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Single-crystal Structure of Porphyrin Bicapped with Trimethyl-β-cyclodextrins: A Novel Dye-oriented Material

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Complexes formed between porphyrins and cyclodextrins are among the most fascinating targets of host–guest complexes. So far, the structural details have been discussed on the basis of the solution properties. However, the real complex structure determined from single-crystal analysis is not known up to the present. In this paper, we report the first successful example for formation of a single crystal and its X-ray analysis. We believe that the resultant dye-oriented crystalline material would lead to novel host–guest chemistry applicable to new photo and electronic devices.

It is well-known that porphyrin derivatives act as important players in various new photo- and electrochemical research fields. Particularly, their role in the design of solar cells mimicking the natural photosynthetic system is a conspicuous example.[1] In fact, many researchers have so far constructed various artificial light-harvesting systems and charge separation systems utilizing functionalized porphyrins and their assemblies.[2,3] Through these studies, it is now well-established that to control the aggregation mode of porphyrins is a decisive factor to achieve high light-harvesting efficiency. In solution phase, however, regular control is rather difficult because of the predominantly strong π–π stacking force among the porphyrin rings, which in most cases governs the resultant aggregation mode. It thus occurred to us that the crystal phase is a potential alternative to realize a variety of new porphyrin aggregation modes. The first idea was to separate the distance among porphyrin rings through formation of inclusion complexes. In this study, we have succeeded in isolating each porphyrin in the single crystal utilizing host–guest complex formation with methylated β-cyclodextrin (β-CD) (Figure 1). Over a long period, host–guest complexes of CDs have been studied extensively.[4–9] In particular, the interaction between porphyrin and β-CD is interesting from the viewpoint of a biomimetic model for hemoproteins. It has been proposed that porphyrins form bicapped host–guest complexes with β-CDs in solution.[10,11] However, their complex structures have been discussed only on the basis of the spectral properties and theoretical calculations. It is really surprising that so far nobody analyzes the single-crystal complex structures, although the complexation modes have frequently been discussed in the references.[10–16] Here, we report the first example of the crystal structure of porphyrin bicapped with β-CDs.

2,3,6-Trimethyl-β-cyclodextrin (TMβCD) was selected to isolate a single crystal from aqueous solution, because TMβCD has higher inclusion ability for *meso*-aryl groups of tetraarylporphyrins ($K \approx 10^6\,M^{-1}$) than other β-CD derivatives.[12–16] As for a guest porphyrin, we selected 5,10,15,20-tetrapyridin-4-ylporphyrin (TPyP), because the water solubility of this compound can be adjusted by solution pH and the compound disperses well in acidic aqueous solution. Basically, there is scarce interaction between *meso*-tetrapyridiniumporphyrin and the β-CD cavity in acidic solution,[13] whereas in neutral solution TPyP becomes much less water-soluble and the hydrophobic *meso*-pyridyl groups have more chance to be included in the CD cavity.

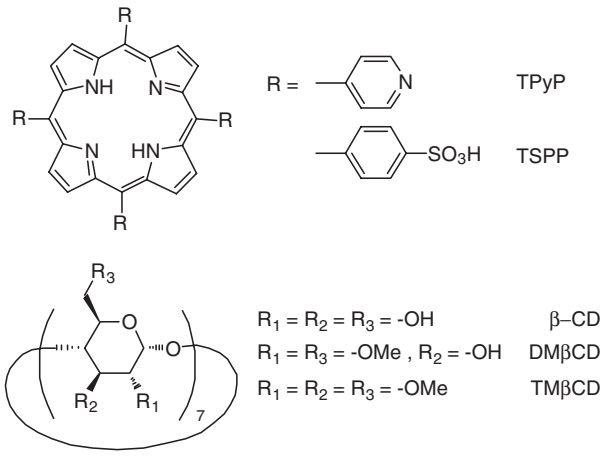

Figure 1. Structures of porphyrins and cyclodextrins.

