Communications

Organogels

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Spontaneous Colorimetric Sensing of the Positional Isomers of Dihydroxynaphthalene in a 1D Organogel Matrix**

Pritam Mukhopadhyay, Yuya Iwashita, Michihiro Shirakawa, Shin-ichiro Kawano, Norifumi Fujita, and Seiji Shinkai*

The recent upsurge of interest in functional and stimuliresponsive $organogels^{[1]}$ has unraveled new and exciting

properties of molecules hitherto unknown in solution and the solid state.^[2] Hydrogen-bonding interactions between amide, urea, and sugar groups as well as the van der Waals interactions between cholesteryl groups have chiefly been utilized so far in the construction of onedimensional (1D) architectures suitable for gelation. In contrast, examples of a relatively new

design strategy that utilizes the π - π -stacking interaction to form 1D low-molecular-weight gels are rather limited.^[3a-d] We employed this concept to produce 1D perylenediimide-based organogels with light-harvesting properties.^[3e,f] Our interest in the development of a 1D naphthalenediimide-based organogel that exhibits recognition properties was driven by the following motives: Firstly, naphthalenediimide is a versatile molecule^[4] with an extended π surface and has been applied in the design of conductive materials, artificial photosynthetic systems, as well as DNA intercalators. Secondly, the naphthalenediimide–alkoxynaphthalene system is an important supramolecular motif that has been applied in the design of a plethora of novel architectures:^[5] for example, Sanders, Stoddart, and co-workers have reported [2]catenanes,

[*] Dr. P. Mukhopadhyay, Y. Iwashita, M. Shirakawa, S.-i. Kawano, Dr. N. Fujita, Prof. Dr. S. Shinkai
Department of Chemistry and Biochemistry
Graduate School of Engineering
Kyushu University
744 Moto-oka, Nishi-ku, Fukuoka 819-0395 (Japan)
Fax: (+81) 92-802-2820
E-mail: seijitcm@mbox.nc.kyushu-u.ac.jp

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[2]rotaxanes, and pseudo[2]rotaxanes, and Iverson and coworkers have designed folded aedamers—artificial duplexes based on this versatile donor–acceptor interaction. Surprisingly, however, this important motif has not been investigated in an organogel system to date.

Herein we present a highly efficient, versatile organogelator (1) that forms a robust 1D gel superstructure. We reasonably envisioned that the gel matrix of 1 would bind to 1,5-dialkoxynaphthalenes following the precedent of supramolecular architectures derived from the naphthalenediimide–alkoxynaphthalene motif.^[5] However, to our astonishment, organogel 1 does not interact with this well-known complementary partner, whereas it shows selective recognition of the polar, hydrophilic dihydroxynaphthalenes. Thus, we have found serendipitously an alternative supramolecular



binding motif that predominantly operates only in the gel state. We utilized this unusual recognition pattern and the remarkably amplified binding in the gel-phase environment to design a simple and straightforward colorimetric detection system. With this system, it is possible to distinguish clearly several positional isomers of dihydroxynaphthalenes with the naked eye; such a process is impossible to carry out in the conventional solution state. To our knowledge, this is the first example of an organogel matrix that has been employed in a colorimetric sensing system.

The gelator molecule **1** was designed to include a combination of π - π stacking, H-bonding, and van der Waals forces. We anticipated that the naphthalenediimide moiety would facilitate the formation of a 1D superstructure because of its propensity to form π -stacked structures. Interestingly, **1** was found to be a versatile gelator; it formed stable gels in 19 of the 26 common organic solvents evaluated.^[6] This gel shows a reversible sol-gel transition, and the temperature-dependent spectral changes strongly indicate the existence of π - π -stacked naphthalenediimide units in the gel which unstack upon heating (see Supporting Information). The 1D morphology constructed from **1** was confirmed by TEM observations (see Supporting Information).

To investigate the recognition characteristics^[7] in the gel matrix of **1**, we first chose 1,5-dimethoxynaphthalene (**4a**) as a substrate as it is known to form a strong donor–acceptor complex with naphthalenediimide that can be visualized by its plum/violet color.^[8] Gelator **1** and compound **4a** were added



in a 1:1 molar ratio to a screw-capped sample vial containing cyclohexane (1 mL),^[9] and the mixture was heated gently until a clear solution was obtained. Gel formation occurred within a few minutes, but contrary to our expectation, no color change was observed even after keeping the gel for a few weeks at ambient temperature, which indicates that no donor-acceptor interaction is present in the gel matrix. Likewise, no color changes were observed for 2,6-dimethox-ynaphthalene (**4c**) and other common donor analogues such as **4b**, **4d**, and pyrene (see Figure 1). This finding is very surprising because a large number of supramolecular architectures have been constructed in which dialkoxynaphthalene or pyrene^[10] derivatives intercalate between naphthalenediimide moieties to form columnar π -stacked donor-acceptor superstructures.



