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Sequential and Spatial Organization of Metal Complexes Inside a Peptide Duplex

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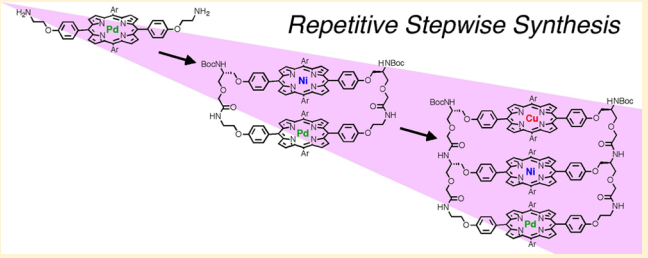
Supporting Information

ABSTRACT: To generate integrated organized molecular properties, multiple molecular components are required to be assembled into the molecular system with sequential and spatial accuracy in accordance with the design of the molecular assembly. Herein, we present a novel programmable synthesis of a cofacially stacked porphyrin array via repetitive construction of a peptide duplex. We designed and synthesized a novel porphyrin having two artificial amino acid moieties at the trans meso-positions. The amino acid moieties can be connected with another porphyrin unit by repetitive doubly coupling reactions to afford the peptide duplex bridged by the porphyrins. In the duplex, the porphyrin units are stacked cofacially, and the efficient electronic communication among the arrayed porphyrin units was characterized by split redox waves in the cyclic voltammograms. We also demonstrated the three different square-planar metal ions, namely Cu^{2+}, Ni^{2+}, and Pd^{2+}, were arranged inside the ladder-type porphyrin array in a programmable fashion.



INTRODUCTION

Organized assemblies of functional molecules occasionally demonstrate chemical and physical properties that are unpredictable from the sum of their individual molecular components.[1] In elaborate molecular systems, the properties of individual molecules translate to the integrated properties of organized molecules via the generation of efficient intermolecular communications, which bring synergy effects.[2] To generate such molecular properties, multiple functional molecular components are required to assemble the molecular system with sequential and spatial accuracy in accordance with the design of the molecular assembly. Although it is generally difficult to synthesize a precise molecular assembly composed of many different molecular components, one practical approach toward the programmed arrangement of building units is to utilize the well-defined nanostructures of biopolymers such as DNA and polypeptides as organizing scaffolds.[3−5] This strategy allows for the use of polymer chains as a chemical elongation method, and predictable folding structures such as helices, sheets, duplexes, triplexes, and higher structures allow structural diversity. Incorporation of such moieties ensures that the building components are precisely arrayed in a monodisperse primary structure that can be folded into a secondary or a tertiary structure to maintain a relative positional, angular, or configurational relationship between the components. For instance, both we and others have developed artificial metallo-DNAs in which metal complexes are aligned along the DNA helix axes inside the duplexes, via the formation of artificial metallo-base pairs (Figure 1a).[6,7] In the artificial metallo-DNAs, the arrayed metal complexes exhibited characteristic spin−spin interactions defined by the spatial arrangements of metallo-base pairs.[7] We have also reported the formation of discrete nanowires of halogen-bridged platinum complexes via duplex formation between a Pt^{II}-pendant peptide and a Pt^{IV}-pendant peptide (Figure 1b).[8] However, as related to the heterogeneous arraying of metals inside a single scaffold, the assembly of only limited kinds of metal ions has been achieved, because the bioinspired strategies are based on self-assembly between metal ions and presynthesized arrays of metal ligands as the template strands. Hence, the development of a novel synthetic strategy composed of the coupling of premetalated building blocks is required to manipulate multiple

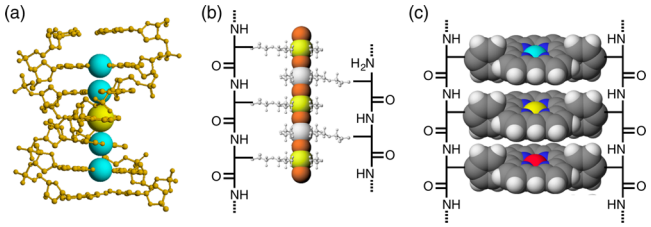


Figure 1. Representations of (a) an artificial metallo-DNA, (b) a discrete one-dimensional halogen-bridged platinum nanowire in a peptide duplex, and (c) a metalloporphyrin stacked array in a peptide duplex.

