Photochemical Processes

Visible-Light-Harvesting Organogel Composed of Cholesterol-Based Perylene Derivatives**

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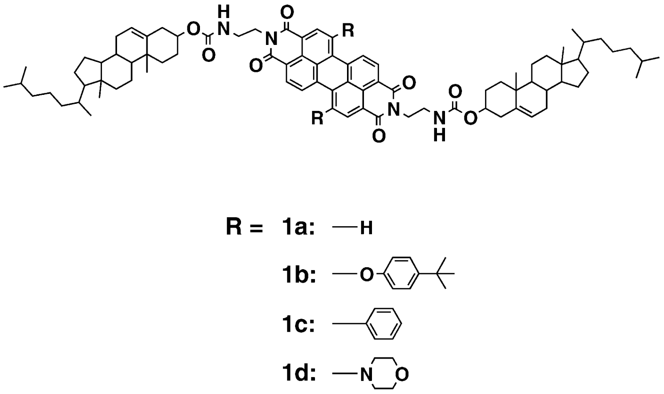
In nature, photosynthesis commences with the absorption of sunlight, and continuous unidirectional energy or electron transfer between chromophores plays a key role in efficient light harvesting.[1] The chromophores (i.e., chlorophyll molecules) are arranged by noncovalent interactions at suitable distances and in an appropriate orientations within the peptide matrix. To mimic a natural photosynthetic system with artificial molecular systems, numerous attempts have been made to arrange chromophores in a one-dimensional (1D) manner utilizing the methodologies developed in self-assembly and supramolecular chemistry. The supramolecular architectures used so far to design light harvesting systems are molecular arrays,[2] supramolecular complexes,[3] dendrimers,[4] monolayer systems,[5] etc. In particular, photochemical studies conscious of the reaction medium (matrix) are very important not only to create efficient energy and electron transfer systems but also to consider what kind of reaction is taking place in green plants.

Recently, novel supramolecular architectures constructed in organogels have attracted the widespread attention of supramolecular chemists. The origin of organogel formation is considered to be through 1D alignment of gelator molecules supported by dipole–dipole, van der Waals, and hydrogen-bonding interactions.[6,7] Such 1D alignment of functional molecules constructed through the gelation process can provide a novel chromophore assembly. Thus, gelators based on porphyrins,[8] phthalocyanines,[9] and conjugate oligomers[10] have been developed. In addition, the gel phase, which is different from either the solid phase or the liquid phase, is so unique as a medium that it is expected to provide a novel environment to arrange functional molecules indispensable to a natural photosynthetic system. Herein, we report on the design of a novel "visible"-light-harvesting system utilizing the 1D alignment nature of perylene-containing cholesterol-based gelators. Perylene and its derivatives are known to be the photofunctional dyes with unique optical and electrochemical properties. They have excellent light fastness, high chemical stability, high photoluminescence yield, and a wide range of colors that are tunable by various substituents at the bay position.[11] The gel-forming ability of cholesterol derivatives is useful to arrange them into a 1D alignment.[12] As a result, it is expected that perylene-containing organogels[13] will provide well-defined nanomaterials that feature a "visible"-light-harvesting function.[14]

The gelation ability of **1a**–**d** (Scheme 1) was evaluated in various solvents. In most of these solvents gels were not formed, however, aromatic solvents (such as benzene, toluene, and *p*-xylene) are partially gelated by **1a,** whereas it is virtually insoluble in most alcoholic solvents (such as methanol, ethanol, 1-propanol, and 1-butanol). Thus, we modified the solubility of **1a** in *p*-xylene by adding alcoholic solvents; as expected, most mixed solvents were finely gelated by **1a** (Figure 1a). We could also use toluene, *o*-xylene, and



Scheme 1. Structure of cholesterol-based perylene derivatives.

