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Synthesis of a Series of Zinc(II)/Freebase Porphyrin Dimers and Trimers with Programmable Sequences from a Common Key Molecule

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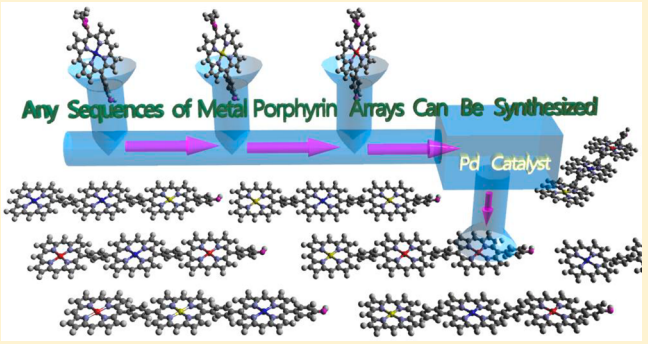
Supporting Information

ABSTRACT: We have developed a new methodology that enables the synthesis of any sequence of metal porphyrin arrays starting from a common key molecule. Using this method, we prepared porphyrin dimers and trimers with varying component unit sequences via consecutive Suzuki coupling reactions using the same key porphyrin compound under the same reaction conditions. The key porphyrin compound was synthesized on a gram scale in one batch, and the coupling reactions afforded the desired oligomers in good yields. Thus, the prepared porphyrin arrays showed unique physical properties depending on the sequence of the central metals. The reaction is potentially applicable for the automated synthesis of porphyrin arrays.



INTRODUCTION

Covalently linked porphyrin arrays have attracted much attention for a wide range of scientific applications such as electronic devices,[1−3] artificial photosynthetic antennas,[4−6] photonic materials,[7−12] spintronic devices,[13] and single-molecule devices.[14−20] Various synthetic methods for these molecules, such as oxidative coupling of meso-free porphyrins by Ag salt,[21] electrochemical reactions,[22−24] Glaser coupling to afford diacetylene-bridged porphyrin arrays,[25,26] reaction of a porphyrin-bearing aldehyde group with dipyrromethane derivatives to afford *p*-phenylene-bridged porphyrin arrays,[27,28] and Suzuki or Sonogashira cross-coupling reactions, have been reported.[29,30] However, these methods can be applied only to homologous porphyrin arrays, and it is difficult to synthesize elaborate porphyrin arrays with a programmable order of each unit. These arrays are not only utilized in biological systems but also are studied for suitability in physical sciences research. Through the programmable synthesis of porphyrin arrays with various ordering of the porphyrin units, these molecules can be utilized in various fields such as self-organization, single-molecule electronics, optical materials, electrical materials, sensors, and fuel cell catalysts.

The application of these molecules to single-molecule electronics has gained much interest[31] because the molecular orbital (MO) levels of the porphyrin unit can be controlled by changing the central metal in each unit. Modification of the MO sequences will modify the single-molecule current−voltage (*I*−*V*) characteristics: for example, Aviram and Ratner[32] reported that the combination of a high highest occupied molecular orbital−lowest unoccupied molecular orbital (HOMO−LUMO, donor) molecule and a low HOMO−LUMO (acceptor) molecule gives rise to a molecular rectifier; this fact was confirmed in several reports.[33−38] Different single-molecule MO sequences can possibly lead to negative differential resistance, switching, or memory functionality.[39−41]

In this study, we aimed to develop an easy method to synthesize a variety of porphyrin arrays with programmed sequences that will enable the investigation of the relationship between the single-molecule *I*−*V* and MO sequences.

Consecutive Suzuki coupling reactions are used for the effective synthesis of elaborate oligoarenes by the repetition of the same reaction in each elongation step.[42,43] The procedure utilizes key compounds that have both nucleophilic (organoboronic acid derivatives) and potential leaving groups (hydroxyl or triflate groups). Consecutive coupling can be performed by varying the reactivity of these nucleophiles or leaving groups. In this study, consecutive Suzuki coupling reactions were applied to synthesize various sequences of porphyrin arrays, as shown in Scheme 1, and their various physical properties were studied.

RESULTS AND DISCUSSION

Synthesis of the Key Monomer Porphyrins 6 and 7. Key porphyrin **6** and terminal porphyrin **7** were synthesized as shown in Scheme 2. Meso-free porphyrin **1** was prepared from dipyrromethane and 3,5-diisopentoxybenzaldehyde in 35% yield.[44] In the first trial, **2-Zn** was prepared in moderate yields[45] by reacting the Zn complex of **1** with a solution of lithium 4-oxidophenyllithium (**R^{1}Li**, Table 1). The **R^{1}Li**

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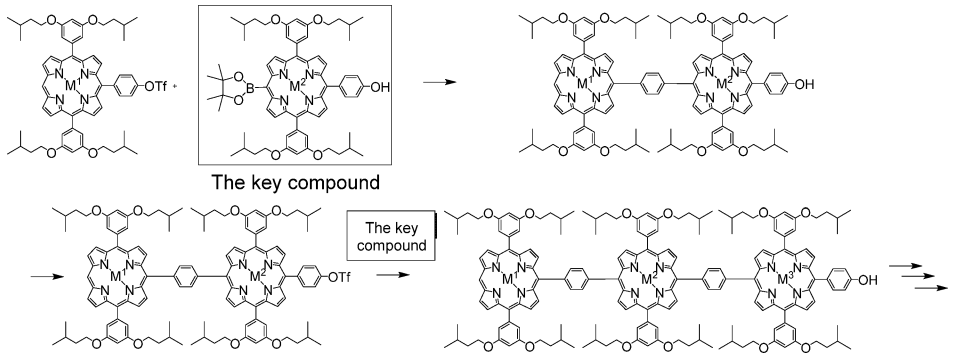
Scheme 1. Synthetic Scheme of Porphyrin Arrays by Consecutive Suzuki Coupling Reactions



Scheme 2. Synthesis of the Key Compound 6 and Terminal Porphyrin 7

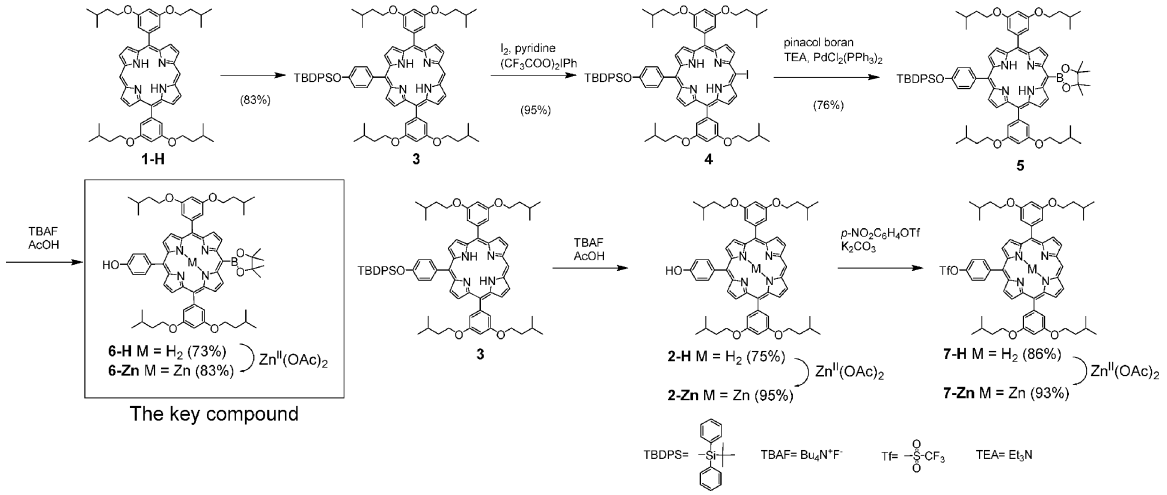
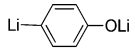
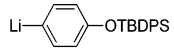


Table 1. Preparation of Phenolated Porphyrins 2-Zn and 3[a]

	meso-free porphyrin (mmol)		lithium reagent[b] (mmol)		method[c]	reaction time (min)	product isolated yield (%)	
1	**1-Zn**	0.21	R^1Li	5.24	A	20	**2-Zn**	71
2	**1-Zn**	0.60	R^1Li	18.1	A	20	**2-Zn**	65
3	**1-Zn**	0.60	R^1Li	17.9	A	20	**2-Zn**	39
4	**1-Zn**	0.65	R^1Li	14.4	A	20	**2-Zn**	18
5	**1-Zn**	1.16	R^1Li	29.2	A	20	**2-Zn**	20
6	**1-Zn**	0.21	R^2Li	1.82	A	160	**3**	trace[d]
7	**1-H**	0.22	R^2Li	1.82	A	420	**3**	13
8	**1-H**	1.24	R^2Li	11.1	B	60	**3**	83

[a]All reactions were performed in THF under dry nitrogen. Detailed reaction conditions are described in the Experimental Section (also, see the Supporting Information).

[b] R^1Li:  R^2Li: 

[c]Method A: the reaction was performed in a flask by modifying the reported conditions.[45] Method B: the reaction was performed using a microreactor. [d]Starting porphyrin **1-Zn** was recovered almost completely.

solution was prepared by the reaction of 4-bromophenol with *n*-butyllithium. However, the reproducibility of the **2-Zn** synthesis was poor, and the yield was reduced when the reaction was performed on a large scale (Table 1, runs 1−5). In the second trial, 4-(*tert*-butyldiphenylsilyl)oxyphenyllithium (R^2Li, Table 1) was used instead of R^1Li, which afforded a poor yield of product **3** (Table 1, runs 6 and 7). In the next trial, a micro flow system[46] was used to control the reaction's heat, and the reaction afforded good scalability. As a result, we succeeded in obtaining a reproducible, good yield (83%) of porphyrin **3** by using the micro flow system with the freebase porphyrin (**1-H**) and R^2Li (Table 1, run 8). Porphyrin **3** was obtained on a gram scale by a one-batch reaction using this method. Iodoporphyrin **4** was prepared by the iodination of **3**[47] followed by substitution with a pinacol borane by a Pd-catalyzed reaction[48] to afford porphyrin **5** in 76% yield. Deprotection of the *tert*-butyldiphenylsilyl (TBDPS) group with tetra-*n*-butylammonium fluoride (TBAF) afforded key

