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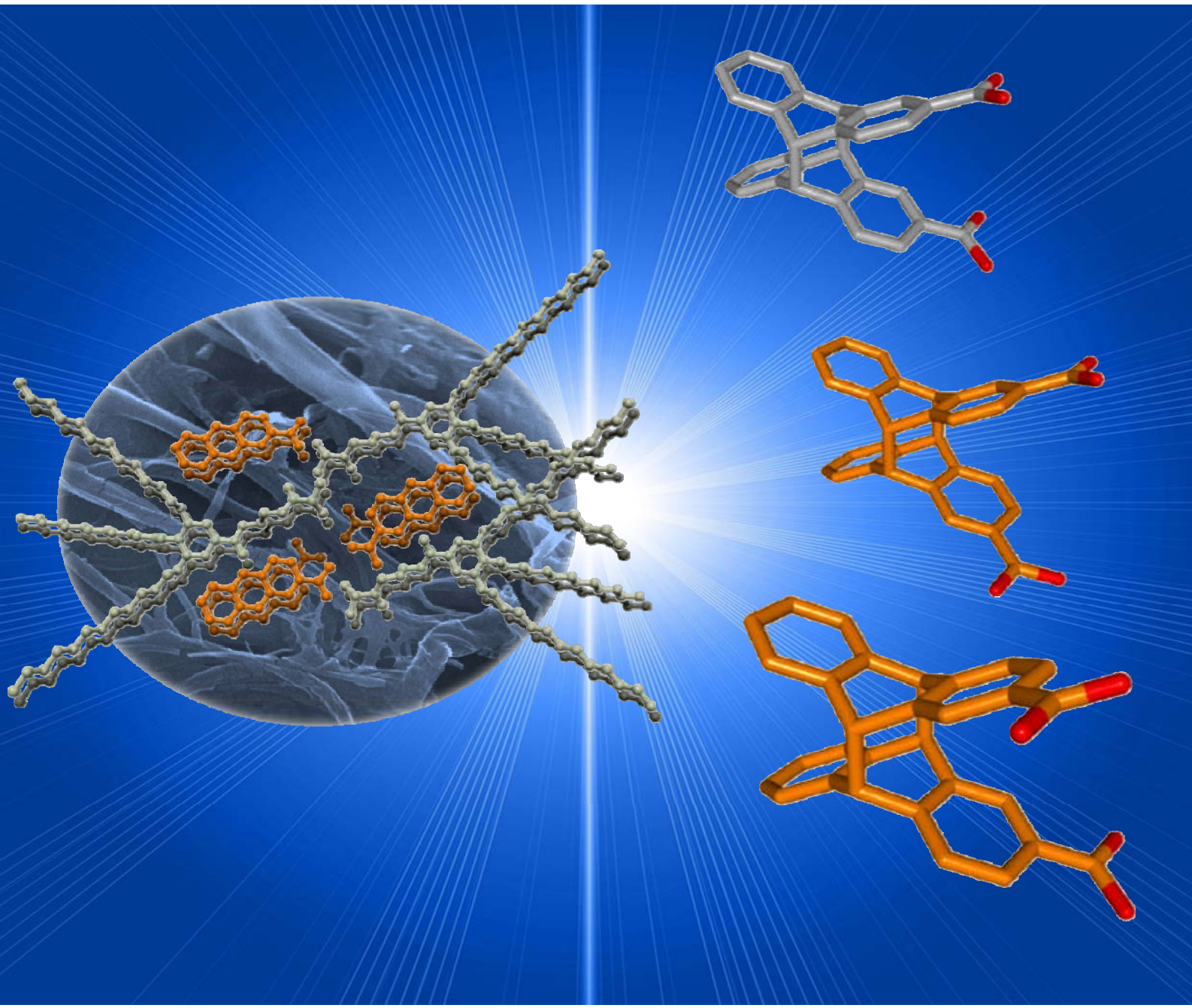

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An organogel system can control the stereochemical course of anthracene photodimerization†‡