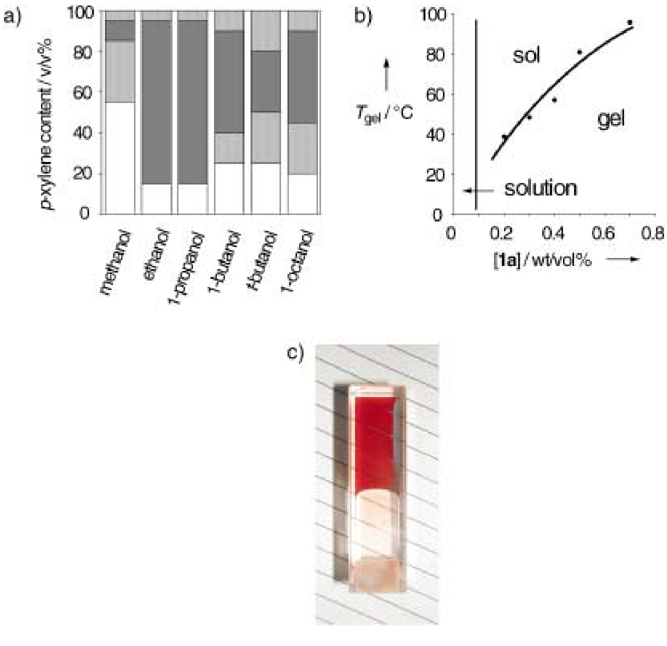


Figure 1. a) Gelation test for **1a** in *p*-xylene and alcoholic solvent mixtures: dark gray = gel, light gray = precipitate, white = insoluble material; b) plot of T_{gel} versus **1a** concentration in *p*-xylene/1-propanol (3:1 v/v); c) photo of **1a** gel prepared from *p*-xylene/1-propanol (3:1 v/v), [**1a**] = 0.5 wt/vol% (3.8 mM).

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nitrobenzene for gelation instead of *p*-xylene. The **1a** gel was formed very stably above 0.5 wt/vol% (3.8 mM) and showed a high sol–gel phase-transition temperature (T_{gel}; Figure 1 b) as well as high transparency even in the high gelator concentration region (Figure 1 c), which is a condition that is indispensable for applying this system to photochemical purposes. In contrast, **1b–d** could not gelate these mixed solvents. However, mixtures containing more than 50 mol% of **1a** formed stable, transparent organogels from the mixed solvents. Hereafter, we used a mixed solvent of *p*-xylene and 1-propanol (3:1 v/v) as a standard medium.

First, to obtain visual images of the **1a** gel we took pictures with confocal laser scanning microscope (CLSM), SEM, and AFM (Figure 2). Although the scale of the pictures is increased 10 times from Figure 2c (AFM) to Figure 2b (SEM) and from Figure 2b to Figure 2a (CLSM), one can consistently observe a network structure composed of fibrous aggregates. This means that the gel fibers present consist of hierarchical structures. The smallest fiber diameter observed with AFM is ≈3 nm, which is almost comparable with the length of the molecular long axis of **1a**.[15] On the other hand, an SEM picture of the precipitate formed from *p*-xylene showed a cubic structure (Figure 2d). The difference indicates that added 1-propanol plays a role in changing the aggregation mode of **1a** from the 3D aggregate to the 1D aggregate.

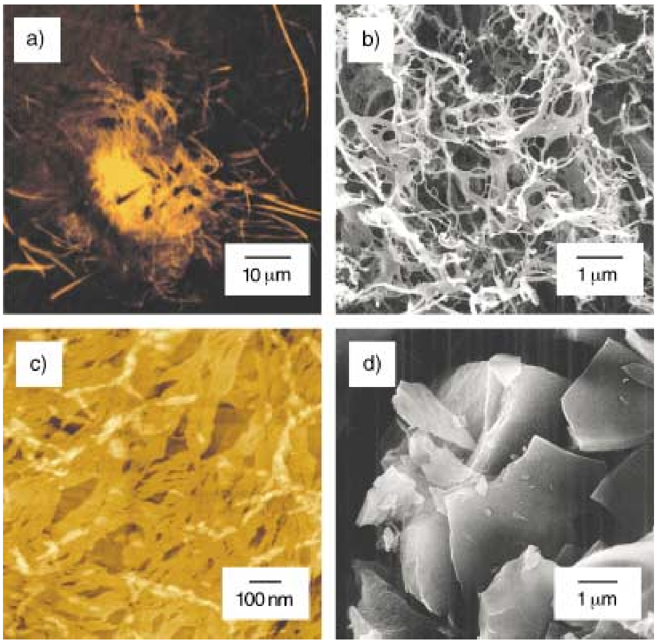

Figure 2. a–c) CLSM (λ_{ex} = 488 nm, prepared from *p*-xylene/1-propanol (3:1 v/v)), SEM (*p*-xylene/*tert*-butanol (4:1 v/v)), and AFM images (*p*-xylene/1-propanol (3:1 v/v)) of a **1a** gel; d) SEM image of **1a** crystals precipitated from *p*-xylene.

