3

Supramolecular Organization in the Solid State and Intermolecular Electron Delocalization
<table>
<thead>
<tr>
<th>Section</th>
<th>Duration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Introduction and Overview</td>
<td>1 h</td>
</tr>
<tr>
<td>2. Electron Delocalization in Organic Molecules and Polymers</td>
<td>3 h</td>
</tr>
<tr>
<td>2.1. Chemical Bonding in Organic Molecules</td>
<td>1 h</td>
</tr>
<tr>
<td>2.2. Intramolecular Electron Delocalization in $\pi$-Conjugated Systems</td>
<td>2 h</td>
</tr>
<tr>
<td>3. Supramolecular Organization in the Solid State and Intermolecular Electron Delocalization</td>
<td>3 h</td>
</tr>
<tr>
<td>3.1. The Origin of $\pi-\pi$ Interactions</td>
<td>1 h</td>
</tr>
<tr>
<td>3.2. Supramolecular Organization of $\pi$-Conjugated Molecules in the Solid State</td>
<td>1 h</td>
</tr>
<tr>
<td>3.3. Intermolecular Electron Delocalization</td>
<td>1 h</td>
</tr>
<tr>
<td>4.1. General Strategies for the Synthesis of Conjugated Oligomers and Polymers</td>
<td>1 h</td>
</tr>
<tr>
<td>4.2. Poly(phenylene), Poly(phenylene vinylene)s, and Poly(thiophene)s (and Their Oligomers)</td>
<td>2 h</td>
</tr>
<tr>
<td>4.3. Acenes, Coronenes, Perylenes, Porphyrins, and Other Selected Examples</td>
<td>2 h</td>
</tr>
<tr>
<td>4.4. Fullerenes, Carbon Nanotubes, and Graphene</td>
<td>1 h</td>
</tr>
<tr>
<td>5. Charge Transport in Organic Materials</td>
<td>6 h</td>
</tr>
<tr>
<td>5.1. Interaction of $\pi$-Conjugated Systems with Light</td>
<td>1 h</td>
</tr>
<tr>
<td>5.2. Charge Carrier Generation in Organic Molecules</td>
<td>2 h</td>
</tr>
<tr>
<td>5.3. Charge Transport in Organic Materials</td>
<td>2 h</td>
</tr>
<tr>
<td>5.4. Interplay of Supramolecular Packing, Microstructure, Defects, and Charge Transport</td>
<td>1 h</td>
</tr>
<tr>
<td>6. Fabrication and Characterization of Organic Electronic Devices</td>
<td>6 h</td>
</tr>
<tr>
<td>6.1. Organic Field-Effect Transistors</td>
<td>2 h</td>
</tr>
<tr>
<td>6.2. Organic Photovoltaic Devices</td>
<td>2 h</td>
</tr>
<tr>
<td>6.3. Organic Light-Emitting Diodes</td>
<td>2 h</td>
</tr>
</tbody>
</table>
3.1

The Origin of $\pi-\pi$ Interactions
Charge Transport in Organic Thin Film Devices

- charge transport in organic thin film devices occurs in thin 2D layer parallel to substrate
- gate electrode induces charge carriers in the channel, serves as to “switch on/off” the device

organic field-effect transistor

transistor output curves

- linear regime
- saturation regime

\( V_G = 0 \text{ V} \)
\( V_G = -60 \text{ V} \)
• device performance (e.g., electron/hole mobility) due to structure/order on various length scales

- for good 2D transport properties, one needs large domains and/or symmetric 2D packing
- molecular structure determines supramolecular arrangement and crystal growth
- crystal packing is dense packing determined by van der Waals, dipole, and quadrupole interactions
Electron Density Distribution in Molecules with $\pi$-Conjugated Systems

- due to C–H electronegativity difference, carbons are partially negatively charged
- $\pi$-system above/below molecular plane is polarizable, electron-rich, partially negatively charged
- rim of the molecule is electron-poor, partially positively charged
- benzene has no dipolar moment due to symmetry, but a quadrupolar moment
• -M substituents determine electron density and reactivity patterns in π-conjugated systems

\[
\begin{align*}
\text{ROSO}_2\text{C}_6\text{H}_4 & > \text{ONO}_2\text{C}_6\text{H}_4 > \text{NCS}\text{C}_6\text{H}_4 > \text{ROCO}_2\text{C}_6\text{H}_4 > \text{RNOC}_6\text{H}_4 \\
\end{align*}
\]

