

Fabrication of Light-Triggered Soft Artificial Muscles via a Mixed-Matrix Membrane Strategy

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Abstract: Artificial muscles triggered by light are of great importance, especially for the development of non-contact and remotely controlled materials. Common materials for synthesis of photoinduced artificial muscles typically rely on polymer-based photomechanical materials. Herein, we are able to prepare artificial muscles using a mixed-matrix membrane strategy to incorporate photomechanical molecular crystals with connective polymers (e.g. PVDF). The formed hybrid materials inherit not only the advantages of the photomechanical crystals, including faster light response, higher Young's modulus and ordered structure, but also the elastomer properties from polymers. This new type of artificial muscles demonstrates various muscle movements, including lifting objects, grasping objects, crawling and swimming, triggered by light irradiation. These results open a new direction to prepare light-driven artificial muscles based on molecular crystals.

Bio-inspired artificial muscles or actuators have recently been of considerable interest owing to their ability to convert chemical energy into mechanical motions for a wide range of potential applications in industry, medicine, and robotics.^[1] The energy transforming process of muscle-like movements in actuators can be realized by reversible deformation (contraction, expansion, rotation, bending, folding, curling and rotating) due to an external stimulus such as electric, thermal, photo energies, pH, chemical energy and pressure.^[2] Among those stimuli, light possesses many advantages

including cost-effectiveness, wireless actuation, fast response and various remoting methods (e.g. adjusting light wavelength, intensity, polarization and irradiation position).^[3] Therefore, artificial muscles remoted by light possess remarkable superiority compared to other stimuli. To date, various photomechanical materials have been reported, such as polymers, hydrogels, liquid crystal elastomers and molecular crystals, which contain light-sensitive chromophores (e.g. azobenzenes, diarylethenes, stilbenes and anthracenes) in the systems.^[4] Common materials for the synthesis of light-triggered artificial muscles typically rely on polymer-based photomechanical materials.^[5,3b] For example, the Ikeda group recently reported a liquid-crystalline polymer containing azobenzene moieties, which is capable of inducing three-dimensional movement controlled by light.^[2] Harada reported a reversible photoresponsive supramolecular hydrogel with α -cyclodextrin and azobenzene that exhibited an expansion-contraction behavior dependent on the photo stimuli.^[6]

Recently, photomechanical molecular crystals are attracting increasing attentions because of their considerable advantages compared with polymer-based materials including rapid response, faster relaxation recovery, higher Young's modulus and ordered structure.^[7] In particular, the ordered and well-defined crystal structure facilitates the understanding of mechanisms during the photoresponsive process which can be tracked easily by X-ray diffraction techniques. However, it remains a challenge to use molecular crystals to construct macroscale actuators, mainly attributed to the lack of a suitable strategy to combine the motions of randomly dispersed microscale crystals into one organized macroscale system without cancelling out the crystals' motions. Chen and co-workers reported a hybrid photoresponsive actuator incorporating nanocrystals with a polymer matrix through a dissolution-precipitation method.^[8] However, crystals were not uniformly dispersed and of low loading in the polymer system due to the low solubility of crystals. Therefore, the dissolution-precipitation method lacks universality in preparation of artificial muscles. In this study, inspired by the components of animal muscles, we adopted a mixed matrix membrane (MMM) strategy to fabricate artificial muscles, for the first time in which photomechanical crystals serve as muscle fibers and polymers as connective tissues. Benefiting from the features of both photomechanical crystals and connective polymers, the hybrid materials deemed as artificial muscles with extends of elasticity and motility, and demonstrated controllable mobility that can reversibly lift/grasp objects, crawl and swim triggered by visible light irradiation.