Second, we measured the absorption and fluorescence spectra of **1a–d** (2.0×10^{-5} M) in homogeneous solutions to obtain an insight into their photochemical properties. As shown in Figure 3, **1a**, **b**, **c**, and **d** have their absorption maxima at 527 (and weaker maxima 490 and 457), 550 (and 513), 557, and 660 nm, respectively, and their emission maxima at 540 (and 575), 580, 602, and 718 nm, respectively. We estimated the fluorescence quantum yields of **1a–d** in the solution phase using a reported compound *N,N'*-di(1-hexylheptyl)-3,4,9,10-perylenetetracarboxylic diimide as a standard: the fluorescence quantum yield is 0.93.[16] We could thus determine the quantum yields of **1a**, **b**, **c**, and **d** to be 0.93, 0.49, 0.28, and ≈0.001, respectively. Comparison of Figure 4a with Figure 3a reveals that the relative absorbance of the 0→0 transition (527 nm) against the 0→1 transition (490 nm) is decreased in the gel phase. This change indicates that the gel formation intensifies the π–π stacking interaction among perylene moieties.[17] It was found that the fluorescence intensity of **1a** in the gel phase is decreased by about two orders of magnitude from that in the solution phase, but the relative intensity of a fluorescence peak at 630 nm is rather intensified. Interestingly, only the gel phase (but not the sol phase) showed CD activity, which features a negative exciton coupling consisting of a negative first Cotton effect and a

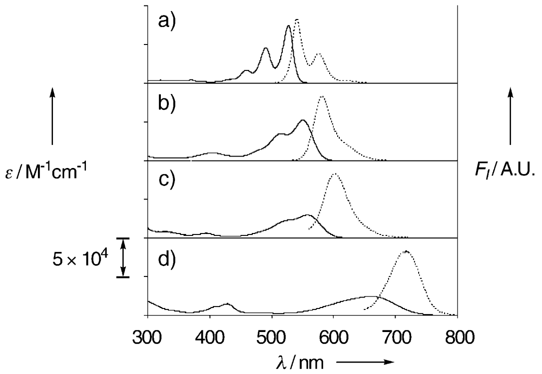

Figure 3. Absorption (——) and fluorescence (•••••) spectra of a) **1a**, b) **1b**, c) **1c**, and d) **1d** in diluted homogeneous solutions; [**1a–d**] = 2.0×10^{-5} M in $CHCl_3$. λ_{ex} = 477 for **1a**, 494 for **1b**, 507 for **1c**, and 622 nm for **1d**, respectively.

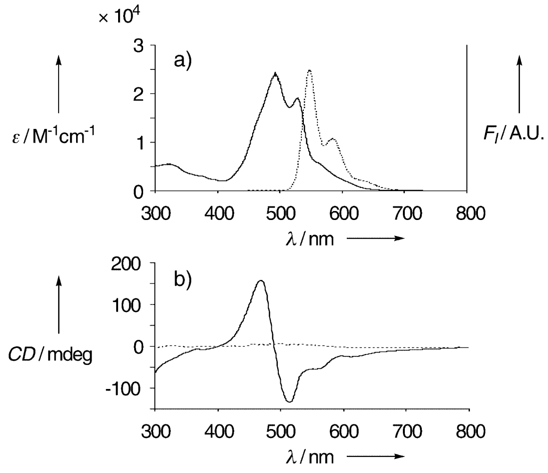

Figure 4. a) Absorption (——) and fluorescence (•••••) spectra of a **1a** gel; b) CD spectra of a **1a** gel (——) and a **1a** sol (•••••, 70 °C): *p*-xylene/1-propanol (3:1 v/v), [**1a**] = 0.2 wt/vol% (1.5 mM), λ_{ex} used for fluorescence measurements was 457 nm.

positive second Cotton effect (Figure 4b). The contribution of linear dichroism (LD) observed under the same measurement conditions was negligibly small. This CD sign implies that the dipole moments in the perylene moiety of **1a** are oriented into an anticlockwise direction (that is, *S* chirality). The π–π stacking interaction among the perylene moieties is so strong that one can imagine an aggregation mode in which a 1D-aligned perylene column is twisted by the chirality of the tethered cholesterol groups. Addition of **1b** to the **1a** gel weakened the CD intensity (Figure 1 in Supporting Information). This is probably because the perylene moiety of **1b** is intercalated into the **1a** gel fibrils and the helical sense of **1a** is reduced by the bulky *p*-*tert*-butylphenoxy substituents of **1b**.[18]