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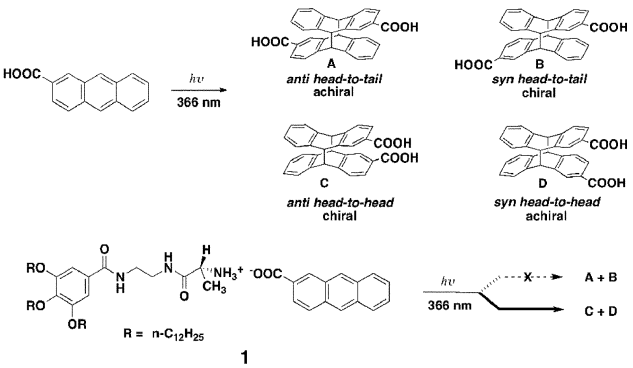
A novel photoresponsive organogel with a binary gelator containing 2-anthracenecarboxylic acid shows a high degree of stereochemical control, resulting in *head-to-head* photocyclodimers exclusively together with significant enantiomeric excess induced by the chiral counterpart of the gelator.

Chirality that is induced, monitored, controlled, or applied *via* the principles of a supramolecular approach is a modern interdisciplinary field of research that deals with the transfer of asymmetry information within molecular systems *via* noncovalent interactions from a chiral entity to a prochiral substrate.[1] Primarily, they include electrostatic, hydrogen-bonding,[2] van der Waals and π–π interactions,[3] in addition to steric effects,[4] acting individually or cooperatively to produce the chiral structures. In this context, stereochemical control in a chiral photochemical process such as photocycloaddition is one of the most intriguing issues from the mechanistic and synthetic points of view.[5] Substrate preorientation prior to photoirradiation, governed by supramolecular interactions, has recently been exploited to achieve high regio-[6] and enantioselectivities.[7] Among different stereochemical processes, anthracene photodimerization is one of the oldest known photochemical reactions.[8] However, the stereochemistry of photocyclodimerization of unsymmetrically substituted anthracenes has been less studied until recently, probably due to the complex nature of their photoproducts which include four [4 + 4] cyclodimers (Scheme 1), *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. Among the different hosts or template molecules, the inherently chiral cavity of γ-cyclodextrin has been utilized to study the stereoselectivity and enantioselectivity of the photodimers obtained from 2-anthracenecarboxylate.[9] Those approaches could improve the low selectivity for h–h photodimers by manipulating the electrostatic interaction between host and guest, controlling external stimuli such as temperature, solvent, pressure and also by a steric effect operating outside the binding site. A solid state approach with a similar system, in which stereodifferentiation and chiral information are provided by the rigid solid environment, gives more h–h photoproducts though the conversion is very low.[10] On the other hand, reaction media like a Langmuir–Blodgett assembly, micelles, liquid crystals and polymer aggregates have not been employed extensively or the rate of success is very low. Even in this series, however, one phase is really missing, that is the gel state which is capable of affording novel supramolecular architectures created by low molecular-weight gelator (LMG) assemblies. Photo-induced *trans-to-cis* isomerization of azobenzene in cholesterol based gelator has been developed.[11a,b] Chiral silver nanoparticles and chiral nanoparticulate films have been prepared through the *in situ* reduction of an organogel formed by a silver(I)-coordinated organogelator.[11c] Photoresponsive LMG-containing stilbene,[11d] 9-anthracenecarboxylate,[11e] and LMG based on monomeric and dimeric derivatives of anthracene have also been studied.[11f] However, the product analysis and the stereochemical control over the photoproducts have not been explored properly, probably because of their complexity. It should be an encouraging step to explore the stereochemical control of anthracene derivatives using the gel matrix.



Scheme 1 Schematic presentation of [4 + 4] photocyclodimerization of 2-anthracenecarboxylic acid in the free state and in the cyclohexane gel of binary system **1**.

