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# “Self-Lockable” Liquid-Crystalline Diels-Alder Dynamic Network Actuators with Room Temperature Programmability and Solution-Reprocessability

Zhi-Chao Jiang, Yao-Yu Xiao, Lu Yin, Li Han and Yue Zhao*

**Abstract:** Novel main-chain liquid crystalline polyesters were designed and synthesized to demonstrate liquid crystalline Diels-Alder dynamic networks (LCDANs) for soft actuator applications. These materials exhibit unprecedented ease for actuator programming and reprocessing compared to existing liquid crystalline network (LCN) systems. Following cooling from around 125 °C, LCDANs can be deformed with aligned mesogens self-locked at room temperature by slowly formed DA bonds, which allows for the making of solid 3D actuators capable of reversible shape transformation, and strip walker and wheel capable of light-driven locomotion upon either thermally or optically induced order-disorder phase transition. Any actuator can readily be erased at 125 °C and reprogrammed into a new one under ambient conditions. Moreover, LCDANs can be processed directly from melt (e.g. fiber drawing) and, being dissolvable in solution, from solution as well (e.g. casting tubular actuators), which cannot be achieved with liquid crystalline dynamic networks using exchangeable covalent bonds (vitrimers). The combined attributes of LCDANs are a significant progress toward developing easily programmable/processable LCN actuators.

Polymer soft actuators have aroused great scientific interest for use as stimuli-controlled shape changing and moving devices for soft robots,[1] micromechanical systems,[2] artificial muscle[3] and energy generators.[4] Liquid crystal polymer networks including elastomers (LCNs) possess both entropy elasticity of polymer networks and anisotropic property arising from ordered mesogens, which makes them stand out among the many polymeric materials for soft actuator applications.[5] LCN actuators are typically fabricated by firstly orienting the mesogens through mechanical stretching or surface alignment, and subsequently locking the ordered structure through a chain crosslinking reaction.[6] Upon reversible order-disorder phase transition of the mesogens, LCNs can exhibit macroscopic and reversible shape change. Although substantial progress has been made in the development of LCN actuators in terms of actuation performance in the past decade,[7] their large-scale applications are still hampered by the demanding actuator fabrication and the lack of ease for processing. First, most LCN actuators require photo-crosslinking or photo-initiated reaction during the preparation process.[8] Due to the limited penetration of light, LCN actuators can only be prepared into thin films for the sake of complete crosslinking. Secondly, like thermosetting polymers and elastomers, LCNs cannot be melted or dissolved in soliton for reprocessing due to crosslinked polymer chains. To address these issues, liquid crystal vitrimers have first been developed using exchangeable ester bonds to replace traditional permanent covalent bonds in LCNs.[8] Through the transesterification reaction, the network topology can be rearranged, which makes it possible to reprogram the shape of the actuator or reprocess it at high temperatures (>130 °C). Subsequently, a variety of reactions promoting exchangeable covalent bonds have been applied in making LCN actuators, such as transcarbamoylation,[10] boronic-ester exchange reaction,[11] and photo-exchange reactions of disulfide[12] and allyl sulfide,[13] all of which allow an actuator to be reshaped under external force at high temperature or under illumination.

