Light-Driven Molecular Crystal Actuators

Oct. 2, 2013
Overview

- Importance of solar energy harvesting
- Reversible surface morphology change
- Reversible microcrystal shape change
- Reversible bending of microcrystals
- Reversible bending of composites that contain tiny crystals
- Irreversible bending of macrocrystals
- Reversible bending of macrocrystals
Primary energy demand is growing with population and the population is growing rapidly.
The primary energy source has been mostly fossil fuels

1973

Coal/peat
Natural gas
Oil
Hydro
Biofuels And waste
Renewable 0.1%

6,107 Mtoe

2010

Coal/peat
Natural gas
Oil
Hydro
Biofuels And waste
Nuclear
Renewable 0.9%

12,717 Mtoe

Mtoe: Million ton oil equivalent

Burning fossil fuels should be decreased

Renewable energy sources need to grow

Solar

Geothermal

Wind

Solar energy harvesting

- Solar heating
- Solar cells
- Artificial photosynthesis
- ...
- Light-driven molecular crystal actuators
What is a light-driven molecular actuator?

This image is the first frame of a video that could be found in the supporting information of the cited paper.
Evolution of light-driven molecular crystal actuators

- Reversible surface morphology change
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Solid phase photoinduced isomerization

What is atomic force microscopy (AFM)?
Reversible steps and valleys form on two faces of the crystal

Longer irradiation time forms more 1 nm height steps on surface A

Comparison of closed and open-ring isomers shows a considerable molecular shape change upon isomerization.

Molecular shape change results in crystal deformation

Evolution of light-driven molecular crystal actuators

- Reversible surface morphology change

- **Reversible microcrystal shape change**

- Reversible bending of microcrystals

- Reversible bending of composites that contain tiny crystals

- Irreversible bending of macrocrystals

- Reversible bending of macrocrystals
Reversible single to single crystal transformation accompanied with crystal deformation

As the reaction proceeds, the tension increases in the lattice

The solid phase conversion is 70% under photostationary state.

Crystal packing explains the crystal shape change

Single crystals have Fast response time

Each frame is 25 micro second

355 nm (8 ns)

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- **Reversible bending of microcrystals**
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- Reversible bending of macrocrystals
Azo-dye crystals bend reversibly

What is X-ray diffraction (XRD)?

Bragg’s law
\[ n\lambda = 2d\sin\theta \]
The crystal deforms reversibly

Around 1% of molecules react in solid phase

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- Reversible bending of macrocrystals
Crystal phase salicylideneaniline isomerization

HNAN crystals dispersed in PVDF–HFP forms composites that bend reversibly upon UV illumination.

2-hydroxynaphthylidene-1’-naphthylamine (HNAN)

Polyvinylidene fluoride–hexafluoropropylene (PVDF–HFP)

75 mm x 25 mm x 52 μm

λ=360 nm

dark

Average displacement/ mm g

HNAN mass percentage

The bending is reversible and relatively strong

The direction of bending depends on the concentration gradient direction of HNAN in the composite

HNAN crystals are responsible for bending

1. Large single crystals of HNAN responds to light:

![Image of HNAN crystals]

![Graph showing displacement over time]

2. XRD shows that HNAN is crystalline in the composite:

![Graph of XRD spectra for PVDF–HFP and HNAN with peaks indicating crystallinity]

3. PVDF-HFP does not respond to light.

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- Reversible bending of macrocrystals
π–π interactions and hydrogen-bondings increase the flexibility
Highest flexibility ever seen among macroscopic crystals

Contraction of one side of the crystal bends the crystal towards itself

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- Reversible bending of macrocrystals
Macro crystals bend reversibly

Electrocyclic reaction increases the height of the molecule

\[
\begin{align*}
\lambda &= 365 \text{ nm} \\
\lambda &> 440 \text{ nm}
\end{align*}
\]

Molecular geometry change increases the surface area on one side of the crystal and bends it away.
A 0.17 mg piece of crystal pulls up 46.77 mg of a lead ball

A cocrystal of two similar diarylalkenes bends towards light

The crystal works reversible

1st cycle  →  500th cycle  →  1000th cycle

0.5 mm

tip displacement /mm

cycle number

The crystal bends under water remotely

[Images showing the crystal bending under UV and visible light, with a label indicating 1 mm in each step]

The crystal spins a gearwheel

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Conclusions

- Molecular crystals can convert light to mechanical motion
- Small sized crystals are able to result in macroscopic motion if they are used in composites
- Inter molecular interactions could be established by molecular design
- Additives can increase the strength and flexibility of the crystal
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Thank You For Your Attention
Light-Driven Molecular Crystal Actuators

Tayeb Kakeshpour

Since 1950 human use of energy has been increasing along with dramatic population growth. This huge energy demand, which is predicted to keep rising, is being supplied mostly by fossil fuels. However, burning fossil fuels not only consumes and destroys them as chemical building blocks, but also introduces massive quantities of combustion products into the atmosphere leading to global warming, natural ecosystem interruption, urban pollution, etc. One solution to this energy-environmental crisis is solar energy harvesting. Light-driven molecular crystal actuators are one of the options that are able to convert light into their own mechanical motion and movement of other objects.

In molecular crystal actuators, the shape change of organic molecules resulting from solid phase reactions leads to a local tension in the lattice (Figure 1). This oriented tension has proven strong enough to change the shape of a crystal, bending it and moving the other objects. This presentation covers the initial experiments that led to this idea, and explains how exactly the molecular geometry change is related to the bulk crystal shape deformation for a variety of substrates reported in this area.

Figure 1. An example of a plate shaped single crystal which bends away upon irradiation on one side.

Wednesday, October 2, 2013, Room 136