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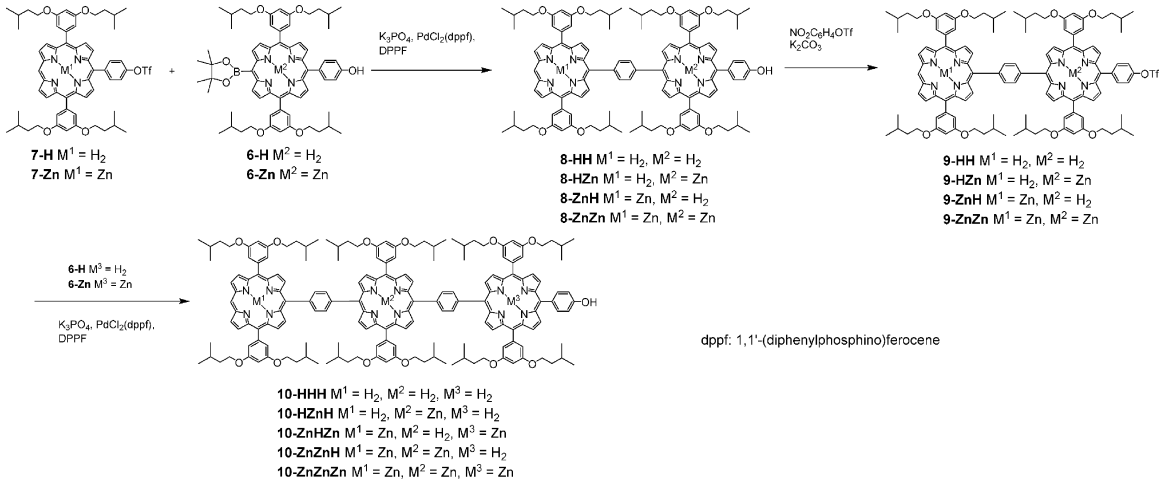
Scheme 3. Consecutive Coupling Reactions Using Key Compound 6



porphyrin **6-H** in 73% yield. A moderate yield (44%) of porphyrin **6-H** was achieved in four steps, and all of the steps can be carried out on a gram scale. Thus, we developed a novel method for the synthesis of key porphyrin **6** for the consecutive coupling reaction of the porphyrin arrays. Porphyrin **7-H**, which bears a triflate group, was prepared from **3** in two steps: (1) deprotection with TBAF and (2) triflation with *p*-nitrophenyltriflate.[49] Zinc acetate was reacted with the free-base porphyrins (**2-H**, **6-H**, and **7-H**) to give the corresponding Zn(II) porphyrin complexes (**2-Zn**, **6-Zn**, and **7-Zn**).

Synthesis of Porphyrin Dimers and Trimers by Consecutive Suzuki Coupling Reactions. The coupling reaction of **6-H** and **7-H** was performed by using $PdCl_2$(dppf) (dppf = 1,1′-bis(diphenylphospino)ferrocene) as the catalyst along with dppf ligand and K_3PO_4 base[50] in THF−H_2O (10:1)[51] at 70 °C for 1 h, as shown in Scheme 3. The reaction afforded dimer **8-HH** in 88% yield after purification by silica-gel column chromatography and gel permeation chromatography (GPC). In the absence of water, the reaction time was longer, and the amount of byproducts increased. As shown in Table 2, starting from common freebase porphyrins **6-H** and **7-H** and Zn(II) porphyrins **6-Zn** and **7-Zn** in various combinations, a series of porphyrin dimers **8-HZn**, **8-ZnH**, and **8-ZnZn** could be obtained in 81, 79, and 85% yields, respectively, under the same conditions as those for **8-HH**.

Table 2. Isolated Yields of Various Sequences of Dimers 8 and 9 and Trimers 10 by Consecutive Suzuki Coupling Reactions[a]

run	triflate	borate	array-OH		array-OTf	
				(%)		(%)
1	**7-H**	**6-H**	**8-HH**	88	**9-HH**	91
2	**7-H**	**6-Zn**	**8-HZn**	81	**9-HZn**	87
3	**7-Zn**	**6-H**	**8-ZnH**	79	**9-ZnH**	99
4	**7-Zn**	**6-Zn**	**8-ZnZn**	85	**9-ZnZn**	95
5	**9-HH**	**6-H**	**10-HHH**	75		
6	**9-HZn**	**6-H**	**10-HZnH**	71		
7	**9-ZnH**	**6-Zn**	**10-ZnHZn**	76		
8	**9-ZnZn**	**6-H**	**10-ZnZnH**	88		
9	**9-ZnZn**	**6-Zn**	**10-ZnZnZn**	70		

[a]The isolated yields were obtained after silica-gel column chromatography and gel permeation chromatography at every step.

Triflation of the hydroxyl groups in **8-HH**, **8-HZn**, **8-ZnH**, and **8-ZnZn** using 4-nitrophenyltriflate gave dimers **9-HH**, **9-HZn**, **9-ZnH** and **9-ZnZn** in sufficiently good yields (87−99%, Table 2). Subsequent coupling of dimer triflate **9** with key porphyrin monomer **6** afforded five different porphyrin trimers, **10-HHH**, **10-HZnH**, **10-ZnHZn**, **10-ZnZnH**, and **10-ZnZnZn**, in 75, 71, 76, 88, and 70% yields, respectively, after the purification by silica-gel column chromatography and GPC (Table 2). All new compounds (**2**−**10**) were characterized by UV−vis absorption, ^{1}H NMR, ^{13}C NMR, infrared (IR) spectroscopy, and high-resolution mass spectrometry (HRMS).

Optical and Electrochemical Properties of the Monomers, Dimers, and Trimers. Optical and electrochemical properties were studied in order to identify the electronic interactions between the porphyrin units within the arrays. The absorption and emission spectra of the dimers and trimers are shown in Figure 1, and the absorption data of compounds **2**, **8**, and **10** in dichloromethane (CH_2Cl_2) are tabulated in Table S1. The Soret bands of the dimers and trimers are split into two peaks because of the exciton coupling. As shown in Table S1, the exciton coupling constants (ΔE) in the dimers were in the order **8-HZn** (619 cm^{-1}), **8-ZnZn** (561 cm^{-1}), **8-HH** (509 cm^{-1}), and **8-ZnH** (506 cm^{-1}), and those in the trimers were in the order **10-HZnH** (997 cm^{-1}), **10-ZnZnZn** (992 cm^{-1}), **10-ZnZnH** (939 cm^{-1}), **10-HHH** (890 cm^{-1}), and **10-ZnHZn** (886 cm^{-1}). However, further experiments are needed for the clear interpretation of the relationship between the array structure and ΔE. The observed Q bands in the dimers and trimers (see solid blue lines in Figure 1) were different from the mathematical summation of the unit monomers (broken blue lines in Figure 1). In all cases, the arrays showed larger molar absorptivity coefficient (ε) values than those of the mathematical summation of the components, which indicated that the asymmetric structures of the arrays perturbed the forbidden Q transitions into more allowed ones.

The emission spectra obtained by exciting the Soret absorption maxima (λ_{max}, ca. 416 nm) of the dimers and trimers are shown in Figure 1 and summarized in Table S1. The optical energy gaps of the porphyrin units are in the order Zn-triarylporphyrin > Zn-tetraarylporphyrin > H_2-triarylporphyrin > H_2-tetraarylporphyrin. In all cases, the emission was observed from the lowest energy gap porphyrin unit, which indicated efficient energy transfer to the lowest energy gap porphyrin unit in the arrays.[30] For example, dimer **8-HH** emits at 719 nm,

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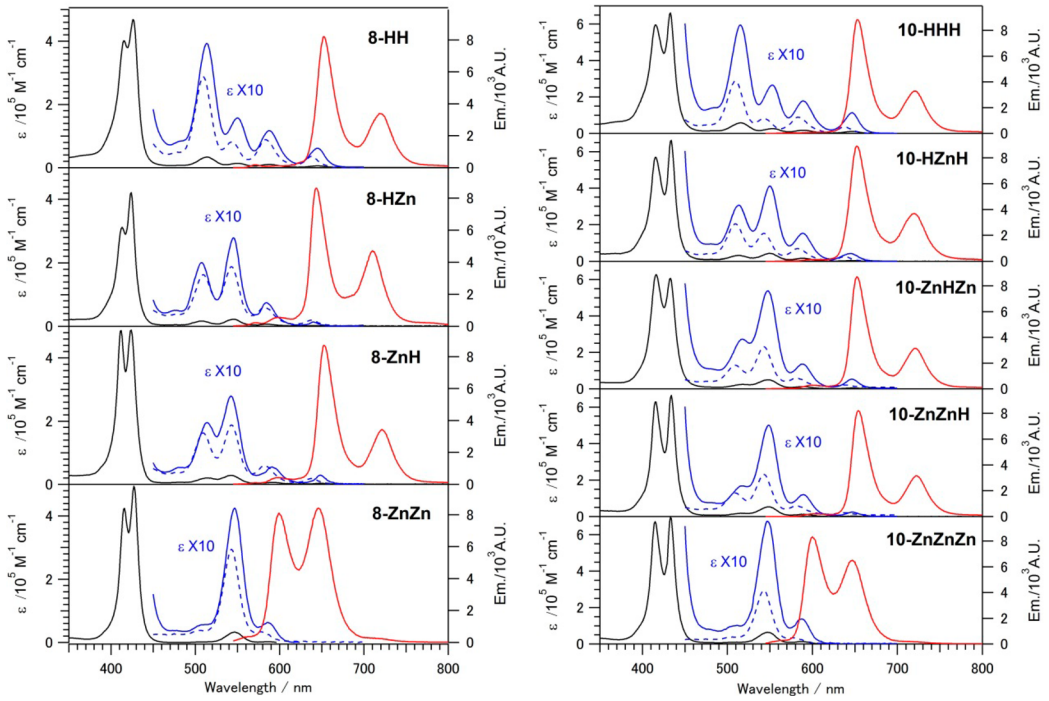

Figure 1. Absorption spectra in dichloromethane (black lines) and emission spectra in toluene (red lines) of dimers **8** (top) and trimers **10** (bottom). The solid blue lines are a magnified view, and the broken blue lines are the summation of each spectrum of the component monomers around the Q region. The left axes denote absorption spectra, and the right axes denote emission spectra.

which is of lower energy than that of monomer **2-H** (711 nm) because the emission is from the H_2-tetraarylporphyrin unit of **8-HH**. Dimer **8-HZn**, which has H_2-triarylporphyrin and Zn-tetraarylporphyrin units, emits at 711 nm, which is similar to the wavelength for monomer **2-H**, indicating that the emission is from the H_2-triarylporphyrin unit. Similar results were observed for trimers: the emission of trimer **10-HZnH** is mostly from the H_2-tetraarylporphyrin unit, and for trimer **10-ZnZnZn**, it is from the Zn-tetraarylporphyrin unit.

