Supramolecular Gels

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Formation of Nanoporous Fibers by the Self-Assembly of a Pyromellitic Diimide-Based Macrocycle**

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Construction of one-dimensional (1D) nanostructures based on self-assembly of small molecules has received much attention.[2] Supramolecular gels derived from the 1D self-assembly of low-molecular-weight organogelators (LMOGs) have potential applications in various areas, such as drug delivery systems, biomaterials, electronic devices, and templates for nanostructures.[3] Therefore, much effort has been made to develop novel LMOGs and to elucidate their nanostructures and new physical properties.[2,3] Among the various LMOGs, macrocycles are the attractive candidates. The first example of the macrocyclic gelator is the calix[8]-arene with long alkanoyl chains at the *para* position of the phenol groups reported by Shinkai and co-workers.[4] Since then, gelators based on β-[5a] and γ-cyclodextrins,[5b] peptidomimetic cyclophane,[6] resorcinarene,[7] crown ether,[8] arylene ethynylene macrocycle,[2b,9] as well as cucurbit[7]uril (CB[7])[10] have been developed. However, the construction of supramolecular gel based on the self-assembly of well-defined macrocycles remains challenging since the rational design of the macrocycles capable of forming gels by 1D self-assembly is not possible at the present stage. If we can find such macrocycles, an additional function based on the guest-binding properties of macrocycles[11] may be added to the fibril structures formed by stacking of the macrocycles. For example, crown ether based gelators formed gels by inclusion of tetraammonium cationic guests.[8a,b] In the CB[7]-based hydrogel, a guest-induced stimuli-responsive system was achieved by the use of the inclusion ability of CB[7].[10] The development of a new type of macrocyclic gelator may lead to the formation of a supramolecular gel with new structural and physical properties pertaining to the macrocycle itself.

Recently, we found that pyromellitic diimide-based macrocycle **1** (Figure 1) gelated *N*,*N*-dimethylaniline. We reported that **1** preferentially includes π-donating guests with a charge transfer (CT) interaction as the driving force.[12] Further investigation of the inclusion properties of **1** with π-donating compounds led us to discover the solvent-selective gelation of **1** in *N*,*N*-dimethylaniline. By taking advantage of 1D assembling of **1** in *N*,*N*-dimethylaniline, we prepared functional porous organic nanofibers, in which the pores were constructed by the tubular assembly of **1**. Herein, we report the preparation and the structural study of new porous organic nanofibers along with their potential application as chemosensors.

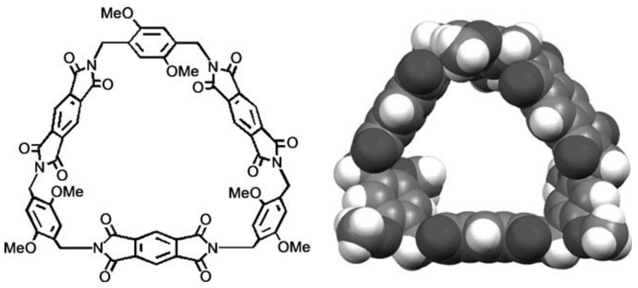

Figure 1. Structure of pyromallitic diimide-based macrocycle **1** and its CPK representation.

When a hot solution of **1** (1.0 wt%) in *N*,*N*-dimethylaniline was allowed to cool to room temperature, a deep-violet colored gel was formed (Figure 2). The color of the gel is ascribed to the CT interaction between π-accepting **1** and π-donating *N*,*N*-dimethylaniline ($\lambda_{max} = 530$ nm). Of all the aniline derivatives that were tested, only *N*,*N*-dimethylaniline

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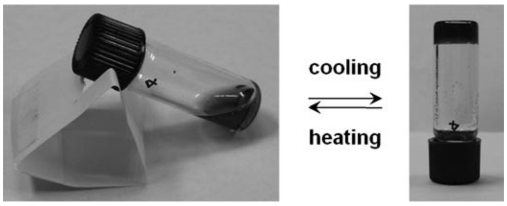


Figure 2. Pictures of the gelation behavior of **1** in *N*,*N*-dimethylaniline (1.0 wt %).

had the ability to induce gelation of **1** (Table 1 and see the Supporting Information).[13] After centrifugation of the gel, the deep-violet precipitate was collected and gave a solid-state UV/Vis spectrum displaying a CT band similar to that of the gel (see the Supporting Information). The composition of the precipitate was predicted to be **1**·(*N*,*N*-dimethylaniline)$_3$ based on analysis of its ^{1}H NMR spectrum in $CDCl_3$. CT complexation between **1** and *N*,*N*-dimethylaniline may be a driving force of the gelation.