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metal ions at a time and assemble them into a preplanned fashion.

Porphyrins satisfy such criteria as premetalated units, and their metal complexes are key building blocks within a wide range of molecular materials due to their unique photophysical, electrochemical, magnetic, and catalytic properties.[9] Organized porphyrin assemblies are also demonstrating promise in the construction of higher functionalized systems,[10] while the arraying of multiple porphyrins has been investigated by employing bioinspired templates and regulated stacking interactions.[11−15]

We have recently reported supramolecular stacked arrays of porphyrins and phthalocyanines connected by two- or four-fold rotaxanes,[16] demonstrating that connection of the structural units by two or four columns is an effective way to control their relative spatial arrangements via $\pi-\pi$ stacking interactions. In this paper, we describe the organized arraying of metalloporphyrins in a peptide duplex (Figure 1c), achieved via the layering of various metalloporphyrins possessing two amino acid side chains through repetitive peptide bond formation. Accordingly, the parallel peptide duplexes are bridged by stacked arrays of metalloporphyrins, and the cofacially stacked porphyrins are aligned along and in the middle of the peptide duplex.

RESULTS AND DISCUSSION

Molecular Design. Before the synthesis of the porphyrin monomer containing two amino acid linker moieties, we assessed the structure of the peptide duplex by using computer-assisted molecular modeling. The sequential length of natural α-amino acids was judged to be too short to allow efficient stacking of the arrayed porphyrins. To circumvent this problem, we designed the monomer **1** with longer artificial amino acids in the trans meso-positions to increase the number of atoms of the repeating unit; from the amino (N) to carboxy (C) termini is same distance as found in a repeating DNA or peptide nucleic acid (PNA) units, in which planar aromatic moieties are stacked in the middle of the helical double strands (Figure 2).

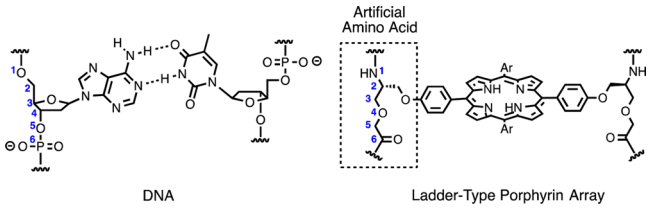
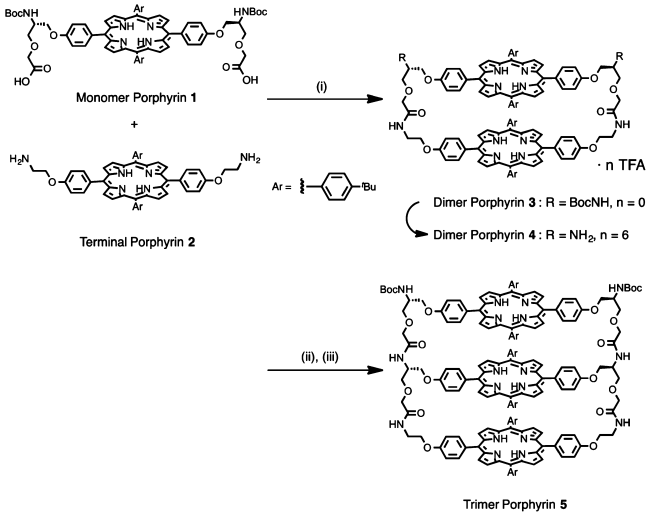


Figure 2. Structural comparison of the peptide duplexes and DNA.

Stepwise Chemical Elongation of Ladder-Type Peptide Arrays. The peripheral artificial amino acid was subsequently synthesized from L-serine in a good yield and introduced to the porphyrin center by Stille coupling to afford a monomer porphyrin **1**, as described in Scheme S1.

