doi:10.1246/cl.2011.1290

Published on the web October 26, 2011

Self-organized Structure Generated by Molecular Symmetry/Asymmetry Regulation

Keisuke Kaneda,[1] Kazuhiro Shikinaka,[1] Nozomu Fujii,[1] Keiichi Noguchi,[1] Eiji Masai,[2] Yoshihiro Katayama,[3] Masaya Nakamura,[4] Yuichiro Otsuka,[4] Seiji Ohara,[4] and Kiyotaka Shigehara*[1]
[1]*Graduate School of Engineering, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588*
[2]*Department of Bioengineering, Nagaoka University of Technology, Nagaoka, Niigata 940-2188*
[3]*College of Bioresource Science, Nihon University, Fujisawa, Kanagawa 252-0880*
[4]*Forestry and Forest Products Research Institute, Tsukuba, Ibaraki 305-8687*

(Received July 27, 2011; CL-110631; E-mail: jun@cc.tuat.ac.jp)

The self-organization of polyfunctional molecules, leading to specific molecular assemblies, is often determined by the molecular symmetry/asymmetry of constitution. By using structurally isomeric pyronedicarboxylic acids, the molecular symmetry/asymmetry was revealed to discriminate the structure and the thermodynamic stability of self-organized architecture.

Self-organization is scientifically interesting and technologically important because it provides routes to a range of materials with regular structures.[1–5] The concept of self-organization has come from studying molecular assembling mechanisms. Final structure of self-organized architecture is dominated by the structure of components which give the driving force for assembly. Understanding the complementarity between the self-organized structure and its components is also crucial for designing of architecture.

Chelidonic acid is a dicarboxylic acid with 4-pyrone ring (abbreviated as CDA; Figure 1a). CDA formed well-organized structures with various metals.[6] 2-Pyrone-4,6-dicarboxylic acid (abbreviated as PDC; Figure 1b), that is the structural isomer of CDA and has the asymmetric structure originated from the 2-pyrone ring, was first obtained in a massive scale from lignin biodegradation intermediates by the action of transformed bacterium.[7] PDC also forms specific structures with alkali metal[8] ions and heavy metal[9] ions. The self-organized structure of PDC with sodium ion was completely different from that of CDA regardless of the same molecular formula.[6,8] This result experimentally indicates that molecular symmetry/asymmetry regulates the self-organization.

In this letter, we report the generation of self-organized structure by molecular symmetry/asymmetry of components. Here, CDA or PDC was combined with amines to obtain the self-organized assemblies. There are a variety of amines with different formulae and charge ratios. Therefore, by using amines as partners of complex formation, the self-organization of CDA and PDC can be studied systematically. Especially, the effect of molecular symmetry/asymmetry and activity of functional groups (i.e., carboxylic acid) for self-organized structure were revealed herein.

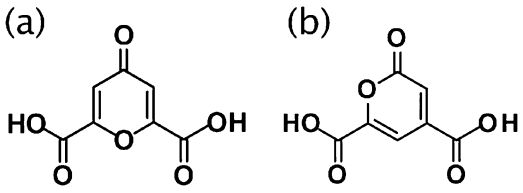

Figure 1. Molecular structure of CDA (a) and PDC (b).

Pyrazine (abbreviated as PY), a typical bifunctional aromatic amine, was combined with CDA or PDC for estimation of correlation between the self-organized structure and the molecular symmetry/asymmetry of components. Starting from any mixing ratio, the resulting self-organized assembly of CDA–PY (abbreviated as **I**) included each component as the molar ratio of CDA:PY = 2:1. Similarly starting from any mixing ratio, the resulting self-organized assembly of PDC–PY (abbreviated as **II**) had each component as the molar ratio of PDC:PY = 2:3. The single-crystal structure essentially differs by the molecular symmetry of pyrone rings as shown in Figure 2. CDA and PY in **I** made two-dimensional networks (Figure 2a-1), by contrast, PDC and PY in **II** formed pentamer (Figure 2b-1). Furthermore, the number of hydrogen bonds was different in two architectures; although every PY unit in **I** had two hydrogen bonds (Figure 2a-2), there are one PY unit bearing two hydrogen bonds and two terminal PY units bearing only one hydrogen bond in **II** (Figure 2b-2). Thermogravimetric analysis (TGA) revealed that the thermal stability of PY in the complex **I** is clearly higher than that in the complex **II** (Figure 3). This indicates that the molecular symmetry/asymmetry determines the stability of self-

