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A self-recovering mechanochromic chiral π-gelator†

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Mechanochromism is a stress induced perturbation of electronic property in molecular materials. It is shown here that the presence of a branched chiral chain facilitates mechanochromic response in a molecular assembly as illustrated with a chiral oligo(*p*-phenylenevinylene) derived π-gelator (**OPVC**). **OPVC** exhibits a reversible mechanochromism while the analogous achiral derivative (**OPVA**) having a linear side chain does not, as established from the fluorescence and circular dichroism (CD) studies. The helically twisted chromophore packing in **OPVC** allows mechanical reorganization of the self-assembly and the associated fluorescence intensity variation at different wavelength positions in the broad emission spectrum, resulting in a perturbation in the colour ratio leading to the observed mechanochromic emission color change. This exciting new finding may have wide ranging implications in the design of stimuli responsive molecular materials with reversible optical properties.

Solid-state fluorescence switching of supramolecular functional materials in response to a mechanical stress has been extensively studied to design sensors, memory chips, and security inks.[1–4] Reversible mechanochromic fluorescence change has immense applications in the area of secret documentation and imaging.[1,5] In several of the mechanochromic systems, a stress-induced change in the effective molecular packing at the condensed phase is the main reason for the mechanochromic behaviour.[1,3d–f] In most of the cases, mechanochromic change could be reversed only with application of a second stimulus. Therefore, self-reversible/self-recovering mechanochromic systems have been a target of interest to chemists for reusable applications.[4]

In the recent past, supramolecular gels derived from fluorescent π-systems have been shown to undergo fluorescence change during gelation.[6] Subsequently, an effect of mechanical stress on the fluorescence modulation of gels/xerogels based on supramolecular π-systems has been reported.[6c–e] This property of π-gelators can be used for the design of stimuli responsive materials.[6f] Recently, we reported an amplification of NIR emission upon mechanical agitation of a xerogel film derived from a π-extended BODIPY.[6e] While studying the properties of several amide functionalized OPV gelators,[7] we came across an interesting observation of a mechanical stress induced fluorescence colour change only with a chiral OPV amide (**OPVC**) and not with an analogous achiral derivative (**OPVA**). Supramolecular assembly of chiral π-gelators is known to weaken the gel strength and excitonic interaction between molecules due to the presence of branched/chiral chain, which in turn reflect upon properties such as fluorescence and circular dichroism.[8] Since aggregation and disaggregation pathways in chiral self-assembly of π-systems are controlled by kinetic and thermodynamic parameters,[9] mechanical intervention of such processes can strongly influence on their electronic properties. As a proof of concept to this hypothesis, we establish here that the branched chiral chain in a π-gelator not only helps to express supramolecular helicity but also facilitates mechanically induced fluorescence colour change, leading to a new mechanochromic system.

We synthesized two OPV based π-gelators **OPVA**[7c] and **OPVC** (Chart 1) from achiral and chiral OPV bisester derivatives (**1a** and **1b**) as depicted in Scheme S1 (ESI†). All compounds

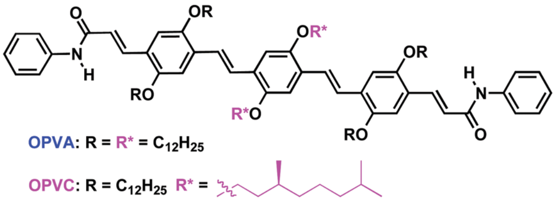

Chart 1 Chemical structures of achiral and chiral OPVs.

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were characterized using FT-IR, ^{1}H NMR, ^{13}C NMR and MALDI-TOF techniques. **OPVC** and **OPVA** self-assemble to form fibrous aggregates and gels in *n*-decane (minimum gelator concentration = 1.3 mM, Fig. 1). Transmission electron microscopy (TEM) analysis of the greenish-yellow fluorescent gels showed entangled helical fibres of micrometer length and 100–200 nm width (Fig. 1b and c). The fluorescence spectra of the gelators in *n*-decane (c = 1.3 mM) exhibited a broad emission with two prominent peaks at 530 and 570 nm and shoulder bands at 620 and 680 nm (Fig. S1, ESI†). The xerogel obtained after evaporation of the solvent showed significant reduction in the intensity of the 530 nm band with increase in the 620 and 680 nm bands (Fig. S1, ESI†). Reversible self-assembly and gelation of the molecules were confirmed by variable temperature fluorescence spectral changes (Fig. S1, ESI†). Upon increasing the temperature of xerogel from 30 to 150 °C, a significant reduction in the intensity of higher wavelength bands with a slight blue-shift was observed, indicating the disaggregation of self-assembled **OPVC** (Fig. S2a, ESI†). Upon cooling, the initial emission was retained; indicating the reformation of **OPVC** aggregates (Fig. S2b, ESI†). From the observed broad yellow emission with different peak intensities, it is inferred that different emitting species, particularly green and red emitting components are present in the self-assembly. Hence, it is possible to manipulate the emission colour by varying the ratio of the emitting species with an external stimulus.