The results of the electrochemical measurements of the porphyrin arrays in dry CH_2Cl_2 by differential pulse voltammetry (DPV) using 0.1 M Bu_4NPF_6 as the supporting electrolyte at room temperature under an Ar atmosphere vs the ferrocene/ferricinium couple (Fc/Fc^+) are depicted in Figure 2 and summarized in Table S3.

The **2-H** and **2-Zn** porphyrin monomers exhibited two one-electron oxidation peaks and two one-electron reduction peaks. For the porphyrin arrays with no freebase porphyrin unit, the oxidative peaks appeared at almost the same potentials as those of the monomer, whereas the reductive peaks exhibited lower potentials than those of the monomer. Specifically, porphyrin dimer **8-ZnZn** showed two oxidation peaks at +0.38 and +0.66 V, and porphyrin trimer **10-ZnZnZn** showed two oxidation peaks at +0.36 and +0.67 V, which are similar to those of monomer **2-Zn** (+0.34 and +0.66 V). For reductive peaks, the Zn-arrays (**8-ZnZn**, −2.27, −1.88 V; **10-ZnZnZn**, −1.93 V) showed lower potentials than those of the monomer (**2-Zn**, −2.34, −1.99 V). Different results were obtained for the arrays containing the freebase porphyrin units: the first oxidative peak split into two peaks, whereas the reductive peaks remained at the same potentials as those of the monomer. Thus, dimer **8-HH** showed three oxidative peaks at +0.45, +0.60, and +0.95 V, whereas monomer **2-H** exhibited two oxidative peaks at +0.48 and +0.79 V. Trimer **10-HHH** exhibited potentials similar to

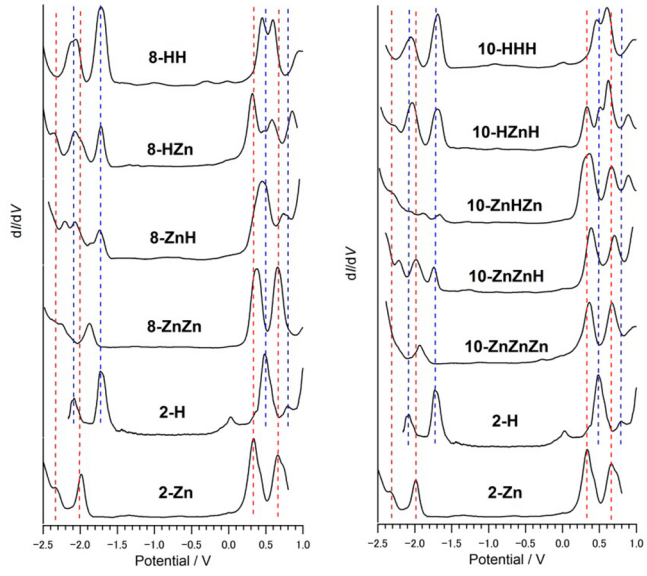

Figure 2. Differential pulse voltammetry of compounds **2**, **8**, and **10** in dichloromethane.

those of dimer **8-HH**. These results are discussed in the next section.

Interaction between Component Units in the Porphyrin Arrays Using DFT Calculations. Optical measurements of the series of porphyrin arrays showed that despite the presence of the exciton coupling between each unit the electronic interaction between the component units was insignificant in the ground state, as observed from the small absorption wavelength shifts in the arrays. These experimental results were also supported by DFT calculations of the porphyrin arrays, as shown in Figure 3. In the array **10′**-

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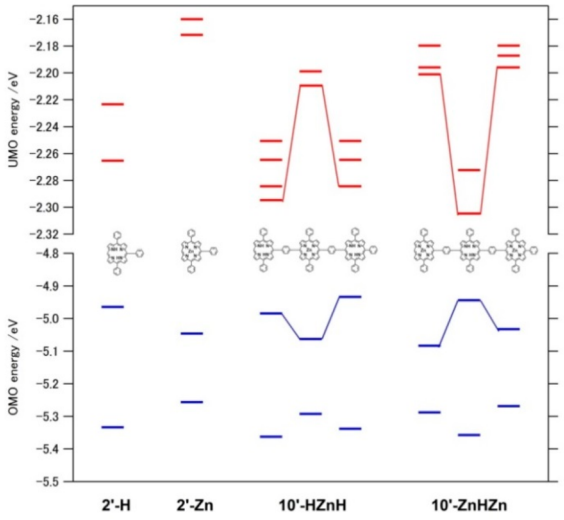

Figure 3. Calculated frontier orbital energies of **2′-H**, **2′-Zn**, **10′-HZnH**, and **10′-ZnHZn** (b3lyp/6-31G). Detailed energies and orbital shapes are shown in Tables S4 (monomers), S5 (dimers), and S6 (trimers) in the Supporting Information.

HZnH, the energies of the frontier orbitals are lower than those of the corresponding model units **2′-H** and **2′-Zn**.

However, the maintenance of electronic independence of each unit generates a zigzag potential in the molecule, i.e., a high−low−-high potential in the HOMO level and a low−high−low potential in the LUMO level. In the array **10′-ZnHZn**, the electronic potential was low−high−low in the HOMO level and high−low−high in the LUMO level. With this potential structure, the central freebase porphyrin can function both as an electron and a hole trap, whereas the two neighboring Zn porphyrin units will function as barriers for the trapped carrier. Since molecules exhibit such complex potential curves, elaborate *I*−*V* curves might be observed in single-molecule electronic measurements.

Electrochemical measurements of the porphyrin arrays showed that each unit interacted in a complex manner. As mentioned above, with the freebase porphyrin arrays (**8-HH** and **10-HHH**), the first oxidative peak split into two peaks, whereas the reductive peaks were similar to those of monomer **2-H**. Contrastingly, in the Zn porphyrin arrays (**8-ZnZn** and **10-ZnZnZn**), the oxidative peaks were similar to those of monomer **2-Zn**, whereas the reductive peaks shifted to lower potentials.

Charge distribution of the cation and anion radicals of the model monomer porphyrins **2′-Zn** and **2′-H** are depicted in Figure 4, as obtained by DFT calculations. As clearly indicated in the **2′-Zn** cation radical, the positive charge is strongly localized on the Zn atom, whereas in the **2′-H** cation radical, it is delocalized around the outer rim of the porphyrin core. For the anion radicals, the negative charge is distributed around the inner part of the porphyrin core in **2′-Zn**, whereas in **2′-H**, it is strongly localized in the center of the molecule. Thus, the differences between the Zn porphyrin arrays and freebase porphyrin arrays can be explained as follows: The cation radical of the freebase porphyrin has its positive charge around the outer rim of the porphyrin core. Hence, Coulombic repulsion with the neighboring porphyrin units will be large, which increases the second oxidation potential above the first oxidation potential. In contrast, for the Zn porphyrin arrays, the positive charge localizes on the central Zn atom. Hence, the

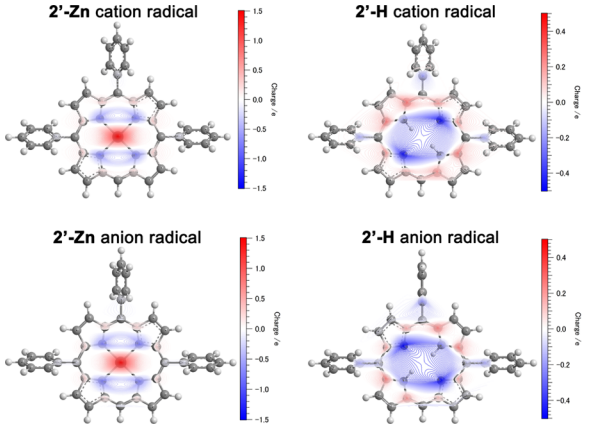

Figure 4. Charge distribution of the cation radicals of **2′-Zn** (upper left) and **2′-H** (upper right) and anion radicals of **2′-Zn** (lower left) and **2′-H** (lower right) calculated by ub3lyp/6-311G(d, p) with full structural optimization. Red color denotes positive charge, and blue color denotes negative charge.

repulsion with the neighboring units will be minimal, which leads to the similarity of the first and second oxidation potentials. For the reductive peaks, the negative charge of the anion radicals in both Zn and freebase porphyrins are within the inner core of the porphyrin units. Hence, the repulsive interaction between the neighboring units will be minimal, which makes the second reductive peaks similar to those of the monomers.

■ CONCLUSIONS

In this study, we established a synthetic method for a series of porphyrin arrays with various ordering of the component units by using the same key compound under the same reaction conditions. In the near future, the proposed method can be applied for the automated synthesis of DNA or protein.

Although the porphyrin arrays synthesized by this method exhibit various strengths of exciton coupling, minimal electronic interactions were observed between each unit in the ground state. The electrochemical studies reveal that the interactions between the units of charged species are strongly dependent on the order of the units within the arrays. In general, the oxidized state of the freebase porphyrins can have strong Coulombic interaction with the neighboring porphyrin units, whereas the same does not hold true for Zn porphyrins. This knowledge is important for the design of single-molecule devices using porphyrin units because the porphyrin arrays that are longer than trimers exhibit the hopping conduction mechanism.[14,52] In this mechanism, the charges remain on the molecule and hence the electric conduction properties can be controlled by the charge interaction between each component unit. Single-molecule conduction experiments of the synthesized molecules are in progress.

■ EXPERIMENTAL SECTION

General. The experiments with moisture- or air-sensitive compounds were performed in anhydrous solvents under a nitrogen atmosphere in well-dried glassware. All reactions using porphyrin were performed under dark conditions. THF and CH_2Cl_2 were dried and distilled over calcium hydride. Hexane, $CHCl_3$, 1,2-dichloroethane, and DMF were stored over molecular sieves 4Å. Porphyrin **1**[44] and 1-((*tert*-butyldiphenylsilyl)oxy)-4-bromobenzene[53] were synthesized according to literature procedures. All other chemicals were of reagent grade and used without further purification. Column chromatography

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was performed with silica-gel (spherical, neutral, 63−200 μm, Kishida Chemical Co., Ltd.). GPC was performed with Bio-Beads S-X1 (Bio-Rad Laboratories). A T-shaped microreactor (YMC-P-0022) with an inner diameter (φ) of 500 μm was purchased from YMC Co., Ltd.

Chemical shifts are quoted in ppm and referenced to the signals of tetramethylsilane (TMS) and $CHCl_3$, which were used as the internal standards. IR spectra were recorded with KBr pellets. Electrochemical experiments were performed using a conventional three-electrode cell, which consisted of a glassy carbon working electrode, a platinum wire counter electrode, and a Ag/Ag^+ reference electrode. All experiments were performed in dry CH_2Cl_2 with 0.1 M Bu_4NPF_6 as the supporting electrolyte. All potentials obtained in this study were experimentally referenced against the Ag/Ag^+ couple but were manipulated to be referenced against the Fc/Fc^+ couple.