Third, we evaluated whether efficient energy transfer can take place from **1a** to others or in a stepwise manner from **1a** to **1d** using **1b** and **1c** as stepping stones (Figure 5). In diluted homogeneous solutions ($[\mathbf{1a}] = 2.0 \times 10^{-5}$ M), perceptible energy transfer from **1a** to other forms was not detected, although the mixtures (**1a**/**1b**/**1c**/**1d** = 10:3:0:0, 10:0:3:0, 10:3:3:0, and 10:3:3:3 molar ratios) were excited at various wavelengths: that is, the presence of **1b**, **1c**, and/or **1d** scarcely affects the fluorescence intensity of **1a** (Figure 2 in the Supporting Information). In contrast, when the **1a**/**1b**/**1c**/**1d** (10:3:3:3 molar ratio) mixed gel was excited at 457 nm where **1a** mainly absorbs light (Figure 3 in the Supporting Information), it was confirmed that efficient energy transfer from **1a** takes place. Figure 5 illustrates the fluorescence spectra of **1a**/**1b**, **1a**/**1c**, and **1a**/**1d** (all 10:3 molar ratio) binary systems, which clearly show that energy is transferred from excited **1a** to **1b**, **1c**, and **1d**, respectively. Energy-transfer efficiency was estimated by the quenching efficiency for **1a** at the emission maximum of 544 nm, which appeared in the order of **1b** (68 %), **1c** (53 %), and **1d** (34 %). This order is consistent with the order of the overlap between the fluorescence of **1a** and the absorbance of **1b**, **1c**, and **1d**, respectively. We have found that $FI_{\mathrm{acceptor}}/FI_{\mathrm{donor}}$ values in the gel phase are increased 10-fold for the **1a**/**1b** system and 19-fold for **1a**/**1c** system when compared to the solution phase.[19]

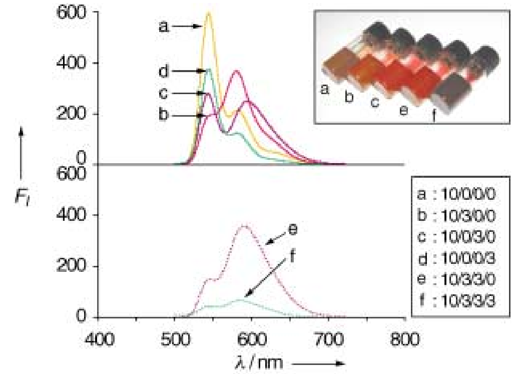

Figure 5. Fluorescence spectra of **1a**/**1b**/**1c**/**1d** mixed gels: [**1a**] = 0.5 wt/vol% (3.8 mM), [**1b**–**d**] = 0 or 1.3 mM, *p*-xylene/1-propanol (3:1 v/v), $\lambda_{\mathrm{ex}} = 457$ nm. the numbers in inset denote the molar ratios for **1a**/**1b**/**1c**/**1d**. Inset: a photograph displaying the **1a**/**1b**/**1c**/**1d** mixed gels.

It should be noted that fluorescence of **1b** and **1c** becomes stronger in the mixed-gel systems in spite of their low fluorescence quantum yields relative to **1a**. As shown by spectrum e in Figure 5, the emission band of a **1a**/**1b**/**1c** (10:3:3 molar ratio) ternary system is decreased in the shorter wavelength region whereas it is increased in the longer wavelength region. This change supports the view that energy transfer from **1b** to **1c** is also taking place. Overall, the emission spectrum of the **1a**/**1b**/**1c** ternary system is similar to that of **1c**. This means that even though the ternary system has a broad absorption wavelength region that is photo-irradiated by visible light, the excited energy is collected by **1c** and thus it is mainly the emission from **1c** is observable. In a quaternary system including **1d**, 1D alignment of four different perylene groups constitutes an energy gradient, and consequently, the excited energy of **1a** was given to **1b** and **1c**, and finally collected by **1d**. Because of the low emissive nature of **1d** arising from the twisted intramolecular charge-transfer (TICT) band,[20] it acts rather as an energy sink (note the weak fluorescence intensity of spectrum f in Figure 5). These trends are visually shown in the inset in Figure 5.[21]

In conclusion, we have demonstrated that a new visible-light-harvesting system can be designed utilizing a superstructure created in an organogel medium. As is common to organogel systems, gelator molecules tend to assemble into 1D aggregates and thus energy transfer among such 1D aligned chromophores can take place.[22] Since perylene derivatives can absorb a wide range of light energy by subtle modification of the substituents, one can harvest sunlight to the energy sink through perylene-stacked assemblies in the gel system. Well-defined nanoscale 1D alignment of photofunctional molecules, ease of fabrication,[23] and thermo-reversible properties of organogels will lead to the development of novel photofunctional materials from the organogel system. We believe that these soft materials based on molecular assemblies can be applied as model systems for light-emitting diodes, signal amplifiers, fluorescence sensors, energy filters, and other photonic devices.

