

Two-Dimensional Porphyrin Array Assembled by Self-Coordination

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Abstract: A novel cross-shaped porphyrin pentamer having four imidazolyl-porphyrinatozinc(II) moieties, one at each *meso*-position, was prepared. AFM measurements confirmed the formation of a large two-dimensional porphyrin array structure: a thin layer of 6~7 porphyrins was assembled over a $350 \times 350 \text{ nm}^2$ area, representing linkage of approximately 120 pentamer units along the line of the cross.

Keywords: Porphyrin, Nanostructure, Scanning probe microscopy, Self-assembly, Supramolecular chemistry, Confocal fluorescence microscopy.

INTRODUCTION

Multi-porphyrin arrays are attractive candidates for molecular electronics and in optical devices and for use in organic dye-based solar cells. Recently, considerable attention has been focused on molecular electronic and photonic devices [1] because the miniaturization of metal-oxide-semiconductor-based LSI (large-scale integration) is close to its absolute limit [1d]. Novel materials for use in molecular-scale integrated circuits, such as carbon nanotubes [2] and multi-porphyrin arrays [3], are now available. The large conjugated π -electron system of porphyrin molecules is interesting due to its small HOMO-LUMO energy gap. Its light absorbing and emitting properties give it desirable electronic and photonic properties and lend it to applications as an artificial light-harvesting antenna complex for converting light energy to electrical power. Several covalently linked multi-porphyrin molecules have been synthesized for potential applications as electric wires [4], optoelectronic gates [5], in non-linear optics [6], as light-harvesting antenna [7], and in other applications [8].

We first proposed complementary coordination of imidazolyl to Zn(II) to form a slipped co-facial porphyrin dimer **2**, as shown in Fig. (1). This dimer had a high stability constant of over 10^{10} M^{-1} in CHCl_3 [9]. Combination of imidazolyl and Zn(II) in porphyrin created an ideal and extremely stable supramolecular assembly, opening the way for multi-porphyrin arrays without the need for covalent linkages. The energy transfer and energy emitting properties of Zn-porphyrin made them useful as opto-electronic materials. However the penta-coordinate zinc ion did not give higher-order aggregates even if more than two imidazolyl groups were attached at the *meso*-positions of the monomeric porphyrin. In order to overcome this limitation, we coupled two imidazolyl porphyrins, and extended the idea to obtain a large one-dimensional porphyrin array **4** [9b]. Propagated in one-dimension, this complementary coordination linked at least 160 porphyrin units, even in a dilute solution. The molecular weight and

length of the assembly were at least 1×10^5 and 120nm, respectively. Furthermore, its oligomeric species containing free base porphyrins as acceptors at molecular terminals showed a large third-order non-linear optical response [9c]. Propagation of the array structure in two-dimensions would give a more stable array, because the coordination network would not be disrupted even if defects were present. To this end, we have designed a porphyrin pentamer **5**, that contains four imidazolyl groups at each corner of the cross. Its zinc complex **6** was anticipated to produce a two-dimensional network of porphyrins **7** by complementary coordination of imidazolyl to Zn(II) at each corner of the cross. To date, the largest planar array comprised of 21 porphyrins linked by covalent bonds [8a] and several two-dimensional supramolecular arrays, produced by using coordination of pyridyl to Ru(II) center [10a] or outer Pd(II) ion [10b,c] and by hydrogen bonds [10d], have been reported.

RESULTS AND DISCUSSIONS

The pentamer **5** was synthesized in three steps, as shown in Fig. (2). First, porphyrin aldehyde **8** was prepared as a precursor from 5-mesityl-dipyrromethane, terephthalaldehyde, and 1-methylimidazole-2-carboxyaldehyde with trifluoroacetic acid (TFA), in 8.4% yield. The porphyrin aldehyde **8** was converted into dipyrromethane **9** as the second precursor. Finally, **5** was synthesized from an equimolar mixture of **8** and **9** with TFA, in 13.2% yield. The absorption spectrum of free base **5** in CHCl_3 showed a relatively broad Soret band at 419nm (hbw 38nm), representing a small exciton coupling between chromophores, as was also reported in the similar 21-mer [8a]. Since two-dimensionally arranged Zn-porphyrin **7** was insoluble in CHCl_3 , zinc insertion experiments were conducted in CHCl_3 containing 30% MeOH. This prevented the coordination of imidazole to zinc [9b] and favored the complete insertion of zinc. The formation of the highly organized complex **7** was effected by a reorganization from the monomeric species **6** by eliminating the pyridine that had been added as a ligand to inhibit the complementary coordination of imidazole to Zn. Therefore, $0.44 \mu\text{M}$ of **6** in a pyridine/nitrobenzene mixture (1:10, v/v) was prepared and $1 \mu\text{l}$ of this solution was dropped on a glass plate. The