The synthetic procedure for the porphyrin array in a peptide duplex is summarized in Scheme 1. Two-fold peptide bond formation between **1** and the terminal porphyrin **2** was successfully achieved by using 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride (DMT-MM) as a coupling reagent at comparatively low concentrations of each component in *N,N*-dimethylacetamide (DMA) (<0.5 mM) to give the dimer **3** in 17% yield. In the coupling reaction, the use of more bulky coupling reagents such as *N,N′*-dicyclohexyl carbodiimide (DCC) was not practical, and therefore the sterically hindered structure of **3** was expected. After deprotection of the Boc groups by treatment with trifluoroacetic acid, structural elongation was carried out via a second round of two-fold peptide formation, between $[\mathbf{4}\cdot 6H]^{6+}\cdot 6TFA^{-}$ and **1** analogous to the preparation of **3**, to afford the trimer **5** in 27% isolated yield. During the course of the repetitive coupling reactions, the structures of the formed porphyrin arrays were fully characterized by ^{1}H NMR spectroscopy and ESI-TOF MS, the results of which clearly demonstrated the stepwise elongation of the peptide duplexes (Figure S11).

Scheme 1. Synthesis of the Porphyrin Trimer in the Peptide Duplex 5, through Two-Fold Peptide Elongation Reactions[a]



[a]Reagents and conditions: (i) DMT-MM, DBU in DMA, 17%, (ii) TFA in CH_2Cl_2, 80%, (iii) monomer **1**, DMT-MM, DBU in DMA, 27%.

NMR Study of Ladder-Type Stacked Arrays. The stacking interactions among the porphyrin units inside the duplex were revealed by the NMR signals of the pyrrolic NH protons; the ^{1}H NMR N−H resonances of the dimer **3** (observed at −3.24 and −3.25 ppm) and the trimer **4** (observed at −3.34, −3.47, and −4.22 ppm) are shifted to high field as compared to those in the monomer **1** (observed at −2.74 ppm) (Figure 3). Similar phenomena have been observed for supramolecular porphyrins stacked with a phthalocyanine unit as a result of the shielding effects of the adjacent phthalocyanine.[15] In addition, although the C_2-symmetric structure of the dimer **3** was revealed by ^{1}H NMR spectroscopy at 140 °C in 1,1,2,2-tetrachloroethane-d_2 as shown in Figure S8, significant broadening of the signals in the aromatic region was observed at room temperature. This is considered to be a result of a temperature-dependent folding via efficient $\pi-\pi$ stacking interactions between the porphyrin rings, and the dimer seems to form a single folding structure. In fact, the pyrrolic NH protons showed a couple of single and sharp signals as mentioned above. For the trimer **5**, the aromatic signals were still broadened even at elevated temperature in 1,1,2,2-tetrachloroethane-d_2 as shown in Figure S10, indicating a more tightly folded elongated duplex structure. Hence, the porphyrins are located in specific spatial arrangements within the duplexes.

UV−vis and Electrochemical Studies of Ladder-Type Stacked Arrays. The distinct stacking interactions between

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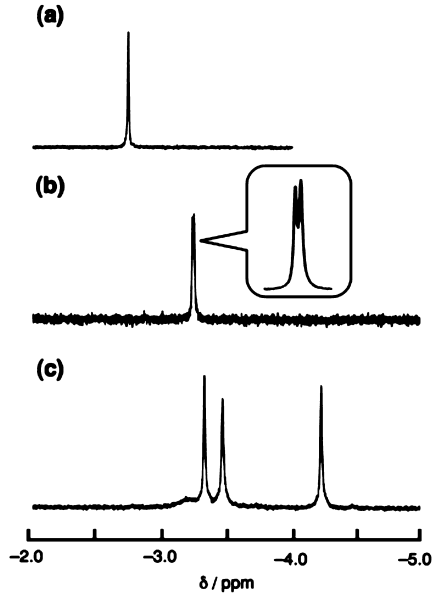

Figure 3. Partial ^{1}H NMR spectra (600 MHz, $CDCl_3$/TMS): (a) porphyrin monomer **1**; (b) porphyrin dimer **3**; (c) porphyrin trimer **5** at 20 °C.

