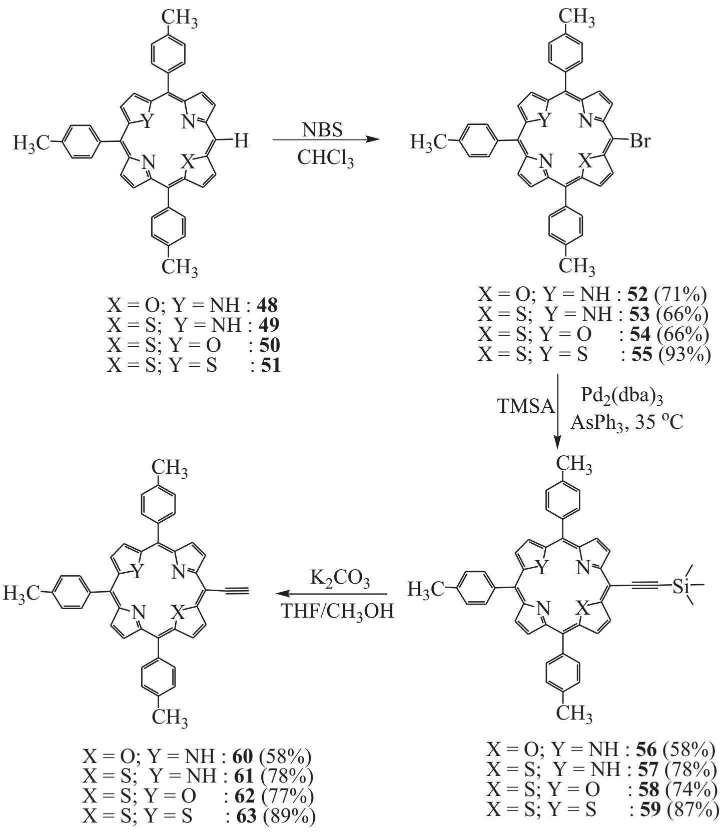


C. No.	X	Y	R	R'	Yield
33	S	S			19
34	S	S			10%
35	S	S			11%
36	S	O			7%
37	S	S			11%
38	S	O			10%
39	S	S			11%
40	S	S			10%
41	S	S			11%
42	S	S			10%
43	O	S			8%
44	S	S			10%
45	O	S			6%
46	S	S			8%
47	S	S			12%

Scheme 5. Synthesis of mono-functionalized 21,23-diheteroatom substituted porphyrins.

one porphyrin unit. For example, the hetero porphyrin dyad **67** containing ZnN_4 porphyrin and N_2S_2 porphyrin sub-units [76,85], on excitation at 550 nm where ZnN_4 porphyrin sub-unit absorbs strongly as compared to N_2S_2 porphyrin sub-unit, the emission of ZnN_4 porphyrin quenched by 93% and the strong emission from N_2S_2 porphyrin sub-unit was observed. However, as shown in Fig. 1, when 1:1 mixture of its corresponding monomers **71** and **72** was irradiated at 550 nm, a strong emission was observed mainly from the ZnN_4 porphyrin sub-unit (Fig. 1). These observations supported an efficient energy transfer from the ZnN_4 porphyrin sub-unit to N_2S_2 porphyrin sub-unit in hetero porphyrin dyad **67**. The time-resolved fluorescence studies indicated that the rate of excitation energy transfer, K_{ENT} was 152 ps and the yield of energy transfer, Φ_{ENT} was 93% for dyad **67**. Similarly, the studies on other hetero porphyrin dyads **64**–**70** also confirmed the efficient energy transfer from donor porphyrin sub-unit to acceptor porphyrin sub-unit.

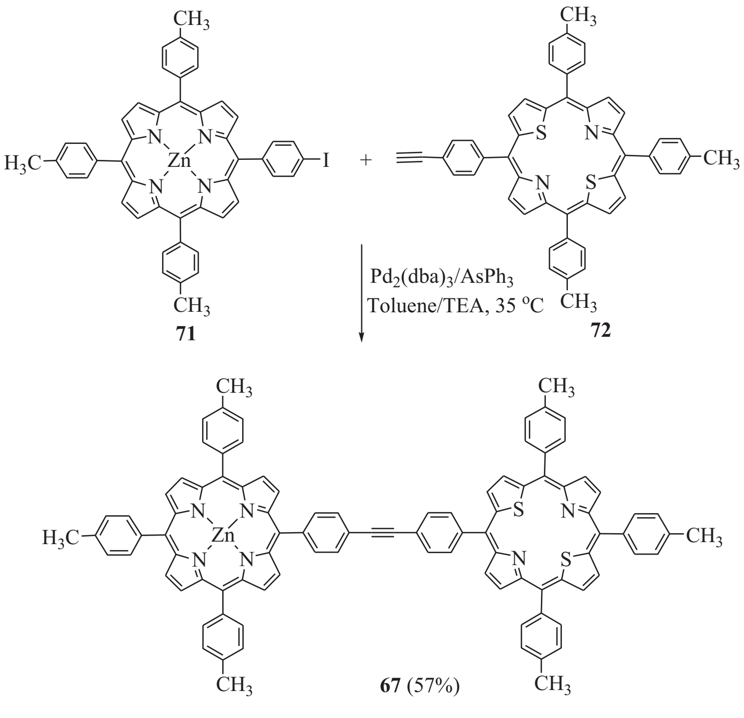
Ravikanth and co-workers [86] also synthesized diphenyl ethyne bridged hetero porphyrin dyads **73**, **74** and **75** containing *meso*-tolyl and *meso*-furyl porphyrin sub-units, under mild Pd(0) mediated coupling conditions (Chart 4). In these dyads, the singlet state energy of porphyrin having six membered *meso*-aryl groups is at higher energy and acts as energy donor and the singlet state energy of porphyrin having five membered *meso*-furyl groups is at lower energy and acts as energy acceptor. The comparison of fluorescence spectra of dyad **74** with its 1:1 mixture of porphyrin monomers **39** and **80** shown in Fig. 2a supported >90% efficient energy transfer from *meso*-tolyl porphyrin sub-unit to *meso*-furyl porphyrin sub-unit in dyads **73**–**75**. The K_{ENT} and Φ_{ENT} were almost same as other diphenylethyne bridged hetero porphyrin dyads described above but the energy transfer rates were relatively lower in dyads **73**–**75.** The energy level diagram shown in Fig. 2b also supported energy transfer from *meso*-tolyl porphyrin to *meso*-furyl



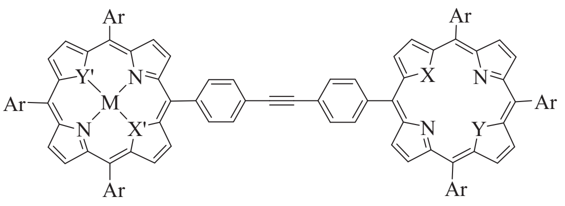
Scheme 6. Synthesis of mono *meso*-functionalized core-modified porphyrins **52**–**63**.

porphyrin and ruled out the possibility of electron transfer in dyads **73**–**75**.

The phenyl ethyne bridged hetero porphyrin dyads **76**–**79** containing two different porphyrin sub-units were also synthesized under mild Pd(0) mediated coupling conditions (Scheme 8) [81,82]. The *meso*-bromo N_3S porphyrin [81] **53**, was the key building block for the synthesis of phenyl ethyne bridged hetero porphyrin dyads **76**–**79**. The dyads **76**–**79** were synthesized



Scheme 7. Synthesis of diphenylethyne bridged covalently linked hetero dyad **67**.



X = S; Y = NH; X' = Y' = N; Ar = mesityl; Ar' = O-n-octyl; M = Zn : **64**
X = S; Y = NH; X' = Y' = N; Ar = mesityl; Ar' = O-n-octyl; M = 2H : **65**
X = O; Y = NH; X' = Y' = N; Ar = mesityl; Ar' = O-n-octyl; M = Zn : **66**
X = S; Y = S; X' = Y' = N; Ar = tolyl; Ar' = tolyl; M = Zn : **67**
X = S; Y = S; X' = Y' = N; Ar = tolyl; Ar' = tolyl; M = 2H : **68**
X = S; Y = NH; X' = O; Y' = NH Ar = tolyl; Ar' = O-n-octyl : **69**
X = S; Y = S; X' = S; Y' = NH Ar = tolyl; Ar' = tolyl : **70**

Chart 3. Diphenyl ethyne bridged covalent hetero porphyrin dyads **64**–**70**.

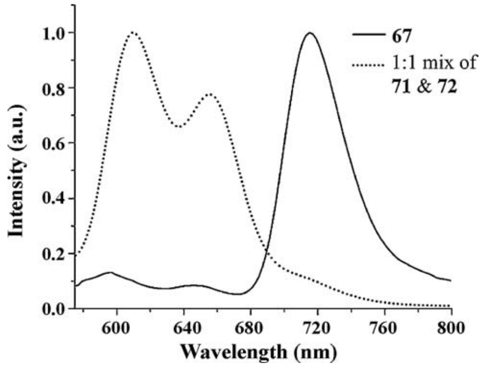
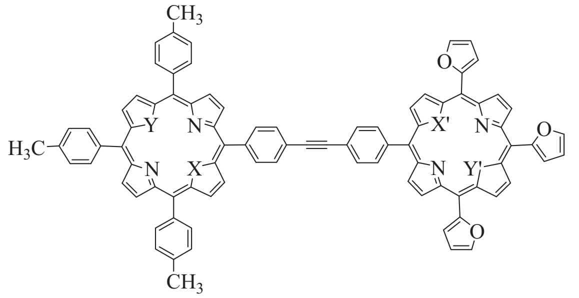


Fig. 1. Comparison of steady-state emission spectra of dyad **67** (—) and 1:1 mixture of **71** and **72** (···). The excitation wavelength used was 550 nm.

by coupling of *meso*-bromo N_3S porphyrin **53** with corresponding *meso*-phenylethyne porphyrins **80**–**83** in the presence of a catalytic amount of $Pd_2(dba)_3/AsPh_3$ at 35 °C for 15 h (Scheme 8). Unlike diphenylethyne bridged dyads described above, in phenylethyne bridged dyads **76**–**79**, the porphyrin sub-units interact strongly and the electronic properties of porphyrin sub-unit having ethynyl group at direct *meso*-position altered significantly with almost no affect on the electronic properties of the other porphyrin sub-unit having *meso*-phenyl group [82]. The fluorescence studies supported energy transfer from one porphyrin sub-unit to another in dyads **76**–**79**. This is illustrated in the fluorescence spectrum of dyad **76** containing ZnN_4 and N_3S porphyrin sub-units (Fig. 3). On excitation of ZnN_4 porphyrin sub-unit at 550 nm where ZnN_4 porphyrin absorbs strongly, the emission was noted from N_3S porphyrin sub-unit supporting the energy transfer from ZnN_4 porphyrin sub-unit to N_3S porphyrin sub-unit. Furthermore, the rate of energy transfer in phenyl ethyne bridged dyad **76** (26 ps^{-1}) was relatively faster than diphenyl ethyne bridged dyad **64** (59 ps^{-1}). This is attributed



X = Y = NH; X' = S; Y' = NH : **73**
X = Y = NH; X' = Y' = S : **74**
X = S; Y = NH; X' = Y' = S : **75**

Chart 4. Diphenyl ethyne bridged covalent hetero porphyrin dyads **73**–**75** containing *meso*-tolylporphyrin and *meso*-furylporphyrin sub-units.

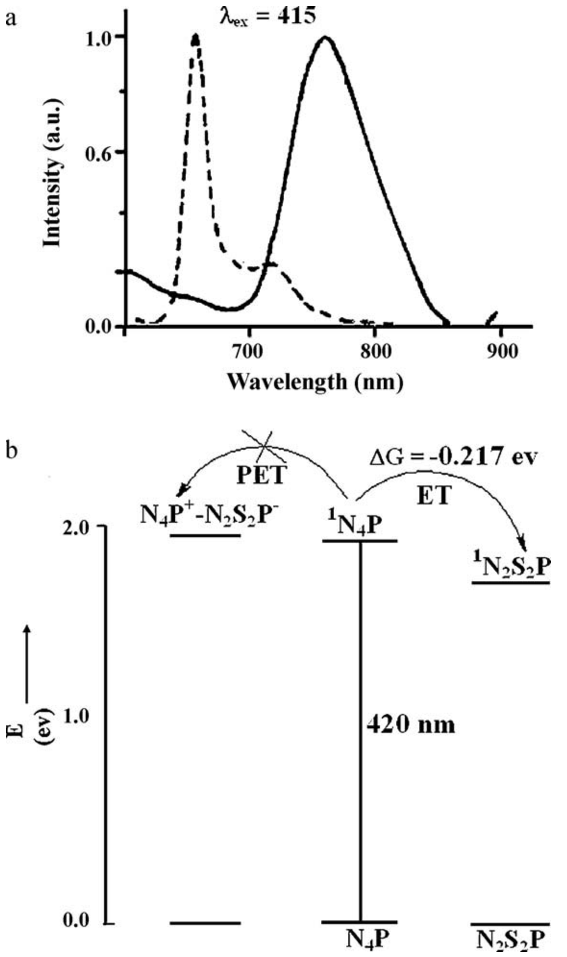


Fig. 2. (a) Comparison of normalized emission spectra of dyad **74** (—) with its corresponding 1:1 mixture of porphyrin monomers **39** and **80** (- - -) recorded in toluene. (b) Energy level diagram of **74** depicting free energy values for electron and energy transfer processes from lowest singlet excited state.

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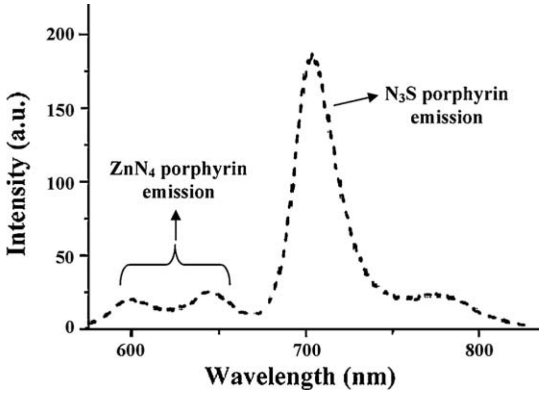

Fig. 3. The steady-state emission spectra of phenyl ethyne bridged dyad **76** recorded in toluene at λ_{ex} = 550 nm.

