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Construction of Polymeric Self-Assembly Based on $2\lambda^5,4\lambda^5,6\lambda^5$-Cyclotriphosphazene and Its Inclusion Behavior of Iodine

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The self-assembling of 2,2,4,4,6,6-hexakis(4-pyridylmethoxy)-$2\lambda^5$, $4\lambda^5$, $6\lambda^5$-cyclotri(phosphazene) (PyPN) and 1, 4-naphthalenedicarboxylic acid (DCN) in DMF gives needle-like crystals. From elemental analysis, the stoichiometry of the crystal was PyPN/DCN = 1 : 3. The FT-IR, fluorescence and X-ray diffraction data showed that the self-assemblies [PyPN·3(DCN)]$_n$ (**1**) formed by the hydrogen bonding with an alternating sequence of one PyPN and three DCN molecules take a cylindrical structure and are laterally packed into a hexagonal arrangement, where the naphthalene rings are placed to avoid steric congestion. The assembly **1** has an ability to include iodine molecules. From FT-Raman spectroscopy, the iodine in **1** was found to exist as a polyiodine linear I_5^- ion, indicating that the crystal of **1** has a tunnel-like void.

Design of supramolecular architectures with potentially useful properties for relevant scientific and technological applications by means of coordination bonding, hydrogen bonding, or other weak intermolecular interactions is of great interest in organizing solid-state chemistry.[1—3] A particular effort is being directed toward the synthesis of nanoporous molecular-based solids which reveal structural and functional similarity to the inorganic zeolites, because the channels of supramolecular porous materials are potentially tunable by choosing unit size or functionalities of building block.[5—7]

Cyclic phosphazenes have attracted much interest since unique properties and functionalities are attainable through the introduction of organic groups into P-Cl group in 2,2, 4,4,6,6-hexachloro-$2\lambda^5$, $4\lambda^5$, $6\lambda^5$-cyclotri(phosphazene). Recently, Allcock et al. have shown that 2, 4, 6-tris-(*o*-phenylenedioxy)-$2\lambda^5$, $4\lambda^5$, $6\lambda^5$-cyclotri(phosphazene) forms clathrates.[8,9] Furthermore, the X-ray diffraction analysis of 2,2,4,4,6,6-hexaphenoxy-$2\lambda^5$, $4\lambda^5$, $6\lambda^5$-cyclotri(phosphazene) showed that the phenoxy groups are located perpendicularly above and below a nearly planar cyclotri(phosphazene) ring.[9,10] By utilizing such an unique structure, we have recently reported that the cylindrical-shaped supramolecules are formed through the complementary hydrogen bondings between 2,2,4,4,6,6-hexakis(4-carboxyphenoxy)-$2\lambda^5$, $4\lambda^5$, $6\lambda^5$-cyclotri(phosphazene) and 2,2,4, 4,6,6-hexakis(4-pyridylmethoxy)-$2\lambda^5$, $4\lambda^5$, $6\lambda^5$-cyclotri(phosphazene) (PyPN),[12] between PyPN and terephthalic acid (TPA).[13]

In this paper, we report on the construction of a nanoporous assembly **1** from PyPN and 1,4-naphthalenedicarboxylic acid (DCN) in order to develop the phosphazene-based assembly as a material capable of including ions and molecules. The synthetic method, structural features, and inclusion properties of **1** are described.

Experimental

Materials. 2,2,4,4,6,6-Hexakis(4-pyridylmethoxy)-$2\lambda^5$,$4\lambda^5$, $6\lambda^5$-cyclotri(phosphazene) (PyPN) was synthesized from the reaction of 2,2,4,4,6,6-hexachloro-$2\lambda^5$, $4\lambda^5$, $6\lambda^5$-cyclotri(phosphazene) with sodium 4-pyridylmethoxide, prepared from 4-pyridinemethanol (Koei Chemical) and NaH in THF as described in the previous paper.[12] 1,4-Naphthalenedicarboxylic acid (DCN, Wako Chemical) was recrystallized from 1 : 2 water/methanol solution. Other reagents were of analytical grade and were used without further purification.

Preparation of the Assembly 1. A typical preparation of **1** was as follows. A DMF solution (0.25 ml) of PyPN (0.042 g, 5.4×10^{-5} mol) was mixed with a DMF solution (0.25 ml) of DCN (0.036 g, 1.6×10^{-4} mol), and the mixture was allowed to stand for one day at room temperature, giving the assembly as needle crystals in 41% isolated yield. Found: C, 60.32; H, 4.22; N, 8.68%. Anal. Calcd. for $C_{60}H_{54}N_9O_{18}P_3$: C, 60.38; H, 4.22; N, 8.80 %.

