Studies on a new class of organogelator containing 2-anthracenecarboxylic acid: Influence of gelator and solvent on stereochemistry of the photodimers

Arnab Dawn,† Norifumi Fujita,*‡ Shuichi Haraguchi, Kazuki Sada, Shun-ichi Tamaru† and Seiji Shinkai*†

Received 2nd June 2009, Accepted 22nd June 2009
First published as an Advance Article on the web 26th August 2009
DOI: 10.1039/b910741j

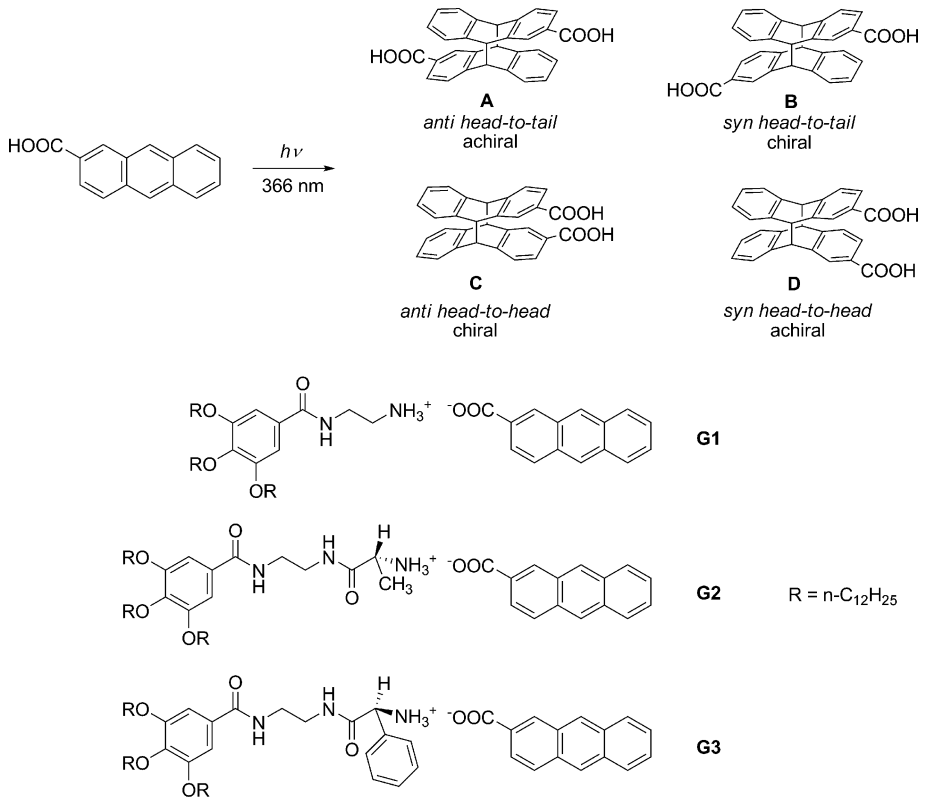
A new class of binary organogelator (**G1**, **G2** and **G3**) based on 2-anthracenecarboxylic acid (2Ac), attached noncovalently with the gelator counterpart containing a 3,4,5-tris(n-dodecyloxy)-benzoylamide backbone has been developed. Among the three gelators, two (**G2** and **G3**) are chiral containing D-alanine or L-2-phenylglycine moieties, respectively. They can act as efficient gelators of organic solvents with varying polarity depending upon the gelator systems. Gelator **G1** even gelates chiral solvents. The photoirradiation of the gel samples produces photocyclodimers having different degrees of stereoselectivity for different systems. Gels with **G1** and **G2** produce *head-to-head* (h–h) photodimers as major products, whereas the stereoselectivity is reversed for the gels with **G3** producing *head-to-tail* (h–t) photodimers as major products. Among those, **G2**/cyclohexane gel shows the highest degree of stereoselectivity, producing only h–h photodimers with some significant amount of chiral induction. Other chiral systems exhibit low to moderate chiral inductions. The gelator **G1** can differentiate between the racemic and enantiomerically pure varieties of a solvent by exhibiting different gel melting temperatures (T_{gel}). For different gel systems, T_{gel} increases in all the cases as a consequence of photoreaction, except for the **G2**/cyclohexane gel, where a prominent gel-to-sol phase transition can be observed during the photoreaction. Hydrogen-bonding and π–π stacking interactions play the principal roles in constructing the gel structure. The morphologies of the gel systems vary between one-dimensional fibrils and a fibrillar network structure. In addition, the influences of the gelator and solvent polarity on the rate of photoreactions, photoproduct distributions as well as gel structures are investigated.

Introduction

Control over stereochemistry and chirality using the principles of supramolecular interactions is an intriguing field of recent advanced research.[1] Primarily, it deals with electrostatic, hydrogen bonding, van der Waals and π–π interactions, and also in some cases steric interactions, acting individually or cooperatively by noncovalent paths to determine the final stereochemistry of the substrates.[2–4] In this context, stereochemical control in a chiral photochemical process such as photocycloaddition is a hot topic from the mechanistic as well as synthetic point of view.