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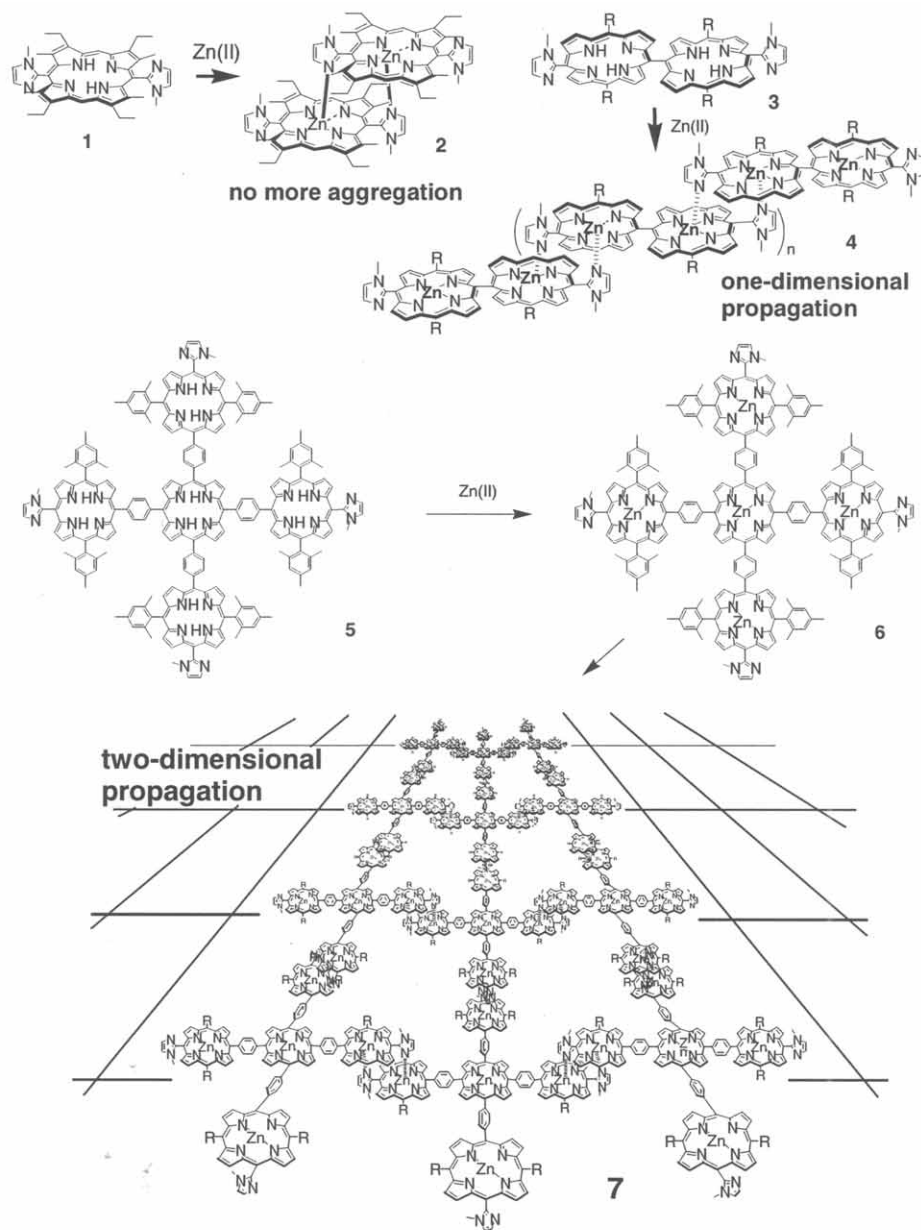


Fig. (1). Self-assembled porphyrin arrays formed by complementary coordination of imidazolyl to zinc.

solvent was dried at 80°C and then completely removed *in vacuo*. The thin film obtained was not soluble in any of the organic solvents tested. Because of its lower boiling point, pyridine was removed first and nitrobenzene kept the organized structure solubilized, so that a large organized structure might be formed.