Synthesis of Compounds. 5-(4-(*tert*-Butyldiphenylsilyoxy)-phenyl)-10,20-bis(3,5-diisopentoxyphenyl)porphyrin (3). A solution of 1-(*tert*-butyldiphenylsilyloxy)-4-bromobenzene (0.2 M, 56 mL) in dry THF (flow rate =1.8 mL min^{-1}) and a solution of *n*-BuLi (0.2 M, 56 mL) in hexane (flow rate = 1.8 mL min^{-1}) were introduced into a T-shaped microreactor (φ = 500 μm). The resulting solution was passed through Teflon tube (450 cm, φ = 500 μm) and added dropwise to porphyrin **1** (997 mg, 1.24 mmol) in THF (77 mL) at 0 °C. After addition, the cold bath was removed, and the mixture was stirred for 1.5 h at room temperature, followed by quenching with THF/H_2O (1:1, 20 mL) and the addition of *p*-chloranil (1.27 g, 5.17 mmol). The obtained solution was washed with water and brine and dried with Na_2SO_4. The organic solvent was evaporated, and the residue was purified by column chromatography (silica-gel, $CHCl_3$/hexane = 2:1) to afford 1.17 g of **3** in 83% yield.

^1H NMR (500 MHz, $CDCl_3$) δ 10.15 (s, 1H), 9.29 (d, J = 4.6 Hz, 2H), 9.14 (d, J = 4.6 Hz, 2H), 9.04 (d, J = 4.7 Hz, 2H), 8.85 (d, J = 4.9 Hz, 2H), 7.99−7.94 (m, 6H), 7.58−7.52 (m, 6H), 7.44 (d, J = 2.1 Hz, 4H), 7.20−7.18 (m, 2H), 6.95 (t, J = 2.2 Hz, 2H), 4.15 (t, J = 6.7 Hz, 8H), 1.87 (m, J = 6.7 Hz, 4H), 1.75 (q, J = 7.0 Hz, 8H), 1.33 (s, 9H), 0.96 (d, J = 6.5 Hz, 24H), −3.0 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.5, 155.6, 146.4, 143.6, 135.8, 135.5, 135.3, 133.1, 131.4, 131.1, 130.6, 130.1, 127.9, 120.5, 119.5, 118.2, 114.5, 104.5, 101.1, 66.8, 38.2, 26.7, 25.1, 22.7, 19.7; UV−vis (CH_2Cl_2) λ_{max} = 415, 510, 544, 583, 638 nm; FTIR (KBr, thin film) 3310, 2955, 1590, 1166, 923 cm^{-1}; HRMS (ESI) m/z for $C_{74}H_{84}N_4O_5Si$ $[M + H]^+$ calcd, 1137.6284; found, 1137.6297.

10-(4-Hydroxyphenyl)-5,15-bis(3,5-diisopentoxyphenyl)-porphyrin (2-H). Porphyrin **3** (213.9 mg, 0.188 mmol) was dissolved in $CHCl_3$ (35 mL) and TBAF (1.0 M in THF, 0.4 mL, 0.4 mmol) followed by the addition of 5.4 μL (0.094 mmol) of acetic acid. The mixture was stirred for 1 h at room temperature, following which it washed with water and brine and dried with Na_2SO_4. The organic solvent was evaporated, and the residue was purified by column chromatography (silica, CH_2Cl_2) to afford 127 mg of **2-H** in 75% yield.

^1H NMR (500 MHz, $CDCl_3$) δ 10.14 (s, 1H), 9.28 (d, J = 4.6 Hz, 2H), 9.14 (d, J = 4.6 Hz, 2H), 9.03 (d, J = 4.6 Hz, 2H), 8.85 (d, J = 4.7 Hz, 2H), 7.94 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 2.3 Hz, 4H), 6.92 (t, J = 2.3 Hz, 2H), 6.86 (d, J = 8.4 Hz, 2H), 4.15 (t, J = 6.7 Hz, 8H), 1.87 (m, J = 6.7 Hz, 4H), 1.75 (q, J = 7.0 Hz, 8H), 0.96 (d, J = 6.5 Hz, 24H), −3.00 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.4, 155.2, 146.5, 135.5, 134.8, 131.5, 131.2, 130.7, 120.3, 119.5, 114.5, 113.4, 104.6, 101.1, 66.8, 38.1, 25.1, 22.6; UV−vis (CH_2Cl_2) λ_{max} = 415, 510, 543, 583, 638 nm; FTIR (KBr, thin film) 3311, 2955, 1590, 1167 cm^{-1}; HRMS (ESI) m/z for $C_{58}H_{66}N_4O_5$ $[M + H]^+$ calcd, 899.5060; found, 899.5114.

5-(4-(*tert*-Butyldiphenylsilyoxy)phenyl)-15-iodo-10,20-bis-(3,5-diisopentoxyphenyl)porphyrin (4). Porphyrin **3** (2.00 g, 1.76 mmol) was dissolved in $CHCl_3$ (1.4 L). Iodine (675 mg, 2.66 mmol) and pyridine (2.6 mL, 2.6 mmol) were added, followed by 757 mg (1.76 mmol) of (bis(trifluoroacetoxy)iodo)benzene. The mixture was stirred for 2 h at room temperature and was washed with saturated sodium thiosulfate solution. The organic solvent was evaporated, and the residue was purified by column chromatography (silica-gel, CH_2Cl_2/hexane = 1:1) to afford 2.12 g of **4** in 95% yield.

^1H NMR (500 MHz, $CDCl_3$) δ 9.61 (d, J = 4.7 Hz, 2H), 8.99 (d, J = 4.9 Hz, 2H), 8.92 (d, J = 4.9 Hz, 2H), 8.76 (d, J = 4.9 Hz, 2H), 7.95−7.93 (m, 4H), 7.91 (d, J = 8.6 Hz, 2H), 7.53−7.48 (m, 6H), 7.37 (d, J = 2.1 Hz, 4H), 7.16 (d, J = 8.4 Hz, 2H), 6.92 (t, J = 2.1 Hz, 2H), 4.15 (t, J = 6.7 Hz, 8H), 1.89 (m, J = 6.8 Hz, 4H), 1.76 (q, J = 6.8 Hz, 8H), 1.29 (s, 9H), 0.96 (d, J = 6.7 Hz, 24H), −2.71 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.4, 155.8, 143.7, 135.8, 135.3, 134.6, 133.0 131.5, 130.1, 127.9, 121.2, 120.8, 118.4, 114.5, 101.2, 78.2, 66. 8, 38.1, 26.7, 25.1, 22.8, 19.7; UV−vis (CH_2Cl_2) λ_{max} = 426, 521, 557, 597, 653 nm; FTIR (KBr, thin film) 3317, 2954, 1589, 1167, 922 cm^{-1}; HRMS (ESI) m/z for $C_{74}H_{83}IN_4O_5Si$ $[M + H]^+$ calcd, 1263.5250; found, 1263.5274.

5-(4-(*tert*-Butyldiphenylsilyoxyphenyl)-10,20-bis(3,5-diiso-pentoxyphenyl)-15-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)porphyrin (5). A 100 mL Schlenk flask was charged with porphyrin **4** (494 mg, 0.391 mmol), pinacolborane (1.7 mL, 11 mmol), triethylamine (1.6 mL, 11 mmol), bis(triphenylphosphine)-palladium(II) dichloride (5.5 mg, 0.008 mmol), and 50 mL of 1,2-dichloroethane. The mixture was stirred at 90 °C for 15 h. The reaction was quenched with MeOH, and the mixture was washed with water and brine and dried with Na_2SO_4. The organic solvent was evaporated, and the residue was purified by column chromatography (silica-gel, CH_2Cl_2/hexane = 2:1) to afford 367 mg of **5** in 74% yield.

^1H NMR (500 MHz, $CDCl_3$) δ 9.84 (d, J = 4.7 Hz, 2H), 9.10 (d, J = 4.6 Hz, 2H), 8.94 (d, J = 4.9 Hz, 2H), 8.80 (d, J = 4.7 Hz, 2H), 7.95−7.92 (m, 6H), 7.54−7.48 (m, 6H), 7.40 (d, J = 2.1 Hz, 4H), 7.17 (d, J = 8.4 Hz, 2H), 6.92 (t, J = 2.2 Hz, 2H), 4.17 (t, J = 6.7 Hz, 8H), 1.90 (m, J = 6.7 Hz, 4H), 1.81 (s, 12H), 1.78 (q, J = 6.8 Hz, 8H), 1.29 (s, 9H), 0.99 (d, J = 6.6 Hz, 24H), −2.79 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.3, 155.7, 144.2, 135.8, 135.3, 134.9, 133.0, 132.1, 130.8, 130.1, 127.9, 121.7, 119.9, 118.3, 114.4, 101.1, 85.2, 66.8, 38.2, 26.7, 25.3, 25.2, 22.7, 19.7; UV−vis (CH_2Cl_2) λ_{max} = 420, 515, 549, 588, 642 nm; FTIR (KBr, thin film) 3314, 2956, 1590, 1167, 922 cm^{-1}; HRMS (ESI) m/z for $C_{80}H_{95}BN_4O_7Si$ $[M + H]^+$ calcd, 1263.7149; found, 1263.7159.

5-(4-(*tert*-Butyldiphenylsilyloxy)phenyl)-10,20-bis(3,5-diiso-pentoxyphenyl)-15-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)porphyrin (6-H). Porphyrin **5** (404 mg, 0.320 mmol) was dissolved in $CHCl_3$ (64 mL) and TBAF (1.0 M in THF, 0.6 mL, 0.6 mmol), and acetic acid (0.004 mL, 0.063 mmol) was added. The mixture was stirred for 1 h at room temperature, following which it was washed with water and brine and dried with Na_2SO_4. The organic solvent was evaporated, and the residue was purified by column chromatography (silica, CH_2Cl_2) to afford 239 mg of **6-H** in 73% yield.

