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One-Flask Synthesis of Mono- and Trifunctionalized 21-Thia and 21-Oxaporphyrin Building Blocks and Their Application in the Synthesis of Covalent and Noncovalent Unsymmetrical Porphyrin Arrays†

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A rapid synthetic route has been developed to synthesize mono- and trifunctionalized 21-thia and 21-oxaporphyrin systems using simple precursors such as 2[α-(aryl)-α-hydroxymethyl] thiophene (thiophene mono-ol) and 2[α-(aryl)-α-hydroxymethyl] furan (furan mono-ol), respectively. Condensation of one equivalent of thiophene or furan mono-ol with two equivalents of aryl aldehyde and three equivalents of pyrrole under porphyrin forming conditions followed by column chromatography resulted in functionalized 21-thia or 21-oxaporphyrins. To synthesize monofunctionalized porphyrins, the mono-ol containing the functionalized aryl group was used. The functionalized aldehydes were used to synthesize trifunctionalized porphyrins. The mono-ol method is versatile and applicable to synthesize mono- and trifunctionalized 21-thia and 21-oxaporphyrins containing functional groups such as iodophenyl, ethynylphenyl, hydroxyphenyl, bromophenyl, and pyridyl groups. The monofunctionalized porphyrin building blocks containing iodophenyl and ethynylphenyl groups were used further to synthesize four unsymmetrical covalent porphyrin dimers containing two different porphyrin cores such as N_3S-N_4, N_3O-N_4, and N_3S-N_3O bridged via diaryl ethyne group and one symmetrical phenylethyne bridged dimer containing two N_3S cores. A preliminary photophysical study on these dimers indicated a possibility of energy transfer from one subunit to another. We also demonstrated the use of trifunctionalized porphyrins in the synthesis of two noncovalent unsymmetrical porphyrin tetramers containing one N_3S and three N_4 porphyrin subunits.

Introduction

The covalent and noncovalent linking of porphyrins and related macrocycles into dimers and larger arrays has been exhaustively studied in recent years to understand the energy and electron-transfer processes of photosynthesis. Most synthetic models for photosynthesis contain two covalently linked porphyrins which are attached to each other by one or more bridging groups such as phenyls, biphenyls, aromatic heterocycles, alkenes, or alkynes.[1] Supramolecular assemblies held together by noncovalent forces[2] such as hydrogen bonding and metal-pyridyl interactions have also been synthesized as model compounds for photosynthetic processes in natural systems. However, most of these covalent and noncovalent porphyrin arrays were symmetrical in nature containing two identical macrocycles; hence, it was difficult to achieve selective excitation of porphyrin unit upon irradiation. The direction of photoinduced energy or electron transfer has been generally induced in porphyrin arrays by selective metalation of the porphyrin subunits. However, since the absorption bands of metalated porphyrin overlaps with the free base porphyrin subunits of porphyrin arrays, the 100% selective excitation is not possible. The selective excitation of the porphyrin unit to induce electron or energy transfer in a particular direction can be achieved easily if the porphyrin units in the array are not identical (unsymmetrical). In the recent past, attention has been directed toward synthesizing covalently linked unsymmetrical arrays[3] containing two different macrocycles such as a porphyrin−pyropheophorbide, porphyrin−chlorin, porphyrin−corrole, or porphyrin−phthalocyanine to obtain fast initial charge transfer and a slow back reaction, so giving a long-lived charge-transfer state. A common feature among the various unsymmetrical dimers reported so far is that they all have similar pyrrole nitrogens as donor atoms (N_4 cores).

One area of porphyrin chemistry that has received less attention but may lead to systems of interesting structural and electronic properties is the characterization of porphyrin dimers with dissimilar cores. One of the most interesting modifications of the porphyrin molecule would be the replacement of the core nitrogens by other heteroatoms such as sulfur, oxygen, selenium, tellurium, and so forth.[4] Thus, a series of heteroatom substituted porphyrins form a group of core-modified porphyrins that exhibit interesting properties in terms of both aromatic

† This paper is dedicated to a porphyrin chemist the late Professor Bhaskar G. Maiya (1956-2004).

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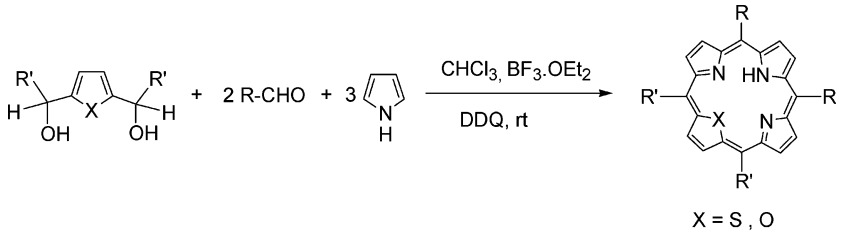
SCHEME 1. General Synthetic Scheme for 21-Thia and 21-Oxaporphyrins



character and their ability to stabilize metals in unusual oxidation states.[4a] An assembly of such heteroatom substituted porphyrin (N_3S, N_3O, N_2S_2, N_2O_2, N_2SO) and normal porphyrin (N_4 core) would offer unique dimers and oligomers which are expected to have unusual electronic structure and interesting properties. Recently, Van Patten and co-workers[5] proposed that a set of heteroatom porphyrins such as N_4, N_3O, N_3S, N_2OS, and N_2S_2 arranged in a linear series with a progressive decrease in energy levels could provide the basis for an energy cascade. There are very few examples of unsymmetrical porphyrin dimers and oligomers containing heteroatom substituted porphyrins available in the literature.[6−8] Since the heteroatom substituted porphyrin building blocks with desired functional groups are very rare in the literature because of limited synthetic methods available, the chemistry of porphyrin arrays containing heteroporphyrins is not very well developed.

The general synthetic scheme used for synthesis of 21-thia[9a,b] and 21-oxaporphyrins[9c] is shown in Scheme 1. Condensation of 2,5-bis(α-aryl- α-hydroxymethyl)thiophene or furan (thiophene diol or furan diol) with an aldehyde and pyrrole under standard porphyrin reaction conditions resulted in the formation of N_3S or N_3O porphyrins. This method is useful to prepare 21-thia or 21-oxaporphyrins bearing only one type of meso-substituent or two types of meso-substituents in a cis configuration. We explored this method extensively and synthesized several heteroatom substituted porphyrins.[10]

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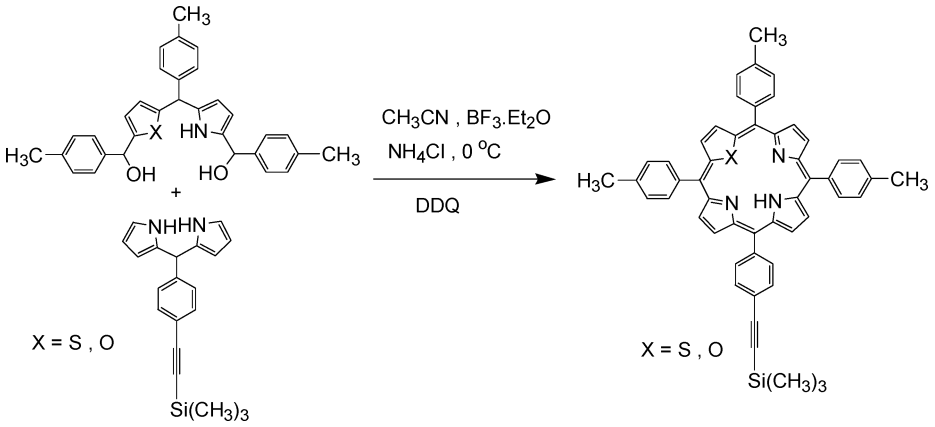
SCHEME 2. Lindsey and Co-Workers Synthetic Scheme for the Preparation of Monofunctionalized 21-Thia and 21-Oxaporphyrin Building Blocks



Furthermore, Cho and co-workers[11] developed a very novel and rational method for the synthesis of 21-thia and 21-oxaporphyrins containing two types of meso-substituents in trans configuration. They further extended the same strategy to synthesize monofunctionalized 21-thia and 21-oxaporphyrins. Thus, 21-thia and 21-oxaporphyrin having ethyne and iodo functional groups at the para position of meso-phenyl group were synthesized by this method as shown in Scheme 2. As evident from the scheme, the method requires two key precursors and involves multistep synthesis, extensive chromatography, and vacuum distillations to purify the intermediate compounds.

We recently developed a one-step rapid synthetic route to prepare mono- and trifunctionalized 21-thiaporphyrins using a very easily available precursor such as 2[α-(aryl)-α-hydroxymethyl] thiophene (thiophene mono-ol).[12] The mono-ol method is versatile and gives an access to several mono- and trifunctionalized 21-thiaporphyrins which were not accessible earlier. In this paper, we describe in detail the synthesis and characterization of a series of thiophene or furan mono-ols and one-pot synthesis of several mono- and trifunctionalized 21-thia and 21-oxaporphyrins. We also showed the application of these mono- and trifunctionalized 21-thia and 21-oxaporphyrin building blocks in the synthesis of five covalently connected unsymmetrical porphyrin dimers with different combinations of porphyrin cores such as N_4-N_3S, N_4-N_3O, and N_3S-N_3O as well as noncovalently connected unsymmetrical porphyrin tetramers composed of one N_3S porphyrin subunit and three N_4 porphyrin subunits.

Results and Discussion

Synthesis of Thiophene Mono-ols 1−9 and Furan Mono-ols 10−12. The preparation of the mono- and trifunctionalized 21-thia and 21-oxaporphyrin building blocks depends on the availability of the suitable thiophene and furan mono-ols which are key precursors in this reaction. A series of thiophene mono-ols were prepared by treating thiophene with 1.2 equivalents of *n*-butyllithium followed by 1.2 equivalents of benzaldehyde or substituted benzaldehyde in THF at 0 °C (Scheme 3).

The TLC analysis of the crude reaction mixture showed two clear spots corresponding to the unreacted aldehyde and the desired thiophene mono-ol. The crude compound was subjected to silica gel column chromatography and the fast moving unreacted aldehyde was collected as a first band with petroleum ether/2−15% ethyl acetate. The required thiophene mono-ol was always moved as a second band and collected with petroleum ether/5−25% ethyl acetate. The solvent was removed on a rotary evaporator under vacuum and the oily compound had been stored in a refrigerator overnight and a white solid formed. Attempts to recrystallize the crude compound without subjecting it first to column chromatography did not afford the pure thiophene mono-ols. Thus, the column chromatography is essential to afford pure thiophene mono-ols in 65−70% yields. Similarly, the furan mono-ols **10**−**12** were prepared by treating furan with 1.2 equivalents of *n*-butyllithium followed by 1.2 equivalents of appropriate aldehyde under same reaction conditions. However, the crude reaction mixture showed more complex TLC with at least four spots unlike thiophene mono-ols. Usually, the third spot on TLC was our desired furan mono-ol. The crude mono-ols were subjected to silica gel column chromatography and afforded the pure furan mono-ols **10**−**12** as gray white solids in 50−70% yields. The low yields observed in some cases such as **2**, **3**, and **10** were due to poor solubility of the corresponding aldehydes. However, all these mono-ols can be prepared easily in multigram quanity and purified by straightforward column chromatoghaphy. The thiophene and furan mono-ols were characterized by mp, IR, elemental analysis, and ^1H and ^{13}C NMR spectroscopic techniques (Supporting Information). The presence of a sharp singlet for the CH proton in the region 5.6−5.9 ppm and broad singlet for OH in 2.6−2.9 ppm region in the ^1H NMR and

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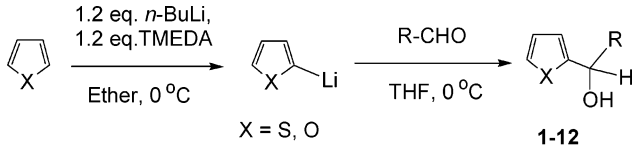
SCHEME 3. Synthesis of Thiophene Mono-ols 1−9 and Furan Mono-ols 10−12



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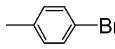
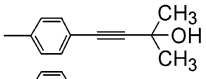
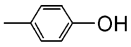
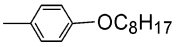
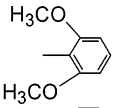
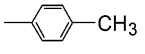
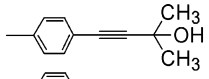
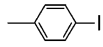
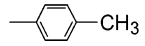
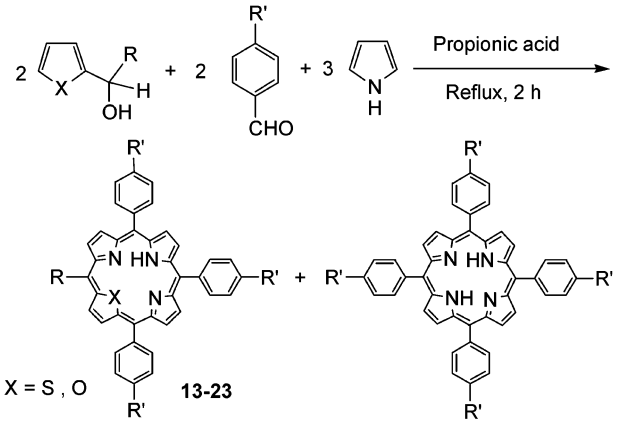
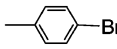
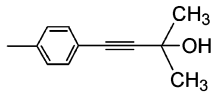
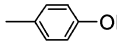
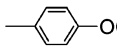
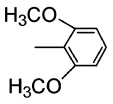
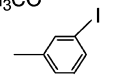
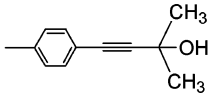
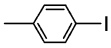
S		1
S		2
S		3
S		4
S		5
S		6
S		7
S		8
S		9
O		10
O		11
O		12

strong peak at ∼3300 cm^{-1} for OH in IR were characteristic features of thiophene and furan mono-ols. The ES-MS spectra showed a weak peak of M^+ ion (10%) and strong peak at M^+-17 (90%) confirming the identities of products.

Synthesis of Monofunctionalized 21-Thia and 21-Oxaporphyrins 13−23. 21-Thia and 21-oxaporphyrin building blocks bearing one functional group provide the basis for the synthesis of dimeric arrays. A series of monofunctionalized 21-thia and 21-oxaporphyrins **13**−**23** were synthesized using thiophene or furan mono-ols in one-pot reaction as shown in Scheme 4. The condensation of two equivalents of thiophene or furan mono-ol with two equivalents of aldehyde and three equivalents of pyrrole in propionic acid[13] at refluxing temperature for 2 h, followed by the removal of propionic acid under vacuum and thorough washing with warm water, gave a crude mixture of two porphyrins: the desired monofunctionalized 21-thia or 21-oxaporphyrin and tetra-aryl substituted normal porphyrin (N_4). Absorption spectroscopy was used to confirm the formation of the above two porphyrins in every porphyrin condensation reaction since absorption bands of 21-thia or 21-oxaporphyrins are quite different from normal porphyrin. Although the absorption spectra of the crude porphyrin mixture mainly show absorption bands corresponding to N_4 porphyrin, a

SCHEME 4. Synthesis of Monofunctionalized 21-Thia and 21-Oxaporphyrins



X	R	R'	Porphyrin
S		—CH_3	13
S		—OC_8H_{17}	14
S		—CH_3	16
S		—H	17
S		—CH_3	18
S		—CH_3	19
S		—CH_3	20
O		—OC_8H_{17}	21
O		—CH_3	23

characteristic peak around ∼680 nm confirms the formation of N_3S or N_3O porphyrin. The crude porphyrin mixture was initially subjected to silica gel column chromatography and removed nonporphyrinic impurities. The TLC analysis of porphyrin mixture after the first column clearly showed two spots corresponding to N_4 and N_3S or N_3O porphyrins. The porphyrin mixture was subjected to second silica gel column chromatography and the desired 21-thia or 21-oxaporphyrin building blocks **13**−**23** were always collected as a second band and afforded purple compounds in 2−7% yields. When we performed porphyrin condensations under Lindsey et al. conditions,[14] the yields of the desired 21-thia or 21-oxaporphyrin building blocks were not improved. Although the yields of monofunctionalized building blocks are relatively low, the method is very simple and the desired porphyrin building block with any functional

(13) Adler, A. D.; Longo, F. R.; Finarelli, J. D.; Goldmacher, J.; Assour, J.; Korsakoff, L. *J. Org. Chem.* **1967**, *32*, 476.