Herein, we report the design and study of a new material system for LCN actuators, namely, liquid crystalline Diels-Alder dynamic networks (LCDANs), which elevates the ease for actuator programming and reprocessing to a new height. The thermally reversible nature of some Diels-Alder reactions has long been utilized for designing recyclable and reprocessable thermoset polymers.[14] Typically, the material network consisting of diene/dienophile adducts is heated to high temperature (usually above 110 °C) to trigger the reverse Diels-Alder reaction (retro-DA) so that it can reach melt state for reprocessing, while the DA bonds reform to restore the network structure on cooling.[15] Although the kinetics and mild reaction conditions of DA bonds appear suitable for LCN actuators, it has not been explored for LCNs to our knowledge. One design consideration is that the material needs to possess an LC (order) to isotropic (disorder) phase transition temperature significantly lower than the dissociation temperatures of the DA bonds, so that the material can be reversibly actuated through back-and-forth phase transition without disrupting the DA bonded network. In this study, we synthesized two LCDANs differing in the mesogenic moiety in the polymer structure. They show unprecedented ease of programmability and reprocessability, which greatly facilitates the making of LCN actuators. More specifically, following a simple thermal treatment for DA bond dissociation, all necessary steps for an actuator fabrication can be accomplished at room temperature: an LCDAN specimen is deformed or processed into a specific 3D shape and the alignment of mesogens in deformed state is self-locked by a slowly formed DA-bonded network, without the need for any photo- or thermal polymer crosslinking. Such LCDAN actuators display reversible shape change upon heating above and cooling below the order-disorder phase transition, and can also be made into a light-fueled walker or wheel. Moreover, unlike liquid crystalline vitrimers using exchangeable covalent bonds, the recycling and reprocessing of LCDANs can be realized not only from melt but also from solution as they can be dissolved in solvent with thermally dissociated DA bonds.

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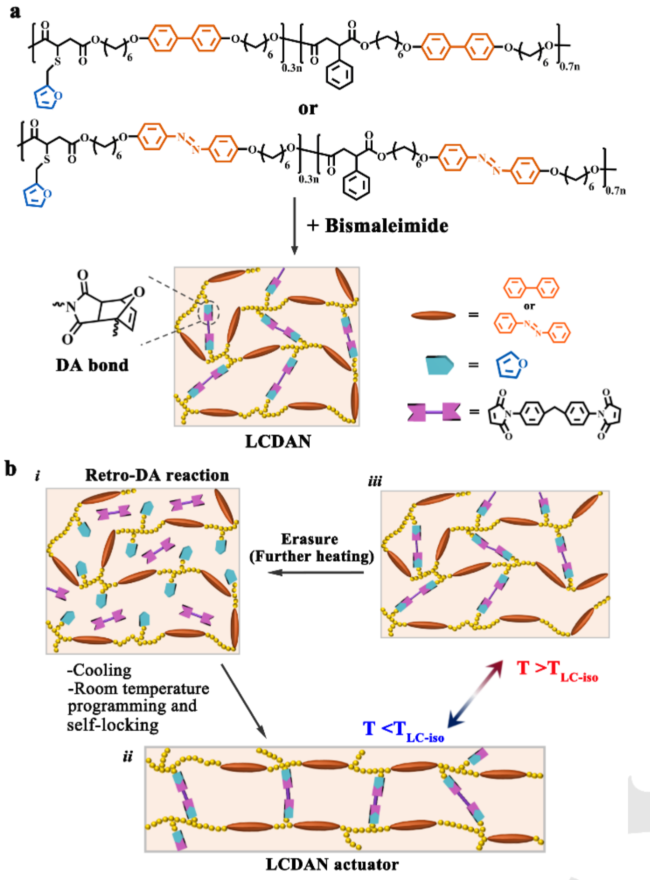

**Figure 1.** Design of the “self-lockable” liquid crystalline Diels-Alder dynamic network (LCDAN) actuators: **a)** Chemical structures of two main-chain liquid crystalline polymers (LCPs) bearing furan side groups and containing either biphenyl or azobenzene as mesogenic moieties, as well as the preparation of their LCDANs through DA bonded-crosslinking in the presence of bismaleimide; and **b)** Schematic showing the room temperature programming and self-locking of LCDAN actuators capable of reversible shape change upon the LC-isotropic (order-disorder) phase transition.

