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Supramolecular Tetrads Containing Sn(IV) Porphyrin, Ru(II) Porphyrin, and Expanded Porphyrins Assembled Using Complementary Metal−Ligand Interactions

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Two examples of supramolecular tetrads containing Sn(IV) porphyrin, expanded thiaporphyrins such as sapphyrin and rubyrin, and Ru(II) porphyrin assembled using non-interfering cooperative tin(IV)−oxygen and ruthenium(II)−nitrogen coordination properties are described. These are the first examples in which the expanded porphyrins are used as axial ligands. The tetrads were prepared by adopting one step as well as stepwise approaches. In a one pot approach, the mono *meso*-pyridyl dihydroxy Sn(IV) porphyrin, *meso*-hydroxyphenyl expanded thiaporphyrin, and Ru(II) porphyrin were reacted in benzene under refluxing conditions followed by column chromatographic purification on alumina to afford tetrads. In a stepwise approach, the axial bonding type of triads containing Sn(IV)porphyrin as central unit and expanded thiaporphyrins as axial ligands were synthesized first by reacting *meso*-pyridyl dihydroxy Sn(IV) porphyrin with *meso*-hydroxyphenyl expanded thiaporphyrin in benzene at refluxing temperature. In the next step, the triads were reacted with Ru(II) porphyrin under mild reaction conditions to afford tetrads in decent yields. Both methods worked efficiently and produced stable, soluble tetrads in decent yields. One-dimensional (1D) and two-dimensional (2D) NMR techniques were used to confirm the identity of these novel tetrads. Absorption and electrochemical studies indicated that the components in tetrads interact weakly and retain their individual characteristic features. The steady state photophysical studies revealed that the quantum yield of Sn(IV) porphyrin in tetrads was reduced significantly because of non-radiative decay pathways operating in these systems.

Introduction

The preferential coordination properties of metal ions present in the porphyrin ring have been exploited to construct novel supramolecular arrays.[1] For example, the strong preference of Sn(IV) porphyrins for coordination to carboxylates and phenolates has been used by several researchers to construct multiporphyrin assemblies.[2] Similarly, the Zn(II), Ru(II), Rh(III), and so forth porphyrin building blocks which have preference to nitrogen coordination have been used extensively for the synthesis of multiporphyrin assemblies.[3] These well-known complementary binding abilities of zinc(II) and ruthenium(II) to nitrogen and that of tin(IV) to oxygen has been used first by Sanders and co-workers[4] and later by others[5] to synthesize a few novel heterometallic porphyrin oligomers shown in Chart 1. Sanders and co-workers synthesized trimeric as well as higher porphyrin arrays by using carboxylate binding to Sn(IV) components

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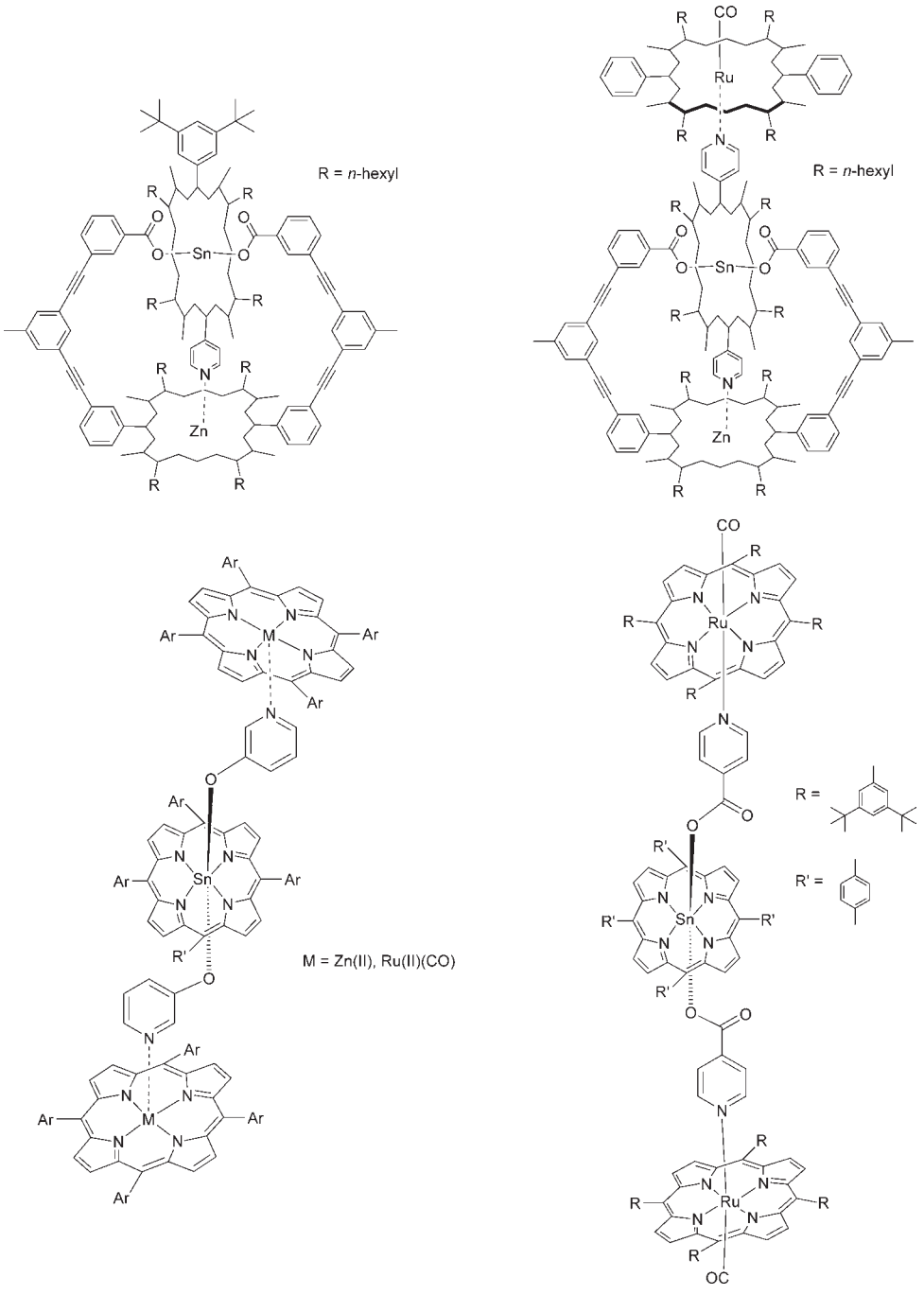
Chart 1. Few Representative Multiporphyrin Assemblies Constructed Based on Complementary Bonding Properties



coupled with complementary binding of pyridines to Zn(II), Ru(II), and Rh(III) porphyrins. These compounds were prepared either by a one-step approach where all components are reacted in one reaction flask or by a stepwise approach in which the intermediate products are collected and reacted further to create elaborate structures. However, the reports available, in which the complementary binding properties of two metal ions are used in synthesizing heterometallic porphyrin assemblies, are few. Furthermore, these reports are limited to assemblies containing only porphyrin macrocycles. To the best of our knowledge, there is no report available on Sn(IV) porphyrin based assemblies containing expanded porphyrin as one of the components. Expanded porphyrins are larger aromatic macrocycles than porphyrins containing five or more heterocyclic rings such as sapphyrins, rubyrins, or more extended structures but preserve the key characteristics of porphyrins.[6] The expanded porphyrins because of the increased number of donor atoms and varying cavity sizes