Table 1: Solvent-selective gelation behavior of **1**.[a]

Solvent	Behavior
aniline	S
N-methylanilne	S
N-ethylaniline	S
N-isopropylaniline	S
N,*N*-dimethylaniline	G (1.0 wt %)
N-methyl-*N*-ethylaniline	S
N,*N*-diethylaniline	P
N,*N*-dimethyl-*o*-toluidine	P
N,*N*-dimethyl-*m*-toluidine	P
N,*N*-dimethyl-*p*-toluidine	P

[a] G: gel formed (critical gel concentration); S: soluble; P: precipitate formed.

The xerogel was prepared by drying in vacuo, and the pale yellow color of the xerogel indicated the absence of *N*,*N*-dimethylaniline in the xerogel, which was supported by the ^{1}H NMR spectrum of the xerogel (see the Supporting Information). These results indicated that the gelation was derived from the complexation between **1** and *N*,*N*-dimethylaniline, and that *N*,*N*-dimethylaniline was removed by drying in vacuo. The morphology of the sample was then investigated by field emission scanning electron microscopy (FE-SEM), which revealed fibril structures and their 3D networks (Figure 3).[14] Further examination of the xerogel by high-resolution transmission electron microscopy (HR-TEM, Figure 4) showed that the tubular hollows along the fiber growth axis have a diameter that is comparable to the size of **1** (ca. 1 nm). This result suggests that the hollow is composed of a one-molecule-thick array of **1**. The tubular stacking was also inferred from X-ray diffraction measurements of the xerogel. The diffractogram is dominated by three sharp peaks at $2\theta = 6.5, 7.6°$, and 15.5°, which can be assigned to the height (13.6 and 11.7 Å) and width (5.7 Å) of the macrocycle **1**, respectively, and is in good agreement with the structure optimized by B3LYP/6-31G* calculations (height: 13.1 and 11.1 Å; width 4.7 Å, see the Supporting Information). XRD measurements of the nanofibers collected by centrifugation showed three similar distinctive peaks, suggesting their similar tubular structures.

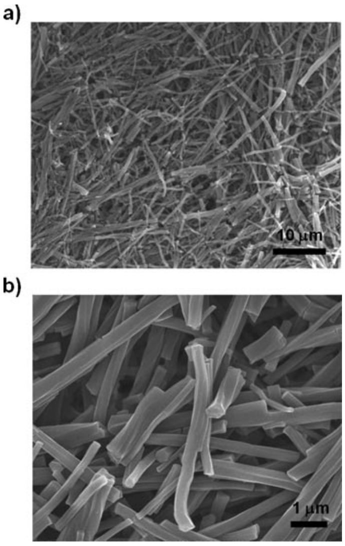


Figure 3. FE-SEM images of the xerogel: a) large-area image; b) magnified image.

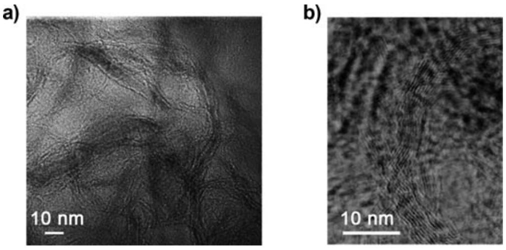


Figure 4. HR-TEM images of the xerogel: a) large-area image; b) magnified image.

Single crystals of (**1**·(*N*,*N*-dimethylaniline)$_2$(tetrachloroethane)$_2$ were obtained by recrystallization of **1** from a mixture of *N*,*N*-dimethylaniline and 1,1,2,2-tetrachloroethane (v/v = 1:1). X-ray crystal structural analysis also showed that **1** stacks regularly to form a tubular structure (Figure 5).[15] This result is in line with our previous study, in

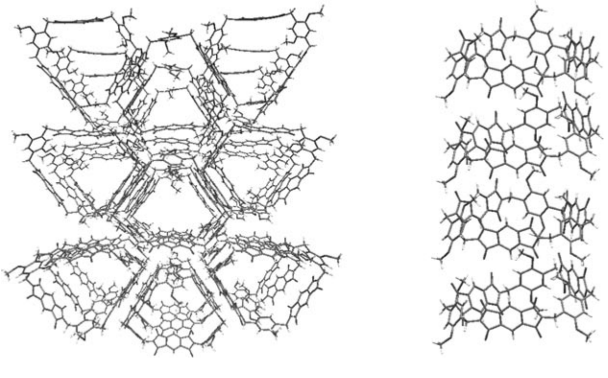
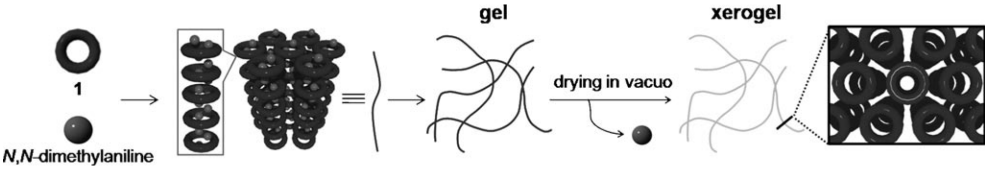