Figure 1a shows the chemical structures of two main-chain liquid crystalline polymers (LCPs) and their use for preparing LCDANs. We designed and synthesized two polyesters bearing a number of furan side groups for DA bonds and containing either biphenyl or azobenzene mesogenic moieties in all monomeric units, denoted as BP-LCP and AZO-LCP, respectively (synthesis and characterization are detailed in Supporting Information). To prepare their LCDANs, either of the polymers dissolved in tetrahydrofuran was mixed with stoichiometric quantity of bismaleimide (BM) and cast into a Teflon mold. After removing the solvent, an LCDAN with DA bonds as crosslinking points was obtained. Using mechanical stretching as an example of shape programming, Figure 1b schematically illustrates the deformation of LCDAN and self-locking of oriented mesogens by DA bonds at room temperature with no need for a separate crosslinking reaction. After heating for dissociation of DA bonds through retro-DA reaction, the LCDAN sample is cooled to room temperature. Since the generated furan and maleimide groups after thermal dissociation need time to react with each other and reform DA bonded network,[16] the slow kinetics allows the LCDAN to have plenty of time to be programmed by mechanical force into a desired shape with oriented mesogens at room temperature. With the reformation of DA bonds over time, the alignment of mesogens and the programmed shape can be self-locked. Without any post-treatment, the obtained monodomain LCDAN actuator can realize reversible contraction and elongation upon order-disorder phase transition. Due to the dynamic nature of DA bonds, the actuation behavior can be erased by heating to 125 °C and the LCDAN sample can be reprogrammed into new actuators with different shapes and actuation behaviors.

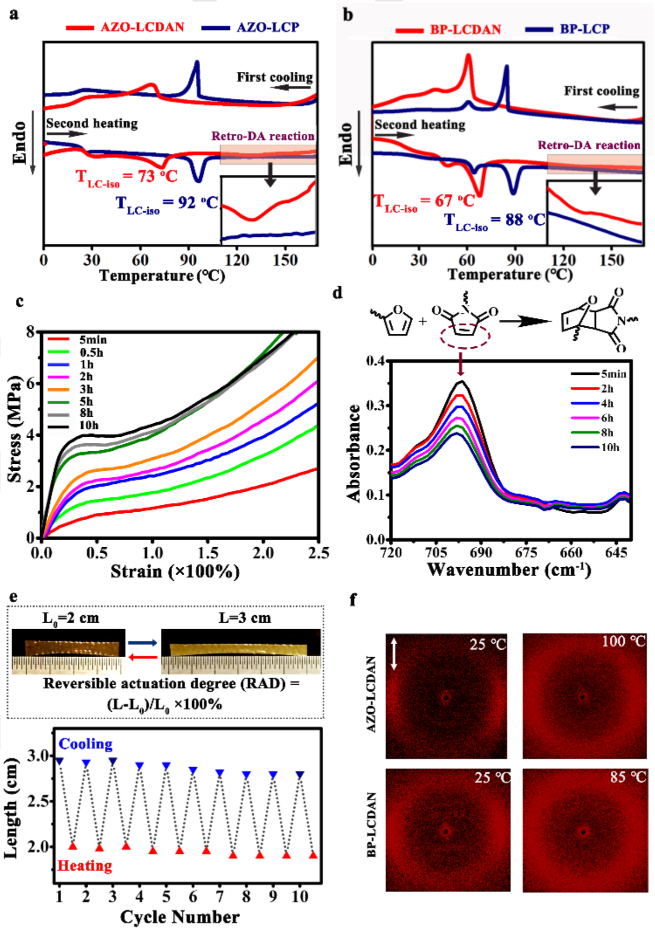

**Figure 2. a)** and **b)** DSC heating and cooling scans for AZO-LCDAN and AZO-LCP, and BP-LCDAN and BP-LCP, respectively. The inset is a magnified region showing a broad endothermic peak on heating the LCDANs. **c)** Tensile test curves of AZO-LCDAN cooled from 125 °C to room temperature for different times prior to the measurement. **d)** Change in the infrared absorbance of out of plane vibration of –C=C–H in maleimide over different waiting time at room temperature, recorded from a thin film of AZO-LCDAN cooled from 125 °C to room temperature. **e)** Photos of an AZO-LCDAN strip actuator displaying reversible contraction (in isotropic phase) and elongation (at room temperature) as well as data showing the stable actuation upon ten heating/cooling cycles. **f)** Two dimensional XRD patterns of AZO-LCDAN actuator (top) and BP-LCDAN actuator (bottom) recorded in the isotropic phase and after cooling to room temperature (the arrow indicates the stretching direction)