Figure 1. The photograph shows there is no change in color upon addition of alkoxynaphthalenes (**4a** and **4c**), methylnaphthalenes (**4b** and **4d**), and pyrene to the gel matrix of **1** ([**1**]=3.5 mM in cyclohexane, RT).

We then turned our attention to dihydroxynaphthalenes, which are also known to be environmental pollutants widely distributed in water and soil. Their recognition, sensing, and immobilization in a gel matrix would therefore be very important. However, carrying out recognition studies of dihydroxynaphthalenes in a nonpolar medium poses a serious challenge because of their hydrophilicity and poor solubility. Presumably, this is why dihydroxynaphthalenes have been studied mainly in aqueous media rather than in nonpolar solvents. Among the polar analogues of naphthalene, 2,6dihydroxynaphthalene (3 f) is known to form stable, violetcolored complexes with various acceptors in aqueous solution.^[11] However, its complexation with naphthalenediimide in solution and the solid state has not been reported to date. Very surprisingly, although **3**f remains completely insoluble in solvents such as cyclohexane and decalin, it dissolves readily with gentle heating in the presence of 1. A deep bluish-green color appears within a few minutes as the solution is cooled and transforms into a gel. The UV/Vis absorption spectrum exhibits a broad band in the visible region ($\lambda_{max} = 600$ nm), which is characteristic of a chargetransfer transition between the donor and acceptor molecules in the gel matrix (Figure 2). The charge-transfer band at 600 nm increases sharply with increasing amounts of **3 f** in the gel matrix of 1, while the intensity of the π - π * transition at 380 nm decreases. This observation indicates the facile transformation of a π -stacked naphthalenediimide structure to a naphthalenediimide-2,6-dihydroxynaphthalene complex in



Figure 2. UV/Vis spectra of gelator 1 (4.0 mM in cyclohexane) at various concentrations of 3 f (0.0–4.8 mM). The inset shows a plot of the molar absorption coefficient at 600 nm versus concentration of 3 f and confirms a 1:1 stoichiometry of the donor–acceptor complex ([1]=4 mM).

the gel matrix. A 1:1 stoichiometry was confirmed by various spectroscopic methods^[12] (e.g., see inset of Figure 2).

Encouraged by this observation, we then investigated the recognition of seven positional isomers of dihydroxynaphthalene (3a-g) in the gel matrix of 1. Interestingly, all of the isomers spontaneously generate distinct colors visible to the naked eye (Figure 3a). To ascertain that the recognition



Figure 3. A) The photograph depicts the spontaneous color changes of organogel 1 upon addition of positional isomers of dihydroxynaphthalene (3a–3g): 1 (yellow), 1·3a (deep purple), 1·3b (green), 1·3c (purple), 1·3d (light brown), 1·3e (reddish-orange), 1·3 f (bluish-green) and 1·3g (orange). B) The photograph shows the significantly reduced color changes in the solution state with nongelling compound 2 upon addition of dihydroxynaphthalenes 3a–3g: 2 (colorless), 2·3a (light violet), 2·3b (colorless), 2·3c (light purple), 2·3d (light purple), 2·3e (yellowish-orange), 2·3 f (yellowish-green), and 2·3g (light yellow). Conditions: 1:1 complexes at 2.5 mM in 1·3a–3g in cyclohexane gel, 2·3a, 2·3d, and 2·3f in cyclohexane/CHCl₃ (1:1), and 2·3b, 2·3c, 2·3e, and 2·3g in cyclohexane.^[9]

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process operates only in the gel matrix, we synthesized the nongelling reference compound 2, which has 2-ethylhexyl groups as solubilizing substituents. Figure 3 b shows that the addition of the same isomers of 3 to the nongelling compound 2 in solution (in the same concentrations as before) generates drastically less-intense and less-distinct color changes. Hence, the determination of the positional isomers of dihydroxy-naphthalenes with the naked eye is not possible in the solution state.

UV/Vis spectra of the various complexes (1·3a–g) in the gel state show clearly the significantly red-shifted and markedly more-intense charge-transfer bands relative to those in the solution state (2·3a–g; Figure 4). For example,



Figure 4. UV/Vis spectra of 1 and the charge-transfer bands of the donor-acceptor complexes (4.0 mm) $1\cdot3a-3g$ in cyclohexane gel, $2\cdot3a$, $2\cdot3d$, and $2\cdot3f$ in cyclohexane/CHCl₃ (1:1), and $2\cdot3b$, $2\cdot3c$, $2\cdot3e$, and $2\cdot3g$ in cyclohexane.^[9]

the bluish-green gel of 1.3f ($\varepsilon = 877 \,\mathrm{M}^{-1} \,\mathrm{cm}^{-1}$) shows an impressive 70-fold enhancement in the molar absorption coefficient of the charge-transfer band relative to that of of 2.3f in solution ($\varepsilon = 12.5 \,\mathrm{M}^{-1} \,\mathrm{cm}^{-1}$) at $\lambda = 600 \,\mathrm{nm}$. Moreover, all the color changes (from pale yellow to the respective colors) were found to be reversed by heating and could be repeated many times with the same sample (see Supporting Information). Furthermore, we found that the number of hydroxy groups is also important, since α - and β -naphthols, which are also insoluble in these solvents, do not show any binding in the gel matrix. These derivatives gradually precipitate from the gel matrix.

