Topologically Different Two Pseudo-decahedral Hydrogen-bond Networks Composed of Triphenylmethylammonium Phosphonates

Tetsuharu Yuge, Nobuyasu Kai, Ichiro Hisaki, Mikiji Miyata,* and Tohnai Norimitsu*
Department of Material and Life Science, Graduate School of Engineering,
Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871

(Received September 3, 2007; CL-070952; E-mail: tohnai@mls.eng.osaka-u.ac.jp)

Novel two pseudo-decahedral hydrogen-bond networks with different topology are constructed with triphenylmethylammonium phosphonates. Phosphonate anions show four different hydrogen-bond manners, which lead to the topological diversity.

Supramolecular clusters based on organic compounds have attracted much attention for future materials because of their nano-order scale and uniform size.[1,2] On these clusters, topological issue is often attendant and has been well discussed with covalent-bonded networks such as catenanes and knots for the further development of molecular informatics.[1]

We also focused on the topology of hydrogen-bond network.[3] Here, we demonstrate that the multiplicity and usefulness of the phosphonate anions for the design of topological diversity by means of the design and construction of two novel pseudo-decahedrons consisting of hydrogen-bond networks (Figures 1a and 1b). Since each pseudo-decahedron consists of two quadrangles and eight triangles, they are topological isomers of square antiprism (Figure 1c). Up to now, some kinds of discrete hydrogen-bond networks, such as pseudo-tetrahedron,[4] pseudo-hexahedron,[3,5–9] and pseudo-octahedron,[10] have been reported with organic components, but we have never seen such asymmetric pseudo-decahedrons.

We designed the pseudo-decahedral networks by the extension of conventional [4 + 4]-type clusters. To date, we and other research groups have reported the [4 + 4] ion pair clusters consisting of organic ammonium with chloride,[5] carboxylate,[3,6] thiolate,[7] phosphonothioate,[8] and sulfonate.[9] Cations and anions act as a tridentate hydrogen-bond donor and acceptor, respectively and link together with robust pseudo-cubic supramolecular synthon.[11]

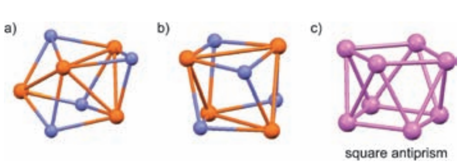
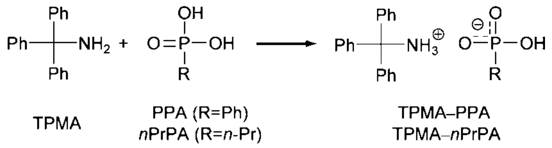


Figure 1. Decahedrons consisting of two quadrangles and eight triangles with different topology.



Scheme 1. Salt formation of triphenylmethylamine with phosphonic acids.

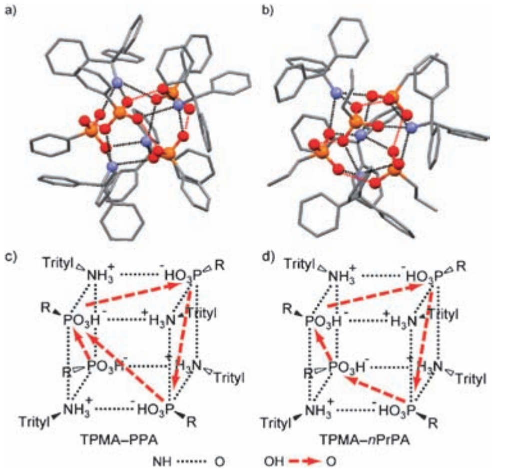


Figure 2. [4 + 4]-Type clusters of (a) TPMA–PPA, and (b) TPMA–*n*PrPA. Phosphorus, nitrogen, and oxygen atoms are orange, blue, and red, respectively. Hydrogen atoms are omitted for clarity. Pattern diagrams of hydrogen-bond networks of (c) TPMA–PPA, and (d) TPMA–*n*PrPA with different OH···O topology. Black and red dashed lines show NH···O and OH···O hydrogen bonds, respectively.

In the aim of extending the conventional [4 + 4]-type clusters, we adopted phosphonic acids which have an additional hydrogen-bond donor as the anion moiety.[12] (Scheme 1).

