

Transcription of Chirality in the Organogel Systems Dictates the Enantiodifferentiating Photodimerization of Substituted Anthracene

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Abstract: An organogelator (**G**) that contains 2-anthracenecarboxylic acid (2Ac) attached covalently to a gelator counterpart that consists of 3,4,5-tris(*n*-dodecan-1-yloxy)benzoic acid by means of a chiral amino alcohol linkage has been synthesized. **G** acts as an efficient gelator of organic solvents, including mixed solvents and chiral solvents. Photodimers isolated after the photoreaction of the gel samples display different degrees of stereoselectivity. In the gel state, the formation of head-to-head (h-h) photodimers is always favored over head-to-tail (h-t) photodimers. Enantiomeric excess (*ee*) values of the major h-h photodimers reached as high as –56% in the case of the gels with enantiomeric glycidyl methyl ethers. Here, the solvent chirality

is outweighed by the intrinsic chirality of the gelator molecule. The packing of the chromophore in the gel state has been characterized by the absorption and the emission behaviors and their variations during the course of gel-to-sol phase transition. Whereas for the hexane gel, emission intensity increases with an increase in temperature, other systems show a decrease in emission intensity. Redshift of the λ_{max} in the gel spectra indicates the J-aggregate arrangement of the chromophores. Chiral transcription in the gel state has been

investigated by CD spectroscopy, which shows a decrease in CD intensity during the gel-to-sol phase transition. The X-ray diffraction study clearly differentiates among the gels in terms of the order of molecular arrangements. The gel systems are categorized as strong, moderately strong, and weak, that originate from the cooperative or individual participations of intermolecular hydrogen-bonding and π - π interactions, fine-tuned by the solvent polarity and the gelation temperature. A simple model based on the experimental findings and the molecular preorientation as evidenced by the stereochemistry of the photodimers has been proposed.

Keywords: chiral induction • enantioselectivity • organogels • photodimerization • supramolecular chemistry

Introduction

Photochirogenesis still remains a big challenge for chemists in spite of recent advancements in ground-state asymmetric

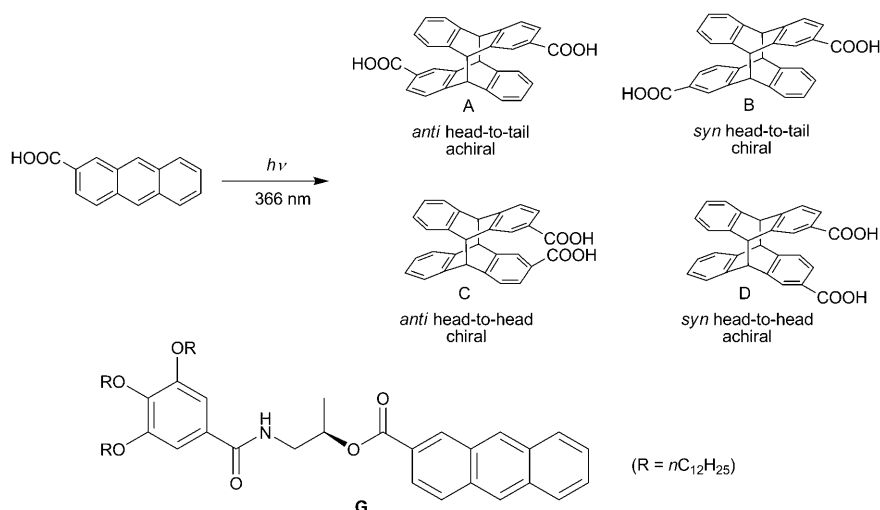
synthesis, mostly because of the nature of the short-lived weak interactions involved in the excited state. In this context, supramolecular photochirogenesis has become a promising interdisciplinary field of research, in which chiral information is induced, monitored, or controlled through the principles of a supramolecular approach that involves different types of noncovalent interactions.^[1] Among the different stereochemical processes, photodimerization of anthracene is one of the oldest known photochemical reactions.^[2] The stereochemistry of unsymmetrically substituted anthracenes such as 2-anthracenecarboxylic acid (2Ac) has been less explored until recently, probably due to the complex nature of their photoproducts, which include four [4+4] photocyclo-dimers: *anti* and *syn* head-to-tail (h-t, A and B) and *anti* and *syn* head-to-head (h-h, C and D), among which B and C are chiral (Scheme 1). In a more positive light, however, one can consider this complexity to be a probe to explore and monitor the molecular phenomena involved in the ste-

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Scheme 1. Schematic presentation of [4+4] photocyclodimerization of 2-anthracenecarboxylic acid in the free state, and gelator **G** used in this study.

reochemical course of a process, especially in terms of molecular arrangement, fine-tuned by noncovalent interactions that participate in supramolecular chirogenesis. Substrate preorientation prior to photoreaction, governed by means of the supramolecular interactions, has recently been exploited to achieve highly regio- and enantioselective photodimerization of 2Ac in solution,^[3] in the solid state^[4] by using the inherently chiral cavity of γ -cyclodextrin derivatives, and in two-component liquid crystalline medium as well.^[5] However, all are sensitive to the design or fine-tuning of the appropriate host molecules.

Thinking in a different way, we have noticed that in the supramolecularly assembled systems that are produced from the low-molecular-weight gelators (LMGs), the chirality within an individual molecule can be transcribed to the nano- and mesoscale fibrous assembly by means of hierarchical self-assembly process.^[6] So far, such types of soft materials have scarcely been employed in the stereochemical process except in some isolated preliminary examples such as photoinduced isomerization of azobenzenes,^[6a,7] the development of photoresponsive LMGs that contain stilbene^[8] or substituted anthracene,^[9] or the study of the gelation behavior of monomeric and dimeric derivatives of anthracene.^[10] There is also an earlier example in which a cholesterol-based organogelator containing 2-substituted anthracene was developed and the effect of photodimerization in the gel, liquid crystalline, and isotropic phases were studied.^[11] In another example, the principle of capturing the translated chiral information has been used to produce helical silica fibers by the polymerization of tetraethoxysilane in the chiral gel template.^[12] Even in these cases, however, an attempt has never been made to analyze the final stereochemistry precisely or to estimate the degree of chiral information transcribed. The principles of organogel formation are considered to be through the one-dimensional alignment of the gelator molecules supported by different types of nonco-

valent interactions, which include electrostatic, hydrogen-bonding, π - π stacking, and van der Waals interactions. Such a highly ordered molecular environment is expected to provide an ideal platform for performing a stereoselective process. On the other hand, quantifying the transcription of chiral message in a supramolecular gel system by means of analyzing the photoactive chromophore as a functional probe might give us real scope to “estimate” the efficiency of such a hierarchical process. In spite of the presence of several chirally well-defined gel systems, such a quantitative result is still missing. Motivated by the

above prospect, our group recently has developed a two-component organogelator system containing a 2Ac molecule attached noncovalently to a gelator counterpart that contains a long alkyl chain substituted gallic acid backbone and a chiral alanine moiety. The photodimerization of this system in the gel phase provided an unprecedented stereoselectivity and produced only h-h photodimers.^[13] However, only a moderate enantiomeric excess (*ee*) could be achieved during the process.

To fulfill the chirality factor, which is indispensable for the application of such a soft template for chirogenesis, here we have designed a 2Ac-bearing chiral organogelator **G** (Scheme 1). Gel samples have been prepared by using different organic solvents. After photodimerization, the 2Ac moiety could easily be cleaved from the gelator backbone by hydrolysis. The photoproducts were analyzed and the photodimer distributions were determined precisely by using chiral HPLC. Remarkably, in the gel states, we obtained variable *ee* values that ranged from low to high, depending on the solvents. The assembly of the gelator molecules prior to the photoreaction has been investigated from absorption and emission behaviors with varying temperatures. For the first time, we have observed here that the phenomenon of emission enhancement occurs during two opposite thermal events, gel-to-sol and sol-to-gel phase transitions, with the same gelator systems differentiated by the solvents only. The transmission of the chiral information within the supramolecular assembly has been investigated by CD spectroscopy. The structural elucidation is carried out based on the X-ray diffraction, spectroscopic data, and analysis of the photodimer distributions. Isotropic and molecularly aggregated systems were also investigated simultaneously to demonstrate the inherent selectivity and chirality in the gel state. The mechanistic background of the chiral selection process has been discussed and correlated with the different aspects of the gel chemistry.

Results and Discussion

Investigation of different gel systems and their selection to perform the photodimerization process: Gelator **G** consists of a 2Ac moiety attached covalently to a gallic acid backbone by means of a chiral amino alcohol linkage. In **G**, the 2Ac molecule is linked directly to the chiral center by an ester bond so that pronounced chiral induction can be transmitted to the ground-state orientation of the 2Ac moiety. **G** is expected to be capable of forming a one-dimensional molecular arrangement by means of intermolecular hydrogen-bonding through the amide linkage, π - π stacking interaction of the anthracene and benzene ring (in the gallic acid part), or even by the van der Waals interaction involved in long alkyl chains. The gelation ability of **G** has been tested in different organic solvents of varying polarity, including mixed solvents and chiral solvents (Table S1 in the Supporting Information). Firstly, to differentiate the systems precisely in terms of the solvent polarity, we have used mixed solvent systems. Secondly, to investigate the probability of inducing chirality directly by the solvent molecules, we have considered gel systems composed of enantiomeric and racemic varieties of the solvent, glycidyl methyl ether.

