Supramolecular Polymers

DOI: 10.1002/ange.201107655

Supramolecular Polymerization Triggered by Molecular Recognition between Bisporphyrin and Trinitrofluorenone**

Takeharu Haino, Akihide Watanabe, Takehiro Hirao, and Toshiaki Ikeda*

Self-assembled supramolecular polymers consist of molecular components that are held together through noncovalent interactions. The reversible noncovalent interactions can be used to produce healable, stimuli-responsive, and switchable supramolecular polymers. This new class of intelligent polymer materials, with macroscopic properties that might be turned on and off by external stimuli, has helped supramolecular polymer chemistry to gain momentum within the field of polymer science.[1] The design of well-organized polymer architectures requires the integration of certain supramolecular components that must be capable of creating the strong noncovalent interactions necessary for producing an appreciable degree of polymerization. Multiple hydrogen-bonding,[2] hydrophobic,[3] cation–dipole,[4] CH/π,[5] and aromatic electron donor–acceptor[6] interactions are often employed in the synthesis of functional supramolecular polymers.

Supramolecular porphyrin polymers have recently attracted attention because of their creative applications in photoactive devices. Coordination-driven self-assembly is one of the most useful approaches for building large and elaborate porphyrin architectures.[7] However, self-assembly of porphyrins in organic media, driven by weak noncovalent forces, such as van der Waals and CH/π interactions, is very limited,[8] even though the porphyrin moiety possesses a flat and electron-rich surface that creates the possibility of attractive van der Waals, stacking, and charge-transfer interactions. Recently, we have developed a bisporphyrin cleft connected by a pyridine dicarboxamide linker that assembles to form a unique complementary dimer in organic media.[9] The competitive complexation of a flat, electron-deficient aromatic guest into the bisporphyrin cleft leads to a π donor–acceptor-type host–guest complex.[10] These supramolecular motifs should be useful for the synthesis of supramolecular porphyrin polymers.[11] To investigate this strategy, a π donor–acceptor-type host–guest motif was incorporated into the heteroditopic monomer **1**. The electron-deficient guest moiety, 4,5,7-trinitrofluorenone-2-carboxylate (TNF), can bind within the bisporphyrin cleft through a charge-transfer interaction, and iterative head-to-tail host–guest complexation should produce a new supramolecular polymer (Figure 1). Herein, we report the novel molecular recognition-directed supramolecular polymerization of monomer **1** in solution and solid state.

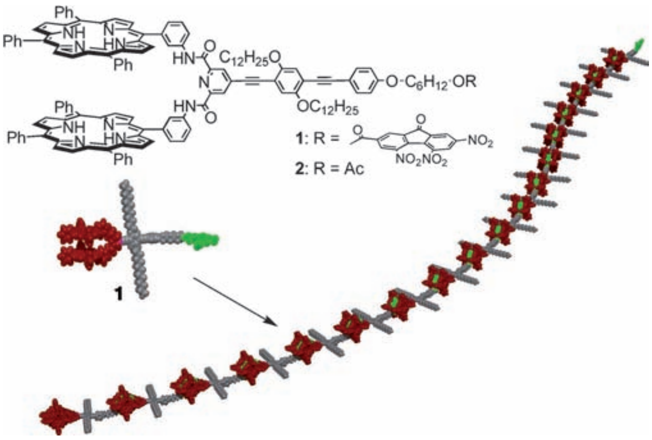

Figure 1. Heteroditopic monomer **1**, its analogue **2**, and the supramolecular polymer.