The formation of DA bonds in both BP-LCDAN and AZO-LCDAN was firstly revealed by the swelling experiment. In contrast to the soluble LCPs bearing furan side groups (without addition of BM), the LCDANs can only swell in chloroform at room temperature after 24h (Figure S9). Figure 2 presents a series of characterization results of LCDANs and their actuators, showing particularly the slow formation of DA bonds that opens the window for room temperature programming and self-locked network structure for reversible shape changes. First, comparing the two linear LCPs with their corresponding LCDANs, the differential scanning calorimetry (DSC) measurements show that the formation of DA bonds has little effect on the glass transition temperature (Tg) appeared at about 25 $^{o}$C, but reduces significantly the LC-isotropic phase temperature, $T_{LC\text{-}iso}$, by some 20 $^{o}$C, to 73 $^{o}$C (on heating) for AZO-LCDAN (Figure 2a) and 67 $^{o}$C for BP-LCDAN (Figure 2b). The lowered $T_{LC\text{-}iso}$ in DA-bonded actuator is a sought-for feature, because a large gap between $T_{LC\text{-}iso}$ and the temperature promoting effective DA network disruption is necessary for repeated shape change of the LCDAN actuator upon the order-disorder phase transition while retaining a stable DA-bonded network. From the DSC heating curves, DA bonds dissociation appears to occur over a temperature range of about 110-150 $^{o}$C, as revealed by a broad endothermic peak for both LCDANs. Interestingly, after cooling to room temperature, the dissociated furan/maleimide groups in LCDANs reform DA bonds slowly at room temperature. This is demonstrated by the tensile tests shown in Figure 2c. A series of AZO-LCDAN films were heated at 125 $^{o}$C for 3 min to dissociate DA bonds, followed by cooling to room temperature. Afterwards, the samples were subjected to the tensile test after various times at room temperature (about 26 $^{o}$C). As can be seen, the LCDAN sample becomes increasingly harder with increasing the time at room temperature prior to the test. Similar results were obtained for BP-LCDAN (Figure S10). Indeed, both Young's modulus and yield stress for the two LCDANs increase significantly by prolonging the waiting time at room temperature, especially over the first 5h (Figure S11). This observation indicates that the number of DA bonds formed at room temperature increases over time, because Young's modulus and yield stress generally increase with increasing density of DA crosslinks.[18] The slow reformation of DA bonds at room temperature was further confirmed by recording the infrared spectra of a thin AZO-LCDAN film after cooling from 125 $^{o}$C (Figure 2d). The intensity of the imide absorption band at 700 cm$^{-1}$, attributed to the out of plane vibration of −C=C−H in maleimide,[19] decreases over time, implying the continuous formation of DA bonds. This slow kinetics of DA reaction makes it possible to program LCDAN actuators with desired shapes at room temperature. As the LCDAN is deformed with aligning mesogens, the forming DA bonds builds up a network structure that self-locks the programmed shape and enables the reversible shape change as long as the DA-bonded network remains.