Figure (3) compares the absorption spectrum of 7 on a glass plate with that of 6 in pyridine (inset). The Soret band of the monomer 6 appeared as a single peak at 431nm while that of the reorganized film 7 split into two peaks at 431 and 449nm, with the split width being 930 cm^{-1} . In a previous report [9a], the split of the Soret band in solution due to the slipped-co-facial arrangement by complementary imidazole-

Zn coordination was 1035 cm^{-1} . This agrees well with the present result. When the reorganization was carried out in pyridine without nitrobenzene being present as a co-solvent, only a minor split of the absorption spectrum was observed. The small degree of peak broadening observed indicated incomplete coordination. From these results, it can be concluded that formation of a self-assembled porphyrin array on a glass plate was achieved by slow evaporation from a pyridine/nitrobenzene solution, but not from pure pyridine.

Figure (4) shows AFM (atomic force microscope) images of 7 on a mica plate prepared in the same manner as that on the glass plate. Figure (4a) shows several spots in a 6 \times 6 μm^2 scales. The sample widths were distributed around an

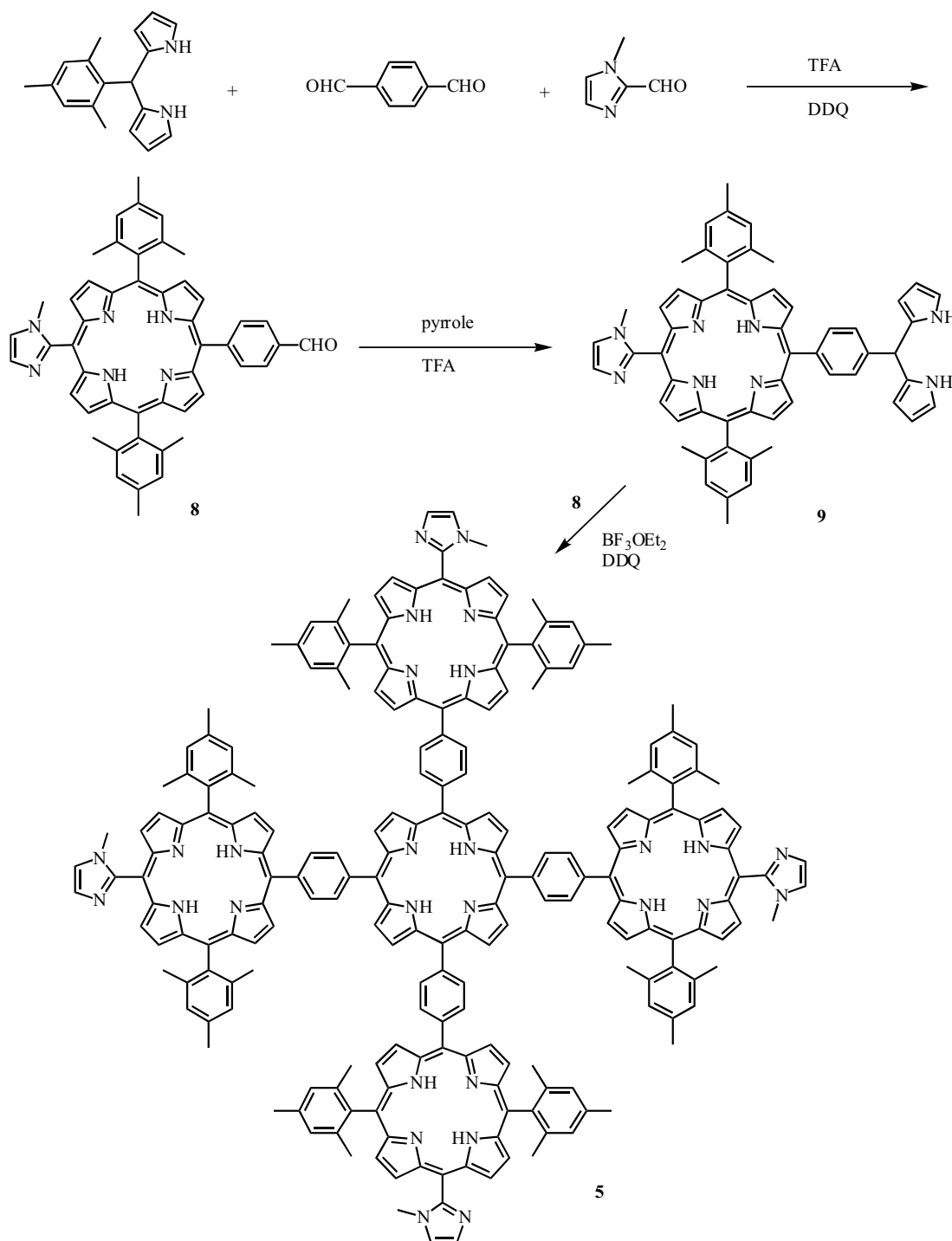


Fig. (2). Synthetic routes to porphyrin pentamer 5.

average of 350nm. As the distance between two diagonal zincs (see Fig. (5)) was 3nm, the average width corresponded to a lining-up of 120 pentamers, i.e. 360 diagonal porphyrins. In the case of previously reported one-dimensional porphyrin array, GPC analysis gave a distribution maximum in solution as 80 links of porphyrin dimer units [9b]. The height of the AFM trace varied between 2 and 6nm, corresponding to between 6 and 18 layers of 6, assuming a molecular thickness of 0.33nm and an inter-planar distance of 0.32nm [11]. As shown in Fig. (5), each nitrogen atom of the *N*-methyl-imidazolyl group can coordinate to the central zinc ion from either axial

