Supramolecular Chemistry

Outline

Lecture 11: Assembly of Materials using Hydrogen Bonding
Lecture 12: Assembly of Materials using Metal Ion Complexation
Lecture 13: Applications of New Materials

Overview of Two Weeks Ago:
Clathrates - Crystalline Host-Guest Systems

Overview of Last Week:
Metal-Ion Complexation in Supramolecular Materials

Handouts:

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Rm 456

Overview of Last Week:
Metal-Ion Complexation in Supramolecular Materials

Metal-Organic Frameworks

- The first ability to design then build materials ("crystal engineering")
Overview of Last Week: Metal-Ion Complexation in Supramolecular Materials

Metal-Organic Frameworks
- Highly robust lattices for host-guest chemistry
  e.g. Hofmann Clathrates, which are well-defined in 2D but have flexibility in the third dimension

Overview of Structure Types and Properties

Interaction
- VDW: Weak, largely non-directional interactions lead to highly flexible clathrates; limited design potential, guest-exchange selectivity depends on phase
- H-bonding: Moderately strong, partially-directional interactions lead to less flexible clathrates; some design potential, good guest-exchange selectivity, microporosity observed
- Coordination: Very strong, directional interactions lead to rigid clathrates with well-defined structures; first true 'crystal design', microporous phases common

Applications of Supramolecular Materials
1) Separations
2) Catalyses
3) Stereoregular Polymerisation
4) Molecular Hosts
5) Controlled Release
6) Sensing
7) Mechanical Properties
8) Optical Properties
9) Conductors/Wires
10) Magnets
11) Data Storage
12) Molecular Computers
13) Light-Harvesting

Separations
Mechanisms:
- Crystallisation: guest selectivity (molecular recognition) occurs in the precipitation step
- Guest-Exchange: reversible exchange of guest species within micropores

Examples:
- Purification of benzene by the Hofmann clathrates, either by precipitation then decomposition, or by chromatography
- Enantioseparations by chiral host lattices of achiral building units (e.g. urea) or chiral units (e.g. cyclodextrins)
Catalysis

**Mechanism:**
Heterogeneous - molecules are constrained to have a certain orientation within micropores, leading to a drastic increase in ‘collision frequencies’

**Examples:**
- Diels-Alder reactions within the bis(resorcinol)anthracene host
- Enantioselective catalyses within POST-1
  
  *Can specific catalytic centres be included, as seen in enzymes?*

Incorporating Catalytic Sites

**Ti(IV)-Catalyzed ZnCl₂ Additions to Aromatic Aldehydes**

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<th>Ar</th>
<th>1-Ti</th>
<th>EnoLUTI(OP)₂</th>
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Incorporating Catalytic Sites

JACS, 127, 8940 (2005)

Stereoregular Polymerisation

Inclusion of monomers into clathrate systems, followed by irradiation by β-, γ- or X-rays, leads to geometrically-constrained polymerisation

*E.g.*

Highly ordered (sterically regular) polymers, which may be isolated following decomposition of the host.

Well-aligned linear polymers with no intertwining

~ 50 different monomers have been polymerised in urea clathrates
Molecular Hosts

**Orientation** - Host lattice provides an environment for the alignment of guests ⇒ matrix for the study and manipulation of individual molecules

**Stabilisation** - Organic radicals may be stabilised inside the pore structure for long periods of time ⇒ matrix for the study of radicals

- e.g. ESR studies of C\textsubscript{6}H\textsubscript{7}\textsuperscript{*} in Hofmann clathrates

Controlled Release

Moderately strong host-guest interactions (controllable by design of the host)

- Slow rate of guest uptake/release

- Applications in controlled release e.g. pharmaceuticals

Sensing

**Mechanism**: Easily-measured properties of the host change in response to the presence of the guest, or *vice versa*. High selectivity of host-guest interaction gives highly selective sensor. High sensitivity if microscopic process affects macroscopic properties.

**Detection**:
- Optical - colour, luminescence
- Electrical - conductivity
- Structure - shape, size

Mechanical Properties

**Negative Thermal Expansion**
- e.g. The crystal volume of Zn(CN)\textsubscript{2} contracts by ~2% in warming from 10 to 300 K

**Mechanism**: shortening of bonds with increase in vibrational amplitude

**Auxetic Properties**
- Compression in one direction leads to contraction *not expansion* in the other two directions / Expansion in one direction leads to expansion *not contraction* in the other two directions.
**Optical Properties**

- **Molecular Lasers**
- **Electroluminescence**

**Non-Linear Optics (NLO)** - inclusion and alignment of chiral guests

**Quantum Dots** - nanoscale particle growth achieved in nanopores

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**Conductors**

- **Construction of Molecular Wires**
  - $\Rightarrow$ electrical components

**Combining Properties**: the first ever conducting host lattice?

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**Magnets**

- e.g. Prussian blues - the only transparent room temperature magnets

**High strength magnets**

\[
M^{2+} + 2 \left[ \begin{array}{c} \text{C-N} \\ \text{C-N} \end{array} \right]^{-} 
\]

- $M^{10}(N(CN)_2)_2$

**Nanoporous Magnets**

- $[\text{Co}_3(\text{OH})_2(\text{C}_4\text{O}_4)_2] \cdot 3\text{H}_2\text{O}$

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*Chem. Commun., 3012 (2005).*
Nanoporous Magnets

Data Storage

Magnetism

Storage of Information at the Molecular Level

Guest location

Switching of Guest

Science, 286, 261 (1999)

Data Storage and Beyond

Course Objectives

Switching of Host

Switching of host in response to guest ⇒ Molecular Sensors.

Switching of host in response to external stimulus ⇒ Molecular Manipulation.

Switching response to stimulus & communication between switching centres ⇒ Molecular Computers.

Principle understandings to be gained from the last three lectures:

- The classification scheme for inclusion compounds
- Understandings of the structures of (as seen in the ability to be able to sketch!) some of the more simple materials, such as the urea clathrate, bis(recorcinol)anthracene, Hofmann clathrates, Prussian blue, MOF-5, ...
- To understand the different properties that arise from different types of host-host and host-guest interactions, ...
- An appreciation of the structural features that impart rigidity (and therefore high guest-selectivity, microporosity, etc.) to host lattices
- To understand the various mechanisms by which chiral separations may be performed with chiral host lattices
- A general appreciation for applications of supramolecular materials, the most important being those that are already proven!