Chiral Amplification

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Autoamplification of Molecular Chirality through the Induction of Supramolecular Chirality**

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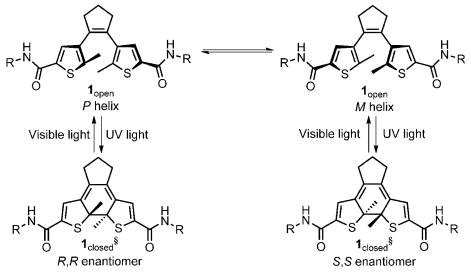
Abstract: *The novel concept for the autoamplification of molecular chirality, wherein the amplification proceeds through the induction of supramolecular chirality, is presented. A solution of prochiral, ring-open diarylethenes is doped with a small amount of their chiral, ring-closed counterpart. The molecules co-assemble into helical fibers through hydrogen bonding and the handedness of the fibers is biased by the chiral, ring-closed diarylethene. Photochemical ring closure of the open diarylethene yields the ring-closed product, which is enriched in the template enantiomer.*

Autoamplification of chirality, a process which allows the emergence of homochirality from a pool of near-racemic compounds,[1] is an intriguing concept with far-reaching implications for asymmetric synthesis[2] and the origin of life.[3] In the seminal work by Soai et al.[4] on asymmetric autocatalysis it is shown that autoamplification of molecular chirality can be achieved by the product of a reaction acting as a chiral ligand for a metal, thus forming a complex which catalyzes the enantioselective formation of this product. Blackmond and Brown and co-workers provided a mechanistic model for this chiral amplification, one involving a catalyst which is able to accelerate its own formation, while simultaneously suppressing other catalytic species which would lead to the formation of the other enantiomer.[3,5]

The concept of chiral amplification has been extended to noncovalent macromolecular systems[6] and the emergence and induction of supramolecular chirality in dynamic macromolecular aggregates was pioneered by Meijer and co-workers.[7] It was shown that doping of achiral, disc-shaped molecules with small quantities of chiral analogues results in the formation of long, chiral, columnar stacks held together by hydrogen bonding.[7] In the columnar stacks, the chiral dopant is distinct from the majority of the achiral entity, as opposed to the Soai system which shows autoamplification of chirality based on chiral catalysts in which the product is identical to the chiral ligand in the catalyst. Moreover, the achiral molecule is not a precursor for the chiral molecule and there is no conversion of one into the other. The key question is: can supramolecular chirality result in the induction of chirality at the molecular level for the constituent molecular component of the chiral supramolecular aggregate?

Here we show that autoamplification of molecular chirality by induction of supramolecular chirality can be achieved. A minor amount of a chiral diarylethene in the closed form induces handedness in a supramolecular aggregate (chiral gel) of the corresponding achiral diarylethene in the open form. Subsequent photochemical ring closure results in the formation of extra chiral diarylethene in the closed form. In other words, we demonstrate that a small amount of a single enantiomer of a chiral molecule can induce its own formation through the intermediacy of a chiral, supramolecular assembly of the same molecules.

The system presented here is based on amide-modified diarylethene molecular photoswitches (Scheme 1).[8] Diarylethenes in their open form ($\mathbf{1}_{open}$) exist in two, rapidly



Scheme 1. Helical conformations of the diarylethene $\mathbf{1}_{open}$ and the formation of the two enantiomers of $\mathbf{1}_{closed}$ upon photochemical ring closing. § = single enantiomer.

exchanging, chiral conformations (*P* and *M* helicity) in solution.[9] During ring closing, which results from irradiation with UV light, two stereogenic centers are generated, thus giving rise to two enantiomers (Scheme 1): (*R*,*R*)-$\mathbf{1}_{closed}$§ from (*P*)-$\mathbf{1}_{open}$ and (*S*,*S*)-$\mathbf{1}_{closed}$§ from (*M*)-$\mathbf{1}_{open}$ (§ denotes that the compound is a single enantiomer). Functionalization of diarylethenes with amide moieties allows the photoswitches to assemble through hydrogen bonding and this results in low-molecular-weight gelators (LMWGs).[10,11]

For the transfer of chirality, we rely on the sergeant-soldier principle as introduced by Green and co-workers.[12] According to this mechanism of chiral amplification, a minor

