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Abstract: In this study we synthesized two- and four-armed porphyrins—bearing two carboxyl and four 2-aminoquinolino functionalities, respectively, at their meso positions—as a complementary hydrogen bonding pair for the self-assembly of a D_2-symmetric porphyrin trimer host. Two units of the two-armed porphyrin and one unit of the four-armed porphyrin self-assembled quantitatively into the D_2-symmetric porphyrin trimer, stabilized through ammidinium–carboxylate salt bridge formation, in CH_2Cl_2 and $CHCl_3$. The porphyrin trimer host gradually bound two units of 1,3,5-trinitrobenzene between the pair of porphyrin units, forming a five-layer aromatic structure. At temperatures below –40 °C, the rates of association and dissociation of the complexes were slow on the NMR spectroscopic time scale, allowing the 1:1 and 1:2 complexes of the trimer host and trinitrobenzene guest(s) to be detected independently when using less than 2 eq of trinitrobenzene. Vis titration experiments revealed the values of K_1 (2.1 ± 0.4 × 10^5 M^{-1}) and K_2 (2.2 ± 0.06 × 10^4 M^{-1}) in $CHCl_3$ at room temperature.

Introduction

Porphyrins have been used widely as supramolecular tools for the development of self-assembled molecular cages[1–3] because of their attractive electronic and photophysical properties[4–8] and catalytic activities,[9–15] as well as their symmetric aromatic structures. For example, the construction of self-assembled multi-porphyrin architectures has been achieved through the intermolecular axial coordination of identical metalloporphyrin units bearing covalently linked ligand moieties[16–20] and the pairing of multi-metalloporphyrins with appropriate multidentate ligands.[21–25] Some of these methodologies have been developed to provide multi-porphyrin systems that are capable of binding guest molecules.[26–28]

Molecular paneling approaches,[29–33] which exploit intermolecular interactions between functionalities located at corner positions of the porphyrins and appropriately designed other molecules, have also been applied extensively for the preparation of a wide variety of three-dimensional porphyrin architectures.[34–39] Multi-porphyrin architectures that feature free space between the surfaces of their porphyrin components can often accommodate guests with stabilization through axial coordination,[40,41] π-stacking,[42–46] and other interactions between the (metallo)porphyrin units and the guest molecules.[47,48]

Furthermore, regulation of the distance between the porphyrin units can lead to the recognition of several guest units and the formation of multi-layer π-aromatic structures. For example, the Nitschke group prepared a porphyrin-faced cubic host that could encapsulate three units of coronene and two of C_{60}; these host–guest complexes contained multi-layer π-aromatic structures.[49, 50] In addition, the Shionoya group synthesized a four-layer π-aromatic structure from a hexameric porphyrin cage having a triangular bipyramidal-shaped cavity and two units of 2,7-dinitro-9-fluorenone.[51] Furthermore, Jacquemin and Zysman-Colmana recently reported the construction of a porphyrin cage that could encapsulate up to three units of fluorescein within its cavity.[52]

These attractive recognition systems of porphyrin cage hosts and several aromatic guests selectively formed uniform multi-layer (in these cases, greater than four layers) π-aromatic structures. These strategies employed cages that bound the multiple guest units in a single large cavity; in the examples above, the self-assembled multi-porphyrin frames were constructed from coordination bonds, which relatively strong among reversible bonds and feature predictable coordination geometries.