Figure 5. Crystal structure of **1**·(*N*,*N*-dimethylaniline)$_2$·(1,1,2,2-tetrachloroethane)$_2$. Solvent molecules are omitted for clarity.

which **1** showed a strong tendency to self-assemble to form channel-type structures in the solid state, and the guest molecules were continuously included in the long cavity of the channel, as was observed in the inclusion complexes of (p-xylene)$_2$@**1** and (toluene)$_3$@**1**.[12] When **1** self-assembles with the aid of π-donating benzene derivatives, the formation of channel-type structure is favorable probably as a result of the adequate structural fitting of the pseudohexagonal shape of **1**.[13] Accordingly, *N*,*N*-dimethylaniline can help **1**, through CT interactions, to self-assemble to form nanofibers of tubular structure, which then accumulate into bundles referred as nanofibers.[16] Because the CT interaction between *N*,*N*-dimethylaniline and pyromellitic diimide moieties in **1** is weak,[17] guest molecules can be removed rather easily by drying in vacuo. The tubular arrangement of **1** would remain intact after the removal of *N*,*N*-dimethylaniline (Scheme 1).



Scheme 1. Schematic representation of the formation of the fibril structure by tubular assembly of **1**.

Thus, the nanofibers of the xerogel have channel-type empty cavities, and the cross section of a nanofiber may have nanoporous structure similar to honeycomb. Therefore, π-electron donating guests can be preferentially included in the π-electron deficient cavities of the nanoporous fibers with CT interactions as the driving force. The adsorption property of the xerogel was thus examined by using *N*,*N*-dimethylaniline, *N*-methylaniline, aniline, and 1,3-dimethoxybenzene as adsorbents. The xerogel was placed in a chamber and filled with vapor of a guest at room temperature under ordinary pressure. The pale yellow color of the xerogel changed after adsorption of the guest, and the color change could be easily differentiated by the naked eye according to the π-donating ability of the guest (Figure 6). Corresponding to this color change, the UV/Vis spectrum of the xerogel exposed to a vapor of the guest is slightly different from that of the xerogel itself (see the Supporting Information). The color after adsorption reflects the π-donating ability of the guest. The strong π-donating guest, *N*,*N*-dimethylaniline, changed the color of the xerogel to deep violet, while light yellow color was observed when the vapor of the weak donor guest, 1,3-dimethoxybenzene, was exposed to the xerogel. The same experiment was carried out for a powder of **1**, which was prepared from a 1.0 wt % solution of **1** in CHCl$_3$. However, it was difficult to detect the color by the naked eye for all the guests, and the UV/Vis spectral curves were almost the same as that of the xerogel itself (see the Supporting Information). The fibril structure was not observed in the powder of **1** by the SEM images, not was the diffraction pattern observed in XRD measurements. Thus, the tubular cavities in the nanofiber are essential for the color change of the xerogel, and this result suggests that the xerogel could be used as a chemosensor for π-electron-donating molecules.

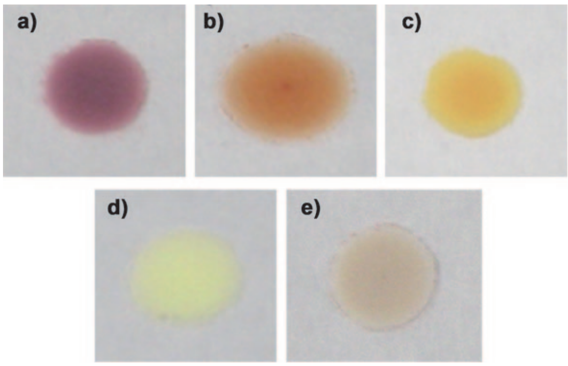


Figure 6. Photographs of the xerogel after adsorption of *N*,*N*-dimethylaniline (a), *N*-methylaniline (b), aniline (c), 1,3-dimethoxybenzene (d), and before adsorption (e).