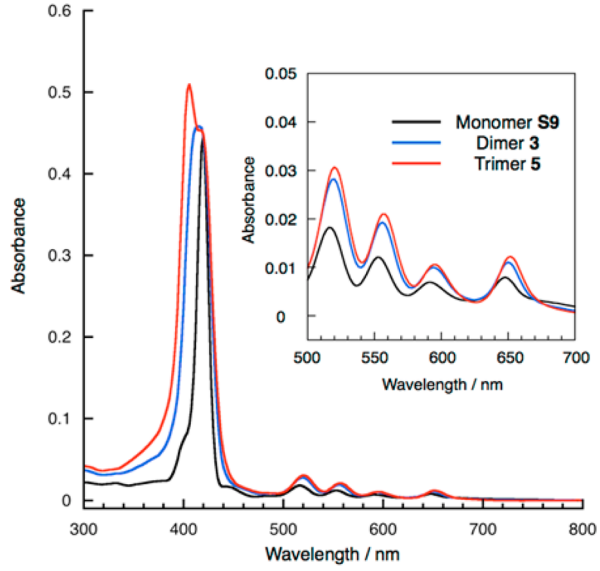

Figure 4. UV−vis absorption spectra of the dimer **3** (red) and the trimer **5** (blue) in comparison with **S9** (a precursor of **1**: the detailed structure is shown in the Supporting Information) (black) in CH_2Cl_2 at 20 °C. [**3**] = [**5**] = [**S9**] = 1.0 μM. Inset: magnified Q-bands.

the porphyrins in the dimer **3** and the trimer **5** were also observed in UV−vis absorption spectra (Figure 4). In the absorption spectrum of **3**, the Soret band showed a slight blue shift with broadening compared to that of the monomer **1**, whereas four Q-bands red-shifted significantly. Similar behavior was observed for **5**. Such observations are characteristic of the H aggregates of stacked porphyrin arrays.[17]

In cyclic voltammetric experiments, only one quasi-reversible redox wave was observed at 0.46 V vs Fc/Fc^+ for the monomer **1**. Conversely, the redox peaks were split into two peaks for **3** (appearing at 0.39 and 0.53 V) and into three different peaks for **5** (appearing at 0.27, 0.42, and 0.52 V) (Figures 5 and S14). The first oxidation of a porphyrin array became easier as the

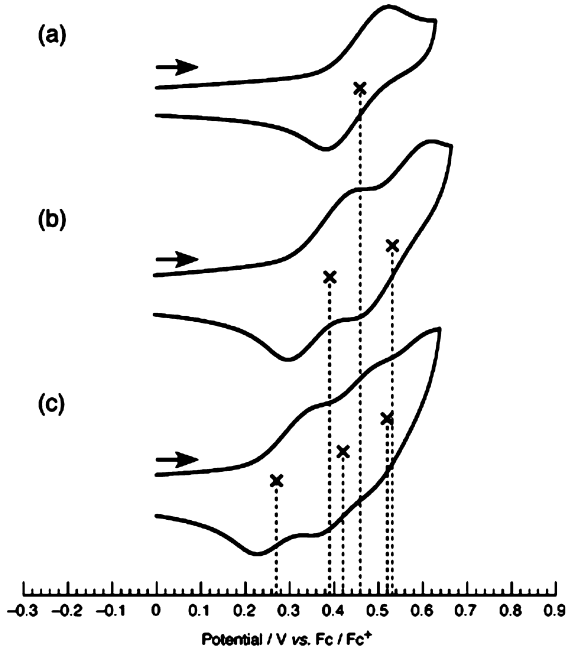

Figure 5. Cyclic voltammograms of (a) porphyrin monomer **1**, (b) porphyrin dimer **3**, and (c) porphyrin trimer **5** in CH_2Cl_2 including 0.1 M $^{n}Bu_4NPF_6$ at 20 °C at a scan rate of 100 mV s^{-1}. [Substrate] = 400 μM.

number of porphyrin units increased. These phenomena reflect the efficient $\pi-\pi$ electronic interaction in the closely stacked system and the Coulombic repulsion between the oxidized porphyrin cations.