Before showcasing the exceptional room temperature shape programmability and easy reprocessability from either melt or solution of the LCDAN actuators, we used the simple uniaxial stretching to investigate their actuation properties and the influencing factors. After 3 min at 125 $^{o}$C followed by cooling, a strip of either AZO-LCDAN or BP-LCDAN was stretched at room temperature to 300% strain and remained under strain for certain time to ensure the self-locking of aligned mesogens by formed DA-bonded network. Such programed actuators of both LCDANs exhibit similar thermal actuation behaviors: contracting upon heating into the isotropic phase (e.g. 80 $^{o}$C) and extending after cooling back to room temperature, with a reversible actuation degree (RAD) around 48% for AZO-LCDAN and 45% for BP-LCDAN (an AZO-LCDAN strip and the definition of RAD are shown in Figure 2e). The reversible shape change remains stable upon repeated heating-cooling cycles (Figure 2e). The reversible shape change arises from the transition between uniaxially oriented and disordered mesogens as confirmed by X-Ray Diffraction (XRD) measurements (Figure 2f, Figure S13-S14). For both LCDAN actuators, at 25 $^{o}$C (extension), mesogens are aligned along the strain direction as can be seen from the wide-angle reflection arcs at $2\theta\approx20^{o}$ (nematic order) and small-angle reflection at $2\theta\approx2.5^{o}$ (ordered smectic layers). In the isotropic phase, the orientation of mesogens disappears. Moreover, experiments revealed the effects of a number of parameters on the actuation performance of the LCDANs. First, to have a stable RAD over repeated heating-cooling cycles, the temperature in the isotropic phase should be below about 100 $^{o}$C to retain a stable DA-bonded network; heating to higher temperatures leads to DA bonds dissociation and, consequently, declined reversible actuation (Figure S15). Secondly, after stretching an actuator at room temperature, it should be kept under deformation for over 5h to obtain a well crosslinked network due to the slow DA bond formation kinetics. If needed, this waiting time can be reduced considerably by heating slightly the actuator under strain (e.g. 40 $^{o}$C) to speed up the formation of DA bonds (Figure S16). Thirdly, following the thermal treatment at 125 $^{o}$C, if wanted, the LCDAN actuator can be stretched at higher temperatures before cooling to room temperature. While a similar RAD (around 54%) was observed when the LCDAN was stretched in the LC phase, stretching in the isotropic phase resulted in a decreased RAD (about 30% when stretched at 120 $^{o}$C, Figure S17). This effect is likely explained by a less efficient orientation of mesogens upon stretching in the isotropic phase.

The attributes of shape programming and self-locking at room temperature leading to reversible actuation greatly enhance the achievable shape morphing complexity and flexibility, as well as shape change-enabled motion of the LCDAN actuators. Examples are given in Figure 3 to illustrate the unique properties of LCDANs. First, after cooling from 125 $^{o}$C, an AZO-LCDAN strip was directly twisted around a metal bar at room temperature, followed by awaiting the fixation of the mesogen alignment and helical shape through gradually formed DA crosslinks. As the temperature goes above $T_{LC\text{-}iso}$, the helix unwinds and the strip recovers the flat shape; while on cooling back to the LC phase, the helical shape reappears (Figure S19 and Movie S1). Secondly, since both the alignment of mesogens and DA crosslinks in LCDAN are lost at 125 $^{o}$C, the previously programmed shape is erased (Figure S15) and the same sample can be reprogrammed into different shapes and endowed with diverse reversible actuation modes. As shown by the example in Figure 3a and Movie S2, a flat AZO-LCDAN sheet was firstly programmed into the dome-shaped actuator. Upon heating and cooling, the actuator undergoes reversible dome-flat shape transformation. Then, the actuator was heated at 125 °C to eliminate the previous network, the cooled and refreshed sheet was then reprogramed to have two reversed pyramids. Using the same procedure, the actuator could be continually reprogramed, in an on-demand manner, to various types of pyramids or dooms. For each architecture, it can be flattened on heating above $T_{LC\text{-}iso}$ and reappeared on cooling below $T_{LC\text{-}iso}$. Moreover, as demonstrated in Figure 3b and Movie S3, using a single sheet of BP-LCDAN, a series of 3D origami structures, including accordion fold, Miura-Ori fold, Origami spiral and Origami tent, were obtained, which can unfold and refold repeatedly on heating/cooling cycles. These origami transformers were easily prepared at room temperature thanks to the properties of the LCDANs. Owing to the stability of reversible actuation during the reprograming process (Figure S20), the number of reprogrammable shapes is infinite in principle. More interestingly, the self-locking LCDAN can be further used to fabricate reprogrammable solid 3D actuator, which can hardly be achieved using other LCN materials. Examples are given in Figure 3c and Movie S4. The cuboid of BP-LCDAN after retro-DA reaction can be shaped to a sphere manually like a playdough at room temperature. After self-locking, the sphere exhibits reversible ball-cuboid transformation by heating and cooling through $T_{LC\text{-}iso}$. The same sample can then be reprogrammed into other solid 3D geometries such as star, pie and parallelepiped, through simple thermal erasure followed by room temperature processing. One mention about the Movies should be made: the apparently slow actuation speed is due to the used slow rate of temperature change.