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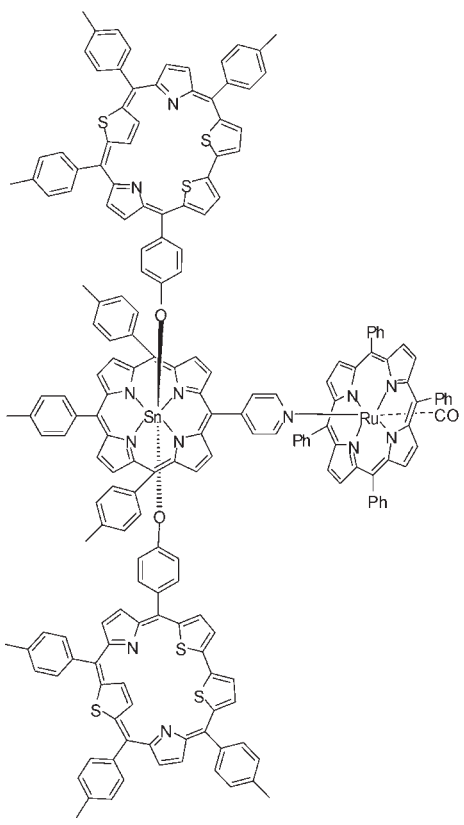
Chart 2. Sn(IV) Porphyrin Based Tetrads **1** and **2** Containing Expanded Thiaporphyrins as One of the Axial Ligands Synthesized in the Present Study



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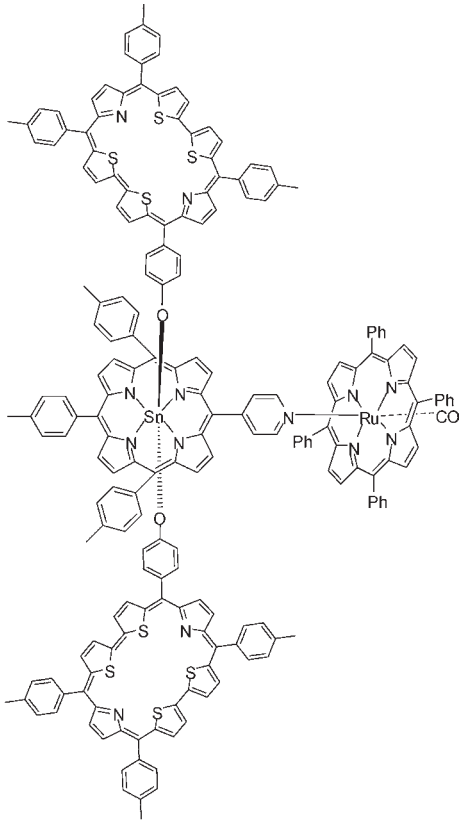

2

are important for studying metal coordination, anion binding, biomedical applications and nonlinear optical properties to name few.[7] In this paper, we report the synthesis of two novel tetrads **1** and **2** containing Sn(IV) porphyrin, Ru(II) porphyrin, and expanded porphyrin such as sapphyrin or rubyrin subunits assembled by using the oxophilic nature of Sn(IV) and the preferential nitrogen coordination ability of ruthenium(II) ions (Chart 2). In these systems, the RuTPP-(CO) is coordinated to *meso*-pyridyl group of Sn(IV) porphyrin and expanded porphyrins such as thiasapphyrin and thiarubyrin containing one *meso*-hydroxyphenyl group are coordinated to Sn(IV) porphyrin as axial ligands. The spectral, electrochemical, and photophysical properties of these novel tetrads and their reference compounds are described.

Results and Discussion

The synthesis of tetrads **1** and **2** were attempted by a one step as well as stepwise approaches. The required starting building units dihydroxo[5-(4-pyridyl)-10,15,20-tri(tolyl)]-porphyrinatotin(IV) **3**, 5-(4-hydroxyphenyl),10,15,20-tritolyl-25,27,29-trithiasapphyrin **4**, 5-(4-hydroxyphenyl)10,19,-24-tritolyl-29,30,32,33-tetrathiarubyrin **5**, and (*meso*-tetraphenylporphyrinato)carbonyl(ethanol)ruthenium(II) **6** were synthesized by following the standard literature protocols.[8] To prepare the compounds **4** and **5**, we first prepared their corresponding methoxy derivatives 5-(4-methoxyphenyl),10,15,20-tritolyl-25,27,29-trithiasapphyrin, 5-(4-methoxyphenyl),10,19,24-tritolyl-29,30,32,33-tetrathiarubyrin by condensing 5-[(*p*-methoxyphenyl)hydroxymethyl]-5′-[(*p*-tolyl) hydroxymethyl]-2,2′-bithiophene with 5,10-di(*p*-tolyl)-16-thia-15,17-dihydrotripyrrane and 20,21-(*p*-tolyl)dithiatetrapyrromethane, respectively, in dichloromethane under acid catalyzed conditions. The methoxy derivatives were treated with 49% HBr-H_2O at reflux conditions to afford hydroxy compounds **4** and **5** in decent yields (Supporting Information, Scheme S1). We adopted three different strategies to synthesize the tetrads **1** and **2** as outlined in Schemes 1 and 2. The tetrads **1** and **2** were initially prepared by a one pot approach (Method 1) by using the appropriate building blocks (Scheme 1). The tetrad **1** was prepared by reacting **3** with **4** and **6** in 1:2:1.2 ratios in benzene at refluxing temperature for 24 h. Similarly the tetrad **2** was prepared by reacting **3** with **5** and **6** in the same ratio under similar reaction conditions. Unfortunately,