A single crystal of TPyP·TMβCD complex was obtained from an aqueous solution of TPyP containing an excess amount of TMβCD at 60 °C.[17] It may be a little curious that crystallization of the TMβCD-based host–guest complex is performed at high temperature.[9,18,19] In general, β-CD and its derivatives are strongly solvated in aqueous solution through hydrogen bonding with water molecules. Under heating, however, the hydrogen bonds are cleaved and as a result, the hydrophobic nature of β-CD and its derivatives can emerge strongly. In particular, TMβCD behaves as a more hydrophobic host molecule, which facilitates the TMβCD complexes leading to crystal growth.[9] On the other hand, crystallization of an inclusion complex between TMβCD and tetrasulfonated phenylporphyrin (TSPP) is very difficult, because TSPP is a hydrophilic molecule and induces electrostatic repulsion among anionic charges in the solid state.

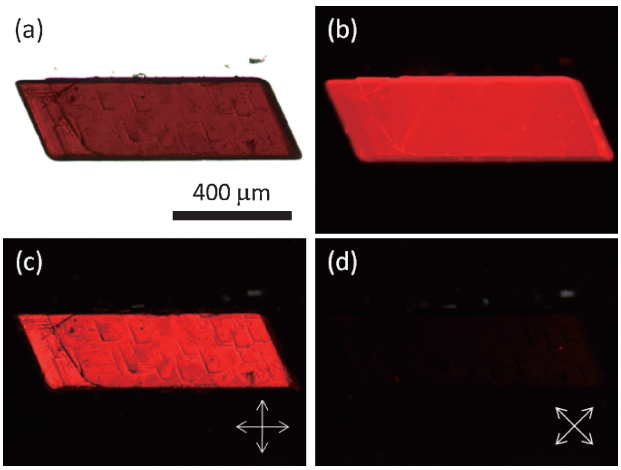

Figure 2. Microscopic images of the single crystal of TPyP bicapped with TMβCD; (a) bright-field, (b) fluorescent, and (c), (d) crossed Nicols polarized images.

The decomposition temperature of TPyP·TMβCD complex is 198–202 °C. At this temperature, the crystal changed to colorless liquid TMβCD and purple precipitate of TPyP. It is worthy to mention that this temperature is higher than the melting point of TMβCD (170–178 °C). From this high temperature, one may presume that the structure of TMβCD becomes more rigid by inclusion of TPyP into the cavity. The isolated crystal was stable without deliquescence, but when it was dispersed into neutral water, it showed good water solubility. Interestingly, the crystal showed optical anisotropy (Figure 2). Oblique extinction was observed under crossed Nicols observation. The extinction angle was 45°. Under one Nicol observation, the extinction of polarized light was observed at 135° for the major axis of the crystal. This angle is approximately between the major and minor axes. In addition, when the fluorescence was observed through the polarizer, the fluorescence intensity was minimized at 60° and maximized at 150° for the major axis of the crystal. These findings are rationalized in terms of the neat arrangement of TPyP molecules in the crystal.

The crystals of TPyP·TMβCD complex were triclinic with the unit cell parameters $a = 16.864$ Å, $b = 17.532$ Å, $c = 17.712$ Å, $\alpha = 99.0°$, $\beta = 103.3°$, and $\gamma = 112.9°$ (Figure 3, Figure S1).[20,24] We can find five water molecules in the crystal structure. Their respective occupation probability is ca. 0.2. From the low probability, we consider that these water molecules are not necessarily indispensable to stabilize the crystal structure. The structure consists of one TPyP capped with two TMβCD molecules. In addition, two *meso*-pyridyl groups of TPyP penetrate into the TMβCD cavity. This bicapped host–guest complex structure is consistent with that proposed on the basis of spectral studies in solution.[10–16] For example, Kano et al. reported that O-methylation of secondary hydroxy groups in β-CD is essential for strong guest binding.[14] They explained on the basis of ROESY and ^{13}C NMR spectra that the induced-fit complex is formed from porphyrin and TMβCD, accompanying the distortion of the β-CD ring. In our structural analysis, it is not so clear whether TMβCD is significantly distorted along the porphyrin in the top view. More obvious is the finding that the π system of the porphyrin ring is twisted to the left by 7.3° (Figure S2).[24]

