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Self-Sorting Organogels with p−n Heterojunction Points

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For the development of organic optoelectronics such as flexible light-emitting diodes, field effect transistors, photovoltaic cells, and so forth, continuous efforts have been devoted.[1] Considering the advantages of the organic substances over inorganic counterparts, (i) preparation by a low-cost solution process, (ii) well-defined stacks of π-conjugated molecules, and (iii) integration of various molecular functions are of fundamental importance for the practical production. Among them, (iii) will lead to more advanced optoelectronic systems; however, the examples are still very limited.

The supramolecular approach is the most promising methodology to meet these demands.[2] Programmed molecules recognize the direction and the number of noncovalent interactions to form precise supramolecular architecture such that intriguing properties appear. Particularly interesting is the example of orthogonal molecular assembly (i.e., "self-sorting") where *different* molecules distinguish between self and nonself.[3] This system will enable us to integrate the supramolecular functions as they are designed, thus leading to accomplish the requirement of (iii).[4–7]

Recently, solution-processible supramolecular materials of organogel systems have attracted much attention.[8–12] Organogels are composed of precisely designed supramolecular assemblies as characterized by X-ray crystallography and unique electronic spectra.[9] In an organogel medium, one-dimensional (1-D) supramoleculer fibers are bundled up together and entangled at nodes, the so-called "junction point", to form three-dimensional (3-D) network structures, by which the solvent molecules are entrapped. The nanostructured functional molecular assembly thus created is a promising candidate for organic devices with intriguing photo- and electrochemical functions. For example, we have previously reported semiconducting molecule-based organogelators, **Thio** and **Pery**, which act as opposite charge carriers of p-type and n-type, respectively.[10–12] They form 1-D fiber structures and gelatinize various organic solvents. Because of the structural similarity of **Thio** and **Pery**, they can form organogel with mutual organic solvent: chlorobenzene. In the meantime, their molecular lengths are slightly different and they have different numbers of noncovalent interaction sites: four hydrogen bonding sites in **Thio** and, on the other hand, two in **Pery**. Here it occurred to us that if these gelators self-sort and assemble to form the p-type and the n-type fibers individually, the mixed organogel system will offer us functional nanocables entangled at p−n heterojunction points (Scheme 1). In this Communication, we described the self-sorting process of **Thio** and **Pery** and preliminarily employed the resultant organogel to design a photoelectronic conversion system. A closely related example of self-sorting behavior of p-type and n-type supramolecular fiber structures has recently been reported by Schenning and Meijer et al. where oligo(*p*-phenylene vinylene) and perylene derivatives were used as p-type and n-type materials, respectively.[6b]

Absorption spectra of **Thio** and **Pery** in the gel phase are blue-shifted in comparison with those of their monomeric state (measured in diluted tetrachloroethane solution: [galator] = 2.0×10^{-6} M), indicating that chromophore moieties are π-overlapped in an H-aggregate manner. We could thus

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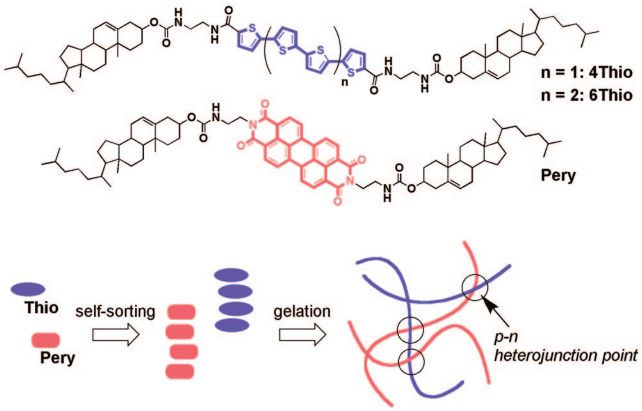
Scheme 1. Chemical Structures of Thio and Pery and Schematic Representation of Their Self-Sorting Organogel Formation Yielding p−n Heterojunction Points