The self-assembly of **1** was studied in solution using fluorescence and UV/Vis absorption spectroscopies (see Figure S1 in the Supporting Information). The fluorescence spectrum of **1** in toluene was temperature dependent; strong emission bands ($\lambda_{ex} = 501$ nm) at 363 K were observed at 657 and 719 nm, which are characteristic of a porphyrin core, but the emission bands gradually diminished upon cooling the solution. When the temperature reached 263 K, 80 % of the emission was quenched. The TNF moiety is a good energy acceptor. Therefore, this quenching can be rationalized by accommodation of the TNF moiety of **1** into the bisporphyrin cleft. The UV/Vis absorption spectrum of **1** was concentration dependent at 298 K in toluene, and plotting the molar extinction coefficients versus the concentrations gave hyperbolic curves. The isodesmic model was applied for the curve-fitting analysis to obtain the association constant ($K_E = 42\,000 \pm 4000\ \mathrm{L\,mol^{-1}}$).[12] In chloroform, the association constant could not be determined in the same way because of competitive protonation of the porphyrin nitrogen. To examine the solvent effect for π donor–acceptor-type host–guest complexation in chloroform and toluene, the associa-

---

[*] Prof. Dr. T. Haino, A. Watanabe, T. Hirao, Dr. T. Ikeda
Department of Chemistry, Graduate School of Science
Hiroshima University, 1-3-1 Kagamiyama
Higashi-Hiroshima 739-8526 (Japan)
E-mail: haino@sci.hiroshima-u.ac.jp

[**] We are grateful to Prof. Dr. Shin-ichi Kihara at the department of chemical engineering, graduate school of engineering, Hiroshima University for helpful discussions about solution rheology. This work is supported by the JSPS (Japan), the Yamada Science Foundation, and the Electric Technology Research Foundation of Chugoku through grant-in-aids for scientific research (B; grant number 21350066) and the challenging exploratory research (grant number 23655105).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201107655.

tion constants of **2** and 2,4,7-trinitrofluorenone were determined ($K_a = 250\,000 \pm 7000$ L mol^{-1} and $35\,000 \pm 1000$ L mol^{-1} for chloroform and toluene), and the results clearly indicated that the host–guest complexation was enhanced more in chloroform than in toluene.

The head-to-tail complexation between the bisporphyrin cleft and the TNF moiety was confirmed using ^{1}H NMR spectroscopy (Figure 2). A large upfield shift ($\Delta\delta = -1.58$ ppm) for the inner porphyrin NH of **1** was observed when the acetyl group of **2** was displaced by the TNF moiety (Figure 2). The aromatic TNF protons of **1** emerged in unusually upfield regions ($\delta = 4.56$, 5.77, 6.36, and 7.05 ppm).[13] Both the porphyrin NH and the TNF moiety obviously experienced a large shielding effect, placing the TNF moiety within the porphyrin cleft. Significant intermolecular nuclear Overhauser effects (NOEs) between the TNF protons and the porphyrin NHs provided evidence for a close contact, implying the formation of head-to-tail supramolecular polymers (see Figure S11 in the Supporting Information).

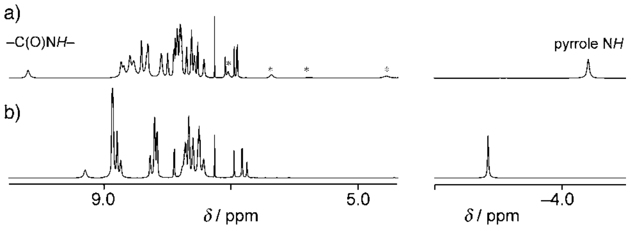

Figure 2. ^{1}H NMR spectra of a) monomer **1** (5.0×10^{-3} mol L^{-1}) and b) analogue **2** (5.0×10^{-3} mol L^{-1}) at 296 K in [D$_1$]chloroform. The asterisks denote the aromatic protons of the TNF moiety.