The synthetic strategy also allows the incorporation of heterogeneous metal arrays into the duplex. To demonstrate the repetitive synthesis, we attempted to arrange three different metalloporphyrins inside the stacked trimer. Figure 6 shows the reaction scheme of the stepwise layering from the terminal Pd^{II}-porphyrin **6** to a $Cu^{II}-Ni^{II}-Pd^{II}$ trimer **8** along with the ESI-TOF MS spectra snapshotted in each elongation step. Although structural information on the trinuclear complex was not obtained from NMR measurements because of the paramagnetic Cu^{II} center, it was confirmed that precise assembly of Cu^{II}-, Ni^{II}-, and Pd^{II}-porphyrins were successfully achieved without any metal migration from the porphyrin centers during the peptide elongation reactions, as demonstrated by the elemental analyses and the ESI-TOF MS spectra (Figure S13). UV−vis spectra of the $Ni^{II}-Pd^{II}$ dimer **7** and the $Cu^{II}-Ni^{II}-Pd^{II}$ trimer **8** showed a slight blue shift with broadening compared to that of their monomers similar to that when the metal-free porphyrins were measured, indicating the stacking interactions between the porphyrins (Figure S15).

CONCLUSION

In summary, we have developed a repetitive stepwise synthesis of programmable cofacially stacked porphyrin arrays in a peptide duplex. The duplex, number, sequence, and spatial arrangement of the porphyrins were precisely controlled and significant electronic communications were observed between the stacked porphyrins. Two peptide backbones connected to the trans meso-positions of each porphyrin effectively minimized the conformational and configurational diversity. Since most metalloporphyrins are stable under Boc/peptide conditions, the synthesis of diverse arrays of metalloporphyrins

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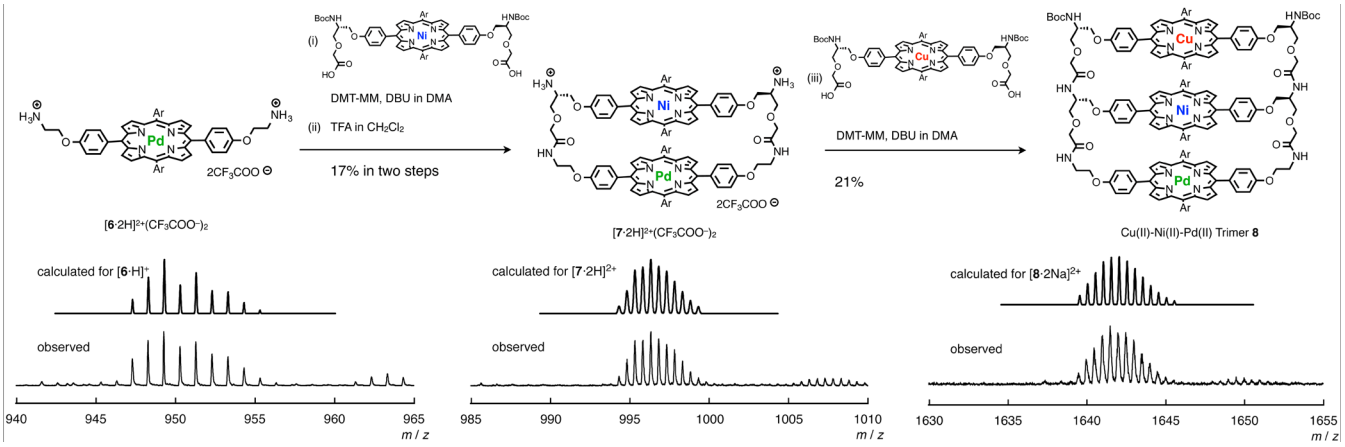

Figure 6. Synthetic procedure for the Cu^{II}–Ni^{II}–Pd^{II} trimer **8** and ESI-TOF mass spectra of (a) Pd^{II} monomer **6**, (b) Ni^{II}–Pd^{II} dimer **7**, and (c) Cu^{II}–Ni^{II}–Pd^{II} trimer **8**.

with designer sequences becomes possible. This concept, therefore, would allow the potential development of programmable molecular wires, spin devices, and supramolecular catalysts.