Measurements. FT-IR spectra were recorded on a JASCO FT-IR 230 spectrophotometer applying the KBr pelleting technique. Fluorescence spectra were recorded on a Shimadzu RF-5000 spectrometer. Differential scanning calorimetry was done using a Shimadzu DSC-50 calorimeter in sealed aluminium pans at heating rates of 10 °C min^{-1}. Wide-angle X-ray diffraction patterns were obtained using the Rigaku RINT 2000 system. FT-Raman spectra were recorded on a JASCO FT-Raman FT-IR 800 spectrophotometer with the RFT-800 system.

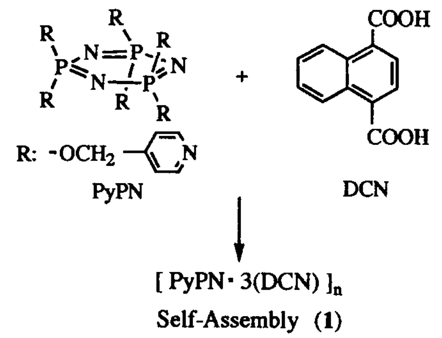
Guest Inclusion Experiments into the Assembly 1. The inclusion of iodine into **1** was performed as follows. The crystals (0.010 g) of **1** were immersed in an aqueous solution (5 ml) containing iodine (9.0×10^{-4} g) for an appropriate time at room temperature and then filtered. The crystals were washed with ether. The iodine content included into **1** was determined from the absorbance at 440 nm in methanol solution. The inclusion of organic compounds such as benzene, hexane, and chloroform was performed by immersing **1** (0.05 g) in these solvents (5 ml). The crystals were dried at room temperature and then the samples were examined by ^{1}H NMR spectroscopy (in DMSO-d_6).

Results and Discussion

Formation of Self-Assembly 1 Composed of PyPN and DCN. The structural symmetry of component molecules is an important key for the construction of a supramolecular assembly with a highly ordered structure.[14] In the supermolecule composed of PyPN and terephthalic acid (TPA), PyPN has an approximate *C*2 symmetry axis along a P–N direction.[13] The single crystal X-ray analysis indicates that the pyridyl groups at each side of the phosphazene ring are located perpendicularly on the ring, i.e., pyridyl units take positions that enable directional and selective interactions with TPA, in spite of having flexible OCH$_2$ groups. The structural features of organocyclotriphosphazenes have been also reported for 2, 2, 4, 4, 6, 6-hexaphenoxy-$2\lambda^5$, $4\lambda^5$, $6\lambda^5$-cyclotri(phosphazene).[9,10] If the geometrical arrangement holds for the assembly formed by PyPN and DCN with bulky aromatic rings, the assembly crystal would be expected to possess a void depending on the packing of the cylindrical-shaped assemblies composed of PyPN and DCN.

The assembly **1** was obtained as needle-like crystals from a DMF solution containing PyPN and DCN (Scheme 1).[15] Since the precise molecular structure of **1** have not been ascertained due to difficulties in obtaining single crystals of **1**, the structure was examined by FT-IR and fluorescence spectroscopic methods, and X-ray diffraction measurements.

Etter[16] has pointed out that the strongest hydrogen bond acceptor binds to the strongest donor, suggesting that carboxy groups form hydrogen bondings with pyridine moieties rather than self-association of carboxylic acids. While the FT-IR spectrum of DCN showed characteristic bands attributed to carboxylic acids at about 2600—3000 cm^{-1}, in the spectrum of **1** the broad band disappeared and two new bands were observed at 2450 and 1940 cm^{-1} due to the carboxylic acid–pyridine hydrogen bonding (Fig. 1). From elemental analysis, the stoichiometry of **1** was PyPN : DCN = 1/3. These results indicate that the hydrogen bonding with an alternating sequence of one PyPN and three DCN molecules gives a polymeric self-assembly **1** composed of [PyPN·3(DCN)]$_n$. This assembly decomposed at 190 °C, which was higher than the decomposition temperature of PyPN (100 °C), indicating that PyPN become thermally stable in the assemblies. In the DSC curve, no endothermic peak due to the hydrogen-bond scission was observed up to 190 °C. This suggests that the decomposition of **1** arises from the pyrolysis of PyPN in the assemblies.