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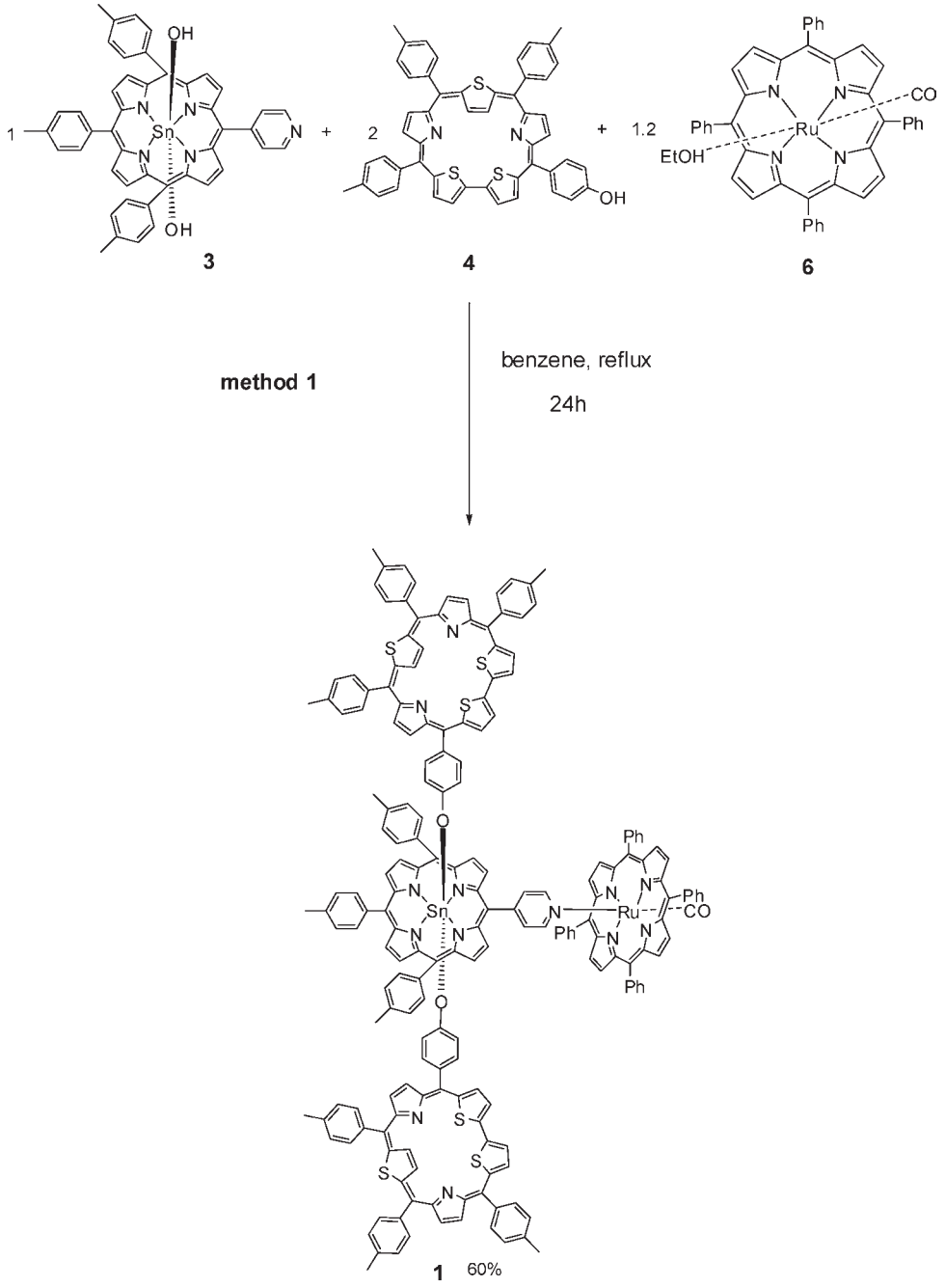
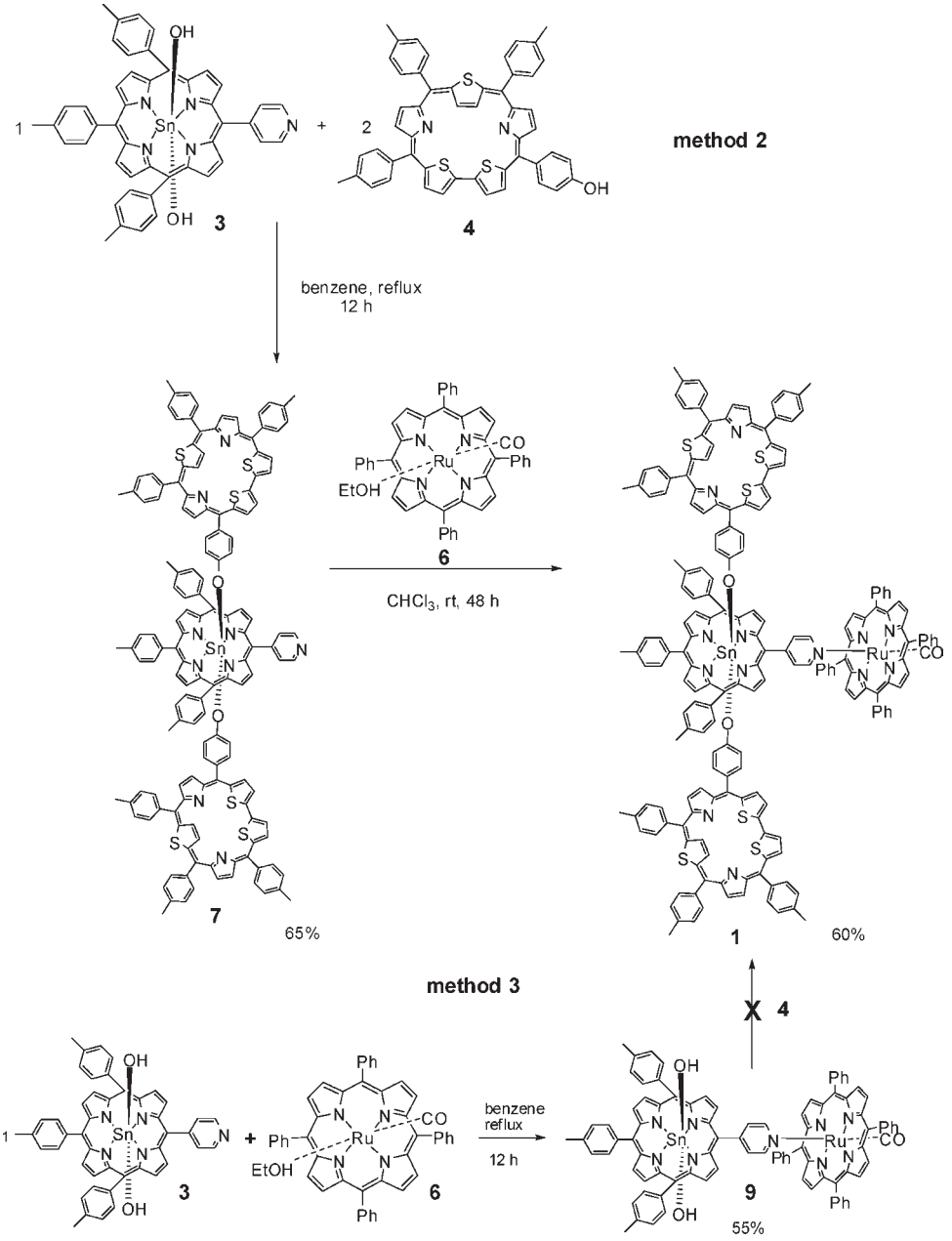
Scheme 1. One-Pot Synthesis of Tetrad **1** Possessing Thiasapphyrin



progress of the reaction cannot be monitored by TLC analysis on silica gel as well as by absorption spectroscopy since the target compounds are not stable on silica and the absorption spectroscopy always showed the features of all three components. The reaction was stopped after 24 h, and the crude compound was subjected to basic alumina column chromatography. The fast moving band was collected with dichloromethane, and the resulted solid was recrystallized using dichloromethane/*n*-hexane to afford the tetrads **1** and **2** as dark colored solids in ~60% yield.

Alternately the tetrads **1** and **2** were synthesized by stepwise approaches (methods 2 and 3) (Scheme 2). In the first step of method 2, the compound **3** was reacted with **4** or **5** in 1:2 ratios in benzene at refluxing temperature for overnight. The crude compounds were purified by basic alumina column chromatography followed by recrystallization to yield the triads **7** or **8** containing expanded thiaporphyrins as axial ligands and free *meso*-pyridyl group on central Sn(IV) porphyrin in ~65% yield. In the next step, the triad **7** or **8** was treated with **6** in 1:1.2 ratio in chloroform at room temperature for 48 h in air. The solvent was removed on a rotary evaporator, and the crude compound was subjected to basic alumina column chromatography followed by recrystallization to afford the tetrad **1** or **2** in 60−65% yield. In method 3, we first prepared dyad **9** containing Sn(IV) and Ru(II) porphyrins by reacting **3** with **6** in 1:1 ratio at refluxing temperature in benzene for overnight. The crude compound was subjected to basic alumina column chromatography and afforded dyad **9** in 55% yield. However, the dyad **9** on reaction with 2 equiv of **4** or **5** in benzene at refluxing

Scheme 2. Stepwise Synthesis of Tetrad **1** Possessing Thiasapphyrin



temperature for 24 h failed to yield the desired tetrad **1** or **2**. Thus, the tetrads **1** and **2** can be prepared easily in decent yields by following any one of the first two methods. The failure of method 3 indicates that in a one pot reaction, the triad containing Sn(IV) porphyrin and axial expanded porphyrins may be forming initially which then react with RuTPP(CO)(EtOH) to form the tetrads **1** and **2**. The tetrads are freely soluble in common organic solvents such as toluene, chloroform, dichloromethane, and so forth and were characterized by mass spectrometry, one-dimensional (1D) and two-dimensional (2D) NMR, absorption, electrochemical, and fluorescence techniques.