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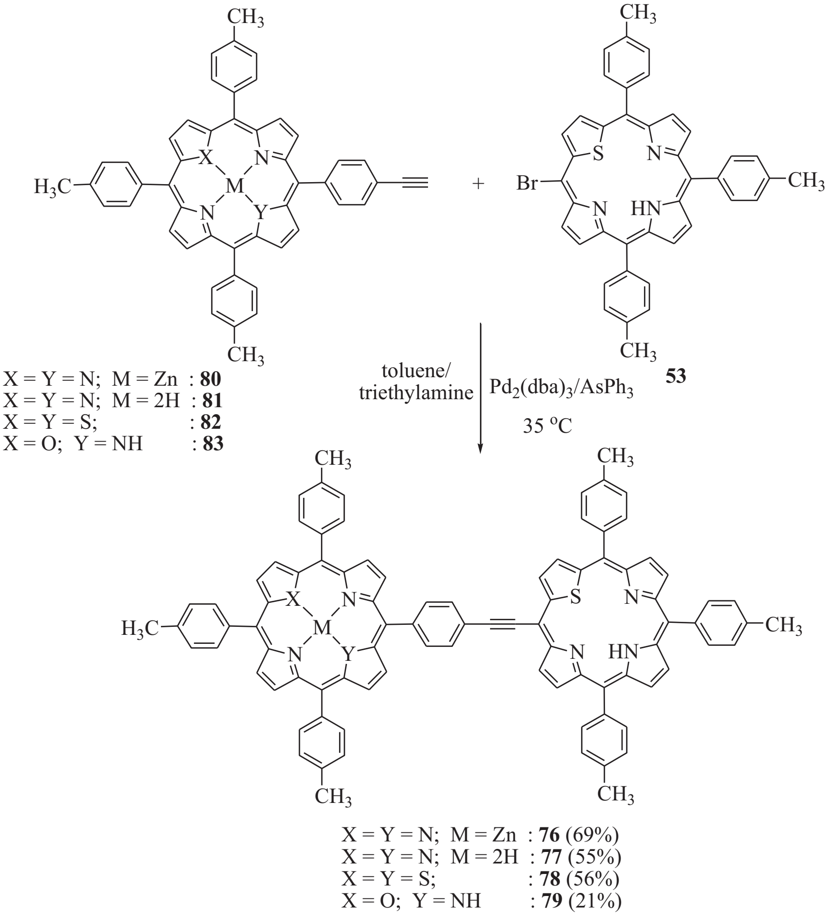
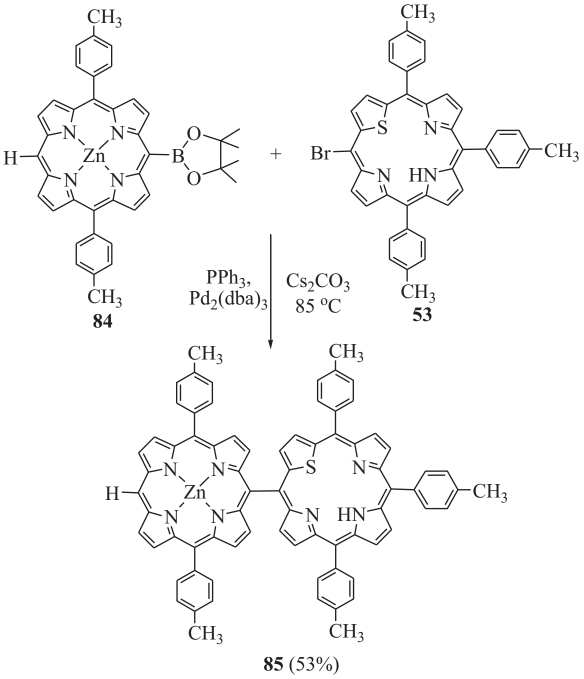


Scheme 8. Synthesis of phenylethyne bridged covalent hetero dyads **76**–**79**.

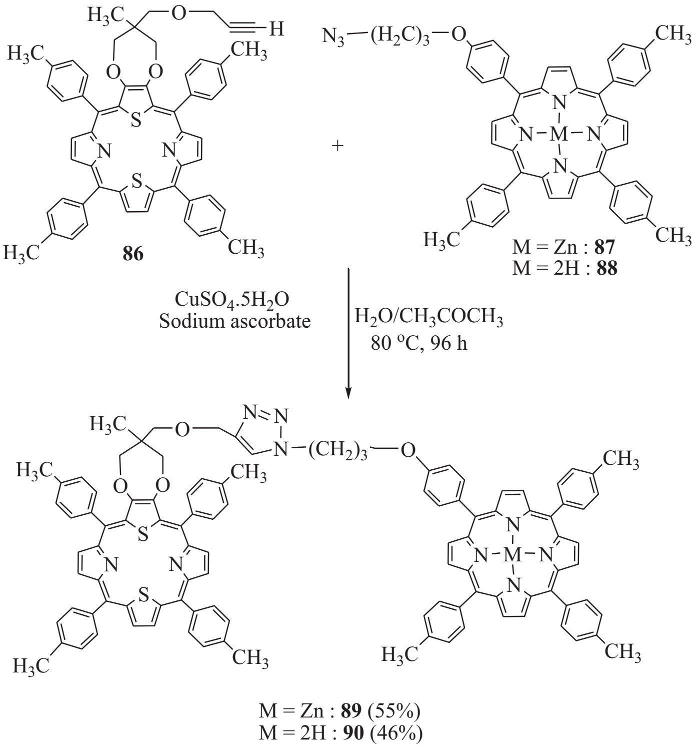
to the short distance between energy donor and energy acceptor in phenyl ethyne bridged dyad **76** compared to diphenyl ethyne bridged dyad **64** [82].

One example of direct *meso*–*meso* linked hetero porphyrin dyad **85** containing ZnN_4 and N_3S porphyrin sub-units was reported [81]. The dyad **85** was synthesized by coupling of *meso*-bromo N_3S porphyrin, 5-bromo-10,15,20-tri(*p*-tolyl)-21-thiaporphyrin [81] **53** with ZnN_4 porphyrin boronate, 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10,20-bis(*p*-tolyl)porphyrinatozinc(II) [87] **84** in toluene/DMSO at 85 °C in the presence of PPh_3, Cs_2CO_3 and $Pd_2(dba)_3$ for 16 h (Scheme 9). The steady-state fluorescence study of dyad **85** showed that the emission of the ZnN_4 porphyrin sub-unit was quenched to a greater extent and the emission was observed mainly from N_3S porphyrin sub-unit, supporting the efficient energy transfer from ZnN_4 porphyrin sub-unit to N_3S porphyrin sub-unit.

Flexible triazole bridged hetero porphyrin dyads [88] **89** and **90** containing ZnN_4 or N_4 and N_2S_2 porphyrin sub-units respectively were prepared under classical Click reaction conditions by reacting N_2S_2 porphyrin having an ethyne functional group **86** with ZnN_4 **87** or N_4 porphyrin **88** having an azide functional group in the presence of sodium ascorbate and $CuSO_4$ in a water–acetone mixture at room temperature for 4 days (Scheme 10). The absorption spectrum of dyads **89** and **90** was essentially a linear combination of absorption spectra of both the porphyrin sub-units which supported no interaction between the porphyrin sub-units. The steady-state fluorescence studies indicated energy transfer from the ZnN_4 or N_4 porphyrin sub-unit to the N_2S_2 porphyrin sub-unit at singlet state in dyads **89** and **90** respectively. For example, the dyad **90** when excited at 420 nm where the N_4 porphyrin sub-unit



Scheme 9. Synthesis of *meso*–*meso* linked hetero porphyrin dyad **85**.



Scheme 10. Synthesis of triazole-bridged porphyrin dyads **89** and **90** under "Click" reaction conditions.

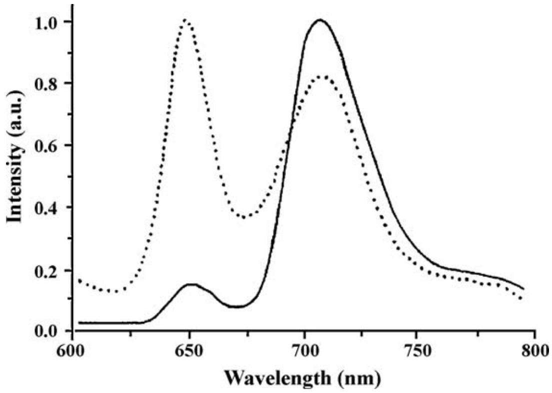
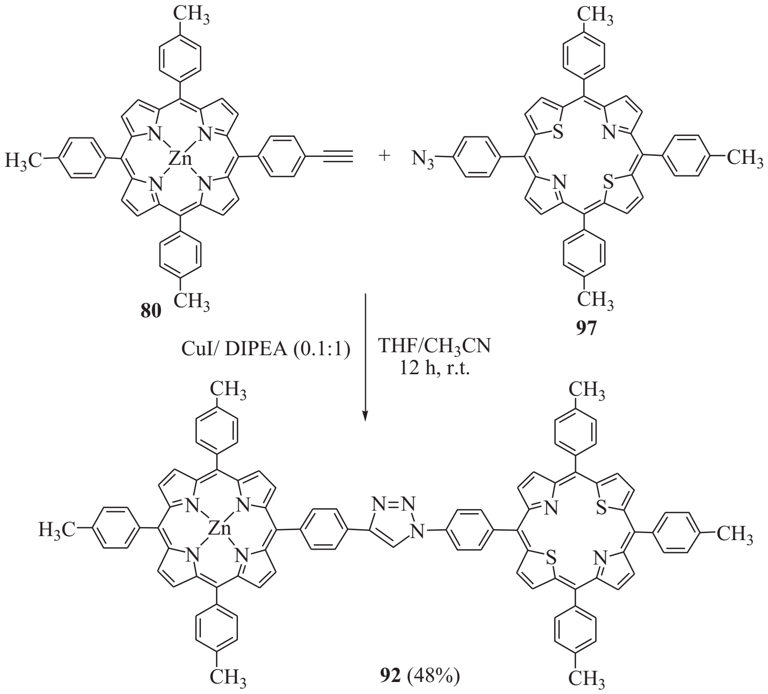


Fig. 4. Comparison of steady-state emission spectra of dyad **90** (—) and **68** (···). The excitation wavelength used was 420 nm.

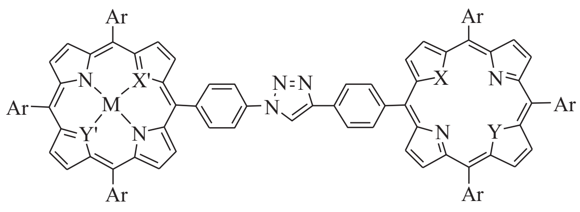
Reproduced with permission from Ref. [88].

absorbs strongly, the emission of the N_4 porphyrin was quenched by 97% and a strong emission from the N_2S_2 porphyrin sub-unit was observed. On the other hand, with the diphenylethyne bridged porphyrin dyad **68** containing the same N_4 and N_2S_2 porphyrin sub-units, emission was noted from both N_4 and N_2S_2 porphyrin sub-units at the same excitation wavelength (Fig. 4). This study indicated that on changing the rigid diphenylethyne bridge in porphyrin dyad **68** to a flexible triazole-bridge in porphyrin dyad **90**, the energy transfer efficiency from the N_4 porphyrin sub-unit to the N_2S_2 porphyrin sub-unit is increased.

Rigid diphenyl triazole bridged hetero porphyrin dyads **91**–**96** (Chart 5) were synthesized under modified Click reaction conditions [89]. The standard Click reaction conditions used for the synthesis of flexible triazole bridged dyads **89** and **90** did not work effectively and copper insertion problems were also observed. Hence, Shetti and Ravikanth optimized alternate conditions to prepare diphenyl triazole bridged hetero porphyrin dyads **91**–**96**. For example, the diphenyl triazole bridged porphyrin dyad **92** was prepared by reacting 5-(4-ethynylphenyl)-10,15,20-tri(*p*-tolyl)porphyrinato zinc (II) [84] **80** with 5-(4-azidophenyl)-10,15,20-tri(*p*-tolyl)-21,23-dithiaporphyrin **97** in THF/CH_3CN (1:1) in the presence of CuI/DIPEA (0.1:1) at room temperature for 12 h (Scheme 11). Similarly, the hetero porphyrin dyads **91**–**96** were also prepared using identical reaction conditions. NMR, absorption and electrochemical studies indicated that there is no specific interaction between the two porphyrin sub-units in dyads **91**–**96**.



Scheme 11. Synthesis of rigid diphenyl triazole-bridged porphyrin dyad **92** under "modified click" reaction conditions.



X = S; Y = NH; X' = Y' = N; M = Zn : **91**
X = S; Y = S; X' = Y' = N; M = Zn : **92**
X = S; Y = O; X' = Y' = N; M = Zn : **93**
X = S; Y = NH; X' = Y' = N; M = 2H : **94**
X = S; Y = S; X' = Y' = N; M = 2H : **95**
X = S; Y = S; X' = S; Y' = NH : **96**

Chart 5. Diphenyl triazole bridged hetero porphyrin dyads **91**–**96**.

The fluorescence studies supported an efficient energy transfer from donor ZnN_4/N_4/core-modified porphyrin sub-unit to acceptor core-modified porphyrin sub-unit on selective excitation of ZnN_4/N_4/core-modified porphyrin sub-unit as shown in Fig. 5 for dyad **92**. The dyad **92** containing ZnN_4 and N_2S_2 porphyrin sub-units, on excitation at 550 nm where the ZnN_4 porphyrin sub-unit absorbs strongly, the emission of the ZnN_4 porphyrin was quenched by 97% and strong emission from the N_2S_2 porphyrin sub-unit was observed. When 1:1 mixture of monomers **80** and **97** was excited at 550 nm, the emission was noted mainly from the ZnN_4 porphyrin sub-unit (Fig. 5). These observations supported the energy transfer from donor porphyrin to acceptor porphyrin on selective excitation of donor porphyrin unit.