Not limited to actuation by direct heating/cooling, AZO-LCDAN based actuators can also achieve light-fueled shape change and locomotion, because the rod-like azobenzene mesogens in the stable *trans* isomer are converted to the bent *cis* isomer upon absorption of UV light (365 nm), while the latter returns to the *trans* state by absorption of visible light (550 nm) (Figure S21). Since azobenzene mesogens upon the reversible *trans–cis* isomerization can lead to reversible order-disorder phase transition, the bending-unbending actuation behavior can be observed with uniaxially aligned monodomain AZO-LCDAN strip actuator upon alternating UV and visible light irradiation (Figure S22). Moreover, when a monodomain AZO-LCDAN strip is laminated with a flexible polyimide film (Kapton), the bilayer actuator can present reversible bending and unbending by turning on/off UV light (320-480 nm, Figure S23 and discussion). Since the actuator can be easily programmed into a desired shape or structure, versatile light-controlled motions can be realized. On the one hand, a bilayer strip was shaped into caterpillar-inspired arching walker (Figure 3d, Figure S24 and Movie S5). When UV light is on, the strip arches up due to contraction of the bottom LCDAN layer, while when the light is turned off, the strip flattens to restore the initial shape. With the two ends adjusted purposely for unbalanced friction with the substrate surface, the walker can crawl forward upon repeated UV light on/off cycles, at an average speed of 3.4 cm/min. On the other hand, the bilayer actuator was programmed into a light-fueled rotating wheel (Figure 3e and Movie S6). Upon UV light irradiation, the curvature of illuminated right side decreases as a result of bending towards the outer AZO-LCDAN layer, while the unexposed left side remains unchanged. This asymmetric change in curvature makes the wheel's center of gravity shifting from right to left, which results in rolling of the wheel away from the light beam at an average speed of 19.4 cm/min. It should be emphasized that all the examples of reversible shape change and light-driven locomotion were realized using the LCDAN actuators programmed and self-locked at room temperature, which is a first-time achievement.