Scheme 1. Formation of the self-assembly composed of PyPN and DCN.

Figure 2a shows the wide-angle powder X-ray diffractogram of **1**. The patterns of sharp peaks were similar to that of the supramolecular assembly of 2,2,4,4,6,6-hexakis(4-carboxyphenoxy)-$2\lambda^5$,$4\lambda^5$,$6\lambda^5$-cyclotri(phosphazene) (CPN) and PyPN determined by single-crystal X-ray analysis, in which all pyridyl and carboxy groups located at perpendicular positions on the $2\lambda^5$, $4\lambda^5$, $6\lambda^5$-cy-

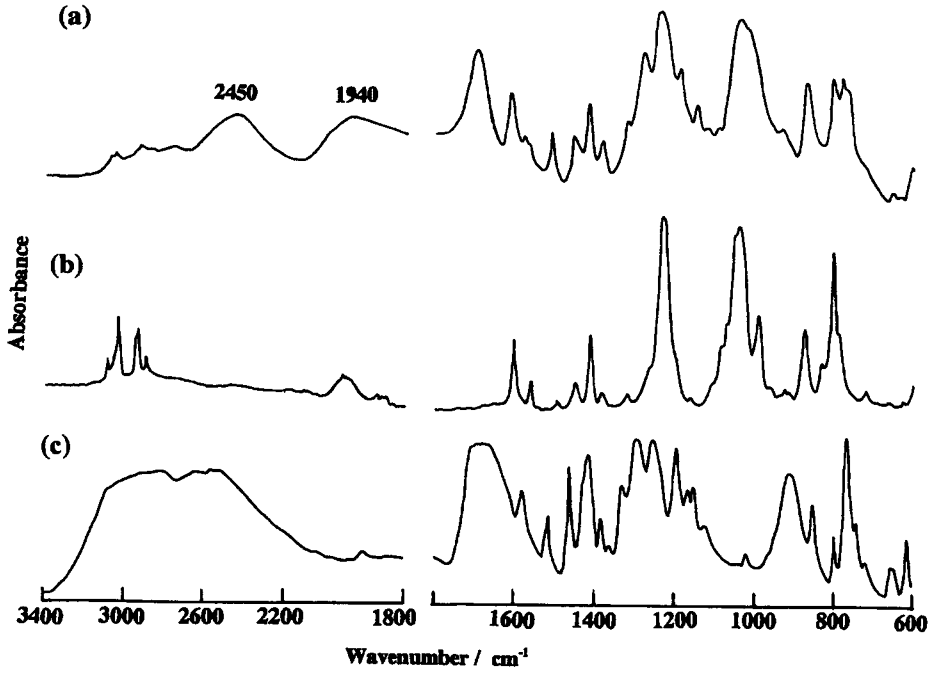


Fig. 1. FT-IR spectra of the assembly of **1** (a), PyPN (b) and DCN (c).