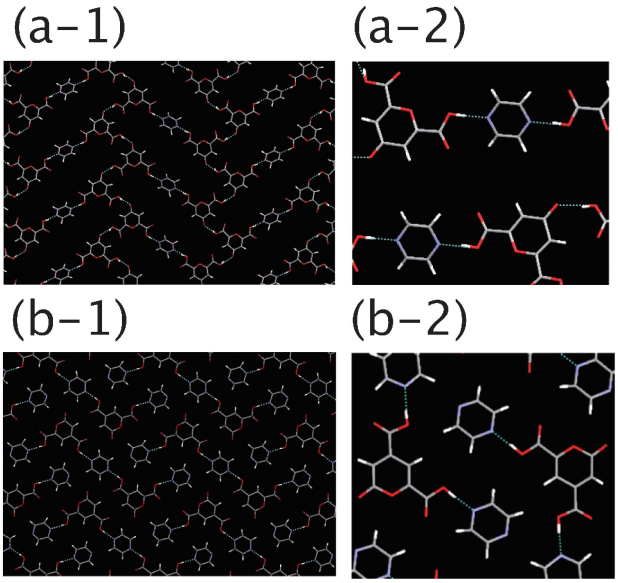

Figure 2. Single-crystal structure of **I**: (a) and **II**: (b). C: gray, N: blue, O: red, H: white. The dotted green lines indicate the hydrogen bond between CDA or PDC and pyrazine.

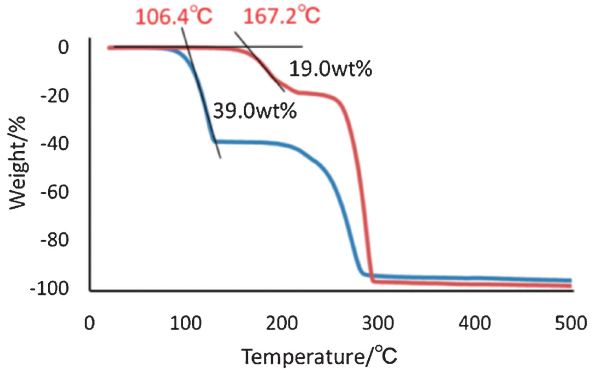

Figure 3. TGA curves of single crystal **I** (red) or **II** (blue). The 1st weight loss was due to the elimination of PY. The ratio of the weight loss is consistent with the molar ratio which is confirmed from the single-crystal structural analysis (Figure 2). The inset temperature corresponds to 5 wt % weight loss.

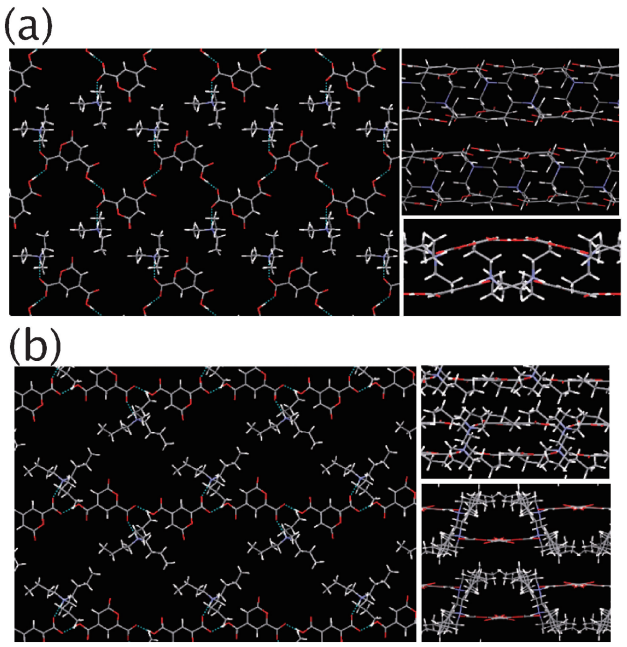

Figure 4. Single-crystal structure of **III**: (a) and **IV**: (b). C: gray, N: blue, O: red, H: white. The dotted green lines indicate the hydrogen bond between PDC and triethylamine or tributylamine.