^1H NMR (500 MHz, $CDCl_3$) δ 9.85 (d, J = 4.7 Hz, 2H), 9.11 (d, J = 4.7 Hz, 2H), 8.93 (d, J = 4.6 Hz, 2H), 8.80 (d, J = 4.7 Hz, 2H), 7.90 (d, J = 7.6 Hz, 2H), 7.40 (d, J = 2.1 Hz, 4H), 6.91 (t, J = 2.1 Hz, 2H), 6.83 (d, J = 7.3 Hz, 2H), 4.15 (t, J = 6.8 Hz, 8H), 1.87 (m, J = 6.7 Hz, 4H), 1.80 (s, 12H), 1.75 (q, J = 6.7 Hz, 8H), 0.96 (d, J = 6.6 Hz, 24H), −2.77 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.3, 155.4, 144.1, 135.5, 134.2, 132.1, 130.9, 121.6, 119.9, 114.5, 113.5, 101.2, 85.2, 66.8, 38.1, 25.3, 25.1, 22.7; UV−vis (CH_2Cl_2) λ_{max} = 419, 515, 548, 588, 642 nm; FTIR (KBr, thin film) 3314, 2955, 1589, 1168 cm^{-1}; HRMS (ESI) m/z for $C_{64}H_{77}BN_4O_7$ $[M + H]^+$ calcd, 1025.5969; found, 1025.5985.

General Procedure for Triflation of the Porphyrin with Hydroxyl Group. The porphyrin (1 equiv), K_2CO_3 (10 equiv), and 4-nitrophenyltriflate (5 equiv) were dissolved in DMF. The mixture was stirred for 5 h at room temperature, washed with water and brine, and dried with Na_2SO_4. The organic solvent was evaporated, and the residue was purified by column chromatography (silica-gel, CH_2Cl_2/hexane = 1:1).

5,15-Bis(3,5-diisopentoxyphenyl)-10-(4-(trifluoromethane-sulfonyloxy)phenyl)porphyrin (7-H). Porphyrin **2-H** (523 mg, 0.582 mmol), K_2CO_3 (805 mg, 5.82 mmol), and 4-nitrophenyltriflate (790 mg, 2.91 mmol) were reacted by the general triflation procedure, which afforded 590 mg of porphyrin **7-H** in 98% yield.

^1H NMR (500 MHz, $CDCl_3$) δ 10.23 (s, 1H), 9.34 (d, J = 4.6 Hz, 2H), 9.14 (d, J = 4.6 Hz, 2H), 9.05 (d, J = 4.7 Hz, 2H), 8.76 (d, J = 4.7

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Hz, 2H), 8.29 (d, J = 8.7 Hz, 2H), 7.68 (d, J = 8.6 Hz, 2H), 7.39 (d, J = 2.1 Hz, 4H), 6.91 (t, J = 2.2 Hz, 2H), 4.05 (t, J = 6.7 Hz, 8H), 1.89 (m, J = 6.7 Hz, 4H), 1.78 (q, J = 6.7 Hz, 8H), 0.98 (d, J = 6.7 Hz, 24H), −3.06 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.5, 149.5, 147.0, 145.7, 143.3, 143.2, 135.8, 131.7, 131.5, 131.3, 130.7, 120.3, 119.9, 119.5, 117.7, 117.5, 114.6, 105.2, 101.1, 66.8, 38.1, 25.1, 22.7; UV−vis (CH_2Cl_2) λ_{max} = 414, 509, 542, 583, 637 nm; FTIR (KBr, thin film) 3311, 2956, 1589, 1211, 1164, 1139, 922 cm^{-1}; HRMS (ESI) m/z for $C_{59}H_{65}F_3N_4O_7S$ $[M + H]^+$ calcd, 1031.4599; found, 1031.4609.

General Procedure for the Metalation of Freebase Porphyrins with Zinc Acetate. Freebase porphyrin (50 mg, 0.05 mmol) was dissolved in 20 mL of $CHCl_3$ and 5 mL of MeOH, 0.3 g of zinc(II) acetate was added, and the mixture was stirred for 2 h at room temperature. It was then washed with water and brine and dried with Na_2SO_4. The organic solvent was evaporated, and the residue was purified by column chromatography (silica-gel, CH_2Cl_2).

(10-(4-Hydroxyphenyl)-5,15-bis(3,5-diisopentoxyphenyl)-porphyrinato)zinc(II) (2-Zn). Porphyrin **2-H** (50 mg, 0.056 mmol) in $CHCl_3$ (20 mL) and zinc(II) acetate (240 mg, 1.09 mmol) in MeOH (6 mL) were reacted by the general metalation procedure, which afforded 51 mg of porphyrin **2-Zn** in 95% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.12 (s, 1H), 9.31 (d, J = 4.4 Hz, 2H), 9.17 (d, J = 4.4 Hz, 2H), 9.10 (d, J = 4.6 Hz, 2H), 8.96 (d, J = 4.6 Hz, 2H), 7.97 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 2.1 Hz, 4H), 6.89 (d, J = 8.2 Hz, 2H), 6.80 (t, J = 2.2 Hz, 2H), 4.08 (t, J = 6.8 Hz, 8H), 1.83 (m, J = 6.7 Hz, 4H), 1.70 (q, J = 6.8 Hz, 8H), 0.93 (d, J = 6.6 Hz, 24H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.2, 155.0, 150.2, 149.92, 149.88, 149.8, 144.6, 135.4, 132.6, 131.9, 131.8, 131.6, 121.1, 120.3, 114.6, 113.3, 102.5, 101.1, 66.8, 38.1, 25.1, 22.6; UV−vis (CH_2Cl_2) λ_{max} = 416, 543, 577 nm; FTIR (KBr, thin film) 2956, 1590, 1167, 998 cm^{-1}; HRMS (ESI) m/z for $C_{58}H_{64}N_4O_5Zn$ $[M + H]^+$ calcd 961.4241, found 961.4237.

(5-(4-Hydroxyphenyl)-10,20-bis(3,5-diisopentoxyphenyl)-15-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)porphyrinato)zinc(II) (6-Zn). Porphyrin **6-H** (60 mg, 0.059 mmol) in $CHCl_3$ (21 mL) and zinc(II) acetate (260 mg, 1.18 mmol) in MeOH (6 mL) were reacted by the general metalation procedure, which afforded 53 mg of porphyrin **6-Zn** in 83% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.89 (d, J = 4.7 Hz, 2H), 9.19 (d, J = 4.7 Hz, 2H), 9.04 (d, J = 4.6 Hz, 2H), 8.95 (d, J = 4.6 Hz, 2H), 8.03 (d, J = 8.2 Hz, 2H), 7.38 (d, J = 2.3 Hz, 4H), 7.13 (d, J = 8.3 Hz, 2H), 6.88 (t, J = 2.2 Hz, 2H), 4.14 (t, J = 6.8 Hz, 8H), 1.87 (m, J = 6.7 Hz, 4H), 1.85 (s, 12H), 1.75 (q, J = 6.8 Hz, 8H), 0.97 (d, J = 6.6 Hz, 24H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.1, 154.9, 154.5, 150.1, 149.69, 149.68, 144.7, 135.3, 135.2, 133.0, 132.7, 132.1, 131.5, 122.2, 120.8, 101.2, 85.2, 66.8, 38.1, 25.3, 25.1, 22.6; UV−vis (CH_2Cl_2) λ_{max} = 419, 547, 582 nm; FTIR (KBr, thin film) 2956, 1588, 1167, 1000 cm^{-1}; HRMS (ESI) m/z for $C_{64}H_{75}BN_4O_7Zn$ $[M + H]^+$ calcd, 1087.5093; found, 1087.5104.

(5,15-Bis(3,5-diisopentoxyphenyl)-10-(4-(trifluoromethanesulfonyloxy)phenyl)porphyrinato)zinc(II) (7-Zn). Porphyrin **7-H** (58 mg, 0.056 mmol) in $CHCl_3$ (20 mL) and zinc(II) acetate (285 mg, 1.30 mmol) in MeOH (5 mL) were reacted by the general metalation procedure, which afforded 57 mg of porphyrin **7-Zn** in 93% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.01 (s, 1H), 9.27 (d, J = 4.6 Hz, 2H), 9.13 (d, J = 4.4 Hz, 2H), 9.12 (d, J = 4.7 Hz, 2H), 8.86 (d, J = 4.6 Hz, 2H), 8.28 (d, J = 8.6 Hz, 2H), 7.66 (d, J = 8.6 Hz, 2H), 7.31 (d, J = 2.1 Hz, 4H), 6.75 (t, J = 2.2 Hz, 2H), 4.05 (t, J = 6.8 Hz, 8H), 1.83 (m, J = 6.7 Hz, 4H), 1.70 (q, J = 6.8 Hz, 8H), 0.95 (d, J = 6.6 Hz, 24H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.1, 150.1, 149.94, 149.92, 149.4, 149.3, 144.2, 143.6, 135.7, 132.8, 132.4, 131.8, 131.2, 122.9, 120.7, 120.3, 119.4, 118.5, 117.7, 115.3, 114.6, 106.1, 101.0, 66.8, 38.1, 25.1, 22.6; UV−vis (CH_2Cl_2) λ_{max} = 415. 542, 577 nm; FTIR (KBr, thin film) 2956, 1588, 1212, 1164, 1140, 997 cm^{-1}; HRMS (ESI) m/z for $C_{59}H_{63}F_3N_4O_7SZn$ $[M + H]^+$ calcd, 1093.3734; found, 1093.3749.

General Procedure for Suzuki Coupling for Dimer Porphyrins. Porphyrin **7** (1 equiv), porphyrin **6** (1.2 equiv), K_3PO_4 (5 equiv), $PdCl_2$ (dppf) (0.5 equiv), and dppf (0.4 equiv) were dissolved in THF/H_2O (10:1). The mixture was stirred for 1 h at 70 °C, washed with water and brine, and dried with Na_2SO_4. The organic solvent was evaporated, and the residue was purified by column chromatography (silica-gel,, CH_2Cl_2) and GPC (Bio-Beads S-X beads, THF).