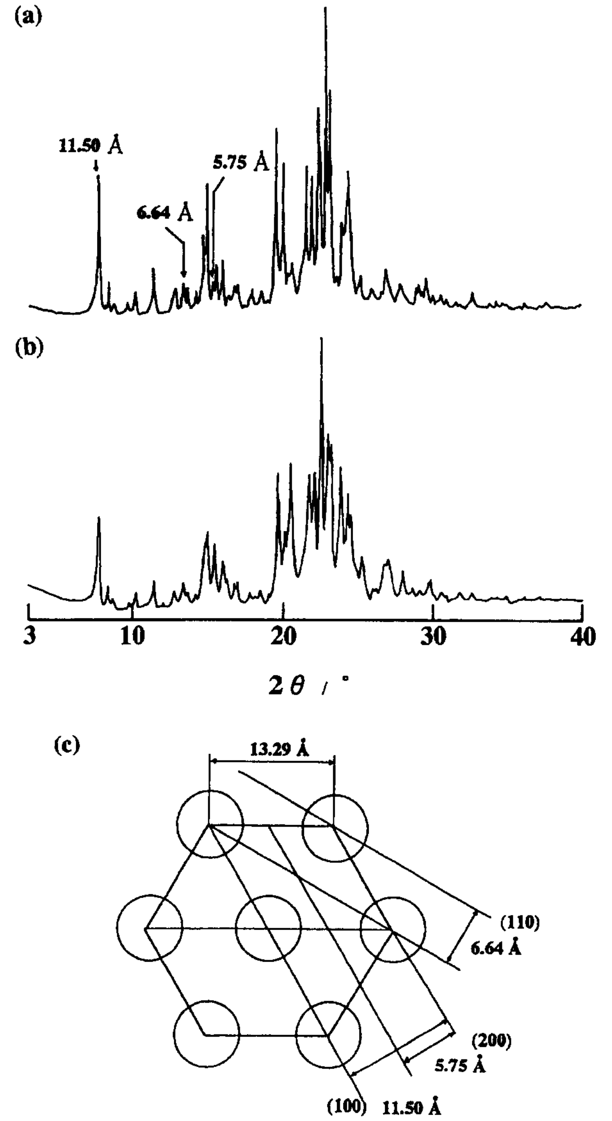
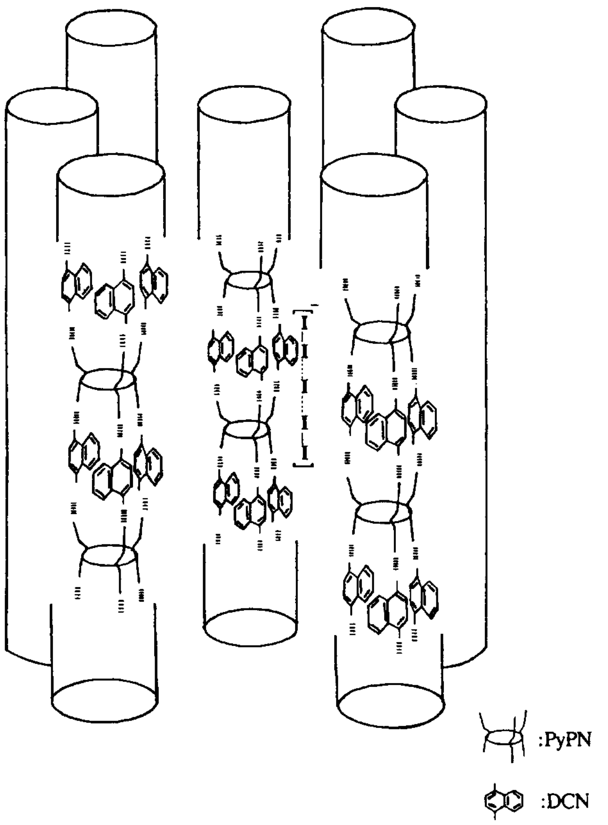


Fig. 2. Powder X-ray diffraction patterns of **1** (a) and **1**–iodine adduct after immersed in an aqueous iodine solution for 5 days (b), and (c) represents the hexagonal packing structure for **1** together with Miller's indices.

clotri(phosphazene) ring form hydrogen bonding to create a cylindrical structure.[12] In the diffractogram of **1**, in addition, the reflections with the lattice spacing of 11.50, 6.64, and 5.75 Å, which are in a ratio of 1, $1/\sqrt{3}$, and 1/2 were observed (Fig. 2c).[17] From these results, it was concluded that the cylindrical-shaped assemblies formed from PyPN and DCN are laterally packed into a hexagonal arrangement with the space of $13.3\ (=11.50\times2/\sqrt{3})$ Å (Scheme 2). This space is larger than that (8.9 Å) observed for the supramolecular coordination polymer composed of PyPN and $AgNO_3$ with a hexagonal packing arrangement.[18] Thus, it seems that the bulkiness of the naphthalene ring leads to enlarging the space among cylindrical-shaped assemblies composed of PyPN and DCN.

The geometrical arrangement of naphthalene rings of DCN in crystals of **1** may be reflected in the fluorescence spectra. The solid-state fluorescence spectra of **1** and DCN are shown in Fig. 3a. While the solid of DCN exhibited the fluorescence spectrum with maximum at 480 nm, the spectrum of **1** had a fluorescence peak centered at 390 nm. The fluorescence spectra of DCN in DMF solution shifted to a shorter wavelength, along with an increase in the fluorescence intensity as the concentration of DCN decreased (Fig. 3b), suggesting that the fluorescence spectrum of **1** appears to correspond to the spectrum of DCN in an infinitely dilute solution. Therefore, the fluorescence spectrum of **1** is due to the monomeric naphthalene ring. This implies that the naphthalene rings of DCN in the crystal are isolated from each other. From the fluorescence spectra and the above-mentioned X-ray diffraction results, it seems likely that the cylindrical assemblies are placed at relatively large distances in the crystal of **1**, leading to creation of space (Fig. 2c).