Interestingly, a film of the gel obtained from **OPVC** exhibited a change in the emission colour from greenish yellow to orange upon shearing with a spatula (Fig. 2a), whereas the achiral **OPVA** did not show fluorescence colour change upon mechanical agitation. Under mechanical stress (grinding/shearing), the initial green emission of the film of **OPVC** turned into orange which reversed to greenish yellow upon keeping at room temperature over a period of time (Fig. 2a and Fig. S3, ESI†). To gain more insight, the emission spectra of **OPVC** in the xerogel form before and after mechanical stress was examined (Fig. 2b). It is interesting to note that the intensity of the band at 535 nm of the fluorescence spectrum of **OPVC** xerogel film has been significantly reduced with a concomitant increase of the band at 620 nm (Fig. 2b–d). The emission spectrum was recovered upon keeping the sheared film over a period of time, however, with reduced intensity (Fig. 2b and c). Shearing with a spatula over the recovered sample recreated the orange emission. Normalized emission spectra of the xerogel and the recovered film were nearly identical (Fig. 2c inset). A 20 nm redshift (430 → 450 nm) in the absorption spectrum of **OPVC** aggregates was also observed upon shearing (Fig. S4a, ESI†). The self-recovered absorption showed a 12 nm blue shift (450 → 438 nm) upon keeping over a period of 1 h (Fig. S4a, ESI†).

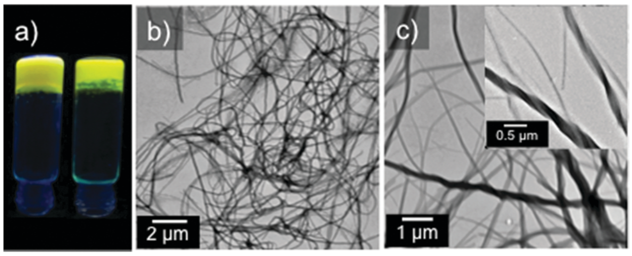

Fig. 1 (a) Photographs (under UV light, λ_{ex} = 365 nm) of **OPVA** (left) and **OPVC** (right) *n*-decane gel (1.3 mM). TEM image of (b) **OPVA** and (c) **OPVC** (inset; zoomed portion of image) from *n*-decane solution (5 × 10^{-5} M). Sample prepared by heating the solution followed by cooling.

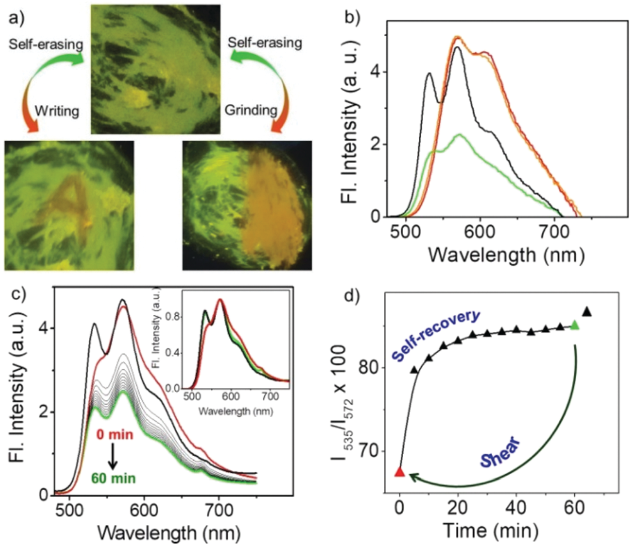

Fig. 2 (a) Photographs showing fluorescence changes upon mechanical writing and grinding of **OPVC** aggregates (under UV light, λ_{ex} = 365 nm). (b) Emission profiles of xerogel (—), ground (—) recovered (—) and re-scratched (—). (c) Time dependent emission spectra showing self-recovery of **OPVC** xerogel (inset; normalized spectra before shearing (—), after shearing (—) and after self-recovery (—)). (d) A plot of fluorescence intensity (ratio of 535 to 572 nm) *versus* time for **OPVC** xerogel (λ_{ex} = 440 nm).