Among the different stereochemical processes, the stereochemistry of unsymmetrically substituted anthracenes has been less explored until recently, probably due to the complex nature of their photoproducts, which include four [4 + 4] cyclodimers (Scheme 1), *anti*- and *syn*- h–t (A and B) and *anti* and *syn*- h–h (C and D), among which B and C are chiral. We consider, however, that this complexity could be useful as a 'probe' to monitor molecular orientation modes and stereochemical course occurring in molecular assemblies. Among the various hosts or template molecules, the inherently chiral cavity of γ-cyclodextrin has been primarily utilized to study the stereoselectivity and enantioselectivity of the photodimers resulting from 2-anthracenecarboxylate. Those approaches involve the manipulation of electrostatic interactions between host and guest, controlling external stimuli such as temperature, solvent, pressure and also steric effects acting outside the binding site.[5–8] The examples of successful use of some other reaction media like Langmuir–Blodgett assemblies, micelles, and polymer aggregates are very limited. Recently, Saigo and Ishida *et al.* utilized the liquid crystalline environment to control the stereo and enantioselectivity of anthracenecarboxylic acid.[9] Apart from those media, there is another interesting phase, the gel phase, which can provide a platform with a high degree of molecular organization of the substrate by means of different noncovalent intra- and intermolecular interactions such as hydrogen-bonding, van der Waals interactions, π–π stacking, solvophobic interaction, *etc.*[10] Photo-induced *trans-to-cis* isomerization of azobenzene in cholesterol-based low molecular-weight gelators (LMGs) has already been studied.[11] Photoresponsive LMGs containing stilbene,[12] substituted anthracenes[13] and LMGs based on monomeric and dimeric derivatives of anthracene[14] have also been developed. Even a few decades back, Weiss *et al.* developed an organogelator containing a cholesterol moiety linked to 2-substituted anthracene and studied the effect of photoirradiation in gel, liquid-crystalline and isotropic phases.[15] However, the

Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Fukuoka, 819-0395, Japan
† Current address: Faculty of Engineering, Sojo University, Kumamoto 860-0082, Japan. Email: shinkai_center@mail.cstm.kyushu-u.ac.jp; Fax: +81 92 805 3814.
‡ Current address: Department of Chemistry and Biotechnology, School of Engineering, The University of Tokyo, Tokyo 113-8656, Japan. Email: fujita@macro.t.u-tokyo.ac.jp; Fax: +81-3-5841-7310.



Scheme 1 Schematic representation of [4 + 4] photocyclodimerization of 2-anthracenecarboxylic acid in the free state, and the binary gelators used for the photoreaction.

product analysis and the insight into the stereochemical control of the photoproducts have not been explored in detail, probably because of their complexity. Keeping the above goal in mind, very recently, our group developed a binary organogelator containing 2-anthracenecarboxylic acid (2Ac) attached noncovalently to a gelator component containing a gallic acid backbone coupled with D-alanine by means of electrostatic and hydrogen-bonding interactions.[16] This approach results in a very high degree of stereochemical control of photodimerization of the 2Ac moiety, affording only h–h photocyclodimers (which are generally the minor products under normal isotropic conditions), together with a significant enantiomeric excess (ee) induced by the chiral counterpart of the gelator. As a consequence of the photoreaction, a significant gel-to-sol phase transition can easily be induced.

In this manuscript, we have elaborated this system to develop two additional similar binary gelator systems containing 2Ac attached noncovalently to the gelator counterpart. Here, we have tried to provide an insight into the stereochemical selection process in the gel phase in which the molecules assemble, in most cases, in a one-dimensional fashion. What we expect is that a change of the substituents, choice of the solvents even can invert the stereoselectivity of the photoproducts. The influence of photodimerization on the sol–gel phase transition for different systems and the kinetics of the photochemical processes are also investigated. Here, we have explored the influence of different factors acting separately or cooperatively to determine the final stereochemistry of the dimers, so that we can develop some generalized systems in which the simple tuning of physical factors would be enough to monitor and control the final stereochemistry of a chemical process.

Results and discussion

The different gelator systems studied

The binary gelator systems, **G1**, **G2** and **G3** used in this study all contain 2Ac attached noncovalently to the gelator counterpart containing a gallic acid backbone. **G1** does not contain any chiral center in the molecule, whereas **G2** and **G3** have D-alanine and L-2-phenylglycine respectively, coupled with the gallic acid moiety covalently to introduce chirality into the system. **G2** and **G3** differ only in the substituents at the terminal C atom of the gelator backbone and in terms of conformation. All these systems are capable of forming one-dimensional arrangements by means of intermolecular hydrogen-bonding *via* amide linkages (one in the case of **G1** and two in the case of **G2** and **G3**) and π–π stacking interaction of anthracene and gallic acid groups. The phenyl group is substituted in **G3** (instead of methyl in **G2**) to introduce the larger steric factor.

The different gel systems investigated are summarized in Table 1. The gelation abilities of **G1**, **G2** and **G3** were tested in different organic solvents (varying from nonpolar to polar) including chiral solvents, among which racemic glycidyl methyl ether was found to be gelated by all three gelators. In addition, **G1** produces partial gels with (*R*)- and (*S*)-glycidyl methyl ether, **G2** forms gel with nonpolar cyclohexane and **G3** gelates polar solvents like ethyl acetate and ethanol.