Scheme 2. Schematic representation of a possible structure of **1**.

Inclusion Behavior of Iodine into 1. As the assemblies **1** contain rigid and bulky naphthalene rings, the assemblies with cylindrical structure are difficult to pack together in a space-saving arrangement. When the assemblies are packed together in the hexagonal arrangement (Fig. 2c), substantial voids seem to appear along the assemblies in the crystal of **1**. If so, linear molecules which can interact with naphthalene ring may be included into the space among the assemblies. The formation of polyiodine chain in the inclusion complex with starch has been investigated in detail for a long time.[19,20] When iodine was mixed with a suspension of **1** in water, **1** changed to blue-black crystals as time went by, suggesting the inclusion of iodine molecules into **1**. Such inclusion behaviors were not observed for benzene, hexane, and chlo-

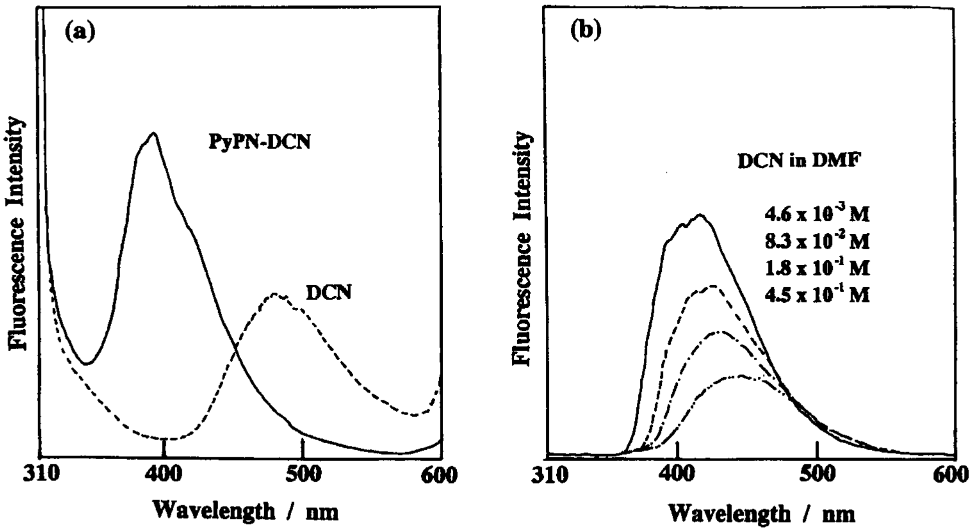


Fig. 3. (a) Solid-state fluorescence spectra of **1** and DCN. (b) Fluorescence spectra of DCN in DMF at various concentrations. The excitation and emission band widths were 3 nm and 1.5 nm, respectively. λ_{ex} = 305 nm.

roform.

The amount of iodine included into **1** increased with time, and, after 5 days, reached 0.038 g per 1g of assembly (Fig. 4), implying that iodine atom is incorporated into **1** with [I]/[repeated unit of **1**] = 0.4. This value was not changed by repeated washing with ether. On the other hand, the inclusion of iodine was not observed for the assembly composed of PyPN and terephthalic acid (TPA), suggesting that a void does not exist in the crystal of the PyPN-TPA assembly. The hexagonal packing of the cylindrical-shaped assemblies composed of PyPN and DCN in such a way that bulky naphthalene rings do not stack each other affords an opportunity to form the **1**-iodine inclusion complex. In the case of the perylene-iodine complex, a discoloration occurred within 10—15 min at room temperature due to a loss of iodine from the complex.[21] On the other hand, a noticeable discoloration of the **1**-iodine inclusion complex was not observed for a week on standing in an open container at room temperature, indicating that iodine molecules are trapped strongly in **1**. When **1** was immersed in ether solution of iodine, the amount of iodine included into **1** decreased to one-quarter of the amount of iodine included from aqueous solution of iodine. Iodine in chloroform and in hexane was not included into **1**. Therefore, it seems that hydrophobic iodine molecules permeate from water phase to hydrophobic void in the crystals of **1**.