Recently, LMG chemistry using cholesterols[12a–c] and substituted gallic acids[12d–f] as the backbone of a gelator has been developed. Keeping the above mentioned goal in mind, we have designed a binary gelator containing 2-anthracenecarboxylic acid (2Ac) attached noncovalently with a gelator component containing the gallic acid backbone coupled with D-alanine by means of electrostatic and hydrogen-bonding interactions. The reasons behind the selection of such a system are three-fold: (i) the noncovalently attached anthracene

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moiety should have sufficient room for cyclodimerization reaction in the closely packed gel state and also this photo-responsive component may induce the gel–sol phase transition by photo-stimuli, (ii) intermolecular hydrogen-bonding through two amide groups and possible π–π stacking of the anthracene molecules are expected to provide an appropriate platform for stereochemical selection of the photoproducts in the 1D arrangement in the gel state, and (iii) there is scope for the chiral alanine moiety to induce enantioselectivity in the anthracene photoproducts *via* perturbation of the pre-orientation in the ground state.

In a typical synthetic procedure, first the D-alanine was condensed with gallic acid based amine, to which was then attached the 2Ac moiety (equimolar) from THF solution to give the binary organogelator **1** (Scheme 1). The product was used in all the studies described here. The gelation ability of **1** was tested in different organic solvents (hexane, cyclohexane, toluene, *p*-xylene, benzene, THF, *etc*.). Among these it was found to gelate cyclohexane reversibly with a low critical gelator concentration (2.5×10^{-3} mol dm^{-3}). High transparency of the system is a really advantageous condition that is indispensable for applying the system to photochemical purposes. For the photoreaction, a gel sample with medium gelator concentration (9.9×10^{-3} mol dm^{-3}) has been chosen because the higher the gelator concentration, the more rigid will be the molecular packing in the gel state but at the same time the efficiency of the photoirradiation would be less.

The gel sample prepared under the inert conditions was photoirradiated at a wavelength of 366 nm with a medium pressure mercury lamp through optical filters for 2 h at 10 °C. Photocyclization is not reversible at this wavelength. With the progress of photoirradiation, the intensity of UV-absorption band (^1L_a) (Fig. S1‡) of 2Ac monomer gradually decreased with a simultaneous change in the physical state from gel to sol. It is worth mentioning that the gel melting temperature (35 °C) for this system is well above the photoirradiation temperature. One can propose, therefore, that the observed phase transition should be ascribed to a photo-induced process. After the photoreaction, the photoproducts and unreacted 2Ac were separated and isolated from the gelator component, which was then subjected to HPLC analysis. The chromatogram (Fig. S2‡) showed no signal for the h–t photodimers which are normally the major products in isotropic conditions. In this process only h–h photodimers were produced with some moderate (10%) enantiomeric excess (ee) (Table 1). This system, even at higher temperature (50 °C, sol state), gave a substantial amount (76%) of h–h dimers but with lesser chiral induction (2% ee). In the solid state, however, a photodimerization process did not take place. In THF, a nongelating medium, the stereoselectivity was reversed to give h–t dimers as major photoproducts. It is thus clear that a high degree of stereoselectivity is inherent in the gel system. One should notice that the condition employed for the photoreaction here is close to the ambient condition even though the system shows a very high degree of stereoselectivity and also some chiral induction. These easily performable reaction conditions definitely enhance the merit of the system.

The presence of excess chirality in the photoproducts has encouraged us to investigate the circular dichroism (CD) of the sample in the ground state. The CD spectrum (Fig. S3‡) of the cyclohexane gel of **1** clearly shows the CD signal corresponding to the wavelength of the 2Ac absorption band. It means that the 2Ac molecules are arranged in a chiral environment induced by the chiral gelator. This is supported by the fact that the photoproduct distribution and ee are determined by the orientation in the ground state. The CD signal in the sol state (at 50 °C) is negligibly weak as is evident from the lower ee obtained in the sol state. It is worth noticing that in the gel state, even the noncovalent interaction can convey the chiral message to the achiral counterpart. This process is facilitated by the orientational rigidity in the gel matrix.