Table 1 Composition of the gel systems studied

Entry	Gelator	Solvent	CGC (% w/v)	Concentration (% w/v)	Quenching temperature/°C
1	**G1**	Glycidyl methyl ether	0.5	1.0	5
2	**G1**	(*R*)-Glycidyl methyl ether	1.0	1.5	0
3	**G1**	(*S*)-Glycidyl methyl ether	1.0	1.5	0
4	**G2**	Cyclohexane	0.25	1.0	25
5	**G2**	Glycidyl methyl ether	0.40	1.0	5
6	**G3**	Glycidyl methyl ether	0.75	1.5	5
7	**G3**	Ethyl acetate	0.75	1.5	5
8	**G3**	Ethanol	1.0	1.5	5

Role of the gelator and the solvent on the sol–gel phase transition temperature

We have examined the influence of the gelator concentration on the sol–gel phase transition by measuring the gel melting temperature (T_{gel}). The results are summarized in Fig. 1. The phase above each curve is the sol, whereas the phase below each curve is the gel. In general, T_{gel} values increase with increasing gelator concentrations and finally tend to saturate. In the given range of concentrations, the T_{gel} values for **G2** do not saturate, in contrast to **G1** or **G3** systems. However, similar patterns of the plots can be observed for a particular type of gelator with different solvents. Thus, it appears that the mechanism of breaking and making of gel structure is mainly controlled by the nature of the gelator. On the other hand, solvent polarity influences the physical binding modes such as intermolecular hydrogen-bonding and electrostatic interaction, resulting in different degrees of compactness or strength for different gel systems. This is also highlighted by the critical gelation concentration (CGC) values for different gel systems (Table 1). In general, **G3** gels possess higher CGC values than **G1** and **G2** gels, among which the **G2**/cyclohexane system has the lowest CGC value. Thus, the presence of a bulky phenyl group in **G3** affects the gel formation markedly.

Looking at the T_{gel} values reveals that for the solvent glycidyl methyl ether at a particular concentration, **G2** exhibits the highest T_{gel} value. This is probably due to the most favorable hydrogen bonding interaction among the gelator molecules operating in **G2**, arising from two amide groups. In contrast, the presence of only one amide group in **G1** and a bulky phenyl group in **G3** (also having two amide groups) dilute the effect.

Influence of the solvent chirality on T_{gel}

To investigate the influence of the solvent chirality, we prepared gels of **G1** with (*R*)- and (*S*)-glycidyl methyl ether, separately. It should be mentioned that the gels produced from enantiomerically pure solvents are rather weak in nature. The probable reason may be that there is a weaker homochiral interaction between the solvent molecules in the enantiomerically pure species that makes the gelator more soluble and favours the gelation only at a comparatively lower temperature, *i.e.* producing a weaker gel with a lower T_{gel} value.[17] Still, it is worth noting that from plots of T_{gel} against concentrations (Fig. 2) one can clearly distinguish the gel with racemic solvent from the gels with enantiomerically pure solvents. At a given gelator concentration, the gel with the racemic solvent has the higher T_{gel} value. In other words, **G1** forms a stronger gel with racemic solvents than with enantiomerically

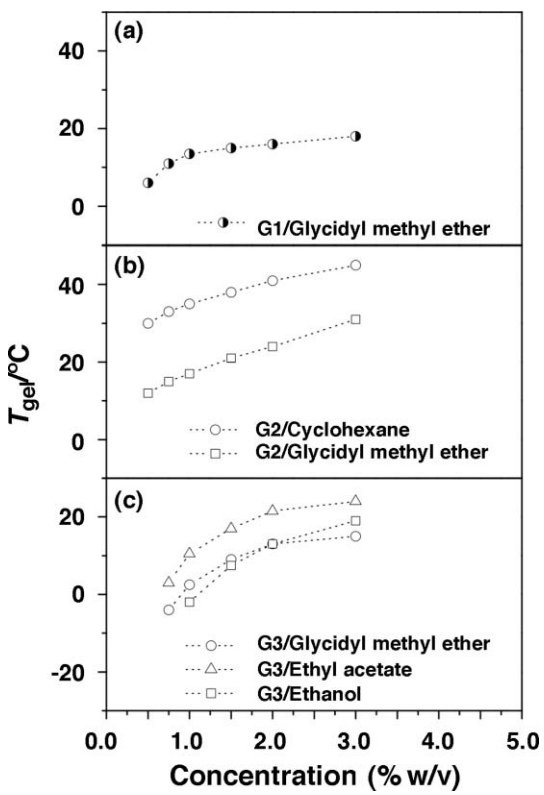


Fig. 1 Plots of T_{gel} *vs.* concentrations for the different gel systems with the gelators (a) **G1**, (b) **G2** and (c) **G3**.

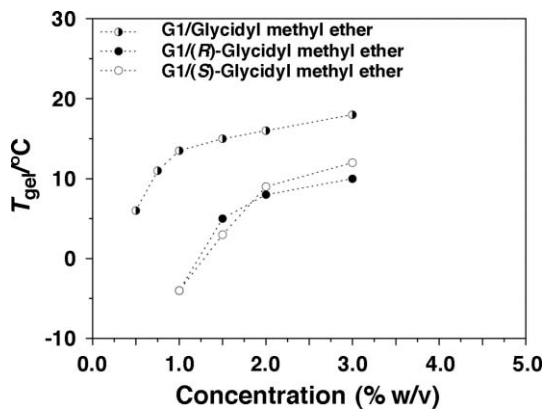


Fig. 2 Plots of T_{gel} *vs.* concentrations for gel systems with gelator **G1** with racemic and chiral varieties of the solvent.

pure solvents. As expected, the difference in the plots between two enantiomerically pure solvents is very small or insignificant. This is therefore a rare example of an organogel system being able to detect the presence of excess chirality in a solvent.

Morphology

To study the morphology of the gel samples, SEM studies of the xerogels were performed (Fig. 3). In general, in nonpolar solvents, as for the **G2**/cyclohexane system, the one-dimensional fibrillar structure, rather than the interconnecting network structure, is prominent, whereas in all other cases (for relatively polar solvents) the fibrillar network pattern is present, and it is mostly prominent and well defined in the case of the gelator **G3** with the highly polar solvent ethanol.