Raman scattering has been extensively used to resonantly probe the vibrational modes in several polyiodide compounds.[22,23] The FT-Raman spectra of **1** and the **1**-iodine inclusion complex (after immersed in an aqueous iodine solution for 5 days) are shown in Fig. 5. In the **1**-iodine inclusion complex, a new band at 163 cm^{-1} appeared. In the Raman spectrum of (trimesic acid $H_2O)_{10}{\cdot}H^+I_5^-$, the peak

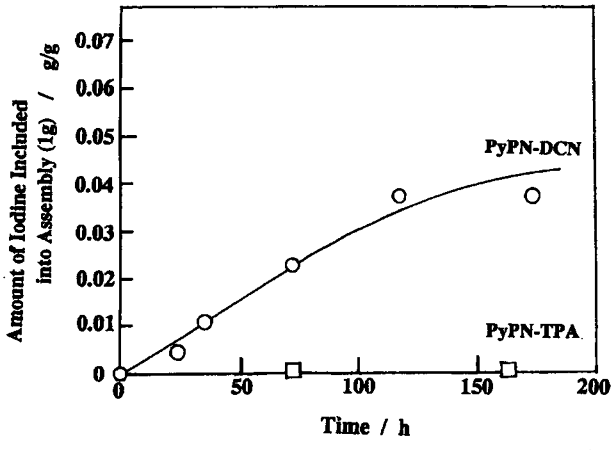


Fig. 4. Time course of the amount of iodine included into **1** and the PyPN–terephthalic acid (TPA) assembly.

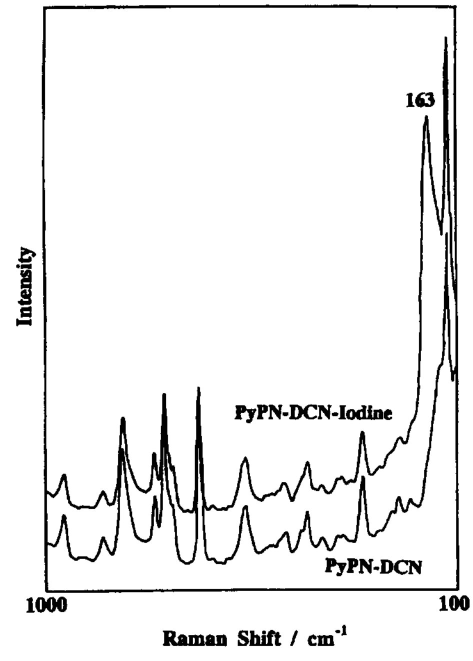


Fig. 5. FT-Raman spectra of **1** and **1**–iodine adduct after immersed in aqueous iodine solution for 5 days.

assignable to the linear and symmetrical I_5^- chain was observed at 162 cm^{-1}.[24] These results suggest that iodine in **1** exists as a polyiodine linear I_5^- ion, indicating that a tunnel-like void is formed in the crystal of **1**.

The X-ray diffraction peaks observed for the **1**-iodine inclusion complex are superimposed on those of **1**, except in the region of $2\theta = 19—25°$, although the I_5^- ions included into **1** cause the broadening of the peaks (Fig. 2b). The observation of the peaks including $d = 11.50$ Å suggests that iodine molecules are incorporated with retaining the hexagonal packing of the assemblies. The difference of the X-ray diffraction pattern between the **1**-iodine inclusion complex and **1** in the wide-angle region ($2\theta = 19—25°$) may be caused by changes in the arrangement of naphthalene rings in the crystal of **1** due to the interaction between naphthalene ring and iodine. As shown in Fig. 5, the Raman spectrum of the **1**-iodine inclusion complex was identical to that of original **1** except for the band of I_5^- ions. In addition, FT-IR spectra showed that the inclusion of iodine does not affect the hydrogen bonding between PyPN and DCN. These results suggest that the assemblies keep cylindrical structure and possess space capable of including iodine, although the inclusion caused by a phase transformation can not be rigorously ruled out.

The fluorescence of **1** observed in Fig. 3a was not detected for the **1**-iodine inclusion complex, indicating the fluorescence of naphthalene rings was quenched by the interaction between naphthalene ring and iodine. These results indicate that the I_5^- ions included in the crystal of **1** are surrounded by naphthalene rings (Scheme 2). However, details of the mechanism of the formation of I_5^- ions and the exact location of I_5^- ions in **1** remain unclear.