The structures of triads **7**, **8**, and tetrads **1**, **2** were clearly deduced by mass spectrometry, ^{1}H NMR and ^{1}H-^{1}H COSY studies. Both electrospray mass spectra (ES-MS) and matrix-assisted laser desorption/ionization-time of flight (MALDI-TOF) mass spectra of triads **7** and **8** showed a weak peak corresponding to M-(O-expanded porphyrin). However, we failed to obtain a molecular ion peak or any relevant fragment peak other than the peak corresponding to the expanded porphyrin unit in mass spectra of tetrads **1** and **2**. The ^{1}H NMR spectra of triad **7** and tetrad **1** is presented in Figures 1 and 2, respectively, along with proton assignments, which are made on the basis of the resonance position and integrated intensity data as well as the proton−proton connectivity information revealed in the ^{1}H-^{1}H COSY spectra. The comparison of selected proton resonances of triads and tetrads along with their corresponding monomers is presented in Table 1. In ^{1}H NMR of triads **7** and **8**, certain protons of the basal Sn(IV) porphyrin and axial expanded porphyrins experienced shifts because of the ring current effect of the adjacent macrocyclic components and appeared at a different region as compared to their monomers. For example in triad **7**, the eight β-pyrrole protons of central Sn(IV) porphyrins appeared as three multiplets at 9.34, 9.47,

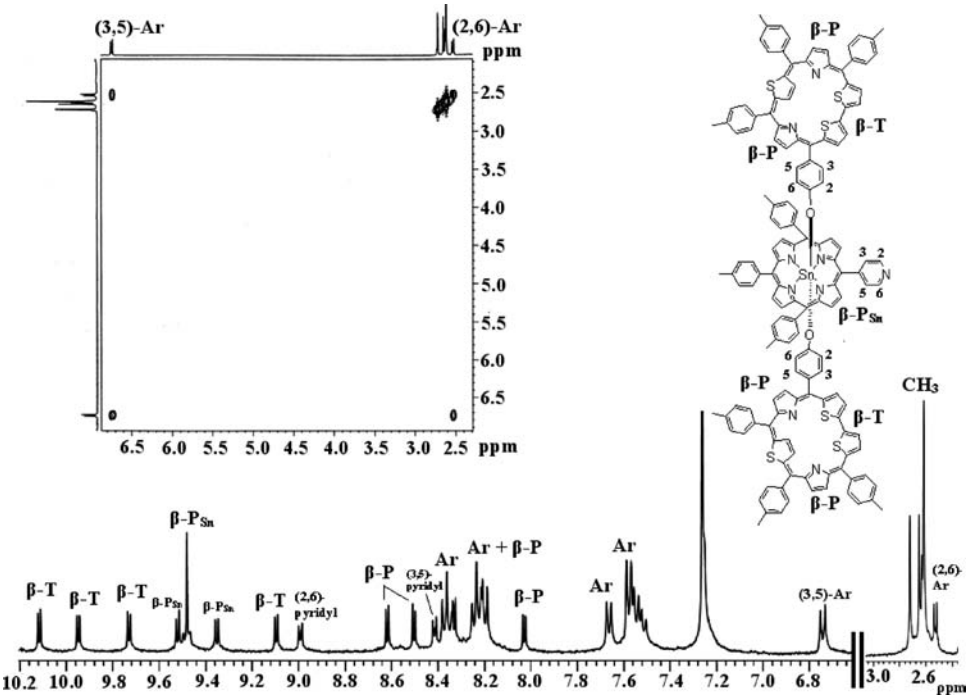


Figure 1. Selected region of the ^{1}H NMR spectrum of triad **7** with proton assignments and the partial ^{1}H-^{1}H COSY spectrum of **7** recorded in $CDCl_3$.

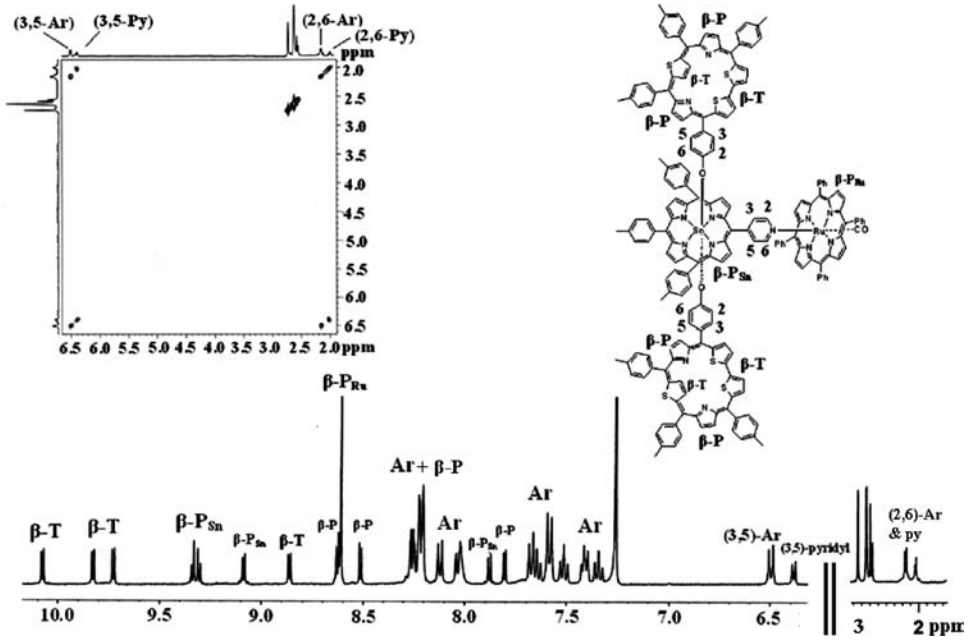


Figure 2. Selected region of the ^{1}H NMR spectrum of tetrad **1** with proton assignments and the partial ^{1}H-^{1}H COSY spectrum of **1** recorded in $CDCl_3$.

and 9.51 ppm which were slightly downfield shifted compared to monomeric Sn(IV) porphyrin **3**. The 2,6- and 3,5-pyridyl proton resonances appeared as two sets of doublets and experienced slightly upfield and downfield shifts, respectively, compared to **3**. The axial sapphyrin units in triad **7** also showed different features compared to the monomeric sapphyrin **4**. In **4**, the two protons of inverted thiophene appeared as singlet at −0.73 ppm and four bithiophene protons appeared as two doublets at 9.70 and 10.2 ppm. However, in triad **7**, the two inverted β-thiophene protons appeared as two doublets and at the upfield region compared to **4**. The four β-bithiophene protons appeared as four doublets and exhibited shifts depending on their proximity to the central Sn(IV) porphyrin. Similarly, the four β-pyrrole protons which existed as three sets of signals in **4**, appeared as four sets of doublets in triad **7** and exhibited shifts compared to **4**. However, the formation of triads **7** and **8** was more clearly evident in the large upfield shifts observed for the *meso*-phenoxo group of axial expanded porphyrins which was connected to the Sn(IV) porphyrin. The 3,5-proton resonance of monomeric thiasapphyrin **4** which appeared as a doublet at 7.60 ppm shifted to upfield and appeared as