Hydrogen bond–directed (metallo)porphyrin oligomers have been reported by some groups,[53–55] and the some of these structures have bound guest molecules, stabilized through coordination bonds.[56–59] Recently, we constructed a hetero-dimer from a pair of porphyrin units, **P1** and **P2**, stabilized by intermolecular hydrogen bonds (Figures 1a and 2).[60] These porphyrin derivatives featured two amidino (2-aminoquinolino) and two carboxyl groups, respectively. A 1:1 mixture of **P1** and **P2** in $CHCl_3$ or CH_2Cl_2 self-assembled quantitatively into their hetero-dimer, featuring two ammidinium–carboxylate salt bridges. This dimer bound electron-deficient π-aromatic compounds, forming three-layer π-aromatic structures that did not feature any metal–ligand interactions. Because this dimer comprised two different porphyrin components, either of which could be modified. In this present study, we prepared the four-armed porphyrin derivative **P3**, presenting four aminoquinolino groups (Figure 2). Herein, we report the D_2-symmetric self-assembled porphyrin trimer **P1·P3·P1** constructed from two equivalents of the two-armed porphyrin **P1** and one equivalent of the four-armed porphyrin **P3**; again, this structure did not feature any coordination bonds (Figure 1). Moreover, we have constructed a five-layer π-aromatic structure from this trimer through encapsulation of aromatic guests between its pairs of porphyrin units.
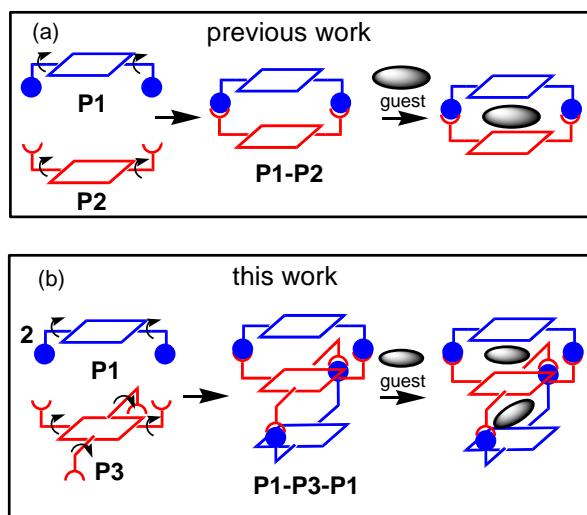
Figure 1. Cartoon representation of the construction of (a) the porphyrin dimer **P1·P2** and (b) the porphyrin trimer **P1·P3·P1** and their encapsulation of guest molecules. The structures of porphyrins **P1**−**P3** are displayed in Figure 2.
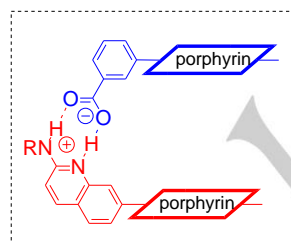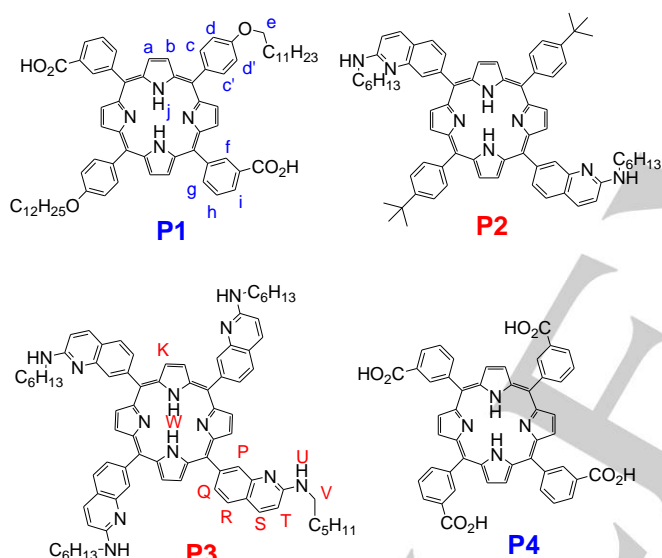

Figure 2. Structures of the porphyrins **P1**−**P4** and of the ammidinium–carboxylate salt bridges.

Results and Discussion

Synthesis of porphyrin P3: When expanding the hetero-dimer **P1·P2**, we had the choice of two pairs of two- and four-armed porphyrin units for construction of self-assembled porphyrin

trimers (either **P1·P3·P1** or **P2·P4·P2**). We chose the porphyrin trimer **P1·P3·P1**, thereby avoiding any potential concerns regarding the solubility of the tetracarboxyporphyrin **P4**. Molecular modeling of the structure formed from the trimer **P1·P3·P1** and two units of trinitrobenzene supported the formation of a five-layer π-aromatic structure (Figure S1). We prepared the four-armed porphyrin **P3** through condensation of pyrrole and the aldehyde **1**[60] (Scheme 1).
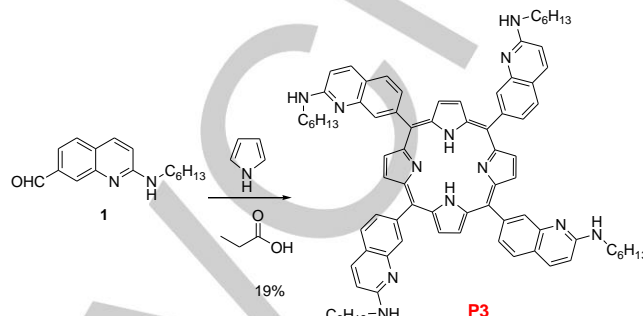
Scheme 1.

Formation of the porphyrin trimer P1·P3·P1: The two-armed carboxy-porphyrin **P1** was not soluble in CH_2Cl_2 and $CHCl_3$. Nevertheless, after mixing a solution of the two-armed porphyrin **P1** (2.0 eq) in THF with a solution of the four-armed amidino-porphyrin **P3** (1.0 eq) in $CHCl_3$, replacement of the solvent with CD_2Cl_2 resulted in a solution of the complex. The ^1H NMR spectrum (CD_2Cl_2, 25 °C) of the solution of a 2:1 mixture of **P1** (0.5 mM) and **P3** (0.25 mM) revealed one set of signals for each porphyrin component (Figure 3b). The signal for the ammidinium proton NH_U appeared at 12.35 ppm (initially at 4.96 ppm in the spectrum of **P1** alone: $\Delta\delta$ = 7.39 ppm; Figure S2); this shifting suggested the formation of an ammidinium–carboxylate complex. The signals of the NH protons at the centers of both porphyrin rings shifted upfield (Hj: from –2.80 to –3.81 ppm; H_W: from –2.68 to –4.50 ppm) (Figure 3), suggesting a cofacial arrangement of the three porphyrin units.
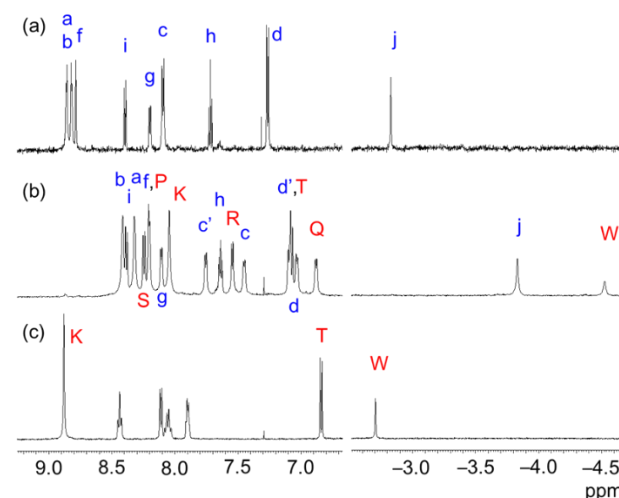

Figure 3. ^1H NMR spectra (600 MHz, CD_2Cl_2) of (a) **P1** in the presence of an excess of Et_3N, (b) a mixture of **P1** (0.5 mM) and **P3** (0.25 mM), and (c) **P3**.