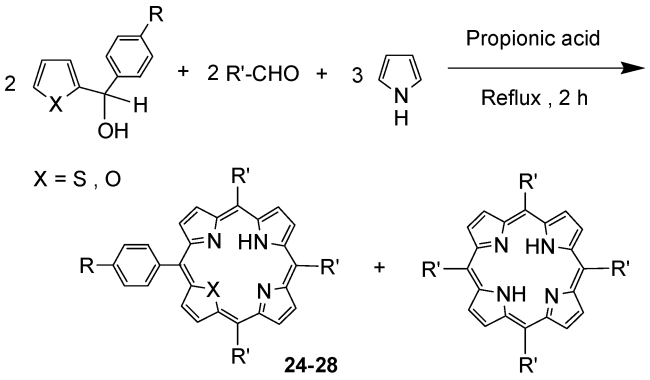
(14) Lindsey, J. S.; Schreiman, I. C.; Hsu, H. C.; Kearay, P. C.; Marguerettaz, A. M. *J. Org. Chem.* **1987**, *52*, 827.

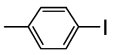
group can be obtained very easily. Furthermore, since the precursor thiophene or furan mono-ol can be synthesized in multigram quantity, the desired porphyrin building block can be obtained in ca. 100-mg quantities in one-pot reaction. We varied the number of equivalents of thiophene or furan mono-ol, aldehyde, and pyrrole to optimize the porphyrin yields. When we used one equivalent of thiophene or furan mono-ol keeping aldehyde and pyrrole equivalents constant, the N_4 porphyrin was formed as a major product with trace amounts of the required N_3S or N_3O porphyrin. When three equivalents of thiophene or furan mono-ol was used, the yield of N_3S or N_3O porphyrin did not increase. We also varied the aldehyde and pyrrole equivalents keeping the mono-ol equivalents constant but the yields were not improved. Thus, two equivalents of thiophene or furan mono-ol, two equivalents of aldehyde, and three equivalents of pyrrole were needed to afford the porphyrin building blocks in reasonable yields. We arrived at this stoichiometry after testing a series of trial reactions. Though no explaination can be offered at this stage, this reaction works well when we used the above-mentioned ratio of reactants. The mono-ol method is versatile and any desired monofunctionalized 21-thia and 21-oxaporphyrin building block can be prepared by using this method. The thiophene or furan mono-ol should contain the functionalized aryl group to synthesize monofunctionalized N_3S or N_3O porphyrin. The mono-ol method is unique and novel and to the best of our knowledge, there are no reports on using mono-ols for porphyrin reaction. The only report on use of mono-ols is when Grazynski and co-workers[15] synthesized 5,10,15-triaryl-21,23-dioxacorrole by condensing one equivalent of 2-phenylhydroxymethyl furan (furan mono-ol) with one equivalent of 2,5-bis(arylhydroxymethyl)-furan and two equivalents of pyrrole under mild acidic conditions. We also anticipated the corrole formation in our condensation reactions but we did not observe any corrole in these reactions.

The monofunctionalized 21-thia and 21-oxaporphyrin building blocks **13**−**23** were characterized with ^{1}H and ^{13}C NMR, ES-MS, elemental analysis, IR, absorption, and emission spectroscopic techniques (Supporting Information). All porphyrins showed M^+ ion peak in mass spectra confirming the product. In the ^{1}H NMR, all N_3S porphyrins clearly showed two signals for the thiophene protons unlike 5, 10, 15, 20-tetraphenyl-21-thiaporphyrin[4a] (STPPH) which showed only one signal for thiophene protons indicating the unsymmetric substitution of 21-thiaporphyrin building blocks. Similarly, unlike one signal observed for furan protons in 5, 10, 15, 20-tetraphenyl-21-oxaporphyrin[4a] (OTPPH), the monofunctionalized 21-oxaporphyrin showed two signals due to unsymmetric substitution. Absorption spectra for N_3S and N_3O porphyrin building blocks exhibited one Soret and four Q-bands and the peak positions were in close match with STPPH and OTPPH, respectively.[4a] Elemental analyses were also in agreement with the composition of the expected porphyrin building blocks.

Synthesis of Trifunctionalized 21-Thia and 21-Oxaporphyrins 24−**28.** The thiophene and furan mono-ols were also useful in the synthesis of trifunctionalized

SCHEME 5. Synthesis of Trifunctionalized 21-Thia and 21-Oxaporphyrin Building Blocks



X	R	R'	Porphyrin
S	—CH_3		**24**
S	—H		**25**
S	—H		**26**
S	—OC_8H_{17}		**27**
O	—CH_3		**28**

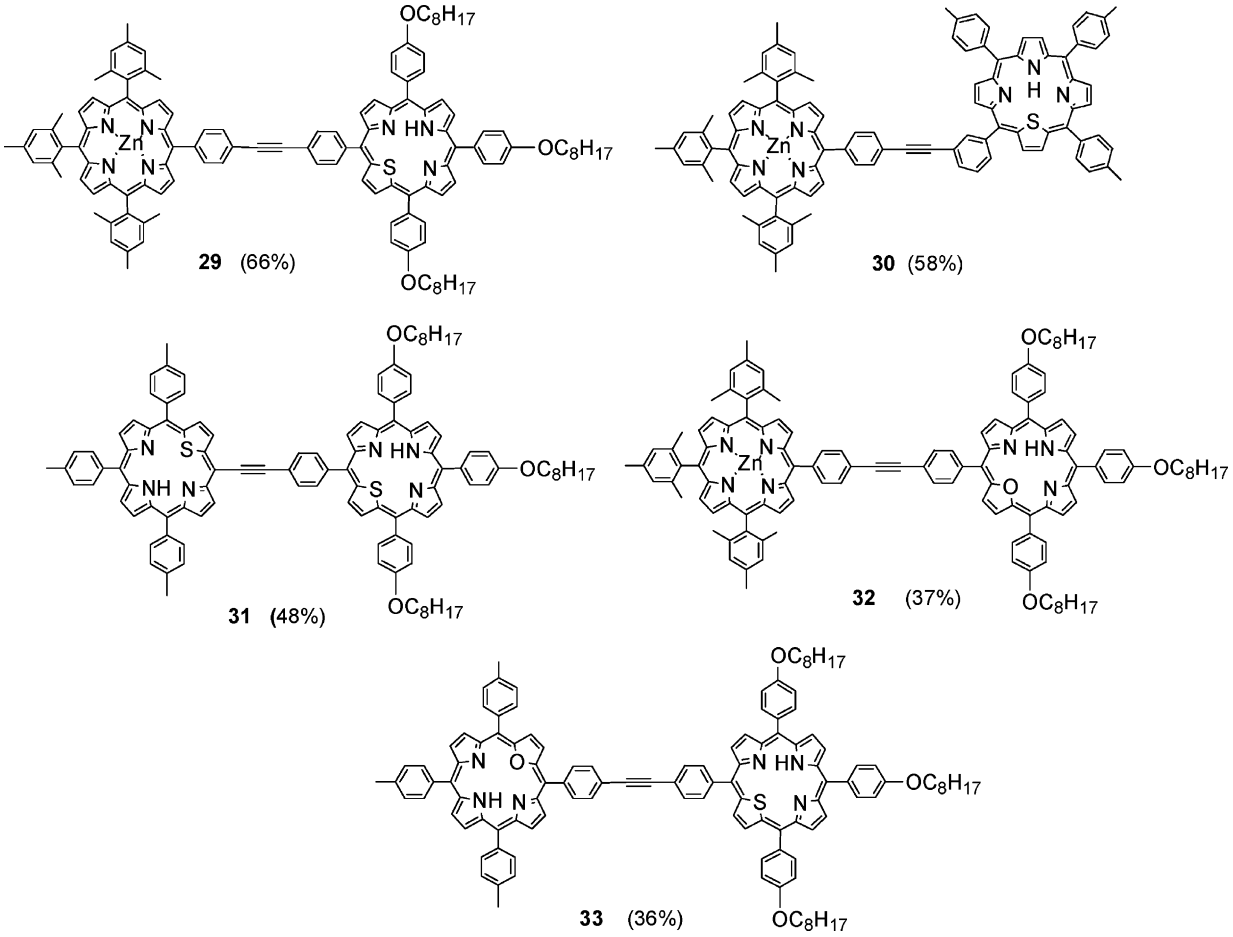
N_3S and N_3O porphyrins, respectively. Prior to our communication,[12] there were no reports available on the synthesis of trifunctionalized 21-thia and 21-oxaporphyrin building blocks. To synthesize the trifunctionalized N_3S and N_3O porphyrin, the thiophene and furan mono-ol, respectively, were condensed with the desired functionalized aryl aldehyde and pyrrole in propionic acid in the same stoichiometry used for monofunctionalized compounds at refluxing temperature (Scheme 5).

Thus, the desired aryl functional groups were incorporated in 21-thia and 21-oxaporphyrin building blocks by using the appropriate functionalized aryl aldehyde. By using the mono-ol method, we synthesized trifunctionalized N_3S and N_3O porphyrins containing pyridyl and iodophenyl groups at the meso positions which are useful building blocks for noncovalent and covalent porphyrin arrays, respectively. The trifunctionalized N_3S and N_3O porphyrin building blocks were purified by column chromataography and characterized by the standard spectroscopic techniques. The ^{1}H NMR spectra of the trifunctionalized N_3S and N_3O porphyrins indicated the unsymmetric substitution of the porphyrin. All porphyrins showed an M^+ ion peak in ES-MS spectra and characteristic absorption and emission spectra (Supporting Information).

Synthesis of Unsymmetrical Covalent Porphyrin Dimers. The monofunctionalized N_3S and N_3O porphyrins with functional groups such as iodophenyl, ethynylphenyl, bromophenyl, and hydroxyphenyl groups at the meso position reported in this paper are highly desirable to synthesize a series of covalently linked porphyrin dimers. They are ideal porphyrin building blocks to

(15) Pawlicki, M.; Latos-Grazynski, L.; Szterenberg, L. *J. Org. Chem.* **2002**, *67*, 5644.

CHART 1



synthesize unsymmetrical covalent dimers containing two different types of porphyrin cores. Porphyrin−porphyrin dimers are of interest for investigating the pairwise interactions of porphyrins in larger arrays. To demonstrate the use of porphyrin building blocks reported in this paper, we synthesized five aryl ethyne bridged covalent dimers **29**−**33** by taking appropriate N_3S and N_3O porphyrin building blocks (Chart 1). The N_3S porphyrin **15** and N_3O porphyrin **22** with monoethynylphenyl group at the meso position were synthesized by deprotecting N_3S porphyrin **14** and N_3O porphyrin **21,** respectively, at 80 °C with KOH in benzene/methanol. The other required porphyrin building block, 5,10,15-tri(mesityl)-20-(4-iodophenyl) zinc(II) porphyrin **34** was synthesized by following the literature method.[16] The dimers **29**−**33** were synthesized by following milder palladium coupling conditions developed by Lindsey and co-workers[17] during their investigation on synthesis of aryl ethyne bridged porphyrin arrays.

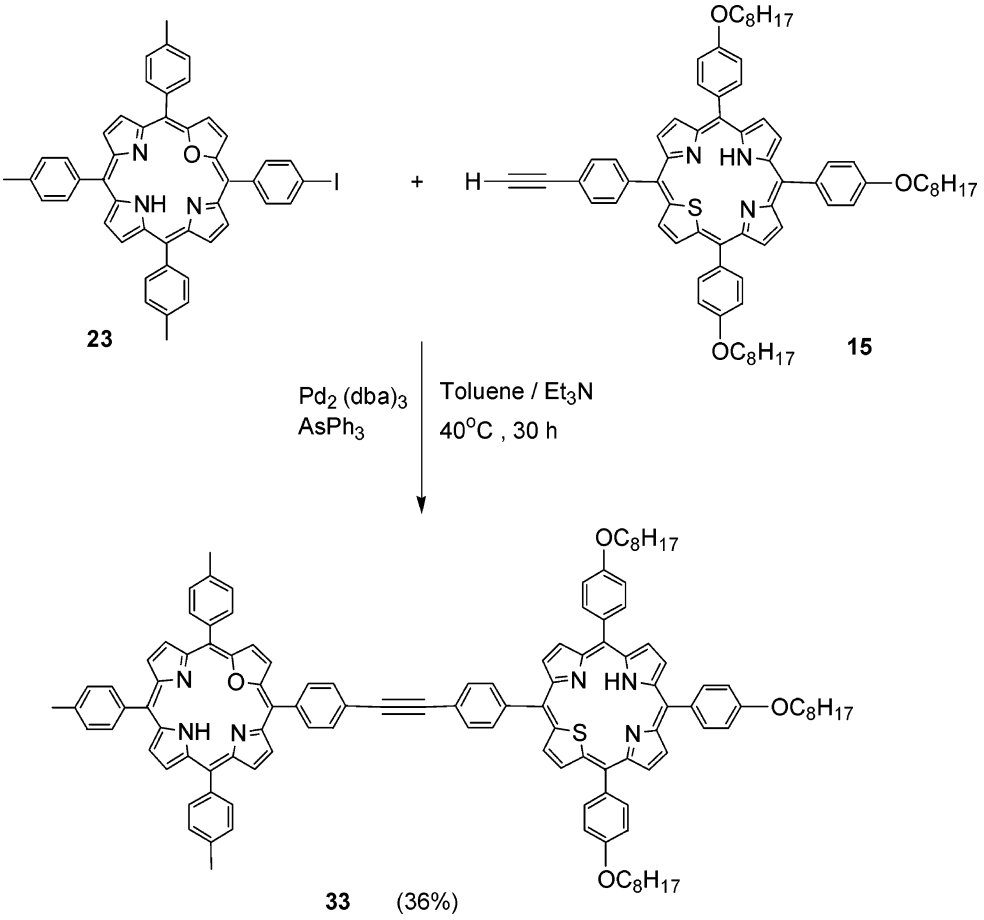
Thus, the dimer **29** was synthesized by coupling N_3S porphyrin **15** with **34** in toluene/triethylamine at 35 °C in the presence of $Pd_2(dba)_3$ and $AsPh_3$. The progress of the reaction was monitored with TLC and absorption spectroscopy. The reaction was stopped after the disappearance of major amounts of starting materials as judged by TLC analysis. The solvent was removed on rotary evaporator and the crude reaction mixture was loaded on alumina column and eluted with petroleum ether/dichloromethane. The small amounts of triphenyl arsine and unreacted porphyrin building blocks were removed with petroleum ether/dichloromethane (70:30) and the dimer with small amounts of impurities was collected with petroleum ether/dichloromethane (20:80). The impure dimer was subjected to a second alumina column and the pure unsymmetrical dimer **29** containing N_3S-N_4 cores was collected with the same solvent mixture as purple solid in 66% yield. Similarly, coupling of 5,10,15-tri(mesityl)-20-(4-ethynylphenyl) zinc(II)[16] **35** with the other N_3S porphyrin building block **20** under the same palladium coupling conditions followed by chromatography on alumina yielded pure unsymmetrical dimer **30** containing N_3S-N_4 cores as purple solid in 37% yield. The symmetrical dimer **31** containing N_3S-N_3S cores bridged via phenyl ethyne instead of diaryl ethyne was prepared in 69% yield by coupling N_3S porphyrin building block **15** with 5-bromo-10,15,20-tris(*p*-tolyl)-21-thiaporphyrin[18] **36** under the same mild palladium coupling conditions. The unsymmetrical dimer **32** with N_3O-N_4 cores was prepared by coupling N_3O porphyrin building block **22** with **34** and the dimer **33** with N_3S-N_3O cores was prepared by coupling N_3S porphyrin building block **15** with N_3O porphyrin building block **23**

(16) Lindsey, J. S.; Prathapan, S.; Johnson, T. E.; Wagner, R. W. *Tetrahedron* **1994**, *50*, 8941.