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amount of the chiral compound (sergeant), used as a dopant, dictates the overall chirality of a system which is made up of mainly achiral material (soldiers). In recent years, this principle has been exploited in the field of supramolecular chemistry.[13,14]

In our earlier study of LMWGs of type $\mathbf{1}_{open}$ (Scheme 1) we showed how $\mathbf{1}_{open}$, bearing chiral side chains [R = (*R*)-phenylethylamine], can undergo ring closure in the gel state to give $\mathbf{1}_{closed}$ with 96% diastereomeric excess.[15] It was also shown that these chiral compounds can co-aggregate with compounds of the same type, which have achiral R groups (R = *c*-hexyl), and induce an enantiomeric excess of up to 94% after subjecting the mixture in the gel to ring-closing conditions.[16] Here we demonstrate how enantiomerically pure $\mathbf{1}_{closed}^{\S}$ can template its own formation in the gel state, that is, how the chiral product of the reaction governs its own formation. The distinctive feature of this system, as compared to earlier studies,[8,14,16] is the fact that the soldier is a precursor of the sergeant, and can be converted into it by photochemical cyclization after the amplification of supramolecular chirality is established. One can consider this an autocatalytic effect in a kinetically trapped state.

We show how the use of the prochiral diarylethene molecular photoswitches $\mathbf{1}_{open}$, which co-aggregate with a small fraction of their enantiomerically pure closed counterparts $\mathbf{1}_{closed}^{\S}$, results in the formation of chiral supramolecular gels (Figure 1, templated pathway). The *S*,*S* molecular chirality present in the dopant [(*S*,*S*)-$\mathbf{1}_{closed}^{\S}$] is translated into a preferred helicity in the chiral supramolecular gel (*M* helicity in Figure 1) consisting of $\mathbf{1}_{open}$ (soldier). In the gel state, the prochiral switches $\mathbf{1}_{open}$ can be photochemically ring-closed to $\mathbf{1}_{closed}$ by UV irradiation, thereby locking the chirality at the molecular level and completing the cycle from molecular chirality, through induction of supramolecular chirality, and finally back to molecular chirality, thus leading to an enriched mixture in the templated enantiomer ((*S*,*S*)-$\mathbf{1}_{closed}^{\S}$ in Figure 1). If chiral dopant is not added to the system (Figure 1, non-templated pathway), the gel consists of an equal amount of *P*- and *M*-helical fibers and, upon irradiation, a statistical 1:1 mixture of the *S*,*S*- and *R*,*R* enantiomer of $\mathbf{1}_{closed}$ (*rac*-$\mathbf{1}_{closed}$) is formed.

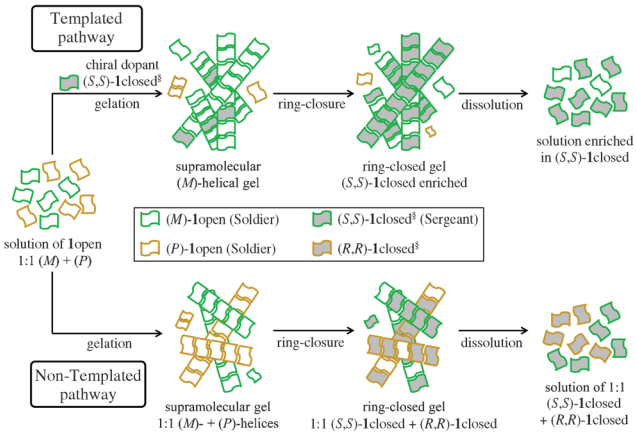
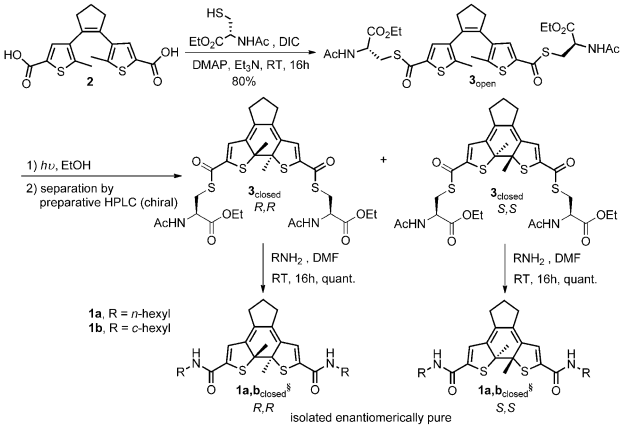


