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Polymeric Hydrogen-Bonded Supermolecules by Self-Assembling of Hexakis(4-Pyridylcarbinoxy) Cyclotriphosphazene and Dicarboxylic Acids

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Hexakis(4-pyridylcarbinoxy)cyclotriphosphazene (PyPN) and terephthalic acid (TPA) self-assembled into polymeric supermolecules through hydrogen bonding between carboxyl and pyridyl groups. Two supermolecular self-assemblies were obtained: crystals 1 composed of 2:1 TPA/PyPN from DMF/DMSO, and crystals 2 composed of 3:1 TPA/PyPN from DMF. The former is monoclinic, space group C2/c with a = 26.029 Å, b = 7.854 Å, c = 28.073 Å, β = 116.47°, V = 5138 Å^3, and Z = 4. The structure was defined to R = 0.064 based on 2832 data, I > 1.5 σ(I). The X-ray analysis revealed that PyPN is joined with two TPA molecules through hydrogen bonding to form a polymeric assembly. The self-assembly obtained from DMF seems to take a cylindrical-shaped structure, *i.e.*, all of pyridyl group in PyPN participate in the formation of the assembly, as evidenced by elemental analysis, FT-IR spectroscopy and X-ray diffraction data. These results and the role of the solvent are described.

INTRODUCTION

Supramolecular architectures by self-assembly from different components through noncovalent, multiple intermolecular interaction have attracted enormous attention from both their academic importance and potential applications in technology [1–11]. The hydrogen bonding between carboxylic acid and pyridyl groups is a useful and powerful organizing force and has been utilized for the formation of supermolecules [9].

Recently, we have found that the complementary hydrogen bonding between hexakis(4-carboxyphenoxy)cyclotriphosphazene (CPN) and hexakis(4-pyridylcarbinoxy)cyclotriphosphazene (PyPN) forms a supermolecule with cylindrical structure [12]. This result suggests that the hydrogen bonding donor and acceptor moieties are located perpendicularly on the phosphazene ring, in other words, the carboxy or pyridyl groups attached to the phosphazene ring are preorganized at fixed positions suitable for assembly formation. This finding prompted us to investigate the formation of new three-dimensional structures from the combination of cyclotriphophazenes and small organic compounds with bifunctional groups. In this paper,

we report on the formation of polymeric supramolecular self-assemblies of PyPN and rigid dicarboxylic acid such as terephthalic acid.

MATERIALS AND METHODS

Materials

Hexakis(4-pyridylcarbinoxy)cyclotriphosphazene (PyPN) was synthesized from the reaction of hexachlorocyclotriphosphazene with sodium 4-pyridylmethoxide, prepared from 4-pyridinemethanol and NaH in THF as described in a previous paper [12]. Other reagents were of analytical grade and used without further purification.

PREPARATION OF ASSEMBLIES

A typical procedure is as follows. A DMF/DMSO (2:1) solution of PyPN (0.02 g, 2.6×10^{-5} mol) was added into a DMF/DMSO (2:1) solution of TPA (0.013 g, 7.8×10^{-5} mol). The mixture (1.0 mL) was allowed to stand at room temperature for 12 h. Prismatic crystals **1** were precipitated. Yield, 36%. Anal. Calcd for $C_{52}H_{48}N_9O_{14}P_3$ for TPA/PyPN = 2:1: C, 55.97; H, 4.34; N, 11.30. Found: C, 55.81; H, 4.37; N, 11.28. FT-IR: 2440, 1935, 1610, 1701, 1245, 1042 cm^{-1}. Similarly, needle cyrstals **2** were obtained from DMF solution of PyPN and TPA. Yield, 57%. Anal. Calcd for $C_{60}H_{54}N_9O_{18}P_3$ for TPA/PyPN = 3:1: C, 56.21; H, 4.25; N, 9.83. Found: C, 56.31; H, 4.45; N, 10.10. FT-IR: 2440, 1935, 1611, 1701, 1245, 1042 cm^{-1}.