Keeping the versatility of the solvents in mind, we have selected the gel systems (Table 1) for performing the photo-reaction. It can be seen that among the different systems, only hexane can form a gel at room temperature. All other gels have been prepared by quenching below room temperature from 5 to 0 °C, depending upon the solvents. However, after formation, the gels **G-Mc**, **G-Mc/Hx**, **G-Mc/Ch**, and **G-Ch/Hx** were found to be stable (to an inversion of the test tube) even at room temperature. To elucidate the inherent strength and stability of the gel systems, we have examined their gel melting temperatures (T_{gel}). The results are presented in Figure 1. The phase above each curve is the sol, whereas the phase below each curve is the gel. In general, the T_{gel} values increase with an increase in the gelator concentration and finally tend to saturate. From these plots, one can clearly notice three distinct zones along the T_{gel} axis. Based on this observation, we have preliminarily categorized different gel systems as strong, such as **G-Hx**; moderately strong, such as **G-Mc**, **G-Mc/Hx**, **G-Mc/Ch**, and **G-Ch/Hx**; and weak gels like **G-Ge**, **G-RGe**, and **G-SGe**. The values of critical gelation concentration (CGC) and quenching temperatures also justify such classifications.

Table 1. Specifications of the investigated gel systems of **G**.

System	Sample	Solvent	CGC ^[a] [% w/v]	[G] ^[b] [% w/v]	T_{q} ^[c] [°C]
1	G-Hx	<i>n</i> -hexane	0.2	1	25
2	G-Mc	methylcyclohexane	0.25	1	5
3	G-Mc/Hx	methylcyclohexane/ <i>n</i> -hexane (1:1 v/v)	0.25	1	5
4	G-Mc/Ch	methylcyclohexane/cyclohexane (1:1 v/v)	0.25	1	5
5	G-Ch/Hx	cyclohexane/ <i>n</i> -hexane (1:1 v/v)	0.25	1	5
6	G-Ge	glycidyl methyl ether	0.8	1.5	0
7	G-RGe	(<i>R</i>)-glycidyl methyl ether	1.0	1.5	0
8	G-SGe	(<i>S</i>)-glycidyl methyl ether	1.0	1.5	0

[a] CGC=critical gelation concentration. [b] [**G**]=Concentration of **G** used. [c] T_{q} =quenching temperature.

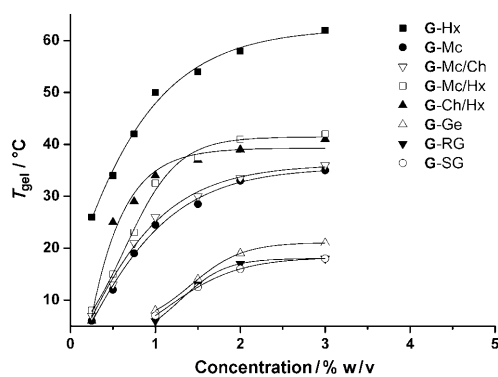


Figure 1. Plots of T_{gel} versus concentration for the gel systems with gelator **G**.

The enantiomeric solvent systems **G-RGe** and **G-SGe** give almost identical plots that also closely resemble those of the racemic variety. That means that the opposite chiralities of the enantiomeric solvents cannot influence the gelation ability of **G**. In the series of moderately strong gels, we can arrange the different solvent systems in order of increasing polarity: Ch/Hx < Mc/Hx < Mc/Ch < Mc, which is indeed reflected in the plots. Throughout the text, we shall discuss the different gel systems with their representative sample names (Table 1) and also when necessary we shall introduce new solvent systems for the discussion depending upon their relevancy. All the forthcoming experiments including the photodimerization process have been carried out using the same gelator concentrations as indicated in Table 1 unless otherwise noted, so that we can safely discuss and correlate among different experimental results.

Morphology of the gel samples: The morphology of the gel samples provides us with direct evidence about the existence of a one-dimensional molecular arrangement. Before proceeding to the photoreaction step, therefore, we have performed SEM studies of the xerogels as presented in Figure 2 (corresponding TEM images are presented in Figure S1 in the Supporting Information). A one-dimensional fibrillar arrangement is evident in all the images. The fibrillar diameters for the different samples lie in the range of 85 to 102 nm on average. The minute variations in the morphologies are likely to originate from the different degrees of participation of the noncovalent interactions responsible for creating the one-dimensional molecular arrangement. The relative solvent polarities probably play the major role in this. TEM images of **G-RGe** and **G-SGe** (Figure S1) give some hints of short-range twisted fibers. Efforts to correlate these findings with the other results will be made in the forthcoming sections. However, it is clear that the above

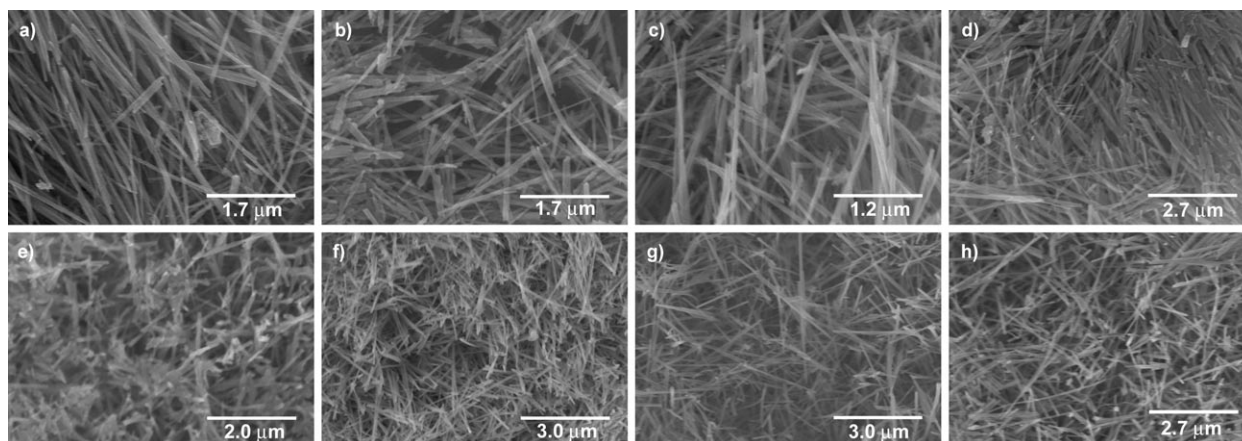


Figure 2. SEM pictures of the xerogels prepared from gelator **G** with varying solvents: a) **G**-Hx, b) **G**-Mc, c) **G**-Mc/Ch, d) **G**-Mc/Hx, e) **G**-Ch/Hx, f) **G**-Ge, g) **G**-RGe, and h) **G**-SGe.

morphological investigation proves not only the presence of a perfect molecular platform to initiate a stereochemical process, but also the scope to fine-tune the selectivity in the photochemical process by the solvent-induced molecularly different gelator arrangements.

Stereochemistry of 2Ac photodimers produced from the photodimerization of **G in the gel matrices:** The gel samples prepared under inert conditions were photoirradiated at a wavelength of 366 nm at constant temperature. Photoreaction is not reversible at this wavelength. As the samples were photoirradiated, the intensity of the 1L_a absorption band of monomeric 2Ac gradually decreased (Figure S2 in the Supporting Information), thus signifying their conversion to the dimer. Simultaneously, the physical state changed from gel to sol. Since the photoreaction temperature remained below the gel melting temperature, the observed phase transition should be ascribed to a photoinduced process. After the reaction the solvents were first removed and then the samples were hydrolyzed in alkaline medium to separate 2Ac dimers and unreacted monomer from the gela-

tor backbone. In the next steps, the photoproducts were isolated and finally subjected to the HPLC analysis (the details of the process are described in the Experimental Section). The relative yields and *ee* values for the different photodimers were calculated from the HPLC chromatogram (Figure S3 in the Supporting Information).

The distribution of the photodimers and corresponding *ee* values obtained from different gel systems are summarized in Table 2. In general, all the gel samples produce h-h photodimers as the major products. It is worth mentioning here that under the isotropic conditions, h-t photodimers are always the major products due to their thermodynamic stability. The abundance of h-h photodimers is almost exclusive to all the gel samples except for the systems with the chiral solvent (racemic and enantiomeric) glycidyl methyl ether, in which h-t photodimers are also present in a substantial fraction. The solvent polarity is probably responsible for such a differentiation. Unlike nonpolar hexane, cyclohexane, and methylcyclohexane, glycidyl methyl ether is relatively polar in nature. The priority of the formation of h-h photodimers in the gel state can be explained well in terms

Table 2. Distribution and enantiomeric excess (*ee*) values of the 2Ac photodimers obtained from [4+4] photocyclodimerization in the gel samples of **G**.^[a]