Here, two important questions came to our mind. First, where can we find the structural characteristics of the induced-fit binding? Second, why is the porphyrin ring so twisted? The answers for these questions are obtained from the arrangement of seven glucose units in each CD ring. The TMβCD ring shape can be seen from the top view of the glucoside oxygen atoms linking glucose units together (Figure S3).[24] Surprisingly, they occupy almost regular positions regardless of the nesting porphyrin plane. This is contrary to our expectation, because the glucose units near the *meso*-pyridyl group should be more expanded owing to the steric crowding. On the other hand, the side view of the TMβCD ring can be illustrated by the C1

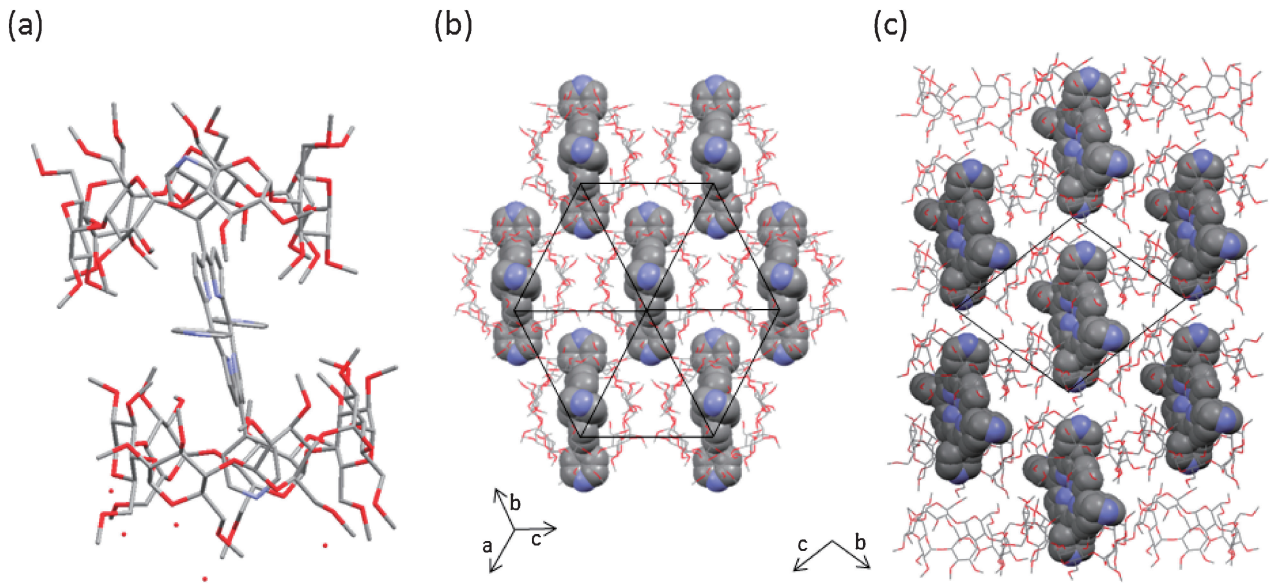

Figure 3. Structures of TPyP·TMβCD complex; (a) unit cell, (b) (111) plane, and (c) along the *a* axis. The hydrogen atoms are omitted.

and C4 atoms connected to the glucoside oxygen atoms (Figure S4).[24] One can clearly recognize that the strain in the glucose ring belt does exist. Probably, this type of strain is more advantageous than the ring strain to enhance the hydrophobic interaction with TPyP. In addition, Kano et al. reported that the bent structure of permethylated cyclodextrins which have no –OH group plays an important role in chiral recognition.[21] As the β-CD ring consists of odd seven glucose units, it is difficult for each glucose unit to sandwich a TPyP and to overlap with each other in the top view. In addition, each glucose ring belt is considerably strained. We consider that these asymmetric factors cause the twisting of the porphyrin π system.