MEASUREMENTS

FT-IR spectra were recorded on a JASCO FT-IR 230 spectrophotometer applying the KBr pelleting technique. Wide angle X-ray diffraction patterns were obtained using Rigaku RINT 2000 system. Differential scanning calorimetry was done using Shimadzu DSC-50 calorimeter in sealed aluminium pans at heating rate of 10°C/min. Thermogravimetry was performed on a Shimadzu TGA-50/50H thermogravimetry system at heating rate of 10°C/min.

X-RAY DATA, STRUCTURE DETERMINATION AND REFINEMENT

The three dimensional X-ray data of the prismatic crystal obtained from DMF/DMSO (2:1) solution were collected by the use of graphite monochromated MoK α radiation ($\lambda = 0.71069$ Å) on an automated Rigaku AFC-5R diffractometer up to a maximum 2θ of 55.0°. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $24.05 < 2\theta < 25.92°$.

The intensities were corrected for Lorentz and polarization effects. The crystal structure was solved by the direct method using the MITHRIL program [13]. The coordination and anisotropic thermal parameters for non-hydrogen atoms were refined using a full matrix least square procedure. The positions of hydrogen atoms were idealized (C—H; 0.95 Å). The intensity data of 6473 independent reflections were collected and 2832 data were used in the solution and refinement (R = 0.064). A summary of data collection and refinement parameters are given in Table I.

RESULTS AND DISCUSSION

Attempts to prepare crystals from PyPN and dicarboxylic acids, 1,4-dicarboxynaphthalene (DCN), terephthalic acid (TPA), and 4,4′-dicarboxybiphenyl (DCB) have been made in various solvents. Among them, only the combination of PyPN and TPA gave crystals in DMF and DMF/

TABLE I Crystal data

Empirical formula:	$C_{52}H_{48}N_9O_{14}P_3$
Formula weight:	1115.92
Crystal system:	monoclinic
Space group:	C2/c
Lattice parameters:	a = 26.029(4) Å
	b = 7.854(1) Å
	c = 28.073(4) Å
	β = 116.47(1)°
Volume:	5138(1) Å^3
Formula units/unit cell:	4
d_{calc}:	1.442 g/cm^3
F(000):	2320
MoK α radiation:	λ = 0.71069 Å
μ:	1.86 cm^{-1}
Number of reflections measured:	6473
observed:	2832
Final R value:	0.064
Goodness of fit:	1.41

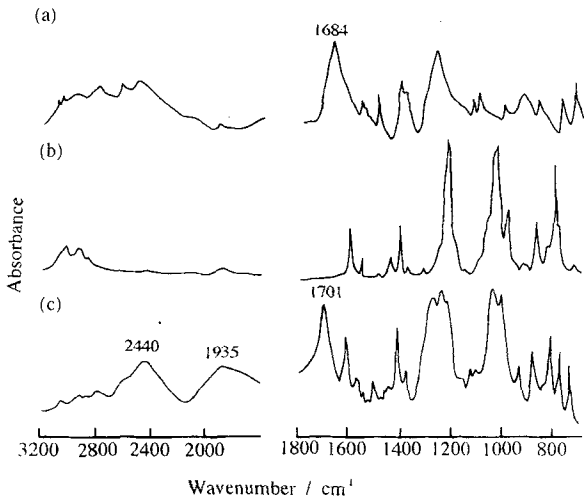


FIGURE 1 FT-IR spectra of TPA (a), PyPN (b) and 1(c).

DMSO solutions. Crystallization from DMF/DMSO (2:1) solution containing TPA and PyPN in 3:1 molar ratio afforded prismatic crystals **1**. The yield of **1** increased as wt% of DMSO decreased, but the isolation of pure **1** became hard due to the formation of crystals composed of TPA/PyPN = 3:1, as will be described later.