Sample-state	Solvent	<i>T</i> [°C]	Conv. ^[b] [%]	Relative yield [%] ^[c]						<i>ee</i> [%] ^[c]	
				A	B	C	D	A+B (h-t)	C+D (h-h)	B (h-t)	C (h-h)
G -Hx-gel	<i>n</i> -hexane	5	25	9	7	47	37	16	84	30	-10
G -Mc-gel	methylcyclohexane	5	60	4	3	50	43	7	93	36	-30
G -Mc-sol		25	88	10	10	44	36	20	80	16	-9
G -Mc/Hx-gel	methylcyclohexane/ <i>n</i> -hexane (1:1 v/v)	5	47	5	3	49	43	8	92	41	-36
G -Mc/Ch-gel	methylcyclohexane/cyclohexane (1:1 v/v)	5	70	4	3	50	43	7	93	30	-30
G -Ch/Hx-gel	cyclohexane/ <i>n</i> -hexane (1:1 v/v)	5	43	4	3	50	43	7	93	41	-33
G -Ch-aggregate ^[d]	cyclohexane	10	81	9	9	44	38	18	82	20	-5
G -Ge-gel	glycidyl methyl ether	5	71	28	18	30	24	46	54	12	-44
G -Ge-sol		25	82	32	26	24	18	58	42	7	-1
G -RGe-gel	(<i>R</i>)-glycidyl methyl ether	5	75	26	17	31	26	43	57	11	-56
G -SGe-gel	(<i>S</i>)-glycidyl methyl ether	5	73	27	17	31	25	44	56	12	-56
G -THF ^[d]	THF	25	88	29	25	26	20	54	46	10	4

[a] Gel samples were photoirradiated for 120 min and all other samples were photoirradiated for 30 min. [b] Conv.=conversion. [c] The absolute configurations of B and C were not determined. The first eluted enantiomer is given a positive sign. Errors in relative yields are $\pm 0.5\%$ and in *ee* values are $\pm 1\%$ for major products and $\pm 2\%$ for minor products. [d] Gelator concentration: 1% w/v.

of the ground-state preorientation of the gelator molecules. Intermolecular hydrogen-bonding and π - π interactions should be the key factors that construct and control the one-dimensional arrangement of the gelator molecules in the gel state. Whereas the former is favored in h-h molecular orientation, the latter can be operative in both kind of orientations, h-h and h-t. In nonpolar solvents, these two factors operate cooperatively, thereby allowing h-h orientation almost exclusively. On the other hand, with a relatively polar solvent like glycidyl methyl ether, intermolecular hydrogen bonding is less favored, thereby resulting in some h-t photodimers as well. These results also resemble our previous studies.^[13,14] That means that the preferential formation of h-h photodimers in the gel state is now a well-documented phenomenon.

The next and most important issue for the "chirogenesis" would be the chirality factor expressed in terms of *ee* values. It is expected that the presence of excess chirality (in other words, *ee*) in the photodimers is governed by the inherent chirality of **G**, which is capable of differentiating preferentially among the preorientations of the gelator molecules in the ground state. However, it is remarkable that, depending upon the solvent, the % *ee* values displayed by the gel systems vary from -10 (minimum) to -56 (maximum) for the major chiral dimer C (h-h), and from +11 (minimum) to +41 (maximum) for the minor chiral dimer B (h-t). Such a high chiral excess value has never been achieved when using a soft template like an organogel. This unprecedented finding means that the present gel systems are truly capable of leading an enantiodifferentiating process. Careful observation of the data reveals that the binary solvent system (Ch/Hx) gives higher *ee* values relative to that of the corresponding single-solvent system (Mc). In addition, considering *ee* values for both the photodimers B and C, the chiral induction is most prominent for the binary solvent system Mc/Hx. For the highly stable and strong gel system **G**-Hx, the *ee* value for h-h photodimers is remarkably small, even though it possesses moderately high *ee* values for h-t photodimers. On the other hand, **G**-RGe produces the highest *ee* values for h-h photodimers, even though it gives the lowest *ee* values for h-t photodimers. The origin of such discriminations is probably the presence and the absence of intermolecular hydrogen bonding for h-h and h-t molecular orientations, respectively. Unlike the π - π stacking interactions, the hydrogen bonding is really sensitive to the solvent polarity. Thus, it is understandable that in the series of nonpolar solvents with little variation, *ee* values for the h-t photodimers do not change too much. However, in relatively polar solvent systems with glycidyl methyl ether (categorized as weak gels), the lack of favorable hydrogen-bonding interactions weakens the systems, especially the domain that consists of h-t molecular orientation, which is dependent solely on π - π stacking interactions and the compactness of the neighborhood. Here a big question comes to mind. Why does the strong gel (**G**-Hx) produce the lowest *ee* values, whereas the weak ones (**G**-Ge/**G**-RGe/**G**-SGe) provide the highest values for the major photodimers? At this stage of

discussion, we can explain this by the compactness of the gelator arrangement in terms of the T_{gel} values. The variation in *ee* values versus the corresponding T_{gel} values is depicted in Figure 3. Here again, one can see three distinct domains

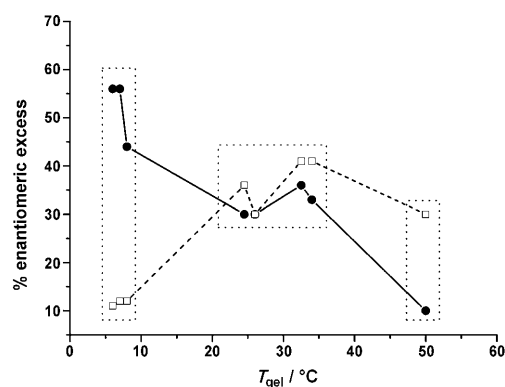


Figure 3. Plots of the *ee* values obtained from the photodimers produced in the gel state against the corresponding gel melting temperature (dotted rectangular boxes indicate different zones in the plot): ●, h-h photodimer C; □, h-t photodimer B.

(as indicated by the dotted rectangular boxes) that belong to strong, moderately strong, and weak gel systems based on the corresponding T_{gel} values. At this point, we should consider the gelation temperature (to initiate the gelation) too, because in principle it should follow a similar trend as that of the corresponding T_{gel} . Whereas the strong gel is formed at room temperature, others are formed only at low temperatures (Table 1). The energy difference between the relative orientations of 2Ac moieties that give enantiomeric photodimers should be very small. Such a differentiation is expected to become more prominent at low temperature. This is the reason why the *ee* values for h-h photodimers follow such an unexpected trend. This phenomenon is nicely supported by the similar *ee* values displayed by the gels formed under the similar quenching conditions. For h-t photodimers, the scenario is completely different, especially due to the lack of intermolecular hydrogen-bonding sites. Here, the environmental rigidity plays the key role in facilitating the excess chirality in the photodimers. Significantly, chiral h-h photodimers (i.e., C) have the highest relative yield in the gel state, thereby implying the environmental preference for chiral moieties. More detailed and informative discussions about such a chiral selection process will be made in the later sections.

To compare the results obtained from the gel state with the other isotropic states, we have performed similar photo-reactions in two additional environments. The sol states of the corresponding gel states for the systems **G**-Mc and **G**-Ge (as representatives) give an increased amount of h-t photodimers for the former system, and for the latter system, the selectivity is reversed to give h-t photodimers as major product. However, the presence of a high percentage of h-h photodimers even in the sol state for the system **G**-Mc indicates that some sort of molecular association is still

taking place therein. Actually, it may not be all that unusual to consider the possibility of hydrogen-bonded molecular association in such a nonpolar solvent. To support our prediction, we have performed similar experiment with cyclohexane (we shall denote the system as **G-Ch**), which forms only the molecular aggregate (Figure S4 in the Supporting Information) rather than the macroscopic gel. This system gives a similar result to those of the sol systems. That means the molecular association is the key factor for the high degree of chiral selection in the gel phase. The decrease in *ee* values in the sol and the aggregate systems justifies the same. The lowest *ee* value for **G-Ge**-sol system is evident due to the absence of any significant fraction of molecular association by means of the intermolecular hydrogen bonding in a relatively polar solvent environment, particularly at elevated temperatures. Similar photodimer distribution, including the *ee* values, is obtained from using THF, a non-gelating solvent. From the above discussion, there is no doubt that the stereochemical and chiral selectivity is inherent in the gel system in which the small difference in molecular orientations is amplified through the tight molecular packing mode.

In spite of the fact that the gelator chirality is likely to be the origin of excess chirality in the photodimers, we still expected some degree of perturbation from the enantiomeric solvent pair based on the preferential interaction of **G** with a particular enantiomer. To our surprise, both of the enantiomeric solvent systems provide almost identical photodimer distributions, including *ee* values with the same “sign.” This result means that solvent chirality has no influence on the preorientation of the gelator molecules. In other words, the gelator chirality apparently outweighed the effect of solvent chirality.

To examine the sensitivity of photodimer distribution towards the different physical parameters, we have performed a series of photoreactions by tuning the external factors. For a given range of concentrations, the product distribution remains almost unaffected for a particular solvent system (Table S2 in the Supporting Information). We have also examined the effect of quenching conditions during the formation of gel on the photodimer distribution (Table S3 in the Supporting Information). Here again, the photodimer distributions show minimal dependency on the quenching rate and even on the quenching temperature. We also have varied the relative proportions of the solvents in a given binary solvent system (Table S4 in the Supporting Information). The results show little variation in stereo- and enantioselectivities, probably due to the minute differences in the resultant solvent polarities. From the above findings, it is worth noting that the current gel systems are less sensitive to the environmental perturbations. In other words, the final stereochemistry is predetermined and maintained in a particular solvent system by immobilizing the orientations of the gelator molecules. This conclusion is a remarkable achievement, especially for a delicate process like chiral photoreaction.

In the forthcoming sections, we shall try to shed some light on the different mechanistic aspects that operate individually or cooperatively to determine the final stereochemistry of the photodimers. Of course, the final molecular orientations analyzed from the stereochemistry of the photodimers will be the key issue, based on which the correlations among the different experimental findings have to be made.