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This structure was supported by the value of $\Delta\delta$ for the NH_W units of **P3**, which would have been positioned at the center of the trimer, being larger than that of those of **P1**, and by the chemical shift of H_i being similar to that of the NH protons of the dimer **P1·P2** (–3.59 and –3.58 ppm, respectively).[60] In addition, the signals of the protons H_c and H_d, in the phenyl rings aligned perpendicular to the porphyrin rings, were split into two signals (Figure 3b), consistent with the desymmetrization of the porphyrin surface of **P1** in the trimer **P1·P3·P1**. We also confirmed the formation of the trimer **P1·P3·P1** in CDCl₃, as characterized by the similar ¹H NMR spectral features of a 2:1 mixture of **P1** and **P3** in this solvent (Figures S3). Furthermore, the ESI mass spectrum of a 2:1 mixture of **P1** and **P3** featured a peak at m/z 1678.96, corresponding to the trimer [**P1·P3·P1** + 2H]²⁺ (Figure 4).
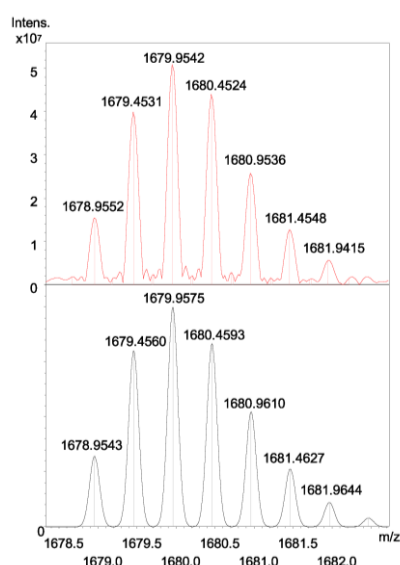

Figure 4. ESI mass spectrum of the porphyrin complex **P1·P3·P1**: experimental (top) and calculated (bottom) isotopic patterns.
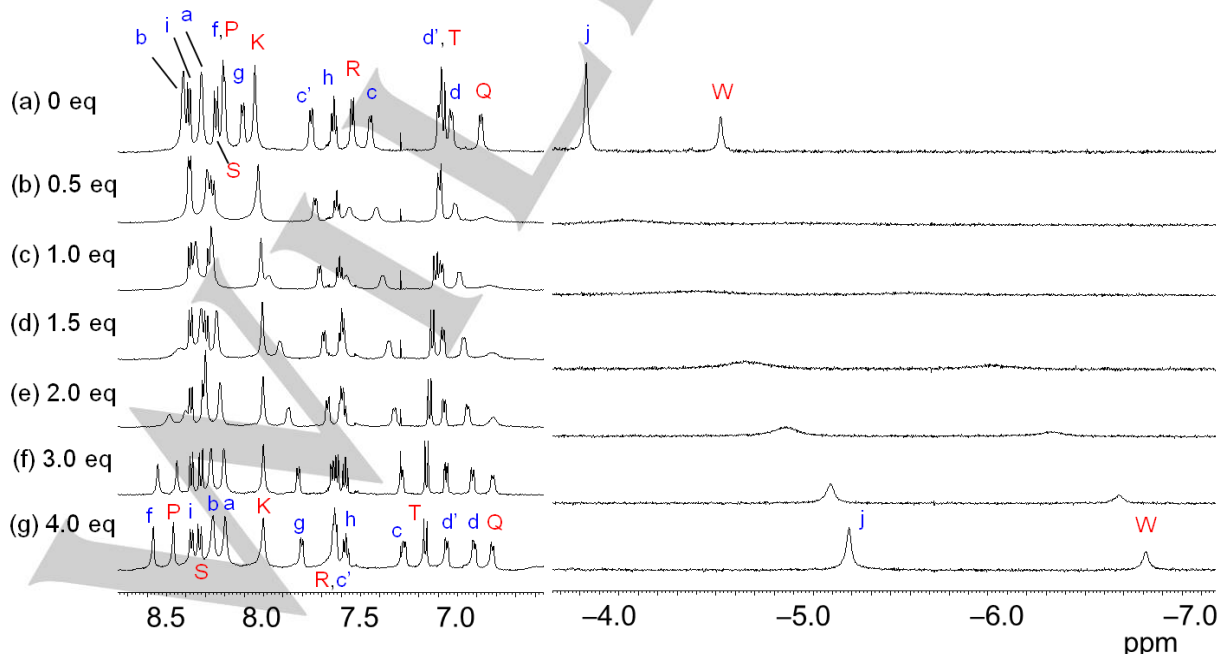
Association of the self-assembled trimer with 1,3,5-trinitrobenzene NMR spectroscopic titration experiments: We performed ¹H NMR spectroscopic titration experiments of the trimer **P1·P3·P1** and 1,3,5-trinitrobenzene (TNB), which was good guest for the dimer **P1·P2** (Figures 5 and S4). Most of the signals of the trimer broadened until 2.0 eq of TNB had been added. After the addition of more than 3.0 eq of TNB (Figures 5f and 5g), these signals became sharp again. Notably, in the presence of 4.0 eq of TNB, the signals of the porphyrin NH protons at the centers of both porphyrin rings shifted upfield significantly (H_i: to –5.17 ppm; H_W: to –6.70 ppm; Figure 5g). These observations, consistent with the shielding effects of TNB, suggested that the trimer **P1·P3·P1** did indeed encapsulate two units of TNB, one between each of its pairs of cofacial porphyrin units. Because the rates of association and dissociation of TNB were faster than the NMR spectroscopic time scale at 25 °C, we recorded variable-temperature (VT) NMR spectra to identify the two possible complexes TNB@**P1·P3·P1** and TNB₂@**P1·P3·P1** (Figures 6 and S5–7). In the presence of 0.5 equivalents of TNB at –40 °C, three equally integrated signals of porphyrin NH protons (H_i and H_W) appeared at –4.20, –5.39, and –5.99 ppm (Figure 6b); these signals decreased in intensity after the addition of more than 1.5 equivalents of TNB. Accordingly, we assigned these three signals to the 1:1 complex TNB@**P1·P3·P1**. Two new signals for the porphyrin NH protons (at –5.58 and –7.11 ppm) appeared after the addition of more than 1.0 equivalent of TNB (Figures 6c–g). Because the integration of these two signals for the porphyrin NH protons was always 2:1, and because they appeared at high field, we assigned them to the 2:1 complex TNB₂@**P1·P3·P1**. Interestingly, changes in the temperature affected the chemical shifts of the signals for the NH units. For example, the signals for the protons H_W and H_i appeared at –5.65 and –7.12 ppm at –40 °C and at –5.80 and –7.20 ppm at –60 °C (Figures S6g–i). This additional shielding effect is consistent with stronger hydrogen bonds at lower temperatures and the likelihood for corresponding decreases in the distances between the three porphyrin and two TNB aromatic units. In addition, we observed a broad signal for free TNB at 8.99 ppm when 4.0 equivalents of