Figure 1. Concept for autoamplification of molecular chirality through the induction of supramolecular chirality. For the templated pathway, a small fraction of chiral dopant (*S*,*S*)-$\mathbf{1}_{closed}^{\S}$ is added to a mixture of prochiral photoswitches [(*M*)-$\mathbf{1}_{open}$ and (*P*)-$\mathbf{1}_{open}$] prior to gelation. The formed fibers that result in gel formation are templated by the chiral dopant (*S*,*S*)-$\mathbf{1}_{closed}^{\S}$ and one helicity (*M*) is dominant. Upon ring closing of the photoswitches with UV light, the chirality of the fibers results predominantly in the formation of the templated enantiomer (*S*,*S*)-$\mathbf{1}_{closed}$. If no chiral dopant is added to the mixture of prochiral photoswitches (non-templated pathway), the gel is made up of an equal mixture of *P* and *M* conformers in the fibers. Subsequent ring closure results in a statistical 1:1 mixture of products.

We envisioned a system in which the chiral information is exclusively transferred from the ring-closed diarylethene core, rather than from auxiliary, peripheral stereogenic centers adjacent to the amide group.[16,17] *n*-Hexyl and *c*-hexyl substituents were chosen to prevent any additional influence from non-innocent groups, such as phenyl moieties. The sergeant $\mathbf{1}_{closed}^{\S}$ (R = *n*-hexyl or *c*-hexyl) was designed to be one of the enantiomers of the ring-closed soldier $\mathbf{1}_{open}$. Predicting the outcome of chiral amplification in supramolecular systems is a daunting task[17] and small structural changes in the chiral dopant can result in formation of the other enantiomer[16] or even loss of amplification.[14] The fact that the soldier and sergeant in our system are the same molecule may have outstanding implications for autoamplification of chirality. The soldiers $\mathbf{1a}_{open}$ and $\mathbf{1b}_{open}$ and enantiopure sergeants $\mathbf{1a}_{closed}^{\S}$ and $\mathbf{1b}_{closed}^{\S}$ were synthesized to investigate the potential for $\mathbf{1}_{closed}^{\S}$ to act as a template in the gel state (Scheme 2).



Scheme 2. Synthesis of the sergeants $\mathbf{1a}_{closed}^{\S}$ and $\mathbf{1b}_{closed}^{\S}$. DIC = *N*,*N*′-diisopropylcarbodiimide, DMAP = 4-(*N*,*N*-dimethylamino)pyridine.

The soldiers $\mathbf{1a}_{open}$ and $\mathbf{1b}_{open}$ are readily prepared by our reported procedure.[18] The chiral sergeant, however, undergoes fast ring opening to the achiral (open) form when exposed to visible light[19] and the synthesis proved to be highly challenging. Using a variety of procedures, including classical resolution, HPLC using a chiral stationary phase, or asymmetric synthesis, did not result in isolation of enantiopure material. We envisioned functionalization of the precursor **2** with a chiral auxiliary in a manner that not only resulted in separation of the closed isomers, but also allowed facile synthesis of the desired enantiomers of the amides $\mathbf{1}_{closed}^{\S}$ (Scheme 2).

Towards this goal, the chiral dithioester $\mathbf{3}_{open}$ was prepared by coupling **2** with Ac-(*R*)-Cys-OEt. Compound $\mathbf{3}_{open}$ was then photocyclized with UV light ($\lambda = 312$ nm) to form a 1:1 mixture of diastereomers ($\mathbf{3}_{closed}$). Separation of the diastereomers, by HPLC using a chiral stationary phase, was followed by reaction of each of the enantiomerically pure $\mathbf{3}_{closed}$[§] with an excess of *n*-hexyl and *c*-hexyl amine at room temperature (shielded from light) to provide the enantiopure amides $\mathbf{1a}_{closed}$[§] and $\mathbf{1b}_{closed}$[§], respectively. These mild reaction conditions resulted in full conversions for the last step and no ring opening was observed.