EXPERIMENTAL SECTION

General Procedure. Synthetic procedures were carried out under dry nitrogen atmosphere, unless otherwise specified. All reagents and solvents were purchased at the highest commercial quality available and used without further purification, unless otherwise stated. A monomer porphyrins **1**, a Cu^{2+} complex of **1** (**Cu-1**), a Ni^{2+} complex of **1** (**Ni-1**), a terminal porphyrin **2**, a Pd^{2+} complex of **2** ($[\mathbf{6}\cdot 2H]^{2+}(CF_3COO^-)_2$) were synthesized according to the procedure shown in the Supporting Information. ^1H and ^{13}C spectra were recorded on a JEOL JNM-A600 (600 MHz for ^1H; 150 MHz for ^{13}C) spectrometer or a JEOL JNM-ECS400 (400 MHz for ^1H; 100 MHz for ^{13}C) spectrometer at a constant temperature of 298 K. Tetramethylsilane (TMS) was used as an internal reference for ^1H and ^{13}C NMR measurements in $CDCl_3$. Elemental analyses were performed on a Yanaco MT-6 analyzer. Silica gel column chromatographies and thin-layer (TLC) chromatography were performed using Merck silica gel 60 and Merck silica gel 60 (F254) TLC plates, respectively. GPC was performed using a JAI LC-9204 equipped with JAIGEL 1H-40/2H-40 columns. ESI mass spectrometry was performed with a Waters LCT-Premier XE Spectrometer controlled using Masslynx software.

Synthesis of a Porphyrin Dimer 2. Monomer porphyrin **1** (317 mg, 0.26 mmol) and DMT-MM (224 mg, 0.81 mmol) were dissolved in DMA (260 mL), and the mixture was stirred at room temperature for 2 h (solution A). On the other hand, porphyrin **2** (283 mg, 0.22 mmol) and DBU (0.090 mL, 0.60 mmol) were dissolved in DMA (260 mL) (solution B). Using two different dropping funnels, the solutions A and B were added simultaneously to a solution of DMT-MM (143 mg, 0.52 mmol) in DMA (200 mL) over 8 h at 0 °C. The mixture was stirred for 10 h. The solvent was removed under reduced pressure. The residual purple precipitate was dissolved in CH_2Cl_2 (300 mL). The organic layer was washed with H_2O (200 mL, twice), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude purple solid was purified by silicagel column chromatography (4 cm ϕ × 10 cm, CH_2Cl_2:MeOH = 20:1, including Et_3N 0.5%) and GPC (JAIGEL 2.5H-2.5H, $CHCl_3$) and crystallization (vapor diffusion, $CHCl_3$/Et_2O) successively to afford the title compound **3** as a reddish purple solid (89 mg, 20%). ^1H NMR (400 MHz, 140 °C, tetrachloroethane-d_2/TMS): δ = 8.26 (m, 8H), 7.80 (m, 10H) 7.16 (br, 8H), 6.99 (br, 3H) 6.79 (br, 7H), 6.59 (br, 6H), 4.98 (d, J = 4.0 Hz, 2H), 4.36 (m, 10H), 4.13 (s, 4H), 3.88 (m, 8H), 1.49 (s, 18H) 1.32 (m, 36H). ESI-TOF MS (positive); m/z calcd for $[M + H]^+$, 2030; found, 2030. Anal. calcd for $C_{410}H_{458}Cl_6N_{36}O_{42}$ (**3**M + 2$CHCl_3$ + 6Et_2O): C, 72.69; H, 6.81; N, 7.44. Found. C, 72.87; H, 6.44; N, 7.23 (0.37% error).

Synthesis of a Deprotected Porphyrin Dimer 4. Porphyrin dimer **3** (74 mg, 36 μmol) was suspended in CH_2Cl_2 (2 mL). To the mixture was added TFA (0.2 mL) at 0 °C. After stirring for 9 h, an additional amount of TFA (0.4 mL) was added, followed by stirring for 7 h at room temperature. The reaction mixture was added dropwise to Et_2O (400 mL) at 0 °C. The resulting precipitate was collected by centrifugation. The resulting purple solid was purified by reprecipitation (MeOH/Et_2O) to afford the title compound **4** was obtained as a purple solid (60 mg, 66%). ^1H NMR (400 MHz, CD_3OD/TMS): δ = 8.53 (br, 8H), 8.14 (m, 10H) 7.78 (br, 8H), 7.58 (m, 12H) 7.15 (m, 8H), 7.44 (d, J = 8.2 Hz, 4H), 5.59 (br, 4H), 5.23 (br, 2H), 4.65 (m, 4H), 4.47 (m, 4H), 4.32 (m, 4H), 4.15 (m, 6H), 4.04 (m, 2H) 3.86 (m, 2H) 1.20 (m, 36H). ESI-TOF MS (positive); m/z calcd for $[M + H]^+$, 1831; found, 1831.