We hypothesized that the branched chiral handle of **OPVC** aggregates has a major role in the observed mechanochromic behavior. Therefore, we compared the mechanoresponsive behaviour of **OPVC** with that of the achiral OPV analogue, **OPVA**. The emission spectrum of **OPVA** gel showed a peak with a maximum at 570 nm and a strong shoulder band around 620 nm, which exhibited a red shift upon mechanical stimulation (Fig. S4b, ESI†). The absence of the short wavelength band at 535 nm must be due to the strong aggregation of **OPVA** molecules. In this case, the mechanochromic effect was not significant and no major changes were observed in the absorption or emission upon mechanical agitation. The fluorescence contour maps (excitation *versus* emission matrix scan) of **OPVC** before and after mechanical stress are shown in Fig. 3. Dilute *n*-decane (1 × 10^{-6} M) solution of **OPVC** showed an emission around 520 nm with an excitation maximum around 450 nm (Fig. S5a, ESI†). However, a film prepared from *n*-decane (1 × 10^{-3} M) solution displayed a red shift in the emission with a blue shift in the excitation (Fig. 3a) indicating the formation of fluorescent H-type aggregates.[10] Mechanical stress showed a red shift in the emission and blue shift in the excitation wavelength (Fig. 3b), which might be due to the strong π–π overlap between OPVs under mechanical stress. After 1 h, the recovered sample showed excitation–emission