Figure 5. ¹H NMR spectra (600 MHz, CD₂Cl₂) of a mixture of **P1** (0.50 mM) and **P3** (0.25 mM) in the presence of TNB (0–4 eq) at 25 °C.

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TNB were present at –40 °C (Figure S6g). We could not, however, detect the signal of encapsulated TNB in the same ^{1}H NMR spectrum. Because the signal of the encapsulated TNB signal appeared near 2.2 ppm in the case of TNB@**P1·P2** under similar conditions,[60] we suspect that the signal for TNB in the complex TNB$_2$@**P1·P3·P1** was obscured by other intense signals in the range 1.0–1.8 ppm. Moreover, the amount of TNB also influenced the intensity of the high-field chemical shift of the proton H$_W$. For example, the signal of H$_W$ appeared at –5.58 and –5.65 ppm in the presence of 2.0 and 4.0 equivalents, respectively, of TNB at –40 °C (Figure 6). We suspect that the signal of the NH units of porphyrin located at the edge of the trimer shifted to the high-field region upon increasing the content of TNB at –40 °C because the excess TNB units interacted with the surface of the complex at low temperature, possibly forming a six-layer π-aromatic structure.
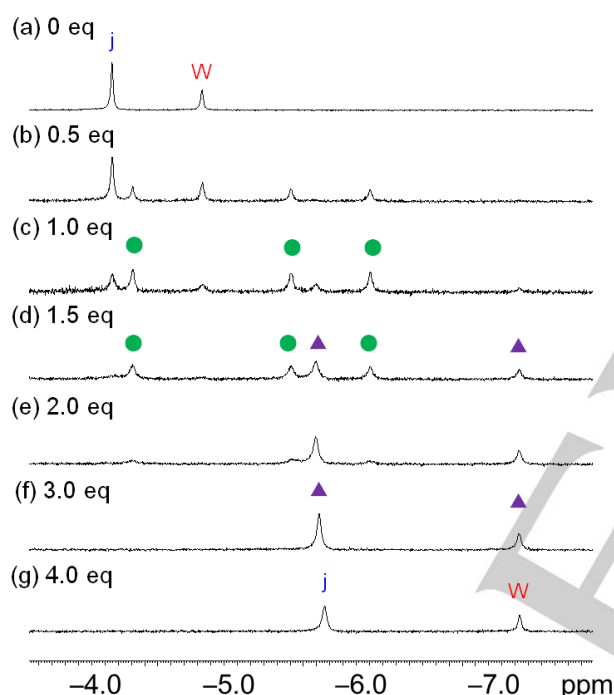

Figure 6. ^{1}H NMR spectra (600 MHz, CD$_2$Cl$_2$) of a mixture of **P1** (0.50 mM), **P3** (0.25 mM), and TNB (0–4 eq) at –40 °C. ● : TNB@**P1·P3·P1**. ▲ : TNB$_2$@**P1·P3·P1**.