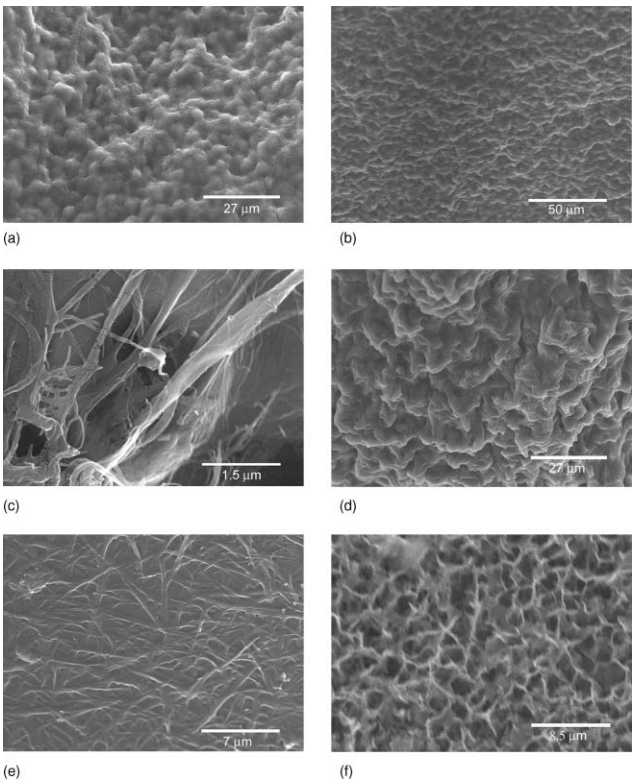


Fig. 3 SEM micrographs of the xerogels prepared from (a) **G1**/glycidyl methyl ether, (b) **G2**/glycidyl methyl ether, (c) **G2**/cyclohexane, (d) **G3**/glycidyl methyl ether, (e) **G3**/ethyl acetate and (f) **G3**/ethanol.

It is also worth mentioning that the morphologies of the different gel systems vary significantly. Thus the gelator and the solvent both have a strong influence on the morphology.

Product distributions of 2Ac dimers produced from the photoirradiation of different gel systems

The gel samples prepared from various gelator systems under inert conditions were photoirradiated at a wavelength of 366 nm at constant temperature. Photocyclization is not reversible at this wavelength. As the samples were photoirradiated, the intensity of the UV-absorption band (^1L_a) of the 2Ac monomer gradually decreased (Fig. 4). After the photoreaction, the photoproducts

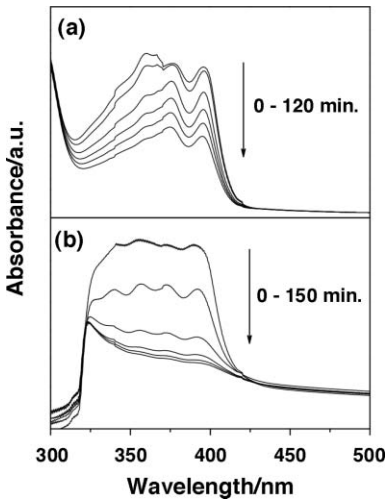


Fig. 4 Representative UV-vis spectra of the gel samples of the gelator **G2** (1% w/v) with the solvents (a) cyclohexane and (b) glycidyl methyl ether with progress of photoirradiation.

and unreacted 2Ac were separated and isolated from the gelator components, which were then subjected to HPLC analysis. The distribution of photodimers and their ee values obtained from different gel systems are summarized in Table 2.

In general, in the case of the gels with **G1** and **G2**, h–h photodimers are the major products, whereas similar systems in the sol state result in h–t photodimers as the major products. This means the molecular arrangements in the gel state favor the h–h molecular orientation. In other words, most of the molecules are oriented in a h–h fashion in the gel state. In more isotropic sol state, no such driving force exists and the gelator molecules are randomly oriented, giving thermodynamically more favored h–t photodimers as major products. As reported previously, particularly in the **G2**/cyclohexane system, all the gelator molecules are oriented in a h–h fashion, giving 100% h–h photodimers.[16] Even in the sol state h–h products are the major products. In contrast, the gels with **G3** produce more h–t photodimers. It should be noticed that **G3** gels are formed in polar solvents only. Here, the difference between the product distribution resulting form either the gel state or the sol state is rather less.

This means that even in the gel state, both h–h and h–t orientations are favored. The gels of **G1** with the enantiomerically pure (*R*- and *S*-) glycidyl methyl ethers give h–t photodimers as major products. The reason may be the weakness of the gel structure compared to the similar system with a racemic solvent, which is also reflected in the higher CGC values for the gels with enantiomerically pure solvents. Even though, it is still interesting that the enantiomerically pure solvents can induce some (though small) ee to the photodimers.