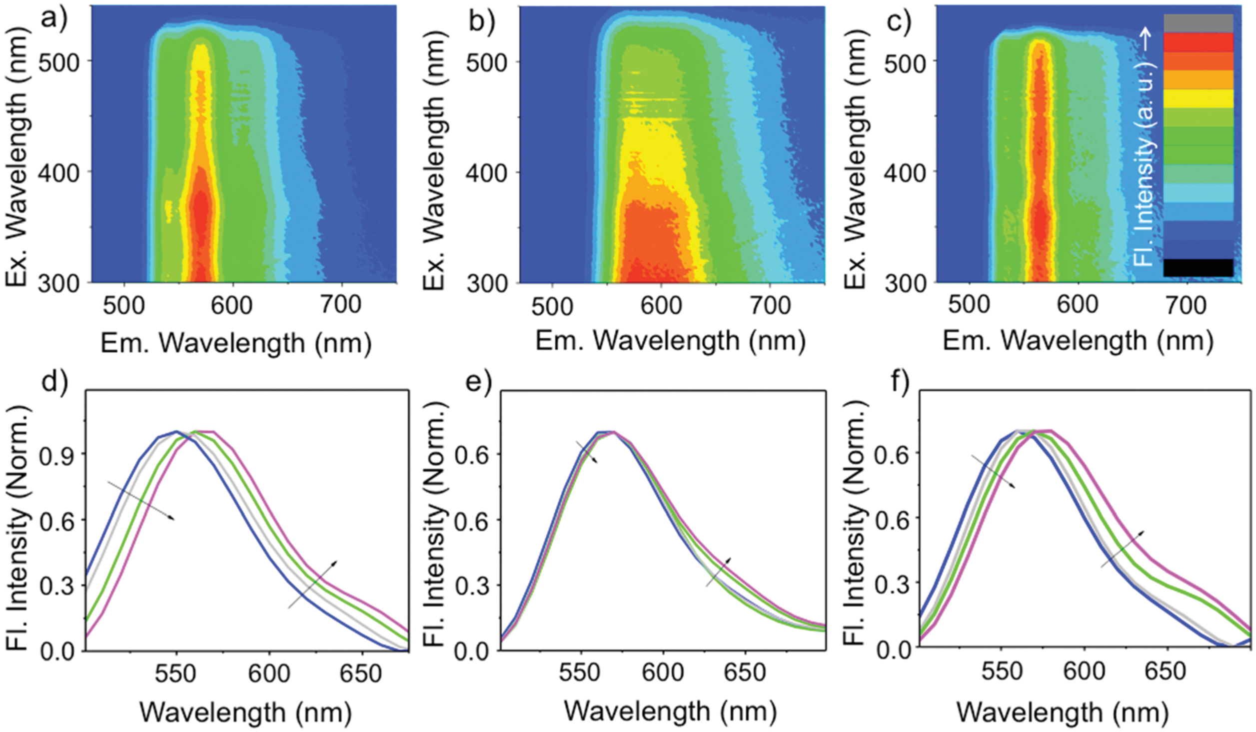

Fig. 3 Contour map of the observed fluorescence intensity (red maximum and blue minimum) of **OPVC** as a function of the fluorescence excitation and emission wavelength (matrix scan) of (a) xerogel, (b) sheared and (c) self-recovered film prepared from *n*-decane solution (1 mM). Time resolved emission spectra of (d) xerogel, (e) sheared and (f) self-recovered **OPVC** aggregates (λ_{ex} = 440 nm) from 56 ps (blue) to 1.5 ns (magenta).

features similar to the initial film (Fig. 3c) indicating the reformation of the initial aggregates.

Fluorescence lifetime decay of the xerogel after shearing and recovery was monitored and the results are summarized in Table 1. **OPVC** in the xerogel state exhibited tri-exponential decay indicating aggregates of different size and HOMO–LUMO energy levels. Upon shearing, a decrease in the lifetime and a reduction in the relative intensity of shorter lifetime species were observed. The reduction in the relative percentage of shorter lifetime species with a concomitant increase of longer lifetime species (Table 1 and Fig. S5b–d, ESI†) can be attributed to the possibility of excited state energy migration from aggregates of different energy levels.[11] An increase in the fluorescence lifetime was observed when the emission was monitored from higher to lower energy, which also point towards possible energy migration among **OPVC** aggregates.[11] In order to confirm the excited state energy migration, we measured time resolved emission spectra (TRES). A dynamic red shift in emission within short period of time after excitation at 440 nm was observed in the case of the xerogel and the recovered film (Fig. 3d and f), which corroborate the migration of excitation energy from lower order **OPVC** stacks (higher energy sites) to higher order **OPVC** stacks (lower energy sites).[11] The TRES profile of the sheared sample was found to be different from that of the initial xerogel and the recovered films. The difference in TRES profile for the sheared sample (Fig. 3e) is presumably due to the absence of aggregates with higher optical band gaps, which is also evident from the fluorescence spectra where the band around 535 nm disappeared after shearing the sample (Fig. 2).

Table 1 Fluorescence decay lifetimes of self-assembled **OPVC** at different conditions (λ_{ex} = 440 nm)

	Fluorescence lifetime, ns		
Emission monitored (λ_{em})	Initial	Sheared	Recovered
535 nm	0.3 (60%)	0.04 (35%)	0.19 (48%)
	0.8 (37%)	0.4 (44%)	0.8 (46%)
	2.8 (3%)	1.6 (21%)	3.2 (7%)
570 nm	0.3 (49%)	0.06 (16%)	0.2 (32%)
	0.79 (45%)	0.4 (55%)	0.8 (54%)
	2.6 (6%)	1.6 (28%)	2.5 (14%)
620 nm	0.36 (51%)	0.25 (30%)	0.27 (39%)
	1.2 (39%)	1.03 (56%)	1.0 (51%)
	3.3 (10%)	2.9 (14%)	3.0 (10%)

The CD spectrum of **OPVC** xerogel displayed two weak positive Cotton signals and a strong negative signal (Fig. 4). After shearing, this CD signal almost disappeared, which suggests absence of the chiral excitonic coupling, due to the mechanical dislocation of chromophore assembly. Surprisingly, the CD signal was not recovered with time, which is in contrast to the fluorescence recovery observed. These contrasting observations suggest that the self-recovered fluorescent aggregates obtained after mechanical stress is a nonhelical assembly, presumably having a phase, different from the kinetically favoured gel assembly, which is helical. However, upon annealing the sample, a slight enhancement in the CD signal intensity was observed indicating a possible reorganization of the molecules to form helical aggregates (Fig. 4 inset). The CD response

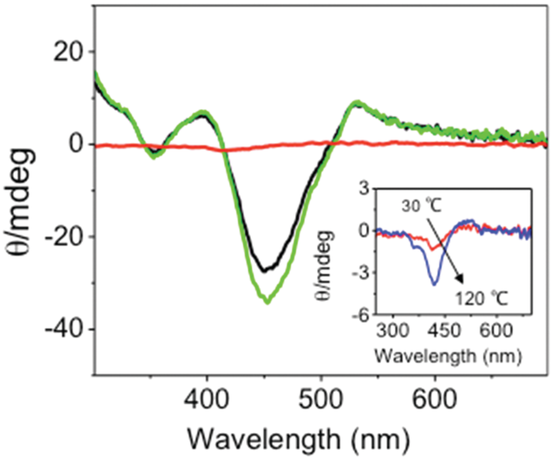

Fig. 4 CD spectra of **OPVC** xerogel (—), sheared (—), and recovered upon a solvent exposure (—) inset: a zoomed region showing the change in CD intensity with increase in temperature.