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To construct artificial muscles based on photomechanical crystals, in the first stage, we prepared a series of novel anthracene derivatives dimers (**BA n DA**, $n=2-8$) using flexible alkyl linkers (Scheme S1 in the Supporting Information). In all the crystal structures, the anthracene molecules are arranged in a parallel face-to-face manner (Figure 1 and

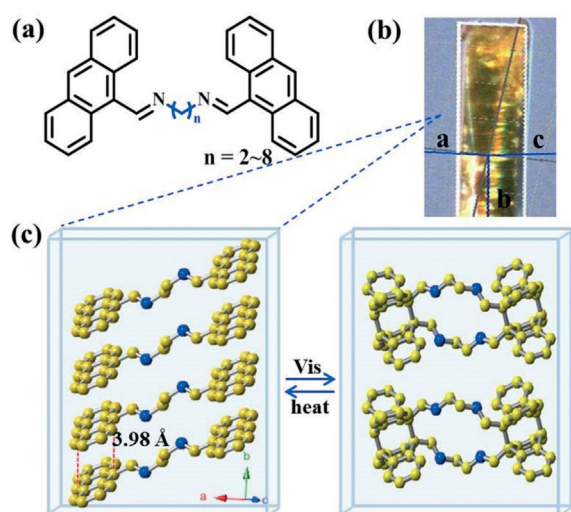


Figure 1. a) Molecular structures of **BA n DA**; b) face index of **BA2DA** view along the b axis; c) structure change of **BA2DA** before and after light irradiation.

Figure S1–S6) via a π - π stacking fashion. The plane to plane distance between two anthracene groups is 3.98–4.40 Å, suitable for [4+4] photodimerization according to Schmidt's rules.^[9] It is noteworthy that all **BA n DA** crystals were photoresponsive to visible light with interesting bending behaviors (Figure S7). **BA2DA** crystals were chosen as a representative to study its photoresponsive properties in detail. We found that **BA2DA** crystals were responsive to white light, blue light and even sunlight (Figure S8,S9). Moreover, **BA2DA** crystals demonstrated various motions including bending, curling, jumping and wriggling behaviors (Figure S10 and Video S1). **BA2DA** crystal was fixed on a glass fiber and irradiated with unilateral white light in vertical direction (Figure 2a). After irradiation for 1 min, the crystal gradually bent away from light to reach a bending angle approximately 45°. When irradiating from the opposite direction, the crystal can bend back to the initial position. Extended the irradiation time for 4 min, the crystal could bend up to 90° (Figure S11). Since structure packing of **BA2DA** is different along a , b , and c directions, the photoresponsive behaviors of **BA2DA** irradiated along different axes were also studied. It was found that the bending behaviors could occur when irradiation was along the a or c axes (Figure S12). In addition, we found **BA2DA** crystals could bend under mechanical force as well. The crystal could bend to an angle greater than 180° and recover its original shape easily when releasing force, which indicates the high elasticity and flexibility of the crystals (Figure 2b). To study whether the flexible alkyl linker of **BA n DA** plays a key role in the crystals' photomechanical performances, a rigid anthra-

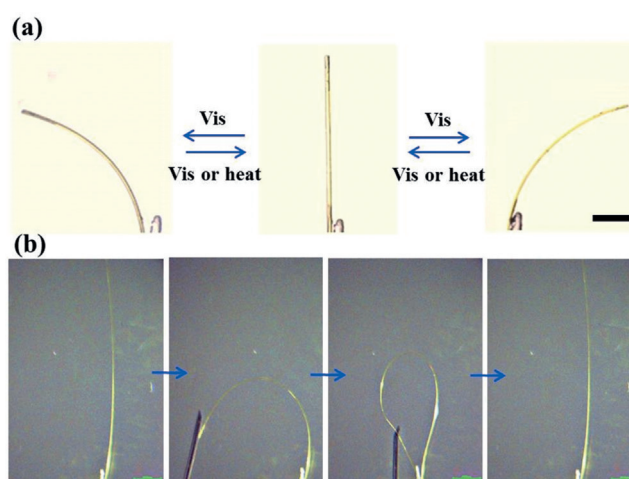


Figure 2. a) Illumination of photoresponsive bending behavior of **BA2DA** crystal and straighten behavior by light irradiation or heating. Scale bar: 1 mm; b) illumination of the bending behavior of **BA2DA** by mechanical force. Scale bar: 2 mm.