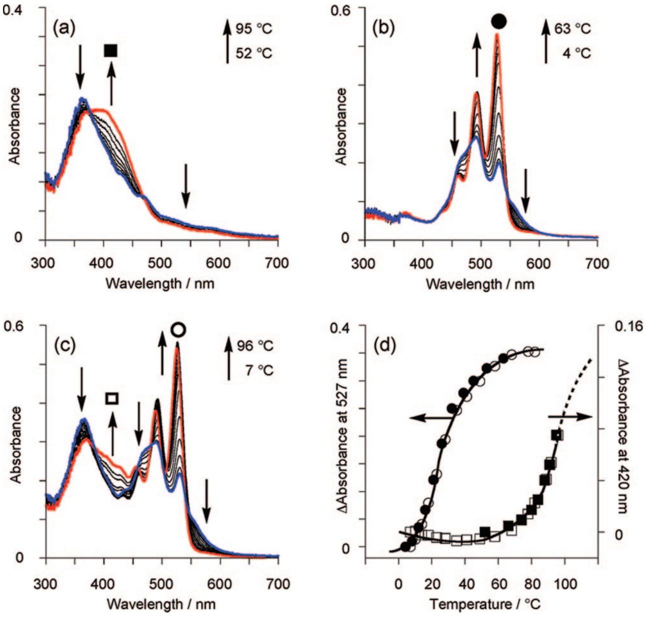


Figure 1. Variable temperature UV−vis spectral changes of (a) **4Thio** gel, (b) **Pery** gel, and (c) **4Thio/Pery** self-sorting gel and (d) plots of absorption intensities versus temperature: [gelator] = 0.5 mM, optical path length = 0.2 mm, chlorobenzene; marks in (d) correspond to those in (a−c).

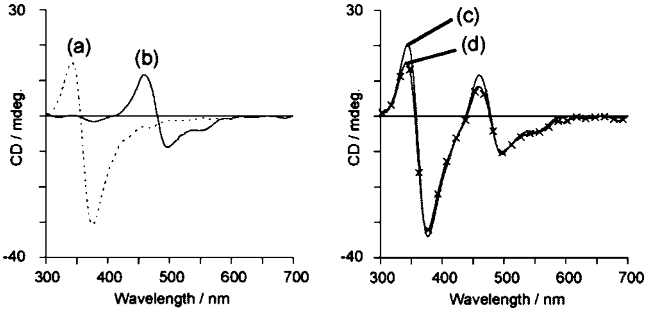


Figure 2. CD spectra of (a) **4Thio** gel, (b) **Pery** gel, (c) **4Thio/Pery** self-sorting gel, and (d) the sum of CD spectra (a) and (b).

determine the self-aggregation constants (K_{agg}) of these gelators to be $>10^5$ M^{-1} for **4Thio** and 1.3×10^3 M^{-1} for **Pery** by concentration dependent absorption spectral changes (Figure S1, Supporting Information).[13] The self-sorting gelation process was monitored by variable temperature UV−vis spectra. Upon elevating the temperature, the absorption spectra of **4Thio** (Figure 1a) and **Pery** (Figure 1b) in the gel phase showed red-shift, indicating their thermal dissociation. Dissociation temperature of **Pery** was about 25 °C and that of **4Thio** was too high to be determined in the measurement conditions (assumed to be about 95 °C). This difference in the dissociation temperatures is consistent with the difference in their self-aggregation constants, which is presumably related to the number of hydrogen bonding sites (four in **4Thio** and two in **Pery**). When these two gelators and chlorobenzene were put in a septum capped test tube and the mixture was heated to dissolve the gelators, transparent and stable organogel was obtained upon cooling. Absorption spectrum of the mixed gel (i.e., self-sorting gel) overlapped with the sum of two spectra of **4Thio** gel and **Pery** gel and did not show any new peaks assignable to the charge transfer complex, indicating that there is no interaction between oligothiophene and perylene molecules. Interestingly, these peaks attributed to **4Thio** and **Pery** independently changed upon heating; that is, absorption bands of **Pery** gradually sharpened first, then that of **4Thio** showed red-shift (Figure 1c and Figure S2, Supporting Information). Plots of the absorption intensities versus temperature are shown in Figure 1d. Very interestingly, dissociation temperatures of these gelators in the self-sorting gel system coincide with those of individual ones. This accordance was also observed in a cooling process. These results indicate that **4Thio** and **Pery** self-assemble independently (self-sorting) and do not interfere in each other's aggregation−dissociation process. We expect that kinetic and inequilibrium nature of the organogel formation are important for self-sorting and segregation of these two gelators.[14] In fact, during the preparation of individual organogels, we noticed that gel formation of **4Thio** is much faster than that of **Pery**: gelation took ~1 min for **4Thio** and more than 10 min for **Pery**; [gelator] = 0.5 mM. The similar phenomena were also observed for the **6Thio/Pery** system, where **6Thio** never dissociated in the measurement condition (measured up to 100 °C) due to its strong aggregation property.[11,15]