Figure 1 shows the FT-IR spectra of TPA, PyPN and **1**. Etter has pointed out that the strongest hydrogen bond acceptor binds to the strongest donor, suggesting that carboxylic groups form hydrogen bonds with pyridine moieties rather than self-association of carboxylic acids [14]. In the FT-IR spectrum of **1**, the broad bands of carboxylic acids of TPA at 2600 cm^{-1} – 3000 cm^{-1} disappeared and the absorptions due to hydrogen bonding between the carboxyl and pyridyl groups appeared at 2440 cm^{-1} and 1935 cm^{-1}, accompanying by the shift of C=O stretching band from 1684 cm^{-1} to 1701 cm^{-1} [9]. In addition, upon the formation of **1**, the characteristic bands of the pyridyl unit at 1605 and 1040 cm^{-1} of PyPN are perturbed. These IR changes indicate that PyPN and TPA are linked through hydrogen bonding between carboxyl and pyridyl units.

In the ^{1}H NMR spectrum of **1** in DMSO-d_6, the peak area at 5.02 and 8.04 ppm assignable to CH_2 and C_6H_4, respectively, showed the integral ratio of 3:2, suggesting that all six pyridyl groups do not participate in the hydrogen bonding and two groups are free. This is also supported by elemental analysis. This result is different from the assembly composed of PyPN and CPN, where all of carboxyl and pyridyl groups attached to the phosphazene ring form hydrogen bond to afford a cylindrical structure [12].

Fortunately, the crystals grew large enough to conduct single crystal X-ray analysis. The selected bond distances and angles, the arrangement of molecules in the assembly in the unit cell and ORTEP diagrams of PyPN and TPA are shown in Table II and Figure 2, respectively. The assembly crystallizes in the space group C2/c and the unit cell contains eight TPA and four PyPN molecules. The complementary hydrogen bonding occurs with two TPA molecules on both sides of the phosphazene ring of PyPN to give a novel assembly with extended structure, **1**, as shown in Scheme 1. The average hydrogen bonded N ···HO distance of 2.66 Å is short compared to the sum of the van der Waal's radii, 3.20 Å, indicating the formation of strong hydrogen bonding. Interestingly, both pyridyl

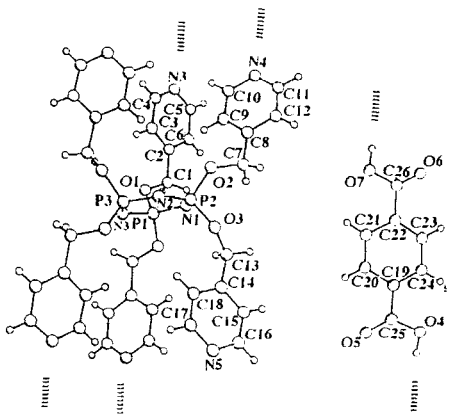


FIGURE 2 ORTEP diagrams of PyPN and TPA in **1**.

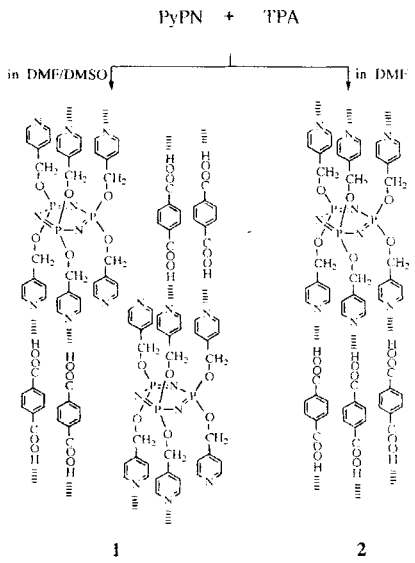
TABLE II Selected bond lengths (Å) and angles (deg)