The absorption and the emission behaviors of the gel samples and their temperature dependency during the course of gel-to-sol phase transition:

It is a well-established and easily understandable phenomenon that the physical organogels are responsive to external stimuli such as temperature, through which the aggregate structure is stabilized or destabilized. During the stabilization process, the organogel structure is transformed to a more ordered, self-assembled mode. On the other hand, in the destabilization process such an aggregate structure is dissociated to reversibly form the molecularly free state, which results in a gel-to-sol phase transition. Thus, it provides us with a great opportunity to use a chromophore-bearing organogelator to follow the optical properties of the resulting assemblies in which the modulation of the chromophore packing involved in a hierarchical process directly influences the absorption and emission behaviors. Keeping in mind the above points, we have investigated the absorption and emission phenomena of the different solvent systems in the gel state (maintaining the conditions close to those of the photoreaction experiments) and also during the gel-to-sol phase transition with varying temperature. Among eight gel systems we had initially selected, the absorption and emission spectra (samples were excited at 400 nm) of the four representative solvent systems are presented in Figure 4. For the purposes of discussion, and where relevant, the rest of the spectra are presented in the Supporting Information. To study the absorption spectra, optically diluted samples (0.75 and 0.5% w/v for **G-Ge** and other gels, respectively) have been used. Here, we have monitored the 1L_a band of the anthracene moiety. The absorption spectra follow a similar response to the temperature enhancement for all the samples. The gel spectra are always less structured, and the absorption maxima are also redshifted relative to the sol phase attained at higher temperatures. One can consider this trend as aggregation-induced broadening, whereas the fine structure remains essentially the same. However, the **G-Ge** gel spectrum shows only a little deviation relative to that of the free state. The polar solvent probably limits the participation of hydrogen bonding, which is expected to be more sensitive to the temperature variation. In spite of that, the appearance of a small shoulder in the high-wavelength region is quite clear, and it also tails over 450 nm. Similar bands are visible for all other systems. Though the exact nature of the self-assembled aggregates formed in a gel structure is difficult to establish unambiguously, the redshifted spectral features suggest that the J-type aggregate structure is likely to be formed in the assembled state.^[15]

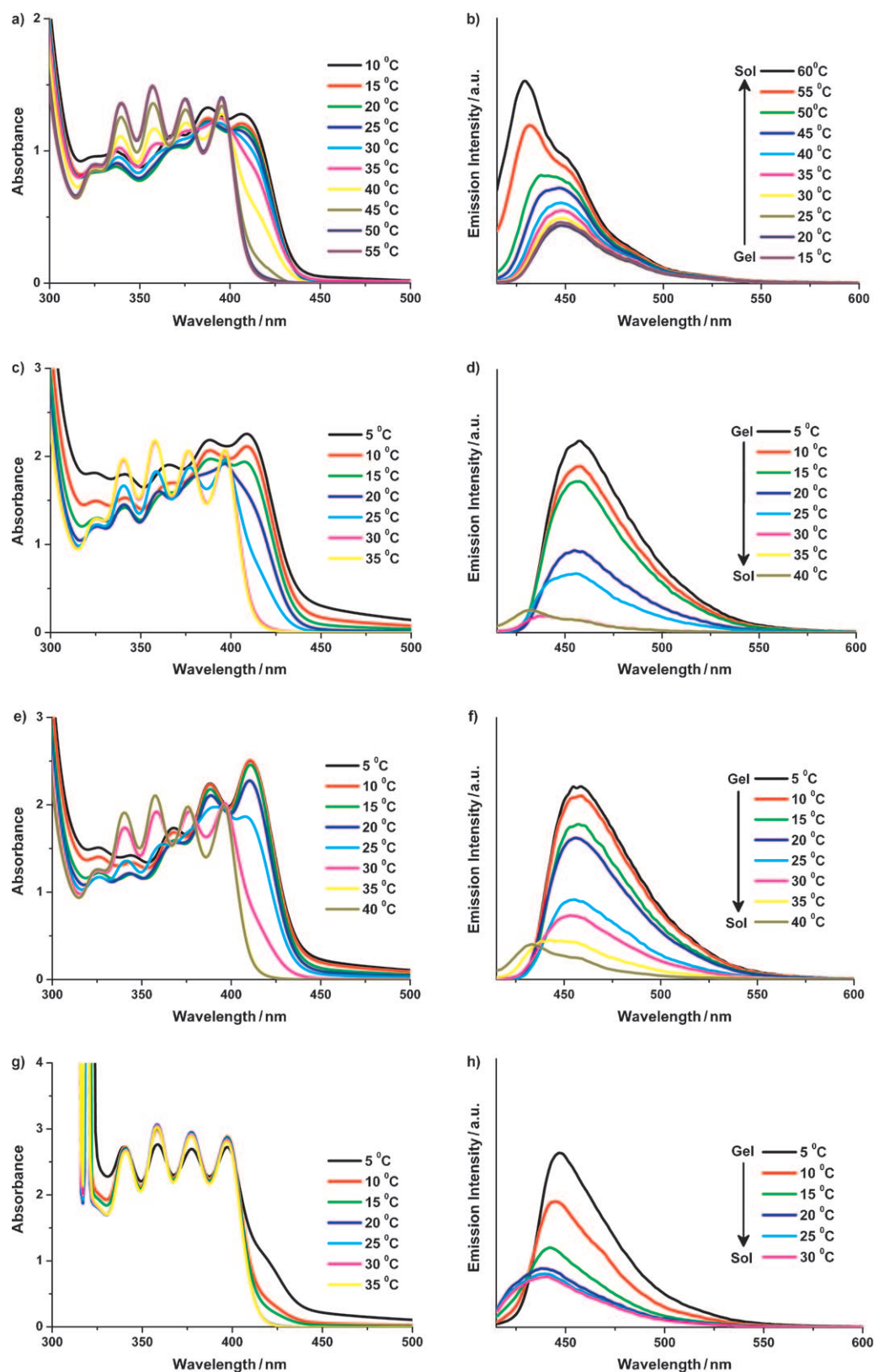


Figure 4. Representative absorption and emission spectra of the gel samples: a,b) G-Hx; c,d) G-Mc; e,f) G-Ch/Hx; g,h) G-Ge with varying temperatures.

The response of the emission spectra to thermal stimulation is even more drastic. In general, the gel-state emission spectra are broad and almost structureless. Similar to the absorption spectra, here, too, the λ_{max} is redshifted in the aggregate state relative to that of the free state, thereby supporting the presence of a J-aggregate structure of the chromophore. The driving forces for the chromophore organization are expected to be the hydrogen-bonding and π - π interactions. Here it should be kept in mind that unlike π - π stacking, the direct hydrogen bonding between two 2Ac molecules is not possible, as they are coupled with the gelator counterpart by means of the ester linkage. However, the amide group present in the gelator backbone can associate two units by intermolecular hydrogen bonding. The presence of the hydrogen-bonding motif away from the 2Ac moiety provides some sort of flexible microenvironment near the chromophore. Maybe this is the reason for the broad nature of the emission spectra. In support of this, **G-Hx**-gel (categorized as a strong gel), which bears the most favorable hydrogen-bonded molecular association produced from the least polar hexane, displays relatively well-defined emission spectra relative to the other systems. At the same time, the presence of two bands that correspond to the aggregate species (at a higher wavelength) and molecularly isolated species (at a lower wavelength) for the **G-Hx** system, even at 60 °C, support the view that still not all the chromophores are in the molecularly free state. This indeed reflects the rigidity of the gel structure. To generalize the idea, we have investigated the absorption and the emission behavior of gelator **G** dissolved in cyclohexane (**G-Ch**), which does not show any gel formation (Figure S4 in the Supporting Information). However, due to the nonpolar nature (similar to hexane and cyclohexane) of the solvent, we still expected the formation of molecular aggregates, particularly at lower temperatures. Modification of the absorption and the emission spectra with varying temperature points to our prediction. The presence of an emission peak that corresponds to the free chromophore, even at low temperatures, and the smaller degree of deviation relative to the other gel samples is justified when one considers the system **G-Ch** as an intermediate between highly organized gel and molecularly free solution state. As expected from the previous investigations, the enantiomeric solvent systems behave similarly (Figure S5 in the Supporting Information). Also, the binary solvent systems show little difference in the emission spectra (Figure S6 in the Supporting Information) because of the similar resultant solvent polarities.

During the investigation of the optical properties, the most remarkable finding was the completely opposite responses of the emission property of the gel samples during the gel-to-sol phase transition. In the **G-Hx** system, the emission intensity increases with the increase in temperature, whereas for all other systems it decreases as a result of temperature enhancement. This unusual behavior is rarely encountered, as it represents a sharp contrast to that exhibited by other typical thermotropic organogels.^[16] For a class of silole fluorogens, the enhancement of the fluorescence in

the aggregate state is explained by the “aggregation-induced enhanced emission” in which the restriction of intramolecular rotation is identified as the main cause.^[17] In another example, the luminescence enhancement of metallo gels at elevated temperatures has been explained in terms of the higher degrees of freedom and motion of the molecules at higher temperatures, thereby enhancing the chance of intermolecular aggregate formation to populate excimer formation.^[18] However, neither of these phenomena may be fully applicable to our systems, as we found opposite behaviors in the systems that have the same gelator molecule but different solvents. Therefore, a more meaningful choice would be to explain things in terms of the differentiating microenvironments created in the vicinity of the chromophore moieties.