Since these gelators have chiral cholesterol moieties, aggregates of these molecules are CD active. Both of the CD spectra of **4Thio** and **Pery** showed negative exciton coupling, due to the structural similarity (Figure 2). These CD signs imply that the dipole moments in the chromophore moieties of these gelator molecules are oriented into an anticlockwise direction (*S* chirality).[10,11] Very interestingly, the CD spectrum of the self-sorting gel was perfectly overlapped with the sum of each CD spectrum of **4Thio** and **Pery**, further demonstrating the self-sorting organogel formation (Figure 2).

In order to obtain the visual insights into the superstructures in the gel phase, we took SEM images of these gel

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(14) Kinetically controlled self-sorting processes of supramolecular assembly are quite rare Prins, L. J.; de Jong, F.; Timmerman, P.; Reinhoudt, D. N. *Nature* **2000**, *408*, 181–184, and see also ref 3b.

(15) The K_{agg} values of **4Thio** and **6Thio** in tetrachloroethane are 0.5×10^3 M^{-1} and 2.7×10^5 M^{-1}, respectively,[11] indicating that **6Thio** aggregates two to three orders of magnitude stronger than **4Thio**.

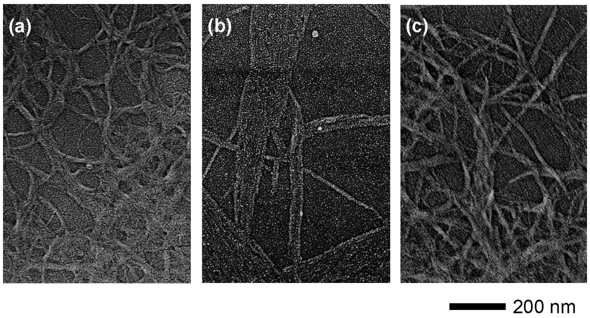

Figure 3. SEM images of (a) **4Thio** gel, (b) **Pery** gel, and (c) **4Thio/Pery** self-sorting gel.

systems (Figure 3). Parts a and b of Figure 3 show fibrous aggregates of **4Thio** and **Pery**, respectively, the diameters of which were ~20 nm. We also observed the similar structures in the self-sorting gel system, indicating that mixing these two kinds of gelators does not affect the aggregation structures. Considering the molecular long axis of these gelators, the fiber structures consist of the bundle of a dozen of unimolecular stacks. These results imply that the interface area between thiophene stack (p-type conductor) and perylene stack (n-type conductor) should be very large.