• every other carbon in the π-conjugated system carries positive formal charge in resonance structures
• in reality, every other carbon in the delocalized π system is electron deficient (positive partial charge $\delta^-$)
**Resonance Structures Involving Electron-Donating Groups**

- +M substituents determine electron density and reactivity patterns in π-conjugated systems

\[
\begin{align*}
R_2&N^* > R^S > RO > I > Br > Cl > F \\
\end{align*}
\]

- every other carbon in the π-conjugated system carries negative formal charge in resonance structures
- in reality, every other carbon in the delocalized π system is electron-rich (negative partial charge \(\delta^-\))

![Charge distribution](image1)

![HOMO](image2)

![LUMO](image3)
Substituents with Mesomeric Effects

- Mesomeric (resonance) effects have strong influence on electron density distribution in π-system.
Substituents with Inductive Effects

- Inductive effect from electronegative substituents (F, O, Cl) affects overall electron density in π-system
Electron Density Distribution of Increasingly Large $\pi$-Conjugated Systems

- benzene
- naphthalene
- anthracene
- tetracene
- pentacene
Examples of Electron-rich and Electron Poor π-Conjugated Systems

- perfluorination inverts quadrupolar moment of aromatic systems no matter what is their size
Examples of Electron-rich and Electron Poor π-Conjugated Systems

- M substituents invert quadrupolar moment of aromatic systems no matter what is their size
Examples of Electron-rich and Electron Poor $\pi$-Conjugated Systems

- heteroatoms with free electron pairs as part of the aromatic system are $+M$ substituents
- heteroatom double bonds connected to the $\pi$-system are $-M$ substituents

- tetrathiafulvalene
- tetracyanoquinodimethane
- π–π interactions are weak (5–50 kJ/mol) and have a short range ($E \sim d^{-6}$)
- π–π interactions are a combination of dispersive interactions with quadrupolar interactions
Types of $\pi$–$\pi$ Interactions

- **face-to-face**
  - $\pi$–$\pi$ stacked
  - *never observed*
  - 3.4–3.8 Å

- **parallel-displaced**
  - $\pi$–$\pi$ stacked
  - 3.4–3.8 Å
  - 4.2–4.8 Å

- **edge-to-face**
  - 4.2–4.8 Å
  - 2.0–2.3 Å

- **edge-to-face**
  - 2.0–2.3 Å

- $\pi$–$\pi$ interactions are weak (5–50 kJ/mol) and have a short range ($E \sim d^{-6}$)
- $\pi$–$\pi$ interactions are a combination of dispersive interactions with quadrupolar interactions
Types of $\pi-\pi$ Interactions

- **face-to-face $\pi-\pi$ stacked**
  - eclipsed
  - 3.4–3.8 Å
  - 3.2–3.6 Å

- **face-to-face $\pi-\pi$ stacked**
  - staggered
  - 3.2–3.6 Å

- **edge-to-edge dipolar**
  - C–H···F hydrogen bond

- electron-poor/rich aromatic systems dominated by **dipolar and quadrupolar interactions**
3.2

Supramolecular Organization of π-Conjugated Molecules in the Solid State
Crystal Structure of Benzene

- Benzene packs into complex 3D herringbone packing.

In side view, benzene molecule has two almost identical dimensions due to π-system.

- Space-filling packing with both edge-to-face and parallel-displaced π–π stacking interactions.
- Optimized for both dispersive interactions (van der Waals) and quadrupolar interactions.