Freebase−Freebase Porphyrin Dimer (8-HH). Porphyrin **7-H** (17 mg, 0.017 mmol), porphyrin **6-H** (20 mg, 0.019 mmol), K_3PO_4 (16 mg, 0.075 mmol), $PdCl_2$(dppf) (6 mg, 0.007 mmol), and dppf (4 mg, 0.007 mmol) in THF/H_2O (10:1, 0.3 mL) were reacted by the general Suzuki coupling procedure for dimers, which afforded 26 mg of porphyrin dimer **8-HH** in 88% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.22 (s, 1H), 9.37−9.34 (m, 6H), 9.27 (d, J = 4.6 Hz, 2H), 9.22 (d, J = 4.4 Hz, 4H), 9.06 (d, J = 4.6 Hz, 2H), 8.90 (d, J = 4.6 Hz, 2H), 8.65 (s, 4H), 8.04 (d, J = 8.3 Hz, 2H), 7.53 (d, J = 2.1 Hz, 4H), 7.51 (d, J = 2.1 Hz, 4H), 7.03 (d, J = 8.3 Hz, 2H), 6.98 (t, J = 2.2 Hz, 2H), 6.97 (t, J = 2.2 Hz, 2H), 4.25−4.20 (m, 16H), 1.96−1.89 (m, 8H), 1.84−1.78 (m, 16H), 1.02 (d, J = 6.7 Hz, 24H), 1.00 (d, J = 6.6 Hz, 24H), −2.60 (s, 2H), −2.84 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.5, 158.4, 155.4, 146.5, 144.0, 143.6, 142.1, 141.7, 135.6, 134.6, 132.9, 132.8, 131.5, 131.2, 120.3, 120.2, 120.1, 119.8, 119.6, 114.63, 114.57, 113.6, 104.9, 101.19 101.15, 66.8, 38.17, 38.15, 25.16, 25.15, 22.69, 22.68; UV−vis (CH_2Cl_2) λ_{max} = 415, 426, 514, 550, 588, 645 nm; FTIR (KBr, thin film) 3312, 2954, 1589, 1166 cm^{-1}; HRMS (ESI) m/z for $C_{116}H_{130}N_8O_9$ $[M + 2H]^{2+}$ calcd, 890.5053; found, 890.5068.

Freebase−Zn Porphyrin Dimer (8-HZn). Porphyrin **7-H** (23 mg, 0.022 mmol), porphyrin **6-Zn** (30 mg, 0.028 mmol), K_3PO_4 (23 mg, 0.108 mmol), $PdCl_2$(dppf) (9 mg, 0.011 mmol), and dppf (6 mg, 0.011 mmol) in THF/H_2O (10:1, 0.5 mL) were reacted by the general Suzuki coupling procedure for dimers, which afforded 34 mg of porphyrin dimer **8-HZn** in 81% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.24 (s, 1H), 9.43 (d, J = 4.6 Hz, 2H), 9.38 (d, J = 4.7 Hz, 2H), 9.36 (d, J = 4.4 Hz, 2H), 9.29 (d, J = 4.6 Hz, 2H), 9.25 (d, J = 4.6 Hz, 2H), 9.21 (d, J = 4.4 Hz, 2H), 9.14 (d, J = 4.6 Hz, 2H), 9.01 (d, J = 4.6 Hz, 2H), 8.64 (s, 4H), 8.07 (d, J = 8.3 Hz, 2H), 7.50 (d, J = 2.1 Hz, 4H), 7.48 (d, J = 2.3 Hz, 4H), 7.07 (d, J = 8.2 Hz, 2H), 6.94 (t, J = 2.2 Hz, 2H), 6.90 (t, J = 2.2 Hz, 2H), 4.21 (t, J = 6.7 Hz, 8H), 4.16 (t, J = 6.7 Hz, 8H), 1.95−1.85 (m, 8H), 1.83−1.75 (m, 16H), 1.01 (d, J = 6.6 Hz, 24H), 0.98 (d, J = 6.7 Hz, 24H), −2.85 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.5, 158.2, 155.2, 150.7, 150.4, 150.11, 150.09, 144.6, 143.5, 142.4, 141.8, 135.5, 135.4, 132.8, 132.7, 132.4, 132.1, 132.04, 131.97, 131.6, 131.2, 121.2, 120.9, 120.6, 120.4, 119.8, 114.6, 114.5, 113.5, 104.9, 101.2, 101.1, 66.84, 66.82, 38.2, 38.1, 25.16, 25.15, 22.69, 22.67; UV−vis (CH_2Cl_2) λ_{max} = 416, 428, 511, 550, 587, 638 nm; FTIR (KBr, thin film) 3310, 2955, 1589, 1166, 999 cm^{-1}; HRMS (ESI) m/z for $C_{116}H_{128}N_8O_9Zn$ $[M + 2H]^{2+}$ calcd, 921.4621; found, 921.4628.

Zn−Freebase Porphyrin Dimer (8-ZnH). Porphyrin **7-Zn** (18 mg, 0.016 mmol), porphyrin **6-H** (20 mg, 0.019 mmol), K_3PO_4 (16 mg, 0.077 mmol), $PdCl_2$(dppf) (7 mg, 0.008 mmol), and dppf (4 mg, 0.008 mmol) in THF/H_2O (10:1, 0.3 mL) were reacted by the general Suzuki coupling procedure for dimers, which afforded 24 mg of porphyrin dimer **8-ZnH** in 79% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.18 (s, 1H), 9.49 (d, J = 4.4 Hz, 2H), 9.38−9.36 (m, 6H), 9.27 (d, J = 4.3 Hz, 2H), 9.22 (d, J = 4.4 Hz, 2H), 9.06 (d, J = 4.4 Hz, 2H), 8.91 (d, J = 4.3 Hz, 2H), 8.69−8.65 (m, 4H), 8.03 (d, J = 7.7 Hz, 2H), 7.51 (d, J = 2.0 Hz, 4H), 7.49 (d, J = 2.0 Hz, 4H), 6.91 (m, 6H), 4.18 (m, 16H), 1.94−1.86 (m, 8H), 1.78 (q, J = 6.7 Hz, 16H), 1.00 (d, J = 6.6 Hz, 48H), −2.58 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.32, 158.28, 155.2, 150.10, 150.05, 150.01, 149.98, 144.5, 144.0, 142.5, 141.5, 135.6, 134.5 132.9 132.8, 132.3, 132.1, 131.8, 131.2, 121.1, 120.7, 120.2 120.0, 119.8, 114.61, 114.60, 113.6, 105.9, 101.2, 101.1, 66.8, 38.12, 38.11, 25.14, 25.13, 22.7; UV−vis (CH_2Cl_2) λ_{max} = 417, 428, 518, 545, 590, 647 nm; FTIR (KBr, thin film) 3317, 2955, 1589, 1166, 997 cm^{-1}; HRMS (ESI) m/z for $C_{116}H_{128}N_8O_9Zn$ $[M + 2H]^{2+}$ calcd, 921.4621; found, 921.4629.

Zn−Zn Porphyrin Dimer (8-ZnZn). Porphyrin **7-Zn** (20 mg, 0.018 mmol), porphyrin **6-Zn** (25 mg, 0.023 mmol), K_3PO_4 (20 mg, 0.094 mmol), $PdCl_2$(dppf) (7 mg, 0.009 mmol), and dppf (5 mg, 0.009 mmol) in THF/H_2O (10:1, 0.4 mL) were reacted by the general Suzuki coupling procedure for dimers, which afforded 29 mg of porphyrin dimer **8-ZnZn** in 85% yield.

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^{1}H NMR (500 MHz, $CDCl_3$) δ 10.19 (s, 1H), 9.50 (d, J = 4.6 Hz, 2H), 9.47 (d, J = 4.6 Hz, 2H), 9.37 (d, J = 4.4 Hz, 2H), 9.34 (d, J = 4.6 Hz, 2H), 9.29 (d, J = 4.6 Hz, 2H), 9.24 (d, J = 4.3 Hz, 2H), 9.12 (d, J = 4.6 Hz, 2H), 9.01 (d, J = 4.6 Hz, 2H), 8.65 (s, 4H), 8.05 (d, J = 8.4 Hz, 2H), 7.44 (d, J = 2.3 Hz, 4H), 7.41 (d, J = 2.3 Hz, 4H), 6.97 (d, J = 8.3 Hz, 2H), 6.79 (t, J = 1.9 Hz, 2H), 6.74 (t, J = 1.7 Hz, 2H), 4.10 (t, J = 6.7 Hz, 8H), 4.06 (t, J = 6.8 Hz, 8H), 1.91−1.80 (m, 8H), 1.76−1.68 (m, 16H), 0.98 (d, J = 6.7 Hz, 24H), 0.96 (d, J = 6.6 Hz, 24H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.2, 158.1, 155.1, 150.7, 150.5, 150.14, 150.12, 150.08, 144.6, 144.5, 142.3, 142.2, 135.5, 135.4, 132.8, 132.72, 132.65, 132.4, 132.3, 132.12, 132.05, 131.8, 121.3, 121.2, 120.9, 120.8, 120.7, 114.7, 114.6, 113.5, 105.9, 101.3, 101.2, 66.9, 38.2, 38.1, 25.18, 25.16, 22.69, 22.67; UV−vis (CH_2Cl_2) λ_{max} = 416, 427, 546, 586 nm; FTIR (KBr, thin film) 2955, 1589, 1166, 999 cm^{-1}; HRMS (ESI) m/z for $C_{116}H_{126}N_8O_9Zn_2$ $[M + 2H]^{2+}$ calcd, 952.4202; found, 952.4188.

Freebase−Freebase Porphyrin Dimer Triflate (9-HH). Porphyrin dimer **8-HH** (52 mg, 0.029 mmol), K_2CO_3 (41 mg, 0.30 mmol), and 4-nitrophenyltriflate (40 mg, 0.15 mmol) were reacted by the general triflation procedure, which afforded 51 mg of porphyrin dimer **9-HH** in 91% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.22 (s, 1H), 9.35 (d, J = 4.4 Hz, 6H), 9.26 (d, J = 4.6 Hz, 2H), 9.22 (m, 4H), 9.10 (d, J = 4.6 Hz, 2H), 8.81 (d, J = 4.6 Hz, 2H), 8.64 (s, 4H), 8.35 (d, J = 8.3 Hz, 2H), 7.72 (d, J = 8.3 Hz, 2H), 7.52 (d, J = 2.0 Hz, 4H), 7.50 (d, J = 2.0 Hz, 2H), 6.98−6.97 (m, 4H), 4.23 (q, J = 6.6 Hz, 16H), 1.97−1.90 (m, 8H), 1.84−1.79 (m, 16H), 1.02 (d, J = 6.7 Hz, 24H), 1.02 (d, J = 6.6 Hz, 24H), −2.63 (s, 2H), −2.85 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.6, 158.5, 149.5, 146.5, 143.7, 143.5, 142.8, 142.2, 141.5, 135.9, 132.9, 132.8, 131.6, 131.3, 120.7, 120.3, 120.1, 119.8, 119.7, 119.0 (q, J_{C-F} = 320 Hz), 117.3, 114.6, 104.9, 101.2, 101.1, 66.8, 38.19, 38.17, 25.2, 22.7; UV−vis (CH_2Cl_2) λ_{max} = 416, 424, 513 549, 587, 644 nm; FTIR (KBr, thin film) 3315, 2958, 1590, 1165 cm^{-1}; HRMS (ESI) m/z for $C_{117}H_{129}F_3N_8O_{11}S$ $[M + 2H]^{2+}$ calcd, 956.4817; found, 956.4800.