The advantages of the self-sorting organogel system should be applied to an efficient photovoltaic system in which an orderly π stacking of the photoactive molecule and a large donor−acceptor interface area are required. So-called "bulk heterojunction" facilitates efficient dissociation of photogenerated excitons and produces continuous carrier pathways.[5,6,16] Here we employed **6Thio/Pery** self-sorting system because of its better donor/acceptor couple compared with the **4Thio/Pery** one.[17] First, we prepared a cast film of organogel on an ITO electrode and measured fluorescence spectra with an excitation wavelength of 390 nm, where **6Thio** mainly absorbs the excitation light. Compared with a simple **6Thio** cast film, fluorescence of a cast film prepared from the **6Thio/Pery** self-sorting system showed the same λ_{max} (600 nm) but was quenched ~63%, indicating the electron and/or energy transfer between **6Thio** and **Pery** (Figure S3, Supporting Information). This notion was also supported by excitation spectra of these films in which both excitation for **6Thio** (λ_{ex} = around 350−450 nm) and **Pery** (λ_{ex} = around 450−550 nm) yielded less emission at 600 nm compared to simple **6Thio** or **Pery** cast film. Next, photocurrent measurements were carried out for the cast film of self-sorting gel on ITO electrode (working electrode) in 100 mM Na_2SO_4 solution containing 50 mM ascorbic acid as an electron sacrifice (water/methanol = 9/1), using a Pt counter electrode and a Ag/AgCl reference electrode. Upon photoirradiation, anodic photocurrent was generated (Figure 4a). This photoresponsive phenomenon could be repeated many times reversibly, and the film was sufficiently robust.

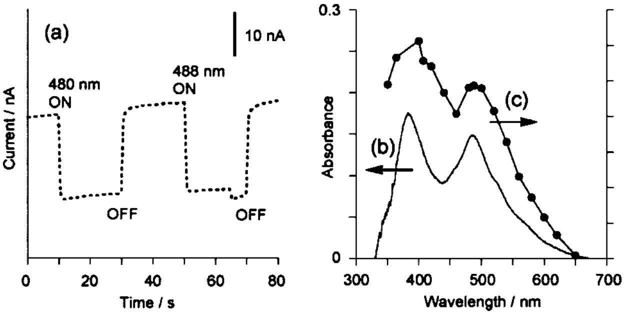

Figure 4. (a) Photoelectrochemical response, (b) absorption spectrum, and (c) photocurrent action spectrum of the cast film prepared from **6Thio/Pery** self-sorting gel on an ITO electrode: applied potential = 0.2 V vs Ag/AgCl.

Figure 4b shows that the photocurrent action spectrum of the film prepared from self-sorting organogel extends to visible light region and perfectly overlaps with its absorption spectrum, indicating that both **6Thio** and **Pery** act as photoactive species for the photocurrent generation.[18]

In conclusion, we have demonstrated the self-sorting organogel formation by π-conjugated molecules. This system is composed of precise π-stacking structures entangled at p−n heterojunction points.[19] Solution-processible material facilitates the preparation of the cast film that shows photoelectrical conversion by visible light irradiation. Future investigations will be directed to kinetic study of organogel formation and detailed photocurrent generation mechanism. We believe that this simple and convenient technique will offer more complicated and advanced design of organic devices.

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Supporting Information Available: Concentration and temperature dependent UV−vis absorption spectral changes of the gel systems and fluorescence spectra of the cast film prepared from **6Thio** gel and **6Thio/Pery** self-sorting gel (PDF). This material is available via the Internet at http://pubs.acs.org.

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(18) Preliminary experiments showed that sequentially prepared cast film (i.e., two-layer films of **6Thio** and **Pery**) generates smaller photocurrent than the cast film prepared from **6Thio/Pery** self-sorting gel. However, the internal quantum yields of these films were quite low (less than 0.1% at 488 nm). One of the reasons for this might be the insulating and bulky cholesteric moieties peripheral to the photoactive core. We are now investigating more proper substituents to improve the performance.

(19) There should be bundles composed of mixture of p-type stacks and n-type stacks since both **Pery** and **Thio** have the same cholesteryl side chains. However, during the sample preparation, we noticed that **Thio** aggregates first when **Pery** is still moleculary dissolved. From this kinetic behavior, it is reasonable to assume that the fiber structures in the self-sorting system are (i) segregated into p-type and n-tpye fibers (as illustrated in Scheme 1) and/or (ii) p-type fibers (as core) surrounded by n-type fibers. Since the diameter of the fiber structures observed in the self-sorting system (Figure 3c) was relatively similar to those of individual fibers of **4Thio** (Figure 3a) and **Pery** (Figure 3b), hypothesis (i) would be more acceptable.