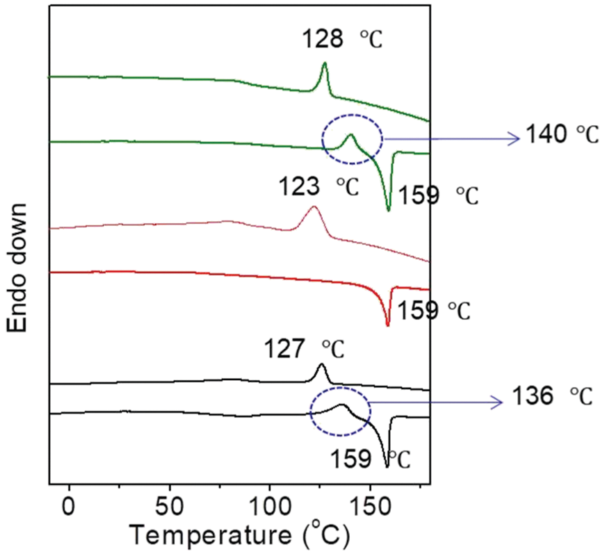

Fig. 5 DSC thermogram of **OPVC** xerogel before grinding (—), after grinding (—) and after recovery (—).

of **OPVC** has a contribution from the linear dichroism in solution, which might be due to the anisotropic orientation of the fibrous assembly (Fig. S6, ESI†).[13]

Interestingly, a complete recovery of the CD signal was observed upon treating the sheared sample with definite volume (0.1 mL mg^{-1}) of *n*-decane followed by removal of the solvent under vacuum (Fig. 4), indicating a reformation of the helical assembly. Such disruption and re-organization of the OPV helical stacks has been further proved with a time dependent FT-IR measurements as shown in Fig. S7, ESI.† The H-bonded N–H stretching peak (3300 cm^{-1}) of **OPVC** upon shearing, resulted in two peaks (3420 and 3300 cm^{-1}), indicating the partial disruption of H-bonds in the assembly due to mechanical stress.[2b] The time dependent recovery of the peak around 3300 cm^{-1} and the decrease of the peak intensity at 3420 cm^{-1} indicate the reorganization of the assembly through amide H-bonding. Changes observed for amide I band further support such a disruption and reorganization of the amide H-bonding in the OPV assemblies. From these experiments it can be assumed that the fast recovery process after mechanical agitation might be driven by amide H-bond, leading to the formation of a nonhelical assembly, whereas point chirality driven kinetically stable helical assembly might have been formed in the presence of *n*-decane.

The lengthy/branched alkyl chain and bulky substituent may also be responsible to the formation of loose molecular stacks, which facilitate the mechano-induced phase transitions. Such a phase transition associated with thermally reversible mechanochromism was reported for various dyes.[12] At the same time, self-recovering mechanochromism has been considered as the result of a crystalline to amorphous transition with a low cold-crystallisation close to room temperature.[12b,c] To get more insights on the mechanism and effect of chiral chain on the reversible mechanochromism, differential scanning calorimetric (DSC) and X-ray diffraction (XRD) experiments were conducted. DSC of **OPVC** xerogel (Fig. 5) showed an exothermic transition around 136 °C, which can be ascribed to either as a phase transition[14] or as a cold-crystallisation.[12b,c] An endothermic transition at 159 °C must be isotropic melting transition of **OPVC**. Interestingly, the sample after grinding showed only a melting transition at 159 °C. The disappearance of the exothermic peak at around 136 °C suggests a plausible mechano-induced transformation of kinetic state (phase I) to energetically more favourable state (phase II). *n*-Decane treated sample displayed a similar transitions as the xerogel sample, indicating the reformation of kinetic state (phase I).