The photochromic properties of $\mathbf{1}_{open}$ were studied using UV/Vis spectroscopy (for $\mathbf{1b}_{open}$, Figure 2a). Upon irradiation with UV light ($\lambda = 312$ nm), the band at $\lambda = 262$ nm decreases

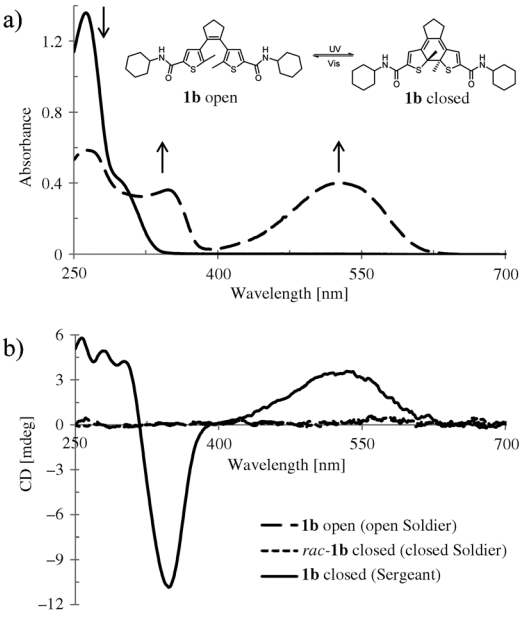


Figure 2. Photochromic properties of $\mathbf{1b}_{open}$, *rac*-$\mathbf{1b}_{closed}$, and $\mathbf{1b}_{closed}$[§]. a) UV/Vis absorption spectra of $\mathbf{1b}_{open}$ (solid line, 5.0×10^{-4} M in EtOH) and *rac*-$\mathbf{1b}_{closed}$ (dashed line, 5.0×10^{-4} M in EtOH). *Rac*-$\mathbf{1b}_{closed}$ was obtained by irradiation ($\lambda = 312$ nm) of $\mathbf{1b}_{open}$. b) CD spectra of the soldier $\mathbf{1b}_{open}$ (dashed line, 3.7×10^{-5} M), ring-closed soldier *rac*-$\mathbf{1b}_{closed}$ (dotted line, 3.7×10^{-5} M), and enantiopure sergeant $\mathbf{1b}_{closed}$[§] (solid line, 3.7×10^{-5} M) in EtOH.

and new bands for *rac*-$\mathbf{1b}_{closed}$ appear at $\lambda = 347$ and 528 nm. CD spectroscopy (Figure 2b) confirmed that $\mathbf{1}_{open}$ closes in a racemic fashion and has no influence on the outcome of the sergeant-soldier asymmetric induction experiment. As expected, no Cotton effect was observed for a solution of neither the open ($\mathbf{1b}_{open}$) nor the closed soldier (*rac*-$\mathbf{1b}_{closed}$). The enantiopure $\mathbf{1b}_{closed}$[§], in contrast, shows a positive Cotton effect with a maximum at $\lambda = 528$ nm and a minimum at $\lambda = 347$ nm.

With the enantiopure sergeants, $\mathbf{1}_{closed}$[§], and soldiers, $\mathbf{1}_{open}$, in hand we set out to probe the concept presented in Figure 1. A suspension of the soldier $\mathbf{1a}_{open}$ in toluene was doped with a small amount of the enantiomerically pure $\mathbf{1a}_{closed}$[§] (for experimental details, see Table 1 and the Supporting Information). The suspension was heated and formed a homogeneous gel upon cooling. The gel was irradiated with UV light ($\lambda = 312$ nm) and the products were analyzed by HPLC, using a chiral stationary phase, after dissolution of the gel in EtOH.

Table 1: Sergeant-soldier experiments of **1a** in toluene.

Entry	Total concentration $\mathbf{1}_{open} + \mathbf{1}_{closed}$[§] (% w/v)	*ee* [%] at no induction[a]	*ee* [%] observed	Δee [%]
1	1.5	0	0	0
2	1.5	3.2	25	22
3	1.5	9.5	50	40
4	1.5	12.5	44	32
5	1.5	16.9	48	31
6	1.5	37.8	84	46
7	0.8	9.0	47	38
8	0.3	15.7	29	13
9	0.2	14.5	31	16
10[b]	0.8	−19.5	−45	25
11[b]	1.5	−19.6	−54	35
12[c]	1.0	9.0	47	38

For experimental details see the Supporting Information. [a] The fraction of enantiopure sergeant added is equal to the *ee* value [%] where there is no indiction. [b] The opposite enantiomer of the sergeant was used as a dopant and the other enantiomer of the product was obtained accordingly. [c] The *c*-hexyl-appended soldier $\mathbf{1b}_{open}$ and sergeant $\mathbf{1b}_{closed}$[§] were used instead of *n*-hexyl $\mathbf{1a}_{open}$ and $\mathbf{1a}_{closed}$[§].