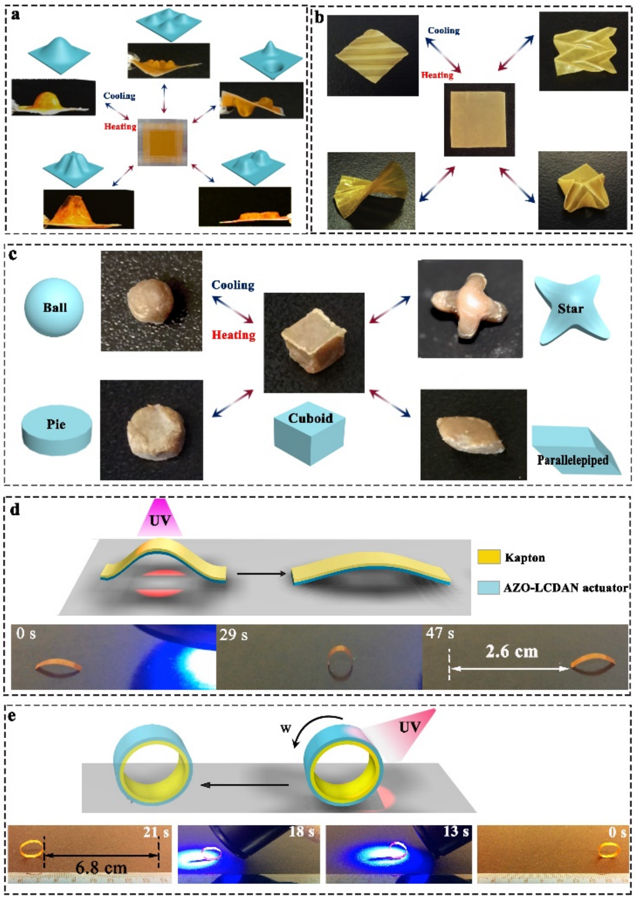

**Figure 3.** Schematic illustrations and photographs of various room temperature programmed and self-locked LCDAN actuators: a) On-demand reprogramming of 3D structures of a single AZO-LCDAN sheet actuator (1cm*1cm*0.15mm in size, see Movie S2 showing reversible 3D-flat transformation). **b)** Different 3D origami architectures programmed from one planar BP-LCDAN actuator (1cm*1cm*0.15mm in size, see Movie S3 for reversible flat-origami transformation). **c)** Reversible 3D-to-3D solid shape conversion based on a bulk BP-LCDAN actuator (3mm*3mm*2.6mm in size, see Movie S4 for reversible 3D-to-3D transformation). **d)** An AZO-LCDAN/Kapton bilayer actuator capable of crawling forward upon UV light on/off cycles (see Movie S5). **e)** An AZO-LCDAN/Kapton bilayer wheel executing rolling motion under UV light irradiation (see Movie S6).

Finally, both BP-LCDAN and AZO-LCDAN display unmatched ease for recycling and reprocessing. Unlike insoluble vitrimers using exchangeable bonds, the LCDANs can be dissolved in organic solvents and processed from solution. This is demonstrated by the preparation of a tubular actuator in Figure 4a and Figures S25-S26. Fragments of BP-LCDAN were dissolved in chloroform at 120 °C in an enclosed pressure vessel filled with $N_2$ gas; when cooled to room temperature, the solution remained clear for at least 2h. By casting the solution into the space between two concentric cylinders, followed by drying and uniaxial stretching, a tubular actuator with thermally induced reversible expanding-shrinking capability was obtained (Figure 4a and Movie S7). Moreover, the LCDANs not only can be remolded under hot-compression like vitrimers (Figure S27), they can also be easily reprocessed from melt. Figure 4b and Figures S28-S29 show LCDAN fiber actuators easily prepared by dipping the tips of a tweezer into the viscous melt (>155 °C) and rapidly drawing it. During the stretching process, the fibers are cooled down in air and the aligned mesogens are locked by DA bond crosslinks over time. As shown, the BP-LCDAN fibers exhibit thermally induced reversible straight-random coil actuation (see Movie S8). Such actuating LCDAN fibers are a potential candidate for smart textile applications. For example, a thin BP-LCDAN yarn (3.5 mg, about 56 mm in length and 0.16 mm in diameter) prepared by twisting four fibers, can easily lift up a clamp (2986.3 mg, 850 times heavier than the yarn's own weight) by 18 mm upon heating (Figure 4b and Movie S9).

