Macroscopic Self-Assembly and Self-Healing through Molecular Recognition

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Molecular Recognition

Host-Guest Chemistry

Supramolecular Chemistry

Development & use of molecules with structure-specific interactions
Biological Systems

Macromolecular Recognition

- Enzyme - Substrate
- Antibody - Antigen
- DNA, RNA

Supramolecular Polymers

- Microtubules, Microfilaments, Cells
Macromolecular Recognition

Main-chain

Side-chain

Supramolecular Polymers

End-group
Cyclodextrins (CD)
Polyrotaxane (Molecular Necklace)

Nature, 1992

Chemistry (Textbook) 2011
Topological Gel

Extension

Disperse

Pulley Effects

Molecular Pulley

◎ Highly Extensible, Swelling
◎ Biocompatible

Venture (Ito et al.)
2010年1月〜2月発売予定
美しさが長持ちする
ナチュラルデザイン＆ウォータープルーフ

防水＆長持ち塗装で、美しさがより長持ち
Nissan brings automotive innovation to the world of technology

Nissan announces unique *self-healing* iPhone case - the Nissan Scratch Shield iPhone case

Nissan's Scratch Shield paint is a world first in paint technology that allows fine scratches to quickly mend themselves.

Addition benefits such as scratch-resistant and *easier-to-grip* than normal glossy phone surfaces.

The outer ‘paint' is made from *polyrotaxane*, when damage occurs to the coating in the form of a fine scratch, the chemical structure is able to react to change back to its original shape and fill the gap - 'healing' the blemish.
Polymeric Materials → Scratch

Polyrotaxanes → Self-healing

From HP of Ito Labo. (Tokyo)
Self-Healing Controlled by Redox

Host (CD) Polymer + Guest (Ferrocene) Polymer
Redox Responsive • Self-Healing Supramolecular Hydrogels

Host - Guest Gel

$(\text{CH}_2\text{CH})_x-r-(\text{CH}_2\text{CH})_y-r-(\text{CH}_2\text{CH}^-)_z$
Self-Healing of Host-Guest Gel

**Self-Healing by Host-guest Interaction**
【2010年】Self-Healing & Self-Replicating systems will be realized
Can you see

Molecular Recognition?
Polyacrylamide Gel

\[ \text{-(CH}_2\text{CH}_2\text{)}^x_r^-\text{-}(\text{CH}_2\text{CH}^-)^y^- \]

1. No Interactions with Protein (Electrophoresis)
2. No Interactions with DNA, RNA (Sequencing)
3. No Interactions with Polysaccharides (GPC, SEC)
4. Little Interactions with small molecules
(CH2CH)x-r-(CH2CH)y-r-(CH2CH-)_z

Host Gel

α-CD
β-CD
γ-CD

Guest Gel

R = Ad (Adamantane)

n-Bu: (CH3CH2CH2CH2O-)
t-Bu:

(CH3)3C- O- CH3
Adamantane Gel (Green)  β-CD Gel (Red)
Adamantane Gel (Green)  β-CD Gel (Red)
\(\beta\)-CD Gel (Red)  Adamantane Gel (Green)
β-CD Gel (Red)  Adamantane Gel (Green)
GENE THERAPY

Small RNAs aid cell transplants

With the help of small RNA molecules called microRNAs, a metabolic and neurodegenerative disorder might be treated using gene therapy.

Patients with Krabbe’s disease lack a functioning version of an enzyme called GALT. Transplants of a microRNA in the stem cells but not in the white blood cells. As the cells developed, they were able to deliver GALC to diseased tissues in a mouse model of Krabbe’s disease.


MATERIALS SCIENCE

Stopping ice before it forms

Ice accumulation on aircraft and other structures can be dangerous, but de-icing procedures are expensive or environmentally unfriendly. Joanna Atzenberg at Harvard University in Cambridge, Massachusetts, and her colleagues show how ice could be prevented from forming on cold surfaces.