If induction of the enantiopure sergeant on the ring-closed soldier does not take place, that is, the ring closure of the soldier molecules proceeds in a racemic fashion, then the amount of added enantiopure sergeant is directly reflected in the observed *ee* value.[20] The difference between the observed *ee* value and the *ee* value if no asymmetric induction occurs, reflects the *ee* value that was induced by the chiral sergeant (Δee) and is referred to henceforth as "induction".

It was found that the sergeant was able to induce its own formation with 40% (Table 1, entry 3) induction (observed $ee = 50\%$, $\Delta ee = 40\%$), when compared to the system in the absence of the sergeant (Table 1, entry 1), after correction for the amount of sergeant initially added. This establishes, to the best of our knowledge, for the first time the autoamplification of molecular chirality by induction of supramolecular chirality. Decreasing the amount of sergeant to 3.2% led to a lower induction of 22% (Table 1, entry 2). Increasing the amount of sergeant (up to 37.8%), in contrast, did not significantly increase the asymmetric induction (Table 1, entries 4–6). Cryo-transmission electron microscopy (cryo-TEM) revealed a fibrous network of very high density in both the gels containing the open and closed forms (Figure 3). We therefore envisioned that decreasing the total concentration of the gelator might have an effect on the outcome of the experiment as the gel would become less dense, but lowering the concentration from 1.5% w/v to 0.8% did not increase the induction (Table 1, entry 7). Further decrease in the concentration below a certain threshold (0.3% w/v) resulted in a drop in induction to approximately 15% (Table 1, entries 8 and 9). When the opposite enantiomer of the sergeant, $\mathbf{1a}_{closed}$[§], was used as the dopant, the other enantiomer of the product was obtained (Table 1, entries 10 and 11), thus providing evidence that the sergeant is responsible for templating its own formation and that one of the enantiomers

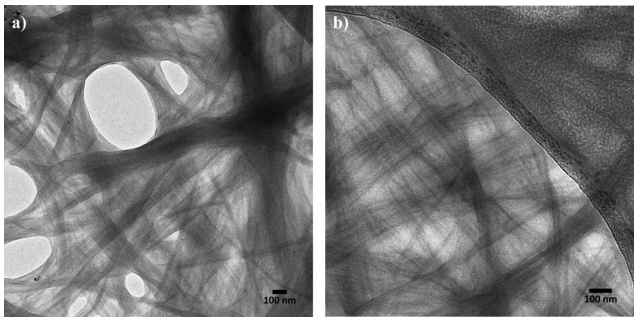


Figure 3. Cryo-TEM images of self-assembled gel morphologies. a) Gel fibers of the soldier $\mathbf{1b}_{open}$ (1.5% w/v in toluene). b) Gel fibers of the soldier *rac*-$\mathbf{1b}_{closed}$ (1.5% w/v in toluene) after irradiation of $\mathbf{1b}_{open}$ with UV light ($\lambda = 312$ nm).

is not simply favored for other reasons. The system gives comparable results for **1b**, which is functionalized with *c*-hexyl instead of *n*-hexyl side chains (Table 1, entry 12), thus demonstrating that the nature of the alkyl moieties has a minor influence. In each case, doping the gels with the enantiopure sergeant $\mathbf{1}_{closed}$[§] resulted in an increase in *ee* value (after correcting for the initial amount of sergeant $\mathbf{1}_{closed}$[§] added) compared to cases where no dopant was added.

As the solvent is an integral part of organogels,[21] a range of other solvents were investigated to assess their effect on the asymmetric autoinduction (Table 2). The use of toluene or cyclohexane gave the best results in these asymmetric autoamplification experiments (Table 2, entries 1 and 2). Benzene and decalin facilitate asymmetric induction, but lower Δee values (ca. 15%) were observed (Table 2, entries 3 and 4). In 1-phenyloctane, the product was formed as a racemate (Table 2, entry 5). Although a gel can still be formed in the more polar dibutylether, the product was obtained as a racemate (Table 2, entry 6). The use of acetonitrile and hexadecane resulted in a precipitate, rather than a gel (Table 2, entries 7 and 8). In conclusion, hydrophobic solvents were required for the observation of an enhancement in *ee* value (with toluene being the preferred solvent), as the use of more polar solvents resulted in poor gel formation or racemic mixtures.