Ravikanth and co-workers [90,91] synthesized the mono-functionalized thiaphlorins with N_3S and N_2S_2 cores containing one sp^3 and three sp^2 *meso* carbons and used them for the synthesis of covalently linked diphenylethyne bridged porphyrin-phlorin dyads **107**–**112** having two different cores (Chart 6). The mono-functionalized 21-monothiaporphotrimethenes **98**–**101** were synthesized by condensing one equivalent of functionalized unsymmetrical di-carbinol having sp^3 carbon with two equivalents of *p*-tolualdehyde and three equivalents of pyrrole under

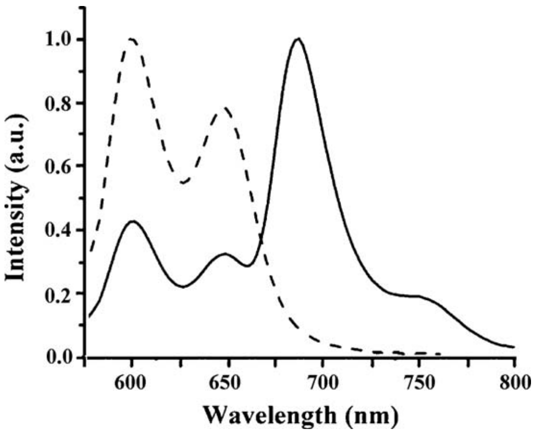
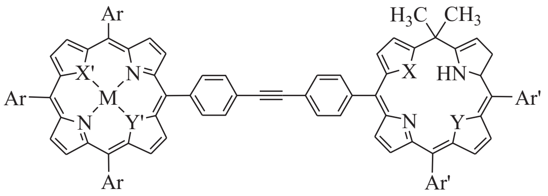
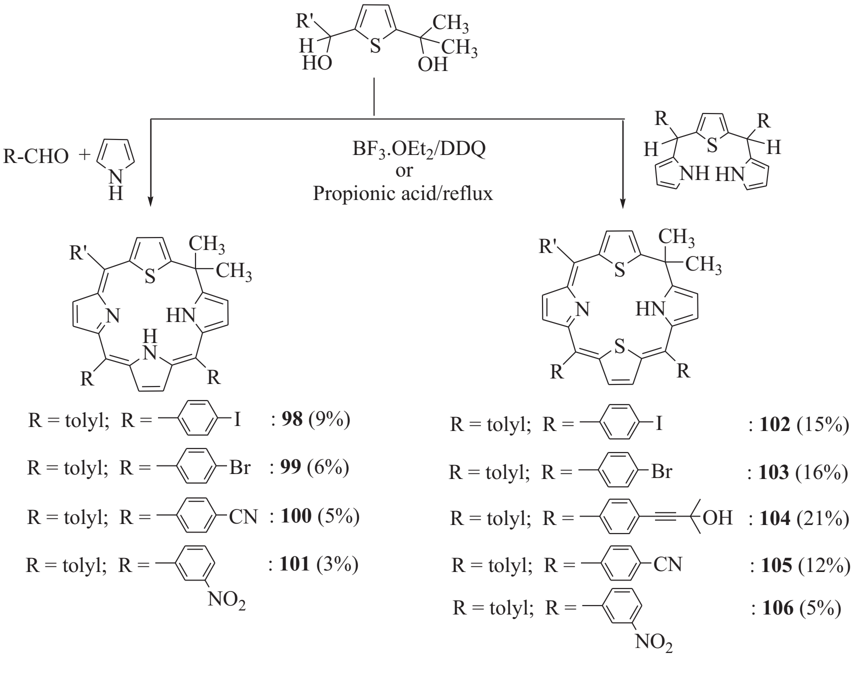


Fig. 5. Comparison of steady-state emission spectra of dyad **92** (—) and 1:1 mixture of **80** and **97** (···). The excitation wavelength used was 550 nm.
Reproduced with permission from Ref. [89].



X = S; Y = NH; X' = Y' = N; Ar = mesityl; Ar' = tolyl; M = Zn : **107**
X = S; Y = NH; X' = Y' = N; Ar = mesityl; Ar' = tolyl; M = 2H : **108**
X = S; Y = S; X' = Y' = N; Ar = mesityl; Ar' = tolyl; M = Zn : **109**
X = S; Y = S; X' = Y' = N; Ar = mesityl; Ar' = tolyl; M = 2H : **110**
X = S; Y = NH; X' = Y' = S; Ar = O-n-octyl; Ar' = tolyl : **111**
X = S; Y = NH; X' = Y' = S; Ar = tolyl; Ar' = tolyl : **112**

Chart 6. Covalently linked thiaphlorin-porphyrin dyads **107**–**112**.



Scheme 12. Synthesis of thiaphlorin building blocks **98**–**106**.

porphyrin forming conditions. Similarly, the mono-functionalized 21,23-dithiaporpho trimethenes **102**–**106** were prepared by condensing one equivalent of functionalized unsymmetrical thiophene di-carbinol with one equivalent of 16-thiatripyrrane under similar reaction conditions (Scheme 12). The X-ray structure solved for compound **103** in its protonated form showed that the macrocycle adopted ruffled conformation with pyrrole and thiophene rings in alternate conformation due to the non-planarity induced by the presence of one *meso* sp^3 carbon (Fig. 6). The thiaphlorin building blocks were used to synthesize novel porphyrin-thiaphlorin dyads **107**–**112** by coupling of appropriate thiaphlorin building blocks containing iodophenyl functional group with porphyrin building blocks with *meso*-ethynyl phenyl functional group under copper free mild Pd(0) coupling conditions [90,91]. The porphyrin-phlorin dyads such as ZnN_4–N_2S_2 dyad **109** and N_3S–N_2S_2 dyad **111** were demonstrated as a fluorescence anion sensors. In porphyrin-phlorin dyads, the flexible protonated thiaphlorin ring was used to bind an anion which was sensed by following the changes in the fluorescence of the porphyrin unit. For example, the protonated dyad **111** which contained N_3S porphyrin and N_2S_2 phlorin, was titrated with tetrabutylammonium iodide. The fluorescence band intensity of the N_3S porphyrin unit was gradually enhanced indicating that the iodide ion was bound at the N_2S_2 phlorin site thus acting as fluorescence anion sensor (Fig. 7).

Very recently, the first examples of β-*meso* acetylenyl bridged hetero porphyrin dyads **113**–**119** containing ZnN_4 or N_4 porphyrin and core-modified porphyrin sub-units were synthesized [92]. The dyads **113**, **114**, **116** and **118** were prepared by coupling of β-ethynyl Zn(II) porphyrin **120** with *meso*-bromo core-modified porphyrin **52**, **53**, **54** and **55** respectively, in the presence of $Pd_2(dba)_3/AsPh_3$ in toluene/triethylamine at 35 °C for 4 h (Scheme 13). The metal free dyads such as **115**, **117** and **119** were

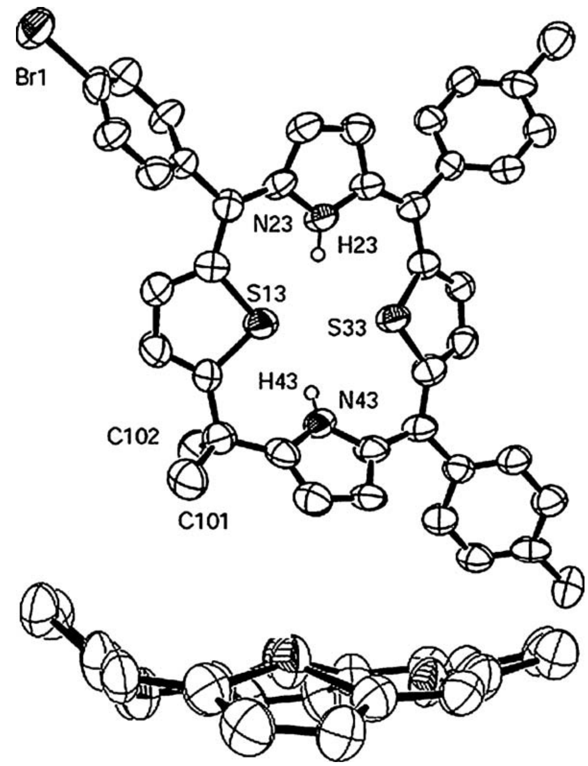


Fig. 6. X-ray crystal structure of **103**·H^+. Thermal ellipsoids are shown at the 50% probability level. In the bottom view, *meso* aryl groups have been removed for clarity. Reproduced with permission from Ref. [91].

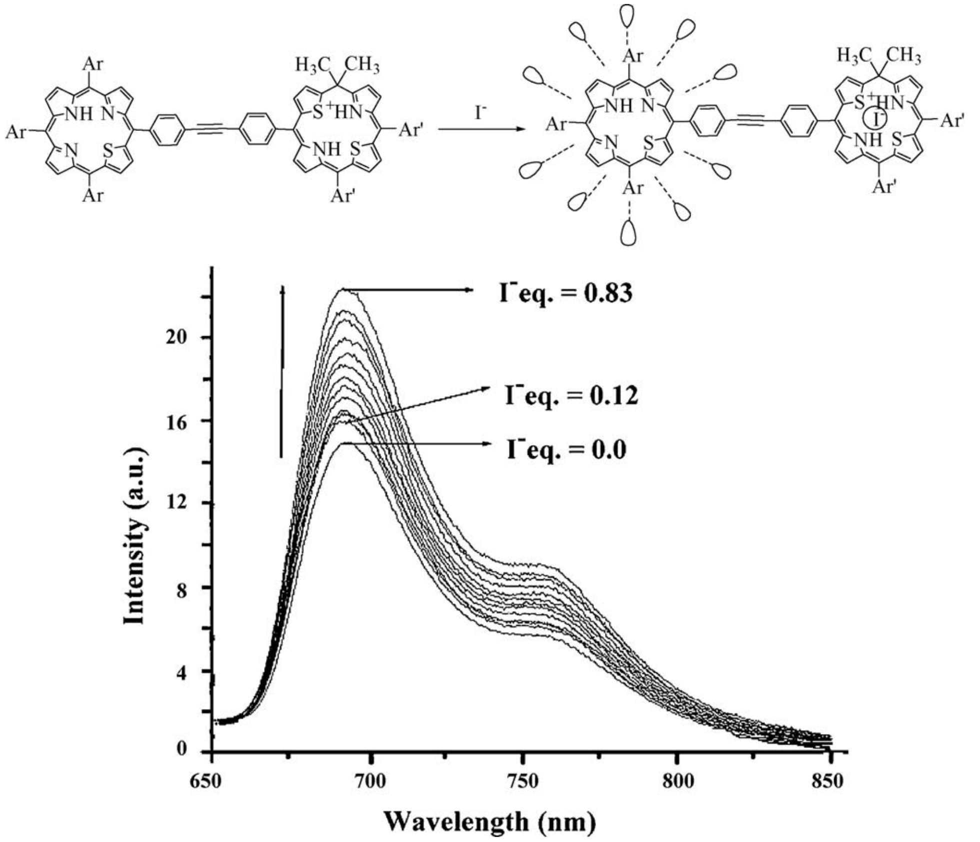
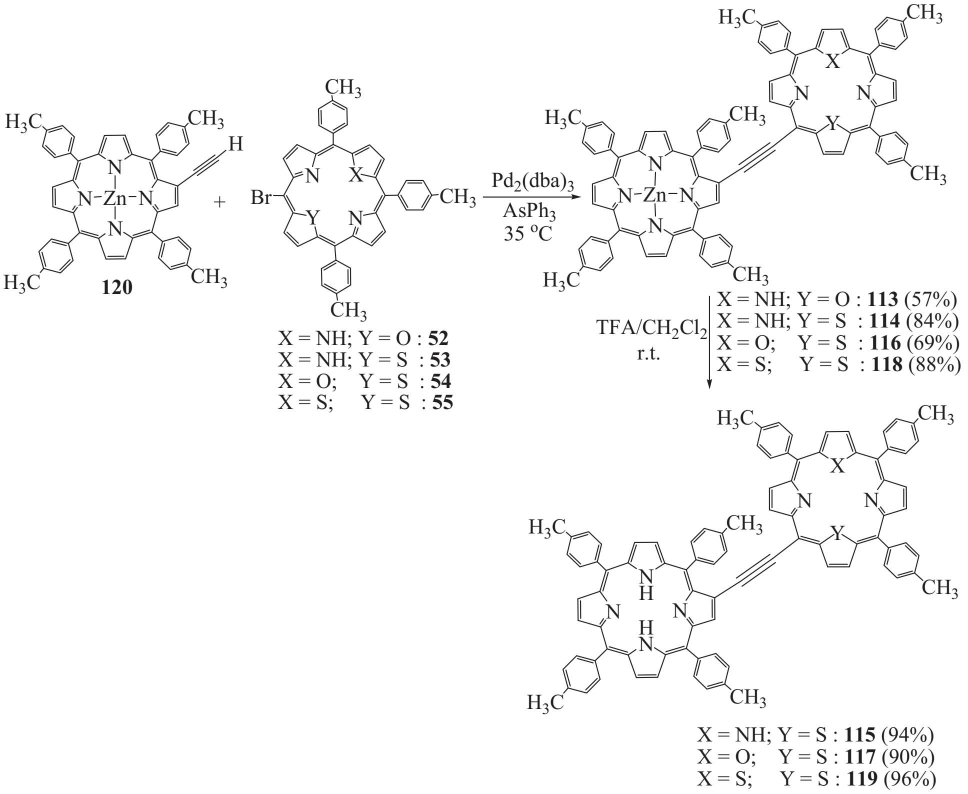
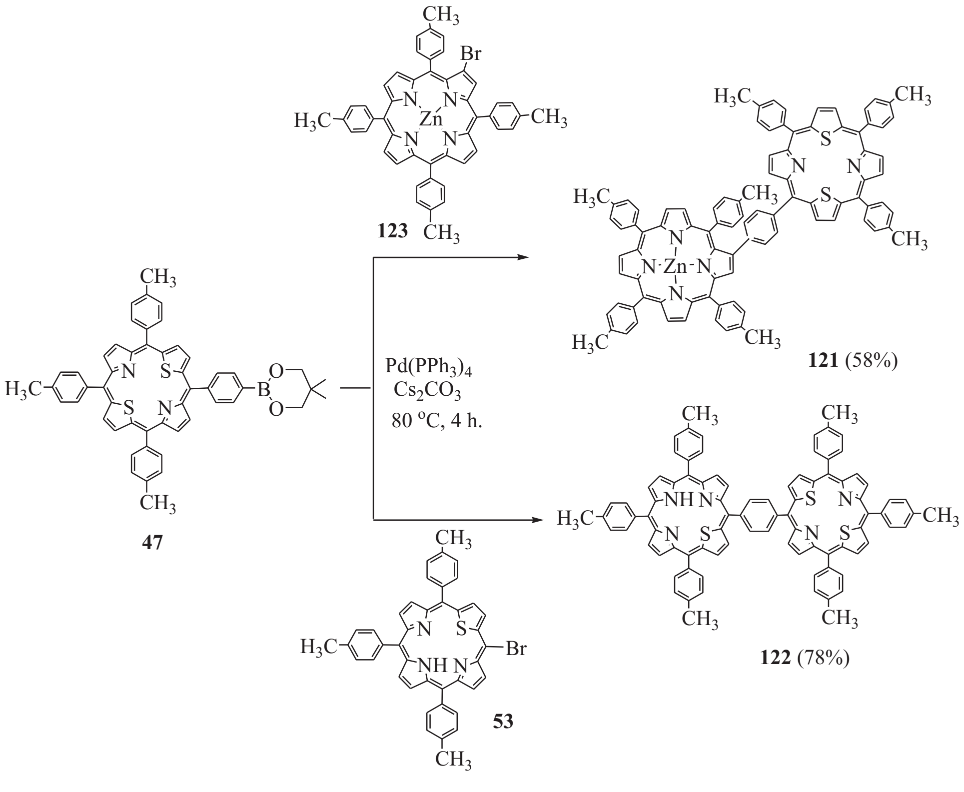


Fig. 7. Fluorescence titration of thiaphlorin–porphyrin dyad **111**·H^+ with increasing amounts of tetrabutylammonium iodide in dichloromethane. Reproduced with permission from Ref. [91].