(17) Wagner, R. W.; Johnson, T. E.; Li, F.; Lindsey, J. S. *J. Org. Chem*. **1995**, *60*, 5266.

(18) Agarwal, N.; Hung, C.-H.; Ravikanth, M. *Eur. J. Org. Chem*. **2003**, 3737.

SCHEME 6. Synthesis of Unsymmetrical Covalent Dimer 33



under the same palladium coupling conditions (Scheme 6). All reactions worked smoothly and involved simple column chromatography for purification. There is no need to use any size exclusion chromatography as all of the dimers were easily separated using alumina column chromatography. The dimers **29**−**33** are highly soluble in all common organic solvents and were characterized by spectroscopic techniques. ES-MS spectrometry of all five dimers showed molecular ion peak confirming the compounds (Supporting Information). The ^{1}H NMR spectroscopy has been used to characterize the dimers **29**−**33** in detail. The resonances of the dimers were assigned on the basis of the spectra observed for the two monomers taken independently. For instance, in the dimer **29** one would expect one set of multiplet for two thiophene protons and three sets of signals for six pyrrole protons of N_3S subunit because of its lower symmetry and also expect one signal for pyrrole protons of N_4 subunit (Supporting Information). In the ^{1}H NMR of **29**, the multiplet resonance observed at 9.81 ppm is due to two thiophene protons and three doublets at 8.79, 8.93, and 8.98 ppm were due to six pyrrole protons of N_3S porphyrin subunit. The strong singlet observed at 8.72 ppm was due to eight pyrrole protons of the ZnN_4 porphyrin subunit. The meso phenyl ortho, meta protons and bridging phenyl group protons appeared in the region 7.32−8.32 ppm methyl and octyloxy groups appeared in the region 0.9−4.25 ppm. The NH proton of N_3S subunit was observed at −2.60 ppm as a broad singlet. A comparison of chemical shifts of the various protons of the dimer **29** with those of individual monomeric units indicates only minor differences suggesting that the two porphyrin subunits in the dimer interact very weakly. Similarly, the dimers **30**, **32**, and **33** were also characterized by comparing the ^{1}H NMR spectra with their corresponding two porphyrin monomeric units. However, the dimer **31** in which two N_3S porphyrin units joined at the meso positions via a phenylethyne linker showed the signals which were shifted because of strong interactions between the two porphyrin units. The chemical shifts of protons of N_3S porphyrin unit of the dimer **31** which has an ethyne group directly at the meso position were altered drastically and the chemical shifts of protons of other N_3S porphyrin unit which has phenyl group at the meso position were not affected as much. The thiophene proton which was adjacent to ethyne linker was shifted to downfield (10.52 ppm) and the other proton of thiophene was shifted to upfield (9.54 ppm) compared to 10, 15, 20-tris (*p*-tolyl)-21-thiaporphyrin (10.00 and 9.95 ppm).[18] The pyrrole protons adjacent to ethyne linker were also shifted to downfield by 0.4 ppm. The bridging phenyl protons also experienced similar downfield shifts. Similarly, the inner NH proton of the same N_3S unit of dimer **31** was shifted to downfield by 0.8 ppm whereas the NH proton of the other N_3S unit remain unaffected.

Absorption Spectra of Dimers 29−33. The absorption spectra of dimers and their corresponding monomers in toluene were measured at room temperature. A comparison of the absorption spectra of dimer **29** with a 1:1 mixture of corresponding monomers is shown in

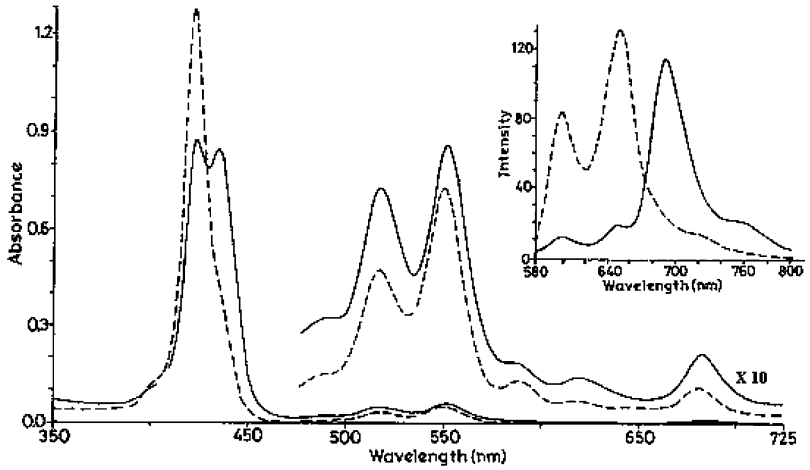


FIGURE 1. UV−vis spectra of dimer **29** (—) and 1:1 mixture of **15** and **34** (---) recorded in toluene. The concentration used was 2×10^{-6} M. The fluorescence spectra ($\lambda_{ex} = 550$ nm) of dimer and 1:1 mixture is shown in inset.

Figure 1 indicating that the covalent dimer **29** shows the absorption bands corresponding to both of the monomers. In the Q-band region, the absorption spectrum of the dimer **29** was almost identical to that of the 1:1 mixture. However, the dimer **29** showed split Soret band compared to 1:1 mixture of monomers indicating an interaction between the subunits. The position, shape, and the width of the Soret band in dimeric systems has been used as a probe for estimating the size of coupling interaction between the two chromophores. Unlike dimer **29**, which showed a split Soret band, the other four dimers **30**−**33** showed a broad Soret band with a bandwidth range of 16−34 nm (fwhm). The maximum broadened Soret band was observed for dimer **31** (fwhm = 34 nm) which also showed a red shifted absorption spectra compared to the 1:1 mixture of corresponding monomers suggesting a strong interaction between the porphyrinic subunits.

Emission and Excitation Spectra of Dimers 29−**33.** The fluorescence spectra of dimers **29**, **30**, and **32** were recorded at 550 and 515 nm and the dimers **31** and **33** were recorded at 515 nm in toluene at room temperature. The data of fluorescence yields of dimers **29**−**33** are presented in Table 1. Excitation of dimer **29** at 515 nm, where the N_3S porphyrin subunit absorbs strongly, results in typical N_3S porphyrin emission with quantum yield resembling that of monomeric STPPH.[19] Illumination of dimer **29** at 550 nm, where ZnN_4 subunit absorbs strongly, causes the emission of ZnN_4 subunit to be quenched by 95% and the strong emission from the N_3S porphyrin subunit was observed. However, when 1:1 mixture of ZnN_4 porphyrin **34** and N_3S porphyrin **15** was excited at 550 nm, the strong emission was observed mainly from ZnN_4 porphyrin subunit. These results indicated that there is an efficient energy transfer from the ZnN_4 subunit to the N_3S subunit in dimer **29**. The excitation spectrum recorded for **29** at $\lambda_{em} = 750$ nm matching exactly with the absorption spectrum further confirmed the efficient energy transfer between the subunits. Similarly, dimer **30** showed an efficient energy transfer from the ZnN_4 porphyrin subunit to the N_3S porphyrin subunit. Interestingly, the dimer **32** with ZnN_4 and N_3O subunits, on excitation at 550 nm, showed the emission mainly from the ZnN_4 subunit with a weak emission from the N_3O subunit (Table 1). This indicates that the energy transfer from ZnN_4 unit to N_3O unit was not efficient. In this system, the emission of ZnN_4 subunit was quenched only 30% suggesting an inefficient energy transfer between the subunits.

In phenyl ethyne linked dimer **31**, which is composed of identical N_3S porphyrin units, the ethyne substitiuted porphyrin is shifted to lower energy and is expected to serve as energy acceptor. The porphyrin with the phenyl substituents is energetically unperturbed and expected to serve as a donor.[20] Similar observations were indeed made for dimer **31**. Upon excitation of dimer **31** at 515 nm, where the N_3S subunit with the phenyl substituents absorbs strongly, the main emission was observed from the N_3S subunit with the ethyne substituent indicating an efficient energy transfer from one N_3S subunit to another N_3S subunit (Table 1).

The emission spectrum recorded for dimer **33** containing N_3S and N_3O porphyrin subunits showed peak maxima at 687 and 750 nm. The excitation spectrum recorded at 750 nm is matching with the absorption spectrum of the dimer indicating that it is true emission. Since the energy levels of N_3S and N_3O porphyrin are close, the energy-transfer dynamics in this dimer cannot be understood with this preliminary study. Although the steady-state fluorescence studies indicated the possibility of energy transfer in the four dimers reported here, detailed time-resolved studies are required to quantify these energy-transfer dynamics.

Synthesis of Unsymmetrical Noncovalent Porphyrin Arrays. The core-modified porphyrins with pyridyl groups at the meso positions are excellent building blocks to construct noncovalent unsymmetrical porphyrin arrays. We earlier demonstrated the utility of *cis*-pyridyl building blocks with the N_3S core in the construction of noncovalent trimer containing one N_3S porphyrin and two N_4 porphyrin cores.[8] Interestingly, except our own report,[8] most of the metal-pyridyl based noncovalent porphyrin arrays were limited to N_4 porphyrins.[2a,b] We used the N_3S porphyrin building blocks **25** and **26** with

(19) Pandian, R. P.; Chandrashekar, T. K.; Saini, G. S. S.; Verma, A. L. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 677.

(20) Tomizaki, K-y.; Lysenko, A. B.; Taniguchi, M.; Lindsey, J. S. *Tetrahedron* **2004**, *60*, 2011.

TABLE 1. Fluorescence Data of Covalent Dimers 29−33 Recorded in Toluene at Excitation Wavelengths 515 and 550 nm

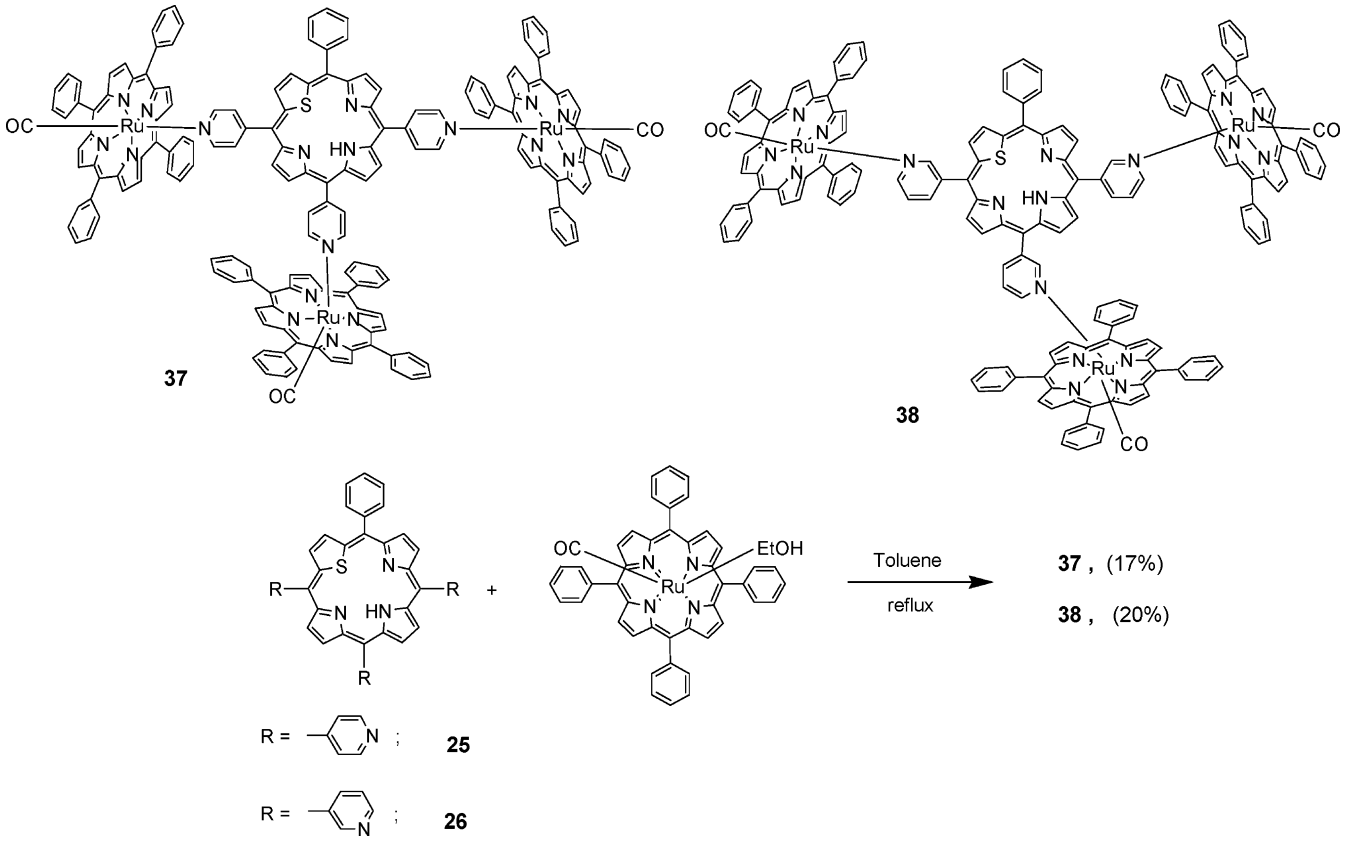
compound		ϕ_{515}	ϕ_{550}
STPPH		0.0168	
OTPPH		0.0758	
ZnTPP			0.033
29	N_3Sem	0.0182	0.0079
	ZnN_4em		0.0015
30	N_3Sem	0.0202	0.0090
	ZnN_4em		0.0057
31	N_3Sem[a]	0.0199	
32	N_3Oem	0.0529	0.0152
	ZnN_4em		0.0233
33	$N_3S + N_3$Oem[b]	0.0309	

[a] The emission bands of monomers N_3S porphyrin with ethyne at the meso position and N_3S porphyrin with the meso aryl although different in emission peak maxima are not distinguishable in dimer **31**. Hence, the total quantum yield is given. [b] The emission peak maxima of N_3S and N_3O porphyrins are close and indistinguishable in dimer **33**.

three 4-pyridyl or 3-pyridyl groups at the meso positions to construct unsymmetrical noncovalent porphyrin tetramers **37** and **38**, respectively, containing one N_3S porphyrin subunit and three N_4 subunits (Scheme 7).