To distinguish among the nature of molecular assemblies involved in the gel systems, we have plotted the emission intensities against the temperature (Figure 5). It is worth

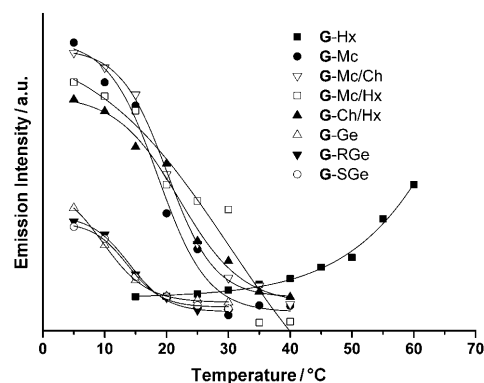


Figure 5. Plots of the emission intensity against the temperature for the gel samples with gelator **G**.

noting that even in this plot there are three distinct zones that consist of the three types of gel samples (strong, moderately strong, and weak). All the samples show a single-step sigmoidal transition, thus indicating the melting of the aggregates to the corresponding isotropic states.^[19] The influence of temperature is mostly prominent for the moderately strong gel systems for which the emission enhancements are six- to eightfold higher than the corresponding sol states. Enhancements are only threefold higher only for the glycidyl methyl ether solvent systems or the weak gels. As expected, **G-RGe** and **G-SGe** behave almost identically and also similar to their racemic counterpart **G-Ge**. In the sol state that usually occurs at elevated temperatures, the molecularly free species of the gelator is conformationally flexible, which typically allows the faster and more efficient nonradiative decay from the excited state. Formation of the gel upon molecular association reduces the conformational flexibility and consequently slows down the nonradiative decay process, thereby resulting in enhanced emission.^[15f] However, the above interpretation may be applicable to all systems except **G-Hx**. For **G-Hx**, the packing of the chromophore is strongest where we can apply the classical theory of concen-

tration quenching caused by the formation of excimers and exciplexes aided by the interactions between the aromatic molecules in the excited and ground states.^[20] This situation is very close to the solid-state fluorescence quenching. In moderately strong gel systems, the chromophores are placed in a comparatively flexible microenvironment that does not allow the concentration quenching due to the lack of chromophore proximity and at the same time reduces the probability of collisional quenching that is likely to occur at higher temperatures in the sol state. We can assume, therefore, that with an increase in temperature, **G-Hx** undergoes a transition from a tightly packed state to a conformationally flexible (however, still assembled) state causing the enhancement of the emission intensity. Here, the strength of the intermolecular association overcomes the effect of thermal agitation, which generally favors the nonradiative decay at elevated temperatures. It is remarkable that even at 60 °C the emission enhancement of **G-Hx** does not plateau (we did not increase the temperature further due the possibility of concentration modification over the boiling point of the solvent). It clearly demonstrates a very high degree of molecular association. As expected, the weak gel systems behave similarly to the moderately strong gels with a lesser extent of emission modification. To the best of our knowledge, this is the first example in which a single gelator molecule executes completely different emission behavior based on the differentiating microenvironments provided by the solvent polarity that fine-tunes the supramolecular interactions.

Transcription of molecular chirality in the gel systems: The high *ee* values of the photodimers, which result from the gel-state photoreaction, encouraged us to investigate the origin of such chiral induction with the help of CD spectroscopy. Representative CD spectra of different gel systems with varying temperatures prior to the photoreaction are presented in Figure 6. All the gels show an intense CD signal in the wavelength range of 2Ac absorption. Though much weakened, the CD signals still remain even in the sol state at elevated temperatures. That signifies the molecular chirality of **G**. However, the enhancement of the CD signals in the gel state definitely points to the existence of supramolecular chirality that originates from the molecular chirality, transcribed through the molecular assembly by means of the noncovalent interactions. The striking difference of **G-Hx** CD spectra compared to other gel systems lies in, firstly, the “sense” (or handedness) of chirality; secondly, very high ellipticity value; and thirdly, the well-defined “structure” of the spectra. At present, it is not fully clear to us why the sign of the CD signals inverts for the **G-Hx** system. However, it may be feasible to explain this phenomenon based on the final stereochemistry of the photodimers. Here, we have considered that in the tightly packed gel phase, the ground-state gelator arrangement does not alter in the short-lived excited state during the photoreaction. From the analysis of the photodimers, we could see that the signs of *ee* values that correspond to h–h and h–t photodimers are opposite (the absolute configurations are not determined). This means that in the ground state, the directions of the resul-

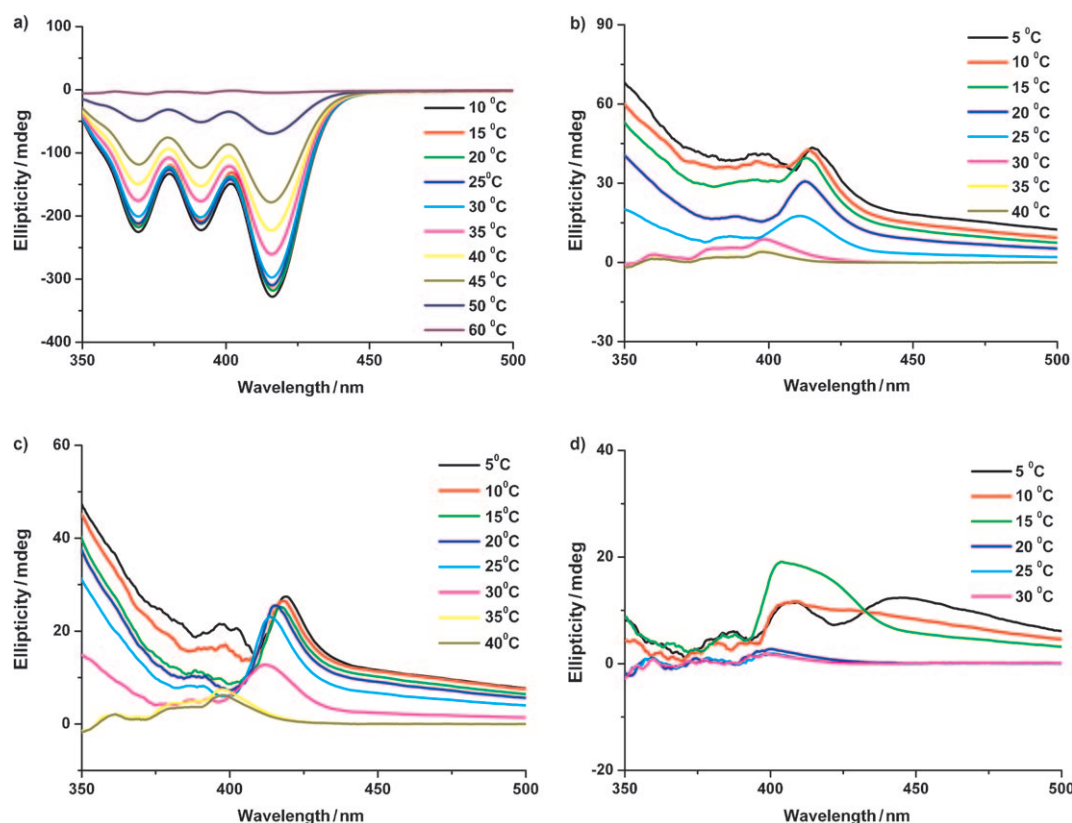


Figure 6. Representative CD spectra of the gel samples: a) **G-Hx**, b) **G-Mc**, c) **G-Ch/Hx**, and d) **G-Ge** with varying temperatures.

tant operating dipoles are likely to be opposite for h–h and h–t molecular orientations. Being major in the gel state, h–h molecular orientation is expected to determine the resultant CD signal. This is probably the reason why all the gel systems (except **G-Hx**) show “positive” CD signals. Our assumption is supported by the fact that **G-Ge** gel comprised of both h–h and h–t molecular orientations in competitive fractions (from the HPLC study) produces a comparatively weak, less-structured and an inconsistent variation of CD signal with temperature. However, in strong **G-Hx** gel dominated by the highly packed and conformationally rigid h–h molecular orientation, the moderately flexible domain that consists of h–t molecular orientation (lacking intermolecular hydrogen bonding) catalyzes and transcribes the chirality through the supramolecular interactions. The presence of higher *ee* values for h–t photodimers than the h–h photodimers justifies the situation. The high intensity of the CD signal probably results from the long-range ordered structure of the **G-Hx** gel. The possibility of the CD artifact originating from the macroscopic anisotropy of the chromophore was tested by measuring the linear dichroism (LD) spectra of the gel samples under similar conditions. Although a nonzero LD spectrum warns of possible CD artifacts, the weak intensity compared to the total observed CD signal at least ensures a confident discussion of the chirality.