We calculated the ratio of the association constants K_1 and K_2 at –40 °C, defined by Equations (1) and (2), based on integration of the signals of the NH units of each of the three species in the ^{1}H NMR spectra of 1:0.5–1:2 mixtures of the porphyrin trimer **P1·P3·P1** and TNB at –40 °C. The value of K_1/K_2 was approximately 12 at –40 °C, suggesting negative allosteric cooperativity. Encapsulation of one unit of TNB would decrease the electron-donating ability of the porphyrin located at the center of the **P1·P3·P1** complex, thereby inducing the negative allosteric effect for the binding of the second TNB unit.

$$K_1 = \frac{[\text{TNB@}\mathbf{P1·P3·P1}]}{[\mathbf{P1·P3·P1}][\text{TNB}]} \quad (1) \qquad K_2 = \frac{[\text{TNB}_2\text{@}\mathbf{P1·P3·P1}]}{[\text{TNB@}\mathbf{P1·P3·P1}][\text{TNB}]} \quad (2)$$

Vis spectroscopic titration experiments: We used Vis spectroscopic titration to identify the association constants for the binding of the porphyrin trimer **P1·P3·P1** with TNB. Figure 7 displays the Vis absorption spectra of **P1·P3·P1** (10 μM) and TNB (0–108 eq) in CHCl$_3$ at room temperature. The Q bands of the trimer **P1·P3·P1** appeared at 517, 553, 592, and 647 nm. Upon addition of TNB to the solution of **P1·P3·P1**, all of these peaks decreased in intensity, with the peaks at 553 and 647 nm red-shifting slightly. From two performances of the Vis spectroscopic titration experiments, we used Bindfit[61] to calculate the association constants K_1 (2.1 ± 0.4 × 10^5 M^{-1}) and K_2 (2.2 ± 0.06 × 10^4 M^{-1}) for the complexation of **P1·P3·P1** with TNB at room temperature, as defined by Equations (1) and (2). The ratio K_1/K_2 was approximately 10 (from Vis spectral titration at room temperature) and close to the value (ca. 12) determined through NMR spectroscopy at –40 °C. The association constant of the original hetero-dimer **P1·P2** (4.86 × 10^4 M)[60] was smaller than the value of K_1, but larger than the value of K_2. In consideration of the number of recognition sites in **P1·P3·P1** (two cavities) and **P1·P2** (one cavity) and the electron density of the center porphyrin moieties in **P1·P3·P1** and TNB@**P1·P3·P1**, these association constants appear to be reasonable.
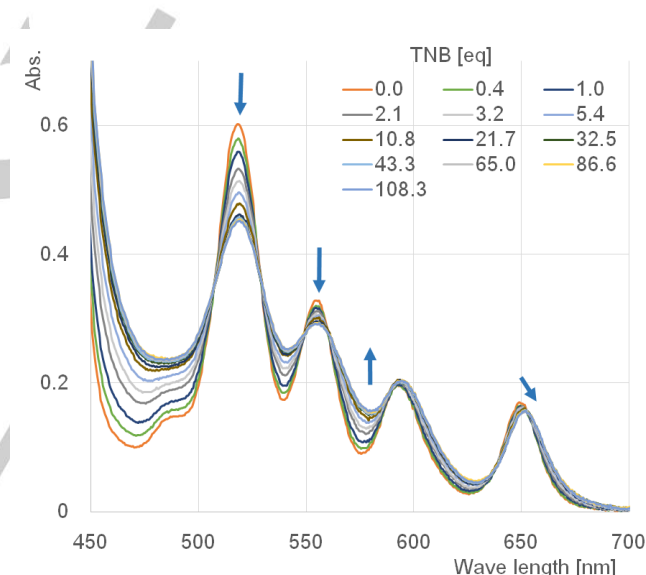

Figure 7. Vis absorption spectra of the trimer **P1·P3·P1** (CHCl$_3$, 10 μM) in the presence of TNB (0–108 eq).

Summary

We have constructed a self-assembled D_2-symmetric porphyrin trimer **P1·P3·P1**, comprising a pair of two- and four-armed porphyrin units, stabilized through ammidinium–carboxylate salt bridges. The trimer **P1·P3·P1** is capable of encapsulating within its two cavities up to two TNB molecules, forming a five-layer π-aromatic structure. The rates of association and dissociation of the complex were fast on the NMR spectral time scale at room temperature. At low temperature, however, the two complexes TNB@**P1·P3·P1** and TNB$_2$@**P1·P3·P1** could be detected independently through NMR spectroscopy. The ratio K_1/K_2 was approximately 12 at –40 °C, as estimated using NMR spectral titration. Vis spectroscopic titration experiments provided values

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for the association constants K_1 ($2.1 \pm 0.4 \times 10^5$ M^{-1}) and K_2 ($2.2 \pm 0.06 \times 10^4$ M^{-1}) for the interaction of the trimer with TNB at room temperature.

Construction of self-assembled multilayer π-aromatic structures has typically been achieved through use of a cage featuring a single large cavity to recognize several aromatic guest molecules. Our strategy in this study involved the use of a cage featuring of two recognition sites and two guests;[62] large allosteric effects would not be expected in comparison with the typical strategy. We could, however, detect the presence of the intermediate aromatic structures in our system. That is, we observed the ^{1}H NMR spectral signals of the NH units of the porphyrins in the intermediate TNB@P1·P3·P1; the changes in the chemical shifts of these signals were consistent with ring current effects in the multilayer structure.