To synthesize unsymmetrical noncovalent porphyrin tetramers **37** and **38**, we treated one equivalent of **25** and **26**, respectively, with 3.2 equivalents of RuTPP(CO)(EtOH) in toluene at refluxing temperature for overnight. As noted previously, the color of the reaction mixture changed from bright red to brownish red as the reaction progressed. The reaction was stopped after the completion of the reaction as judged by the TLC. Column chromatography on silica using petroleum ether/dichloromethane (60:40) gave pure tetramers **37** in 17% yield and **38** in 20% yield as purple solids. The porphyrin tetramers **37** and **38** were highly soluble in all common organic solvents and characterized by NMR, mass, elemental, infrared, and UV−visible spectroscopic techniques. The ^{1}H NMR spectrum of tetramer **37** comparing with monomeric N_3S porphyrin is shown in Figure 2. The ^{1}H NMR spectra of tetramers **37** and **38** are composed of signals from RuTPP(CO) subunit and N_3S porphyrin subunit **25** and **26**, respectively. In the ^{1}H NMR spectra of the tetramers, the chemical shifts of the RuTPP(CO) subunit remain unaltered and the clear evidence of metal-pyridyl nitrogen coordination comes mainly from the dramatic changes in the chemical shifts of the N_3S porphyrin subunit.[8] The large upfield shifts of the 2,6- and 3,5/4,5-pyridyl protons, β-pyrrole, β-thiophene, and inner NH protons of N_3S subunit of tetramers support their formation (Supporting Information). The changes in the chemical shifts of N_3S porphyrin subunit of tetramer **37** compared to N_3S porphyrin building block **25** are as follows: The 2,6-pyridyl protons of **25** which appeared as two multiplets at 9.05 and 9.09 ppm were upfield shifted in tetramer **37** to 1.78 and 1.86 ppm, respectively. Similarly, the 3,5- pyridyl protons of N_3S subunit in tetramer **37** were upfield shifted compared to **25**. The β-pyrrole and β-thiophene protons of N_3S subunit of tetramer **37** also experienced similar upfield shifts compared to **25** (Supporting Information). The inner NH proton that appears at −2.84 ppm in **25** was shifted to −4.33 ppm in tetramer **37**. Similar shifts were observed for N_3S subunit of tetramer **38** compared to N_3S porphy-

SCHEME 7. Synthesis of Unsymmetrical Noncovalent Tetramers 37 and 38



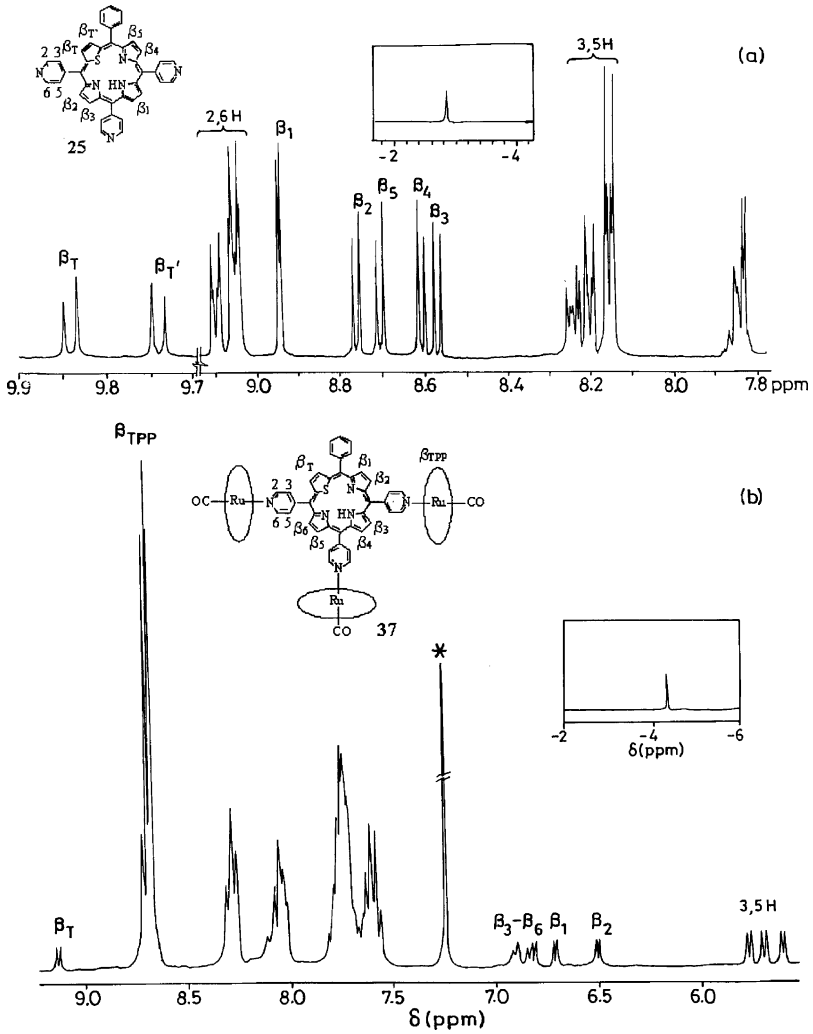


FIGURE 2. ^{1}H NMR spectra of **25** and noncovalent tetramer **37** recorded in $CDCl_3$. The NH signals are shown in insets.

rin building block **26** (Supporting Information). Similar results indicate the coordination of pyridyl groups of N_3S porphyrin **25** and **26** to the ruthenium ion of the RuTPP-(CO) core to form tetramers **37** and **38**, respectively. Further evidence for tetramer formation was obtained from ES-MS spectra that has shown a clear M^+ ion peak, and the elemental analysis also matched with the composition. The infrared measurements on **37** and **38** showed a strong $\nu_{(CO)}$ stretch at ~1953 cm^{-1}. The absorption spectra of **37** and **38** showed that absorption bands correspond to both RuTPP(CO) subunit as well as N_3S porphyrin subunits. Since the number of RuTPP(CO) subunits are three in tetramer, the absorption bands that correspond to RuTPP(CO) subunit are dominating the absorption spectra of tetramers **37** and **38**.

Summary

In summary, we developed a simple and rapid method to synthesize monofunctionalized 21-thia and 21-oxoporphyrin building blocks using an easily available thiophene and furan mono-ols. The mono-ol method reported in this paper is novel and applicable to synthesize any desired monofunctionalized N_3S and N_3O porphyrins. This is the first such method in which the simple precursors such as thiophene or furan mono-ols were used to synthesize the monofunctionalized 21-thia and 21-oxoporphyrins. Furthermore, the same mono-ol precursor can also be used to synthesize the trifunctionalized N_3S and N_3O porphyrin systems. We synthesized a series of trifunctionalized 21-thia and 21-oxaporphyrin building blocks using the same methodology.

To show the use of mono- and trifunctionalized N_3S and N_3O porphyrin building blocks, we synthesized unsymmetrical covalent and noncovalent porphyrins arrays containing two different types of porphyrin cores. We synthesized the first diaryl ethyne bridged four unsymmetrical dimers containing N_3S or N_3O core and N_4 core and one symmetrical phenyl ethyne bridged dimer containing two N_3S cores by following well-established mild palladium coupling conditions. A preliminary steady-state fluorescence study was carried out on all five dimers. In dimers **29** and **30** containing N_3S and ZnN_4 units, an efficient energy transfer was observed from the ZnN_4 unit to the N_3S unit on selective excitation of ZnN_4 subunit. An efficient energy transfer was also noted between two N_3S units in the phenylethyne bridged symmetrical dimer **31**. However, in dimer **32** containing ZnN_4 and N_3O subunits, the energy transfer from ZnN_4 unit to N_3O unit was not efficient and it was difficult to understand the energy-transfer dynamics in dimer **33**

containing N_3S and N_3O cores. The understanding of the photodynamics of this kind of unsymmetrical dimers will be useful in designing efficient molecular photonic devices. Two noncovalent unsymmetrical porphyrin tetramers **37** and **38** containing one N_3S porphyrin subunit and three N_4 porphyrin subunits were also synthesized to demonstrate the use of trifunctionalized porphyrin building blocks. A detailed photodynamics of these novel arrays is presently under investigation in our laboratory.

Experimental Section

Thiophene and Furan Mono-ols. 2-[α-(4-Bromophenyl)-α-hydroxymethyl]thiophene (1). Dry, distilled ether (40 mL) was added to a 250-mL three-necked, round-bottomed flask fitted with a rubber septum and gas inlet tube; the flask was flushed with argon for 10 min. Tetramethylethylenediamine (TMEDA) (3.5 g, 4.6 mL, 30.418 mmol) and *n*-butyllithium (20 mL of ca. 15% solution in hexane) were added to the stirred solution and the reaction temperature maintained at 0° C in an ice bath. Thiophene (2.1 g, 2.0 mL, 25.348 mmol) was added and the solution was stirred for 1 h. As the reaction progressed, a white turbid solution formed indicating the formation of 2-lithiated salt of thiophene. An ice cold solution of 4-bromobenzaldehyde (5.6 g, 30.418 mmol) in dry THF (40 mL) was then added and stirred for an additional 15 min at 0 °C. The reaction mixture was brought to room temperature. The reaction was quenched by adding an ice-cold NH_4Cl solution (50 mL, ca. 1 M). The organic layer was diluted with ether and washed several times with water and brine and dried over anhydrous Na_2SO_4. The solvent was removed in a rotary evaporator under reduced pressure to afford the crude compound. TLC analysis showed two spots mainly corresponding to unchanged aldehyde and the desired mono-ol. The crude compound was loaded on silica and eluted with petroleum ether. The unchanged aldehyde was removed with petroleum ether/ethyl acetate (98: 2) solvent mixture and the desired mono-ol **1** was collected with petroleum ether/ethyl acetate (95: 5) solvent mixture. The solvent was removed in a rotary evaporator to afford **1** as a white solid (5.0 g, 73% yield). M. P. 59−61 °C. IR (KBr film, cm^{-1}) 3282 (OH). ^1H NMR (400 MHz, $CDCl_3$, δ in ppm) 2.82 (br s, 1H), 5.92 (s, 1H), 6.83 (d, J = 3.6 Hz, 1H), 6.91 (t, 1H), 7.25 (m, 3H), 7.44 (d, J = 8.4 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 71.7, 121.9, 125.1, 125.8, 126.8, 128.0, 131.6, 142.06, 147.5. ES-MS: $C_{11}H_9SOBr$, calcd. av mass 269.2, obsd m/z 270.3 (M^+, 10%), 252.9 (M^+-17, 90%). Anal. calcd: C, 49.09; H, 3.37; S, 11.91. Found: C, 48.95; H, 3.04; S, 11.69.

2-[α-(*p*-3-Methyl-3-hydroxybut-1-yn-1-yl)phenyl-α-hydroxymethyl]thiophene (2). The 2-lithiothiophene which was prepared similarly as mentioned above was condensed with *p*-(3-methyl-3-hydroxybut-1yn-1-yl)benzaldehyde (5.7 g, 30.418 mmol) under the same experimental conditions mentioned for **1** and gave a crude compound. The crude compound was subjected to silica gel column chromatography and the desired mono-ol **2** was eluted with petroleum ether/ethyl acetate (80:20) to give a white solid in 35% yield (2.4 g). M. P. 78−80 °C. IR (KBr film, cm^{-1}) 3265, 3370 (OH). ^1H NMR (400 MHz, $CDCl_3$, δ in ppm) 1.57 (s, 6H), 2.81 (s, 1H) 5.94 (s, 1H), 6.81 (d, J = 3.6 Hz, 1H), 6.89 (t, 1 H), 7.21 (d, J = 4.8 Hz, 1H), 7.32 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 30.1, 31.6, 65.7, 76.3, 81.9, 94.4, 126.0, 126.2, 126.3, 126.6, 126.7, 127.0, 127.2, 141.1, 145.3, 145.4. ES-MS: $C_{16}H_{16}SO_2$, calcd av mass 272.4, obsd m/z 273.1 (M^+, 10%). Anal. calcd: C, 70.56; H, 5.92; S, 11.77. Found: C, 70.35; H, 5.57, S,11.45.

2-[α-(4-Hydroxyphenyl)-α-hydroxymethyl]thiophene (3). The condensation of 2-lithiothiophene with 4-hydroxybenzaldehyde (3.7 g, 30.418 mmol) under the same experimental conditions mentioned for **1** followed by silica gel column chromatography using petroleum ether/ethyl acetate (75:25) gave compound **3** as white solid in 11% yield (0.6 g). M. P. 134−136 °C. IR (KBr film, cm^{-1}) 3394, 3397 (OH). ^1H NMR (400 MHz, $CDCl_3$, δ in ppm) 1.67 (br s, 1H), 5.98 (br s, 1H), 6.01 (s, 1H), 6.87 (m, 4H), 7.29 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.3, 72.3, 124.8, 125.3, 126.4, 126.7, 129.3, 137.8, 140.4, 148.5. ES-MS: $C_{11}H_{10}SO_2$, calcd av mass 206.3, obsd m/z 206.8 (M^+, 10%), 189.0 (M^+-17, 90%). Anal. calcd: C, 64.05; H, 4.89; S, 15.55. Found: C, 63.78; H, 4.68; S, 15.28.

2-[α-(4-Octyloxyphenyl)-α-hydroxymethyl]thiophene (4). The condensation of 2-lithiothiophene with 4-octyloxy benzaldehyde (7.1 g, 30.418 mmol) under the same experimental conditions as mentioned for **1** followed by silica gel column chromatography using petroleum ether/ethyl aceate (90:10) gave compound **4** as light-pink solid (3.4 g, 42%). M. P. 45−47 °C. IR (KBr film, cm^{-1}) 3439 (OH). ^1H NMR (400 MHz, $CDCl_3$, δ in ppm) 0.88 (t, 3H), 1.34 (m, 8H), 1.44 (m, 2H), 1.77 (m, 2H), 2.44 (br s, 1H), 3.95 (m, 2H), 5.98 (s, 1H), 6.89 (m, 4H), 7.22 (m, 1H), 7.30 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.2, 22.7, 26.1, 29.3, 29.4, 31.9, 68.1, 72.2, 114.5, 124.7, 125.3, 126.6, 127.7, 135.3, 148.6, 159.01. ES-MS: $C_{19}H_{26}SO_2$, calcd av mass 318.5, obsd m/z 318.9 (M^+,10%), 301.2 (M^+-17, 50%). Anal. calcd. C, 71.66; H, 8.23; S, 10.07. Found: C, 71.14; H, 8.36; S, 10.04.

2-[α-(2-Thienyl)-α-hydroxymethyl]thiophene (5). The condensation of 2-lithiothiophene with 2-thienylaldehyde (3.4 g, 2.8 mL, 30.418 mmol) followed by column chromatography using petroleum ether/ethyl acetate (95:5) gave mono-ol **5** as a brown solid (2.8 g, 55% yield). M. P. 46−48 °C IR (KBr film, cm^{-1}) 3447 (OH). ^1H NMR (400 MHz, $CDCl_3$, δ in ppm) 2.71 (br s, 1H), 6.27 (s, 1H), 6.96 (m, 2H), 7.00 (m, 2H), 7.28 (d, J = 4.88 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 68.5, 72.5, 125.1, 125.5, 126.1, 126.2, 126.5, 126.7, 144.6, 147.2. ES-MS: $C_9H_8S_2O$, calcd av mass 196.3, obsd m/z 196.9 (M^+, 10%), 178.9 (M^+-17, 90%). Anal. calcd. C, 55.07; H, 4.11; S, 32.67. Found: C, 54.91; H, 3.96; S, 32.37.