Diffusion-ordered spectroscopy (DOSY) was used to determine the hydrodynamic radii for molecular aggregates formed in solution. The DOSY experiments for **1** and **2** were performed in [D$_1$]chloroform (Figure 3). Compound **2** did not form any aggregates in solution; in fact, its diffusion coefficient ($D_{avg} = 3.02(8) \times 10^{-10}$ m^2 s^{-1}) was not noticeably influenced by its concentration. In contrast, the diffusion coefficient of **1** was strongly dependent on its concentration. At a concentration of 2.34 mmol L^{-1}, **1** had a diffusion constant of $2.96(2) \times 10^{-10}$ m^2 s^{-1}. The similarity to **2** indicates that, at this concentration, **1** exists in its monomeric form. Upon concentrating the solution, the diffusion coefficient of **1** decreased nonlinearly to $0.340(5) \times 10^{-10}$ m^2 s^{-1}. The large difference between the D values of **1** at high and low concentrations indicates considerably different hydrodynamic radii, implying that large polymeric aggregates were formed through self-assembly at the higher concentrations. The average degree of aggregation can be estimated by simplistically assuming that all aggregates are hydrodynamically spherical.[14] The average size of the supramolecular polymer (DP) was calculated to be approximately 660 at a concentration of 66.0 mmol L^{-1}.

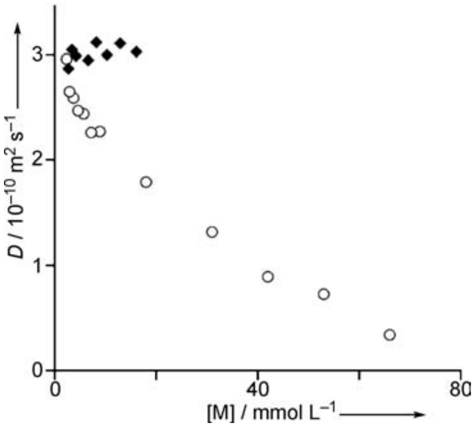

Figure 3. Diffusion coefficients D of **1** (○) and **2** (◆) at 298 K in [D$_1$]chloroform.

Viscometry provides fruitful information concerning the size and structure of supramolecular assemblies in solution. The specific viscosities for solutions of **1** in chloroform and in toluene were measured as a function of the concentration at 293 K using a micro-Ubbelohde viscometer (Figure 4). A double-logarithmic plot of the specific viscosity (η_{sp}) versus the concentration of **1** in chloroform or toluene yielded a linear relationship below the critical polymerization concentration (CPC). The change of viscosity in dependence of the concentration is indicative of a transition from the dilute to the semidilute concentration regime where overlap between chains contributes to a viscous drag. The change was sharper in chloroform than in toluene, but it occurred in approximately the same concentration region for each solvent (CPCs: 23.7 mmol L^{-1} and 24.1 mmol L^{-1} in chloroform and in toluene).

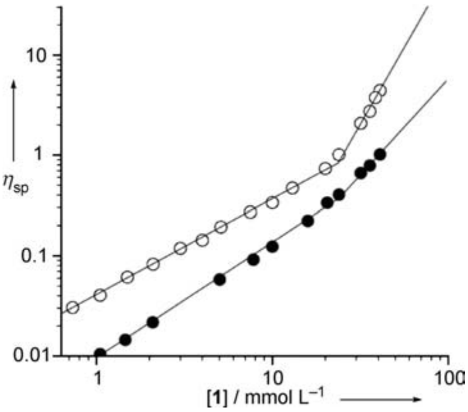

Figure 4. Specific viscosity (η) of **1** in chloroform (○) and toluene (●) at 293 K. The values denote the slopes.

In the dilute concentration regime, the viscosities are low, and the plots have slopes of 0.95 and 1.15 in chloroform and toluene, suggesting that the oligomeric assemblies are too short to be entangled. Above the critical concentrations, the plots curve upward, reaching a slope of 3.07 in the case of chloroform. Sizable supramolecular polymers are clearly formed, and their chains become entangled when the polymers come into contact, which is commonly observed in polymer solutions.