P(1)—N(1)	1.584(3)	C(13)—C(14)	1.503(6)
P(2)—N(1)	1.578(3)		
P(2)—N(2)	1.577(3)	P(1)—O(1)—C(1)	120.9(2)
P(1)—O(1)	1.581(3)	P(2)—O(2)—C(7)	119.4(2)
P(2)—O(2)	1.576(3)	P(2)—O(3)—C(13)	125.7(3)
P(2)—O(3)	1.575(3)	O(1)—P(1)—O(1)	105.9(2)
O(1)—C(1)	1.434(5)	O(2)—P(2)—O(3)	101.4(2)
O(2)—C(7)	1.450(4)	O(1)—C(1)—C(2)	110.6(3)
O(3)—C(13)	1.410(5)	O(2)—C(7)—C(8)	109.3(3)
C(1)—C(2)	1.502(5)	O(3)—C(13)—C(14)	111.6(4)
C(7)—C(8)	1.501(5)		

groups attached to the P1 atom form hydrogen bonds with TPA, whereas one of two groups attached to the P2 and P3 atoms remained without hydrogen bonding.

Crystals **2** obtained from DMF solution present a different structure from **1**. From elemental analysis of the needle crystals the stoichiometry was found to be TPA/PyPN = 3:1. Consistent with this, the highest yield of the assembly was achieved at TPA/PyPN = 3 in the continuous variation plot. The disappearance of the peak at 2600 cm^{-1} – 3000 cm^{-1} and the absorptions due to hydrogen bonding between the carboxyl and pyridyl groups at 2440 cm^{-1} and 1935 cm^{-1} were again observed for the IR spectrum of **2**. These results suggest that all pyridyl groups in PyPN form hydrogen bonds with TPA to constitute a supramolecular assembly. The crystals were, unfortunately, too small to conduct single-crystal X-ray analysis. The wide-angle powder X-ray diffractograms show sharp peaks, indicating that **2** takes an ordered structure. The pattern of **2** was very similar to that of the supermolecule of hexakis(4-carboxyphenoxy)cyclotriphosphazene (CPN) and PyPN determined by single-crystal X-ray analysis, [12] in which all carboxyl and pyridyl groups located at perpendicular positions on the phosphazene ring form hydrogen bond to create a cylindrical structure. From these results, it seems that crystals obtained from DMF also take a cylindrical structure as shown in Scheme 1.

Thus, the assembly composed of PyPN and TPA is affected by the solvents. The carboxyl group is solvated with DMF and DMSO, but the binding ability of these solvents is significantly different, *i.e.*, DMSO binds strongly with the carboxyl group, compared to DMF. It appears that the insertion of strongly solvated TPA with DMSO into the binding site (that two pyridyl groups have already bound with TPA) among three hydrogen bonding sites located at the each side of phosphazene ring, is limited spatially, whereas loosely solvated TPA with DMF could



SCHEME 1

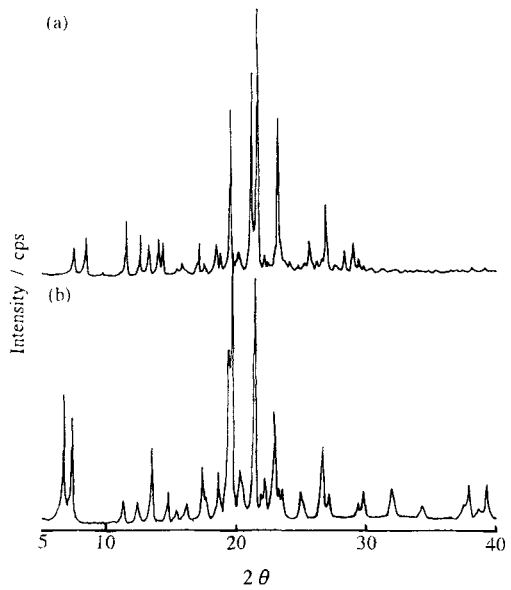


FIGURE 3 Powder X-ray diffraction patterns of the assembly of PyPN and hexakis(4-carboxyphenoxy)cyclotriphosphazene (a) and **2** (b).

exchange hydrogen bonding acceptors and insert into the binding site to form triple hydrogen bonds. Thus, the presence of free pyridyl group in **1** obtained in DMF/DMSO might be due to the strong hydrogen bonding ability of DMSO, although details of the role of solvents remain unclear.