The 1.3 f complex exhibits the most-intense and redshifted charge-transfer band of all of the complexes. We carried out molecular modeling studies of this complex to gain an insight into this unusually amplified recognition phenomenon. Close inspection of the energy-minimized structure of the 1.3 f complex suggested that 3 f can form the most complementary motif because the symmetrical disposition of its hydroxy groups and the carbonyl groups of the naphthalenediimide moiety result in cooperative interplay of weak H-bonding and π -stacking interactions between

the electron-rich and electron-deficient rings along the 1D superstructure (see Supporting Information) of the gel matrix. Attenuated total reflectance infrared (ATR-IR) spectrometry of the xerogels (see Supporting Information) conclusively supports this view; the symmetrical and asymmetrical carbonyl group vibrations of the naphthalenediimide unit in **1** at 1706 and 1665 cm^{-1} shift to 1700 and 1659 cm^{-1} , respectively, as a result of this weak H-bonding in the 1.3 f complex. This remarkably unusual binding property can now be rationalized as follows: a successful intercalation of the donor molecule in the gel matrix of 1 can take place only if it is energetically feasible to break the cooperatively associated π -stacked naphthalenediimides, amide H-bonds, and the closely packed alkyl chains. The dihydroxynaphthalenes, which show a cooperative H-bonding effect and π -stacked donor-acceptor interactions, can easily cross this uphill energy process, while alkoxynaphthalenes, which have a single donor-acceptor interaction, cannot compensate for the overall process.

It is notable that the solvophobic effect can facilitate the binding of the dihydroxynaphtahlenes in the organogel matrix. However, a solvophobic effect alone cannot explain this recognition process in the organogel matrix. The degree of color change with the various dihydroxynaphthalene isomers and the inability of the other hydrophilic and insoluble naphthalene derivatives (i.e. α - and β -naphthols) to bind show that a combination of various interactions such as H-bonding and donor–acceptor interactions have to be taken into account to explain this recognition process in the oragnogel matrix.^[13]

The recognition of the dihydroxynaphthalene triggers a morphological modulation of the 1D fibers of organogel **1** as can be seen clearly from the SEM images (Figure 5). The long



Figure 5. SEM images of the xerogel of A) 1 and B) the 1.3 f complex prepared from the cyclohexane gel (4.0 mm); the scale bar denotes 1 μ m.

1D fibrous network of **1** with fiber diameters of 100-200 nm, which is typical for organogels, has been transformed into a 2D sheetlike structure in the **1**·**3 f** complex. This tranformation is not unsurprising when it is considered that the intercalation of the donor moiety creates a gap of around 7 Å between the gelator molecules (see Supporting Information); this intercalation triggers the 2D aggregation to maintain the close-packed nature of the alkyl chains.

Importantly, even minute quantities (0.2 equiv) of the dihydroxynaphthalenes (0.16 mg of 3 f in 5.0 mm of 1) can be sensed by the naked eye with the gelator 1. Furthermore, we found that the gel superstructure is extremely sensitive even to the upper limit of added donor molecules, since the

addition of more than 1.2 equivalents can readily transform the gel matrix into a sol phase (Figure 6). Therefore, this organogel-based approach becomes quite attractive, considering that conventional colorimetric sensors that operate in



Figure 6. Photograph of organogel 1 (5.0 mM in cyclohexane): A) without 3 f; B) with 0.2 equivalents of 3 f; C) with 1.0 equivalent of 3 f, and D) with 1.2 equivalents of 3 f.

solution require 10–100 equivalents of the analyte for sensing with the naked eye.^[14] Although the present organogel matrix can detect analytes on the milligram scale, an improved design could lead to attractive systems that operate on the ppm scale. This development would make organogels attractive for future applications to determine environmental pollutants.

In summary, we have found a rare example of an organogel in which a multiple set of noncovalent interactions confers hostlike character to the gel matrix^[15], and by virtue of this character, the organogel can perform several exciting functions. It can differentiate different classes of electron-rich naphthalene compounds such as dihydroxynaphthalenes from alkoxy- and hydroxynaphthalenes. Naked-eye differentiation of several positional isomers of dihydroxynaphthalene becomes possible as a result of an unprecedented coerced H-bonding-driven recognition that significantly amplifies the binding in the gel state.

Experimental Section

Organogelator **1** and the nongelling reference compound **2** were synthesized from 1,4,5,8-naphthalenetetracarboxylic dianhydride. See the Supporting Information for experimental details on the synthesis, gelation tests, ¹H NMR, ATR-FTIR, and UV/Vis spectrometry, MALDI TOF mass spectrometry, and SEM/TEM measurements.

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