Fluorescence spectra (Fig. S4‡) of the gel sample at room temperature show a decrease in the fluorescence intensity together with a significant red shift of λ_{max} compared to that in the sol state. The red shift of the fluorescence maxima can be attributed to the π–π stacking of anthracene molecules in the gel state.[13] The decrease in the intensity probably results from the concentration quenching of the fluorescence in the closely packed gel state compared to the more isotropic sol state.[14] The investigation of the morphology (Fig. S5‡) of the gel sample gives a clear view of a one-dimensional fibrillar arrangement. XRD analysis of the xerogel prepared from **1** in cyclohexane shows two peaks (Fig. S6‡) at $2\theta = 4.30°$ (20.5 Å) and 9.60° (9.2 Å) which are assigned to the different spacings in the proposed molecular packing (Fig. S7‡) based on energy minimization.

The goal of this work is to control the stereochemical selectivity of photodimers by taking advantage of the probable one-dimensional supramolecular assembly in the gel phase. In this regard, the gel structure or in other words orientation of the 2Ac molecules in the gel matrix should be the key factor. The HPLC analysis of the photoproducts provides direct

Table 1 Distribution and enantiomeric excess (ee) of the products obtained from [4 + 4] photocyclodimerization of 2Ac in sample **1**

				Relative yield (%)[a]						% ee[a]	
Sample	Temp./°C	Irradiation time/min	Conversion (%)	A	B	C	D	A + B	C + D	B	C
Gel of **1** in cyclohexane	10	120	51	0	0	48	52	0	100	—	−10
Sol of **1** in cyclohexane	50	30	61	10	14	36	40	24	76	1	−2
1 in solid state	10	120	0	—	—	—	—	—	—	—	—
1 in THF (nongelating)	10	30	80	40	26	20	14	66	34	0.5	−0.7

[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% and in % ee are ±1% for major products and ±3% for minor products.

evidence for the gel structure. Formation of only h–h photodimers from the gel state definitely indicates that 2Ac molecules are placed only in a h–h fashion (Fig. S7‡). The arrangement is so compact and directional that the noncovalent interaction becomes enough to transfer the chirality to the ground state packing of 2Ac molecules and this preorientation in the ground state actually determines the ee of the photoproducts. On the other hand, a photo-induced structural change (gel to sol transition) that is fairly difficult in the gel system can easily be attained in the present system. Attachment of 2Ac molecules in the binary gelator *via* hydrogen-bonding is evident from FT-IR spectra of the xerogel (Fig. S8‡) where the C=O stretching frequency (at 1682 cm^{-1}) of 2Ac shifts to lower energy in the gel state. In addition, unlike the previously reported system,[11e] the ammonium counterpart is capable of forming intermolecular hydrogen-bonding (*via* two amide groups) to align itself in the gel structure, even though this does not seem to be enough to resist the structural change during the photoreaction. This situation means that 2Ac molecules definitely have an active participation in constructing the gel structure *via* their π–π stacking interaction which is more favourable in a h–h orientation. The π–π stacking together with the intermolecular hydrogen-bonding *via* two amide linkages cooperatively construct the one-dimensional arrangement of the gelator molecules (Fig. S7‡) which is facilitated by the nonpolar environment of the cyclohexane.

In conclusion, we have demonstrated that a binary gelator containing 2Ac noncovalently linked with 3,4,5-tris(*n*-dodecyloxy)-benzoylamide substituted D-alanine can act as an efficient gelator of a nonpolar solvent like cyclohexane. The photocyclodimerization of the 2Ac in the gel matrix gives only h–h photodimers which are the minor products under the normal isotropic condition. It is also worth noticing that a low but still significant ee (10%) in the photodimer could be induced from the chiral component of the gelator. As a consequence of the photoreaction, a significant gel to sol phase transition can easily be induced. Thus, the present system is the first example in which the stereochemical control of the anthracene photodimerization has been investigated in the gel phase and as a result a very high degree of stereoselectivity is achieved under simple conditions. This study is believed to open a new door towards stereochemical control in a supramolecular assembly created by organogel systems.

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