Scheme 13. Synthesis of β-*meso* acetylenyl hetero porphyrin dyads **113–119**.



Scheme 14. Synthesis of β-*meso* and *meso*–*meso* linked hetero porphyrin dyads **121** and **122**.

synthesized by demetallation of dyads **114**, **116** and **118** respectively by treating the corresponding metallated dyad in $CHCl_3$ with TFA for 15 min (Scheme 13). Spectroscopic and electrochemical studies indicated that the two porphyrin sub-units maintain their independent identity in dyads **113**–**119**. The photophysical studies carried out on hetero porphyrin dyads **113**–**119** indicated a possibility of efficient energy transfer from one porphyrin sub-unit to another on selective excitation of one porphyrin unit. For example, the porphyrin dyad **114** containing ZnN_4 porphyrin sub-unit and N_3S porphyrin sub-unit, on excitation at 550 nm, the emission of ZnN_4 porphyrin quenched by 98% and the strong emission from N_3S porphyrin sub-unit was observed due to energy transfer from ZnN_4 porphyrin sub-unit to N_3S porphyrin sub-unit. Similarly, the hetero porphyrin dyads **113**–**119** also showed an energy transfer from donor porphyrin unit to acceptor porphyrin unit as confirmed by steady state fluorescence studies.

The phenyl bridged β-*meso* **121** and *meso*–*meso* **122** hetero porphyrin dyads containing ZnN_4/N_3S and ZnN_4/N_2S_2 porphyrin sub-units respectively were also reported recently [93]. The β-*meso* phenyl bridged hetero porphyrin dyad **121** was synthesized by coupling of [2-bromo-5,10,15,20-tetra(*p*-tolyl)porphyrinato] zinc (II) [94] **123** with (5,5-dimethyl-1,3,2-dioxaborinan-2-yl)-5,10,15-tri(*p*-tolyl)-21,23-dithiaporphyrin [93] **47** in toluene/triethylamine (5:1) in the presence of catalytic amounts of $Pd(PPh_3)_4/CsCO_3$ at 80 °C for 4 h (Scheme 14). Similarly, the *meso*–*meso* phenyl bridged hetero porphyrin dyad **122** was synthesized by coupling of 5-bromo-10,15,20-tri(*p*-tolyl)-21thiaporphyrin [81] **53** with **47** under the identical reaction conditions (Scheme 14). Absorption studies of dyads **121** and **122** showed a split Soret band with slight shifts in their peak maxima and altered extinction coefficients when compared to their corresponding 1:1 mixture of monomers, which supported an excitonic interaction between the two porphyrin sub-units within the dyads (Fig. 8a).

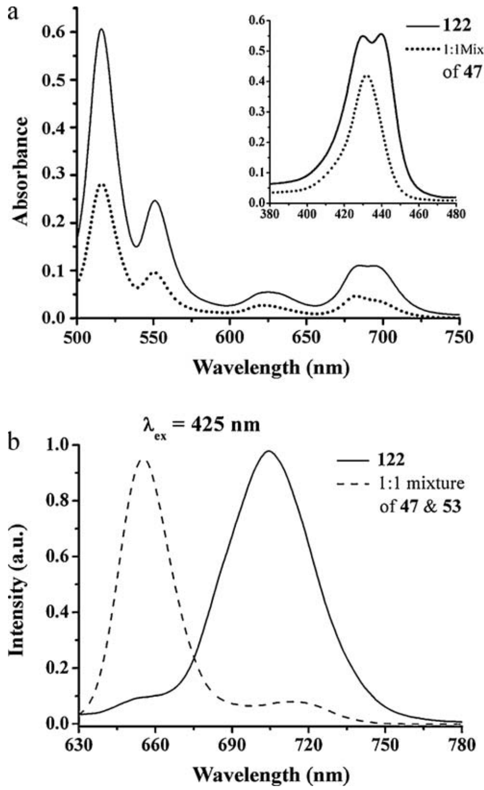
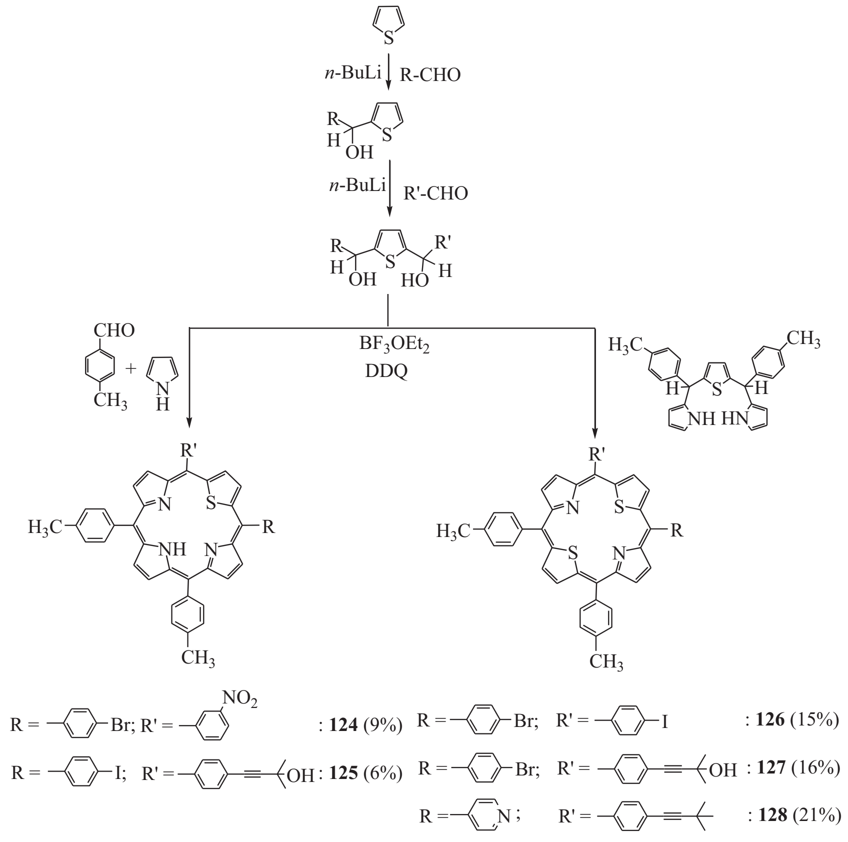
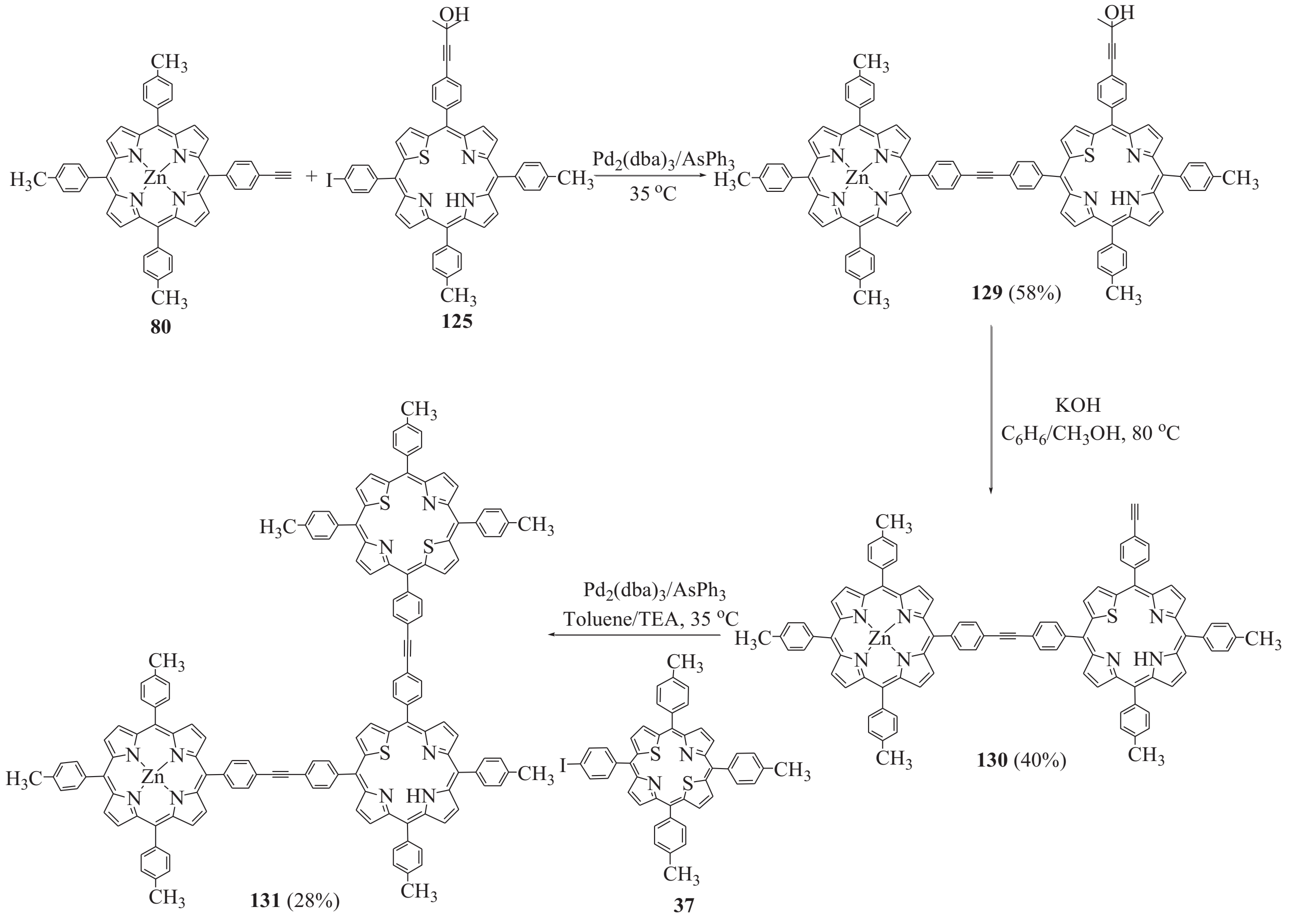


Fig. 8. (a) Comparison of Q-bands (1×10^{-5} M) and Soret band (1×10^{-6} M) (inset) absorption spectra of dyad **122** and a 1:1 mixture of its monomers **47** and **53** recorded in CH_2Cl_2. (b) Comparison of emission spectra of dyad **122** and a 1:1 mixture of its monomers **47** and **53** recorded at λ_{ex} = 425 nm in CH_2Cl_2.
Reproduced with permission from Ref. [93].



Scheme 15. Synthesis of *cis* di-functionalized thiaporphyrin building blocks **124**–**128**.



Scheme 16. Synthesis of L-shaped porphyrin triad **131** comprised of three different porphyrin sub-units.