2-[α-(2-6-Dimethoxyphenyl)-α-hydroxymethyl]thiophene (6). The 2-lithiothiophene was prepared by treating thiophene (0.5 g, 0.5 mL, 6.337 mmol) with *n*-BuLi (4.8 mL of ca. 15% solution in hexane) in the presence of TMEDA (1.2 mL, 7.604 mmol) in ether (20 mL). The condensation of 2-lithiothiophene with 2-6-dimethoxybenzlaldehyde (1.3 g, 7.604 mmol) followed by column chromatography on silica using petroleum ether/ethyl acetate (75:25) gave **6** as white solid in 76% yield (1.2 g). M. P. 73−75 °C. IR (KBr film, cm^{-1}) 3507 (OH). ^1H NMR (400 MHz, $CDCl_3$, δ in ppm) 3.79 (s, 6H), 4.66 (d, J = 10.9 Hz, 1H), 6.45 (d, J = 12.2 Hz, 1H), 6.59 (d, J = 8.5 Hz, 2H), 6.75 (d, J = 3.7 Hz, 1H), 6.86 (t, 1H), 7.15 (d, J = 4.8 Hz, 1H), 7.22 (t, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.9, 65.9, 104.6, 118.9, 123.6, 124.3, 126.5, 129.3, 149.5, 157.8. ES-MS: $C_{13}H_{14}SO_3$, calcd av mass 250.3, obsd m/z 250.1 (M^+, 10%), 233.1 (M^+-17, 90%). Anal. calcd: C, 62.38; H, 5.64; S, 12.81. Found: C, 62.07; H, 5.32; S, 12.60.

2-[α-(*p*-Tolyl)-α-hydroxymethyl]thiophene (7). The condensation of 2-lithiothiophene with *p*-tolylaldehyde (3.6 g, 3.5 mL, 30.418 mmol) followed by silica gel column chromatography using petroleum ether/ethyl acetate (95:5) afforded mono-ol **7** in 79% yield (4.1 g). M. P. 44−47 °C. IR (KBr film, cm^{-1}) 3381 (OH). ^1H NMR (400 MHz, $CDCl_3$, δ in ppm) 2.34 (s, 3H), 2.50 (s, 1H), 5.98 (s, 1H), 6.86 (m, 1H), 6.92 (m, 1H), 7.16 (d, J = 7.6 Hz, 2H), 7.23 (m, 1H), 7.27 (d, J = 7.6 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.3, 72.3, 124.8, 125.3, 126.4, 126.7, 129.3, 137.8, 140.4, 148.5. ES-MS: $C_{12}H_{12}SO$, calcd av mass, 204.3 obsd m/z 205.2 (M^+, 10%), 187.1 (M^+-17, 50%). Anal. calcd: C, 70.55; H, 5.92; S, 15.70. Found: C, 70.17; H, 5.74; S, 15.52.

2-[α-Phenyl-α-hydroxymethyl]thiophene (8). The condensation of 2-lithiothiophene with benzaldehyde (3.2 g, 3.2 mL, 30.418 mmol) followed by column chromatography on silica using petroleum ether/ethyl acetate (95:5) gave **8** as white solid (3.8 g, 77% yield). M. P. 53−55 °C. IR (KBr film, cm^{-1}) 3250 (OH). ^1H NMR (400 MHz, $CDCl_3$, δ in ppm) 2.45 (br s, 1H), 6.05 (s, 1H), 6.88 (m, 1H), 6.92 (m, 1H), 7.27 (m, 1H) 7.36 (m, 3H), 7.44 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ

72.3, 124.8, 125.4, 126.4, 126.8, 129.3, 137.8, 140.4, 148.5. ES-MS: $C_{11}H_{10}SO$, calcd av mass 190.3, obsd *m*/*z* 191.0 (M^+, 10%), 173.0 (M^+-17, 90%). Anal. calcd: C, 69.44; H, 5.30; S, 16.85. Found: C, 69.38; H, 5.19; S, 16.83.

2-[α-(*m*-Iodophenyl)-α-hydroxymethyl]thiophene (9). The 2-lithiothiophene was prepared by treating thiophene (0.6 g, 0.6 mL, 7.609 mmol) with *n*-BuLi (5.7 mL of ca. 15% solution in hexane) in the presence of TMEDA (1.1 g, 1.4 mL, 9.131 mmol) in ether (20 mL). The 2-lithiothiophene was then condensed with *m*-iodobenzaldehyde (2.1 g, 9.131 mmol) and purified the resulted crude compound by column chromatography on silica using petroleum ether/ethyl acetate (90:10) gave compound **9** as white solid (1.4 g, 58% yield). M. P. 76−78 °C. IR (KBr film, cm^{-1}) 3386 (OH). ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm) 2.59 (br s, 1H), 5.95(s, 1H), 6.43 (m, 1H), 6.94 (m, 1H), 7.08 (t, 1H), 7.26 (m, 1H), 7.33 (m, 1H), 7.63 (m, 1H), 7.79 (m, 1H).^{13}C NMR (75 MHz, $CDCl_3$): δ 71.5, 94.5, 125.2, 125.6, 125.9, 126.8, 130.3, 135.3, 137.0, 145.3, 147.3. ES-MS: $C_{11}H_9SOI$, calcd av mass 316.2, obsd *m*/*z* 316.0 (M^+, 10%), 299.0 (M^+-17, 90%). Anal. calcd: C, 41.79; H, 2.87; S, 10.14. Found: C, 41.85; H, 2.59; S, 9.99.

2-[α-(-*p*-3-Methyl-3-hydroxybut-1yn-1-yl)phenyl-α-hydroxymethyl]furan (10). The treatment of furan (2.8 g, 3.0 mL, 41.282 mmol) with *n*-BuLi (31 mL of ca. 15% solution in hexane), TMEDA (5.8 g, 7.5 mL, 49.538 mmol) in 50-mL dry ether under nitrogen atmosphere at 0 °C on ice bath for 1 h gave 2-lithiofuran. An ice-cold solution of *p*-(3-methyl-3-hydroxybut-1yn-1-yl)benzaldehyde (9.3 g, 49.538 mmol) in 50-mL dry THF was then added and the reaction mixture was allowed to stir for 15 min at 0 °C. The TLC analysis of crude reaction mixture showed two major spots corresponding to the unchanged aldehyde and the desired mono-ol. The crude compound was purified by silica gel column chromatography using petroleum ether/ethyl acetate (80:20) and obtained mono-ol **10** as white solid (2.4 g, 23% yield). M. P. 81−83 °C. IR (KBr film, cm^{-1}) 3372 (OH). ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm) 1.61 (s, 6H), 2.30 (br s, 1H), 5.80 (s, 1H), 6.08 (d, J = 2.4 Hz, 1H), 6.31 (d, J = 3.6 Hz, 1H), 7.37 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 31.5, 65.73, 69.8, 81.9, 94.1, 107.7, 110.4, 122.5, 126.6, 127.4, 131.6, 131.8, 140.9, 142.8, 155.7. ES-MS: $C_{16}H_{16}O_3$, calcd av mass 256.3, obsd *m*/*z* 257.2 (M^+,10%), 239.1 (M^+-17, 90%). Anal. calcd: C, 74.98; H, 6.29. Found: C, 74.52; H, 6.15.

2-[α-(*p*-Iodophenyl)-α-hydroxymethyl]furan (11). The 2-lithiofuran was prepared by treating furan (1.8 g, 2 mL, 27.521 mmol) with *n*-BuLi (20.6 mL of ca. 15% solution in hexane) in the presence of TMEDA (3.8 g, 4.9 mL, 33.025 mmol) in ether (40 mL). The condensation of 2-lithiothiophene with *p*-iodobenzaldehyde (7.6 g, 33.025 mmol) followed by column chromatography on silica using petroleum ether/ethyl acetate (95:5) afforded furan mono-ol **11** as white solid (4.9 g, 59% yield). M. P. 134−136 °C. IR (KBr film, cm^{-1}) 3381 (OH). ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm) 2.56 (br s, 1H), 5.71 (s, 1H), 6.08 (m, 1H), 6.29 (m, 1H), 7.14 (m, 2H), 7.36 (m, 1H), 7.66 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 69.5, 93.7, 107.7, 110.3, 128.5, 128.8, 137.5, 137.6, 140.4, 142.8, 155.3. ES-MS $C_{11}H_9O_2I$, calcd av mass 300.1, obsd *m*/*z* 300.8 (M^+, 10%). Anal. calcd: C, 44.03; H, 3.02. Found: C, 43.87; H, 2.93.

2-[α-(4-Tolyl)-α-hydroxymethyl]furan (12). The 2-lithiofuran (1.8 g, 2 mL, 27.521 mmol) which was prepared similarly as above was condensed with *p*-tolyl aldehyde (4.0 g, 3.9 mL, 33.025 mmol) and purification by column chromatography using petroleum ether/ethyl acetate (99:1) gave mono-ol **12** as gray low-melting solid in 56% yield (2.9 g). IR (neat, cm^{-1}) 3341 (OH). ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm) 2.35 (s, 3H), 2.39 (br s, 1H), 5.76 (s, 1H), 6.11 (d, J = 3.6 Hz, 1H), 6.29 (d, J = 3.6 Hz, 1H), 7.17 (d, J = 7.6 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 7.37 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.3, 70.1, 107.4, 110.2, 110.3, 126.7, 127.6, 129.3. 137.9, 138.1, 142.6, 142.8, 156.3. ES-MS: $C_{12}H_{12}O_2$, calcd av mass 188.2, obsd *m*/*z* 189.2 (M^+, 10%), 171.1 (M^+-17, 90%). Anal. calcd: C, 76.57; H, 6.43. Found: C, 76.52; H, 6.46.

Monofunctionalized Porphyrin Building Blocks. 5-(*p*-Bromophenyl)-10,15,20-tri(*p*-tolyl)-21-monothiaporphyrin (13). The samples of thiophene mono-ol **1** (0.8 g, 2.972 mmol), *p*-tolylaldehyde (0.4 g, 0.35 mL, 2.972 mmol), and pyrrole (0.3 g, 0.3 mL, 4.458 mmol) were dissolved in 80 mL propionic acid and gently refluxed for 3 h. The progress of the reaction was checked by absorption spectroscopy which showed bands mainly characteristic of normal porphyrin (N_4 core) with slight indication of the desired N_3S porphyrin. The propionic acid was removed under vacuum and the resultant black solid was washed several times with warm water and dried in an oven at 100 °C. The crude black solid was passed through silica gel column using dichloromethane as solvent to remove nonporphyrinic impurities. The TLC analysis of the compound after the filtration column showed clearly two spots corresponding to 5, 10, 15, 20-tetratolyl porphyrin (N_4) and the desired N_3S porphyrin. The crude mixture of two compounds was subjected to second silica gel column chromatography and eluted with petroleum ether. The N_4 porphyrin was collected as first band with petroleum ether/dichloromethane (90:10) and the desired porphyrin **13** was then collected using petroleum ether/dichloromethane (80:20) mixture. The solvent was removed in a rotary evaporator to afford **13** as purple solid in 3% yield (20 mg). M. P. > 300 ° C. IR (neat, cm^{-1}) 3335 (NH), 2920, 2854, 801. ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm) −2.70 (s, 1H), 2.69 (s, 9H), 7.54 (d, J = 7.7 Hz, 4H), 7.62 (d, J = 7.7 Hz, 2H), 7.94 (m, 2H), 8.09 (m, 8H), 8.62 (m, 3H), 8.69 (d, J = 4.8 Hz, 1H), 8.95 (d, J = 4.8 Hz, 2H), 9.67 (d, J = 5.5 Hz, 1H), 9.76 (d, J = 5.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.5, 29.7, 126.9, 127.4, 128.3, 128.5, 128.9, 130.7, 131.8, 132.5, 132.8, 133.1, 133.6, 134.2, 134.4, 134.6, 135.5, 135.8, 137.6, 138.0, 139.1, 139.5, 141.8, 146.9, 148.3, 154.6, 156.8, 157.6. ES-MS: $C_{47}H_{34}N_3SBr$, Calcd av mass, 752.7 obsd *m*/*z* 752.7 (M^+). Anal. calcd: C, 74.99; H, 4.55; N, 5.58; S, 4.26. Found: C, 74.85; H, 4.47; N, 5.52; S, 4.22. UV−vis λ_{max}/nm (ϵ/mol^{-1} dm^3 cm^{-1}): 431 (335717), 487 (sh), 515 (24699), 550 (8644), 618 (3172), 679 (4866). Fluorescence: (λ_{ex} = 515 nm, in toluene) λ_{em}/nm 684, 747 (sh), ϕ = 0.0208.

5-(*p*-3-Methyl-3-hydroxybut-1-yn-1-yl)phenyl-10,15,20-tris(*p*-octyloxyphe nyl)- 21-monothiaporphyrin (14). The thiophene mono-ol **2** (3.5 g, 12.849 mmol), *p*-octyloxybenzaldehyde (3.0 g, 12.849 mmol), and pyrrole (1.3 g, 1.4 mL, 19.274 mmol) in 300 mL propionic acid were refluxed for 3 h. The propionic acid was removed under vacuum and the black solid was washed several times with warm water. The crude compound was subjected to silica gel column chromatography two times. After removing the nonporphyrinic impurities on the first silica gel column, the mixture of two porphyrins were separated on the second silica gel column and the desired N_3S porphyrin **14** was collected as second band using dichloromethane/methanol (99:1) mixture. The solvent was removed in rotary evaporator and the compound **14** collected as soft brown waxy solid in 6% yield (440 mg). IR (neat, cm^{-1}) 3335 (NH), 2927, 2855, 1242, 1176, 808. ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm) −2.64 (s, 1H), 0.93 (m, 9H), 1.09−1.60 (m, 30H), 1.75 (s, 6H), 1.95 (m, 6H), 4.19 (m, 6H), 7.22 (m, 4H), 7.29 (d, J = 8.4 Hz, 2H), 7.86 (d, J = 8 Hz, 2H), 8.06 (m, 4H), 8.12 (d, J = 8 Hz, 2H), 8.19 (d, J = 7.6 Hz, 2H), 8.62 (s, 3H), 8.69 (d, J = 4.4 Hz, 1H), 8.95 (s, 2H), 9.68 (d, J = 5.2 Hz, 1H), 9.76 (d, J = 5.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.3, 22.9, 26.4, 29.5, 29.9, 31.8, 32.1, 65.9, 68.5, 82.3, 95.2, 112.8, 113.8, 122.4, 123.9, 124.2, 129.2, 130.0, 130.9, 131.7, 132.8, 133.8, 133.9, 134.3, 134.8, 135.7, 141.3, 147.2. ES-MS: $C_{73}H_{83}N_3SO_4$, calcd av mass 1098.5, obsd *m*/*z* 1098.7 (M^+). Anal. calcd: C, 79.81; H, 7.62; N, 3.83; S, 2.92. Found: C, 79.75; H, 7.59; N, 3.81; S, 2.90. UV−vis λ_{max}/nm (ϵ/mol^{-1} dm^3 cm^{-1}): 434 (37049), 517 (4232), 552 (2689), 614(1152), 678 (1075). Fluorescence: (λ_{ex} = 515 nm, in toluene) λ_{em}/nm 680, 746 (sh), ϕ = 0.0287.