As evident from the SEM images, in the gel state, the one-dimensional arrangement of the gelator molecules is created, firstly by the intermolecular hydrogen-bonding between amide moieties and secondly by the π–π stacking of the 2Ac molecules. The intermolecular hydrogen-bonding is favored in nonpolar solvents and in a h–h molecular orientation. Depending on different gel systems, these two factors operate cooperatively or individually to determine the molecular arrangement and in turn the final stereochemistry of the photodimers. In a nonpolar solvent like

Table 2 Distribution and enantiomeric excess (ee) of the products obtained from [4 + 4] photocyclodimerization of 2Ac in different gel samples

					Relative yield (%)[a]						ee (%)[a]	
Entry	Gelator/solvent/state	Temperature/°C	Irradiation time/min	Conversion (%)	A	B	C	D	A + B	C + D	B	C
1	**G1**/Glycidyl methyl ether/gel	5	120	63	20	15	36	29	35	65	—	—
2	**G1**/Glycidyl methyl ether/sol	25	30	82	37	26	19	18	63	37	—	—
3	**G1**/(*S*)-Glycidyl methyl ether/gel	5	180	75	37	26	19	18	63	37	–2	–3
4	**G1**/(*R*)-Glycidyl methyl ether/gel	5	180	77	36	25	21	18	61	39	–3	–3
5	**G2**/Cyclohexane/gel	10	120	51	0	0	48	52	0	100	—	–10
6	**G2**/Cyclohexane/sol	50	30	61	10	14	36	40	24	76	1	–2
7	**G2**/Glycidyl methyl ether/gel	5	120	64	24	17	32	27	41	59	–2	–2
8	**G2**/Glycidyl methyl ether/sol	25	30	85	38	26	19	17	64	36	1	–1
9	**G3**/Glycidyl methyl ether/gel	5	180	75	37	25	22	16	62	38	–1	–2
10	**G3**/Glycidyl methyl ether/sol	25	30	85	37	28	19	16	65	35	–2	–1
11	**G3**/Ethyl acetate/gel	5	180	65	36	23	20	21	59	41	–0.2	–3
12	**G3**/Ethyl acetate/sol	25	30	82	38	26	19	17	64	36	1	–1
13	**G3**/Ethanol/gel	5	180	69	37	24	19	20	61	39	–4	–3
14	**G3**/Ethanol/sol	25	30	80	42	29	18	11	71	29	0.6	1

[a] The absolute configurations of B and C were not determined. The first eluted enantiomer is given a positive sign. Errors in relative yields are ±0.5%. Errors in ee are ±1% for major products and ±2% for minor products.

cyclohexane, these two factors operate cooperatively, allowing only a h–h molecular arrangement. On the other hand, with relatively polar solvents like glycidyl methyl ether, intermolecular hydrogen-bonding is less favored, resulting in some h–t photodimers, though it is minor. In the case of the gels with **G3**, the bulky phenyl group probably opposes the h–h orientation, favoring the h–t molecular orientation energetically. The nonpolar solvent environment facilitates such a type of orientation, making intermolecular hydrogen-bonding less favored and resulting in a preference for the π–π stacking interaction.

The chiral induction is most significant (10% ee) for the **G2**/cyclohexane system. In addition, this system gives only h–h photodimers.[16] In other cases low-to-moderate chiral inductions are observed. Thus, the selectivity of molecular orientation in the gel phase actually determines the order of chiral influence transformed from the chiral counter part of the gelators: the higher the selectivity is, greater the chiral induction will be.

Effect of photodimerization on the gel-to-sol phase transition

To study the effect of conversion of monomeric gelator molecules to dimers on the gel structure, we measured the T_{gel} of different gel systems after exposing the samples to the photoirradiation for a substantial period. The results are summarized in Table 3. In all cases (except in **G2**/cyclohexane), the T_{gel} values increase after the photoirradiation. That means that more energy is now required to break the gelator arrangement. In other words, the gels become more organized and compact as a result of the photoreaction. The finding supports the view that the photodimers are also taking part in constructing the gel structure. However, the gelation ability of the h–t dimeric form of LMG containing anthracene and urea moieties is already reported.[14] In our current study, it should be noticed that in all the gel systems the low-to-high fractions of h–t-oriented gelator molecules are present as evident from the HPLC analysis.

As an exception, for the **G2**/cyclohexane system, the gel-to-sol phase transformation takes place during the photoreaction even at low temperature (~10 °C).[16] That means that as a result of photoreaction, the one-dimensional molecular arrangement in the gel structure is collapsed. Thus, the monomeric anthracene units should have an active participation in constructing the gel structure and at the same time the produced h–h photodimers are not able to maintain the gel structure. In general, in relatively polar solvents the π–π stacking interaction mainly operates due to the absence of strong intermolecular hydrogen-bonding, as a consequence, photodimerization of 2Ac molecules makes the gel structure more compact by attaching the two gelator units, increasing the T_{gel} after the photoreaction.

Table 3 Influence of photodimerization on the gel melting temperature (T_{gel})

Gelator/solvent/concentration (% w/v)	T_{gel} (°C)	
	Before irradiation	After irradiation
G1/Glycidyl methyl ether/1.0	13.5	24.5
G2/Glycidyl methyl ether/1.0	17	28
G2/Cyclohexane/1.0	35	—
G3/Glycidyl methyl ether/1.5	9	17
G3/Ethyl acetate/1.5	17	23
G3/Ethanol/1.5	7.5	15

Kinetics of photodimerization in the gel state

The decrease in the ^1L_a band intensity corresponds to the consumption of the monomeric anthracenes, or in other words their conversion to the dimers. Thus to compare the rates of the photoreaction processes for different gel systems, the absorbance of the ^1L_a band (at ~390 nm) was plotted against the time of the photoreaction under the similar experimental conditions (Fig. 5). For the gelator **G2**, in the nonpolar solvent cyclohexane, the rate is almost uniform, whereas in a relatively polar solvent, glycidyl methyl ether, the initial rate is high followed by a sudden decrease and final saturation (Fig. 5a). The slower rate for the nonpolar solvent may be due to the strong intermolecular hydrogen-bonding, making a rigid one-dimensional gel structure. In the polar solvent, on the other hand, hydrogen-bonding is less strong and gel structure is less compact, giving more room for 2Ac molecules to undergo the photoreaction. With the progress of the