Combining theoretical predictions with experiments, the authors fabricated a silicon surface with honeycomb-like microstructures and coated it with a water-repellent polymer film. There was minimal contact time and heat transfer between the surface and a falling water droplet, such that after it made contact (pictured, left), the droplet fully retracted (right) before it could freeze. This prevented ice formation in temperatures down to about −25 °C. ACS Nano doi:10.1021/nn102557p (2010)

CHEMISTRY

Molecular matchmaking

Structures up to centimetres long have been created by the self-assembly of gel particles that ‘recognize’ each other at the molecular level. Such molecular recognition has previously been used to self-assemble molecules at the microscopic scale.

Akira Harada of Osaka University in Japan and his colleagues prepared acrylamide-based ‘host’ gels bearing cyclodextrin rings, and other gels with smaller ‘guest’ hydrocarbons. The rings and the guest molecules bound to each other, allowing small pieces of gel to self-assemble in specific ways (pictured).


ZOOLOGY

Fish cocoons block biting bugs

The mucus cocoons in which some fish sleep seem to protect them from attacks by parasitic invertebrates.

Alexandra Grutter at the University of Queensland in Brisbane, Australia, and her colleagues placed coral-reef parrotfish (Chlorurus sordidus) in bins of water with parasitic gastropods overnight. They found that only 10% of fish in cocoons were attacked by the parasites, compared with 94.4% of fish that had been teased out of their shelters.

Secreting the mucus to prevent parasite attacks — a mechanism thought to be unique to these fish — costs around 2.5% of a fish’s daily energy budget, the researchers calculate.

\(\beta\text{-CD Gel (Red)}\), \(n\text{-Bu Gel (Yellow)}\), \(t\text{-Bu Gel (Green)}\)
β-CD Gel (Red), $n$-Bu Gel (Yellow),
t-Bu Gel (Green)
β-CD Gel (Red), α-CD Gel (Blue), n-Bu Gel (Yellow), t-Bu Gel (Green)
β-CD Gel (Red), α-CD Gel (Blue), n-Bu Gel (Yellow), t-Bu Gel (Green)
Host-Guest interaction

$\beta$-CD-gel - Ad-gel

$\alpha$-CD-gel - n-Bu-gel

$\beta$-CD-gel - t-Bu-gel
Macroscopic Self-Assembly through Molecular Recognition

Nature Chem., 2011
Self-Assembly

1) Molecular Self-Assembly
   Well-defined Hydrogen-Bonds
   Ligand-Metal Bonds

2) Self-Assembly of Objects
   Capillary Forces
   Electrostatics
   Magnetics

(Whitesides et al.)
Chemical Structures of Host and Guest gels

Host Gel

Guest Gel
Dissociation of Gel Assembly by UV Light

α-CD Gel (Blue) & Azo Gel (Yellow)
Switching of Gel Assembly by UV Light

\[ \alpha - \text{CD Gel (Blue)}, \quad \beta - \text{CD Gel (Red)}, \quad \text{Azo Gel (Yellow)} \]
Sol-Gel Transition by Light

CD-CUR + PAA-Azo

UV (365 nm) → visible light or Δ (60 C)

Angew. Chem. 2010, Nature Asia Highlight
Photo-Responsive Materials formed by CD Polymer and Azobenzene Polymer

Partially Cross-linked between Host polymers & Guest Polymers (Chemical Cross-linking)

Reversible Cross-linking by Formation of Inclusion Complexes between Side-Chains

UV (λ = 365 nm) ↔ Vis (λ = 430 nm)
Bending & Stretching of $\alpha$-CD-Azo gel by Photo-Irradiation

Nature Commun., Accepted
Macroscopic Self-Assembly

Nature Chem., 2011
Nature Highlight, 2010

Sol-Gel Transition

Nature Asia, Highlight, 2010

Nature Chem., 2011
Nature Highlight, 2010

Mol. Tube

Mol. Necklace
Nature, 1992

Mol. Abacus
JACS, 2000, 2003

Self-Healing

Nature Commun., 2011

Artificial Polymerase

Acc. Chem. 2009
Angew. Chem. 2011, Nature, Highlight

Angew. Chem. 2008, Hot Paper

Artificial Muscle

Nature Commun., accepted

Photoswitchable Gel Assembly

Shape Memory

Nature Commun., 2011


Solvent Switching
Harada Lab.
(Osaka Univ.)