In summary, we discovered a new member of a unique class of LMOGs. The pyromellitic diimide based macrocycle **1** selectively gelates *N*,*N*-dimethylaniline to form the supramolecular gel with the nanofibril structure. Nanofibril structures were fabricated from a macrocycle through a gelation process assisted by CT interactions between a host and a guest. The nanofibers may be constructed by the bundles of tubular assembly of **1** with *N*,*N*-dimethylaniline serving as a glue to form the tubular structures. By utilizing the gelation of **1**, functional organic nanofibers with channel-type empty cavities formed by the stacking of **1** were prepared. In the channel-type empty cavities in the fiber, π-donating guests can be included, and the pale yellow color of the xerogel changes to yellow or to orange depending on the π-donating ability of the guests. To the best of our knowledge, this is the first example of the construction of self-assembled organic nanoporous fibers from a macrocycle that can respond to outer stimuli. This preliminary finding may be extended to chemosensors, and studies along this line are in progress.

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[1] T. Nakagaki, S.-i. Kato, A. Harano, T. Shinmyozu, *Tetrahedron* **2010**, *66*, 976–985 (part 5). References to parts 1–4 are therein.

[2] For reviews, see: a) B.-K. Cho, H.-J. Kim, Y.-W. Chung, B.-I. Lee, M. Lee, *Adv. Polym. Sci.* **2008**, *219*, 60–106; b) L. Zang, Y. Che, J. S. Moore, *Acc. Chem. Res.* **2008**, *41*, 1596–1608; c) L. C. Palmer, S. I. Stupp, *Acc. Chem. Res.* **2008**, *41*, 1674–1684; d) T. Shimizu, *Bull. Chem. Soc. Jpn.* **2008**, *81*, 1554–1566; e) M. Llusar, C. Sanchez, *Chem. Mater.* **2008**, *20*, 782–820; f) H. Cui,

M. J. Webber, S. I. Stupp, *Pept. Sci.* **2010**, *94*, 1–18; g) D. K. Smith, *Chem. Soc. Rev.* **2009**, *38*, 684–694.

[3] For reviews, see: a) P. Terech, R. G. Weiss, *Chem. Rev.* **1997**, *97*, 3133–3159; b) L. A. Estroff, A. D. Hamilton, *Chem. Rev.* **2004**, *104*, 1201–1217; c) N. M. Sangeetha, U. Maitra, *Chem. Soc. Rev.* **2005**, *34*, 821–836; d) A. Vintiloiu, J.-C. Leroux, *J. Controlled Release* **2008**, *125*, 179–192; e) A. R. Hirst, B. Escuder, J. F. Miravet, D. K. Smith, *Angew. Chem.* **2008**, *120*, 8122–8139; *Angew. Chem. Int. Ed.* **2008**, *47*, 8002–8018; f) M. Suzuki, K. Hanabusa, *Chem. Soc. Rev.* **2009**, *38*, 967–975; g) M.-O. M. Piepenbrock, G. O. Lloyd, N. Clarke, J. W. Steed, *Chem. Rev.* **2010**, *110*, 1960–2004.

[4] M. Aoki, K. Murata, S. Shinkai, *Chem. Lett.* **1991**, 1715–1718.

[5] a) C. de Rango, P. Charpin, J. Navaza, N. Keller, I. Nicolis, F. Villain, A. W. Coleman, *J. Am. Chem. Soc.* **1992**, *114*, 5475–5476; b) T. Kida, Y. Marui, K. Miyawaki, E. Kato, M. Akashi, *Chem. Commun.* **2009**, 3889–3891.

[6] J. Becerril, M. I. Burguete, B. Escuder, S. V. Luis, J. F. Miravet, M. Querol, *Chem. Commun.* **2002**, 738–739.

[7] S. R. Haines, R. G. Harrison, *Chem. Commun.* **2002**, 2846–2847.

[8] a) S. i. Kawano, N. Fujita, S. Shinkai, *Chem. Commun.* **2003**, 1352–1353; b) Z. Ge, J. Hu, F. Huang, S. Liu, *Angew. Chem.* **2009**, *121*, 1830–1834; *Angew. Chem. Int. Ed.* **2009**, *48*, 1798–1802.

[9] K. Balakrishnan, A. Datar, W. Zhang, X. Yang, T. Naddo, J. Huang, J. Zuo, M. Yen, J. S. Moore, L. Zang, *J. Am. Chem. Soc.* **2006**, *128*, 6576–6577.

[10] I. Hwang, W. S. Jeon, H. J. Kim, D. Kim, H. Kim, N. Selvapalam, N. Fujita, S. Shinkai, K. Kim, *Angew. Chem.* **2007**, *119*, 214–217; *Angew. Chem. Int. Ed.* **2007**, *46*, 210–213.