Experimental Section

Materials and General Methods: The porphyrin **P1** and compound **1** were prepared according to literature procedures.[60] All solvents and commercially available chemicals were used as received. ^{1}H and ^{13}C NMR spectra were recorded using JEOL ECX-500II and ECA-600II spectrometers, with tetramethylsilane (TMS) as the internal standard. Vis absorption spectra were recorded using a Hitachi U-3900 spectrometer. Mass spectra were recorded using Bruker Daltonics autoflex (MALDI), and Bruker Daltonics solarix-JA (ESI) spectrometers. Infrared spectra were recorded using a Shimadzu FTIR-8600PC spectrometer. All reactions were performed under a positive atmosphere of dry N$_2$. All solvents were removed through rotary evaporation under reduced pressure. Silica gel column chromatography was performed using Kanto Chemical silica gel 60 N. Thin layer chromatography (TLC) was performed using Merck Kieselgel 60PF$_{254}$.

5,10,15,20-Tetra-2-hexylaminoquinolinyl-21H-23H-porphyrin   P3: Pyrrole (320 μL, 4.95 mmol) was added to a solution of 2-hexylamino-7-formylquinoline (1.00 g, 3.90 mmol) in propionic acid (26 mL) at 140 °C. The mixture was heated under reflux for 90 min and then stirred for 4 h under air at room temperature. After evaporation of the solvent, the residue was diluted in CH$_2$Cl$_2$ (40 mL). The solution was washed with sat. sodium carbonate (aq.) and brine and then dried over sodium sulfate. After concentration of the solution, the residue was purified through silica gel column chromatography (toluene/acetone, 10:1) to afford the crude product, which was washed with MeOH to give **P3** (229 mg, 19%) as a purple powder. IR (KBr, vmax) cm^{-1}: 3420, 3316, 2952, 2924, 2854, 1617, 1521, 1388, 1341, 1248, 1215, 1147, 1126, 967, 937, 821, 802, 732. ^{1}H NMR (600 MHz, CDCl$_3$) δ: −2.65 (s, 2H), 0.87 (t, J = 7.2 Hz, 12H), 1.27–1.48 (m, 24H), 1.65–1.74 (m, 8H), 3.50–3.58 (m, 8H), 4.86 (br s, 4H), 6.80–6.85 (m, 4H), 7.84–7.91 (m, 4H), 8.02–8.14 (m, 8H), 8.51–8.59 (m, 4H), 8.87 (br s, 8H). ^{13}C NMR (150 MHz, CDCl$_3$, 22 °C) δ: 14.0, 22.6, 26.8, 29.8, 31.6, 41.9, 111.7, 120.0, 122.7, 124.99, 125.06, 125.11, 129.3, 132.0, 137.3, 143.6, 146.7, 157.9. ^{13}C NMR (150 MHz, CDCl$_3$, 55 °C) δ: 13.9, 22.6, 26.8, 29.9, 31.6, 42.0, 111.7, 120.1, 122.9, 125.0, 129.4, 131.2, 132.4, 137.2, 143.7, 147.0, 158.1. HRMS (MALDI): calcd. for C$_{70}$H$_{74}$N$_8$ [M + H]+ m/z 1215.7171, found 1215.7177.

NMR spectroscopic titration: A solution of **P1·P3·P1** (**P1**: 0.5 mM; **P3**: 0.25 mM) in CD$_2$Cl$_2$ (0.6 mL) was prepared in a 5-mm-diameter NMR tube and initial ^{1}H NMR spectra were recorded at temperatures from +25 to −40 °C. Additional VT NMR spectra were recorded after injecting aliquots of a solution of TNB (25 mM) in CD$_2$Cl$_2$, sequentially, using a microsyringe.

Vis spectroscopic titration: A solution of **P1·P3·P1** (**P1**: 20 μM, **P3**: 10 μM) in CHCl$_3$ (3.0 mL) was prepared and its initial Vis spectrum recorded. Additional spectra were recorded after injecting a solution of TNB (1 mM for 0–3.0 eq; 10 mM for 4.0–10 eq; 100 mM for 20–100 eq) in CHCl$_3$,

sequentially, using a microsyringe. The titration experiment was performed twice.

[1] C. M. Drain, A. Varotto, I. Radivojevic, *Chem. Rev.* **2009**, *109*, 1630–1658.

[2] I. Beletskaya, V. S. Tyurin, A. Y. Tsivadze, R. Guilard, C. Stern, *Chem. Rev.* **2009**, *109*, 1659–1713.

[3] S. Durot, J. Taesch, V. Heitz, *Chem. Rev.* **2014**, *114*, 8542–8578.

[4] N. Aratani, D. Kim, A. Osuka, *Acc. Chem. Res.* **2009**, *42*, 1922–1934.

[5] J. Aimi, Y. Nagamine, A. Tsuda, A. Muranaka, M. Uchiyama, T. Aida, *Angew. Chem., Int. Ed.* **2008**, *47*, 5153–5156.

[6] A. Takai, C. P. Gros, J.-M. Barbe, S. Fukuzumi, *Chem. Eur. J.* **2011**, *17*, 3420–3428, S3420/1–S3420/12.

[7] L. Flamigni, B. Ventura, A. I. Oliva, P. Ballester, *Chem. Eur. J.* **2008**, *14*, 4214–4224.