Synthesis of a Porphyrin Trimer 5. Monomer porphyrin **1** (14 mg, 11 μmol) and DMT-MM (11 mg, 39 μmol) were dissolved in DMA (14 mL) to make solution A. The solution A was stirred at room temperature for 1 h. Porphyrin dimer **4** (23 mg, 9.1 μmol) and DBU (4.0 μL, 27 μmol) were dissolved in DMA (14 mL) to make solution B. Using dropping funnels, the solutions A and B were then added simultaneously over 50 min to a solution of DMT-MM (7.1 mg, 26 μmol) in DMA (10 mL) at 0 °C. The mixture was stirred for 16 h. The mixture was poured into brine (300 mL), and the resulting purple precipitate was dissolved in CH_2Cl_2 (200 mL). The organic layer was washed with H_2O (100 mL, twice), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude purple solid was purified by silica gel column chromatography (2.5 cm ϕ × 11 cm, CH_2Cl_2:MeOH = 20:1, including Et_3N 0.5%) and GPC (JAIGEL 2.5H-2.5H, $CHCl_3$) and recrystallization (vapor diffusion, $CHCl_3$/Et_2O) to afford the title compound (9.0 mg, 33%) as a reddish purple solid. ^1H NMR (400 MHz, 120 °C, 1,2-tetrachloroethane-d_2/TMS): δ = 8.21–6.21 (br, 74H), 5.63 (br, 2H), 6.59 (br, 6H), 5.13 (d, J = 5.6 Hz, 2H), 4.82 (m, 2H), 4.65 (m, 2H), 4.24–4.51 (m, 20H), 4.05 (m, 10H), 3.86 (m, 2H), 1.62 (s, 18H) 1.38 (m, 54H). ESI-TOF MS (positive); m/z calcd for $[M + H]^+$, 3014; found, 3014. Anal. calcd for $C_{410}H_{458}Cl_6N_{36}O_{42}$ (**2**M + 3$CHCl_3$ + 4Et_2O): C, 71.68; H, 6.44; N, 7.54. Found. C, 71.34; H, 6.10; N, 7.35 (0.34% error).

Synthesis of a Deprotected Ni^{II}–Pd^{II} Porphyrin Dimer $[\mathbf{7}\cdot 2H]^{2+}(CF_3COO^-)_2$. A Ni^{II} complex of **Ni-1** (93 mg, 73 μmol) and DMT-MM (60 mg, 220 μmol) was dissolved in DMA (80 mL), and the mixture was stirred at room temperature for 2 h to make solution A. On the other hand, a Pd^{II} porphyrin $[\mathbf{6}\cdot 2H]^{2+}(CF_3COO^-)_2$ (86 mg, 73 μmol) and DBU (27 μL, 113 μmol) were dissolved in DMA (80 mL) to make solution B. Using two different dropping funnels, the solutions A and B were added simultaneously to a mixture of DMT-MM (40 mg, 140 μmol) in DMA (60 mL) over 5 h at 0 °C. The reaction mixture was stirred for 19 h. After the solvent was removed

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under reduced pressure. The residual purple solid was purified by silica gel column chromatography (4.5 cm ϕ × 12 cm, CH_2Cl_2:MeOH = 20:1 including 0.5% Et_3N), GPC (JAIGEL 2.5H-3H, $CHCl_3$, twice), and reprecipitation ($CHCl_3$/Et_2O, CH_3CN) successively to afford a Boc-protected form of a Ni^{II}–Pd^{II} dimer as a reddish purple solid (32 mg, 20%). ^{1}H NMR (400 MHz, 120 °C, tetrachloroethane-d_2/TMS): δ = 8.43 (d, J = 4.8 Hz, 4H), 8.18 (d, J = 4.2 Hz, 4H), 8.11 (d, J = 4.2 Hz, 4H), 7.91–7.85 (m, 8H), 7.70 (m, 4H), 7.27–6.96 (m, 20H), 6.78 (d, J = 7.8 Hz, 4H), 5.11 (d, J = 7.8 Hz, 2H), 4.49–4.36 (m, 10H), 4.23 (s, 4H), 4.18–3.94 (m, 8H), 1.59 (s, 18H) 1.45–1.43 (m, 36H). ESI-TOF MS (positive); m/z calcd for $[M]^+$, 2188; found, 2188. Anal. calcd for $C_{257}H_{257}Cl_3N_{24}Ni_2O_{24}Pd_2$ (2**M** + $CHCl_3$): C, 68.56; H, 5.75; N, 7.47. Found. C, 68.45; H, 5.81; N, 7.43 (0.11% error).