direction. From this viewpoint, the self-assembly cannot always be alternating, and the thickness should be more than $(0.33 + 0.32)\text{nm}$. Figure (4b) presents an AFM image with an enlarged scale of $400 \times 400\text{nm}^2$ and a cross-section profile. A thin layer of 2.0 ~ 2.4nm, corresponding to 6 ~ 7 porphyrin layers, developed over 390nm. This length corresponds to linking of approximately 130 porphyrin pentamer units along the line indicated in Fig. (4b). AFM experiments using free base 5 cast onto a mica plate in a manner similar to that of 7 showed only small spots without any aggregation. The average widths of these spots were approximately 30nm.

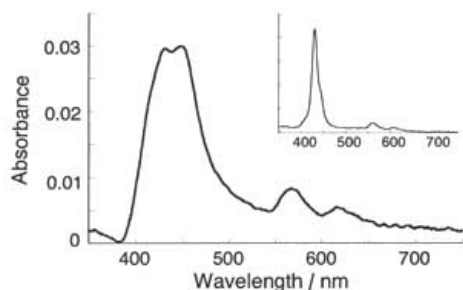


Fig. (3). Absorption spectrum of **7** evaporated from nitrobenzene/pyridine on glass plate and of **6** in pyridine (inset).

Figure (6a) shows the fluorescence mapping image of a film of **7** imaged with a scanning confocal microscope on a glass plate which was prepared in the same manner as that used in the AFM experiments. Several emitting spots were observed. The size of these spots was distributed between 200 and 400nm, in agreement with the results of the AFM measurements. Although the spatial resolution of this technique was 200nm, the distribution of samples in the fluorescence image was similar to the AFM images. Figure (6b) represents the fluorescence spectrum of the film at the point indicated by an arrow. Two peaks, at 620 and 670nm, were observed, corresponding to emissions typical of self-organized Zn-porphyrin. This spectrum was observed at any emitting spot and indicated that the thin layer observed by AFM was composed of porphyrin.