Triphenylmethylamine (TPMA) and phenylphosphonic acid (PPA) or *n*-propylphosphonic acid (*n*PrPA) were mixed in methanol with a 1:1 molar ratio. Evaporating the solutions yielded their powdered salts, which were recrystallized from 1,2-dichloroethane. Single-crystal X-ray analysis revealed that TPMA–PPA and TPMA–*n*PrPA formed the [4 + 4]-type clusters (Figures 2a and 2b).[13,14]

The clusters are built with discrete hydrogen-bond networks which are surrounded by bulky substituents. Four anions and four cations align alternately and are linked by twelve NH···O charge-assisted hydrogen bonds similar to the networks composed of carboxylates[6] or sulfonates.[9] However, unlike these conventional networks, the surplus hydrogen atoms of phosphate anions behave as hydrogen-bond donors for additional four OH···O hydrogen bonds. In these two crystals, different OH···O hydrogen-bond networks are observed. Thereby, two novel pseudo-decahedral hydrogen-bond networks with different topology are formed with totally sixteen hydrogen bonds (Figures 2c and 2d). Each pseudo-decahedron of TPMA–PPA and TPMA–*n*PrPA corresponds to the decahedron shown in Figures 1a and 1b, respectively.

Since four faces in the pseudo-cube are parted by the OH···O hydrogen bonds (see Figures 2c and 2d, red dashed arrows), pseudo-decahedral hydrogen-bond networks are constructed

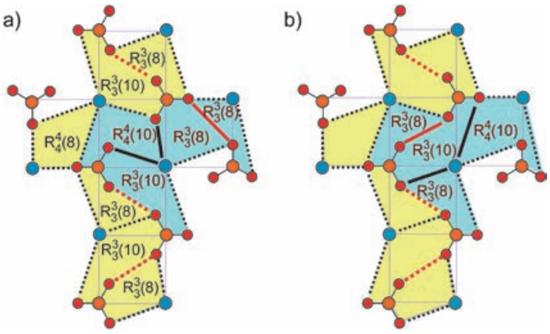


Figure 3. [4 + 4]-Type clusters and hydrogen-bond networks with graph sets on opened-up cube of (a) TPMA–PPA and (b) TPMA–*n*PrPA. Phosphorus, nitrogen, and oxygen atoms are orange, blue, and red, respectively. Hydrogen atoms are omitted for clarity. Black and red bold lines show the difference between two networks. Light-blue- and yellow-colored areas show different and the same network areas, respectively.

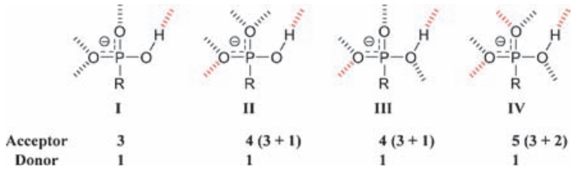


Figure 4. Four manners of phosphonate anions on the corner of the pseudo-cube (black dash lines and red dash lines show NH···O and OH···O hydrogen bonds, respectively).

with ten ringed hydrogen-bond networks. Two networks of TPMA–PPA and TPMA–*n*PrPA look very similar in graph sets[15] which represent the numbers of molecules, hydrogen bonds, and atoms of the rings. However, from the topological point of view, linking mode of four rings among ten (light-blue-colored area) differs Owing to recombination of three hydrogen bonds (bold lines shown in Figure 3).

These topological differences in hydrogen-bond networks originate from distinctive hydrogen-bond manners of each phosphonate anion (Figure 4). Different from other anions which act as tridentate hydrogen-bond acceptor,[3,5–9] in the two crystals of phosphonates, four different manners of phosphonate anions (Figure 4 I–IV) are confirmed: TPMA–PPA consists of one I, two II and one IV, TPMA–*n*PrPA consists of two II and two III. In these manners, phosphonate anions accept at least three hydrogen bonds in a similar fashion to sulfonate and carboxylate anions.[3,6,9] However, depending on the topology of the additive four OH···O hydrogen bonds, phosphonate anions have possibility to accept extra one or two hydrogen bonds (Figure 4 II–IV). The topological diversity depends heavily on the conformational diversity of anion moiety. Therefore, the diversity and adjustability of the phosphonate anion play an important role in constructing a variety of supramolecular assemblies. We also confirmed these assemblies in solution (see Supporting information).[16] These results give us the possibility for the dynamic control of the topology, which may contribute the molecular informatics.

In conclusion, we demonstrated that design and construction of novel pseudo-decahedral hydrogen-bond networks from the conventional hydrogen-bond networks. In the networks, newly four OH···O hydrogen bonds participated into the network through the extra hydrogen atoms of phosphonate anions. In the crystals, phosphonate anions play multimodal hydrogen-bond manners, which turn to be widely engaged in topological diversity. These results give us novel insight into the topology of hydrogen-bond network as well as an instrumental method to design further complicated nano-order fabrications. Topology–property correlations are under investigation for the realization of molecular informatics.