Since the host–guest complexation of the bisporphyrin and the TNF moieties is driven by noncovalent interactions, the dissociation and recombination of the supramolecular polymers occurs on an experimental time scale. The supramolecular relaxation regime should obey the mixed reputation-breakage regime.[15] When the noncovalent bond lifetime τ_{break} is greater than τ_{rep}, the relaxation time τ is approximately equal to τ_{rep}. This leads to a scaling law exponent of 3.0–3.4, which is quite consistent with the slope of 3.07 observed in chloroform. In contrast, the slope of 1.92 in toluene is a little smaller, most likely suggesting that shorter supramolecular polymers are formed because of the weaker head-to-tail connections, which leads to a large polydispersity index (PDI).

Atomic force microscopy visualizes the surface morphology of the supramolecular polymer (Figure 5). Well-developed supramolecular polymer networks are shown in Figure 5a. The fibers have a uniform height of (1.8 ± 0.1) nm. The fibrous morphology disappeared upon addition of 2,4,7-trinitrofluorenone, which interfered with the host–guest association (see Figure S5 in the Supporting Information). In addition, **2** randomly aggregated to form a particle-like morphology with a diameter of (23 ± 3) nm because of the lack of the guest moiety. These substantial morphological differences clearly indicate that the head-to-tail host–guest complexation between the bisporphyrin cleft and the TNF moiety drives the directional growth of the supramolecular polymer.

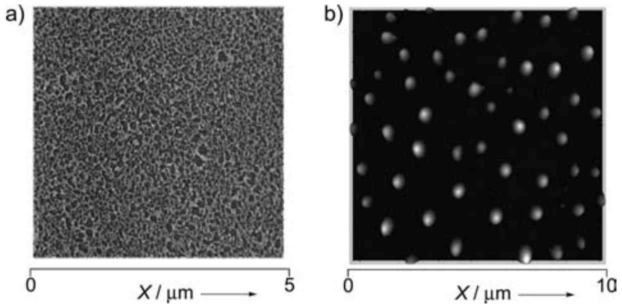

Figure 5. AFM images of the drop-cast films: a) solution of **1** (5.4×10^{-5} mol L^{-1}) and b) solution of **2** (2×10^{-5} mol L^{-1}).

Judging from the calculated structure of the oligomers (see Figure S6 in the Supporting Information), the width (1.7 nm) of the tetraphenylporphyrin moiety is close to the observed height, implying that the porphyrin moieties adopt a perpendicular alignment that stabilizes the oriented fibrillar nanonetwork through the stacking of the porphyrin moieties and van der Waals interactions between the alkyl side chains.

In summary, we have shown that monomer **1**, which possesses a bisporphyrin cleft and a TNF moiety, self-assembled to form supramolecular polymers in solution and solid state. NMR studies confirmed that the polymer was formed through a head-to-tail host–guest complexation. DOSY and viscosity experiments provided evidence for the formation of entangled supramolecular polymers. Atomic force microscopy indicated that the porphyrin moiety adopts a perpendicular alignment that enhances the oriented fibrillar nanoassemblies. The development of supramolecular functional materials is currently underway.

Received: October 31, 2011
Revised: December 6, 2011

Keywords: charge transfer · host–guest systems · molecular recognition · porphyrins · supramolecular chemistry

---

[1] a) M. Burnworth, L. Tang, J. R. Kumpfer, A. J. Duncan, F. L. Beyer, G. L. Fiore, S. J. Rowan, C. Weder, *Nature* **2011**, *472*, 334–337; b) R. Yerushalmi, A. Scherz, M. E. van der Boom, H.-B. Kraatz, *J. Mater. Chem.* **2005**, *15*, 4480–4487; c) Y. Yamamoto, T. Fukushima, Y. Suna, N. Ishii, A. Saeki, S. Seki, S. Tagawa, M. Taniguchi, T. Kawai, T. Aida, *Science* **2006**, *314*, 1761–1764.