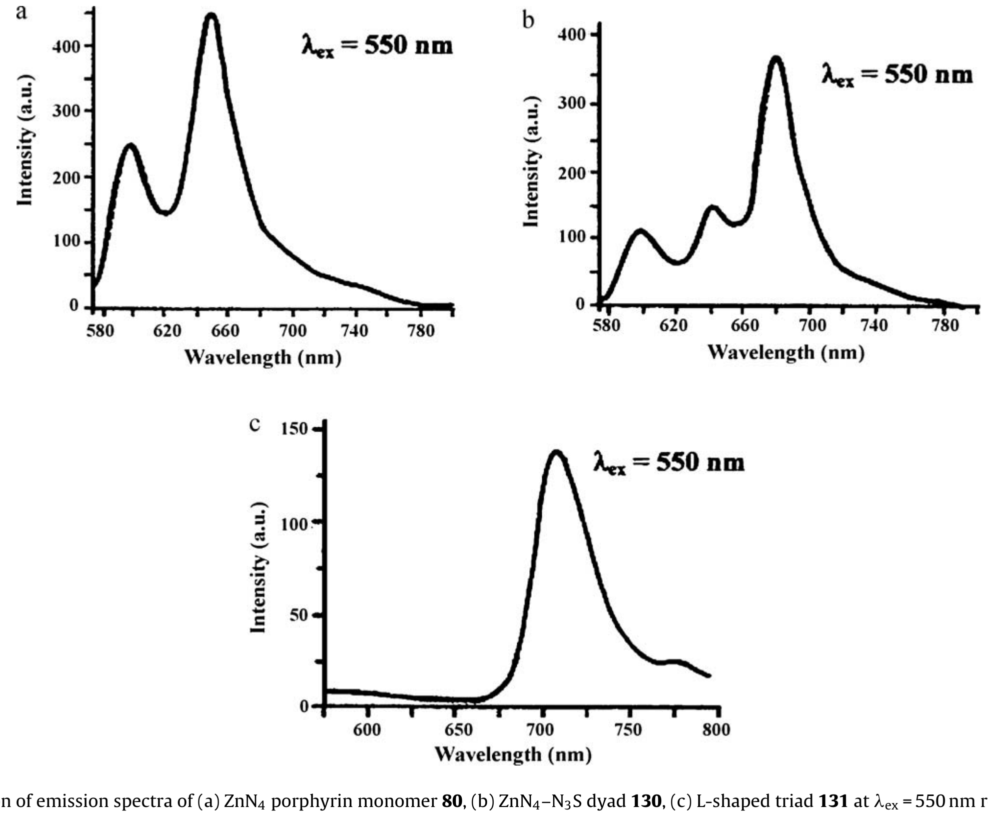
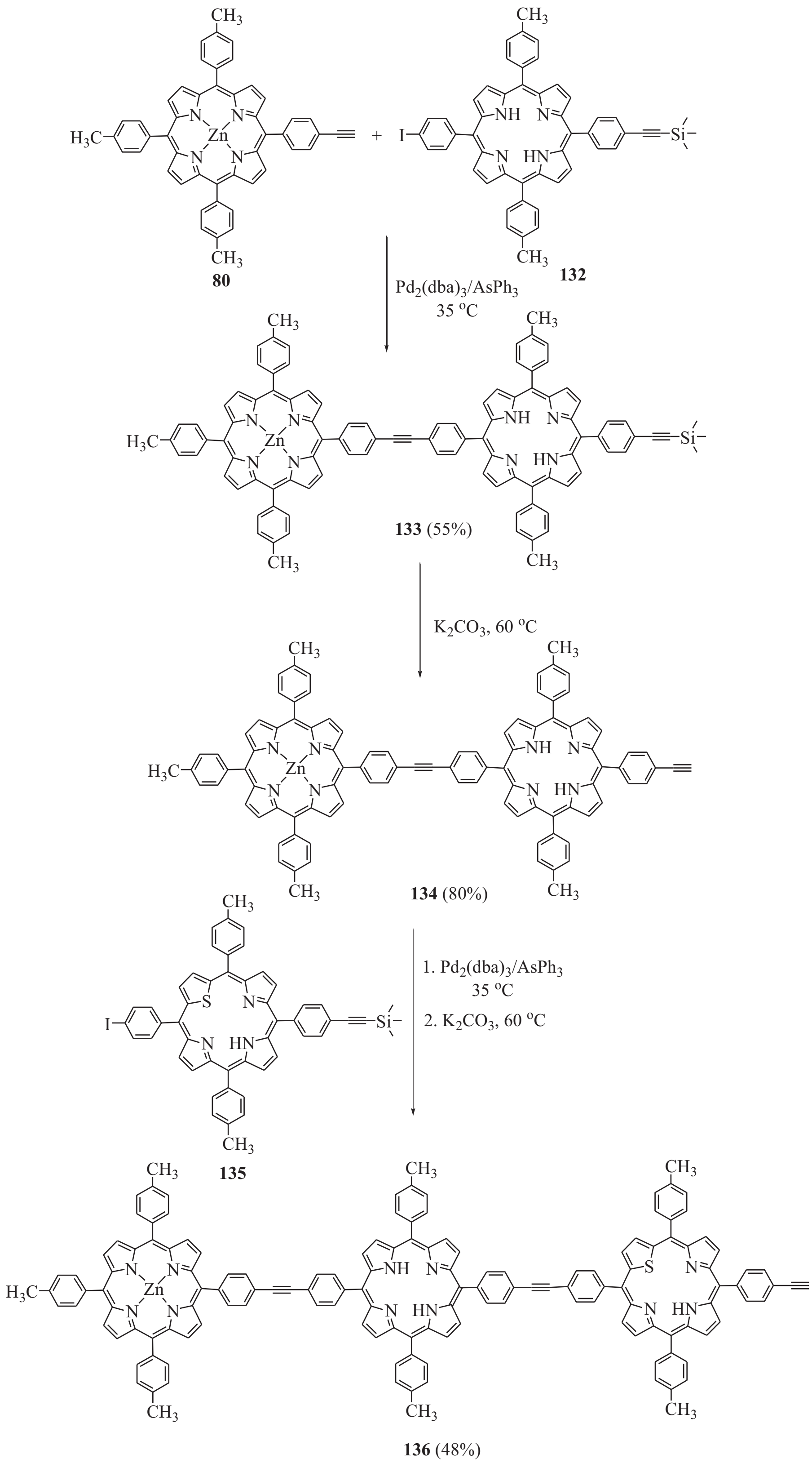
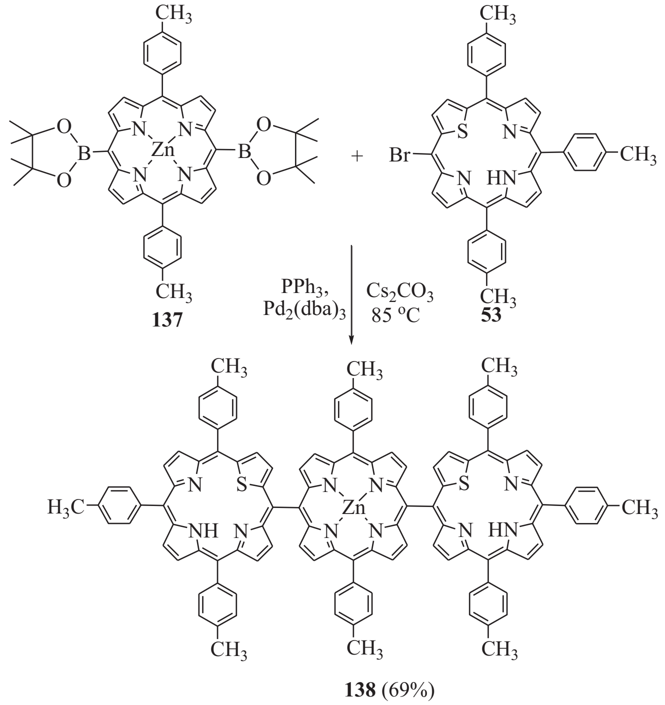


Fig. 9. Comparison of emission spectra of (a) ZnN_4 porphyrin monomer **80**, (b) ZnN_4–N_3S dyad **130**, (c) L-shaped triad **131** at λ_{ex} = 550 nm recorded in toluene.



Scheme 17. Synthesis of linear hetero porphyrin triad **136**.

The steady-state fluorescence properties of dyads **121** and **122** and their 1:1 mixture of monomers were studied by exciting the donor porphyrin sub-unit. The dyad **122** containing N_3S and N_2S_2 porphyrin sub-units, on excitation at 425 nm, the emission of the N_3S porphyrin was quenched by 85% and a strong emission from the N_2S_2 porphyrin sub-unit was observed. However, its 1:1 mixture of porphyrin monomers **47** and **53** on excitation showed emission mainly from the N_3S porphyrin sub-unit (Fig. 8b). These observa-



Scheme 18. Synthesis of *meso–meso* linked hetero porphyrin triad **138**.

tions supported energy transfer from donor porphyrin to acceptor porphyrin on selective excitation of donor porphyrin unit.

2.2. Covalently linked hetero porphyrin triads

The hetero porphyrin triads containing three different types of porphyrin sub-units arranged either in an L-shape [85] or linear [95] were synthesized using *cis* and *trans* di-functionalized core-modified porphyrin building blocks. Ravikanth and co-workers [96,97] synthesized *cis*-difunctionalized thiaporphyrins containing two different types of functional groups at *meso*-positions **124**–**128** in two steps starting from thiophene (Scheme 15). In the first step, the functionalized thiophene mono-carbinols were synthesized by reacting thiophene with functionalized aryl aldehydes under *n*-BuLi conditions and in the second step, the functionalized thiophene mono-carbinols obtained in the first step were reacted with a second functionalized aryl aldehyde under similar reaction conditions. The di-functionalized unsymmetrical thiophene di-carbinols were condensed with appropriate readily available precursors to synthesize the *cis*-difunctionalized thiaporphyrin building blocks. Lee and Lindsey and co-workers [72] synthesized *trans* di-functionalized N_3O and N_3S porphyrin building blocks by condensing the functionalized *meso*-aryl dipyrromethane with functionalized dipyrromethane dicarbinol under mild porphyrin forming conditions as shown in Scheme 2 for the synthesis of mono-functionalized N_3O and N_3S porphyrins.

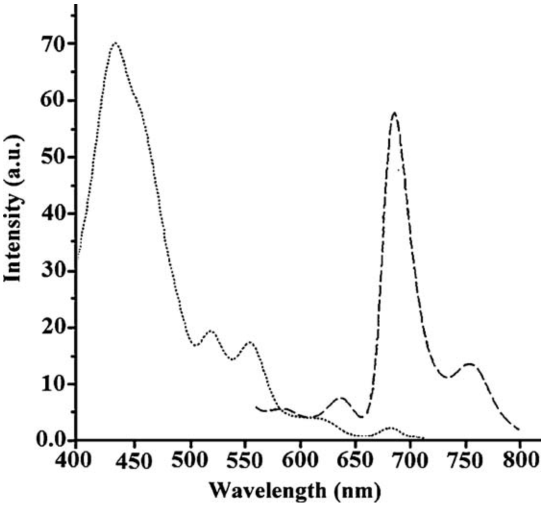


Fig. 10. Steady-state emission (- - -) (λ_{ex} = 550 nm) and excitation (···)(λ_{em} = 750 nm) spectra of **138** recorded in toluene.

Reproduced with permission from Ref. [81].

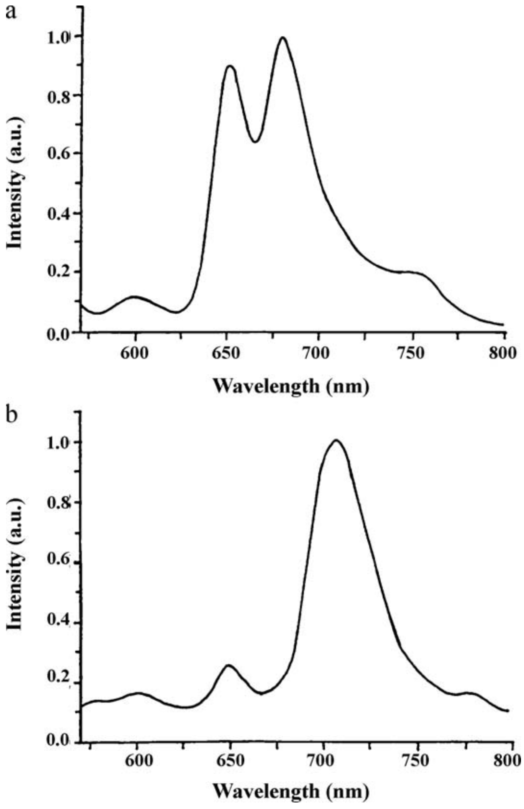
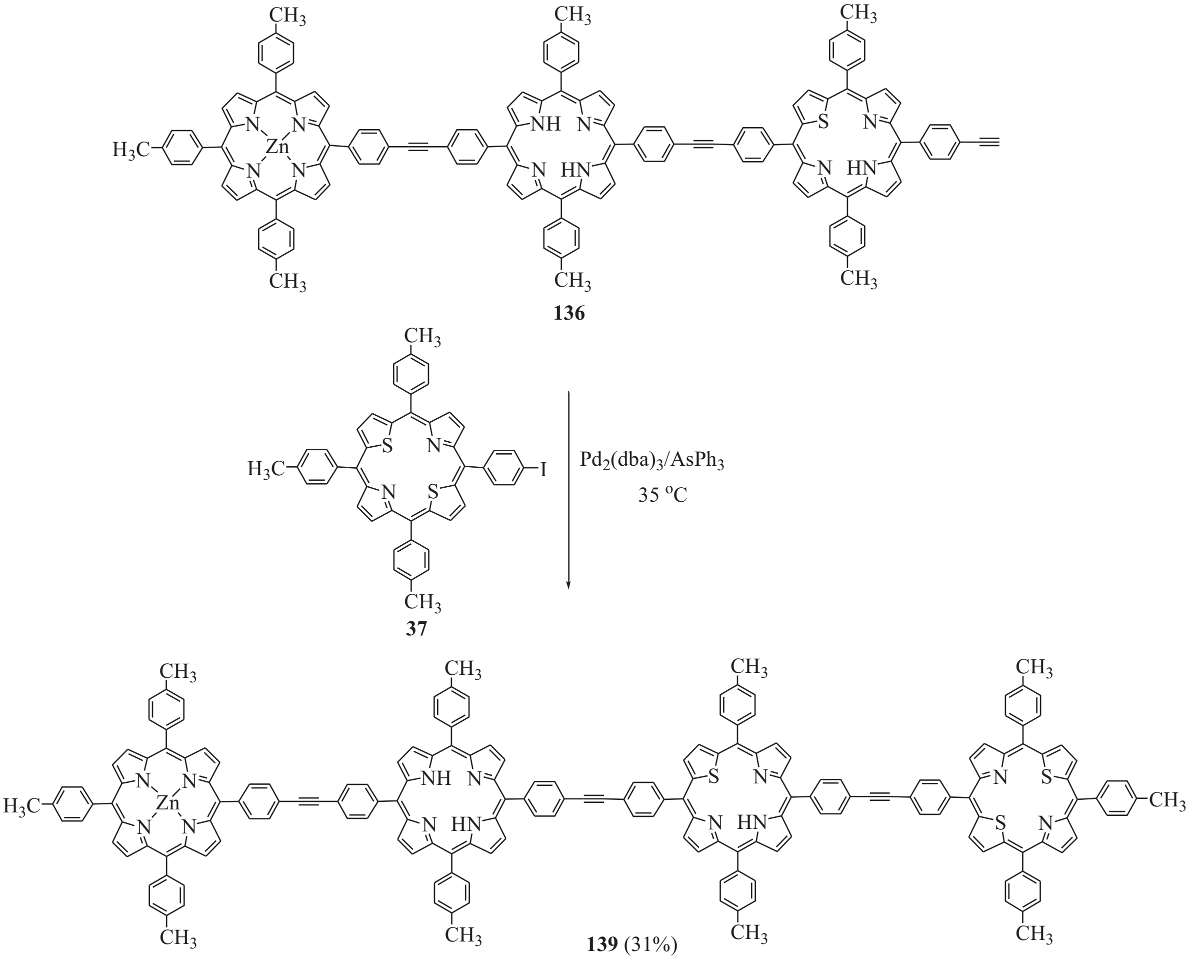


Fig. 11. Steady state emission spectra of (a) **136** and (b) **139** recorded in toluene at λ_{ex} = 550 nm.

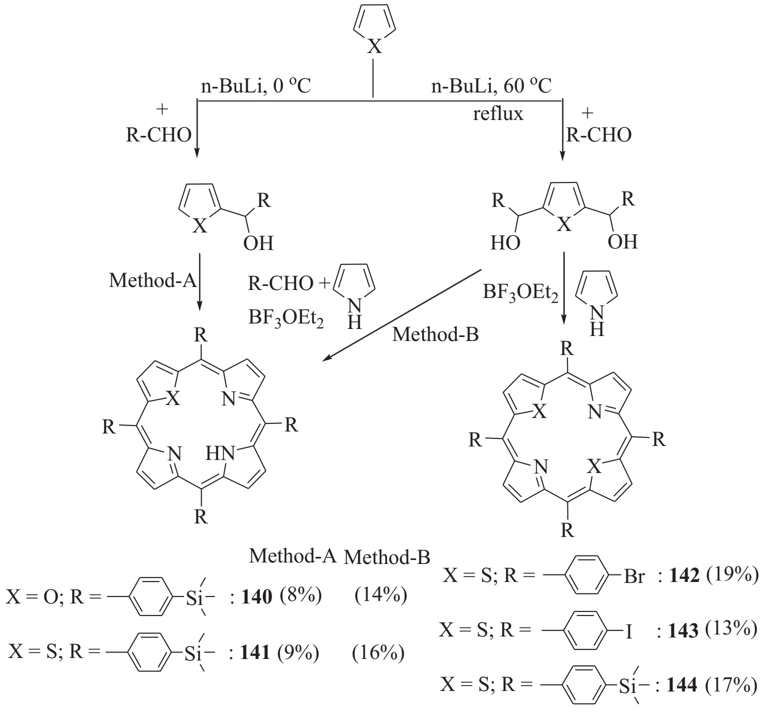
Reproduced with permission from Ref. [95].