Experimental Section

Cholesterol-based perylene derivatives (**1a**, **b**, **c**, and **d**) were synthesized from 3,4,9,10-perylene tetracarboxylic dianhydride. The synthetic procedures are explained in the Supporting Information.[24]

^{1}H NMR spectra were measured on a Bruker DMX 600 spectrometer. IR spectra were obtained using a Perkin Elmer ATR FTIR spectrometer. Mass spectral data were obtained using a Perseptive Voyager RP MALDI TOF mass spectrometer. UV/Vis and CD spectra were measured on a Shimadzu UV-2500PC spectrophotometer and a Jasco J-720WI spectrometer, respectively. Fluorescence spectral measurements were performed using a Hitachi F-4500 spectrometer. The gels were photoexcited with an incidence angle of 45° to the quartz-cell surface and the fluorescence was detected along the normal angle. Comparison of each absorption coefficient reveals that even in the **1a**/**1b**/**1c**/**1d** quaternary gel system, **1a** is mainly photoexcited at an excitation wavelength of 457 nm (Figure 3S).

Gelation test: The gelator and the solvent were put in a septum-capped test tube and heated until the solid was dissolved. The sample vial was cooled in air to 25 °C, then left for 1 h at this temperature. The state of the materials were evaluated by the "stable-to-inversion of a test tube" method.

CLSM measurements: **1a** gel (prepared from *p*-xylene/1-propanol (3:1)) was placed on a glass plate and observed with a BIO-RAD Radiance 2000 AGR3 microscope. The excitation wavelength was 488 nm (argon laser with reflector turret).

SEM measurements: The specimens were obtained by freezing and pumping the sample of **1a** for 12 h (the gel was prepared from *p*-xylene/*tert*-butanol (4:1); the precipitate was prepared from *p*-xylene). The xerogel and precipitate of **1a** thus obtained were shielded by Pt and examined with a Hitachi S-5500 scanning electron microscope. The accelerating voltage of SEM was 15 kV.

AFM measurements: **1a** gel (prepared from *p*-xylene/1-propanol (3:1)) was collapsed by strong vibration and the supernatant was cast on to freshly cleaved highly oriented pyrolytic graphite (HOPG) by spin-coating. The surface was examined by a Topometrix TMX-2100 microscope (non-contact mode).

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[18] **1b**–**d** are not soluble in the mixed solvent of *p*-xylene and 1-propanol but form precipitates. From this fact, it is reasonable to deduce that **1a**–**d** coassemble to form gels.

[19] To determine how many times the fluorescence of the acceptor was intensified, total fluorescence spectra of mixed systems (spectra b and c in Figure 5 and b and c in Figure 2 of the Supporting Information) were divided into those of donor and acceptors. Thus, we could calculate the values for $FI_{\mathrm{acceptor}}/FI_{\mathrm{donor}}$.

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[21] As one of the referees pointed out, the suggested coassembly of **1a**–**d** should lead to assemblies with a random distribution of the four units, and consequently many different decay pathways are likely to exist, instead of a "clean" decay channel to the lowest energy state of **1d**.

[22] We have found that when *N*,*N*′-di-*n*-butyl-1,7-bis(4-*tert*-butylphenoxy)-3,4,9,10-perylenetetracarboxylic diimide (compound **4** without the cholesterol group shown in the Supporting Information) was added as an energy acceptor, emission from **4** was not intensified as for **1b**. This result further supports the view that the structural similarity of the perylene–cholesterol conjugates **1a**–**d** plays an important role in coassembling acceptors and mediating efficient energy transfer.[18]

[23] K. J. C. van Bommel, A. Friggeri, S. Shinkai, *Angew. Chem.* **2003**, *115*, 1010 – 1030; *Angew. Chem. Int. Ed.* **2003**, *42*, 980 – 999.

[24] Cholesterol-based perylene derivatives were synthesized according to the following references: a) H. Quante, P. Schlichting, U. Rohr, Y. Geerts, K. Müllen, *Macromol. Chem. Phys.* **1996**, *197*, 4029 – 4044; b) T. Ishii, R. Iguchi, E. Snip, M. Ikeda, S. Shinkai, *Langmuir* **2001**, *17*, 5825 – 5833; c) A. Böhm, H. Arms, G. Henning, P. Blaschka, US Pat. 6,184,378, **2001**; d) T. Watanabe, N. Miyaura, A. Suzuki, *Synlett* **1992**, 207 – 210.