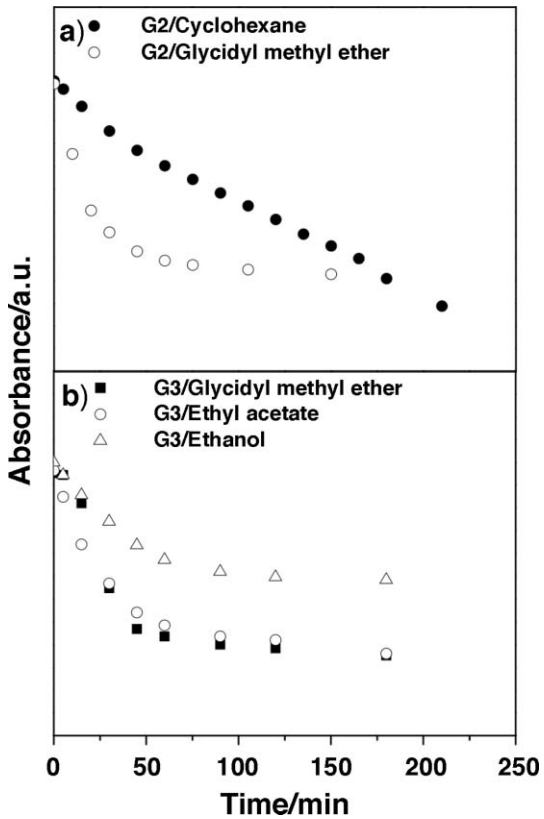


Fig. 5 Plots of absorbance of the ^1L_a band of 2Ac for the gel systems with the gelators (a) **G2** (1% w/v) and (b) **G3** (1.5% w/v) with the progress of photoirradiation.

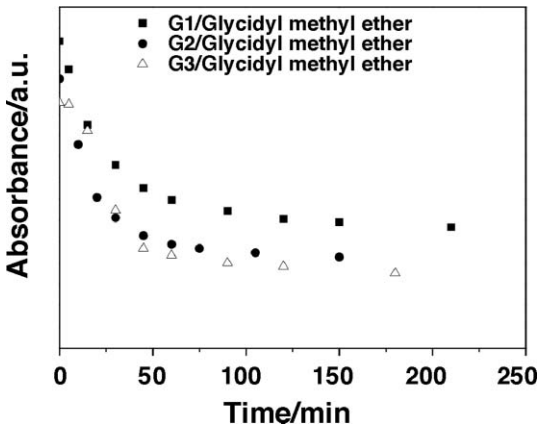


Fig. 6 Plot of absorbance of the ^1L_a band of 2Ac in the gel systems with the solvent glycidyl methyl ether for the gelators **G1**, **G2** and **G3** with the progress of photoirradiation.

photoreaction, after some substantial conversion to photodimers, the gel structure can become more compact (as evident from the increase in T_{gel} after photoreaction), thereby resulting in a sudden decrease in the photoreaction rate followed by saturation. In case of **G3** gels, the rates of photoreaction follows a similar trend (Fig. 5b), as in case of the **G2**/glycidyl methyl ether system. It can be noticed that the reaction rate in the **G3**/EtOH gel is slower than the **G3**/glycidyl ether and **G3**/EtOAc gels. The slower rate for **G3**/EtOH may result from the more rigid gel structure constructed from the h–t arrangement of gelator moieties, especially after the conversion of monomer to dimer, which is also reflected by the greater T_{gel} increase after photoreaction compared to its value before photoreaction. In contrast, the **G3**/EtOAc and **G3**/glycidyl methyl ether gel systems are more isotropic due to the moderate solvent polarity. In general, the higher polarity solvent favors the h–t arrangement (resulting mainly from the π–π stacking interaction), and the nonpolar solvent favors the h–h arrangement (resulting mainly from hydrogen-bonding together with π–π stacking interaction).

To investigate the effect of gelator molecules on the reaction rate, we plotted the absorbance of the ^1L_a band against progress of the photoreaction for three different gelators with the same solvent, glycidyl methyl ether (Fig. 6). The rates of photoreactions follow the similar patterns in all three cases. Thus, the influence of the gelator structure on the photoreaction rate is rather limited, and it is clear that the solvent effect plays a more pronounced role.

General discussion

From all the studies described above, it can be stated that there are two principal scenarios: firstly, the gelator arrangement before the photoreaction, involving only the monomeric gelator units; and secondly, the gelator arrangement after the photoreaction, involving monomeric as well as dimeric gelator units. One of the goals of this work is to control the stereochemical selectivity of the photodimers by taking advantage of the probable one-dimensional supramolecular assemblies in the gel phase. In this regard, the gel structure, or in other words the orientation of 2Ac molecules in the gel matrix, should be the key factor to understand the photodimer distribution. The HPLC analysis of the photoproducts provides direct evidence for the gel structure. The molecular arrangement of the gelator molecules in the gel systems is governed by two types of interactions, namely, the π–π stacking interaction of the anthracene molecules and intermolecular hydrogen-bonding interaction by amide groups. In turn, these are controlled firstly by the solvent polarity, and secondly by the steric influence created by the substituent in the gelator molecules. A nonpolar solvent favors h–h orientation of the gelator molecules and the gel structure is maintained cooperatively by π–π stacking interaction of anthracene molecules and intermolecular hydrogen-bonding through amide moieties. A bulky substituent and polar solvents favor an h–t orientation of the gelator molecules and a one-dimensional arrangement is primarily maintained by the π–π stacking interaction of anthracene molecules. Since these gels are formed only at low temperature, one may still expect some significant contribution from intermolecular hydrogen-bonding, though they may be weak. The stereoselectivity is highest in case of the least polar cyclohexane gel. Similarly, this system results in the highest degree of chiral influence. This implies that the stereoselectivity and enantioselectivity are governed by the directional orientation of the gelator molecules, and this factor is facilitated by the nonpolar solvent environment. Once some photodimers are produced as a result of photoreaction, they influence the existing gel structure crucially. From the above studies it can be stated that the formation of h–t photodimers favors or strengthens the gel structure, whereas h–h photodimers disrupt the gel structure. Thus, in all cases wherever some h–t molecular arrangement exists, the T_{gel} value increases after the photoreaction. Unlike the