5-(*p*-Ethynylphenyl)-10,15,20-tris (*p*-octyloxyphenyl)-21-monothiaporphyrin (15). Compound **14** (0.4 g, 0.364 mmol) was dissolved in dry benzene (50 mL) taken in one-necked round-bottom flask fitted with Dean and Stark ap-

paratus and reflux condenser. The potassium hydroxide (0.03 g, 0.546 mmol) dissolved in methanol (25 mL) was added to it, and the reaction mixture was stirred for 20 h at 80 °C. The solvent mixture collected in Dean and Stark apparatus was removed at regular intervals and the progress of reaction was followed by TLC analysis. After completion of the reaction as judged by TLC, the compound was purified by silica gel column chromatography using petroleum ether/dichloromethane (30:70) followed by recrystallization from acetone that afforded **15** as purple solid in 18% yield (70 mg). M. P. > 300 ° C. IR (neat, cm^{-1}) 3335 (NH), 2927, 2855, 1242, 1183, 808. ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm) −2.64 (s, 1H), 0.94 (m, 9H), 1.25−1.66 (m, 30H), 1.97 (m, 6H), 3.31 (s, 1H), 4.22 (m, 6H), 7.24 (m, 4H), 7.32 (d, J = 5.1 Hz, 2H), 7.93 (d, J = 8.1 Hz, 2H), 8.07 (m, 4H), 8.13 (d, J = 8.4 Hz, 2H), 8.21 (d, J = 8.4 Hz, 2H), 8.62 (d, J = 5.7 Hz, 3H), 8.69 (d, J = 4.5 Hz, 1H), 8.95 (s, 2H), 9.67 (d, J = 5.1 Hz, 1H), 9.76 (d, J = 5.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.3, 22.9, 26.4, 29.5, 29.6, 30.0, 68.5, 112.8, 113.8, 121.8, 123.9, 124.2, 128.9, 129.1, 129.8, 131.4, 131.7, 132.7, 133.2, 133.3, 133.8, 134.3, 134.7, 135.5, 135.6, 135.8, 139.4, 139.6, 141.8, 146.9, 147.2, 154.7, 154.9, 156.9, 157.9, 159.2, 159.3. ES-MS: $C_{70}H_{77}N_3SO_3$, calcd av mass 1040.5, obsd m/z 1040.7 (M^+). Anal. calcd: C, 80.81; H, 7.46; N, 4.04; S, 3.08. Found: C, 80.69; H, 7.38; N, 4.03; S, 3.05. UV−vis λ_{max}/nm (ϵ/mol^{-1} dm^3 cm^{-1}): 434 (196826), 518 (12227), 554 (5996), 621(1615), 682 (3323). Fluorescence: (λ_{ex} = 515 nm, in toluene) λ_{em}/nm 690, 758 (sh), ϕ = 0.0184.

5-(*p*-Hydroxyphenyl)-10,15,20-tri (*p*-tolyl)-21-monothiaporphyrin (16). Condensation of thiophene mono-ol **3** (0.4 g, 1.939 mmol), *p*-tolylaldehyde (0.2 g, 0.2 mL, 1.939 mmol), and pyrrole (0.2 g, 0.2 mL, 2.908 mmol) in 50 mL propionic acid at refluxing temperature followed by standard workup gave a crude compound. Column chromatography of the crude compound on silica gel using dichloromethane/methanol (98:2) mixture gave compound **16** as purple solid in 4% yield (20 mg). M. P. > 300 °C. IR (neat, cm^{-1}) 3328 (NH), 2966, 2921, 2855, 1268, 1025, 802. ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm) −2.68 (s, 1H), 2.69 (s, 9H), 3.05 (br s, 1H), 7.54 (d, J = 7.5 Hz, 6H), 7.61 (d, J = 7.5 Hz, 2H), 8.09 (m, 8H), 8.60 (d, J = 4.5 Hz, 2H), 8.64 (d, J = 4.5 Hz, 2H), 8.93 (s, 2H), 9.75 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.7, 29.5, 29.9, 115.5, 115.6, 116.2, 123.9, 126.6, 127.0, 127.6, 128.2, 128.6, 129.0, 129.3, 130.8, 131.5, 131.9, 132.1, 132.9, 133.2, 133.7, 134.5, 134.7, 135.8, 137.0, 137.8, 139.7. ES-MS: $C_{47}H_{35}N_3SO$, calcd av mass 689.9, obsd m/z 690.5 (M^+). Anal. calcd: C, 81.83; H, 5.11; N, 6.09; S, 4.65. Found: C, 81.75; H, 5.06; N, 6.01; S, 4.59. UV−vis λ_{max}/nm (ϵ/mol^{-1} dm^3 cm^{-1}): 431 (111806), 515 (7747), 551 (3145), 619 (1118), 677 (2791). Fluorescence: (λ_{ex} = 515 nm, in toluene) λ_{em}/nm 682, 751 (sh), ϕ = 0.0227.

5-(Octyloxyphenyl)-10,15,20-tri(phenyl)- 21-monothiaporphyrin (17). A solution of thiophene mono-ol **4** (0.4 g, 1.256 mmol), benzaldehyde (0.1 g, 0.1 mL, 1.256 mmol), and pyrrole (0.1 g, 0.1 mL, 1.884 mmol) in 50 mL propionic acid was refluxed for 3 h. After standard workup, the crude compound was purified by silica gel column chromatography using petroleum ether/dichloromethane (80:20) and afforded the desired N_3S porphyrin **17** as brown-violet solid in 4% yield (40 mg). M. P. > 300 °C. IR (neat, cm^{-1}) 3335 (NH), 3059, 2933, 2861, 1249, 1177, 816, 709. ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm) −2.68 (s, 1H), 0.93 (m, 3H), 1.25−1.48 (m, 8H), 1.61 (m, 2H), 1.96 (m, 2H), 4.22 (m, 2H), 7.32 (d, J = 8.7 Hz, 2H), 7.75 (m, 9H), 8.18 (m, 6H), 8.25 (m, 2H), 8.59 (d, J = 5.5 Hz, 2H), 8.69 (d d, 2H), 8.92 (s, 2H), 9.74 (d, J = 5.2 Hz, 1H), 9.79 (d, J = 5.2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.2, 22.8, 26.3, 29.4, 29.6, 29.8, 31.9, 68.4, 113.7, 123.6, 123.8, 126.7, 127.6, 127.9, 128.9, 131.6, 133.2, 134.3, 134.5, 135.5, 138.9, 139.1, 141.1, 142.5, 147.3, 147.4, 154.3, 154.5, 157.3, 157.7, 159.3. ES-MS: $C_{52}H_{45}N_3SO$, calcd av mass 760.0, obsd m/z 760.2 (M^+). Anal. calcd: C, 82.18; H, 5.97; N, 5.53; S, 4.22. Found: C, 81.97; H, 5.92; N, 5.50; S, 4.18. UV−vis λ_{max}/nm (ϵ/mol^{-1} dm^3 cm^{-1}): 434 (196826), 517 (12227), 554 (5996), 621 (1615), 682 (3323). Fluorescence: (λ_{ex} = 515 nm, in toluene) λ_{em}/nm 683, 752 (sh), ϕ = 0.0154.

5-(2-Thienyl)-10,15,20-tri(*p*-tolyl)-21-monothiaporphyrin (18). Condensation of the thiophene mono-ol **5** (0.4 g, 2.038 mmol), *p*-tolylaldehyde (0.2 g, 0.2 mL, 2.038 mmol), and pyrrole (0.2 g, 0.2 mL, 3.057 mmol) in 50 mL propionic acid at refluxing temperature for 3 h. Column chromatography of the crude compound on silica gel using petroleum ether/dichloromethane (80:20) gave compound **18** in 2% yield (12 mg). M. P. > 300 ° C. IR (neat, cm^{-1}) 3335 (NH), 2934, 2861, 801, 702. ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm) −2.59 (s, 1H), 2.70 (s, 9H), 7.55 (m, 5H), 7.62 (d, J = 2.4 Hz, 2H), 7.90 (m, 1H), 7.94 (m, 1H), 8.07 (d, J = 17.5 Hz, 4H), 8.13 (d, J = 7.9 Hz, 2H), 8.61 (m, 2H), 8.67 (d, J = 4.7 Hz, 1H), 8.87 (d, J = 4.7 Hz, 1H), 8.92 (m, 2H), 9.76 (d, J = 5.2 Hz, 1H), 9.96 (d, J = 5.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.7, 122.6, 124.4, 124.7, 127.2, 127.6, 128.5, 128.7, 129.0, 129.2, 132.2, 132.9, 133.2, 134.3, 134.4, 134.6, 134.8, 135.7, 135.8, 137.8, 138.2, 139.3, 139.5, 139.7,141.9, 147.2, 148.5, 154.7, 154.8, 157.8, 158.1. ES-MS: $C_{45}H_{33}N_3S_2$, calcd av mass 680.1, obsd m/z 681.1 (M^+). Anal. calcd: C, 79.49; H, 4.89; N, 6.18; S, 9.43. Found: C, 79.12; H, 4.68; N, 6.07; S, 9.32. UV−vis λ_{max}/nm (ϵ/mol^{-1} dm^3 cm^{-1}): 433 (344346), 517 (24169), 553 (9685), 620 (3349), 683 (4571). Fluorescence: (λ_{ex} = 515 nm, in toluene) λ_{em}/nm 693, 756 (sh), ϕ = 0.0126.

5-(2,6-Dimethoxyphenyl)-10,15,20-tri(*p*-tolyl)- 21-monothiaporphyrin (19). Compound **6** (0.4 g, 1.598 mmol), *p*-tolylaldehyde (0.2 g, 0.2 mL, 1.598 mmol), and pyrrole (0.2 g, 0.2 mL, 2.397 mmol) were dissolved in 50 mL propionic acid and refluxed for 3 h. Column chromatography of the crude compound on silica gel in petroleum ether/dichloromethane (60:40) mixture gave compound **19** in 2% yield (12 mg). M. P. > 300 ° C. IR (neat, cm^{-1}) 3335 (NH), 3026, 2927, 2835, 1591, 1466, 1439, 1256, 1117, 802, 716. ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm) −2.52 (s, 1H), 2.64 (s, 9H), 3.47 (s, 6H), 6.94 (d, J = 8.4 Hz, 2H), 7.54 (m, 7H), 8.08 (m, 6H), 8.59 (m, 4H), 8.89 (s, 2H), 9.51 (d, J = 5.2 Hz, 1H), 9.68 (d, J = 5.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.6, 29.9, 56.2, 104.6, 118.6, 123.5, 123.9, 124.2, 127.4, 128.4, 128.5, 128.8, 130.6, 131.2, 132.7, 132.7, 133.9, 134.3, 134.5, 135.3, 135.6, 137.6, 138.4, 138.8, 139.3, 139.8, 139.9, 147.2, 147.9, 153.9, 154.6, 158.6, 160.1. ES-MS: $C_{49}H_{39}N_3SO_2$, calcd av mass 733.9, obsd m/z 734.4 (M^+). Anal. calcd: C, 80.19; H, 5.36; N, 5.73; S, 4.37. Found: C, 80.10; H, 5.27; N, 5.69; S, 4.29. UV−vis λ_{max}/nm (ϵ/mol^{-1} dm^3 cm^{-1}): 430 (107607), 513 (8591), 547 (2015), 618 (1058), 679 (1419). Fluorescence: (λ_{ex} = 515 nm, in toluene) λ_{em}/nm 683, 752 (sh), ϕ = 0.0158.

5-(*m*-Iodophenyl)-10,15,20-tritolyl-21-monothiaporphyrin (20). A solution of thiophene mono-ol **9** (0.5 g, 1.581 mmol), *p*-tolylaldehyde (0.2 g, 0.2 mL, 1.581 mmol), and pyrrole (0.2 g, 0.2 mL, 2.372 mmol) were dissolved in 50 mL propionic acid and refluxed for 3 h. Column chromatography of the crude compound on silica gel using petroleum ether/dichloromethane (80:20) gave compound **20** as violet solid in 2% yield (12 mg). M. P. > 300 ° C. IR (neat, cm^{-1}) 3328 (NH), 3033, 2921, 2855, 795, 729. ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm) −2.69 (s, 1H), 2.68 (s, 9H), 7.50 (m, 6H), 7.59 (m, 2H), 8.09 (m, 8H), 8.64 (m, 3H), 8.69 (d, J = 4.0 Hz, 1H), 8.95 (s, 2H), 9.68 (d, J = 5.2 Hz, 1H), 9.77 (d, J = 5.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.5, 93.6, 124.1, 124.4, 127.4, 128.4, 128.8, 128.9, 129.1, 131.9, 132.6, 133.1, 133.4, 133.7, 134.2, 134.4, 134.7, 135.6, 135.8, 136.9, 137.2, 137.6, 138.1, 139.2, 139.3, 139.5, 139.6, 142.6, 143.3, 146.9, 147.1, 154.6, 154.7, 156.9, 157.7. ES-MS: $C_{47}H_{34}N_3$-SI, calcd av mass 799.8, obsd m/z 800.0 (M^+). Anal. calcd: C, 70.58; H, 4.27; N, 5.25; S, 4.01. Found: C, 70.27; H, 4.14; N, 5.20; S, 3.99. UV−vis λ_{max}/nm (ϵ/mol^{-1} dm^3 cm^{-1}): 431 (345675), 549 (6665), 614 (2265), 618 (2751), 679 (4609). Fluorescence: (λ_{ex} = 515 nm, in toluene) λ_{em}/nm 683, 750 (sh), ϕ = 0.0155.

5-(3-methyl-3-hydroxybut-1-yn-1yl)phenyl-10,15,20-Tris (*p*-octyloxyphenyl)- 21-monooxaporphyrin (21). The furan mono-ol **10** (1.5 g, 5.853 mmol), *p*-octyloxybenzaldehyde (1.5 g, 5.853 mmol) and pyrrole (0.6 g, 0.6 mL, 8.780 mmol)

were dissolved in 120 mL propionic acid and refluxed for 3 h. The progress of the reaction was monitored with absorption spectroscopy. After standard work up, the crude reaction mixture was subjected to two clearly showed two spots corresponds to the regular *meso*-tetrakis-(4-octyloxylphenyl) N_4 porphyrin and the desired N_3O porphyrin **21**. The mixture of two porphyrins was separated by column chromatography on silica and the N_3O porphyrin **21** was collected as second band using dichloromethane/ methanol (85:15) mixture. The solvent was removed on rotary evaporator and afforded compound **21** as green solid in 4% yield (120 mg). M. P. >300 ° C. IR (neat, cm^{-1}) 3408 (NH), 2927, 2861, 1611, 1256, 1177, 815, 742. ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm) 0.92 (m, 9H), 1.11−1.68 (m, 30H), 1.77 (s, 6H), 1.99 (m, 6H), 4.25 (t, 6H), 7.83 (t, 4H), 8.12 (m, 12H), 8.49 (t, 1H), 8.58 (d, J = 4.8 Hz, 1H), 8.66 (t, 2H), 8.89 (s, 2H), 9.13 (d, J = 5.1 Hz, 1H), 9.23 (d, J = 4.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.2, 22.8, 26.3, 27.3, 29.4, 29.4, 29.5, 31.5, 31.9, 65.6, 65.8, 68.6, 113.7, 114.2, 128.9, 129.5, 131.2, 131.9, 132.8, 134.2, 135.5, 138.2, 160.4, 160.5, 173.9, 174.2. ES-MS: $C_{73}H_{83}N_3O_5$, calcd. av. mass 1082.5, obsd. m/z 1082.9 (M^+). Anal. Calcd.: C, 81.00; H, 7.73; N, 3.88. Found: C, 79.83; H, 7.59; N, 3.55. UV−vis λ_{max}/nm (ϵ/mol^{-1} dm^3 cm^{-1}): 427 (101856), 512 (11939), 545 (6748), 615 (3599), 678 (3611). Fluorescence: (λ_{ex} = 515 nm, in toluene) λ_{em}/nm 684, 745 (sh), ϕ = 0.0932.