Herringbone angle ≈ 90°
hexaphenylene is a calamitic (rod-like) molecule, one dimension extended compared to benzene

- 2D herringbone packing of molecules along short axes, resulting in layers
- tilt angle relative to layer normal for parallel-displaced packing, smaller herringbone angle

layer with herringbone packing viewed along [0 0 1] axis (“from the top”)
Single-Crystal Structure of Pentacene

- pentacene is a calamitic (rod-like) molecule, with one extended dimension

- layered 2D herringbone packing is a universal packing mode for calamitic molecules
- tilt angle for parallel-displaced packing, herringbone angle smaller with increased lateral dimensions
- quaterthiophene is a calamitic (rod-like) molecule, with one extended dimension

- layered 2D herringbone packing is a universal packing mode for calamitic molecules
- tilt angle for parallel-displaced packing, herringbone angle smaller with increased lateral dimensions

• benzothienobenzothiophene is a calamitic (rod-like) molecule, with one extended dimension

Crystal Structure of Benzothienobenzothiophene (BTBT)

• layered 2D herringbone packing is a universal packing mode for calamitic molecules
• parallel-displaced packing along short axes, herringbone angle smaller with increased lateral size

didodecyl benzothienobenzothiophene is a calamitic (rod-like) molecule with terminal substituents

“phase segregation” of π-conjugated core and alkyl substituents reinforces layered packing
intraplanar space per molecule commensurate with herringbone packing of the π-conjugated cores
layered 2D herringbone packing is a packing mode for calamitic molecules with terminal substituents
• TIPS-pentacene is a calamitic (rod-like) molecule with lateral substituents

- herringbone arrangement, edge-to face interactions impossible due to lateral substituents
- instead, “brickwork” layers enforced by “phase segregation” between pentacene cores and substituents
- space-filling packing of large substituents determines tilt angle, parallel-displaced π–π stacking

rubrene is a calamitic (rod-like) molecule with lateral substituents

- herringbone arrangement, edge-to-face interactions impossible due to lateral substituents
- instead, layers enforced by “phase segregation” between tetracene cores and substituents
- space-filling packing of large substituents determines tilt angle, parallel-displaced π–π stacking
- pyrene is a small discotic (disk-like) molecule
- lateral dimension incommensurate with herringbone packing, would create voids
- instead layered herringbone packing of pairs of molecules (with almost equal lateral dimensions)
• bisbenzocoronene is a large discotic (disk-like) molecule, two extended dimensions, one short axis

Crystal Structure of Bisbenzocoronene

• large discotic molecules cannot assume herringbone packing, not even for dimers
• instead, stacking into densely packed columns along short axes, parallel-displaced π−π stacking
Discotic Molecules with Peripheral Substituents

- hexakis(dodecyl) hexabenzocoronene is a large discotic molecule with peripheral substituents

- phase segregation of alkyl substituents and $\pi$-conjugated core reinforces columnar packing
- $\pi-\pi$ stacked columns along short axis, but peripheral substituents disordered, cannot pack efficiently
- crystallization strongly disfavored, instead formation of liquid-crystalline “hexagonal columnar phases”
3.3

Intermolecular Electron Delocalization
Molecular Orbital Interactions between Closely Packed π-Conjugated Molecules

- crystalline packing of molecules results in electronic coupling between π MO of matching symmetry

- overall electron density and, hence, energy in occupied MO increases (must be compensated)
- interaction (small overlap) of MO can be expressed in new linear combination, very small splitting
- same for unoccupied MO, but orbital energy decreases, hence, HOMO-LUMO gap decreases
Bands in Crystals of Conjugated Molecules (1)

- intermolecular electron delocalization due to \( \pi-\pi \) stacking (parallel displaced)

- molecular orbitals become very narrow bands in the solid state (band width \( \omega < 1 \text{ eV} \))
- small band width representative of low degree of (macroscopic) delocalization
- low charge carrier mobilities, and different for different lattice directions
- upon increasing the size of the conjugated system, the HOMO-LUMO gap narrows
- MO levels get closer, start to interact with one another, but still located MO, no bands
• intermolecular electron delocalization due to \( \pi-\pi \) stacking (parallel displaced)

- but also intermolecular \( \pi \)-interactions become more efficient, stronger coupling
- molecular orbitals become narrow bands (band width \( \omega \approx 1 \text{ eV} \))
- low degree of macroscopic delocalization, low and anisotropic charge carrier mobilities