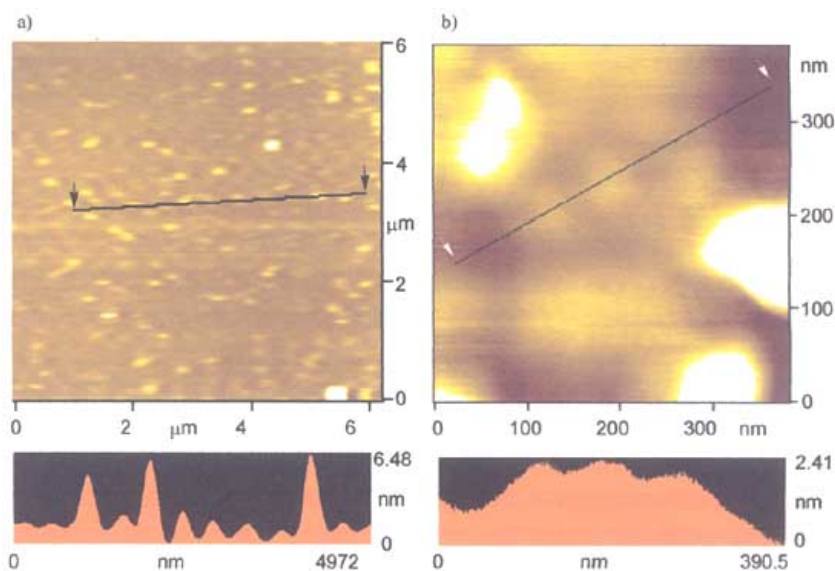


Fig. (4). AFM images of **7** on a mica plate. (a) $6 \times 6 \mu\text{m}^2$ scale with $5\mu\text{m}$ cross-section along the line. (b) $400 \times 400\text{nm}^2$ scale with 390nm cross-section along the line.

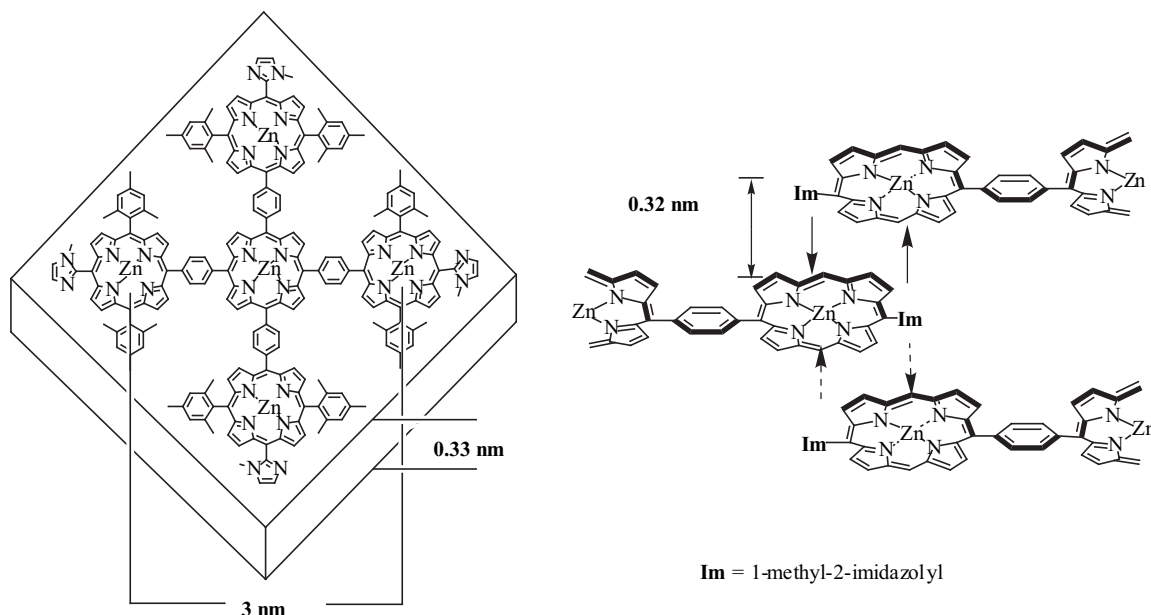


Fig. (5). Schematic representation of repeat length and molecular thickness, and two possible coordination directions of imidazolyl to zinc.