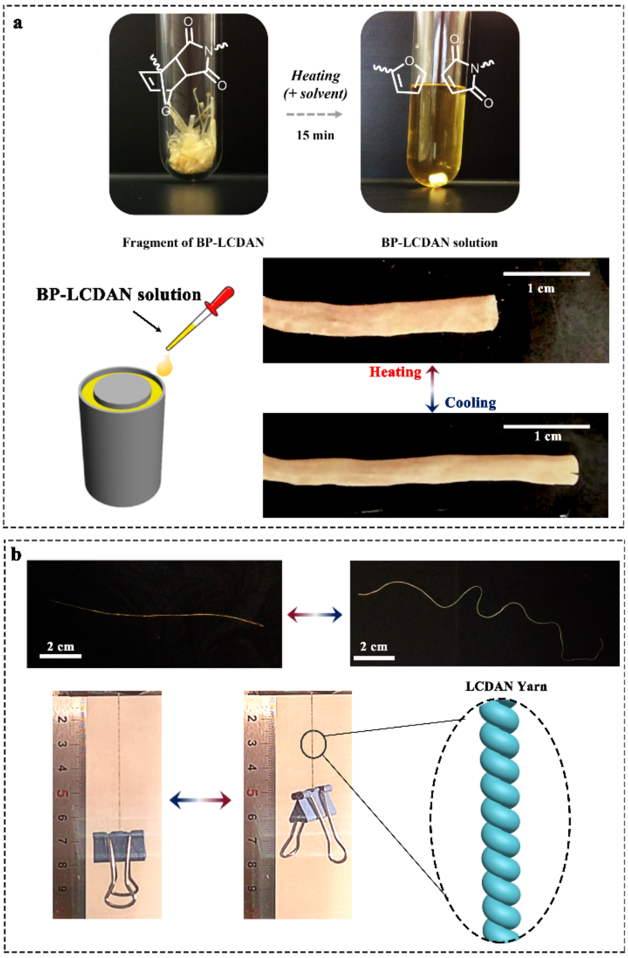

**Figure 4. a)** Photographs showing the solution processing of a tubular actuator of BP-LCDAN and its reversible expanding-shrinking (see also Movie S7). **b)** Reversible straight-random coil actuation behavior of a fiber actuator of BP-LCDAN prepared by direct drawing from melt (see also Movie S8) and photo images of thin LCDAN yarn (3.5 mg) lifting up a load (2986.3 mg) in a heating/cooling cycle (Movie S9).

In summary, we have designed and synthesized two main-chain liquid crystalline polyesters that form Diels-Alder bond-based liquid crystalline dynamic networks. These LCDANs can be shaped or programmed into 3D structured actuators (such as helix, origami and various 3D solid shapes) at room temperature and, surprisingly, self-locked by slowly formed DA bonds for reversible shape transformation, with no need for additional thermally or optically initiated chain crosslinking. If wanted, the DA network formation can be speeded up by slight heating (to about 40 °C). Using oriented AZO-LCDAN strip laminated with a polyimide film (Kapton), UV light-driven caterpillar-like crawling and wheel rotating locomotion can be realized. Furthermore, unlike liquid crystalline vitrimers that generally can only be reshaped or molded by high temperature compressing, the LCDANs can be dissolved in a hot solvent and, after cooling to room temperature, can be solution-processed as demonstrated by the tubular actuator. They can also be processed from the melt. Actuating fibers can be obtained by directly drawing a viscous melt followed by cooling, twisting the fibers together leads to actuating yarns. As compared to existing LCN materials, our LCDANs offer exceptional ease for constructing a stimuli-controlled shape morphing or moving actuator. Indeed, the combined attributes, including room temperature programming and self-locking of aligned mesogens, easy erasure for reprogramming or recycling, and processing from solution or melt, make them a new promising material system for LCN based polymer actuator development and applications.

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## Conflict of interest

The authors declare no conflict of interest.

**Keywords:** liquid crystal polymer actuators • Diels-Alder dynamic networks • room temperature programming • solution-reprocessability • light-driven soft robots

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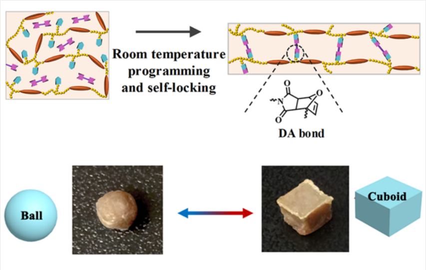
Layout 1:

## COMMUNICATION

Text for Table of Contents

Liquid crystalline dynamic networks can be shaped into 3D objects at room temperature while being stabilized by slowly formed Diels-Alder bonded crosslinks. The actuators can execute thermally or optically induced reversible shape change for doing a mechanical work or locomotion.



**Zhi-Chao Jiang, Yao-Yu Xiao, Lu Yin, Li Han and Yue Zhao***

***Page No. – Page No.***

**“Self-Lockable” Liquid-Crystalline Diels-Alder Dynamic Network Actuators with Room Temperature Programmability and Solution-Reprocessability**

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***Page No. – Page No.***

**Title**

Text for Table of Contents