T. Y. thanks the JSPS Research Fellowships for Young Scientists. This work was also supported by a Grant-in-Aid for Scientific Research on Priority Areas "Super-Hierarchical Structures" (no. 19022022) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References and Notes

1 a) D. B. Amabilino, J. F. Stoddart, *Chem. Rev.* **1995**, *95*, 2725. b) *Molecular Catenanes, Rotaxanes, and Knots*, ed. by J.-P. Sauvage, C. Dietrich-Buchecker, Wiley–VCH, Weinheim, **1999**. c) J. S. Siegel, *Science* **2004**, *304*, 1256. d) K. S. Chichak, S. J. Cantrill, A. R. Pease, S.-H. Chiu, G. W. V. Cave, J. L. Atwood, J. F. Stoddart, *Science* **2004**, *304*, 1308.

2 a) M. Fujita, N. Fujita, K. Ogura, K. Yamaguchi, *Nature* **1999**, *400*, 52. b) B. Moulton, J. Lu, A. Mondal, M. J. Zaworotko, *Chem. Commun.* **2001**, 863.

3 T. Yuge, N. Tohnai, T. Fukuda, I. Hisaki, M. Miyata, *Chem.—Eur. J.* **2007**, *13*, 4163.

4 A. Bacchi, E. Bosetti, M. Carcelli, *CrystEngComm* **2007**, *9*, 313.

5 CSD refcode: BAYXEF, A. D. Bond, E. L. Doyle, *Chem. Commun.* **2003**, 2324.

6 a) CSD refcode: RUTYUA, E. J. Corey, B. E. Roberts, *Tetrahedron Lett.* **1997**, *38*, 8921. b) CSD refcode: LAFDEC, H. Liu, C. Liu, X. Han, B. Zhong, K. Liu, *J. Chem. Res.* **2004**, 7, 482. c) CSD refcode: UMAKOI, B. Szczęsna, Z. Urbanczyk-Lipkowska, *CrystEngComm* **2003**, *5*, 385. d) CSD refcode: IRUOUH, K. Sada, T. Watanabe, J. Miyamoto, T. Fukuda, N. Tohnai, M. Miyata, *Chem. Lett.* **2004**, *33*, 160.

7 CSD refcode: ITIBOC, B. Becker, K. Baranowska, J. Chojnacki, W. Wojnowski, *Chem. Commun.* **2004**, 620.

8 Y. Kobayashi, F. Morisawa, K. Saigo, *Org. Lett.* **2004**, *6*, 4227.

9 N. Tohnai, Y. Mizobe, M. Doi, S. Sukata, T. Hinoue, T. Yuge, I. Hisaki, Y. Matsukawa, M. Miyata, *Angew. Chem., Int. Ed.* **2007**, *46*, 2220.

10 M. Mehring, M. Schürmann, R. Ludwig, *Chem.—Eur. J.* **2003**, *9*, 837.

11 G. R. Desiraju, *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2311.

12 T. R. Kelly, M. H. Kim, *J. Am. Chem. Soc.* **1994**, *116*, 7072.

13 Crystallographic data of TPMA–PPA: $C_{102}H_{100}O_{12}N_4P_4Cl_2$, $M_r = 1768.73$, triclinic, space group $P\bar{1}$, $a = 14.013(3)$, $b = 14.983(3)$, $c = 23.595(5)$ Å, $\alpha = 85.485(13)$, $\beta = 80.455(11)$, $\gamma = 67.351(12)^\circ$, $V = 4508.0(16)$ Å^3, $T = 273$ K, $Z = 2$, $D_{calcd} = 1.303$ g cm^{-3}. 50040 total reflections, 15310 unique, 11995 observed [$I > 2\delta(I)$]. The final R_1 [$I > 2\delta(I)$] and wR_2 (all data) were 0.0594 and 0.1597, respectively. Crystallographic data of TPMA–*n*PrPA: $C_{22}H_{26}O_3N_1P_1$, $M_r = 383.43$, monoclinic, space group Cc, $a = 26.6767(7)$, $b = 13.7847(4)$, $c = 25.0072(6)$ Å, $\beta = 113.0821(12)^\circ$, $V = 8459.7(4)$ Å^3, $T = 213$ K, $Z = 16$, $D_{calcd} = 1.204$ g cm^{-3}. 44341 total reflections, 13954 unique, 7753 observed [$I > 2\delta(I)$]. The final R_1 [$I > 2\delta(I)$] and wR_2 (all data) were 0.1146 and 0.3425, respectively.

14 A. M. Sheldrick, *SHELX 97-Programs for Crystal Structure Analysis*, Göttingen, Germany, **1998**.

15 M. C. Etter, J. C. MacDonald, J. Bernstein, *Acta Cryst.* **1990**, *B46*, 256.

16 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

Published on the web (Advance View) October 24, 2007; doi:10.1246/cl.2007.1390