# Supramolecular Nanoribbons and Nanoropes Generated from Hydrogen-Bonded Supramolecular Polymers Containing Perylene Bisimide Chromophores

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ABSTRACT
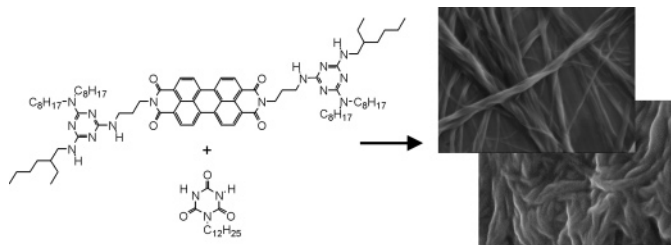
A perylene bisimide anchored with melamine hydrogen-bonding units has been prepared, and its supramolecular polymerization upon binding with *N*-dodecylcyanurate (CA) was examined. The resulting flexible supramolecular polymers self-organized via a π–π stacking interaction between perylene chromophores, affording ribbonlike aggregates in cyclic alkanes and ropelike aggregates in acyclic alkanes to form gels.

The fabrication of well-defined nanoobjects composed of extended π-electronic molecules has attracted much attention because of miniaturization in electronics and photonics.[1] Particularly, one-dimensionally elongated nanoobjects with enough persistent length are quite important to realize dimension-restricted transport of charges and excitation energies.[1,2] Self-organization of extended π-electronic molecules based on the programmed intermolecular noncovalent interactions is a powerful strategy in view of spontaneous and quantitative formation of well-defined nanoobjects.[2]

Perylene bisimide (PBI) is one of the most extensively studied π-electronic molecules because of its prominent optical and electronic properties.[1,3] However, discrete one-dimensional nanoobjects based on PBI are still rare despite the wide scope of their applicability in nanotechnologies.[4] Gelation-induced fabrication of one-dimensional aggregates

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of functional chromophores is a quite attractive way from academic and industrial standpoints.[2,5] Recently, Shinkai and Würthner et al. independently reported PBI-based organogelators using steroidal and urea moieties as gel-forming functionalities, respectively.[6] The former system proved to act as light-harvesting organogels. More recently, Würthner et al. reported PBI derivatives capable of forming helical nanofibers with excellent gelation ability as well as high charge-carrier mobility.[4c] These studies demonstrate that discrete one-dimensional elongated nanoobjects based on PBI are also promising candidates for optoelectronic applications in addition to hitherto reported bulk materials based on this chromophore.[7] Here we report the formation of discrete one-dimensionally elongated nanoobjects from a flexible hydrogen-bonded supramolecular polymer[8] containing PBI chromophores in the main chain (Scheme 1). The
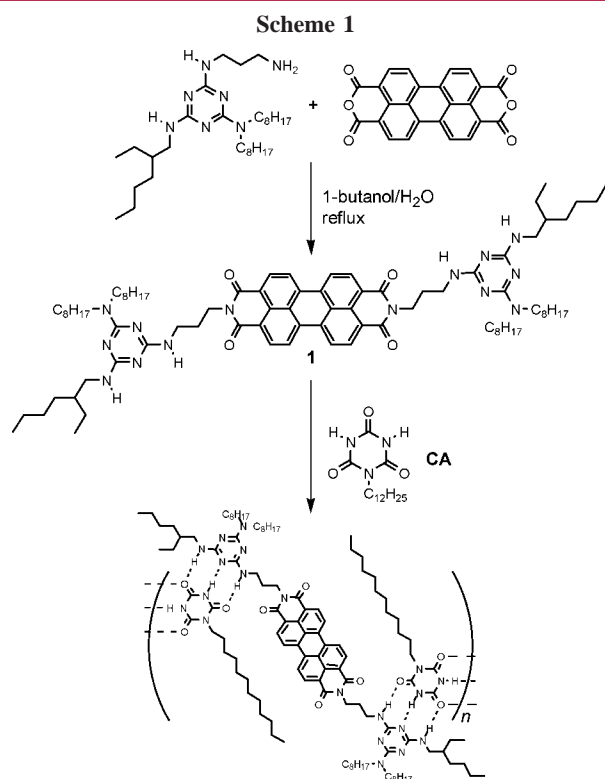
Scheme 1

supramolecular polymers are formed by the triple hydrogen-bonding interactions between melamine and cyanuric acid

functionalities,[9,10] which hierarchically self-organize into ribbonlike or ropelike nanoobjects in aliphatic media via $\pi-\pi$ stacking interactions.