cene dimer (**BABD**) with a conjugated bipyridine linker was prepared for comparison. We found **BABD** crystals, which possessed the similar anthracene packing manner as **BA n DA** crystals (Figure S13), were silent to light irradiation (Figure S7). It indicates the photoresponsive properties are not only related to the packing manner of the chromophore groups but also to the flexible alkyl linker in **BA n DA** crystals. The high elasticity and reversible bending behavior of **BA n DA** crystals are essential to construct artificial muscles.

To reveal the mechanism behind the photomechanical motions that we observed, FT-IR, ¹H NMR, and fluorescence spectroscopy were used to study the chemical reactions during light irradiation. The appearance of a new sp^3 peak at 6.01 ppm could be resulted from the cross-linking C–H of anthracene dimerization (Figure S14). Two doublet peaks (6.62 and 6.82 ppm) and two triplet peaks (6.29 and 6.47 ppm) can be attributed to the dimerization of anthracenes as well.^[10] In the FT-IR spectrum, the new peak at 698 cm^{-1} can be ascribed to deformation vibrations of the cycloaddition of anthracene, which reveals that the photomechanical properties are related to the photocycloaddition reactions of parallel anthracene groups (Figure S15).^[11] In addition, fresh **BA2DA** exhibits fluorescence emission peaks centered at 488 and 528 nm (excitation at 388 nm), which are characteristic peaks of excimer species of π - π anthracene stacking.^[12] The intensity of fluorescence peaks gradually decreased as irradiation time extended, which is attributed to the resulting [4+4] photodimerization (Figure S16).^[13] In situ X-ray diffractions were also employed to track the crystal change during light irradiation. We found the intensities of powder X-ray diffraction (PXRD) patterns and single X-ray diffraction (SCXRD) reflections decreased as the irradiation time proceeded (Figure S17,S18). This result implied that the crystallinity of **BA2DA** sample remained yet with some kind of deformation after photoirradiation. We also tracked the bending behavior shown in Figure 2a via in situ single-crystal XRD (SCXRD) analyses. Crystal unit cells were measured every 2 min under light irradiation. We found that

the length of *b* axis gradually expanded by approximately 1.6% after irradiation for 20 min (Figure S19). Therefore, the crystal bending could be caused by the expansion of the crystal along the *b* axis. In addition, we observed that the whole crystal length (Figure S11) can increase around 2.2% after irradiation for 4 min (Figure S20), which further confirmed the expansion of *b* axis. To investigate the mechanism that is responsible for the elongation of *b* axis, DFT calculations were conducted. The [4+4] photoreaction of **BA2DA** can form dimer, oligomer or polymer. In order to simplify the calculation task, we proposed an aggregation model of **BA2DA-dimer** to explain the experiment results. The projection distance of adjacent **BA2DA** dimers along the stacking direction is 7.201 Å, while the corresponding anthracene groups in **BA2DA** is 6.922 Å after geometrical optimization (Figure S21). This result suggested that the crystal length could elongate approximately 4.0% along the *b* axis after intermolecular [4+4] photodimerization, which is consistent with our observation in SCXRD measurement.^[14] In addition, the bending behavior of **BA2DA** crystal was reversible by thermal treatment.^[15] The disappearance of characteristic ¹H NMR signals ascribed to anthracene dimerization (Figure S14) revealed **BA2DA** can completely recover after thermal treatment. Moreover, we found that higher temperatures can shorten the recovery time (Figure S22).^[7]