The L-shaped covalently linked hetero porphyrin triad **131** having three different porphyrin sub-units such as N_4, N_3S and N_2S_2 porphyrin sub-units was synthesized [85] using *cis*-difunctionalized 21-thiaporphyrin building block over sequence of steps (Scheme 16). In the first step, the hetero porphyrin dyad **129** containing ZnN_4 and N_3S porphyrin sub-units was synthesized by coupling of ZnN_4 ethynylphenyl porphyrin **80** with *cis*-difunctionalized N_3S porphyrin building block **125** in toluene/triethylamine at 35 °C in the presence of catalytic amount of $Pd_2(dba)_3$/$AsPh_3$. In the next step, the deprotection of ethyne group on N_3S porphyrin unit of dyad **129** to afford **130** was carried out by treating dyad **129** with KOH in benzene/methanol at 80 °C overnight. In the final step, the L-shaped hetero porphyrin triad **131** was prepared by coupling of ethynylphenyl porphyrin dyad **130** with iodophenyl N_2S_2 porphyrin **37** under similar palladium(0) coupling conditions. The absorption spectroscopic studies of L-shaped triad **131** indicated a weak interaction between the porphyrin sub-units.

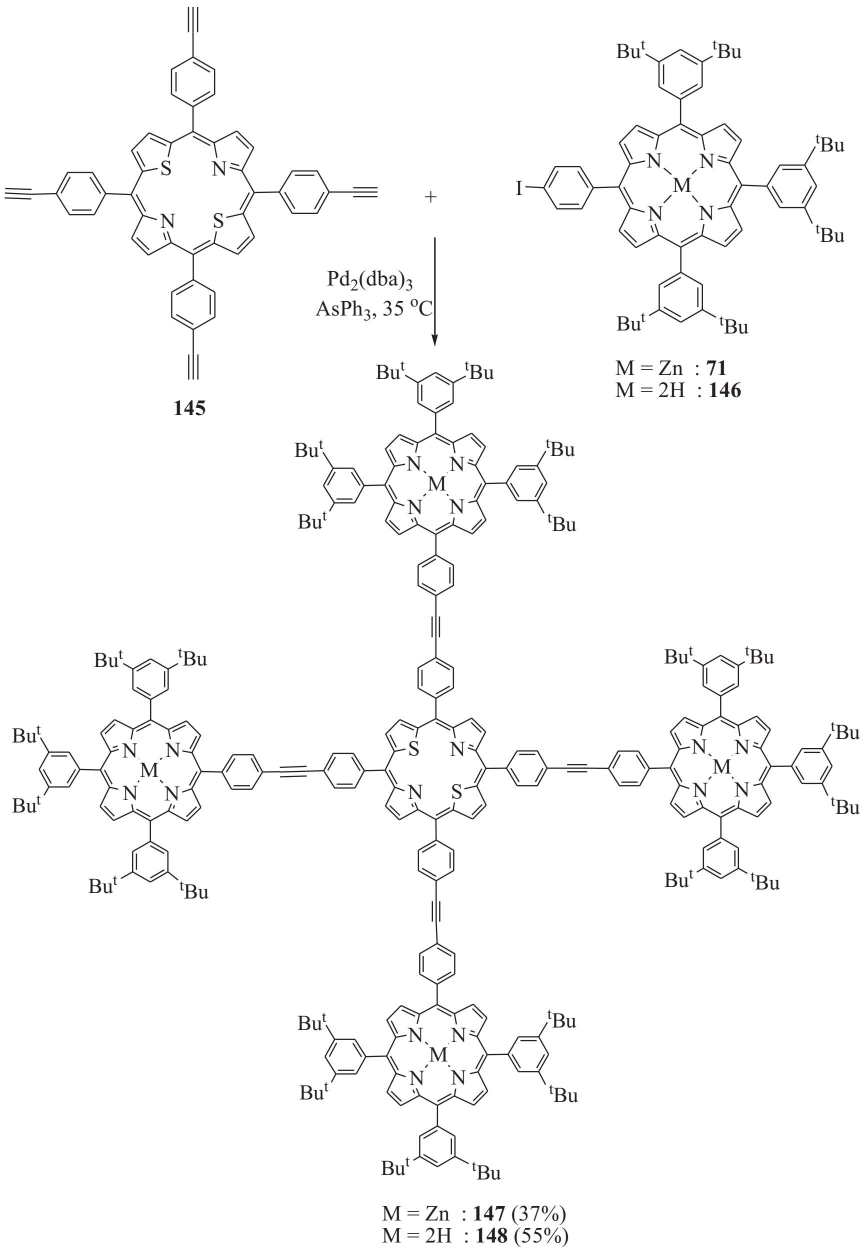
The steady state fluorescence spectra of triad **131** along with its ZnN_4 monomer **80** and functionalized hetero ZnN_4–N_3S dyad



Scheme 19. Synthesis of covalently linked linear hetero porphyrin tetrad **139**.



Scheme 20. Synthesis of A$_4$ type tetra functionalized core-modified porphyrin building blocks **140–144**.

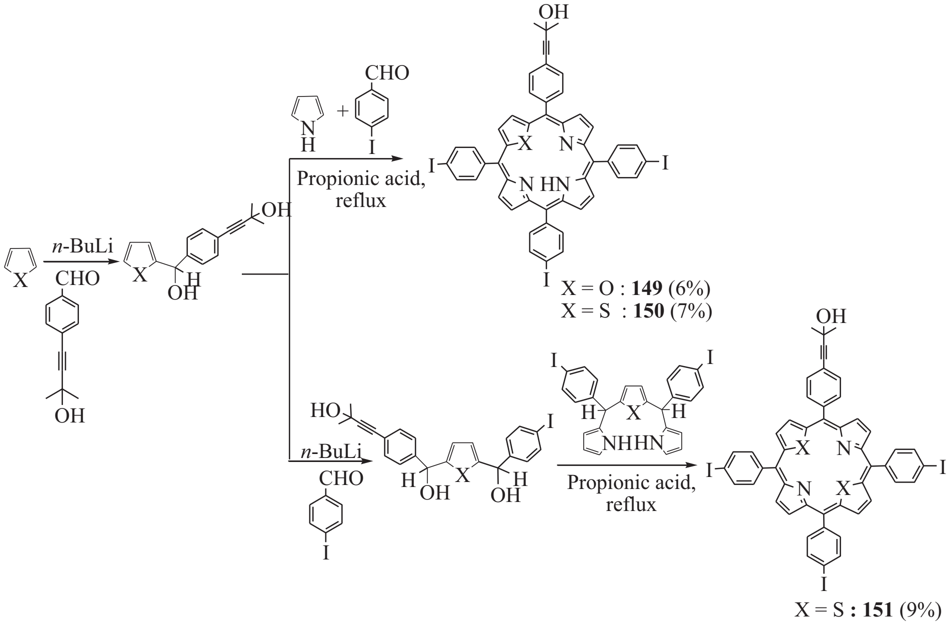


Scheme 21. Synthesis of star shaped hetero porphyrin pentads **147** and **148**.

130 are shown in Fig. 9. As is clear from Fig. 9 the emission from ZnN_4 and N_3S porphyrin sub-units was quenched completely and emission occurred only from the N_2S_2 porphyrin sub-unit in triad **131** supporting the step-wise energy transfer from ZnN_4 porphyrin sub-unit to N_3S porphyrin sub-unit. Then the energy was finally transferred to the N_2S_2 porphyrin sub-unit.

A linear hetero porphyrin triad [95] **136** containing ZnN_4, N_4 and N_3S porphyrin sub-units was synthesized as shown in Scheme 17. The ZnN_4–N_4 porphyrin dyad **133** was synthesized in the first step by coupling of **80** and **132** in toluene/triethylamine at 35 °C in the presence of a catalytic amount of $Pd_2(dba)_3$/$AsPh_3$ (Scheme 17). The dyad **134** having a free phenylethynyl group at the *meso* position was obtained by refluxing the dyad **133** with K_2CO_3 in THF/CH_3OH at 60 °C for 6 h. In the final step, the hetero ZnN_4–N_4–N_3S porphyrin triad **136** was prepared by coupling of **134** and **135** under identical palladium coupling conditions used for dyad **133** (Scheme 17). The ground-state properties of triad **136** indicated a weak interaction between the three porphyrin moieties. The fluorescence properties of the triad **136** was studied using excitation wavelength of 550 nm where ZnN_4 porphyrin sub-unit absorbs strongly. On excitation at 550 nm, the triad **136** showed major emission from both N_4 and N_3S porphyrin sub-units indicating that the energy transfer from ZnN_4 porphyrin sub-unit to N_3S porphyrin sub-unit mediated by N_4 porphyrin sub-unit in this linear triad was not efficient (Fig. 11a) and the energy was leaked from N_4 porphyrin sub-unit instead of complete transfer to the final N_3S porphyrin sub-unit.

One example of direct *meso*–*meso* linked hetero porphyrin triad **138** containing one ZnN_4 porphyrin sub-unit and two N_3S porphyrin sub-units was reported recently [81]. The triad **138** was synthesized by coupling of 2 equivalents of 5-bromo-10,15,20-tri(*p*-tolyl)-21-thiaporphyrin [81] **53** with 1 equivalent of bis[5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)]-10,20-bis(*p*-tolyl) porphyrinato zinc(II) [87] **137** in toluene/DMSO at 85 °C in the presence of PPh_3, Cs_2CO_3 and $Pd_2(dba)_3$ for 16 h (Scheme 18). The steady-state fluorescence study of triad **138** at wavelength where the ZnN_4 porphyrin sub-unit absorbs strongly



Scheme 22. Synthesis of A3B type tetra functionalized core-modified porphyrin building blocks **149**–**151**.

showed that the emission of the ZnN_4 porphyrin sub-unit was quenched by 95% and emission was mainly observed from N_3S porphyrin sub-unit (Fig. 10). Furthermore the excitation spectrum of triad **138**, recorded at $\lambda_{max} = 750$ nm, matched exactly the absorption spectrum (Fig. 10). These results confirm an efficient energy transfer from the middle ZnN_4 porphyrin sub-unit to the peripheral N_3S porphyrin sub-units.

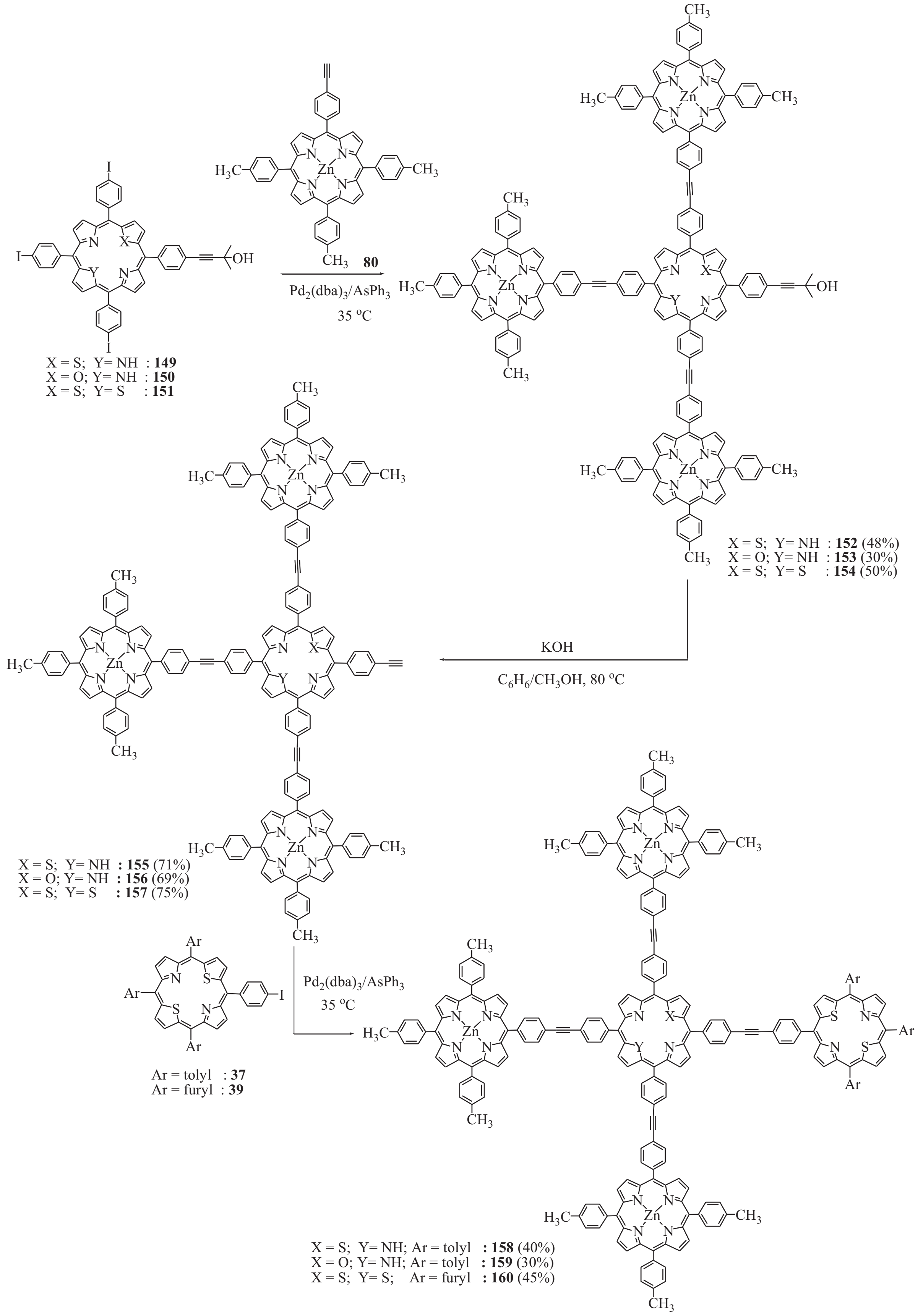
2.3. Covalently linked hetero porphyrin tetrad

Punidha and Ravikanth [95] reported the synthesis of one linear hetero porphyrin tetrad **139** containing ZnN_4, N_4, N_3S and N_2S_2 porphyrin sub-units by coupling linear triad **136** having *meso* phenylethynyl group on N_3S porphyrin sub-unit and N_2S_2 porphyrin building block **37** under standard palladium(0) coupling conditions (Scheme 19). The fluorescence spectra of ZnN_4–N_4–N_3S–N_2S_2 porphyrin tetrad **139** recorded at 550 nm where ZnN_4 porphyrin absorbs relatively strong, the emission from ZnN_4, N_4, and N_3S porphyrin sub-units was quenched significantly and the major emission was noted from terminal N_2S_2 porphyrin sub-unit (Fig. 11b). This is in contrast to the earlier described linear triad **136** where the emission was noted from both N_4 and N_3S porphyrin sub-units (Fig. 11a). Thus, this tetrad demonstrates that it is possible to transfer singlet state energy from one end to the other by connecting four different porphyrin sub-units whose singlet state energy levels are arranged in a cascade manner.