On account of the thermal responsiveness of self-assembled fibers, variable-temperature CD spectroscopy provides an ideal approach for demonstrating the formation of nanoscale chiral aggregates. In Figure 7, the ellipticity values of

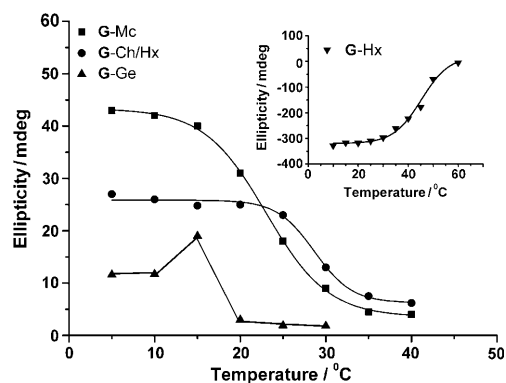


Figure 7. Plots of CD intensity against the temperature for the representative gel samples with gelator **G** (due to the difference in scale, the **G-Hx** system is presented as an inset).

the CD spectra (at $\lambda_{\text{max}} \approx 415$ nm) for the gel samples are plotted against the temperature. In all the cases, the CD signals diminish with heating, thus signifying that the self-assembled nanostructure has nanoscale chirality.^[6e,21] Again, the sigmoidal pattern of the plots indicates a one-step sequential disassembly similar to what we observed from the luminescence study. Here, too, we did not find any influence of the solvent chirality on the supramolecular chirality, as evident from the similar CD signals obtained with enantio-

meric solvent systems (Figure S7 in the Supporting Information). This clearly demonstrates that the inherent molecular chirality of **G** overcomes the effect of solvent chirality. However, with glycidyl methyl ether gel systems, the reason for an unusual hike in the CD signal near 15 °C is not clear to us. In none of the above samples could nanoscale chirality be visualized by electron microscopy, probably due to the absence of any helical twist in the fibrillar assemblies.

From the above discussions, it is clear that the molecular chirality of the gelator molecule is indeed transmitted to the nanoscale supramolecular chirality through the ordering of the chromophore in the assembled phase. One may therefore expect that a simple correlation might exist between the degree of supramolecular chirality and the *ee* values obtained from the photodimers as a result of photodimerization. To our surprise, however, the results are just the reverse. This means that the supramolecular chirality in the ground state is not enough to control the final chirality obtained from the photochemical process through the transition state. It is the molecular chirality that actually determines the preorientation of the gelator molecules depending upon other physical factors that control the hierarchical process. This might be the reason for the low *ee* values obtained in our previous noncovalent approach.^[13] The possible correlations of the molecular chirality with other factors will be discussed in the latter sections.

Structural investigation: To differentiate among the molecular arrangements in different gel samples, we have performed X-ray diffraction experiments of the xerogels. The results are presented in Figure 8. All four xerogel samples show a diffuse halo in the wide-angle region that corresponds to the distance of 4.0–4.5 Å, which is usually attribut-

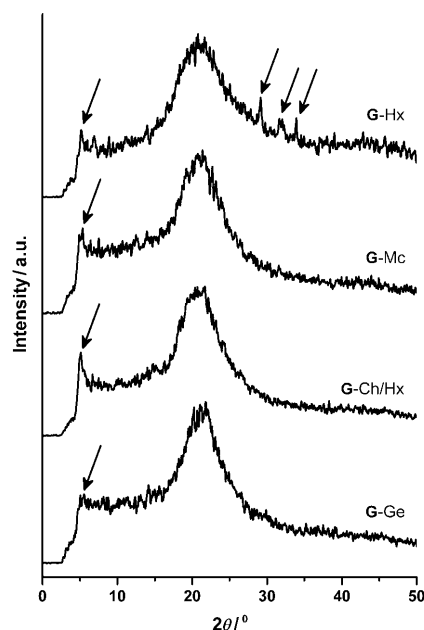


Figure 8. X-ray diffractograms of the xerogels prepared from the gel samples with gelator **G** (diffraction peaks are indicated with arrows).

ed to the disordered alkyl chains.^[15c] The sharp peak observed in the low-wavelength region varies slightly between 17.1, 16.5, 17.3, and 16 Å for the systems **G-Hx**, **G-Mc**, **G-Ch/Hx**, and **G-Ge**, respectively. In addition, the **G-Hx** system possesses diffraction peaks that correspond to the distances of 3.2, 2.8, and 2.6 Å, which are significantly absent for other gel systems. To satisfy the cooperative contribution of intermolecular hydrogen-bonding and π - π stacking interactions, we have approximated that the benzene ring in the gallic acid moiety and the anthracene moiety are placed in more or less same molecular plane. However, some offsets are likely to have taken place due to the interaction among the similar groups. Now, we can consider a typical columnar arrangement, as represented in Figure 9, in which the gelator molecules are stacked in a one-above-the-other fashion. The width of the column as calculated from the energy minimized orientations is longer (≈ 25 Å) than the distance we obtained from the low-angle diffraction peaks present in all four samples. To rationally explain this deviation, we considered some degree of tilt for the stacking planes. This situation would also satisfy the J-

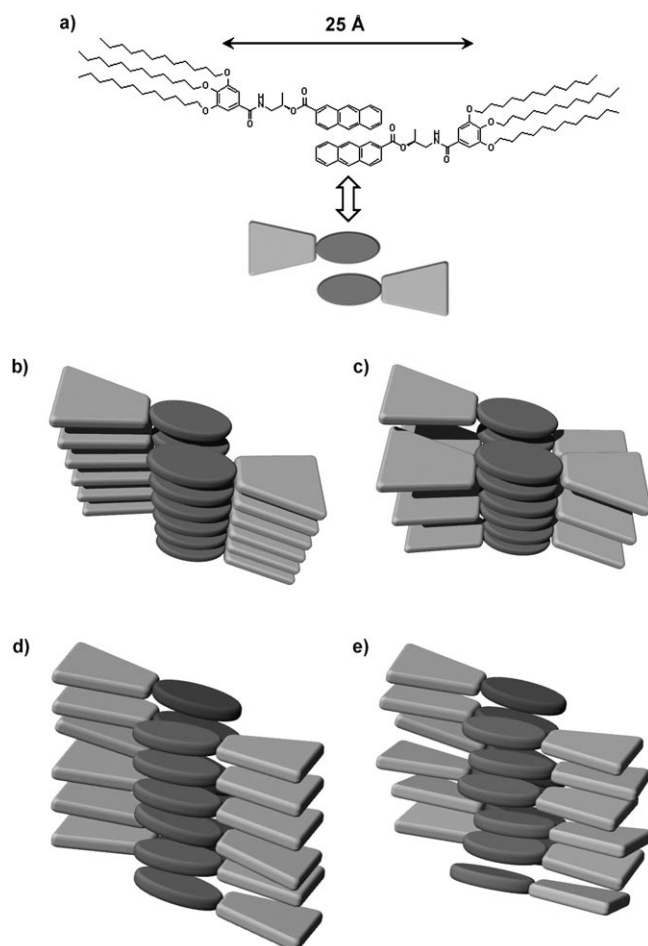


Figure 9. Models for the gelator arrangements in the gel samples with gelator **G** based on their orientations: a) molecular scale of **G**; b) h-h for strong gel; c) h-t; d) h-h for moderately strong gel; and e) h-h for weak gel.

aggregate molecular assembly. The origin of the unique wide-angle diffraction peak for the **G-Hx** system for a distance approximately 3.2 Å can be attributed to the intracolumnar spacing between two stacked molecular planes. This distance is a little shorter than that of typical π -stacked systems.^[15c,f,16d] However, in a very tightly packed gelator arrangement, the stacking distance can be shortened. The absence of similar diffraction peaks for other gel systems signifies the lack of such compactness. For **G-Ge**, even the low-angle peak is less prominent. Also, the FTIR spectra (Figure S8 in the Supporting Information) of the xerogels clearly demonstrate the lower N-H stretching frequency for **G-Hx** (3263 cm^{-1}) relative to other systems ($\approx 3286\text{ cm}^{-1}$). That means that the **G-Hx** system possesses the strongest hydrogen bonding.

From the above observations, we can now safely conclude **G-Hx** to be a strong gel, **G-Mc**, **G-Ch/Hx**, and similar systems to be moderately strong gels, and **G-Ge** and enantiomeric solvent systems to be weak gels. To explain the abundance of the photodimers in terms of relative orientations (h-h or h-t), we have proposed two separate packing models for h-h and h-t molecular orientations (Figure 9). Similar arrangement modes are evident from the similar columnar thicknesses, as indicated by the presence of low-angle diffraction peaks irrespective of the nature of the solvents. We can then consider a gelator arrangement that comprises the domains for either h-h or h-t molecular orientations. The gel systems other than the glycidyl methyl ether solvent systems consist almost exclusively of a single domain that has h-h molecular orientation. On the other hand, **G-Ge** gels include both kinds of domains in competitive proportions. The resultant chirality and relative compactness are not demonstrated in this model because it would require detailed molecular modeling based on precise energy considerations, especially for the gels that have the same gelator molecule differentiated only by the nature of solvents. Relative strengths of the gels are also taken into account in the proposed model. Here, such categorization has been made based on h-h molecular orientation only, because we consider h-t orientation to be inherently weak due to the absence of intermolecular hydrogen bonding. However, it is significant to find the evidence for different degrees of compactness from the X-ray data based solely on the nature of the solvents.