Freebase−Zn Porphyrin Dimer Triflate (9-HZn). Porphyrin dimer **8-HZn** (49 mg, 0.027 mmol), K_2CO_3 (37 mg, 0.27 mmol), and 4-nitrophenyltriflate (36 mg, 0.13 mmol) were reacted by the general triflation procedure, which afforded 46 mg of porphyrin dimer **9-HZn** in 87% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.23 (s, 1H), 9.45 (d, J = 4.6 Hz, 2H), 9.37 (d, J = 4.7 Hz, 2H), 9.35 (d, J = 4.6 Hz, 2H), 9.31 (d, J = 4.6 Hz, 2H), 9.25 (d, J = 4.6 Hz, 2H), 9.19 (m, 4H), 8.91 (d, J = 4.6 Hz, 2H), 8.64 (s, 4H), 8.34 (d, J = 8.6 Hz, 2H), 7.70 (d, J = 8.6 Hz, 2H), 7.49 (d, J = 2.1 Hz, 4H), 7.45 (d, J = 2.3 Hz, 4H), 6.91 (t, J = 2.2 Hz, 2H), 6.87 (t, J = 2.2 Hz, 2H), 4.19 (t, J = 6.7 Hz, 8H), 4.14 (t, J = 6.8 Hz, 8H), 1.95−1.85 (m, 8H), 1.82−1.74 (m, 16H), 1.01 (d, J = 6.6 Hz, 24H), 0.99 (d, J = 6.6 Hz, 24H), −2.85 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.5, 158.3, 150.6, 150.4, 150.2, 149.9, 149.4, 146.4, 144.4, 143.5, 142.2, 142.0, 135.7, 132.8, 132.7, 132.6, 132.3, 131.6, 131.4, 131.2, 121.6, 121.3, 120.2, 119.8, 119.5, 119.0 (q, J_{C-F} = 320 Hz), 118.3, 114.6, 114.5, 104.9, 101.17, 101.15, 66.8, 38.2, 38.1, 25.16, 25.15, 22.69, 22.67; UV−vis (CH_2Cl_2) λ_{max} = 415, 426, 510, 548, 585, 638 nm; FTIR (KBr, thin film) 3309, 2956, 1590, 1212, 1163, 1141, 1000 cm^{-1}; HRMS (ESI) m/z for $C_{117}H_{127}F_3N_8O_{11}SZn$ $[M + 2H]^{2+}$ calcd, 987.4367; found, 987.4374.

Zn−Freebase Porphyrin Dimer Triflate (9-ZnH). Porphyrin dimer **8-ZnH** (64 mg, 0.035 mmol), K_2CO_3 (48 mg, 0.35 mmol), and 4-nitrophenyltriflate (47 mg, 0.17 mmol) were reacted by the general triflation procedure, which afforded 68 mg of porphyrin dimer **9-ZnH** in 99% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.26 (s, 1H), 9.44 (d, J = 4.6 Hz, 2H), 9.42 (d, J = 4.4 Hz, 2H), 9.35 (d, J = 4.6 Hz, 2H), 9.34 (d, J = 4.4 Hz, 2H), 9.28 (d, J = 4.4 Hz, 2H), 9.21 (d, J = 4.4 Hz, 2H), 9.08 (d, J = 4.4 Hz, 2H), 8.81 (d, J = 4.4 Hz, 2H), 8.64 (m, 4H), 8.35 (d, J = 8.4 Hz, 2H), 7.73 (d, J = 8.4 Hz, 2H), 7.50 (d, J = 2.1 Hz, 4H), 7.47 (d, J = 2.1 Hz, 4H), 6.93 (m, 4H), 4.20 (t, J = 6.2 Hz, 16H), 1.96−1.88 (m, 8H), 1.80 (q, J = 6.7 Hz, 16H), 1.01 (d, J = 6.6 Hz, 24H), 1.00 (d, J = 6.6 Hz, 24H), −2.64 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.4, 158.3, 150.12, 150.11, 150.0, 149.5, 144.5, 143.7, 142.8, 142.6, 141.3, 135.9, 132.9, 132.8, 132.3, 132.0, 131.8, 121.0, 120.8, 120.6, 120.5, 119.7, 119.0 (q, J_{C-F} = 320 Hz), 117.2, 114.6, 114.5, 106.0, 101.2, 101.1, 66.8, 38.18, 38.15, 25.18, 25.16, 22.69; UV−vis (CH_2Cl_2) λ_{max} = 416, 424, 516, 544, 588, 645 nm; FTIR (KBr, thin film) 3316, 2955, 1589, 1212, 1165, 1142, 1000 cm^{-1}; HRMS (ESI) m/z for $C_{117}H_{127}F_3N_8O_{11}SZn$ $[M + 2H]^{2+}$ calcd, 987.4367; found, 987.4366.

Zn−Zn Porphyrin Dimer Triflate (9-ZnZn). Porphyrin dimer **8-ZnZn** (93 mg, 0.049 mmol), K_2CO_3 (68 mg, 0.49 mmol), and 4-nitrophenyltriflate (66 mg, 0.24 mmol) were reacted by the general triflation procedure, which afforded 96 mg of porphyrin dimer **9-ZnZn** in 96% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.28 (s, 1H), 9.46−9.43 (m, 6H), 9.32 (d, J = 4.6 Hz, 2H), 9.29 (d, J = 4.6 Hz, 2H), 9.27 (d, J = 4.4 Hz, 2H), 9.29 (d, J = 4.6 Hz, 2H), 9.27 (d, J = 4.4 Hz, 2H), 9.16 (d, J = 4.6 Hz, 2H), 8.89 (d, J = 4.6 Hz, 2H), 8.63 (s, 4H), 8.35 (d, J = 8.4 Hz, 2H), 7.71 (d, J = 8.4 Hz, 2H), 7.47 (d, J = 2.3 Hz, 4H), 7.44 (d, J = 2.1 Hz, 4H), 6.90−6.87 (m, 4H), 4.18−4.14 (m, 16H), 1.94−1.85 (m, 8H), 1.80−1.74 (m, 16H), 1.00 (d, J = 6.6 Hz, 24H), 0.99 (d, J = 6.6 Hz, 24H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.28, 158.26, 150.6, 150.4, 150.13, 150.11, 150.0, 149.8, 149.4, 144.5, 144.4, 143.5, 142.4, 142.0, 135.7, 132.8, 132.7, 132.6, 132.31, 132.29, 132.0, 131.8, 131.3, 121.5, 121.4, 121.1, 120.7, 120.3, 119.5, 118.3, 117.7, 114.54, 114.52, 106.0, 101.12, 101.05, 66.8, 38.2, 38.1, 25.17, 25.16, 22.68, 22.67; UV−vis (CH_2Cl_2) λ_{max} = 416, 426, 546, 585 nm; FTIR (KBr, thin film) 2956, 1589, 1212, 1164, 1142, 999 cm^{-1}; HRMS (ESI) m/z for $C_{117}H_{125}F_3N_8O_{11}SZn_2$ $[M + 2H]^{2+}$ calcd, 1018.3935; found, 1018.3939.

General Procedure for Suzuki Coupling of Porphyrin Trimers. Porphyrin dimer **9** (1 equiv), porphyrin **6** (1.2 equiv), K_3PO_4 (5 equiv), $PdCl_2$(dppf) (0.5 equiv), and dppf (0.4 equiv) were dissolved in THF. The mixture was stirred for 1 h at 70 °C, following which it was washed with water and brine and dried with Na_2SO_4. The organic solvent was evaporated, and the residue was purified by column chromatography (silica-gel, CH_2Cl_2) and GPC (Bio-Beads S-X beads, THF).

Freebase−Freebase−Freebase Porphyrin Trimer (10-HHH). Porphyrin **9-HH** (25 mg, 0.013 mmol), porphyrin **6-H** (16 mg, 0.016 mmol), K_3PO_4 (13 mg, 0.061 mmol), $PdCl_2$(dppf) (5 mg, 0.006 mmol), and dppf (4 mg, 0.006 mmol) in THF/H_2O (10:1, 0.3 mL) were reacted by the general Suzuki coupling procedure for trimers, which afforded 25 mg of porphyrin trimer **10-HHH** in 75% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.23 (s, 1H), 9.38−9.35 (m, 8H), 9.33 (d, J = 4.6 Hz, 2H), 9.26 (d, J = 4.6 Hz, 6H), 9.20 (d, J = 4.6 Hz, 4H), 9.04 (d, J = 4.6 Hz, 2H), 8.91 (d, J = 4.4 Hz, 2H), 8.67 (m, 8H), 8.07 (d, J = 8.3 Hz, 2H), 7.58 (d, J = 2.3 Hz, 4H), 7.51 (d, J = 2.3 Hz, 4H), 7.49 (d, J = 2.3 Hz, 4H), 7.12 (d, J = 8.3 Hz, 2H), 7.00 (t, J = 2.2 Hz, 2H), 6.97 (t, J = 2.3 Hz, 2H), 6.95 (t, J = 2.2 Hz, 2H), 4.27−4.19 (m, 24H), 1.98−1.88(m, 12H), 1.85−1.78 (m, 24H), 1.03 (d, J = 6.4 Hz, 24H), 1.01 (d, J = 6.7 Hz, 24H), 1.00 (d, J = 6.6 Hz, 24H), −2.47 (s, 2H), −2.61 (s, 2H), −2.85 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.6, 158.5, 158.4, 155.5, 146.4, 144.0, 143.6, 143.2, 142.1, 141.73, 141.69, 135.6, 134.6, 133.0, 132.94, 132.88, 131.7, 131.2, 120.5, 120.3, 120.1, 120.03, 119.95, 119.94, 119.8, 119.6, 114.7, 114.63, 114.57, 113.7, 104.9, 101.3, 101.18, 101.15, 66.87, 66.85, 66.8, 38.21, 38.19, 38.17, 25.20, 25.18, 25.17, 22.72, 22.69; UV−vis (CH_2Cl_2) λ_{max} = 416, 433, 516, 553, 589, 647 nm; FTIR (KBr, thin film) 3314, 2955, 1589, 1164 cm^{-1}; HRMS (ESI) m/z for $C_{174}H_{194}N_{12}O_{13}$ $[M + 3H]^{3+}$ calcd, 887.5036; found, 887.5043.