The distances from one porphyrin to contiguous porphyrins in the crystal lattice are estimated (Figure S5).[24] The nearest one and farthest one are 1.7 and 2.9 nm, respectively. However, all porphyrins can be connected in less than 1.8 nm. Takagi et al. reported that porphyrins can be regularly arranged in a clay sheet as an inorganic host.[22] Therein, the distance between porphyrins was estimated to be about 2.4 nm. Important is their finding that the energy transfer between porphyrins can take place very efficiently. We believe, therefore, that the efficient energy transfer between porphyrins can also take place in the present crystal system.

When we used 2,6-dimethyl-β-cyclodextrin (DMβCD) instead of TMβCD, colorless crystals of DMβCD and microcrystals of TPyP were obtained separately. In aqueous solution, the binding constants between DMβCD and porphyrins are relatively large ($K \approx 10^4\,M^{-1}$), but they are smaller by two orders of magnitude than those of TMβCD.[14] Judging from the X-ray structure of the TPyP·TMβCD complex, this difference can be attributed to the CD ring rigidity. The secondary hydroxy groups in DMβCD can still form hydrogen bonds. This should suppress the induced-fit conformational change necessary to stabilize the complex.

In conclusion, we have found a new preparation method for single crystals of a porphyrin·TMβCD inclusion complex that had been repeatedly attempted but unsuccessful so far. The key points are the pH-dependent solubility change in porphyrin, the "flexibility" of TMβCD enabling the induced-fit guest inclusion, and the high temperature advantageous for the hydrophobic force. We have confirmed that this crystallization method is also applicable to a few other porphyrins bearing pH-dependent dissociable groups. The structure of TPyP and TMβCD in the single crystal is very unique, reflecting the packing mode of the inclusion complex. In addition, it has been found that TPyP molecules are oriented in the same direction within energy-transferrable distance. These structural characteristics suggest that this crystal would show interesting electrochemical and optoelectronic properties. Furthermore, we believe that this system can be extended to chiral chemistry and metalloporphyrin chemistry. In the TPyP·TMβCD crystal structure, TPyP is already twisted to the left. However, further chiral control becomes possible by introduction of chiral substituents. Thereby, these inclusion crystals would be applicable to circularly polarized luminescence (CPL).[23] Also, introduction of central metals into the porphyrin ring would change the redox potential of the metalloporphyrins, from which one can exploit a new class of photo- and electrochemical materials. We thus believe that the present study has important implications not only for basic crystal analysis but also for applide research to design new functional materials.

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20 Diffractometer, Rigaku Saturn724; radiation, Mo Kα ($\lambda = 0.71070$ Å); temperature of measurement, −149.8 °C; empirical formula: $C_{166}H_{250}N_8O_{71}$ (TPyP·2TMβCD·H_2O); fw: 3493.81, crystal size: 0.9 × 0.3 × 0.1 mm^3, triclinic crystal system, space group $P1$, $a = 16.864(4)$ Å, $b = 17.532(4)$ Å, $c = 17.712(4)$ Å, $\alpha = 98.9688(10)°$, $\beta = 103.336(3)°$, $\gamma = 112.9167(2)°$, $V = 4514(2)$ $Å^3$, $Z = 1$, $D_{calcd} = 1.285$ g cm^{-3}, $2\theta_{max} = 55.0°$, absorption coefficient $\mu = 1.002$ cm^{-1}, reflections collected: 19721, independent reflections: 19721 ($R_{int} = 0.0000$). SHELXL-97 suite of programs was used to refine the structure (G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *64*, 112). Some non-hydrogen atoms were refined anisotropically, while the rest were refined isotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement on F^2 was based on 19721 observed reflections and 2443 variable parameters. Goodness of fit on $F^2 = 1.059$, final R indices [$I > 2.00\sigma(I)$] $R1 = 0.0552$, R indices (all data) $R1 = 0.0677$, $wR2 = 0.1567$, largest diff. peaks and holes 1.02 and −0.32 eA^{-3}. CCDC: 802112.
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24 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/.