Table 1. ^{1}H NMR Data of Selected Protons of Triads and Tetrads with Its Corresponding Monomers

compound	β−pyrrole Sn	β−pyrrole Sap	β−pyrrole Rub	β−thiophene Sap	β−thiophene Rub	bridging phenyl	pyridyl
3	9.05 (d)						8.28 (d)
	9.16 (s)						
	9.19 (d)						9.08 (d)
4		8.52−8.55 (m)		−0.73 (s)		7.17 (d)	
				9.70 (d)		8.20 (d)	
		8.60 (d)		9.76 (d)			
		8.64 (d)		10.14−10.16 (m)			
5			9.04−9.06 (m)		10.46−10.48 (m)	7.18 (d)	
						8.39 (d)	
					11.57 (d)		
Triad **7**	9.34 (d)	8.02 (d)		−0.69 (d)		2.52 (d)	8.41 (d)
	9.47 (s)	8.18−8.25		−0.61 (d)		6.74 (d)	
	9.52 (d)	(merged in Aryl cluster)		9.09 (d)			8.98 (d)
				9.72 (d)			
		8.50 (d)		9.94 (d)			
		8.61 (d)		10.11 (d)			
Triad **8**	9.50 (d)		8.84 (d)		10.42−10.48 (m)	2.72 (d)	8.56 (d)
	9.63 (s)		9.02−9.05 (m)			6.99 (d)	
	9.66 (d)				11.26 (d)		9.07 (d)
			9.70 (d)		11.47 (d)		
					11.54−11.59 (m)		
Tetrad **1**	7.87 (d)	7.80 (d)		−0.70 (d)		2.15 (d)	2.02 (d)
	9.08 (d)	8.20−8.29		−0.59 (d)		6.49 (d)	
	9.30 (d)	(merged in Aryl cluster)		8.86 (d)			6.38 (d)
				9.72 (d)			
	9.33 (d)	8.51 (d)		9.82 (d)			
		8.62 (d)		10.07 (d)			
Tetrad **2**	7.99 (d)		8.67−8.70 (m)		10.40−10.48 (m)	2.34 (d)	2.02 (d)
	9.23 (d)					6.76 (d)	
	9.48−9.51 (m)		8.74 (d)		11.15 (d)		6.47 (d)
			9.02−9.06 (m)		11.43 (d)		
					11.54−11.59 (m)		

doublet at 6.74 ppm in triad **7**. Similarly, the 2,6-proton resonance of *meso*-phenoxo group of **4** which appeared as doublet at 7.90 ppm were upfield shifted to 2.52 ppm in triad **7** because of the large ring current effect of central Sn(IV) porphyrin experienced by these protons in triad **7**. The upfield shift of proton resonances of *meso*-phenoxo group was further confirmed by the cross peak analysis in the ^{1}H-^{1}H COSY spectrum (Figure 1). Similar observations were made for triad **8** confirming its formation (Supporting Information, Figures S6 and S7).

Upon formation of tetrads **1** and **2**, the protons of all three components such as Sn(IV) porphyrin, Ru(II) porphyrin, and expanded porphyrins exhibited shifts in their resonance positions compared to their corresponding triads **7** and **8** respectively and monomeric Ru(II) porphyrin. In tetrad **1**, the eight β-pyrrole protons of central Sn(IV) porphyrin which appeared as three sets of signals in triad **7**, appeared as four sets of signals in tetrad **1** with prominent upfield shift for two protons which were facing the Ru(II) porphyrin. In tetrad **1**, the protons of pyrrole, inverted thiophene, and bithiophene groups of axial sapphyrin units showed similar pattern with minimal shift in resonance positions compared to the triad **7**. The protons of phenoxo connectors also experienced upfield shifts in tetrad **1** compared to triad **7**. The clear evidence of formation of tetrad **1** comes from the significant upfield shifts of 2,6- and 3,5-pyridyl proton resonances of tetrad **1** compared to triad **7**. In triad **7**, the 2,6 and 3,5-pyridyl proton resonances appeared as two doublets at 8.98 and 8.41 ppm, respectively, which were shifted to 2.02 and 6.38 ppm in tetrad **1**. This is attributed to the ring current effect of Ru(II) porphyrin on *meso*-pyridyl protons of central Sn(IV) porphyrin in tetrad **1** because of coordination of

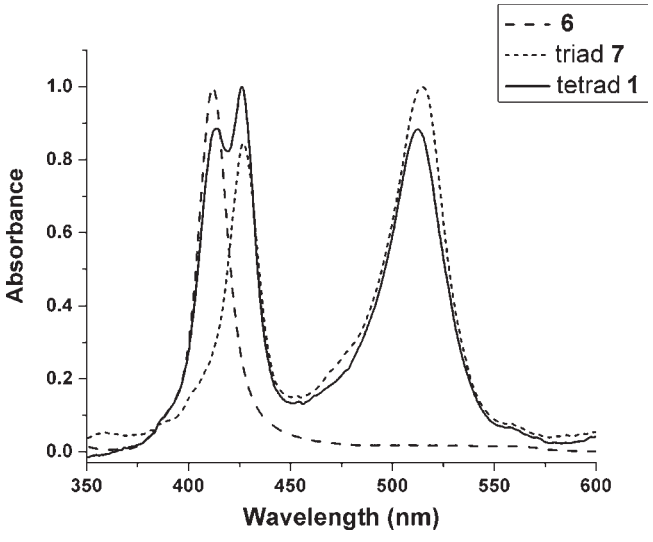


Figure 3. Comparison of Soret band absorption spectra of Ru(II)TPP **6**, triad **7**, and tetrad **1** recorded in dichloromethane.

meso-pyridyl "N" with Ru(II) porphyrin. The ^{1}H-^{1}H COSY spectrum of tetrad **1** also showed clear cross peak correlations for 2,6- and 3,5-pyridyl proton resonances (Figure 2). The NMR features of tetrad **2** were also similar to tetrad **1** supporting its formation (Supporting Information, Figures S9 and S10).

Absorption, Electrochemical, and Fluorescence Properties. The properties of tetrads **1** and **2** along with triads **7** and **8** and associated reference monomers **3**, **4**, **5**, and **6** were studied using absorption, electrochemical, and fluorescence techniques. The comparison of absorption

Table 2. Absorption Data of Triads and Tetrads with Its Constituent Monomers

	UV−vis data	
compound	Soret bands (λ nm, log ε)	Q-bands (λ nm, log ε)
3	427 (5.73)	561 (4.21), 602 (4.08)
4	509 (5.43)	625 (4.15), 682 (4.54), 780 (sh), 882 (3.92)
5	524 (5.30)	662 (3.79), 720 (4.26), 843 (3.33), 960 (3.20)
6	413 (5.61)	532 (4.58), 569 (sh)
7	427 (5.43), 513 (5.52)	559 (sh), 602 (4.33), 629 (sh), 688 (4.74), 784 (3.50), 885 (4.07)
8	426 (4.99), 525 (5.62)	604 (4.36), 661 (4.41), 721 (4.78), 843 (4.17), 960 (4.13)
1	413 (5.64), 427 (5.69), 512 (5.72)	559 (sh), 603 (4.54), 628 (sh), 687 (4.95), 786 (3.01), 885 (4.20)
2	413 (5.64), 426 (5.67), 527 (5.96)	605 (4.55), 663 (4.60), 724 (5.15), 844 (3.94), 961 (4.15)

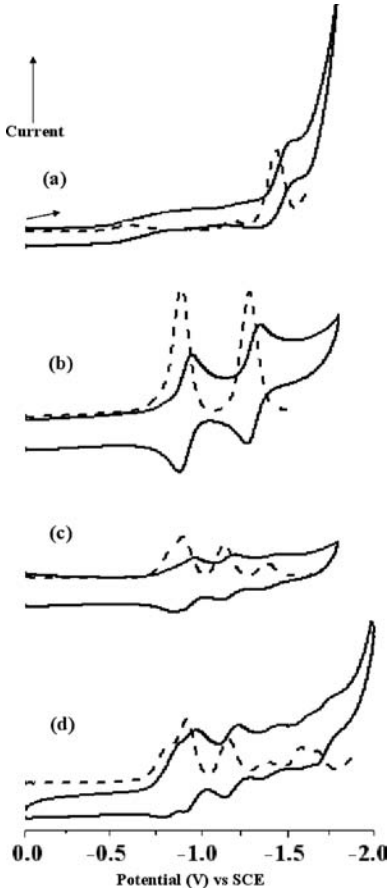


Figure 4. Reduction waves of Cyclic Voltammograms (solid line) and Differential Pulse Voltammograms (dashed line) of (a) **6**, (b) **3**, (c) triad **7**, and (d) tetrad **1** recorded in dichloromethane containing 0.1 M TBAP as supporting electrolyte (scan rate 50 mV/s).

