Miniaturization of Nanofibers Composed of Melamine-appended Perylene Bisimides and Cyanurates

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Miniaturization of nanofibers formed from melamine-appended perylene bisimides and cyanurates are achieved by elongating the linker moieties between perylene bisimide core and melamine moieties. The resulting nanofibers gelate aliphatic solvents with low concentrations and the resulting gels are optically transparent, which are advantageous for photonic devices because no scattering of visible light takes place.

Self-assemblies of extended π-conjugated dyes are topics of current interest because of their potential application in organic optoelectronic devices.[1] By a proper molecular design, these dyes form well-organized nanostructures through a variety of noncovalent interactions, affording various functional soft materials. For instance, organogels based on π-conjugated dyes are one of the major material morphologies in supramolecular electronics.[2] Among various dyes, perylene bisimides (PBIs) have attracted much attention because of their pronounced light-absorptivity in visible region, high fluorescent quantum yield as well as n-type conductivity.[3] Several organogelators based on PBI dyes have been fabricated recently as a new material morphologies of this dye by introducing specific noncovalent interaction sites that can induce gelation of organic solvent, such as amide, urea, or cholesteryl groups.[4] We have also reported that PBI **1** possessing hydrogen-bonding melamine moieties can form organogels in acyclic alkanes upon mixing with a cyanurate (dCA).[5] The most important factor for the gel formation of this system is the supramolecular co-polymerization of **1** and dCA through complementary triple hydrogen-bonding interactions between melamine and cyanurate moieties.[6] The resulting gel was, however, optically not transparent due to the formation of thick supramolecular fibers with average width of 1 μm. This may become a major drawback when we use pristine gels as photonic devices because scattering of visible light occur for such micrometer-width fibers.

To improve our supramolecular organogels in this aspect, herein we employed three different strategies based on the structural alternation of building blocks: i) the introduction of solubilizing substituents to melamine moieties, ii) the introduction of a gel-forming group to the cyanurate components, and iii) the increase in the flexibility of building blocks. We synthesized melamine-appended PBIs **2**–**4** according to the same methods reported previously (Figure 1).[5] PBI **2** structurally differs from PBI **1** only in alkyl substituents of the melamine moieties, i.e., 2-ethylhexyl and *n*-dodecyl chain, respectively. The combination of PBI **2** and dCA can be compared to other combinations based on strategies i)–iii). PBI **3** has tri(dodecyloxy)phenyl (TDP) groups, which is mixed with dCA based on strategy i). PBI **4** has longer alkyl linker moieties between PBI core and hydrogen-bonding sites, which is mixed with dCA based on strategy iii). In contrast to these strategies, strategy ii) is based on the structural alteration on the cyanurate component and cCA possessing gel-forming cholesteryl group was used as a partner of PBI **2**.

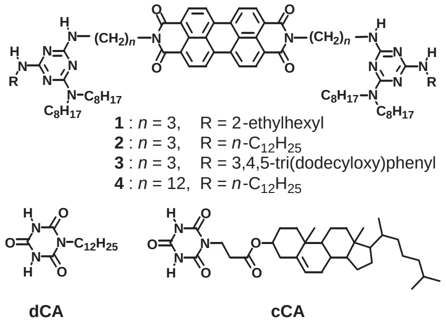

Figure 1. Chemical structures of PBI dyes **1**–**4** and cyanurate derivatives.

Gelation properties of these combinations were investigated in aliphatic solvents. The 1:1 mixture of **2** and dCA affords organogel by being heated together in cyclohexane until all the materials were dissolved and cooled to ambient temperature. The critical gel concentration (*cgc*) was determined as 4.5 mM (= [**2**] = [dCA]) by the "stable-to-inversion of a vial" test. This *cgc* value is relatively lower than those of other organogelators reported previously.[2] In addition, the resulting gel is not transparent and turbid (left in Figure 2a), indicating phase separation between supramolecular assemblies and solvent molecules occur in the micrometer scale because of the efficient crystalline packing of the supramolecular polymers of **2**·dCA.

We next investigated PBI **3** whose TDP wedges are expect to make the resulting supramolecular polymer **3**·dCA more soluble (strategy i). Although TDP group generally facilitates gelation of low molecular-weight organogelators, no gelation was observed for **3**·dCA in cyclohexane, affording precipitates.[5b] This indicates that additional π–π stacking and van der Waals interactions in TDP groups promotes agglomeration of supramolecular polymers. Therefore, we next examined strategy ii), i.e., the use of cCA possessing a gel-forming cholesteryl group.[4a] When cCA was used as a partner of PBI **2**, cyclohexane was gelated as a transparent gel. It is suggested that the bulky cholesteryl group of cCA prevents the close packing of supramolecular polymers into thicker fibers. The *cgc* of **2**·cCA in cyclohexane is, however, above 10.0 mM, which is considerably higher than that of gel **2**·dCA. Such a high *cgc* is disadvantageous when gel is used as light-harvesting materials because of high concentration of chromophoric components.