The melamine-anchored PBI **1** was prepared according to Scheme 1. Compound **1** is highly soluble in aliphatic solvents such as hexane and readily purified by flash column chromatography. The purified compound was characterized by ^{1}H and ^{13}C NMR, FAB mass spectrometry, and elemental analysis. Non-bay-substituted PBIs display a strong tendency to form $\pi-\pi$ stacked aggregates in aliphatic media.[11] The solid lines in Figure 1 show the UV/vis spectra of **1** recorded
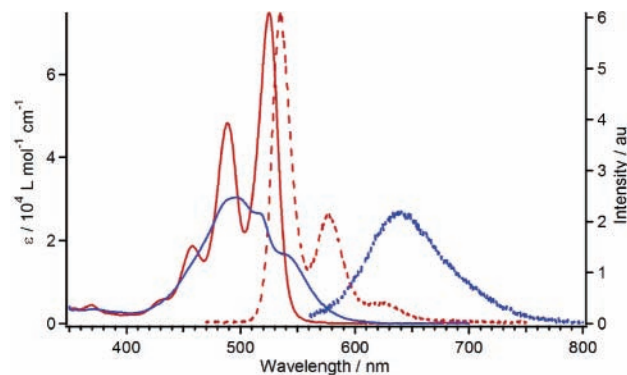

Figure 1. UV/vis (solid line, left axis) and fluorescence spectra (dashed line, right axis) of **1** (10 μM) in dichloromethane (red line) and in MCH (blue line). The excitation wavelengths in the fluorescence spectra are 460 nm in dichloromethane and 550 nm in MCH, respectively.

in dichloromethane and methylcyclohexane (MCH) at a concentration of 10 μM. Compared to the spectrum of the molecularly dissolved state in dichloromethane (red solid line, $\lambda_{max} = 459$, 489, and 526 nm), the spectra in MCH (blue solid line) show a significant loss of fine structure with a new maximum at 497 nm and a shoulder at around 540 nm, characteristic of excitonically coupled PBIs with a face-to-face stacking arrangement.[11,12] The fluorescence spectra

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of **1** in the same set of solvents are shown by dotted lines in Figure 1. Compared to the vibronically-structured spectrum of molecularly dissolved **1** in dichloromethane (red dashed line, λ_{em-max} = 535, 576, and 625 nm), self-aggregated **1** in MCH showed a largely red-shifted, broadened, and structureless fluorescence band at λ_{em-max} = 638 nm (blue dashed line), typical of excimer-like fluorescence from H-aggregates of PBIs.[11,12] The $\pi-\pi$ stacked aggregates of **1** persist over 90% even at a concentration of 1 μM.[13]

The 1:1 complexation of **1** with complementary hydrogen-bonding components such as *N*-dodecylcyanurate (CA) is expected to afford flexible hydrogen-bonded supramolecular polymers where the PBI chromophores are uniformly arranged within the main chain. Figure 2a and Figure S1
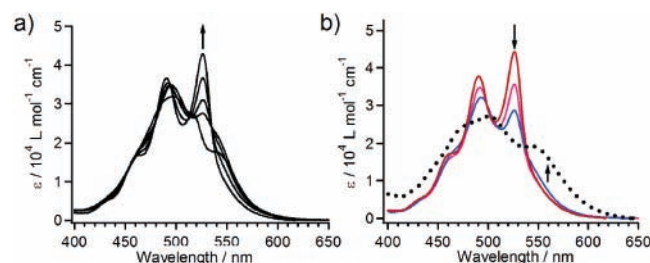

Figure 2. (a) UV/vis titration of **1** (10 μM) with CA (0, 2.5, 5.0, 7.5, and 10 μM) in MCH. The arrows indicate spectral changes upon addition of CA. (b) Concentration-dependent UV/vis spectra of $\mathbf{1}_n \cdot CA_n$ in MCH (10, 50, and 250 μM, from red to blue). The arrows indicate spectral changes upon increasing concentration. Dotted line: the absorption spectrum of the filamentous precipitates obtained from a 300 μM solution.