5-(*p*-Ethynylphenyl)-10,15,20-tris (*p*-octyloxyphenyl)-21-monooxaporphyrin (22). Compound **21** (0.1 g, 0.092 mmol) in dry benzene (40 mL) was treated with potassium hydroxide (0.019 g, 0.139 mmol) in 15 mL methanol for 20 h at 80° C. The completion of the reaction was judged by TLC. The crude porphyrin **22** was purified by silica gel column chromatography using dichloromethane/methanol (93:7) mixture as green solid (43 mg, 41%). M. P. > 300 °C. IR (neat, cm^{-1}) 3342 (NH), 2934, 2861, 1604, 1256, 1183, 815. ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm) 0.94 (m, 9H), 1.27−1.62 (m, 24H), 1.64 (t, 6H), 2.01 (t, 6H), 3.39 (s, 1H), 4.29 (t, 6H), 7.39 (br s, 6H), 7.97 (m, 2H), 8.29 (m, 8H), 8.69 (m, 4H), 8.83 (d, J = 7.2 Hz, 2H), 9.36 (br s, 1H), 9.44 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.3, 22.9, 23.7, 26.4, 29.5, 29.6, 29.6, 29.8, 32.0, 68.6, 113.7, 114.2, 128.9, 130.0, 131.1, 131.8, 132.1, 133.2, 135.6, 137.2, 138.4, 142.9, 160.3, 160.5. ES-MS: $C_{70}H_{77}N_3O_4$, calcd av mass 1023.5, obsd m/z 1024.3 (M^+). Anal. calcd: C, 82.07; H, 7.58; N, 4.10. Found: C, 81.90; H, 7.49; N, 4.02. UV−vis λ_{max}/nm (ϵ/mol^{-1} dm^3 cm^{-1}): 426 (174996), 512 (13267), 546 (5293), 617 (2376), 678 (2844). Fluorescence: (λ_{ex} = 515 nm, in toluene) λ_{em}/nm 684, 750 (sh), ϕ = 0.1221.

5-(*p*-Iodophenyl)-10,15,20-tri(*p*-tolyl)-21-monooxaporphyrin (23). The samples of furan mono-ol **11** (4.8 g, 15.995 mmol), *p*-tolylaldehyde (1.9 g, 1.9 mL, 15.995 mmol), and pyrrole (1.6 g, 1.7 mL, 23.993 mmol) were dissolved in 360 mL propionic acid and refluxed for 3 h. Column chromatography of crude compound on silica gel in dichloromethane/ methanol (92:8) gave compound **23** in 2% yield (82 mg). M. P. > 300 °C. IR (neat, cm^{-1}) 3427 (NH), 2921, 2848, 802, 729. ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm) −1.55 (s, 1H), 2.69 (s, 9H), 7.54 (m, 6H), 7.85 (m, 2H), 8.10 (m, 8H), 8.49 (d, J = 4.2 Hz, 2H), 8.55 (d, J = 4.5 Hz, 1H), 8.63 (t, 2H), 8.89 (s, 1H), 9.14 (d, J = 4.8 Hz, 1H), 9.19 (d, J = 4.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.2, 21.6, 22.6, 29.5, 29.8, 32.0, 94.6, 127.6, 127.8, 128.4, 134.4, 134.7, 236.1, 136.2, 137.4, 137.7, 138.0, 138.7, 139.0, 154.2, 154.8. ES-MS: $C_{47}H_{34}N_3OI$. calcd av mass 783.7, obsd m/z 784.4 (M^+). Anal. calcd: C, 72.03; H, 4.37; N, 5.36. Found: C, 71.92; H, 4.29; N, 5.29. UV−vis λ_{max}/nm (ϵ/mol^{-1} dm^3 cm^{-1}): 423 (281708), 509 (23004), 540 (9297), 614 (4347), 673 (4401). Fluorescence: (λ_{ex} = 515 nm, in toluene) λ_{em}/nm 678, 746 (sh), ϕ = 0.0171.

Trifunctionalized Porphyrin Building Blocks. 5,10,-15-Tris(2-thienyl)-20-(*p*-tolyl)-21-monothiaporphyrin (24). A solution of thiophene mono-ol **7** (0.4 g, 1.958 mmol), 2-thienylaldehyde (0.2 g, 0.2 mL, 1.958 mmol), and pyrrole (0.2 g, 0.2 mL, 2.937 mmol) in 50 mL propionic acid was refluxed for 3 h. Column chromatography of crude compound on silica gel using petroleum ether/dichloromethane (60:40) mixture gave compound **24** as brown-violet solid in 3% yield (20 mg). M. P. > 300 °C. IR (neat, cm^{-1}) 3335 (NH), 3105, 2927, 2855, 802, 709. ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm) −2.68 (s, 1H), 2.71 (s, 3H), 7.49 (m, 2H), 7.57 (m, 1H), 7.63 (d, J = 7.7 Hz, 2H), 7.85 (d, J = 5.2 Hz, 2H), 7.94 (m, 4H), 8.13 (d, J = 7.9 Hz, 2H), 8.69 (d, J = 4.7 Hz, 1H), 8.77 (m, 2H), 8.89 (d, J = 4.4 Hz, 1H), 9.16 (s, 2H), 9.78 (d, J = 5.2 Hz, 1H), 9.98 (d, J = 5.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.5, 29.7, 114.8, 115.1, 123.5, 125.9, 127.1, 127.9, 128.4, 128.8, 129.0, 129.1, 133.0, 133.4, 133.6, 134.0, 134.2, 134.4, 134.9, 135.2, 135.3, 137.7, 137.8, 139.9,140.1, 141.4, 143.1, 147.5, 148.7, 155.6, 155.8, 157.6, 157.9. ES-MS: $C_{39}H_{25}N_3S_4$, calcd av mass 663.9, obsd m/z 664.1 (M^+). Anal. calcd: C, 70.56; H, 3.80; N, 6.33; S, 19.32. Found: C, 70.45; H, 3.68; N, 6.30; S, 19.21. UV−vis λ_{max}/nm (ϵ/mol^{-1} dm^3 cm^{-1}): 437 (239977), 521 (17583), 557 (7479), 624(2679), 687 (3244). Fluorescence: (λ_{ex} = 515 nm, in toluene) λ_{em}/nm 699, 765 (sh), ϕ = 0.0075.

5,10,15-Tris -(4-pyridyl)-20-phenyl-21-monothiaporphyrin (25). The samples of thiophene mono-ol **8** (0.4 g, 2.102 mmol), pyridyl-4-carboxaldehyde (0.2 g, 0.2 mL, 2.102 mmol), and pyrrole (0.2 g, 0.2 mL, 3.153 mmol) were dissolved in 50 mL propionic acid and refluxed for 3 h. Column chromatography of the crude compound on silica gel using dichloromethane/methanol (94:6) mixture gave compound **25** as violet solid in 7% yield (45 mg). ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm) −2.84 (s, 1H), 7.84 (m, 3H), 8.16 (m, 4H), 8.20 (m, 2H), 8.24 (m, 2H), 8.57 (d, J = 4.7 Hz, 1H), 8.61 (d, J = 4.7 Hz, 1H), 8.70 (d, J = 4.6 Hz, 1H), 8.76 (d, J = 4.4 Hz, 1H), 8.94 (d, J = 1.9 Hz, 2H), 9.05 (m, 4H), 9.09 (m, 2H), 9.73 (d, J = 5.5 Hz, 1H), 9.85 (d, J = 5.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.5, 29.7, 126.9, 127.4, 128.3, 128.5, 128.9, 130.7, 131.7, 132.6, 132.8, 133.1, 133.6, 134.2, 134.4, 134.6, 135.5, 135.7, 137.6, 138.0, 139.1, 139.5, 141.8, 146.9, 148.3, 154.6, 156.8, 157.6. ES-MS: $C_{41}H_{26}N_6S$, Calcd av mass, 634.7, obsd m/z 635.1 (M^+). Anal. calcd: C, 77.58; H, 4.13; N, 13.24; S, 5.05. Found: C, 77.26; H, 4.04; N, 13.02; S, 4.92. UV−vis λ_{max}/nm (ϵ/mol^{-1} dm^3 cm^{-1}): 428 (155601), 512 (17086), 545 (6339), 616 (3626), 676 (4387). Fluorescence: (λ_{ex} = 515 nm, in toluene) λ_{em}/nm 680, ϕ = 0.0134.

5,10,15-Tris-(3-pyridyl)-20-phenyl-21-monothiaporphyrin (26). Compound **8** (0.7 g, 3.678 mmol), pyridyl-3-carboxaldehyde (0.4 g, 0.3 mL, 3.678 mmol), and pyrrole (0.4 g, 0.4 mL, 5.517 mmol) were dissolved in 70 mL propionic acid and refluxed for 3 h. The crude compound was purified by silica gel column chromatography and the desired compound **26** was collected in dichloromethane/methanol (94:6) mixture in 6% yield as violet solid (68 mg). M. P. > 300 °C. IR (neat, cm^{-1}) 3421 (NH), 2934, 2861, 802, 696. ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm) −2.74 (s, 1H), 7.79 (m. 7H), 8.24 (br s, 2H), 8.53 (m, 3H), 8.60 (d, J = 4.4 Hz, 1H), 8.69 (d, J = 4.4 Hz, 1H), 8.76 (d, J = 4.4 Hz, 1H), 8.94 (s, 2H), 9.04 (br s, 3H), 9.44 (m, 3H), 9.72 (d, J = 5.2 Hz, 1H), 9.83 (d, J = 5.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 29.7, 119.6, 119.8, 121.9, 122.8, 127.5, 127.7, 128.2, 128.8, 128.9, 132.8, 133.3, 134.1, 134.2, 135.2, 135.5, 135.6, 136.6, 138.0, 138.7, 138.9, 140.4, 140.8, 147.6, 147.8, 149.3, 153.4, 154.5, 157.2, 157.9. ES-MS: $C_{41}H_{26}N_6S$, calcd av mass 634.7, obsd m/z 635.1 (M^+). Anal. calcd: C, 77.58; H, 4.13; N, 13.24; S, 5.05. Found: C, 76.89; H, 4.02; N, 13.05; S, 4.94. UV−vis λ_{max}/nm (ϵ/mol^{-1} dm^3 cm^{-1}): 430 (285065), 515 (23886), 548 (7299), 619 (3696), 679 (4689). Fluorescence: (λ_{ex} = 515 nm, in toluene) λ_{em}/nm 683, 753 (sh), ϕ = 0.0139.

5,10,15-Tris (*p*-iodophenyl)-20-(octyloxyphenyl)-21-monothiaporphyrin (27). Samples of thiophene mono-ol **4** (1.0 g, 3.140 mmol), *p*-iodobenzaldehyde (0.7 g, 3.140 mmol), and pyrrole (0.3 g, 0.3 mL, 4.710 mmol) were dissolved in 90 mL propionic acid and refluxed for 3 h. Column chromatography of crude compound on silica gel in petroleum ether/ dichloromethane (80:20) mixture gave compound **27** as purple solid in 3% yield (60 mg). M. P. > 300 °C. IR (neat, cm^{-1}) 3332 (NH), 2934, 2861, 1485, 1249, 795, 703. ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm) −2.78 (s, 1H), 0.94 (m, 3H), 1.25−1.60 (m,

10H), 1.98 (m, 2H), 4.23 (m, 2H), 7.33 (d, J = 7.6 Hz, 2H), 7.92 (m, 6H), 8.11 (m, 8H), 8.62 (t, 2H), 8.67 (d, J = 4.4 Hz, 1H), 8.72 (d, J = 4.4 Hz, 1H,), 8.92 (s, 2H), 9.70 (d, J = 5.2 Hz, 1H), 9.79 (d, J = 4.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1, 53.5, 70.4, 71.9, 121.4, 124.0, 124.7, 126.3, 126.3, 126.5, 129.1, 129.4, 137.4, 140.3, 140.4, 146.2, 146.3, 148.6, 149.6, 149.8, 153.2. ES-MS: $C_{52}H_{42}N_3SOI_3$, calcd av mass 1137.7, obsd m/z 1137.9 (M^+). Anal. calcd: C, 54.90; H, 3.72; N, 3.69; S, 2.82. Found: C, 53.88; H, 3.54; N, 3.41; S, 2.54. UV−vis λ_{max}/nm (ϵ/mol^{-1} dm^3 cm^{-1}): 433 (384448), 516 (26574), 551 (11272), 620 (3850), 679 (8829). Fluorescence: (λ_{ex} = 515 nm, in toluene) λ_{em}/nm 682, 745 nm (sh), ϕ = 0.0066.

5,10,15-Tris (4-pyridyl)-20-(*p*-tolyl)-21-monooxaporphyrin (28). Condensation of the furan mono-ol **12** (2 g, 10.627 mmol), 4-pyridylcarboxaldehyde (1.1 g, 1.0 mL, 10.627 mmol), and pyrrole (1.0 g, 1.1 mL, 15.941 mmol) in 220 mL propionic acid at refluxing temperature for 3 h followed by column chromatography of the crude compound on silica gel using dichloromethane/methanol (86:14) gave compound **28** as greenish-violet solid in 2% yield (56 mg). M. P. > 300 °C. IR (neat, cm^{-1}) 3414 (NH), 3046, 2927, 2855, 1591, 1472, 1407, 808, 736. ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm) 2.72 (s, 3H), 7.59 (d, J = 7.6 Hz, 2H), 8.12 (m, 8H), 8.58 (m, 2H), 8.65 (m, 2H), 8.84 (m, 2H), 9.04 (m, 6H), 9.19 (br s, 1H), 9.34 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 21.6, 22.7, 31.9, 52.9, 70.6, 119.0, 120.0, 121.2, 122.2, 127.9, 129.1, 129.3, 129.8, 134.32, 134.7, 136.3, 138.4, 148.3, 148.7, 149.6, 150.3, 150.6, 154.0, 155.3. ES-MS: $C_{42}H_{28}N_6O$, calcd av mass 632.7, obsd m/z 633.2 (M^+). Anal. calcd: C, 79.73; H, 4.46; N, 13.28. Found: C, 79.62; H, 4.29; N, 13.05. UV−vis λ_{max}/nm (ϵ/ mol^{-1} dm^3 cm^{-1}): 420 (95449), 506 (15025), 536 (6440), 611 (4063), 672 (3119). Fluorescence: (λ_{ex} = 515 nm, in toluene) λ_{em}/nm 675, 743 (sh), ϕ = 0.0611.