Mechanistic aspects behind the stereo- and the enantioselectivities:

From all the above-mentioned discussions, we can now interpret that the key factors behind the selective nature of photodimerization in the gel state are, firstly, the solvent polarity, which controls the participation of the intermolecular hydrogen bonding, and secondly, the gelation temperature. Nonpolar solvents and low gelation temperatures favor intermolecular hydrogen bonding, thereby leading to the cooperative participation with π - π interactions to result in h-h molecular orientation; conversely, higher gelation temperatures and a polar solvent environment favor h-t molecular orientations based on π - π interactions and

steric factors due to the weak nature of intermolecular hydrogen bond. Thus, it is understandable why the nonpolar solvents systems result in h–h photodimers almost exclusively. Similarly, the gels with the relatively polar glycidyl methyl ether result in both h–h and h–t photodimers in competitive proportions. Among the different gel systems studied, the rigid nature of the **G**-Hx system is also evident from the least conversion during the photoreaction, thereby indicating the unfavorable microenvironment for undergoing such a process. Photoresponsive gel-to-sol phase transition during the photodimerization definitely corresponds to the disruption of molecular arrangement as a result of dimer formation. This fact means that such a process demands some degree of environmental flexibility (see Figure 9). In the case of chiral induction, the situation is not so straightforward. Here, the gelation temperature plays a crucial role. As the energy difference between the two molecular orientations that give the enantiomeric photodimers is very small, lower temperatures should facilitate such a differentiation. At the same time, the connection of the anthracene moiety to the chiral center demands conformational flexibility that leads to some sort of deviation from ideal coplanar molecular arrangements. Such an orientational freedom is permissible in relatively flexible gelator arrangements, or, in other words, for moderately strong and weak gel systems. These factors are mostly prominent in **G**-RGe and **G**-SGe gels, which possess the lowest gelation temperature and weaker molecular arrangement, thereby giving rise to the highest *ee* values for h–h photodimers. However, if temperature were to be the sole factor, then even h–t photodimers would result in high *ee* values. In fact, among the different gel systems, these systems possess the lowest *ee* values for the h–t photodimers, thus signifying that in the absence of intermolecular hydrogen bonding the h–t molecular arrangement is too weak to induce the chirality. The high *ee* values of the h–t photodimers for the **G**-Hx system confirm the same, because in the absence of intermolecular hydrogen bonding, the h–t molecular arrangement gains the desired conformational flexibility. In the moderately strong gel systems, we obtained the medium *ee* values for both h–h and h–t photodimers. From the variation of *ee* values with T_{gel} (Figure 3), it can be concluded that for the highly ordered h–h molecular orientation, gelation temperature dictates the resultant chirality induced in the photodimers, whereas for the inherently weak h–t molecular orientation, the effect of gelation temperature is not reflected on account of the lack of molecular arrangement. As expected, the stereochemical selection is low in the sol state, lower in the molecular aggregate state, and lowest in nongelating THF. This means that a one-dimensional molecular arrangement created in the gel state is the mandatory factor for a high degree of stereo- and enantioselectivity. In this molecular platform, other physical parameters operate individually or cooperatively to control the gelator preorientation, which in turn determines the final stereochemistry of the photodimers. In gel chemistry the stronger gel generally demands priority. However, this is an extraordinary finding in which even the “weak”

gel demonstrates its superiority over the stronger member. Here, for the first time, we have executed a highly stereoselective and enantiodifferentiating chiral photochemical process using a soft template. Moreover, the stereochemistry of the photoproducts can be tuned simply by the solvent selection. This study will certainly bring new prospects to the wealth of gel chemistry.

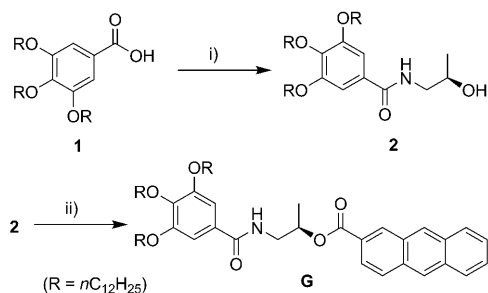
Conclusion

In conclusion, we have demonstrated the highly stereoselective and enantiodifferentiating photodimerization process performed in the gel state with an anthracene-bearing chiral organogelator. Different degrees of stereo- and enantioselectivities have been obtained from the gels prepared from different organic solvents. Interestingly, the **G**-Hx system behaves differently from the rest of the members due to having the highest degree of molecular packing. A one-dimensional molecular arrangement mode and the gelation temperature are found to be responsible for fine-tuning the final stereochemistry of the photodimers. Photoluminescence measurements demonstrated unprecedented variations in which the emission intensity of the **G**-Hx system increases during the gel-to-sol phase transition, unlike the other systems, which show a decrease in the emission intensity during this course. In the gel state, the *ee* values of h–h (major) photodimers increase from strong to moderately strong to weak gel systems, whereas h–t (minor) photodimers maintain the reverse trend. On the basis of spectroscopic findings, gel melting temperatures, and X-ray diffraction patterns, the gel systems are categorized as strong, moderately strong, and weak gels. This “model” can satisfactorily explain the different experimental findings. This is the first example in which a chiral photochemical process is performed in the gel medium and, as a result, a high degree of chiral induction has been achieved and controlled precisely by the one-dimensional gelator assembly created by the supramolecular interactions. This study is believed to add a new dimension in the field of supramolecular chirogenesis.

Experimental Section

General: All starting materials and solvents were purchased from Tokyo Kasei Organic Chemicals or Wako Organic Chemicals and used as received. The ^1H NMR spectra were recorded using a Bruker 300 (300 MHz) spectrometer. Chemical shifts are reported in ppm downfield from tetramethylsilane (TMS) as the internal standard. Mass spectra data were obtained using a Perspective Biosystems Voyager DE RP MALDI-TOF mass spectrometer. UV/Vis, circular dichroism (CD), luminescence, and IR spectra were recorded using a Shimadzu UV-2500 PC spectrophotometer, a JASCO J-720WI spectropolarimeter, a Perkin–Elmer LS 55 luminescence spectrometer, and Perkin–Elmer Spectrum One FTIR spectrometer, respectively.

Synthesis: Gelator **G** was prepared by the esterification of 2-anthracene-carboxylic acid (2Ac) and alcohol **2** (Scheme 2). Compound **1** was synthesized according to the method described earlier.^[13]



Scheme 2. Reagents and conditions: i) (*R*)-(-)-1-amino-2-propanol, BOP, TEA, CH_2Cl_2 , RT, 3 h; ii) 2-anthracenecarboxyl chloride, pyridine, dry benzene, RT, 3 h.

Synthesis of 2: Compound **1** (1 gm, 1.5 mmol) and benzotriazole-1-yloxytris(dimethylamino)phosphonium hexafluorophosphate (BOP) reagent (721 mg, 1.6 mmol) were dissolved in dry CH_2Cl_2 . (*R*)-(-)-1-Amino-2-propanol was added, followed by triethylamine (TEA), and the reaction mixture was stirred for 3 h at RT under an Ar atmosphere. The progress of the reaction was checked by TLC. The reaction mixture was first diluted by adding excess CH_2Cl_2 and then the organic layer was washed three times with distilled water, 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, hexane/ethylacetate=1:1 (v/v)) to give compound **2** (890 mg, 82%) as white solid. ^1H NMR (300 MHz, CDCl_3 , TMS): δ =0.88 (t, J =6.8 Hz, 9H), 1.26–1.47 (m, 54H), 1.56 (m, 3H), 1.73–1.82 (m, 6H), 2.52 (s, 1H), 3.65 (m, 1H), 3.96–4.02 (m, 8H), 6.45 (m, 1H), 6.97 ppm (s, 2H); MALDI-TOF MS (dithranol): m/z : calcd for $[\text{M}+\text{Na}^+]$: 754.63; found: 754.56; elemental analysis calcd (%) for $\text{C}_{46}\text{H}_{85}\text{NO}_5$: C 75.46, H 11.7, N 1.91; found: C 75.45, H 11.64, N 1.93.

Synthesis of 2-anthracenecarboxyl chloride: 2Ac (289 mg, 1.3 mmol) was dispersed in dry benzene (50 mL) at 50°C and a catalytic amount of DMF was added. Oxalyl chloride (1.7 g, 13 mmol) was added dropwise and the reaction mixture was stirred at approximately 70°C under reflux conditions for 18 h. After cooling to RT, the solvent and excess oxalyl chloride were distilled off, washed with dry benzene, and again evaporated to obtain a yellow solid that was used in the next step without further purification.

Synthesis of G: Compound **2** (800 mg, 1.1 mmol) was dissolved in dry benzene (10 mL) that contained a trace of pyridine, and 2-anthracenecarboxyl chloride dissolved in dry benzene (20 mL) was added slowly with constant stirring. The reaction mixture was allowed to stir for 4 h at RT. The progress of the reaction was checked with TLC. Distilled water (20 mL) was added and the mixture was extracted with chloroform several times. The organic layer was washed three times with distilled water, 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, hexane/ethylacetate=1:1 (v/v)) to give compound **G** (757 mg, 74%) as a yellow solid. ^1H NMR (300 MHz, CDCl_3 , TMS): δ =0.88 (t, J =6.8 Hz, 9H), 1.26–1.47 (m, 54H), 1.56 (m, 3H), 1.69–1.77 (m, 6H), 3.79 (m, 2H), 3.93 (m, 6H), 5.45 (m, 1H), 6.63 (m, 1H), 6.91 (s, 2H), 7.52 (m, 2H), 7.98–8.02 (m, 4H), 8.44 (s, 1H), 8.57 (s, 1H), 8.82 ppm (s, 1H); MALDI-TOF MS (dithranol): m/z : calcd for $[\text{M}+\text{Na}^+]$: 958.69; found: 958.78; elemental analysis calcd (%) for $\text{C}_{61}\text{H}_{93}\text{NO}_6$: C 78.24, H 10.01, N 1.50; found: C 78.10, H 9.98, N 1.49.