[2] a) T. Gulik-Krzywicki, C. Fouquey, J.-M. Lehn, *Proc. Natl. Acad. Sci. USA* **1993**, *90*, 163–167; b) R. K. Castellano, D. M. Rudkevich, J. Rebek Jr., *Proc. Natl. Acad. Sci. USA* **1997**, *94*, 7132–7137; c) R. P. Sijbesma, F. H. Beijer, L. Brunsveld, B. J. B. Folmer, J. H. K. K. Hirschberg, R. F. M. Lange, J. K. L. Lowe, E. W. Meijer, *Science* **1997**, *278*, 1601–1604; d) E. A. Fogleman, W. C. Yount, J. Xu, S. L. Craig, *Angew. Chem.* **2002**, *114*, 4198–4200; *Angew. Chem. Int. Ed.* **2002**, *41*, 4026–4028; e) D. Garozzo, G. Gattuso, F. H. Kohnke, A. Notti, S. Pappalardo, M. F. Parisi, I. Pisagatti, A. J. P. White, D. J. Williams, *Org. Lett.* **2003**, *5*, 4025–4028; f) V. Stastny, D. M. Rudkevich, *J. Am. Chem. Soc.* **2007**, *129*, 1018–1019.

[3] a) M. Miyauchi, A. Harada, *J. Am. Chem. Soc.* **2004**, *126*, 11418–11419; b) Y. Hasegawa, M. Miyauchi, Y. Takashima, H. Yamaguchi, A. Harada, *Macromolecules* **2005**, *38*, 3724–3730; c) Y. Xu, M. Guo, X. Li, A. Malkovskiy, C. Wesdemiotis, Y. Pang, *Chem. Commun.* **2011**, *47*, 8883–8885; d) U. Rauwald, O. A. Scherman, *Angew. Chem.* **2008**, *120*, 4014–4017; *Angew. Chem. Int. Ed.* **2008**, *47*, 3950–3953; e) Y. Liu, Y. Yu, J. Gao, Z. Q. Wang, X. Zhang, *Angew. Chem.* **2010**, *122*, 6726–6729; *Angew. Chem. Int. Ed.* **2010**, *49*, 6576–6579.

[4] a) S. Shinkai, T. Yoshida, O. Manabe, Y. Fuchita, *J. Chem. Soc. Perkin Trans. 1* **1988**, 1431–1437; b) N. Yamaguchi, D. S. Nagvekar, H. W. Gibson, *Angew. Chem.* **1998**, *110*, 2518–2520; *Angew. Chem. Int. Ed.* **1998**, *37*, 2361–2364; c) H. W. Gibson, N. Yamaguchi, J. W. Jones, *J. Am. Chem. Soc.* **2003**, *125*, 3522–3533; d) F. Wang, C. Han, C. He, Q. Zhou, J. Zhang, C. Wang, N. Li, F. Huang, *J. Am. Chem. Soc.* **2008**, *130*, 11254–11255; e) F. Wang, J. Zhang, X. Ding, S. Dong, M. Liu, B. Zheng, S. Li, L. Wu, Y. Yu, H. W. Gibson, F. Huang, *Angew. Chem.* **2010**, *122*, 1108–1112; *Angew. Chem. Int. Ed.* **2010**, *49*, 1090–1094; f) Y.-S. Su, J.-W. Liu, Y. Jiang, C.-F. Chen, *Chem. Eur. J.* **2011**, *17*, 2435–2441.

[5] a) F. Tancini, R. M. Yebeutchou, L. Pirondini, R. De Zorzi, S. Geremia, O. A. Scherman, E. Dalcanale, *Chem. Eur. J.* **2010**, *16*, 14313–14321; b) Z. Zhang, Y. Luo, J. Chen, S. Dong, Y. Yu, Z. Ma, F. Huang, *Angew. Chem.* **2011**, *123*, 1433–1437; *Angew. Chem. Int. Ed.* **2011**, *50*, 1397–1401.