(Supporting Information) show UV/vis and fluorescence titration experiments of **1** (c = 10 μM) with CA, respectively.[13] Interestingly, the addition of CA induced the spectral transitions from $\pi-\pi$ stacked to free PBI chromophores. This result implies that $\pi-\pi$ stacked aggregates of **1** are disrupted by the addition of CA to form new hydrogen-bonded aggregates ($\mathbf{1}_n \cdot CA_n$) where the PBI chromophoric segments are free from $\pi-\pi$ stacking interactions at this diluted condition. When the molar amount of CA exceeds that of **1**, excess CA remained insoluble and the spectra did not change at all. This verifies the 1:1 stoichiometry between **1** and CA with quantitative binding at this concentration (c = 10 μM).

When the above stoichiometric mixture of **1** and CA in MCH was condensed, $\pi-\pi$ stacking of the PBI chromophores again started as judged from UV/vis spectroscopy (Figure 2b). At a concentration of 250 μM (blue line), approximately 70% of PBI chromophores stack,[13] above which precipitates start to form within minutes. The formation of the precipitates occurs almost quantitatively because the marginal absorption band of PBI was detected for the supernatant after several days. Optical microscopic observa-

tion showed that the precipitates are composed of agglomerated crystalline filaments with widths less than 1 μm and lengths ranging from 10 to 100 μm.[13] The filaments are birefringent when examined under crossed polarizer conditions, indicating a high degree of molecular anisotropy within the filaments.[13] Observation by field emission scanning electron microscopy (FE-SEM) revealed that the filaments are composed of intertwined thinner fibrils (Figure 3a and
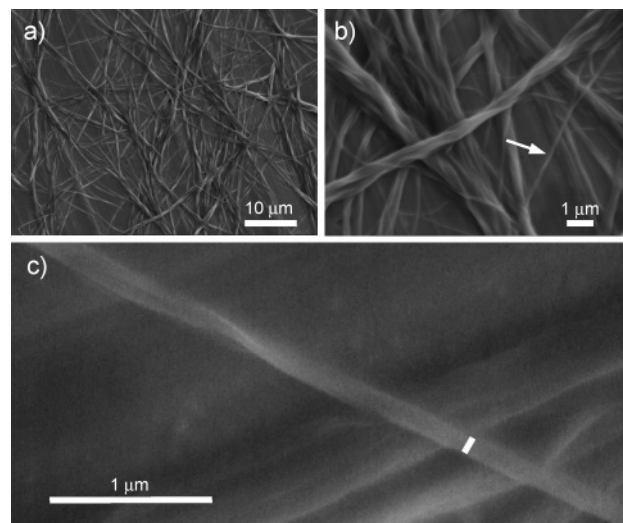

Figure 3. FE-SEM of the filamentous precipitates of $\mathbf{1}_n \cdot CA_n$ generated from the 300 μM solution of MCH. The length of the white bar across the ribbon in the image (c) is 100 nm.

b). From a magnified image, fibrils have ribbonlike morphology with widths of approximately 100 nm (Figure 3c). The almost identical nanoscopic filaments were obtained when cyclohexane was used as a medium.[13]

The absorption spectrum of the filamentous precipitates shows the absorption maximum at 502 nm with a pronounced shoulder at 544 nm (dotted line in Figure 2b), analogous to that of the self-aggregated **1** (Figure 1). The spectrum is also characterized by the complete loss of the monomeric absorption at 525 nm (see Figure 1), indicating the PBI chromophores in the hydrogen-bonded supramolecular polymers are fully aggregated in the filaments. For the present supramolecular polymers where the π-electron-rich segments are uniformly introduced in a flexible main chain, folding or self-assembling might be possible as intrachain or interchain organization, respectively.[14] The former organization can be characterized by concentration-independent secondary interactions (i.e., $\pi-\pi$ stacking interactions). However, the aforementioned UV/vis results shown in Figure 2 unambiguously demonstrate the disruption of the $\pi-\pi$ stacked aggregates of **1** upon addition of CA at lower concentrations