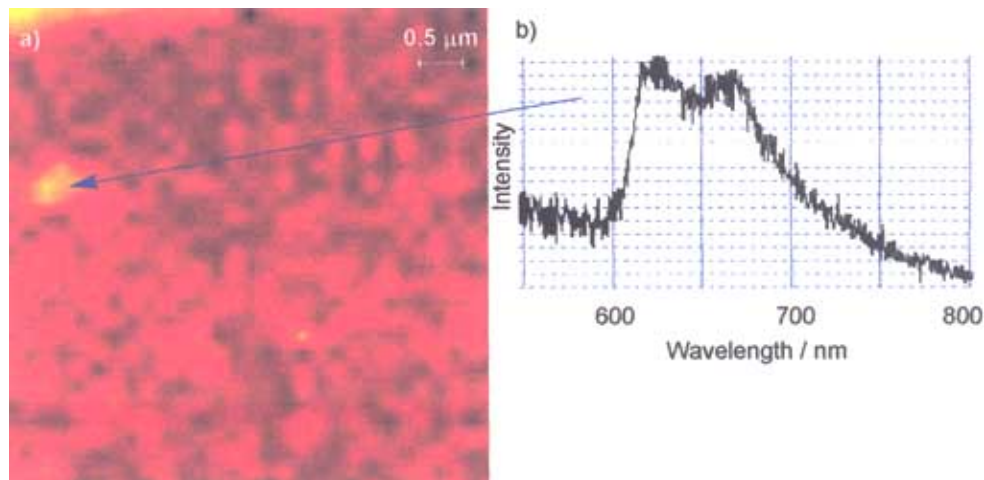


Fig. (6). a) Fluorescence image of a thin film of **7** on a glass plate measured by scanning confocal microscope and b) fluorescence spectrum of the film at the point indicated by the arrow.

CONCLUSIONS

From observations of Zn-porphyrin films by UV/VIS spectroscopy, AFM, and fluorescence confocal microscopy, it was concluded that the organization of a porphyrin array developed two dimensionally with molecular lengths reaching over a 100 ~ 200nm scale. This size corresponds to the present limit of the down-sizing technology [1d]. The structural details of such films are currently being investigated using high resolution STM (scanning tunneling microscopy). The complementary coordination of imidazolyl to zinc can be manipulated to start with a monolayer on a solid surface and to be terminated by the addition of specific porphyrins or further to be broken by the addition of ligand such as methanol or pyridine [9b]. Two-dimensional propagation of a multi-porphyrin array may lend these substrates to applications in molecular photonic and electronic devices [1b,1c].

EXPERIMENTAL

Synthesis of 5-(1-Methyl-2-Imidazolyl)-10,20-bis(Mesityl)-15-(4-Formylphenyl) Porphyrin (**8**)

Under an argon atmosphere, 1-methylimidazole-2-carboxyaldehyde (5.0mmol), terephthalaldehyde (5.0mmol), and 5-(mesityl)dipyrromethane (10mmol) were dissolved in 1 L of chloroform, and then trifluoroacetic acid (40mmol) was added. After stirring for 3 h at room temperature, 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ, 15mmol) was added and the reaction mixture was stirred for a further 1 h. The reaction solution was washed with aqueous sodium bicarbonate, and the organic layer was then evaporated. The crude product was purified by silica gel column chromatography (eluent: chloroform/hexane/acetone = 20:6:1) to yield 0.42mmol of **8**, in 8.4% yield. MS (MALDI-TOF) found, 731.90 ($[M+H]^+$), Calculated 731.90 ($[M+H]^+$); λ_{abs} (chloroform) 419.5, 513.5, 551.0, 589.5, 627.8nm; $^1\text{H NMR}$ (270 MHz, CDCl_3) δ 10.38 (s, formyl, 1H), 8.74 (br, 2, 8, 12, 13, 17, 18, 6H), 8.72 (br, 3, 7, 2H), 8.28-8.45 (m, phenyl, 4H), 7.65 (s, im-5, 1H), 7.48 (s, im-4, 1H), 7.29 (s, mesityl, 2H), 7.28(s, mesityl, 2H), 3.52 (s,

$\text{CH}_3(\text{im})$, 3H), 2.63 (s, $\text{CH}_3(\text{mesityl})$, 6H), 1.90 (s, $\text{CH}_3(\text{mesityl})$, 6H), 1.76 (s, $\text{CH}_3(\text{mesityl})$, 6H), -2.64 (s, NH, 2H).

Synthesis of 5-(4-(5-(1-Methyl-2-Imidazolyl)-10,20-bis(Mesityl)-15-Porphinyl)-Phenyl)Dipyrromethane (**9**)