spectra of tetrad **1** along with its corresponding triad **7** and Ru(II) porphyrin **6** in the Soret region is presented in Figure 3, and data of all compounds are presented in Table 2. The absorption spectra of triads **7** and **8** as well as tetrads **1** and **2** showed features of their constituted monomeric macrocycles and appeared as nearly the sum of the spectra of the corresponding monomers with negligible shifts in peak maxima. For example, the triad **7** which contains central Sn(IV) porphyrin and axial sapphyrin units showed two very clear Soret like absorptions at 427 and 513 nm and six Q-band like absorptions at 559, 602, 629, 688, 784, and 885 nm. In this, the band at 427 nm is the Soret band of Sn(IV)TTP, and the band at 513 nm is due to sapphyrin. Similarly the bands at 559 and 602 nm are mainly due to Sn(IV)TTP, and the rest of the Q-bands are due to the sapphyrin unit. In tetrad **1**, the additional Ru(II)TPP(CO) unit is attached to Sn(IV)TTP unit, hence the tetrad exhibited absorption features of all three constituted macrocycles, Sn(IV)TTP, sapphyrin, and RuTPP(CO) units (Figure 3 and Table 2). The tetrad **1** showed three Soret like absorptions at 413, 427, and 512 nm and five Q-bands at 605, 663, 724, 844, and 961 nm. The Soret band at 413 nm is exclusively due to RuTPP-(CO) unit, and the other two Soret bands at 427 and 512 nm are due to Sn(IV)TTP and sapphyrin units, respectively, which are not changed much from the corresponding triad **7**. However, some of the Q-bands of three components in tetrad **1** overlapped with each other resulting in less number of absorption bands in the Q-band region. Thus, Soret band region is very useful to identify the components present in the triads and tetrads. It is clear from the above discussion that the components in triads and tetrads retain their independent absorption features with minimum perturbation of the electronic structures of the individual macrocyclic systems indicating that the macrocycles in triads and tetrads interact weakly thus acting like supramolecular assemblies.

The redox properties which are investigated by using cyclic voltammetric measurements also indicated the absence of strong electronic interaction between the various macrocycles in triads and tetrads and retain their individual characteristic features. The reduction waves of Ru(II) porphyrin, Sn(IV) porphyrin, triad **7** and tetrad **1** are presented in Figure 4, and data of tetrads, triads, and appropriate monomers are presented in Table 3. The oxidation and reduction waves which are quasi-reversible or irreversible in triads and tetrads were assigned with the help of their constituted monomers. For instance, the triad **7** showed two irreversible oxidations at 0.68 and 1.00 V and three quasi-reversible reductions at −0.90, −1.14, and −1.38 V. In this, the redox waves at 0.68, 1.00, and −1.14 V are exclusively due to axial sapphyrin unit; the redox wave at −0.90 is due to both Sn(IV) porphyrin and sapphyrin unit, and the redox wave at −1.38 is exclusively due to Sn(IV) porphyrin. Similarly, the tetrad **2** showed four irreversible oxidations at 0.58, 0.91, 1.13, and 1.42 V and three quasi-reversible reductions at −0.83, −1.30, and −1.62 V. In this system, 0.91, 1.42, and −1.62 V are due to Ru(II) porphyrin and the other waves are due to the remaining components of the tetrad (Table 3). The triad **8** and tetrad **1** also showed features of their corresponding constituted monomers. Thus, the redox data of triads and tetrads are in the same range as those of its corresponding monomers supporting a weak interaction among the constituted components.

The steady state fluorescence properties of triads **7** and **8** and tetrads **1** and **2** were studied in dichloromethane by using excitation wavelength 427 nm. In triads and tetrads,

Table 3. Electrochemical Data of Triads and Tetrads along with Its Corresponding Monomers Recorded in Dichloromethane

	potential V vs SCE	
compound	oxidation	reduction
3	1.53	−0.89, −1.28
4	0.68, 1.22	−0.94, −1.18, −1.63
5	0.58, 1.05, 1.15	−0.80, −1.03, −1.66
6	0.87, 1.43	−1.59
7	0.68, 1.00	−0.90, −1.14, −1.38
8	0.57, 1.11	−0.84, −1.05, −1.35, −1.66
1	0.68, 0.91, 1.23, 1.43	−0.82, −0.92, −1.16, −1.38, −1.59, −1.66
2	0.58, 0.91, 1.13, 1.42	−0.83, −1.30, −1.62

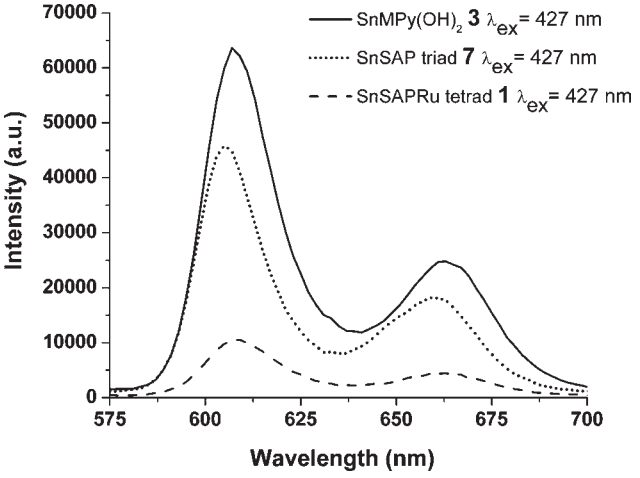


Figure 5. Comparison of emission spectra of **3**, triad **7** and tetrad **1** at λ_{ex} = 427 nm. (the concentartion used was 2×10^{-6} in all cases).

Table 4. Emission Data of Triads and Tetrads Recorded in Dichloromethane

compound	λ_{em} nm		quantum yield of SnP	% quenching
3	607	663	0.026	
7	607	663	0.012	54
8	607	663	0.016	39
1	607	663	0.0026	90
2	607	663	0.0066	75

only the Sn(IV) porphyrin unit is fluorescent and the other components are nonfluorescent. The triads **7** and **8**, on excitation at 427 nm where Sn(IV) porphyrin absorbs strongly, showed bands at 607 and 663 nm which are typical bands of Sn(IV) porphyrin. However, the quantum yield of Sn(IV) porphyrin component in triads calculated by the comparative method[9] are reduced to 40−50% with respect to **3** (Figure 5 and Table 4). This supports that non-radiative decay pathways are operating in triads resulting in reduction of quantum yields. In tetrads **1** and **2**, the quantum yield of the central Sn(IV) porphyrin is reduced to 75−90% with respect to **3** because of the Ru(II) porphyrin which further enhances the non-radiative decay pathways.[10]

Conclusions

In conclusion, we synthesized two novel supramolecular tetrads based on non-interfering cooperative Sn(IV)-oxygen and Ru(II)-nitrogen coordination properties by following both one pot and stepwise approaches. These are the first examples of supramolecular arrays containing expanded porphyrins as axial ligands. Both triads and tetrads are quite stable and can be purified by column chromatography. The compounds were confirmed by 1D and 2D NMR studies. Absorption and electrochemical studies indicated that the components in both triads and tetrads interact weakly and retain their individual properties. These compounds are weakly fluorescent. With suitable modifications, these types of novel supramolecular arrays may find applications in materials chemistry.

Experimental Section

All general chemicals and solvents were procured from SD. Fine Chemicals, India. Column chromatography was performed by using basic alumina obtained from Sisco Research Laboratories, India. Tetrabutylammonium perchlorate was purchased from Fluka and used without further purifications.