Although photomechanical crystals demonstrate interesting reversible bending behavior which is an essential feature of muscles, it is still very challenging to construct macroscale artificial muscles based on photomechanical crystals. Herein, for the first time, we developed a “mixed-matrix membrane” synthesis strategy to combine the motions of dispersed crystals into one synergetic system. A series of **BAnDA-polymer** hybrid materials was fabricated by mixing crystalline **BAnDA** with PVDF polymer (Figure S23).^[16] In these hybrid materials, the polymer serves as connective tissues and **BAnDA** crystals act as mechanical muscle fibers. We optimized the ratio of **BAnDA**/polymer and found a ratio of 1:1 (wt %) provided the best balance of materials' processability and photoresponsive efficiency (Figure S24). **BA2DA-PVDF** hybrid materials were chosen as a representative to study their performance in detail. The stress-strain curve was employed to evaluate the elastic modulus changes of **BA2DA-PVDF** and compared with blank PVDF (Figure S25). The results showed that the elastic modulus increased after introducing **BA2DA** crystals into PVDF, which indicated the good mechanical property of **BA2DA-PVDF**. PXRD patterns revealed that **BA2DA-PVDF** retained the crystallinity of **BA2DA** (Figure S26). SEM images (Figure S24) revealed that particles (after ball milling) in **BA2DA-PVDF** possess a size of approximately 1 μm and were uniformly dispersed into the PVDF matrix. We found that **BA2DA-PVDF** actuators inherited the photoresponsive behavior of **BA2DA** crystals, and can bend away from light and recover its original shape with light from the opposite side or thermal treatment. This reversible bending process can

undergo >100 cycles through heating at 100°C for 4 min (Figure S27). We studied whether **BA2DA-PVDF** actuator can be used as an artificial muscle to lift weight and release it in response to light. Firstly, **BA2DA-PVDF** was fixed with a clip on one side with the other side hung with an object. Upon light irradiation, the bottom of **BA2DA-PVDF** started to bend like an arm. The object (10.0 mg, containing a metal handle) was lifted up to a height of 5.0 mm and can return to the initial state upon light irradiating from the opposite direction (Figure 3 a–c, Video S2). This lifting and releasing

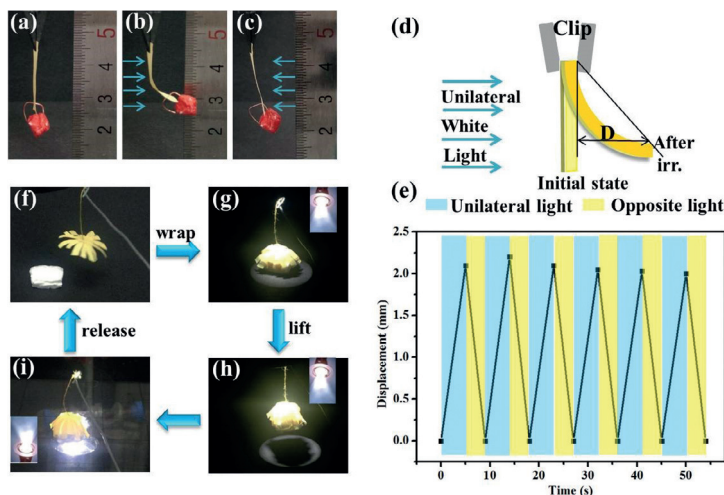


Figure 3. a)–c) Optical images of **BA2DA-PVDF** used as artificial muscles with a red object hung from an “arm” (blue arrows show the direction of light irradiation); d) illustration of **BA2DA-PVDF** hung with a clip, showing how the displacement (*D*) is defined; e) the repeating experiment of **BA2DA-PVDF** irradiated with unilateral light and opposite light. Plots show the correlation between the irradiation time and displacement (*D*); f)–i) **BA2DA-PVDF** robot with multiple arms grasped objects.

process can be repeated for many cycles without significant reduction as shown in Figure 3 e. In addition, **BA2DA-PVDF** was found to be able to mimic muscles to grasp objects. We fabricated an octopus-inspired **BA2DA-PVDF** robot with multiple arms and successfully drove this robot to grasp small objects under the control of visible light (Video S3). The robot can pick an object of over 50.0 mg (Figure 3 f–i). In a black room, the robot was firstly placed on the object, and then each finger of the robot started to bend after the light irradiation for a few seconds, and thus the object was embraced by the robot. The robot was then lifted with artificial force in a fishing fashion, and the contact force between the object and robot was strong enough to hold the object. We also rotated the robot for 360° in a circular motion and observed no detachment of the object. In addition, the robot can release the object via light irradiation in the opposite direction or by putting it into a thermal atmosphere. This process could be repeated more than 20 times.