A Ni^{II}–Pd^{II} dimer (12 mg, 5.3 μmol) was suspended in CH_2Cl_2 (2 mL). To the mixture was added TFA (0.2 mL) at 0 °C. After stirring for 1 h, an additional amount of TFA (0.2 mL) was added, followed by stirring for 1.5 h at room temperature. The reaction mixture was added dropwise to Et_2O (300 mL) at 0 °C. The precipitate was collected by centrifugation. The resulting purple solid was purified by reprecipitation (MeOH, $CHCl_3$/Et_2O) to afford the title compound $[7\cdot 2H]^{2+}(CF_3COO^-)_2$ was obtained as a purple solid (9.7 mg, 83%). ESI-TOF MS (positive); m/z calcd for $[M]^+$, 1988; found, 1988.

Synthesis of a Cu^{II}–Ni^{II}-Pd^{II} Porphyrin Trimer 8. A Cu^{II} complex of **Cu-1** (2.5 mg, 1.9 μmol) and DMT-MM (1.7 mg, 6.1 μmol) was dissolved in DMA (2 mL) to make solution A. The solution A was stirred at room temperature for 1 h. A deprotected Ni^{II}–Pd^{II} dimer $[7\cdot 2H]^{2+}(CF_3COO^-)_2$ (4.3 mg, 1.9 μmol) and DBU (5 μL, 33 μmol) were dissolved in DMA (4 mL) to make solution B. Using dropping funnels, solutions A and B were then added simultaneously over 15 min to a solution of DMT-MM (3.4 mg, 12 μmol) in DMA (2.5 mL) at 0 °C. The mixture was stirred for 12 h. An additional amount of DMT-MM (3.4 mg, 14 mmol) was added portionwise within 48 h. Then the solvent was removed under reduced pressure to give purple residue, which was filtered and dissolved in CH_2Cl_2 (100 mL). The organic layer was washed with H_2O (100 mL, twice), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude red solid was purified by silicagel column chromatography (2 cm ϕ × 18 cm, CH_2Cl_2:MeOH = 20:1, including Et_3N 0.5%) and GPC (JAIGEL 2.5H-2.5H, $CHCl_3$) to afford the title compound **8** as a red solid (1.3 mg, 21%). ESI-TOF MS (positive); m/z calcd for $[M + 2Na]^{2+}$, 1641.6; found, 1641.5. Anal. calcd for $C_{199}H_{207}Cl_3CuN_{18}NiO_{20}Pd$ (**M** + $CHCl_3$ + 2Et_2O): C, 68.18; H, 5.95; N, 7.19. Found. C, 67.82; H, 5.98; N, 7.22 (0.36% error).

Spectroscopic and Electrochemical Measurements. The absorption spectra were recorded with a Hitachi U-4100 spectrophotometer in CH_2Cl_2 solutions at 20 ± 0.1 °C in 1.0 cm quartz cells. Cyclic voltammetry measurements were performed with a BAS Electrochemical Analyzer Model 750Ds at room temperature in CH_2Cl_2 solutions containing 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in a standard one-component cell under an N_2 atmosphere equipped with a 3 mm OD glassy carbon disk working electrode, platinum wire counter electrode as Ag/AgCl reference electrode. All solutions were deoxygenated by N bubbling for at least 10 min. Obtained E^0 vs Ag/AgCl were converted to those vs Fc/Fc^+ based on measured redox potential of ferrocene.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed synthesis for the porphyrin monomer **1** and the terminal porphyrin **2** as well as additional experimental results. 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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