Table 2: Sergeant–soldier experiments of **1a** in various solvents.[a]

Entry	Solvent	*ee* [%] at no induction[b]	*ee* [%] observed	Δee [%]
1[c]	toluene	9.5	50	35 ± 6
2[c]	*c*-hexane	11.0	44	33
3	benzene	9.6	27	17
4[c]	decalin	10.0	24	14
5	1-phenyloctane	12.5	*rac*	–
6	dibutyl ether	6.0	*rac*	–
7[d]	acetonitrile	11.3	–	–
8[d]	hexadecane	11.9	–	–

[a] The total gelator concentration was 1.5% w/v. For experimental details see the Supporting Information. [b] The fraction of enantiopure sergeant added is equal to the *ee* value [%] where there is no indiction. [c] The error indicated is the standard deviation ($n = 7$, see also the Supporting Information). At a concentration of 0.8% w/v, Δee was the same. [d] Solid precipitated from the solution upon cooling.

This observation supports the hypothesis that hydrogen bonding in the supramolecular gel state helps to preorganize the achiral $\mathbf{1}_{open}$ soldier with a preferred helical conformation. In other words, one of the dynamic (and interconverting) helical conformers (Scheme 1) is selected in the supramolecular aggregate, which is governed by the chirality of the dopant $\mathbf{1}_{closed}$[§].

The gel-to-solution temperature (T_{gel}) of gelated $\mathbf{1b}_{open}$ and *rac*-$\mathbf{1b}_{closed}$, using dropping-ball experiments[22] (see the Supporting Information for experimental details), were also determined. The gel of $\mathbf{1b}_{open}$ has a T_{gel} of 82 °C and the gel of *rac*-$\mathbf{1b}_{closed}$ has a T_{gel} of 74 °C, thus suggesting a lower stability of the aggregates of the closed form.

The data indicate that upon irradiation of the gel, the closed form goes into solution preferentially over the open form, a process that would limit the amount of sergeant present in the gel fibers and be a possible origin of a modest asymmetric induction. Indeed, it has been shown by the groups of Sijbesma and Meijer that the presence of chiral monomers in solution has little or no effect on the chirality of assemblies if the monomers are not part of the assembly.[23]

In summary, we present herein, to the best of our knowledge, the first example of autoamplification of molecular chirality by induction of supramolecular chirality. We have shown how diarylethene photochemical switches can be used in autocatalytic induction. A small amount of a chiral sergeant ($\mathbf{1}_{closed}$[§]) can be added to its precursor $\mathbf{1}_{open}$ without inhibiting gel formation. The chirality of the gel is controlled by the chiral sergeant, thereby favoring the formation of either a *P*- or *M*-helical gel. The chiral information is subsequently locked at the molecular level as the prochiral soldiers undergo ring closure by irradiation of the gel with UV light to form one of the enantiomers in excess. This completes the cycle from molecular chirality by supramolecular chirality back to molecular chirality of the same molecules and places this system among the very few examples where a chiral product of a reaction can template its own asymmetric synthesis. This process is reminiscent of so-called autocatalytic reactions, however here the autoamplification takes place in a kinetically trapped state.

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Communications

Chiral Amplification

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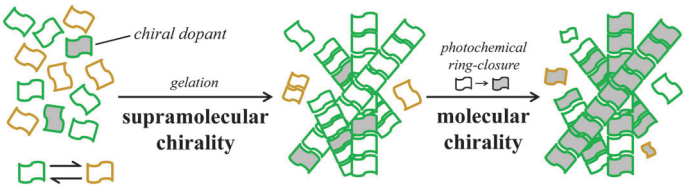
Autoamplification of Molecular Chirality through the Induction of Supramolecular Chirality



There and back again: Doping a mixture of rapidly interconverting prochiral, open diarylethenes (left) with their enantiopure, closed counterparts, led to formation of gel fibers of preferred helicity (center). This supramolecular chirality was transferred to the molecular level by photochemical ring closing, thus yielding a chiral product (right) which is enriched in the enantiomer originally used as a template.