It has been reported that the symmetry and preorganization of component molecules are important keys for the construction of a highly ordered structure [15]. TPA has a C_2 symmetry axis and two carboxylic groups are almost coplanar with the benzene ring. The pyridyl groups of PyPN are linked to the phosphazene ring with are average P—O—C bond angle of 122.0°, O—C—C bond angle of 110.5°, and P—O—C—C torsion angle of 131.6°, and an average P—N bond length of 1.58 Å. This indicates that PyPN has an approximate C_2 symmetry axis along the P1—N2 direction, and that three pyridyl groups at each side of the phosphazene are located perpendicularly on the phosphazene ring, *i.e.*, pyridyl units preorganize and take positions that enable directional and selective interactions with TPA, in spite of having flexible OCH_2 groups [12]. For the DCB-PyPN system, the formation of directional hydrogen bonding is possible, but the rotation around the C—C bond connecting the phenyl groups brings about a disordered arrangement of biphenyl units. This might be the reason why the assembly did not form. Similarly, the disordered hydrogen bonding of DCN units might be operative for the PyPN-DCN system.

Finally, the thermal behavior of **1** and **2** was examined by using differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) (Fig. 4). The thermal analyses of **1** and **2** show an exothermic peak around 210°C due to hydrogen bond scission, followed by the decomposition. The temperature of the observed exothermic peaks was higher than that of the decomposition of PyPN (110°C), indicating that PyPN is thermally stable in the assembly. In addition, the value of 210°C is high compared to the decomposition temperature (165°C) [10] of a

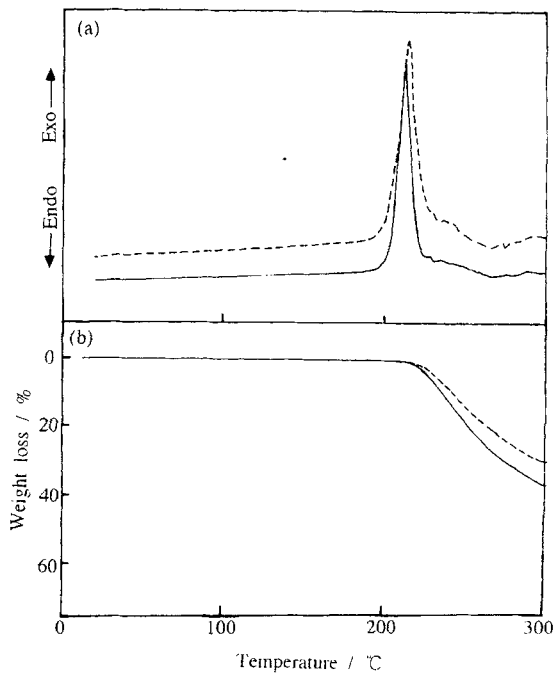


FIGURE 4 DSC heating curves (a) and thermal gravimetrical analysis (b) of **1** (—) and **2** (----).

conventional carboxylic acid-pyridine complex. The ordered molecular packing of assemblies **1** and **2** contributes to the thermal stability of the hydrogen bonding between pyridyl-carboxyl groups.

In conclusion, we have found that the cyclotriphosphazene with six pyridyl groups (PyPN) and TPA form novel polymeric self-assemblies, which originate from the molecular shape of cyclotriphosphazene. These results suggest that the cyclotriphosphazene derivative is a useful building block to create polymeric and three-dimensional supermolecules.

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