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(chain elongation by hydrogen bonding, first step in Figure 4) and subsequent reformation of the $\pi-\pi$ stacked state upon
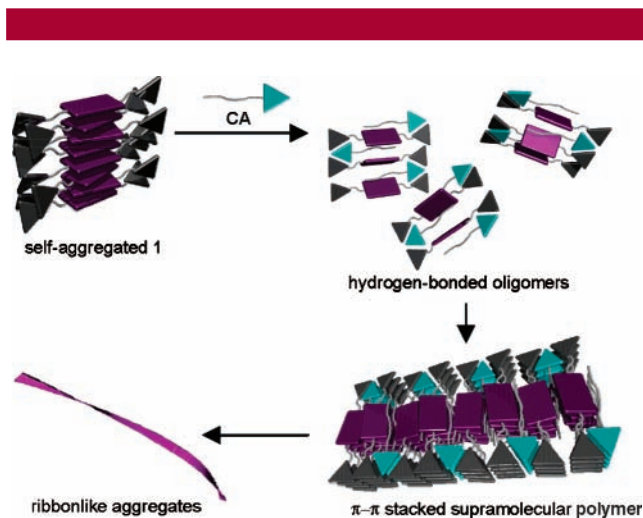

Figure 4. Schematic representation of the aggregation of **1** and CA in cyclic alkanes.

increasing concentration of the mixtures (interchain organization, second step in Figure 4). This argument leads us to conclude that the present hydrogen-bonded supramolecular polymers $\mathbf{1}_n \cdot CA_n$ experience interchain organization (self-assembling) to form ribbonlike nanoscopic aggregates.

Although the formation of the above crystalline filaments is not accompanied by gelation of the solvents employed (cyclic alkanes), self-organization of $\mathbf{1}_n \cdot CA_n$ in acyclic solvents from hexane and decane resulted in gelation at concentrations above 2 mM (0.45−0.51 wt %, inset in Figure 5a). FE-SEM observation of a dried decane gel visualized heavily entangled ropelike objects with diameters of approximately 100 nm in a dense region of the specimen (Figure 5a,b).[13] In the edge of the specimens where the ropes are loosened (Figure 5c,d), the thinnest ropes with widths of several tens of nanometers could be observed (the white arrows in Figure 5d). The lengths of thicker ropes reach several micrometers. It is noteworthy that the ropelike aggregates are rather soft and thereby well-entangled in comparison with the filaments obtained from cyclic alkanes. This is consistent with the gelation of the solvent. In the case of hexane, gel morphology is not ropelike but granular, the surface of which is characterized by the entangled fibrous fine structures with diameters of several tens of nanometers.[13]
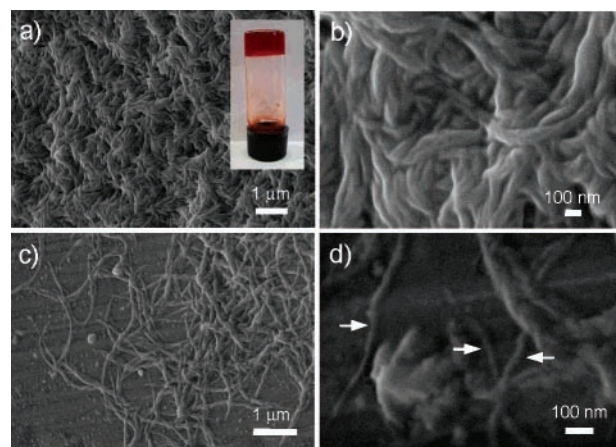

Figure 5. FE-SEM images of the dried decane gel of $\mathbf{1}_n \cdot CA_n$ in the heavily (a and b) and loosely (c and d) entangled region. Inset in (a) shows a photograph of the decane gel (2 mM). The white arrows in (d) indicate the thinnest ropes.

The UV/vis spectra of these gels are almost identical to those of the filaments generated from cyclic alkanes, indicating the same stacking arrangements of the PBI chromophores. Therefore, such solvent-dependent nanoscopic morphologies might be derived from the difference in the crystallinity of the self-organized supramolecular polymers in the solvents employed.

In conclusion, discrete nanoribbons and nanoropes, in which perylene bisimide chromophores are tightly $\pi-\pi$ stacked, could be realized by supramolecular polymerization and hierarchical organization. In the case of the former, the formation of the nanoobjects occurs quantitatively. These one-dimensional elongated nanoobjects consisting of electronically active chromophores would be applicable to nanoscale conducting wires. We are now investigating electronic properties of these nanoobjects as well as the effect of spacer moieties between perylene bisimide chromophores and melamine anchors on the morphology of self-organized nanoobjects.

Supporting Information Available: Synthetic and experimental details and additional spectroscopic and microscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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