The development of supramolecular materials based on $2\lambda^5$, $4\lambda^5$, $6\lambda^5$-cyclotriphosphazene may represent an important step toward a new class of microporous substances. With the purpose of creating the supramolecular assemblies containing channels or voids of various sizes and shapes, further studies utilizing $2\lambda^5$, $4\lambda^5$, $6\lambda^5$ -cyclotriphosphazene derivative are now in progress.

In conclusion, we have found that the $2\lambda^5$, $4\lambda^5$, $6\lambda^5$-cyclotriphosphazene with six pyridyl groups (PyPN) and 1,4-naphthalenedicarboxylic acid (DCN) form a polymeric self-assembly with cylindrical structure, which originate from the molecular shape of PyPN. In addition, the cylindrical assemblies were laterally packed into a hexagonal arrangement and, consequently, a tunnel-like void capable of including iodine was created among them. These results clearly show that the self-assembly based on $2\lambda^5$, $4\lambda^5$, $6\lambda^5$-cyclotriphosphazene is useful as a microporous material.

References

1 D. B. Ambabilino and J. F. Stoddart, *Chem. Rev.*, **95**, 2725 (1995).

2 W. A. Herrmann, N. W. Huber, and O. Runte, *Angew. Chem., Int. Ed. Engl.*, **34**, 2187 (1995).

3 L. R. MacGillivray and J. L. Atwood, *Nature*, **389**, 469 (1997).

4 Y. Aoyama, K. Endo, T. Anzai, Y. Yamaguchi, T. Sawaki, K. Kobayashi, N. Kanehisa, H. Hashimato, Y. Kai, and H. Masuda, *J. Am. Chem. Soc.*, **118**, 5562 (1996).

5 L. Halian, E. D. Charles, L. G. Thomas, G. K. Douglas, and O. M. Yaghi, *J. Am. Chem. Soc.*, **120**, 2186 (1998).

6 S. Kitagawa and M. Kondo, *Bull. Chem. Soc. Jpn.*, **71**, 1739 (1998).

7 S. S. -Y. Chui, S. M. -F. Lo, J. P. H. Charant, A. G. Orpen, and I. D. Williams, *Science*, **283**, 1148 (1999).

8 H. R. Allcock, *Acc. Chem. Res.*, **11**, 81 (1978).

9 A. P. Primrose, M. Parvez, and H. R. Allcock, *Macromolecules*, **30**, 670 (1997).

10 W. Marsh and J. Trotter, *J. Chem. Soc.* A:, **1971**, 169.

11 G. Bandoli, U. Casellato, M. Grassi, E. Montoneri and G. C. Pappalardo, *J. Chem. Soc., Dalton Trans.*, **1989**, 757.

12 K. Inoue, T. Itaya, and N. Azuma, *Supramol. Sci.*, **5**, 163 (1998).

13 T. Itaya, N. Azuma, and K. Inoue, *Supramol. Chem.*, **9**, 121 (1998).

14 J. W. Lauher, S. J. Coe, J. Kane, T. L. Nguyen, L. M. Toledo, E. Wininger, and F. W. Fowler, *J. Am. Chem. Soc.*, **119**, 86 (1997).

15 The assembly crystals also were obtained from a DMSO solution containing PyPN and DCN. The spectroscopic and X-ray diffraction data were identical with those of **1** obtained from DMF solution.

16 M. C. Etter, *Phys. Chem.*, **95**, 4601 (1991).

17 M. Tabata, T. Sone, and Y. Sadahiro, *Macromol. Chem. Phys.*, **200**, 265 (1999).

18 T. Itaya and K. Inoue, *Bull. Chem. Soc. Jpn.*, in press.

19 L. Fredin and B. Nelander, *J. Am. Chem. Soc.*, **96**, 1672 (1974).

20 M. Noltemayer and W. Saenger, *Nature*, **254**, 629 (1976).

21 R. C. Teitelbaum, S. L. Ruby, and T. J. Marks, *J. Am. Chem. Soc.*, **101**, 7568 (1979).

22 R. C. Teitelbaum, S. L. Ruby, and T. J. Marks, *J. Am. Chem. Soc.*, **100**, 345 (1978).

23 H. Sakai, M. Mizota, Y. Maeda, T. Yamamoto, and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, **58**, 926 (1985).

24 F. H. Herbstein and M. Kapon, *Acta Crystallogr., Sect. A*, **28**, 74 (1972).