G2/cyclohexane system, the existence of a very prominent three-dimensional network structure for the gelator **G3** in highly polar ethanol definitely indicates relatively homogeneously distributed molecules of both h–h and h–t orientations. It is clear, therefore, that the formation of h–t photoproducts in the significant fraction is not due to the lack of gelator arrangement but actually arises from the well organized gelator molecules comprising both h–h and h–t orientations. This suggests that the precise tuning of the gelator–solvent pair has a substantial influence on the preorientation of the gelator molecules, which determines the final stereochemistry of the products. This will be a step forward to design some organogel systems which can tune the photoproduct selectivity precisely in a wide distribution range.

Conclusions

In conclusion, we have demonstrated that a new class of binary organogelators containing 2Ac molecules noncovalently linked with 3,4,5-tris(n-dodecyloxy)benzoylamide can act as efficient gelators of the organic solvents with varying polarity, even including chiral solvents depending upon the system. One gelator is even capable of distinguishing between racemic and chiral varieties of the solvent in terms of the gel melting behavior. The photocyclodimerization of 2Ac in the gel matrix results in h–h dimers as the major products for two gelators. On the other hand, the product selectivity can be inverted only by using bulky substituents producing h–t photodimers as major products. The chiral induction in the photodimers from the chiral counterpart of the gelator is small but still significant, especially for the nonpolar solvent system. In addition, the photoreaction can influence the existing gel structure in a constructive or destructive manner depending upon the gel systems. We believe that this study will help to develop versatile gel systems that could be used as new reaction media, which are even able to determine the final stereochemical outcome of a reaction.

Experimental

General

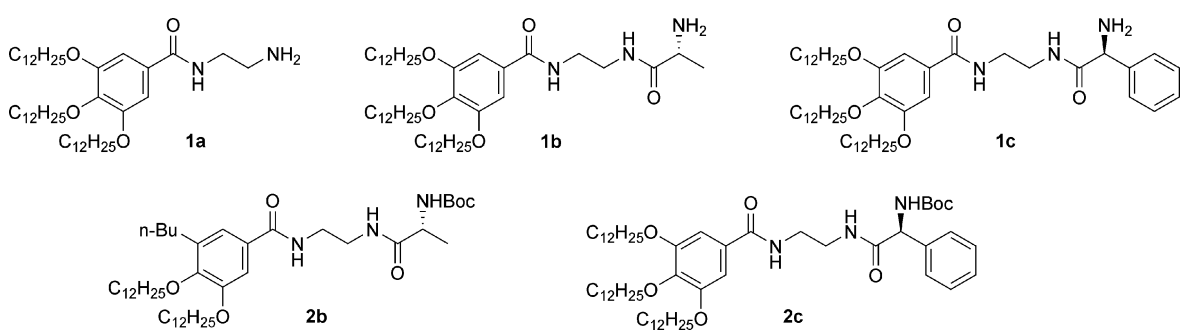
All starting materials and solvents were purchased from Tokyo Kasei Organic Chemicals or Wako Organic Chemicals and used as received. The ^{1}H NMR spectra were recorded on a Bruker 300 (300 MHz) spectrometer. Chemical shifts are recorded in ppm downfield from tetramethylsilane as the internal standard. Mass spectral data were obtained using a Perspective Biosystems Voyager – DE RP MALDI-TOF mass spectrometer. UV spectra were recorded in a Shimadzu UV-2500 PC UV-VIS recording spectrophotometer.

Synthesis of gelators

Gelators **G1**, **G2** and **G3** were prepared from corresponding amines **1a**, **1b** and **1c** and a carboxylic acid, 2-anthracenecarboxylic acid (2Ac). Compound **1a** was synthesized according to the methods described earlier.[16] **1b** was synthesized from the corresponding protected compounds **2b**.[16]

Synthesis of 2c. Compound **1a** (1.0 g, 1.4 mM), *N*-Boc-L-2-phenylglycine (402 mg, 1.6 mM) and BOP reagent (680 mg, 1.5 mM) were dissolved in dry CH_2Cl_2 (25 ml). TEA (151 mg, 1.5 mM) was added and the reaction mixture was stirred for 4 h at room temperature under Ar atmosphere. The organic layer was washed three times with brine, dried over anhydrous Na_2SO_4, filtered and the filtrate was dried under reduced pressure. The dried solid was subjected to column chromatography [silica gel, $CHCl_3$/MeOH = 20:1 (v/v)] to give compound **2c** (1.1 g, 85%) as a white solid. ^{1}H NMR (300 MHz; $CDCl_3$; TMS): δ = 0.86–0.88 (9H, m), 1.26–1.31 (48H, m), 1.38 (9H, s), 1.45–1.49 (6H, m), 1.72–1.74 (2H, m), 1.76–1.79 (4H, m), 3.51 (4H, m), 3.97 (6H, m), 5.10 (1H, m), 5.59 (1H, m), 6.73 (1H, m), 6.95 (3H, m), 7.31 (4H, m), 7.40 (1H, m); MS (MALDI-TOF, matrix; dithranol): *m/z* calcd for $[M + Na]^+$; 972.80 found 973.18; Elemental analysis: calcd for $C_{58}H_{99}N_3O_7$; C 73.30, H 10.50, N 4.42, found C 73.60, H 10.53, N 4.41.