8 (0.012mmol) was dissolved in 3mL of pyrrole and degassed with a stream of N_2 for 5 minutes and then trifluoroacetic acid (0.060mmol) was added. After stirring for 3 h at room temperature, the solution was diluted with 50mL of chloroform and washed with 0.1N aqueous sodium hydroxide. The solvent was removed by evaporation and the unreacted pyrrole was then removed by vacuum distillation at room temperature. Recrystallization from chloroform/hexane gave the title compound (0.010mmol, 81%). $^1\text{H NMR}$ (270 MHz, CDCl_3): δ 8.82 (d, $J=4.8$ Hz, 3' and 7', 2H), 8.75 (br, 12', 13', 17', and 18', 4H), 8.69 (d, $J = 4.8$ Hz, 2' and 8', 2H), 8.26 (br, NH, 2H), 8.19, 8.11 (m, phenylene, 2H), 7.64 (s, im-5, 1H), 7.59 (d, $J = 8.4$ Hz, phenylene, 2H), 7.47 (s, im-4, 1H), 7.29 (s, mesityl, 4H), 6.87, 6.30, 6.17 (each m, pyrrole, 2H \times 3), 5.82 (s, meso-H, 1H), 3.51 (s, $\text{CH}_3(\text{im})$, 3H), 2.64 (s, $\text{CH}_3(\text{mesityl})$, 6H), 1.89 (s, $\text{CH}_3(\text{mesityl})$, 6H), 1.76 (s, $\text{CH}_3(\text{mesityl})$, 6H), -2.62 (s, NH, 2H). MS (MALDI-TOF) found, 848.06 ($[M+H]^+$), Calculated 848.06 ($[M+H]^+$).

Synthesis of 5,10,15,20-Tetrakis(4-(5-(1-Methyl-2-Imidazolyl)-10,20-bis(Mesityl)-15-Porphinyl)Phenyl)Porphyrin (**5**)

Under an argon atmosphere, **8** (6.3 μmol) and **9** (6.3 μmol) were dissolved in 1.3mL of chloroform, and then trifluoroacetic acid (0.16mmol) was added. After stirring for 3 h at room temperature, the precipitate was filtered off. The solid was re-dissolved in 3mL of chloroform/methanol (2:1) followed by addition of 0.16mmol of triethylamine and 50.6 μmol of *p*-chloranil. After stirring for 10 h at room temperature, the reaction solution was washed with 0.1N aqueous sodium hydroxide, and then the organic layer was evaporated to dryness. The crude product was purified by

silica gel column chromatography (eluent: chloroform/acetone = 10:1 to 5:1) followed by recrystallization from chloroform/methanol to give the title compound (0.42 μmol, 13.2%). MS (MALDI-TOF) found, 3112.43 ([M+H]⁺), Calculated 3112.45 ([M+H]⁺); λ_{abs} (chloroform) 419.5, 514.5, 550.0, 588.0, 626.8 nm; ¹H NMR (270 MHz, CDCl₃) δ 9.59 (s, 2,3,7,8,12,13,17,18, 8H), 9.38 (d, J=4.6 Hz, 13', 17', 8H), 8.97 (d, J=4.6 Hz, 3', 7', 8H), 8.70-8.83 (m, 2',8',12',18', phenylene, 32H), 7.70 (s, im-5, 4H), 7.52 (s, im-4, 4H), 7.39 (s, mesityl, 4H), 7.38 (s, mesityl, 4H), 3.58 (s, CH₃(im), 12H), 2.72 (s, CH₃(mesityl), 12H), 2.03 (s, CH₃(mesityl), 12H), 1.89 (s, CH₃(mesityl), 12H), -2.18 (s, NH, 2H), -2.41 (s, NH, 8H).

Synthesis of 5,10,15,20-Tetrakis(Zinc 4-(5-(1-Methyl-2-Imidazolyl)-10,20-bis(Mesityl)-15-Porphinyl)Phenyl)Porphyrinatozinc(II) (6)

A saturated solution of zinc acetate dihydrate in methanol (5 μL) was added to a solution of free base porphyrin-pentamer **3** (0.3 mmol) in 0.5 mL of chloroform/methanol (10:3). After stirring for 3 h at room temperature, the solution was washed with water. The insoluble product, which was self-assembled polymer **7**, was filtered off and the solid was washed with chloroform and then water. MS (MALDI-TOF) found for 3429.67 ([M+H]⁺), Calculated 3429.71 ([M+H]⁺); λ_{abs} (pyridine) 431.0, 561.0, 608.0 nm (observed as pentamer **6**).

AFM (Atomic Force Microscopy) Measurements

AFM measurements were performed with a SEIKO SPI 3800N using the dynamic force (non-contact) mode. Sample preparation onto a mica plate is described in the main text.

Fluorescence Mapping Image and Spectrum Measurements

Fluorescence mapping images and spectra were measured with a scanning confocal microscopy system, *Nanofinder*, made by Tokyo Instruments, Inc. An argon ion laser was used for excitation at 488 nm with laser power of 5 μW. The spatial resolution was approximately 200 nm. Exposure times were 50 ms per point for mapping measurement and 60 s for spectrum measurement, respectively.

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