organized structure. The carbonyl groups of pyrone ring form hydrogen bonds with carboxylic groups of CDA only in the complex **I**. Thus, the hydrogen bonding of carbonyl groups in a pyrone ring is also influenced by the molecular symmetry/asymmetry, and this should be due to the steric hindrance originating from the planarity of 2-pyrone ring in PDC as shown in Figure S1.[10]

When CDA and trialkylamines were mixed, they merely formed the corresponding 1:2 molar ratio salts. However, PDC–triethylamine (**III**) and PDC–tributylamine (**IV**) formed a 1:1 molar ratio network crystals. The single-crystal structures are shown in Figure 4, where the main ladder-like frameworks were composed of the hydrogen bondings among PDC molecules

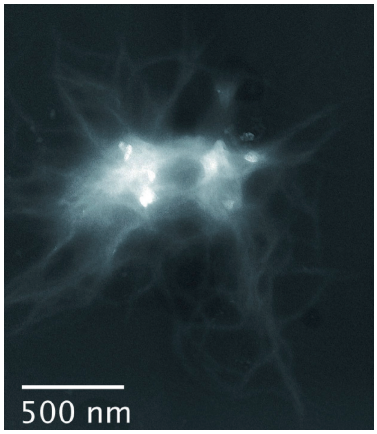

Figure 5. TEM image of the complex of PDC and tributylamine crystallized from ethyl acetate.

such as (4-position)-COOH···O=C<(6-position). Trialkylamines were anchored only to the 6-position carboxylic group in the fashion of $R_3NH^+\cdots{}^-OOC$-(6-position) or $R_3N\cdots HOOC$-(6-position). Such results revealed not only the difference between the symmetric/asymmetric structural isomers of CDA and PDC, but also the discrimination of activity of two carboxylic groups in PDC. We already know pK_a values of PDC are 1.13 and 2.52,[8] however, it was unclear which carboxylic group is more acidic. This result suggests that the activity of two carboxylic groups in PDC differs and the carboxylic group at 6-position is plausibly more acidic, i.e., the activity of functional groups is regulated by molecular asymmetry.

Transmission electron microscopy (TEM) revealed that **IV** consisted of filamentous assembles whose length is several μm (Figure 5). This result emerges us for usage of PDC–amine complexes as organic nanodevices (e.g., conductive nanowire).

In conclusion, the molecular symmetry/asymmetry regulates the structure and the properties of self-organized architecture. Such discrimination would originate from the difference of activity in the functional groups of component molecules depending on their molecular symmetry/asymmetry.

References and Notes

1 B. Alberts, D. Bray, J. Lewis, M. Raff, K. Roberts, J. D. Watson, *Molecular Biology of the Cell*, Garland, New York, **1994**.
2 K. E. Schwiebert, D. N. Chin, J. C. MacDonald, G. M. Whitesides, *J. Am. Chem. Soc.* **1996**, *118*, 4018.
3 L. Schmidt-Mende, A. Fechtenkötter, K. Müllen, E. Moons, R. H. Friend, J. D. MacKenzie, *Science* **2001**, *293*, 1119.
4 C. De Rosa, C. Park, E. L. Thomas, B. Lotz, *Nature* **2000**, *405*, 433.
5 G. M. Whitesides, *Sci. Am.* **1995**, *273*, 146.
6 J. F. Eubank, V. Ch. Kravtsov, M. Eddaoudi, *J. Am. Chem. Soc.* **2007**, *129*, 5820.
7 Y. Otsuka, M. Nakamura, K. Shigehara, K. Sugimura, E. Masai, S. Ohara, Y. Katayama, *Appl. Microbiol. Biotechnol.* **2006**, *71*, 608.
8 T. Michinobu, M. Bito, Y. Yamada, Y. Katayama, K. Noguchi, E. Masai, M. Nakamura, S. Ohara, K. Shigehara, *Bull. Chem. Soc. Jpn.* **2007**, *80*, 2436.
9 M. Bito, T. Michinobu, Y. Katayama, Y. Otsuka, M. Nakamura, S. Ohara, E. Masai, K. Shigehara, *Trans. Mater. Res. Soc. Jpn.* **2008**, *33*, 1165.
10 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