[8] H. Ube, K. Endo, H. Sato, M. Shionoya, *J. Am. Chem. Soc.* **2019**, *141*, 10384–10389.

[9] S. S. Nurttila, W. Brenner, J. Mosquera, K. M. van Vliet, J. R. Nitschke, R. Jonathan, J. N. H. Reek, *Chem. Eur. J.* **2019**, *25*, 609–620.

[10] S. Tanaka, T. Nakazono, K. Yamauchi, K. Sakai, *Chem. Lett.* **2017**, *46*, 1573–1575.

[11] W. Brenner, T. K. Ronson, J. R. Nitschke, *J. Am. Chem. Soc.* **2017**, *139*, 75–78.

[12] A. N. Oldacre, M. R. Crawley, A. E. Friedman, T. R. Cook, *Chem. Eur. J.* **2018**, *24*, 10984–10987.

[13] M. Otte, P. F. Kuijpers, O. Troeppner, I. Ivanović-Burmazović, J. N. H. Reek, B. de Bruin, *Chem. Eur. J.* **2014**, *20*, 4880–4884.

[14] S. J. Lee, S. H. Cho, K. L. Mulfort, D. M. Tiede, J. T. Hupp, S. T. Nguyen, *J. Am. Chem. Soc.* **2008**, *130*, 16828–16829.

[15] C. Colomban, G. Szaloki, M. Allain, L. Gomez, S. Goeb, M. Salle, M. Costas, X. Ribas, *Chem. Eur. J.* **2017**, *23*, 3016–3022.

[16] C. Ikeda, Y. Tanaka, T. Fujihara, Y. Ishii, T. Ushiyama, K. Yamamoto, N. Yoshioka, H. Inoue, *Inorg. Chem.* **2001**, *40*, 3395–3405.

[17] M. R. Johnston, M. J. Latter, R. N. Warrener, *Org. Lett.* **2002**, *4*, 2165–2168.

[18] I. W. Hwang, T. Kamada, T. K. Ahn, D. M. Ko, T. Nakamura, A. Tsuda, A. Osuka, D. Kim, *J. Am. Chem. Soc.* **2004**, *126*, 16187–16198.

[19] A. Tsuda, H. Hu, R. Tanaka, T. Aida, *Angew. Chem., Int. Ed.* **2005**, *44*, 4884–4888.

[20] T. Kamada, N. Aratani, T. Ikeda, N. Shibata, Y. Higuchi, A. Wakamiya, S. Yamaguchi, K. S. Kim, Z. S. Yoon, D. Kim, A. Osuka, *J. Am. Chem. Soc.* **2006**, *128*, 7670–7678.

[21] E. Alessio, M. Casanova, E. Zangrando, E. Iengo, *Chem. Commun.* **2012**, *48*, 5112–5114.

[22] S. Ikeda, N. Aratani, A. Osuka, *Chem. Commun.* **2012**, *48*, 4317–4319.

[23] L. Flamigni, B. Ventura, A. I. Oliva, P. Ballester, *Chem. Eur. J.* **2008**, *14*, 4214–4224.

[24] S. J. Lee, K. L. Mulfort, X. Zuo, A. J. Goshe, P. J. Wesson, S. T. Nguyen, J. T. Hupp, D. M. Tiede, *J. Am. Chem. Soc.* **2008**, *130*, 836–838.

[25] M. Nakamura, K. Kishimoto, Y. Kobori, T. Abe, K. Yoza, K. Kobayashi, *J. Am. Chem. Soc.* **2016**, *138*, 12564–12577.

[26] A. Ikeda, K. Sonoda, S. Shinkai, *Chem. Lett.* **2000**, 1220–1221.

[27] Y. Kuramochi, A. Satake, Y. Kobuke, *J. Am. Chem. Soc.* **2004**, *126*, 8668–8669.

[28] P. Ballester, A. I. Oliva, A. Costa, P. M. Deya, A. Frontera, R. M. Gomila, C. A. Hunter, *J. Am. Chem. Soc.* **2006**, *128*, 5560–5569.

[29] M. D. Pluth, R. G. Bergman, K. N. Raymond, *Acc. Chem. Res.* **2009**, *42*, 1650–1659.

[30] M. Yoshizawa, M. Fujita, *Bull. Chem. Soc. Jpn.* **2010**, *83*, 609–618.

[31] M. M. J. Smulders, I. A. Riddell, C. Browne, J. R. Nitschke, *Chem. Soc. Rev.* **2013**, *42*, 1728−1754.

[32] T. Nakamura, H. Ube, M. Shionoya, *Chem. Lett.* **2013**, *42*, 328−334.

[33] T. R. Cook, P. J. Stang, *Chem. Rev.* **2015**, *115*, 7001−7045.

[34] Y. F. Han, Y. J. Lin, L. H. Weng, H. Berke, G. X. Jin, *Chem. Commun.* **2008**, 350−352.

[35] N. P. E. Barry, P. Govindaswamy, J. Furrer, G. Süss-Fink, B. Therrien, *Inorg. Chem. Commun.* **2008**, *11*, 1300−1303.

[36] Y. Yao, R. Zhao, Y. Shi, Y. Cai, J. Chen, S. Sun, W. Zhang, R. Tang, *Chem. Commun.* **2018**, *54*, 8068−8071.