Freebase−Zn−Freebase Porphyrin Trimer (10-HZnH). Porphyrin **9-HZn** (25 mg, 0.013 mmol), porphyrin **6-H** (15 mg, 0.015 mmol), K_3PO_4 (13 mg, 0.061 mmol), $PdCl_2$(dppf) (5 mg, 0.006 mmol), and dppf (4 mg, 0.006 mmol) in THF/H_2O (10:1, 0.3 mL) were reacted by the general Suzuki coupling procedure for trimers, which afforded 24 mg of porphyrin trimer **10-HZnH** in 71% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.29 (s, 1H), 9.51−9.50 (m, 4H), 9.43−9.38 (m, 10H), 9.29 (d, J = 4.6 Hz, 2H), 9.25−9.23 (m, 4H), 9.08 (d, J = 4.6 Hz, 2H), 8.95 (d, J = 4.4 Hz, 2H), 8.70 (s, 8H), 8.13 (d, J = 8.2 Hz, 2H), 7.62 (d, J = 1.9 Hz, 4H), 7.54 (d, J = 2.1 Hz, 4H), 7.52 (d, J = 2.0 Hz, 4H), 7.20 (d, J = 8.0 Hz, 2H), 7.03 (t, J = 2.0 Hz, 2H), 6.99 (t, J = 2.1 Hz, 2H), 6.97 (t, J = 2.2 Hz, 2H), 4.30−4.22 (m, 24H), 2.01−1.91 (m, 12H), 1.88−1.81 (m, 24H), 1.06−1.03 (m,

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72H), −2.58 (s, 2H), −2.82 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.5, 158.4, 155.5, 150.5, 150.3, 144.6, 144.0, 143.6, 143.1, 142.4, 141.9, 141.5, 135.7, 134.7, 132.9, 132.8, 132.7, 132.6, 132.2, 131.6, 131.2, 121.5, 120.9, 120.3, 120.2, 120.0, 119.8, 119.7, 114.63, 114.57, 114.5, 113.7, 104.9, 101.18, 101.15, 66.87, 66.85, 66.8, 38.22, 38.19, 38.17, 25.21, 25.18, 25.17, 22.72, 22.71, 22.69; UV−vis (CH_2Cl_2) λ_{max} = 416, 434, 514, 550, 589, 644 nm; FTIR (KBr, thin film) 3312, 2954, 1589, 1166, 999 cm^{-1}; HRMS (ESI) *m*/*z* for $C_{174}H_{192}N_{12}O_{13}Zn$ $[M + 2H]^{2+}$ calcd, 1361.7084; found, 1361.7096.

Zn−Freebase−Zn Porphyrin Trimer (10-ZnHZn). Porphyrin **9-ZnH** (25 mg, 0.013 mmol), porphyrin **6-Zn** (16 mg, 0.015 mmol), K_3PO_4 (13 mg, 0.061 mmol), $PdCl_2$(dppf) (5 mg, 0.006 mmol), and dppf (3 mg, 0.006 mmol) in THF/H_2O (10:1, 0.3 mL) were reacted by the general Suzuki coupling procedure for trimers, which afforded 27 mg of porphyrin trimer **10-ZnHZn** in 76% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.31 (s, 1H), 9.49−9.35 (m, 12H), 9.30(d, *J* = 4.4 Hz, 4H), 9.26 (d, *J* = 4.2 Hz, 4H), 9.15 (d, *J* = 4.6 Hz, 2H), 9.03 (d, *J* = 4.4 Hz, 2H), 8.68 (s, 8H), 8.11 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 2.0 Hz, 4H), 7.51 (d, *J* = 2.0 Hz, 4H), 7.49 (d, *J* = 2.0 Hz, 4H), 7.19 (d, *J* = 7.9 Hz, 2H), 6.98 (t, *J* = 2.5 Hz, 2H), 6.95 (t, *J* = 2.3 Hz, 2H), 6.92 (t, *J* = 2.1 Hz, 2H), 4.26−4.17 (m, 24H), 1.98−1.87 (m, 12H), 1.85−1.77 (m, 24H), 1.04−0.99 (m, 72H), −2.46 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.5, 158.4, 158.3, 155.2, 150.7, 150.4, 150.2, 150.1, 144.6, 144.5, 144.0, 142.5, 142.4, 141.5, 135.5, 135.4, 132.88, 132.85, 132.4, 132.3, 132.2, 132.1, 131.8, 121.3, 121.1, 120.97, 120.95, 120.8, 120.7, 120.5, 120.0, 114.7, 114.4, 113.6, 106.1, 101.3, 101.14, 101.10, 66.9, 66.84, 66.83, 38.20, 38.19, 38.17, 25.19, 25.18, 22.72, 22.70, 22.69; UV−vis (CH_2Cl_2) λ_{max} = 416, 433, 518, 548, 589, 647 nm; FTIR (KBr, thin film) 3315, 2956, 1589, 1166, 998 cm^{-1}; HRMS (ESI) *m*/*z* for $C_{174}H_{190}N_{12}O_{13}Zn_2$ $[M + 2H]^{2+}$ calcd, 1392.6652; found, 1392.6655.

Zn−Zn−Free-Base Porphyrin Trimer (10-ZnZnH). Porphyrin **9-ZnZn** (20 mg, 0.010 mmol), porphyrin **6-H** (12 mg, 0.012 mmol), K_3PO_4 (9.2 mg, 0.043 mmol), $PdCl_2$(dppf) (3.8 mg, 0.005 mmol), and dppf (2.4 mg, 0.004 mmol) in THF/H_2O (10:1, 0.2 mL) were reacted by the general Suzuki coupling procedure for trimers, which afforded 24 mg of porphyrin trimer **10-ZnZnH** in 88% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.30 (s, 1H), 9.50−9.45(m, 8H), 9.37−9.35(m, 8H), 9.29 (d, *J* = 4.4 Hz, 2H), 9.20 (d, *J* = 4.6 Hz, 2H), 9.04 (d, *J* = 4.6 Hz, 2H), 8.92 (d, *J* = 4.6 Hz, 2H), 8.67 (m, 8H), 8.10 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 2.1 Hz, 4H), 7.51 (d, *J* = 2.1 Hz, 4H), 7.48 (d, *J* = 2.3 Hz, 4H), 7.17 (d, *J* = 8.3 Hz, 2H), 6.97 (t, *J* = 2.2 Hz, 2H), 6.94−6.92 (m, 4H), 4.24−4.18 (m, 24H), 1.96−1.88 (m, 12H), 1.84−1.78 (m, 24H), 1.03−1.00 (m, 72H), −2.62 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.4, 158.31, 158.28, 155.4, 150.59, 150.57, 150.52, 150.50, 150.33, 150.30, 150.28, 150.14, 150.13, 150.11, 150.06, 150.05, 144.6, 144.5, 144.0, 142.4, 142.3, 142.2, 141.5, 135.7, 134.7, 132.9, 132.8, 132.73, 132.67, 132.6, 132.5, 132.3, 132.2, 132.1, 131.8, 121.5, 121.3, 121.10, 121.08, 120.9, 120.7, 120.23, 120.21, 119.99, 119.97, 119.8, 114.6, 113.7, 106.0, 101.2, 101.1, 66.8, 38.18, 38.16, 25.19, 25.16, 25.15, 22.7; UV−vis (CH_2Cl_2) λ_{max} = 417, 434, 517, 550, 592, 646 nm; FTIR (KBr, thin film) 3317, 2954, 1589, 1165, 999 cm^{-1}; HRMS (ESI) *m*/*z* for $C_{174}H_{190}N_{12}O_{13}Zn_2$ $[M + 2H]^{2+}$ calcd, 1392.6652; found, 1392.6639.

Zn−Zn−Zn Porphyrin Trimer (10-ZnZnZn). Porphyrin **9-ZnZn** (21 mg, 0.010 mmol), porphyrin **6-Zn** (13 mg, 0.012 mmol), K_3PO_4 (11 mg, 0.050 mmol), $PdCl_2$(dppf) (4 mg, 0.005 mmol), and dppf (3 mg, 0.005 mmol) in THF/H_2O (10:1, 0.2 mL) were reacted by the general Suzuki coupling procedure for trimers, which afforded 20 mg of porphyrin trimer **10-ZnZnZn** in 70% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.29 (s, 1H), 9.50−9.49 (m, 6H), 9.46(d, *J* = 4.6 Hz, 2H), 9.44 (d, *J* = 4.3 Hz, 2H), 9.35 (m, 6H), 9.30 (d, *J* = 4.4 Hz, 2H), 9.28 (d, *J* = 4.4 Hz, 2H), 9.13 (d, *J* = 4.6 Hz, 2H), 9.03 (d, *J* = 4.6 Hz, 2H), 8.67 (m, 8H), 8.11 (d, *J* = 7.9 Hz, 2H), 7.52 (d, *J* = 2.1 Hz, 4H), 7.48 (d, *J* = 2.3 Hz, 4H), 7.45 (d, *J* = 2.3 Hz, 4H), 7.16 (d, *J* = 7.7 Hz, 2H), 6.88 (m, 4H), 6.84 (t, *J* = 2.4 Hz, 2H), 4.18−4.12 (m, 24H), 1.95−1.84 (m, 12H), 1.80−1.74 (m, 24H), 1.00 (d, *J* = 6.6 Hz, 24H), 1.00 (d, *J* = 6.7 Hz, 24H), 0.98 (d, *J* = 6.7 Hz, 24H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.23, 158.21, 158.15, 155.2, 150.7, 150.6, 150.5, 150.3, 150.13, 150.10, 150.06, 144.58, 144.57, 144.5, 142.3, 142.19, 142.17, 135.5, 135.4, 132.8, 132.7, 132.6, 132.5, 132.4, 132.2, 132.1, 132.0, 131.8, 121.4, 121.3, 121.2, 121.1, 120.9, 120.8, 120.7, 114.62, 114.59, 114.5, 113.6, 106.0, 101.3, 101.2, 101.1, 66.9, 66.8, 38.13, 38.10, 25.2, 25.1, 22.69, 22.67; UV−vis (CH_2Cl_2) λ_{max} = 415, 433, 548, 587 nm; FTIR (KBr, thin film) 2956, 1589, 1166, 999 cm^{-1}; HRMS (ESI) *m*/*z* for $C_{174}H_{188}N_{12}O_{13}Zn_3$ $[M + 2H]^{2+}$ calcd, 1423.6178; found, 1423.6219.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C NMR of new compounds. Absorption data of compounds **2**, **8**, and **10**. Emission data of compounds **2**, **8** and **10**. Electrochemical redox data of compounds **2**, **8**, and **10**. Energies and shapes of the frontier orbitals of monomers **2′-H** and **2′-Zn**. Energies and shapes of the frontier orbitals of dimers **8′-HH**, **8′-HZn**, **8′-ZnH**, and **8′-ZnZn**. Energies and shapes of the frontier orbitals of trimers **10′-HHH**, **10′-HZnH**, **10′-ZnHZn**, **10′-ZnZnH**, and **10′-ZnZnZn**. Summary of calculations, including absolute energies and atom coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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