Besides grasping behaviors, we also designed and fabricated various artificial muscles (robots) to study if they can perform more complex movements of muscles such as crawling and swimming. **BA2DA-PVDF** robot was found to possess a kind of memory property. For example, the robot in

a rectangle shape was first folded into a wavy shape (Figure S28, Video S4,S5), and then unfolded to become flat and placed on a glass surface. Surprisingly, the robot can transform into a wavy shape in seconds under light irradiation. After switching the light irradiating direction, **BA2DA-PVDF** robot can crawl forward for about 2.0 mm (Figure 4b).

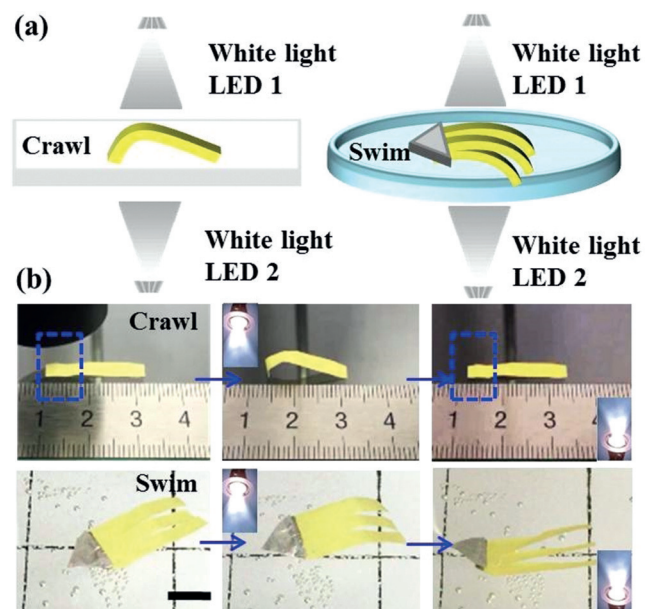


Figure 4. Schematic diagram (a) and photographs (b) showing that the robots can crawl and swim controlled by light irradiation.

By contrast, **BA2DA-PVDF** robot without folding into a wavy shape in advance did not exhibit crawling behavior using the same operation (Figure S29). Hence, the crawling performance of the robot should be resulted from the inhomogeneous strain forces accumulated in the pre-folded robot under light irradiation. We also prepared **BA2DA-PVDF** robots (length: 2.0 cm) with a fish shape by attaching a triangle aluminum foil as a fish head with three **BA2DA-PVDF** tails. By suspending the robot into solution, the tails of the fish robot can flap up and down through switching the light irradiation directions. The fish robot can swim about 5 mm triggered by light irradiation for only two cycles (Figure 4b, Video S6).

In conclusion, for the first time, we developed a “mixed-matrix membrane” synthesis strategy to construct a series of artificial muscles based on photomechanical anthracene crystals. Seven new anthracene-dimer crystals were successfully synthesized, which are photoresponsive to visible light with various motions including bending, curling, jumping and wriggling. The mechanism of the photoresponsive behavior was revealed by in situ XRD, NMR, modelling, FT-IR and fluorescence spectroscopy. In addition, hybridization of photoresponsive crystals with PVDF polymers afforded a series of artificial muscles which demonstrate various muscle movements including lifting, grasping, crawling, and swimming. Moreover, these artificial muscles exhibit excellent reusability. This study develops a versatile, powerful and

facile strategy to prepare artificial muscles and actuators based on photomechanical crystals.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: artificial muscles · mixed-matrix membrane · photomechanical crystals · photoresponsive materials · soft materials

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