These results indicate that the mechanochromism of **OPVC** is due to an amorphous–amorphous transition, say conversion of phase I to phase II (Fig. 6). Further, the effect of mechanical and thermal stimuli on **OPVC** xerogel was studied using XRD technique (Fig. S8, ESI†). The decrease in intensity of the diffraction patterns after shearing the film indicates the possible dissociation of **OPVC** aggregates. More importantly, thermal treatment further decreased the intensity of the diffraction peaks, indicating the amorphous nature of the assembly. These findings underline that the **OPVC** mechanochromism is due to a transition from the kinetic helical amorphous state (phase I) to a

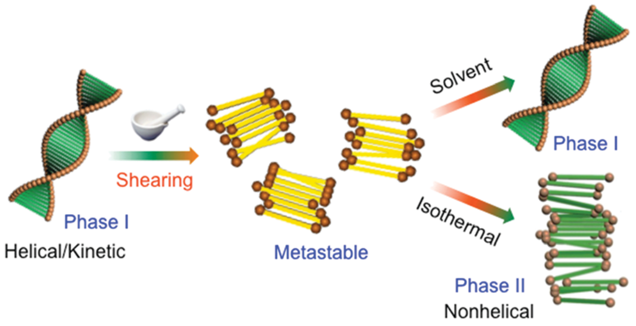

Fig. 6 Proposed pathways for the mechanochromism in **OPVC** from phase I to phase II transition.

nonhelical amorphous state (phase II). XRD of *n*-decane treated sample showed diffraction pattern with relatively high intensity, once again establishing the solvent assisted formation of kinetically favoured helical assembly (phase I). This observation is in analogy to a previous report as in the case of perylene bisimide organogelators where two different types of aggregates have been interconverted using two different stimuli (solvent and heat).[15]

The difference in the mechanochromic fluorescence colour change of **OPVC** and **OPVA** are clear from the Commission Internationale de l'Éclairage (CIE) 1931 chromaticity diagram (Fig. S9, ESI†). The CIE coordinates of **OPVC** before shearing is $x = 0.47$ and $y = 0.52$. After shearing, the values are changed to $x = 0.51$ and $y = 0.46$, and returned to $x = 0.45$ and $y = 0.50$ which are closer to the initial value, after 1 h. In case of **OPVA**, the CIE coordinates of the initial fluorescence are $x = 0.47$ and $y = 0.52$ and those after shearing changed to $x = 0.53$ and $y = 0.47$, which remained more or less the same after 1 h. The observed fluorescence colour change during mechanical stress can be explained on the basis of the formation of aggregates with different size (or overlap strength) and energy levels. **OPVC** forms polydispersed aggregates of varying energy levels as evident from the time resolved emission studies. Upon mechanical stress, the broad dispersity of aggregates become narrow and the resulting fluorescence colour would have less contribution from the short wavelength emitting aggregates thereby shifting the emission to the orange.

Based on the above experimental data, the mechanism of shearing induced fluorescence colour change, self-recovery of fluorescence and the solvent induced recovery of chirality in **OPVC** can be depicted as in Fig. 6. Initially, the **OPVC** xerogel is composed of helically twisted and kinetically favoured green and red emitting aggregates as inferred from the overall yellow emission. Under mechanical stress, these helical aggregates are disturbed to form metastable aggregates having less percentage of the green emitting species. With time, these metastable aggregates slowly reorganize to form a fluorescent but CD silent assembly as evident by the absence of CD signal. In the presence of a solvent, the CD silent aggregates reorganize back to the helical assembly as revealed by the restoration of the CD spectrum.

In conclusion, we have demonstrated an interesting case of a self-recoverable mechanochromism in a chiral π-gelator. The role of the chiral handle in the gelator for the observed phenomenon is clear when the properties were compared with an analogous achiral gelator. Interestingly, the reorganization of the mechanically disturbed chiral gelator leads to the recovery of the initial fluorescence colour but not the initial CD response, which indicated distinct pathways of the molecular reorganization. The fact that the mechanically strained gelator regained the original fluorescence and CD response in presence of a solvent underlines this hypothesis. The present case is a unique example for a self-recoverable amorphous (CD active-phase-I) to amorphous (CD silent-phase-II) change induced by mechanical stress where presence of a branched chiral chain plays an important role in the manifestation of mechanochromism. The strategy described here may be applicable towards the design of a variety of fluorescent chiral π-gelators based reversible mechanochromic systems.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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