^{1}H NMR spectra were recorded with Varian and Bruker 400 MHz instrument using tetramethylsilane as an internal standard. ^{1}H-^{1}H COSY experiments were performed on Bruker 400 MHz instrument. All NMR measurements were carried out at room temperature in deuterochloroform. Absorption and steady state fluorescence spectra were obtained with Perkin−Elmer Lambda-35 and PC1 Photon Counting Spectrofluorometer manufactured by ISS U.S.A., respectively. The fluorescence quantum yield (Φ_f) of Sn(IV) porphyrin in triads **7** and **8** and tetrads **1** and **2** were estimated from the emission and absorption spectra by the comparative method[9] using **3** as standard (Φ_f = 0.026). ES-MS spectra were recorded with a Q-Tof Micromass spectrometer. MALDI-TOF spectra were obtained from Bruker Daltonics instrument. Cyclic Voltammetric (CV) and Differential Pulse Voltammetric (DPV) studies were carried out with BAS electrochemical system utilizing the three electrode configuration consisting of a glassy carbon (working electrode), platinum wire (auxiliary electrode), and saturated calomel (reference electrode) electrodes in dry dichloromethane using 0.1 M tetrabutylammonium perchlorate (TBAP) as supporting electrolyte.

Dihydroxo[5-(4-pyridyl)-10,15,20-tri(tolyl)]porphyrinatotin(IV) (3). A sample of 5-(4-pyridyl)-10,15,20-tri(tolyl)]porphyrin (50 mg, 75 μmol) was dissolved in 15 mL of chloroform in a one-neck round-bottom flask. The solution of $SnCl_2 \cdot 2H_2O$ (171 mg, 0.75 mmol) in 15 mL of ethanol was added to it, and the reaction mixture was stirred at refluxing temperature. The porphyrin solution turned green on addition of $SnCl_2 \cdot 2H_2O$. The progress of the reaction was monitored by thin layer chromatography (TLC) analysis and absorption spectroscopy. The metalation was completed in 4 h as judged by absorption spectroscopy. Triethylamine (0.5 mL) was added to the reaction mixture, and the reaction mixture was stirred for additional 5 min. The solvent was removed on a rotary evaporator, and the crude compound was subjected to alumina column chromatographic purification. The residual unreacted free base porphyrin was collected first with CH_2Cl_2, and the desired dihydroxo[5-(4-pyridyl)-10,15,20-tri(tolyl)]porphyrinatotin(IV) **3** was eluted with CH_2Cl_2/2%

(9) Gupta, I.; Ravikanth, M. *Inorg. Chim. Acta* **2007**, *360*, 1731–1742.
(10) Prodi, A.; Kleverlaan, C. J.; Indelli, M. T.; Scandola, F.; Alessio, E.; Iengo, E. *Inorg. Chem.* **2001**, *40*, 3498–3504.

CH_3OH. The solvent was removed on a rotary evaporator and afforded the pure Sn(IV) porphyrin **3** as purple solid. (55 mg, Yield 90%). Mp >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ −7.38 (br s, 2H, OH), 2.73 (s, 9H, CH_3), 7.62 (d, J = 7.7 Hz, 6H, Ar), 8.20 (d, J = 7.7 Hz, 6H, Ar), 8.28 (d, J = 5.9 Hz, 2H, pyridyl), 9.05 (d, J = 4.9 Hz, 2H, β-P_{Sn}), 9.08 (d, J = 5.7 Hz, 2H, pyridyl), 9.16 (s, 4H, β-P_{Sn}), 9.19 (d, J = 4.9 Hz, 2H, β-P_{Sn}) ppm; HRMS (ES+) m/z calcd for $C_{46}H_{36}N_5O_2Sn$ $(M+H)^+$ 810.1891, found 810.1884.

General Synthesis of Compounds (4) and (5). Samples of 1 equiv of 5-[(*p*-methoxyphenyl)hydroxymethyl]-5′-[(*p*-tolyl)hydroxymethyl]-2,2′-bithiophene and 1 equiv of 5,10-di(*p*-tolyl)-16-thia-15,17-dihydrotripyrrane or 20,21-(*p*-tolyl)dithiatetrapyrromethane were condensed in CH_2Cl_2 in the presence of 1 equiv of trifluoroacetic acid at room temperature for 1 h followed by oxidation with DDQ (1 equiv) and column chromatographic purification on alumina to afford monomethoxy derivatives, 5-(4-methoxyphenyl),10,15,20-tritolyl-25,27,29-trithiasapphyrin, and 5-(4-methoxyphenyl),10,19,24-tritolyl-29,30,32,33-tetrathiarubyrin, respectively, in ∼20% yield. The monomethoxy derivatives of sapphyrin/rubyrin (100 mg) were then refluxed in 40 mL of 49% HBr-water for 4 h, and the reaction mixture was extracted with dichloromethane and washed thoroughly with water and dilute ammonia solution. The organic layer was evaporated, and the resulting compound was purified by basic alumina column chromatography to afford 5-(4-hydroxyphenyl),10,15,20-tritolyl-25,27,29-trithiasapphyrin **4** and 5-(4-hydroxyphenyl),10,19,24-tritolyl-29,30,32,33-tetrathiarubyrin **5** in 50−70% yields.

5-(4-Hydroxyphenyl),10,15,20-tritolyl-25,27,29-trithiasapphyrin (4). Yield 70%; Mp >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ −0.73 (s, 2H, β-thiophene), 2.61 (s, 6H, CH_3), 2.72 (s, 3H, CH_3), 7.17 (d, J = 8.2 Hz, 2H, Ar), 7.57 (d, J = 6.7 Hz, 4H, Ar), 7.66 (d, J = 7.9 Hz, 2H, Ar), 8.08 (d, J = 8.5 Hz, 2H, Ar), 8.20 (d, J = 7.9 Hz, 2H, Ar), 8.25−8.28 (m, 4H, Ar), 8.52−8.55 (m, 2H, β-pyrrole), 8.60 (d, J = 4.2 Hz, 1H, β-pyrrole), 8.64 (d, J = 4.2 Hz, 1H, β-pyrrole), 9.70 (d, J = 4.5 Hz, 1H, β-thiophene), 9.76 (d, J = 4.5 Hz, 1H, β-thiophene), 10.14−10.16 (m, 2H, β-thiophene) ppm; ES-MS: m/z (%) = 790.8 $(M+H)^+$ (100).

5-(4-Hydroxyphenyl),10,19,24-tritolyl-29,30,32,33-tetrathiarubyrin (5). Yield 50%; Mp >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.85 (s, 9H, CH_3), 7.18 (d, J = 8.0 Hz, 2H, Ar), 7.77 (d, J = 7.9 Hz, 6H, Ar), 8.39 (d, J = 8.0 Hz, 2H, Ar), 8.43 (d, J = 7.9 Hz, 6H, Ar), 9.04−9.06 (m, 4H, β-pyrrole), 10.46−10.48 (m, 4H, β-thiophene), 11.57 (d, J = 4.8 Hz, 4H, β-thiophene) ppm; ES-MS: m/z (%) = 872.3 $(M+H)^+$ (100).

General Synthesis of Triads (7) and (8). The triads **7** and **8** were synthesized by refluxing **3** (12 μmol), and monohydroxyphenyl expanded thiaporphyrins **4** and **5** (24 μmol) respectively in dry benzene (10 mL) for 12 h under nitrogen atmosphere. The solvent was evaporated under reduced pressure, and the resulted residue was subjected to basic alumina column chromatography. The desired product was eluted with dichloromethane and was recrystallized using dichloromethane/*n*-hexane mixture to afford triads **7** and **8** in 65% yield.