Synthesis of 1c. In the deprotection step, compound **2c** (1.0 g) was dissolved in dry CH_2Cl_2 (3 ml) and TFA (40 eq) was added slowly at room temperature. Stirring was continued until TLC showed the consumption of all the starting material. Then the mixture was concentrated. Methanol was coevaporated several times to remove traces of TFA to give the TFA salt of the deprotected amino compound. The salt was neutralized by stirring with TEA (2 eq) in dry CH_2Cl_2 at room temperature with simultaneous checking of the completion of neutralization by TLC. The mixture was then washed three times with brine. The organic layer was dried over anhydrous Na_2SO_4, filtered, and the filtrate was dried under reduced pressure to give compound **1c** (805 mg, 90%) as pale white solid. ^{1}H NMR (300 MHz; $CDCl_3$; TMS): δ = 0.88–0.90 (9H, m), 1.27–1.32 (48H, m), 1.45–1.50 (6H, m), 1.72–1.74 (2H, m), 1.76–1.79 (4H, m), 2.75 (2H, m), 3.52 (4H, m), 3.97 (6H, m), 4.50 (1H, m), 6.9 (2H, s), 7.10 (1H, m), 7.29 (5H, m), 7.85 (1H, m); MS (MALDI-TOF, matrix; dithranol): *m/z* calcd for $[M + Na]^+$; 872.69 found 873.10; Elemental analysis: calcd for $C_{53}H_{91}N_3O_5$; C 74.86, H 10.79, N 4.94, found C 74.82, H 10.79, N 4.95.



Preparation of G1, G2 and G3. Compounds **1a**, **1b** and **1c** were stirred with 2Ac (equimolar) in THF separately at room temperature for 2 h. The reaction mixtures were concentrated under reduced pressure and finally dried in vacuum to give binary gelators **G1**, **G2** and **G3** respectively, as yellow solids. Elemental analysis: calcd for **G1** ($C_{60}H_{94}N_2O_6$); C 76.71, H 10.09, N 2.98, found C 76.75, H 10.07, N 2.98; calcd for **G2** ($C_{63}H_{99}N_3O_7$); C 74.88, H 9.88, N 4.16, found C 74.85, H 9.91, N 4.14.; calcd for **G3** ($C_{68}H_{101}N_3O_7$); C 76.15, H 9.49, N 3.92, found C 75.91, H 9.49, N 3.93.

Preparation of gel

Gelator and solvent were taken in a capped glass tube and the mixture was heated until the solid dissolved. The sample was then quenched (at 25 °C to 0 °C depending upon the systems) and left for 1 h at this temperature. The gelation state of the material was evaluated by assessing whether it was stable to inversion of the test tube.

Gel–sol transition temperature (T_{gel})

T_{gel} values were measured by the test-tube-tilting method where a test tube containing the gel was immersed inversely in a thermostatted bath and the temperature was raised at 0.5 °C/min. The T_{gel} was considered as the temperature when the mass started to flow. The error involved in measuring T_{gel} was ±1 °C.

SEM measurements

A thin layer of gel samples were prepared over a carbon-coated copper grid and dried in vacuum for 24 h to obtain the xerogels. The samples were then shielded by Pt and examined with a Hitachi S-5000 scanning electron microscope.

General procedure for photochemical reaction, product isolation and product analysis

The different gel samples of the binary gelators **G1**, **G2** and **G3** were prepared in capped quartz cell of 1 mm path length under argon atmosphere and were photoirradiated at a wavelength 366 nm with a USHIO Optical Modulex Deep UV 500 through the optical filters UV-35 and UV-D36C at constant temperature. After the photoreaction, first the solvents were removed by heating and finally in high vacuum for 24 h. The dried products were then dissolved in minimum amount of THF and poured in to a 25 mM borate buffer solution of pH 9 to precipitate the gelator backbone containing gallic ester. The mixtures were then filtered to collect the photoproducts and unreacted 2Ac as filtrate. 10 μl of the filtrate solutions (50 mM) were subjected to HPLC analysis. The same procedure was employed for the sol systems.

Analysis of the photoproducts was performed using chiral HPLC with tandem columns Inertsil ODS-2 (GL Sciences) and CHIRALCEL OJ-RH (Daicel).[5,16] The columns were kept at 35 °C. A mixture of 0.2 M potassium dihydrogen phosphate (adjusted to pH 2.5 by phosphoric acid) and acetonitrile (62:38 by volume) was used as an eluent. Relative yield and ee were determined from the peak area on the HPLC chromatogram detected by the absorbance at 254 nm.

Acknowledgements

Financial support was provided by Grant-in-Aid (Nos. 19022031, 20045014, and 20685010) and Global COE program: 'Science for future molecular systems' from MEXT of Japan and JSPS fellowship for A. D.

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