[11] a) J. M. Lehn, *Supramolecular Chemistry: Concept and Perspectives*, VCH, Weinheim, **1995**; b) J. W. Steed, J. L. Atwood, *Supramolecular Chemistry*, Wiley, Chichester, **2000**.

[12] T. Iwanaga, R. Nakamoto, M. Yasutake, H. Takemura, K. Sako, T. Shinmyozu, *Angew. Chem.* **2006**, *118*, 3725–3729; *Angew. Chem. Int. Ed.* **2006**, *45*, 3643–3647 (part 1).

[13] Single crystals of the clathrates **1**·(aniline)$_6$ and **1**·(*N*-ethylaniline)$_5$ were obtained by recrystallization from aniline and *N*-ethylaniline, respectively. In the channel-type cavities formed by the stacking of **1**, the cyclic oligomers of the guests formed by the N−H··π and N−H···N interactions are continuously arranged to form a 1D array of the cyclic oligomers. The IR spectra of these complexes support the presence of the N−H···π and N−H···N interactions. This type of the structure of the complex may promote crystallization. In other aniline derivatives without an N−H group, such as *N*-methy-*N*-ethyl- and *N*,*N*-diethylanilines, as well as *N*,*N*-dimethyltoluidines, the formation of the fibril structures were not observed except for *N*,*N*-dimethylaniline. Some of these crystal data will be published elsewhere.

[14] The precipitate collected by centrifugation was also measured by FE-SEM and the FE-SEM images, and these data supported the formation of the fibril structures.

[15] CCDC 781784 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[16] In the crystal structure of **1**·(*N*,*N*-dimethylaniline)$_2$·(1,1,2,2-tetrachloroethane)$_2$, one dimethylaniline and two tetrachloroethane molecules are included in the cavity of **1**, and the remaining *N*,*N*-dimethylaniline interacts with the imide moiety of another neighboring macrocycle outside of the cavity. The included dimethylaniline is located parallel to the benzene ring of the pyromellitic diimide moiety via a CT interaction (see the Supporting Information). A plausible mechanism for the formation of the complex **1**·(*N*,*N*-dimethylaniline)$_2$·(1,1,2,2-tetrachloroethane)$_2$ is considered as follows: *N*,*N*-dimethylaniline may be fixed in the cavity of the macrocycle **1** with the pyromellitic diimide moieties by CT interactions and the remaining cavity may be filled with tetrachloroethane molecules. However, the guest molecules cannot be included completely in the cavity of a macrocycle and the remaining part of the guests is included in another macrocycle, which is stacked on the original one. Repetition of this process as the guest molecules are encapsulated in the macrocycle may lead to the formation of a one-dimensional array of the guest molecules in the tubular cavity of the macrocycles. The formation of this type of tubular host–guest complex should be favorable for host–guest interactions.[12] Formation of **1**·(*N*,*N*-dimethylaniline)$_3$ may follow a similar mechanism to that of **1**·(*N*,*N*-dimethylaniline)$_2$·(1,1,2,2-tetrachloroethane)$_2$. Although short contacts between a carbonyl oxygen atom of the imide moiety of a macrocycle and the methoxy protons of the dimethoxybenzene moiety of the neighboring stacked macrocycle are observed in the crystal structure of **1**·(*N*,*N*-dimethylaniline)$_2$·(1,1,2,2-tetrachloroethane)$_2$, significant interaction among the stacked macrocycles of a given tube is unlikely. In the crystal packing diagram, π-stacking interactions between the pyromellitic diimide moieties, the dimethoxybenzene moieties, as well as the pyromellitic diimide and dimethoxybenzene moieties in the macrocycles of neighboring tubes are observed. These π-stacking interactions may play an important role as an adhesive that binds the tubes. In addition, the pseudohexagonal shape of macrocycle **1** is adequate for the stacking and π–π interactions for the formation of bundles of the tubes. The xerogel obtained from **1** is considered to have similar tubular structure of significant stability.

[17] a) R. Foster, *Organic Charge-Transfer Complexes*, Academic Press, New York, **1969**; b) H. J. Schneider, *Angew. Chem.* **1991**, *103*, 1419–1439; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1417–1436; c) C. A. Hunter, R. Lawson, J. Perkins, C. J. Urch, *J. Chem. Soc. Perkin Trans. 2* **2001**, 651–669; d) E. A. Meyer, R. K. Castellano, F. Diederich, *Angew. Chem.* **2003**, *115*, 1244–1287; *Angew. Chem. Int. Ed.* **2003**, *42*, 1210–1250.