Covalent Dimers. 4-[(5,10,15-Trimesityl-20-porphyrinato) zinc(II)]-4′-[5,10,15-trioctyloxyphenyl-21-monothia-20-porphinyl]diphenylethyne (29). A solution of N_3S porphyrin **15** (15.0 mg, 14.4 μmol) and 5,10,15-tri(mesityl)-20-(4-iodophenyl) zinc porphyrin **34** (16.0 mg, 17.3 μmol) were dissolved in dry toluene-triethylamine (5:1, 18 mL) in a 25 mL-round-bottomed flask. The flask was fitted with a reflux condenser and a gas inlet tube was inserted through the top of the condenser into the solution for argon purging. The reaction vessel was placed in an oil bath preheated to 35 °C. The nitrogen was purged for 15 min. To this solution, $Pd_2(dba)_3$ (2.0 mg, 2.2 μmol) and $AsPh_3$ (5.4 mg, 17.5 μmol) were added and the reaction was stirred at 35 °C for 12 h. TLC analysis of the reaction mixture indicated the virtual disappearance of spots corresponding to starting materials and the appearance of a new spot corresponding to dimer. The solvents were removed in vacuo and the crude compound was passed through a small silica column using petroleum ether/dichloromethane (60:40) to remove the excess of $AsPh_3$, and the crude mixture of small amounts of monomeric porphyrins along with desired dimer was collected with petroleum ether/dichloromethane (20:80). The Pd species remained bound to the top of the column. The solution was concentrated in vacuo and the resulting crude mixture of porphyrinic monomers and dimer was dissolved in dichloromethane (3 mL) and dry slurry was prepared by adding neutral alumina powder. The slurry was loaded on neutral alumina column packed with petroleum ether. The small amounts of porphyrinic monomers were removed first with petroleum ether/dichloromethane and the desired dimer **29** was collected with petroleum ether/dichloromethane (20:80). Concentration of the solution gave porphyrin dimer as violet solid in 66% yield (12 mg). M. P. > 300 °C. IR (neat, cm^{-1}) 3335 (NH), 2934, 1611, 1505, 1453, 1236, 998, 821, 735. ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm) −2.60 (s, 1 H), 0.86−0.99 (m, 15H), 1.25−1.66 (m, 24H), 1.87 (s, 18H), 1.99 (m, 6H), 2.64 (m, 9H), 4.25 (m, 6H), 7.32 (m, 12H), 8.12 (m, 10H), 8.32 (m, 4H), 8.72 (m, 8H), 8.79 (d, J = 4.8 Hz, 2H), 8.93 (d, J = 4.8 Hz, 2H), 8.98 (s, 2H), 9.81 (m, 2H). ES-MS: $C_{123}H_{121}N_7SO_3Zn$, calcd av mass 1842.7, obsd m/z 1843.9 (M^+). Anal. calcd: C, 80.17; H, 6.62; N, 5.32; S, 1.74. Found: C, 80.64; H, 6.32; N, 5.57; S, 1.93. UV−vis λ_{max}/nm (ϵ/mol^{-1} dm^3 cm^{-1}): 424 (535799), 435 (510645), 518 (28439), 552 (34376), 588 (5762), 621 (3892), 683 (7256).

4-[(5,10,15-Trimesityl-20-porphyrinato) zinc(II)]-3′-[5,-10,15-tritolyl-21-monothia-20-porphinyl]diphenylethyne (30). A solution of N_3S porphyrin **20** (12.0 mg, 15.0 μmol) and 5,10,15-tri(mesityl)-20-(4-ethynylphenyl) zinc porphyrin **35** (15.0 mg, 18.1 μmol) in dry toluene-triethylamine (5:1, 15 mL) was purged with nitrogen for 10 min. The coupling was initiated by adding $AsPh_3$ (5.5 mg, 18.0 μmol) followed by $Pd_2(dba)_3$ (2.1 mg, 2.3 μmol) and the reaction mixture was then stirred at 40 °C for 12 h. The excess $AsPh_3$ and other impurities were removed on silica gel column using petroleum ether/dichloromethane (50:50) and the crude mixture of small amounts of monomers and dimer were then separated using neutral alumina column. The required dimer **30** was collected with petroleum ether/dichloromethane (60:40) mixture as a second band. The solvent was removed in a rotary evaporator to afford dimer **30** in 58% yield (13.0 mg). Violet solid, M. P. > 300 °C. IR (neat, cm^{-1}) 3322 (NH), 2940, 2661, 1736, 1604, 1453, 1006, 998, 808, 735. ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm) −2.64 (s, 1H), 1.84 (s, 18H), 2.62 (s, 9H), 2.72 (s, 9H), 7.29 (m, 6H), 7.40 (t, 2H), 7.62 (m, 8H), 7.97 (m, 2H), 8.20 (m, 8H), 8.62 (m, 2H), 8.74 (m, 8H), 8.87 (m, 2H), 8.97 (s, 2H), 9.83 (m, 2H). ES-MS: $C_{102}H_{79}N_7SZn$, calcd av mass 1500.3, obsd m/z 1500.9 (M^+). UV−vis λ_{max}/nm (ϵ/mol^{-1} dm^3 cm^{-1}): 424 (407869), 483 (4982), 515 (18868), 550 (19016), 591 (3241), 617 (2275), 677 (4201).

[5,10,15-Tritolyl-21-monothia-20-porphinyl]-4-[5,10,15-trioctyloxyphenyl-21-monothia-20-porphinyl]phenylethyne (31). A solution of N_3S porphyrin, 5-bromo-10,15,20-tris(*p*-tolyl)-21-thiaporphyrin **36 (**17.0 mg, 25.1 μmol), and N_3S porphyrin **15** (26.1 mg, 25.1 μmol) in dry toluene (20 mL) was purged with nitrogen for 10 min. To this solution were added $Pd_2(dba)_3$ (3.5 mg, 3.8 μmol), $AsPh_3$ (9.4 mg, 30.1 μmol), and Et_3N (8 mL). The resulting solution was then stirred at 40 °C for 24 h. After this period, TLC analysis indicated the presence of a new spot. The solution was concentrated in vacuo and the resulting crude product was purified by neutral alumina column chromatoghaphy. The expected compound **31** collected in petroleum ether/dichloromethane (20:80), in 48% yield (20.0 mg). Violet solid, M. P. > 300 °C. IR (neat, cm^{-1}) 3421 (NH), 3348 (NH), 2934, 2861, 1525, 1459, 1249, 973, 815, 729.^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm) −2.59 (s, 1H), −2.10 s, 1H), 0.95 (m, 9H), 1.21−1.64 (m, 30H), 2.00 (m, 9H), 2.73 (m, 6H), 4.28 (m, 6H), 7.53 (m, 12H), 8.15 (m, 12H), 8.55 (m, 4H), 8.68 (m, 6H), 8.91 (m, 4H), 9.33 (br s, 1H), 9.39 (br s, 1H), 9.54 (d, J = 4.5 Hz, 1H), 9.93 (m, 2H), 10.52 (d, J = 5.1 Hz, 1H). ES-MS: $C_{111}H_{106}N_6S_2O_3$ calcd av mass 1636.2, obsd m/z 1636.9 (M^+). Anal. calcd: C, 81.48; H, 6.53; N, 5.14; S, 3.92. Found: C, 81.02; H, 6.61; N, 5.56; S, 4.14. UV−vis λ_{max}/nm (ϵ/mol^{-1} dm^3 cm^{-1}): 439 (418923), 519 (43155), 578 (40541), 623 (7537), 688 (12499), 697 (12820).

4-[(5,10,15-Trimesityl-20-porphyrinato) zinc(II)]-4′-[5,-10,15-trioctyloxyphenyl-21-monooxa-20-porphinyl]diphenylethyne (32). A solution of N_3O porphyrin **22** (15.0 mg, 14.7 μmol) and 5,10,15-tri(mesityl)-20-(4-iodophenyl) zinc porphyrin **34** (17.9 mg, 17.5 μmol) in dry toluene-triethylamine (5:1, 15 mL) was purged with nitrogen for 10 min. To this solution, $AsPh_3$ (5.4 mg, 17.6 μmol) and $Pd_2(dba)_3$ (2.0 mg, 2.2 μmol) were added and stirred at 35 °C for 30 h. The solution was concentrated in vacuo and the resulting crude product was first subjected to silica gel column using petroleum ether/dichloromethane (50:50) to remove excess $AsPh_3$ and other impurities. The resultant crude compound was then subjected to neutral alumina column chromatoghaphy and afforded the dimer **32** using dichloromethane/methanol (99:1) in 37% yield as violet-green solid (10.0 mg). M. P. > 300 °C. IR (neat, cm^{-1}) 3408 (NH), 2934, 2854, 1604, 1466, 1249, 998, 815, 729. ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm) −2.54 (s, 1H), 0.83−0.95 (m, 21H), 1.25−1.74 (m, 18H), 1.86 (br s, 18H), 2.13 (m, 4H),

2.31 (m, 2H), 2.64 (m, 9H), 3.65 (br s, 2H), 4.27 (br s, 4H), 7.32 (m, 10H), 8.21 (m, 12H), 8.68 (m, 8H), 8.88 (m, 8H), 9.06 (d, J = 4.2 Hz, 1H), 9.10 (d, J = 5.1 Hz, 1H), 9.44 (m, 2H). ES-MS: $C_{123}H_{121}N_7O_4Zn$, calcd av mass 1826.7, obsd m/z 1827.9 (M^+). UV−vis λ_{max}/nm (ϵ/mol^{-1} dm^3 cm^{-1}): 424 (386895), 514 (9826), 550 (19686), 607 (sh) (6129).

4-[5,10,15-Tritolyl-21-mono oxa-20-porphinyl]-4′-[5,10,-15-trioctyloxyphenyl-21-monothia-20-porphinyl]diphenylethyne (33). Samples of N_3S porphyrin **15** (12.0 mg, 11.5 μmol) and N_3O porphyrin **23** (10.8 mg, 13.8 μmol) in dry toluene (15 mL) was purged with nitrogen for 10 min. To this solution were added $Pd_2(dba)_3$ (1.6 mg, 1.7 μmol), $AsPh_3$ (4.2 mg, 13.8 μmol), and Et_3N (5 mL). The resulting solution was then stirred at 50 °C for 30 h. After this period, TLC analysis indicated the presence of a new spot. The solution was concentrated in vacuo and the resulting crude product was purified by neutral alumina column chromatoghaphy. The expected compound **33** collected as violet-green solid, in dichloromethane/methanol (98:2) mixture, in 36% yield (7 mg). M. P. > 300 °C. IR (neat, cm^{-1}) 3441 (NH), 3335 (NH), 2927, 2861, 1604, 1453, 1249, 1766, 985, 802. ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm) −2.61 (s, 1H), 0.83−0.95 (m, 15H), 1.39−1.68 (m, 24H), 1.95−2.02 (m, 6H), 2.76 (m, 6H), 3.66 (m, 3H), 4.20−4.28 (m, 6H), 7.29−7.39 (m, 8H), 7.51−7.65 (m, 8H), 7.68−7.78 (m, 8H), 8.09−8.20 (m, 8H), 8.35−8.38 (m, 4H), 8.48−8.55 (m, 4H), 8.64−8.85 (m, 4H), 8.87−9.03 (m, 2H), 9.81 (m, 2H). ES-MS: $C_{117}H_{110}N_6SO_4$, calcd av mass 1696.2, obsd m/z 1696.6 (M^+). UV−vis λmax/nm (ϵ/mol^{-1} dm^3 cm^{-1}): 435 (211581), 517 (17327), 555 (11131), 619 (5262), 682 (4133).

Noncovalent Tetramers. Unsymmetrical Noncovalent Tetramer (37). The N_3S porphyrin **25** (15.0 mg, 0.024 mmol) was dissolved in 20 mL of toluene in two-necked round-bottomed flask and nitrogen was purged for 10 min. Ru TPP-(CO)(EtOH) (64.6 mg, 0.082 mmol) was then added and the solution was refluxed overnight. The color of the reaction mixture changed from bright red to dark brownish red as the reaction progressed. After 12 h, the TLC analysis showed the virtual disappearance of starting porphyrins and the presence of an additional spot corresponding to unsymmetrical porphyrin tetramer. The solvent was removed under reduced pressure and the resulting crude compound was dissolved in a minimum amount of dichloromethane and a dry slurry powder was prepared by adding a small amount of silica gel followed by the removal of the traces of solvent under reduced pressure. The slurry was loaded on a silica gel column and eluted with petroleum ether. The desired tetramer **37** was eluted as first band and collected with petroleum ether/dichloromethane (60:40) and the excess unreacted RuTPP(CO)(EtOH) was collected as second band with petroleum ether/dichloromethane (50:50). The tetramer **37** with small impurities was then subjected to size exclusion chromatography using toluene and the pure dimer **37** was collected as reddish-brown solid in 17% yield (12 mg). M. P. > 300 °C. IR (neat, cm^{-1}) 3427 (NH), 2927, 2855, 1953, 1078, 1018, 1006, 998, 802, 716. ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm) −4.33 (s, 1H), 1.78 (t, 4H), 1.86 (d, J = 6.9 Hz, 2 H), 5.60 (d, J = 6.6 Hz, 2H), 5.69 (d, J = 6.6 Hz, 2H), 5.77 (d, J = 6.6 Hz, 2H), 6.50 (d, J = 4.5 Hz, 1H), 6.71 (d, J = 4.5 Hz, 1 H), 6.82 (m, 2H), 6.90 (m, 2H), 7.56−7.81 (m, 41H), 8.06 (m, 12H), 8.29 (m, 12H), 8.69 (m, 24H), 9.13 (d, J = 5.4 Hz, 2H). ES-MS: $C_{176}H_{110}N_{18}SO_3Ru_3$, calcd av mass 2860.2, obsd m/z 2861.2 (M^+). Anal. calcd: C, 73.91; H, 3.88; N, 8.81; S, 1.12. Found: C, 74.23; H, 4.11; N, 8.56; S, 1.16. UV−vis λ_{max}/nm (ϵ/mol^{-1} dm^3 cm^{-1}): 410 (740119), 434 (sh), 530 (48797), 564 (sh), 618 (3751), 680 (4472).

Unsymmetrical Noncovalent Tetramer (38). The reaction of N_3S porphyrin **26** (23.0 mg, 0.036 mmol) and Ru TPP-(CO)(EtOH) (97.1 mg, 0.123 mmol), in toluene (40 mL) under the same reaction conditions as mentioned for compound **38** followed by chromatogarphic purification gave **38** in 20% yield (21 mg). M. P. > 300 °C. IR (neat, cm^{-1}) 3440 (NH), 3065, 2934, 2855, 1953, 1078, 1018, 1006, 998, 802, 716. ^{1}H NMR (300 MHz, $CDCl_3$, δ in ppm) −3.90 (s, 1H), 1.99 (m, 6H), 5.46 (br s, 1H), 5.57 (br s, 1H), 5.73 (m, 2H), 5.99 (br s, 1H), 6.15 (br s, 1H), 6.59 (m, 2H), 6.77 (m, 2H), 6.92 (m, 2H), 7.25−7.96 (m, 53H), 8.16 (m, 12H), 8.53 (m, 24H,), 9.55 (br s, 1H), 9.68 (br s, 1H). ES-MS: $C_{176}H_{110}N_{18}SO_3Ru_3$, calcd av mass 2860.2, obsd m/z 2861.2 (M^+). UV−vis λ_{max}/nm (ϵ/mol^{-1} dm^3 cm^{-1}): 411 (491530), 431 (sh), 531 (74966), 564 (sh), 621 (4619), 682 (5822).

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Supporting Information Available: The characterization data including ES-MS, ^{1}H NMR, ^{13}C NMR, absorption, and emission spectra of selected compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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