Triad (7). Mp >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ −0.69 (d, J = 5.5 Hz, 2H, β-thiophene), −0.61 (d, J = 5.2 Hz, 2H, β-thiophene), 2.52 (d, J = 8.2 Hz, 4H, Ar), 2.61 (s, 15H, CH_3), 2.65 (s, 6H, CH_3), 2.72 (s, 6H, CH_3), 6.74 (d, J = 8.5 Hz, 4H, Ar), 7.52−7.58 (m, 14H, Ar), 7.66 (d, J = 7.6 Hz, 4H, Ar), 8.02 (d, J = 4.6 Hz, 2H, β-pyrrole), 8.18−8.25 (m, 14H, Ar + β-pyrrole), 8.32−8.38 (m, 6H, Ar), 8.41 (d, J = 5.9 Hz, 2H, pyridyl), 8.50 (d, J = 4.6 Hz, 2H, β-pyrrole), 8.61 (d, J = 4.6 Hz, 2H, β-pyrrole), 8.98 (d, J = 5.9 Hz, 2H, pyridyl), 9.09 (d, J = 4.6 Hz, 2H, β-thiophene), 9.34 (d, J = 4.9 Hz, 2H, β-pyrrole Sn), 9.47 (s, 4H, β-pyrrole Sn), 9.52 (d, J = 4.9 Hz, 2H, β-pyrrole Sn), 9.72 (d, J = 4.6 Hz, 2H, β-thiophene), 9.94 (d, J = 4.6 Hz, 2H, β-thiophene), 10.11 (d, J = 4.3 Hz, 2H, β-thiophene) ppm; ES-MS: m/z (%) = 1562.7 $(M\text{-}C_{57}H_{35}N_2OS_3)^+$ (28)

Triad (8). Mp >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.63 (s, 3H, CH_3), 2.66 (s, 6H, CH_3), 2.72 (d, J = 8.3 Hz, 4H, Ar), 2.85 (s, 18H, CH_3), 6.99 (d, J = 8.3 Hz, 4H, Ar), 7.57 (d, J = 8.3 Hz, 2H, Ar), 7.60 (d, J = 8.2 Hz, 2H, Ar), 7.75−7.79 (m, 12H, Ar), 8.39−8.44 (m, 16H, Ar), 8.49−8.52 (m, 4H, Ar), 8.56 (d, J = 5.9 Hz, 2H, pyridyl), 8.84 (d, J = 4.5 Hz, 2H, β-pyrrole), 9.02−9.05 (m, 4H, β-pyrrole), 9.07 (d, J = 5.9 Hz, 2H, pyridyl), 9.50 (d, J = 4.9 Hz, 2H, β-pyrrole Sn), 9.63 (s, 4H, β-pyrrole Sn), 9.66 (d, J = 4.9 Hz, 2H, β-pyrrole Sn), 9.70 (d, J = 5.0 Hz, 2H, β-pyrrole), 10.42−10.48 (m, 8H, β-thiophene), 11.26 (d, J = 5.1 Hz, 2H, β-thiophene), 11.47 (d, J = 5.1 Hz, 2H, β-thiophene), 11.54−11.59 (m, 4H, β-thiophene) ppm; ES-MS: m/z (%) = 1644.9 $(M\text{-}C_{55}H_{37}N_2OS_4)^+$ (25)

General Synthesis of Tetrads (1) and (2). One Pot Approach. The tetrads **1** and **2** were synthesized by refluxing dihydroxySn-(IV) porphyrin **3** (12 μmol), monohydroxyphenyl expanded porphyrins **4** and **5** (24 μmol), and RuTPP(CO)EtOH **6** (14.4 μmol), respectively, in dry benzene (15 mL) for 24 h under nitrogen atmosphere. The solvent was evaporated under reduced pressure, and the resulted residue was subjected to basic alumina column chromatography. The desired product was eluted with dichloromethane and was recrystallized using dichloromethane/*n*-hexane mixture to afford tetrads **1** and **2** in 60% yield.

Stepwise Approach. The tetrads **1** and **2** were also synthesized by treating 1 equiv of triads **7** and **8** with 1.2 equiv of RuTPP-(CO)EtOH **6**, respectively, in chloroform at room temperature for 48 h in air. The solvent was evaporated under the reduced pressure, and the resulted residue was subjected to basic alumina column chromatography. The desired product was eluted with dichloromethane and was recrystallized using dichloromethane/*n*-hexane mixture to afford tetrads **1** and **2** in 60 and 65% yields, respectively.

Tetrad (1). Mp >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ −0.70 (d, J = 5.4 Hz, 2H, β-thiophene), −0.59 (d, J = 5.36 Hz, 2H, β-thiophene), 2.02 (d, J = 6.6 Hz, 2H, pyridyl), 2.15 (d, J = 8.3 Hz, 4H, Ar), 2.55 (s, 3H, CH_3), 2.58 (s, 3H, CH_3), 2.62 (s, 3H, CH_3), 2.63 (s, 3H, CH_3), 2.73 (s, 3H, CH_3), 2.88 (s, 6H, CH_3), 2.95 (s, 6H, CH_3), 6.38 (d, J = 6.7 Hz, 2H, pyridyl), 6.49 (d, J = 8.4 Hz, 4H, Ar), 7.34−7.53 (m, 14H, Ar), 7.58 (d, J = 8.0 Hz, 6H, Ar), 7.63−7.68 (m, 10H, Ar), 7.80 (d, J = 4.4 Hz, 2H, β-pyrrole), 7.87 (d, J = 4.9 Hz, 2H, β-pyrrole Sn), 8.03 (d, J = 7.6 Hz, 8H, Ar), 8.12 (d, J = 7.9 Hz, 4H, Ar), 8.20−8.29 (m, 16H, Ar + β-pyrrole), 8.51 (d, J = 4.4 Hz, 2H, β-pyrrole), 8.61 (s, 8H, β-pyrrole Ru), 8.62 (d, J = 4.4 Hz, 2H, β-pyrrole), 8.86 (d, J = 4.5 Hz, 2H, β-thiophene), 9.08 (d, J = 4.9 Hz, 2H, β-pyrrole Sn), 9.30 (d, J = 4.8 Hz, 2H, β-pyrrole Sn), 9.33 (d, J = 4.8 Hz, 2H, β-pyrrole Sn), 9.72 (d, J = 4.5 Hz, 2H, β-thiophene), 9.82 (d, J = 4.5 Hz, 2H, β-thiophene), 10.07 (d, J = 4.5 Hz, 2H, β-thiophene) ppm.

Tetrad (2). Mp >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.02 (d, J = 6.8 Hz, 2H, pyridyl), 2.34 (d, J = 8.3 Hz, 4H, Ar), 2.53 (s, 3H, CH_3), 2.61 (s, 9H, CH_3), 2.85 (s, 12H, CH_3), 2.95 (s, 3H, CH_3), 6.47 (d, J = 6.8 Hz, 2H, pyridyl), 6.76 (d, J = 8.3 Hz, 4H, Ar), 7.31−7.68 (m, 18H, Ar), 7.77 (d, J = 7.5 Hz, 12H, Ar), 7.99 (d, J = 4.9 Hz, 2H, β-pyrrole Sn), 8.05 (d, J = 7.5 Hz, 2H, Ar), 8.18−8.22 (m, 6H, Ar), 8.29 (d, J = 7.8 Hz, 4H, Ar), 8.31−8.44 (m, 14H, Ar), 8.63 (s, 8H, β-pyrrole Ru), 8.67−8.70 (m, 2H, β-pyrrole), 8.74 (d, J = 4.5 Hz, 2H, β-pyrrole), 9.02−9.06 (m, 4H, β-pyrrole), 9.23 (d, J = 4.9 Hz, 2H, β-pyrrole Sn), 9.48−9.51 (m, 4H, β-pyrrole Sn), 10.40−10.48 (m, 8H, β-thiophene), 11.15 (d, J = 5.1 Hz, 2H, β-thiophene), 11.43 (d, J = 5.1 Hz, 2H, β-thiophene), 11.54−11.59 (m, 4H, β-thiophene) ppm.

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Supporting Information Available: Copies of MS, ^{1}H NMR and UV−vis spectra of selected compounds. This material is available free of charge via the Internet at http://pubs.acs.org.