2.4. Covalently linked hetero porphyrin pentads

Star shaped hetero porphyrin pentads **147** and **148** containing four peripheral ZnN_4 and N_4 porphyrin sub-units respectively and one central N_2S_2 porphyrin were synthesized using a tetra-functionalized N_2S_2 porphyrin [98–101]. The A_4 type tetra functionalized core-modified porphyrin building blocks **140**–**144** were synthesized by condensing the symmetrical di-functionalized dicarbinols with appropriate precursors (Scheme 20) under mild acid catalyzed conditions. The symmetrical tetra-functionalized core-modified porphyrins **140**–**144** were used to synthesize the star shaped hetero porphyrin pentads **147** and **148** containing two different types of porphyrin sub-units. Coupling of one equivalent of tetra ethynyl functionalized N_2S_2 porphyrin **145** with 4.5 equivalents of mono-iodophenyl ZnN_4 porphyrin **71** or N_4 porphyrin **146** under copper free Sonogashira coupling conditions afforded star shaped hetero porphyrin pentads **147** and **148** respectively (Scheme 21). Like other diphenyl ethyne bridged hetero porphyrin arrays, the porphyrin components in hetero porphyrin pentads **147** and **148** retain their individual characteristic features. The fluorescence studies carried out on pentad **147** supported the singlet–singlet energy transfer from peripheral ZnN_4 porphyrin sub-units to central N_2S_2 porphyrin unit.

Recently, the hetero porphyrin pentads [102] **158**–**160** containing three peripheral ZnN_4 porphyrins, one central core-modified porphyrin and another peripheral N_2S_2 porphyrin with their energy levels are arranged in cascade manner were synthesized over sequence of steps. The required AB_3 type tetra-functionalized mono-heteroatom substituted porphyrins (N_3O, N_3S cores) **149** and **150** were synthesized by condensing 1 equivalent of functionalized thiophene mono-carbinol with 1.5 equivalents of the other type of functionalized aryl aldehyde and 1.5 equivalent of pyrrole under porphyrin forming conditions (Scheme 22). Similarly, AB_3 type tetra-functionalized di-heteroatom substituted porphyrin (N_2S_2 core) **151** was prepared by condensing 1 equivalent of di-functionalized unsymmetrical di-carbinol with 1 equivalent of di-functionalized symmetrical tripyrrane under porphyrin forming conditions (Scheme 22). One equivalent of AB_3 type functionalized core-modified porphyrins **149**–**151** was coupled with three equivalents of ZnN_4 porphyrin **80** under Pd(0) coupling conditions followed by deprotection yielded mono-functionalized hetero porphyrin tetrads **155**–**157** with ethynyl functional group on core-modified porphyrins (Scheme 23). In last step, the mono-functionalized tetrads **155**–**157** were coupled with mono-functionalized N_2S_2 porphyrins **37** and **39** under the same Pd(0) coupling conditions and afforded a series of hetero porphyrin pentads **158**–**160** containing three different types of porphyrin sub-units (Scheme 23). The ground state properties indicated that all three types of porphyrin sub-units retain their individual features. Since the singlet state energy levels of these three porphyrins are arranged in cascade fashion, these hetero porphyrin pentads **158**–**160** showed an efficient energy flow from peripheral ZnN_4 porphyrins to the other peripheral N_2S_2 porphyrin mediated via



Scheme 23. Synthesis of covalently linked hetero porphyrin pentads **158–160**.

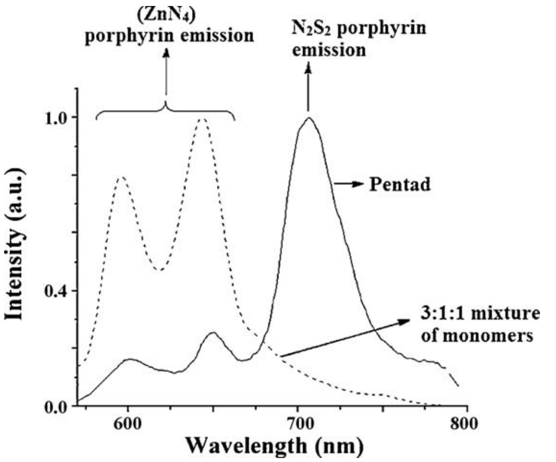
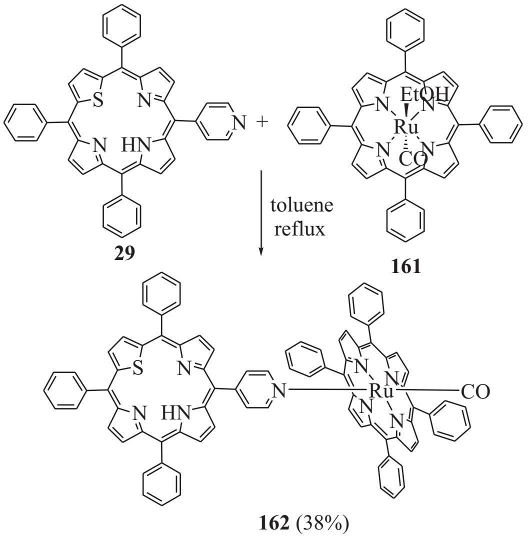


Fig. 12. Comparison of emission spectra of hetero porphyrin pentad **158** (—) and 3:1:1 mixture of its monomers (- - -) recorded in toluene at $\lambda_{ex} = 550$ nm. Reproduced with permission from Ref. [102].

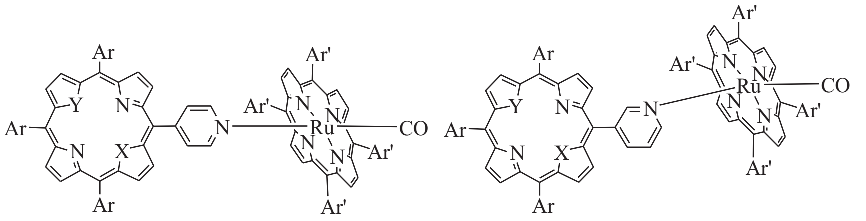
central heteroatom substituted porphyrin sub-unit. This is clearly evident in the comparison of fluorescence spectra of pentad **158** with its corresponding 3:1:1 mixture of monomers shown in Fig. 12. On excitation at 550 nm where the three peripheral ZnN_4 porphyrin sub-units absorb strongly, the emission was noted mainly from the other peripheral N_2S_2 porphyrin sub-unit. However, in 3:1:1 mixture of its corresponding porphyrin monomers, on excitation at 550 nm, the emission was noted only from ZnN_4 porphyrin sub-unit. These results supported an efficient energy transfer from three peripheral ZnN_4 porphyrin sub-units to central heteroatom substituted porphyrin sub-unit and then from central heteroatom substituted porphyrin sub-unit to the other peripheral N_2S_2 porphyrin sub-unit in all these pentads **158**–**160**.



Scheme 24. Synthesis of non-covalent hetero porphyrin dyad **162**.

3. Non-covalently linked hetero porphyrin arrays

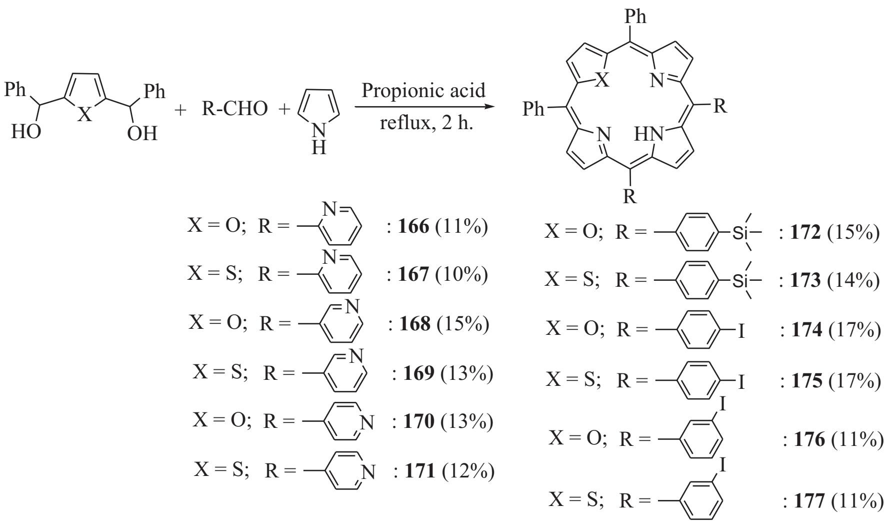
There are relatively few reports available on non-covalent hetero porphyrin dyads, triads and tetrads containing two or more different types of porphyrin sub-units compared to covalently linked hetero porphyrin arrays. In the literature, self-assembly strategies [20] have been used to synthesize unique metalloporphyrin based oligomers linked non-covalently by hydrogen bonding, electrostatic interactions and coordination using ligating porphyrins containing *meso*-pyridyl, *meso*-carboxyphenyl, *meso*-hydroxyphenyl groups, etc. Although it was shown that core-modified porphyrins with various porphyrin cores including N_2S_2 form metal complexes [103] which possess interesting structural and electronic properties, these metallo core-modified porphyrins, unlike metalloporphyrins, were not explored for the synthesis of non-covalent multi-porphyrin assemblies. However, the free base core-modified porphyrins containing *meso*-pyridyl and *meso*-hydroxyphenyl groups were used effectively to construct non-covalent assemblies containing core-modified porphyrin as one of the sub-unit. Ravikanth and co-workers [104,105] reported the synthesis of hetero porphyrin dyads **162**–**165** (Chart 7) assembled using Ru-pyridine "N" interaction. The dyads containing RuN_4 porphyrin and N_3S or N_2S_2 porphyrin sub-units were constructed by reacting the thiaporphyrin building blocks having pyridyl group at *meso*-position with RuTPP(CO)(EtOH) in toluene at refluxing temperature as illustrated in Scheme 24 for the synthesis hetero dyad **162**. The dyad **162** was prepared by reacting **29** with RuTPP(CO)(EtOH) **161** in toluene at refluxing temperature for overnight (Scheme 24). The dyad formation was clearly confirmed by the large upfield shifts of *meso*-pyridyl protons of thiaporphyrin unit which experienced ring current shifts of RuTPP(CO) moiety. These compounds were weakly fluorescent [105] because of the presence of Ru(II) ion which quenches the fluorescence of thiaporphyrin sub-unit. Furthermore, these dyads are not suitable to study energy transfer at the singlet state. Hence, Santosh and Ravikanth synthesized the Re(I) bridged hetero porphyrin dyad **179** containing N_3O and N_3S porphyrin sub-units by following Hupp's methodology [106]. The required *cis*-pyridyl heteroatom substituted porphyrin building blocks with N_3O and N_3S were synthesized [107,108] by condensing the symmetrical furan or thiophene dicarbinol with 3- or 4-pyridine carboxaldehyde under Adler's porphyrin forming conditions (Scheme 25). The Re(I) bridged hetero porphyrin dyad **179** was synthesized [109] by reacting *cis*-dipyridyl



X = S; Y = NH : **162**
X = S; Y = S : **163**

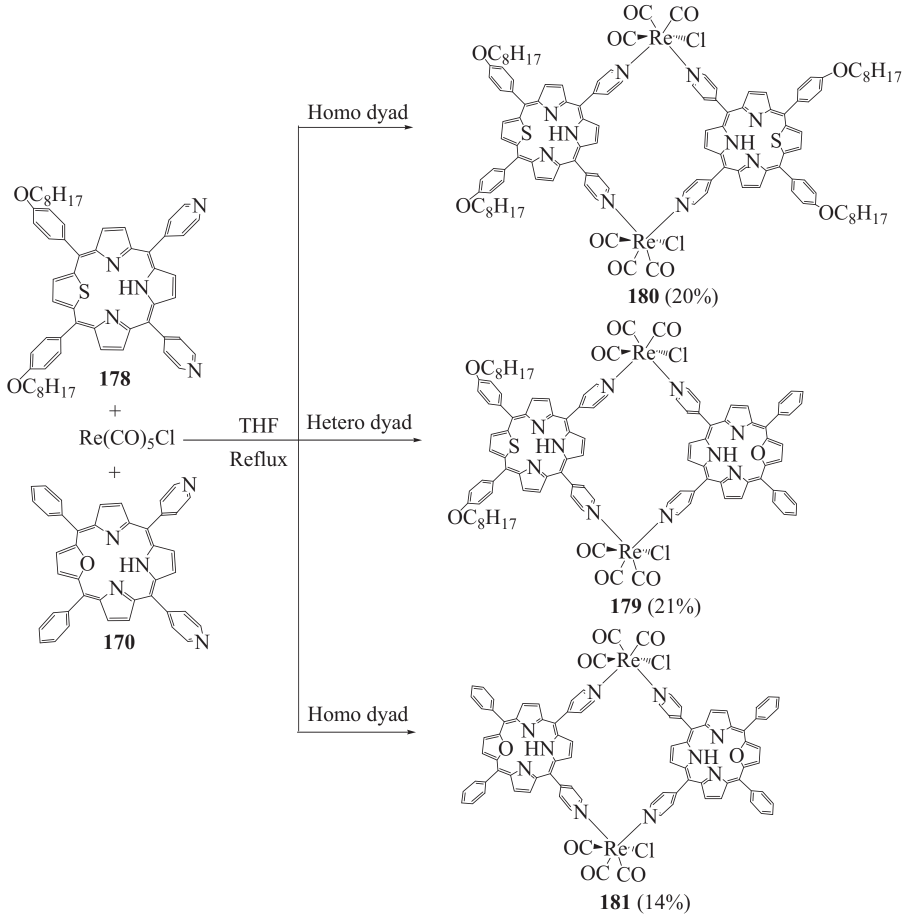
X = S; Y = NH : **164**
X = S; Y = S : **165**

Chart 7. Non-covalently linked hetero porphyrin dyads **162**–**165**.



Scheme 25. Synthesis of *cis* di-functionalized core-modified porphyrin building blocks **166**–**177**.

N_3S porphyrin, 5,10-bis(4-octyloxyphenyl)-15,20-bis(4-pyridyl)-21-thiaporphyrin **178** with *cis*-dipyridyl N_3O porphyrin, 5,10-diphenyl-15,20-di(4-pyridyl)-21-oxaporphyrin **170** and $Re(CO)_5Cl$ in THF at refluxing temperature (Scheme 26). The reaction resulted in the formation of mixture of three dyads and the required hetero porphyrin dyad **179** was separated from the other two homo dyads **180** and **181** by column chromatography. The formation of Re(I) bridged dyad **179** was confirmed by the downfield shifts of *meso*-pyridyl protons. These compounds were sufficiently fluorescent and were also useful for singlet–singlet energy transfer studies. The steady state fluorescence spectra of porphyrin dyads **179**, **180** and **181** recorded in toluene at room temperature are shown in Fig. 13. In hetero dyad **179**, on excitation of N_3O porphyrin sub-unit, major emission was noted from N_3S porphyrin sub-unit supporting the energy transfer from N_3O porphyrin to N_3S porphyrin at singlet state [109].