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

Gel-sol transition temperature (T_{gel}): T_{gel} values were measured by the test-tube-tilting method in which a test tube containing the gel was immersed inversely in a thermostatted bath and the temperature was raised at 0.5°C min⁻¹. The T_{gel} was considered to be the temperature at which

the mass started to flow. The error involved in the measurement of T_{gel} was $\pm 1^\circ\text{C}$.

SEM measurements: A thin layer of the gel sample was prepared over a carbon-coated copper grid and dried under vacuum for 24 h to obtain the xerogel. The sample was then shielded by Pt and examined using a Hitachi S-5000 scanning electron microscope.

TEM measurements: A thin layer of the gel sample was prepared over a carbon-coated copper grid and dried under vacuum for 24 h to obtain the xerogel. TEM studies were carried out using a JEOL JEM-2010.

XRD studies: X-ray data were recorded using a Rigaku R-axis instrument. The gel sample was prepared in a sample tube and frozen in liquid nitrogen. The frozen specimen was evaporated under vacuum for 24 h. The obtained xerogel was put into a glass capillary ($d=0.7$ mm). The diffractogram was recorded on an imaging plate using Cu radiation ($\lambda=1.54178$ Å).

General procedure for photochemical reaction, product isolation, and product analysis:

The different gel samples of gelator **G** were prepared in a capped quartz cell of 1 mm path length under an argon atmosphere and irradiated at a wavelength of 366 nm using a USHIO Optical Modu-lex Deep UV 500 instrument through UV-35 and UV-D36C optical filters at a constant temperature. After the photoreaction, the solvent was first removed at 55°C and then under high vacuum for 24 h. The dried product was then hydrolyzed in a 1,4-dioxane/water mixture with 1 M KOH for 15 h and poured into a 25 mM borate buffer solution of pH 9. The reaction mixture was filtered to isolate 2Ac photodimers and unreacted monomer, and then they were neutralized partially (to a pH $\approx$ 9). This solution (50 mM, 10 μL) was subjected to HPLC analysis. The same procedure was employed for the sol, aggregate, and THF systems. Analysis of the photoproducts was performed using chiral HPLC with tandem columns Inertsil ODS-2 (GL Sciences) and Chiralcel OJ-RH (Daicel). 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 the eluent. Relative yield and *ee* values were determined from the peak area on the HPLC chromatogram, detected by the absorbance at 254 nm.

Acknowledgements

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- [1] G. A. Hembury, V. V. Borovkov, Y. Inoue, *Chem. Rev.* **2008**, *108*, 1.
- [2] a) H. D. Becker, *Chem. Rev.* **1993**, *93*, 145, and references therein; b) H. D. Roth, *Angew. Chem.* **1989**, *101*, 1220; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1193.
- [3] a) A. Nakamura, Y. Inoue, *J. Am. Chem. Soc.* **2005**, *127*, 5338; b) C. Yang, A. Nakamura, T. Wada, Y. Inoue, *Org. Lett.* **2006**, *8*, 3005; c) H. Ikeda, T. Nihei, A. Ueno, *J. Org. Chem.* **2005**, *70*, 1237; d) C. Yang, T. Mori, Y. Origane, Y. H. Ko, N. Selvapalam, K. Kim, Y. Inoue, *J. Am. Chem. Soc.* **2008**, *130*, 8574; e) C. Ke, C. Yang, T. Mori, T. Wada, Y. Liu, Y. Inoue, *Angew. Chem.* **2009**, *121*, 6803; *Angew. Chem. Int. Ed.* **2009**, *48*, 6675.
- [4] C. Yang, M. Nishijima, A. Nakamura, T. Mori, T. Wada, Y. Inoue, *Tetrahedron Lett.* **2007**, *48*, 4357.
- [5] Y. Ishida, Y. Kai, S. Kato, A. Misawa, S. Amano, Y. Matsuoka, K. Saigo, *Angew. Chem.* **2008**, *120*, 8365; *Angew. Chem. Int. Ed.* **2008**, *47*, 8241.
- [6] a) K. Murata, M. Aoki, T. Suzuki, T. Harada, H. Kawabata, T. Komori, F. Ohseto, K. Ueda, S. Shinkai, *J. Am. Chem. Soc.* **1994**, *116*, 6664; b) A. Ajayaghosh, R. Varghese, S. J. George, C. Vijayakumar, *Angew. Chem.* **2006**, *118*, 1159; *Angew. Chem. Int. Ed.* **2006**, *45*, 1141; c) S. J. George, A. Ajayaghosh, P. Jonkheijm, A. P. H. J. Schenning, E. W. Meijer, *Angew. Chem.* **2004**, *116*, 3504; *Angew. Chem. Int. Ed.* **2004**, *43*, 3422; d) V. K. Praveen, S. S. Babu, C. Vi-

- jayakumar, R. Varghese, A. Ajayaghosh, *Bull. Chem. Soc. Jpn.* **2008**, *81*, 1196; e) D. K. Smith, *Chem. Soc. Rev.* **2009**, *38*, 684, and references therein.
- [7] a) K. Murata, M. Aoki, T. Nishi, A. Ikeda, S. Shinkai, *J. Chem. Soc. Chem. Commun.* **1991**, 1715; b) Y.-L. Zhao, J. F. Stoddart, *Langmuir* **2009**, *25*, 8442; c) K. Uchida, S. Yamaguchi, H. Yamada, M. Akazawa, T. Katayama, Y. Ishibashi, H. Miyasaka, *Chem. Commun.* **2009**, 4420.
- [8] J. Eastoe, M. Sanchez-Dominguez, P. Wyatt, R. K. Heenan, *Chem. Commun.* **2004**, 2608.
- [9] a) M. Ayabe, T. Kishida, N. Fujita, K. Sada, S. Shinkai, *Org. Biomol. Chem.* **2003**, *1*, 2744; b) Y. Sako, Y. Takaguchi, *Org. Biomol. Chem.* **2008**, *6*, 3843.
- [10] C. Wang, D. Zhang, J. Xiang, D. Zhu, *Langmuir* **2007**, *23*, 9195.
- [11] a) Y. C. Lin, R. G. Weiss, *Macromolecules* **1987**, *20*, 414; b) P. Terech, R. G. Weiss, *Chem. Rev.* **1997**, *97*, 3133.
- [12] J. H. Jung, Y. Ono, S. Shinkai, *Angew. Chem.* **2000**, *112*, 1931; *Angew. Chem. Int. Ed.* **2000**, *39*, 1862.
- [13] A. Dawn, N. Fujita, S. Haraguchi, K. Sada, S. Shinkai, *Chem. Commun.* **2009**, 2100.
- [14] A. Dawn, N. Fujita, S. Haraguchi, K. Sada, S.-i. Tamaru, S. Shinkai, *Org. Biomol. Chem.* **2009**, *7*, 4378.
- [15] a) M. Shirakawa, N. Fujita, T. Tani, K. Kaneko, S. Shinkai, *Chem. Commun.* **2005**, 4149; b) M. Shirakawa, S.-i. Kawano, N. Fujita, K. Sada, S. Shinkai, *J. Org. Chem.* **2003**, *68*, 5037; c) F. Würthner, C. Thalacker, S. Diele, C. Tschierske, *Chem. Eur. J.* **2001**, *7*, 2245; d) S. Yao, U. Beginn, T. Gress, M. Lysetska, F. Würthner, *J. Am. Chem. Soc.* **2004**, *126*, 8336; e) J. W. Chung, B.-K. An, S. Y. Park, *Chem. Mater.* **2008**, *20*, 6750; f) Y.-T. Shen, C.-H. Li, K.-C. Chang, S.-Y. Chin, H.-A. Lin, Y.-M. Liu, C.-Y. Hung, H.-F. Hsu, S.-S. Sun, *Langmuir* **2009**, *25*, 8714.
- [16] a) Y. Kamikawa, T. Kato, *Langmuir* **2007**, *23*, 274; b) S. Manna, A. Saha, A. K. Nandi, *Chem. Commun.* **2006**, 4285; c) F. Camerel, L. Bonardi, M. Schmutz, R. Ziessel, *J. Am. Chem. Soc.* **2006**, *128*, 4548; d) G. Palui, A. Banerjee, *J. Phys. Chem. B* **2008**, *112*, 10107; e) S. Qu, L. Zhao, Z. Yu, Z. Xiu, C. Zhao, P. Zhang, B. Long, M. Li, *Langmuir* **2009**, *25*, 1713.
- [17] a) B.-K. An, D.-S. Lee, J.-S. Lee, Y.-S. Park, H.-S. Song, S.-Y. Park, *J. Am. Chem. Soc.* **2004**, *126*, 10232; b) Y. Hong, J. W. Y. Lam, B. Z. Tang, *Chem. Commun.* **2009**, 4332, and references therein.
- [18] A. Y.-Y. Tam, K. M.-C. Wong, V. W.-W. Yam, *J. Am. Chem. Soc.* **2009**, *131*, 6253.
- [19] S. S. Babu, S. Mahesh, K. K. Kartha, A. Ajayaghosh, *Chem. Asian J.* **2009**, *4*, 824.
- [20] a) J. B. Birks, *Photophysics of Aromatic Molecules*, Wiley, New York, **1970**; b) N. J. Turro, *Modern Molecular Photochemistry*, University Science Books, Mill Valley, **1991**.
- [21] A. R. Hirst, B. Huang, V. Castelletto, I. W. Hamley, D. K. Smith, *Chem. Eur. J.* **2007**, *13*, 2180.

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