[37] Y. R. Zheng, Z. G. Zhao, M. Wang, K. Ghosh, J. B. Pollock, T. R. Cook, P. J. Stang, *J. Am. Chem. Soc.* **2010**, *132*, 16873−16882.

[38] N. P. E. Barry, M. Austeri, J. R. M. Lacour, B. Therrien, *Organometallics* **2009**, *28*, 4894–4897.

[39] A. K. Bar, S. Mohapatra, E. Zangrando, P. S. Mukherjee, *Chem. Eur. J.* **2012**, *18*, 9571–9579.

[40] A. Ikeda, M. Ayabe, S. Shinkai, S. Sakamoto, K. Yamaguchi, *Org. Lett.* **2000**, *2*, 3707–3710.

[41] E. N. Kirichenko, V. S. Tyurin, I. P. Beletskaya, *Prot. Met. Phys. Chem.* **2011**, *47*, 424–434.

[42] M. Schmittel, B. He, P. Mal, *Org. Lett.* **2008**, *10*, 2513−2516.

[43] T. Nakamura, H. Ube, R. Miyake, M. Shionoya, *J. Am. Chem. Soc.* **2013**, *135*, 18790–18793.

[44] S. K. Samanta, M. Schmittel, *Org. Biomol. Chem.* **2013**, *11*, 3108–3115.

[45] C. García-Simón, M. Garcia-Borràs, L. Gómez, I. Garcia-Bosch, S. Osuna, M. Swart, J. M. Luis, C. Rovira, M. Almeida, I. Imaz, D. Maspoch, M. Costas, X. Ribas, *Chem. Eur. J.* **2013**, *19*, 1445–1456.

[46] N. Fujita, K. Biradha, M. Fujita, S. Sakamoto, K. Yamaguchi, *Angew. Chem., Int. Ed.* **2001**, *40*, 1718–1721.

[47] F. J. Rizzuto, J. P. Carpenter, J. R. Nitschke, *J. Am. Chem. Soc.* **2019**, *141*, 9087–9095.

[48] Y. Hatakeyama, T. Sawada, M. Kawano, M. Fujita, *Angew. Chem., Int. Ed.* **2009**, *48*, 8695–8698.

[49] W. Meng, B. Breiner, K. Rissanen, J. D. Thoburn, J. K. Clegg, J. R. Nitschke, *Angew. Chem., Int. Ed.* **2011**, *50*, 3479−3483.

[50] F. J. Rizzuto, J. R. Nitschke, *Nature Chem.* **2017**, *9*, 903−908.

[51] T. Nakamura, H. Ube, M. Shiro, M. Shionoya, *Angew. Chem., Int. Ed.* **2013**, *52*, 720−723.

[52] D. R. Martir, A. Pizzolante, D. Escudero, D. Jacquemin, S. L. Warriner, E. Zysman-Colman, *ACS Appl. Energy Mater.* **2018**, *1*, 2971–2978.

[53] C. M. Drain, R. Fischer, E. G. Nolen, J.-M. Lehn, *J. Chem. Soc., Chem. Commun.* **1993**, 243–245.

[54] Y. Kuroda, A. Kawashima, T. Urai, H. Ogoshi, *Tetrahedron Lett.* **1995**, *36*, 8449–8452.

[55] S. Singh, A. Aggarwal, C. Farley, B. A. Hageman, J. D. Batteas, C. M. Drain, *Chem. Commun.* **2011**, *47*, 7134–7136.

[56] Y. Kuroda, A. Kawashima, Y. Hayashi, H. Ogoshi, *J. Am. Chem. Soc.* **1997**, *119*, 4929–4933.

[57] M. C. Calama, P. Timmerman, D. N. Reinhoudt, *Angew. Chem., Int. Ed.* **2000**, *39*, 755–758.

[58] H. Katagiri, Y. Tanaka, Y. Furusho, E. Yashima, *Angew. Chem., Int. Ed.* **2007**, *46*, 2435–2439.

[59] H. L. Ozores, M. Amorín, J. R. Granja, *J. Am. Chem. Soc.* **2017**, *139*, 776−784.

[60] M. Kimura, J. Miyashita, S. Miyagawa, T. Kawasaki, H. Takaya, Y. Tokunaga, *Asian J. Org. Chem.* **2018**, *7*, 2087−2093.

[61] Bindfit (http://supramolecular.org), P. Thordarson, *Chem. Soc. Rev.* **2011**, *40*, 1305–1323.

[62] K. Kishimoto, M. Nakamura, K. Kobayashi, *Chem. Eur. J.* **2016**, *22*, 2629–2633.

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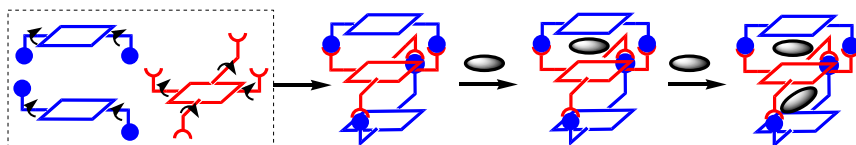
A self-assembled hetero-trimer consisting of a pair of two- and four-armed porphyrin units was constructed by using amidinium–carboxylate salt bridge formation in nonpolar solvent. The porphyrin trimer encapsulated up to two molecules of 1,3,5-trinitrobenzene within the cofacial three porphyrin units, forming five-layer π-aromatic structure.