In contrast, dramatically different results were obtained

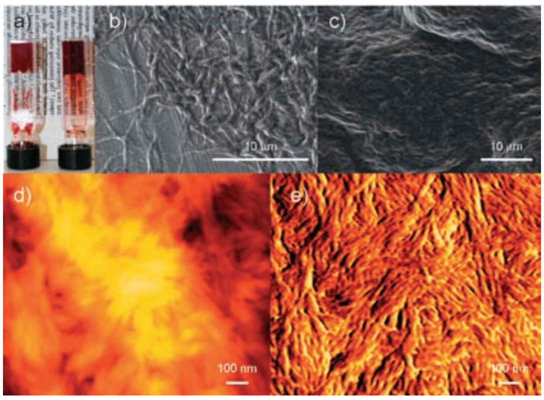

Figure 2. a) Photographs of organogels of **2**•dCA (right) and **4**•dCA (left). SEM images of cyclohexane xerogels of b) **2**•dCA and c) **4**•dCA. d) AFM height (z scale = 75.6 nm) and e) phase images of the **4**•dCA xerogel.

for **4**•dCA. Remarkably, the mixture of **4** and dCA gelated methylcyclohexane, cyclohexane, hexane, and decane at a concentration of 5.0 mM,[7] while the combination of **2** and dCA gelates only cyclic alkanes. The *cgc* of **4**•dCA gel in cyclohexane was less than 1.0 mM,[8] which is much better value than that of **2**•dCA (4.5 mM). More importantly, cyclohexane organogels of **4**•dCA are optically transparent compared to those of **2**•dCA (right in Figure 2a). Such optically transparent gels are promising as photonic device because no scattering of visible light would occur.

Scanning electron microscopy (SEM) images of cyclohexane xerogel of **2**•dCA shows fibrous aggregates whose widths are approaching 1 µm (Figure 2b). In sharp contrast, no fine structure was imaged for **4**•dCA by SEM despite the fact that a good gelation property was observed for this combination (Figure 2c). This implies that **4**•dCA forms fibrous assemblies in more nanoscopic scale that cannot be visualized by our SEM instrument. Thus, atomic force microscopy (AFM) visualized heavily entangled fibrous structures with the width of several tens of nanometer (Figures 2d and 2e). These results clearly demonstrate that the supramolecular polymers of **4**•dCA do not organize into micrometer-widths fibers, probably due to an increase in the structural flexibility of hydrogen-bonded supramolecular polymers which prevents their efficient packing.

To obtain insight into the chromophore packing in **4**•dCA, spectroscopic studies were performed for cyclohexane organogel at a concentration of 5.0 mM. Compared to the absorption spectrum of **4**•dCA in diluted dichloromethane solution with well-resolved vibronic bands characteristic of monomeric PBI dyes ($\lambda_{\max} = 525$ nm, Figure 3), those of the gels exhibited blue-shifted ($\lambda_{\max} = 465$ nm) and broadened absorption bands. The fluorescence spectrum of the gel showed a significant red-shift ($\lambda_{\text{em-max}} = 672$ nm) and a loss of fine structures compared to that of the molecularly dissolved state. These spectral changes are an evidence that PBI moieties in nanofibers of **4**•dCA form H-aggregates.[9,10]

In conclusion, we successfully improved the optical transparency and *cgc* of our PBI-based organogels by the structural alternation in the alkyl linker moieties between the PBI core and the hydrogen-bonding sites, inducing a miniaturization of the resulting nanofibers. Transparent gels can be applied to photonic devices without unfavorable scattering of visible light. Furthermore, miniaturization of fibrous assemblies containing aggregated functional dyes will expand the scope of supramolecular dye assemblies as photonic and electronic nanodevices.

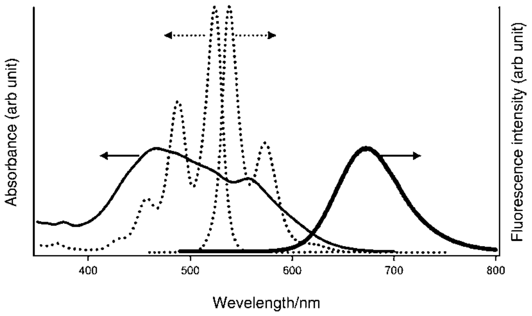

Figure 3. Absorption (left) and fluorescence (right) spectra ($\lambda_{\text{ex}} = 446$ nm) of the **4**•dCA cyclohexane gel ($c = 5.0 \times 10^{-3}$ M, solid lines) and of diluted dichloromethane solution ($c = 1.4 \times 10^{-5}$ M, dotted lines).

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7 The binding stoichiometry between **4** and dCA was determined to be 1:1 by gelation experiments using various amount of dCA. For details, see the Supporting Information which is available electronically on the CSJ-Journal Web site; http://www.csj.jp/journals/chem-lett/.

8 Unexpectedly, the combination **4**•cCA did not show gelation ability higher than **4**•dCA. For details, see the Supporting Information.

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