[6] a) R. S. Lokey, B. L. Iverson, *Nature* **1995**, *375*, 303–305; b) G. J. Gabriel, B. L. Iverson, *J. Am. Chem. Soc.* **2002**, *124*, 15174–15175; c) S. Bhosale, A. L. Sisson, P. Talukdar, A. Fürstenberg, N. Banerji, E. Vauthey, G. Bollot, J. Mareda, C. Röger, F. Würthner, N. Sakai, S. Matile, *Science* **2006**, *313*, 84–86; d) P. Jonkheijm, N. Stutzmann, Z. Chen, D. M. de Leeuw, E. W. Meijer, A. P. H. J. Schenning, F. Würthner, *J. Am. Chem. Soc.* **2006**, *128*, 9535–9540; e) H. Tanaka, S. Litvinchuk, D.-H. Tran, G. Bollot, J. Mareda, N. Sakai, S. Matile, *J. Am. Chem. Soc.* **2006**, *128*, 16000–16001; f) F. B. L. Cougnon, H. Y. Au-Yeung, G. D. Pantoş, J. K. M. Sanders, *J. Am. Chem. Soc.* **2011**, *133*, 3198–

3207; g) J. K. Klosterman, Y. Yamauchi, M. Fujita, *Chem. Soc. Rev.* **2009**, *38*, 1714 – 1725; h) H. Tanaka, G. Bollot, J. Mareda, S. Litvinchuk, D.-H. Tran, N. Sakai, S. Matile, *Org. Biomol. Chem.* **2007**, *5*, 1369 – 1380.

[7] a) U. Michelsen, C. A. Hunter, *Angew. Chem.* **2000**, *112*, 780 – 783; *Angew. Chem. Int. Ed.* **2000**, *39*, 764 – 767; b) K. Ogawa, Y. Kobuke, *Angew. Chem.* **2000**, *112*, 4236 – 4239; *Angew. Chem. Int. Ed.* **2000**, *39*, 4070 – 4073; c) K. Toyofuku, M. A. Alam, A. Tsuda, N. Fujita, S. Sakamoto, K. Yamaguchi, T. Aida, *Angew. Chem.* **2007**, *119*, 6596 – 6600; *Angew. Chem. Int. Ed.* **2007**, *46*, 6476 – 6480.

[8] T. Yamaguchi, T. Kimura, H. Matsuda, T. Aida, *Angew. Chem.* **2004**, *116*, 6510 – 6515; *Angew. Chem. Int. Ed.* **2004**, *43*, 6350 – 6355.

[9] a) T. Haino, T. Fujii, Y. Fukazawa, *Tetrahedron Lett.* **2005**, *46*, 257 – 260; b) T. Ikeda, A. Watanabe, T. Oshita, T. Haino, *Heteroat. Chem.* **2011**, *22*, 590 – 593.

[10] T. Haino, T. Fujii, Y. Fukazawa, *J. Org. Chem.* **2006**, *71*, 2572 – 2580.

[11] T. Haino, T. Fujii, A. Watanabe, U. Takayanagi, *Proc. Natl. Acad. Sci. USA* **2009**, *106*, 10477 – 10481.

[12] a) R. B. Martin, *Chem. Rev.* **1996**, *96*, 3043 – 3064; b) M. Tanaka, T. Ikeda, J. Mack, N. Kobayashi, T. Haino, *J. Org. Chem.* **2011**, *76*, 5082 – 5091.

[13] The assignment of the TNF protons was carried out by using 2D NMR techniques, DQFCOSY, NOESY, HSQC, HMBC (see the Supporting Information).

[14] R. Schmidt, M. Stolte, M. Grüne, F. Würthner, *Macromolecules* **2011**, *44*, 3766 – 3776.

[15] M. E. Cates, *Macromolecules* **1987**, *20*, 2289 – 2296.