Scheme 26. Synthesis of Re(I) bridged thia-oxa porphyrin dyad **179**.

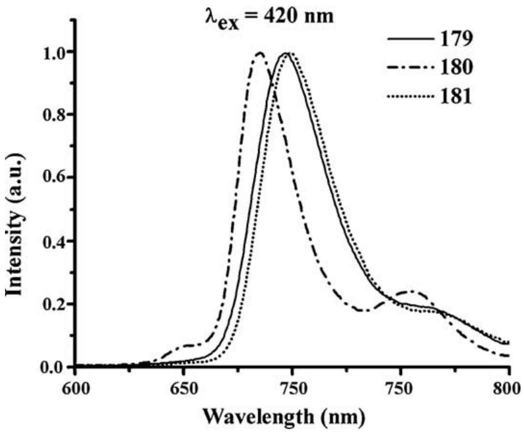
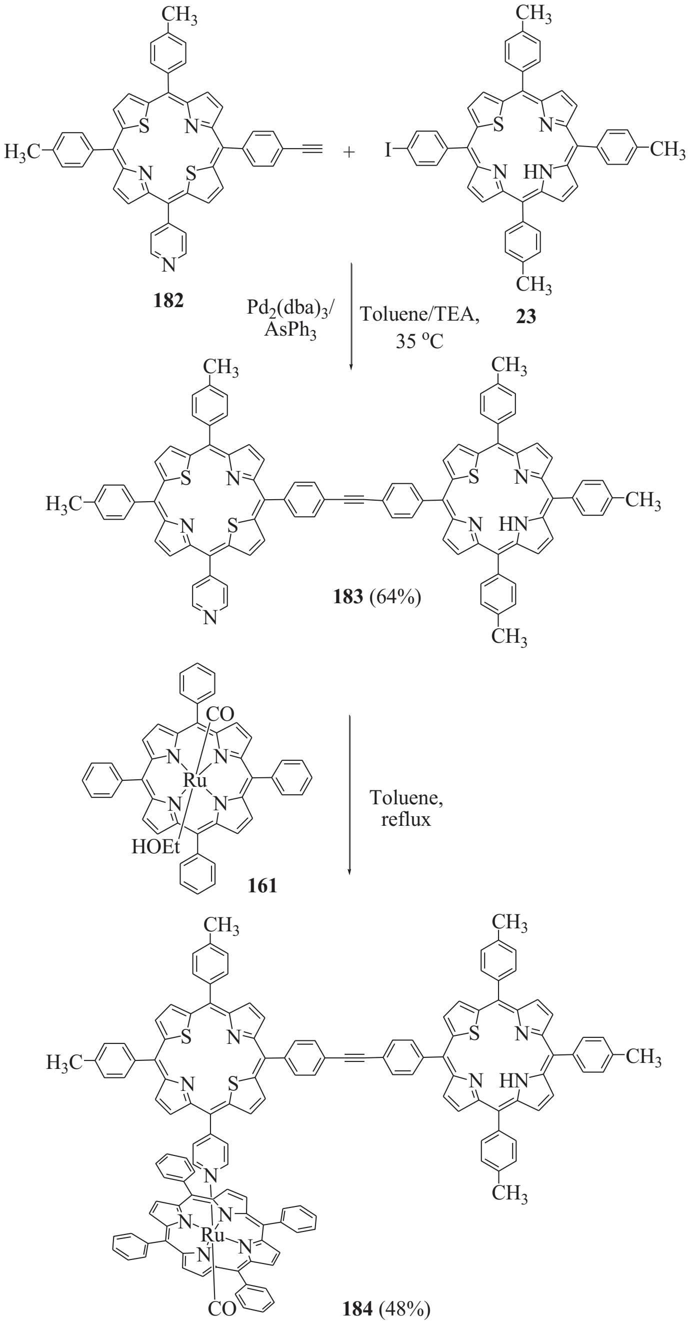


Fig. 13. Normalized emission spectra of Re(I) bridged porphyrin dyads **179**–**181** recorded at λ_{ex} = 420 nm in toluene.
Reproduced with permission from Ref. [109].

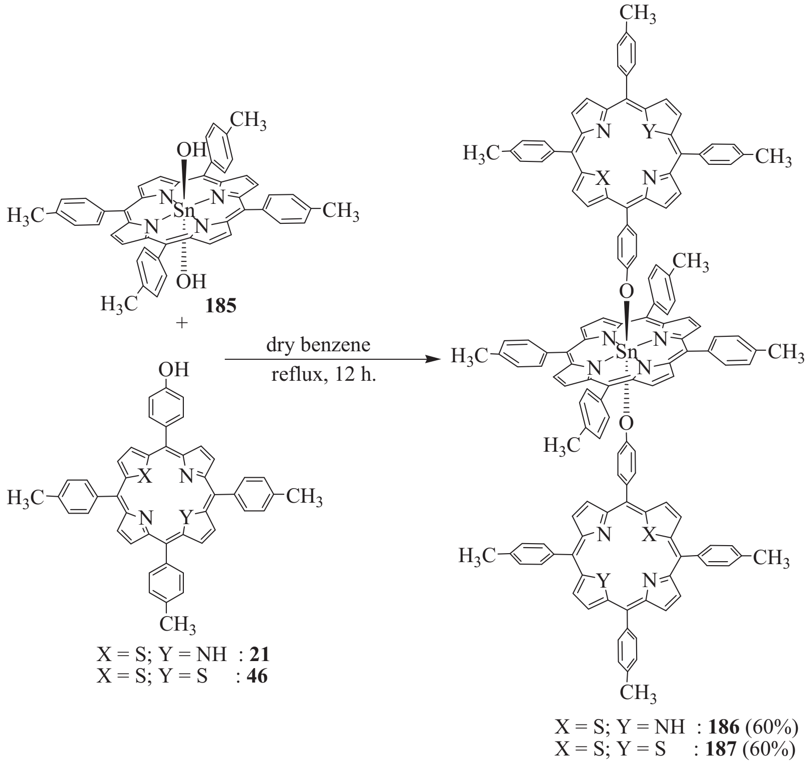
Ravikanth and co-workers [96,97] synthesized hetero triad **184** containing N_4, N_3S and N_2S_2 porphyrin sub-units assembled by using both covalent and non-covalent interactions. The triad **184** was synthesized in two steps as shown in Scheme 27. In the first step, *cis*-difunctionalized N_2S_2 porphyrin building block having *meso*-pyridyl and *meso*-ethynyl phenyl functional groups **182** was coupled with the N_3S porphyrin building block containing *meso*-iodophenyl functional group **23** under mild Pd(0) coupling conditions. The resulting N_3S–N_2S_2 dyad **183** containing *meso*-pyridyl functional group on N_2S_2 porphyrin sub-unit was then reacted with RuTPP(CO)(EtOH) **161** in toluene at refluxing temperature (Scheme 27). The steady state emission spectrum of triad **184** excited at 425 nm, where N_3S porphyrin sub-unit absorbs strongly, the N_3S porphyrin emission was quenched by 87% and the major emission was occurred from N_2S_2 porphyrin sub-unit. When triad **184** was excited at 440 nm, where the N_2S_2 porphyrin absorbs strongly, the N_2S_2 porphyrin emission was quenched by 20%. These results indicated that the fluorescence yields of both N_3S and N_2S_2 porphyrin sub-units in triad **184** were decreased compared to their corresponding monomers due to the heavy ruthenium ion that co-ordinated to the *meso*-pyridyl N_2S_2 porphyrin sub-unit.

Recently, Shetti and Ravikanth [110] synthesized axial-bonding type of Sn(IV) porphyrin triads **186** and **187** in which Sn(IV) porphyrin acts as basal unit and the two core-modified porphyrin units as axial ligands. The triads **186** and **187** containing heteroatom substituted porphyrin sub-units as axial ligands were synthesized by refluxing 1 equivalent of $SnTTP(OH)_2$ **185** with 2 equivalents of **21** and **46** respectively in benzene at refluxing temperature for 12 h (Scheme 28). The absorption and electrochemical studies indicated weak ground state interaction among the porphyrin sub-units within the porphyrin triads **186** and **187**. The fluorescence studies indicated the possibility of energy transfer at the singlet state from basal Sn(IV) porphyrin unit to axial thiaporphyrin units in triads **186** and **187** [110].

Ravikanth and co-workers also synthesized the non-covalent triads [105,107] **188** and **189** (Chart 8) by treating one equivalent of *cis*-dipyridyl-21-thiaporphyrins with two equivalents of RuTPP(CO)(EtOH) **161** in toluene at refluxing temperature for overnight. Furthermore, they also reported the synthesis of two non-covalent hetero tetrads **196** and **197** containing one N_3S and three N_4 porphyrin units using the 21-thiaporphyrin building block containing three *meso*-pyridyl groups. (Chart 8) [75]. The tri-functionalized 21-thiaporphyrin/21-oxaporphyrin building blocks **190**–**195** were synthesized by condensing two equivalents of 2-(α-aryl-α-hydroxymethyl)thiophene or furan with two equivalents of functionalized aryl aldehyde and three equivalents of pyrrole under acid catalyzed conditions (Scheme 29). The non-covalent porphyrin arrays **196** and **197** were synthesized by treating 21-thiaporphyrins, 5,10,15-tris(3 and 4-pyridyl)-20-phenyl-21-thiaporphyrins **192** and **194** respectively, with RuTPP(CO)(EtOH) **161** in toluene at refluxing temperature. The tetrad formation resulted in large ^1H NMR upfield shifts of inner NH, β-pyrrole and pyridyl protons of 21-thiaporphyrin sub-unit in tetrads compared to the corresponding monomers. These compounds are also weakly fluorescent due to presence of the heavy Ru(II) ion. Similar hetero triads and tetrads were not formed when di/tri-functionalized 21-oxaporphyrins such as **193** and **195** were treated with RuTPP(CO)(EtOH) **161** under identical reaction conditions.



Scheme 27. Synthesis of hetero porphyrin triad **184** assembled using covalent and noncovalent interactions.



Scheme 28. Synthesis of Sn(IV) porphyrin based triads **186** and **187**.

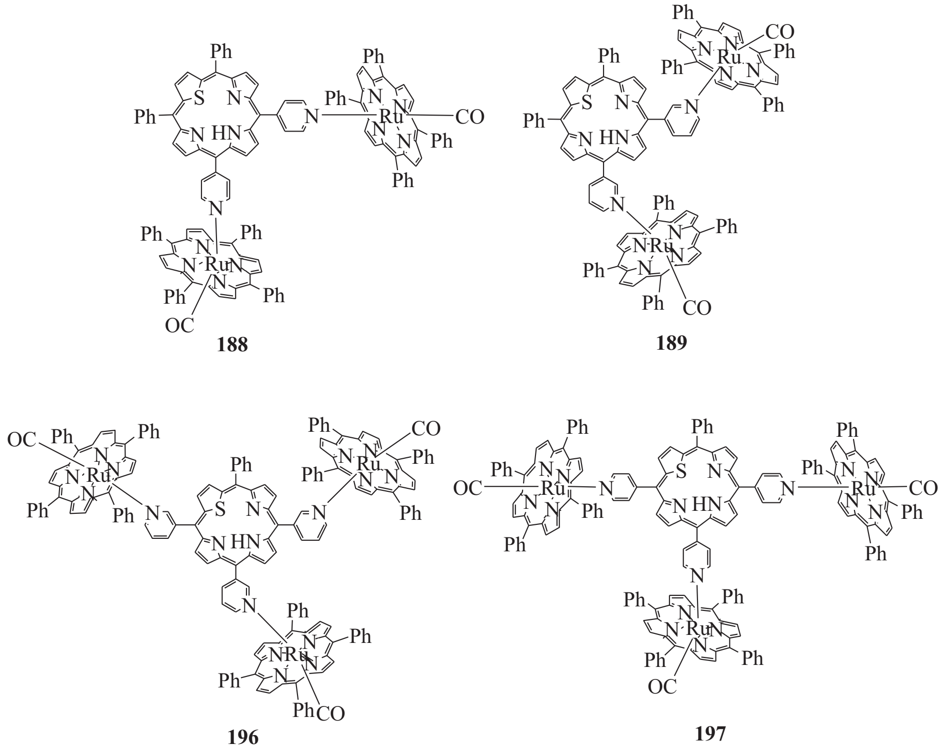
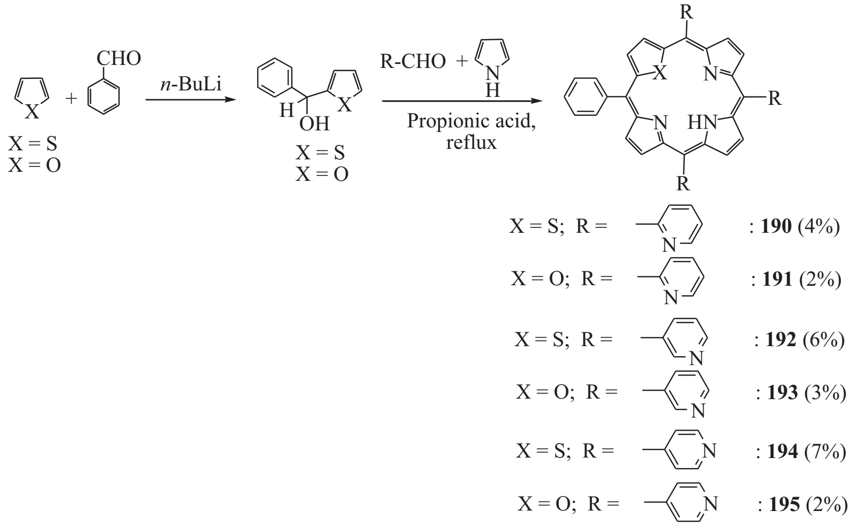


Chart 8. Non-covalent hetero porphyrin triads **188** and **189** and tetrads **196** and **197**.



Scheme 29. Synthesis of tri-functionalized 21-thia and 21-oxaporphyrin building blocks **190**–**195**.

4. Conclusions

Although heteroatom substituted porphyrins were discovered nearly four decades ago, the actual potential use of these compounds as the components in covalent and non-covalent porphyrin arrays has gained significant momentum for the past decade. It is now understood that the energy levels of heteroatom substituted porphyrins can be tuned by systematic alterations in the porphyrin core. Various synthetic methodologies have been developed which gives access to all types of functionalized core-modified porphyrin building blocks. With suitable arrangement of core-modified porphyrins in hetero porphyrin arrays, one can achieve unidirectional flow of electron/energy transfer. Heteroatom substituted porphyrins possess many interesting physico-chemical properties and these can be used as substitutes for tetrapyrrolic porphyrins. Thus, we hope that the availability of methodologies for the synthesis of functionalized core-modified porphyrins will stimulate more research in this area and these hetero porphyrins arrays containing heteroatom substituted porphyrins will find applications in photoactive molecular devices in near future.

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