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Spectroscopic Signature of Perylene π-Stacking

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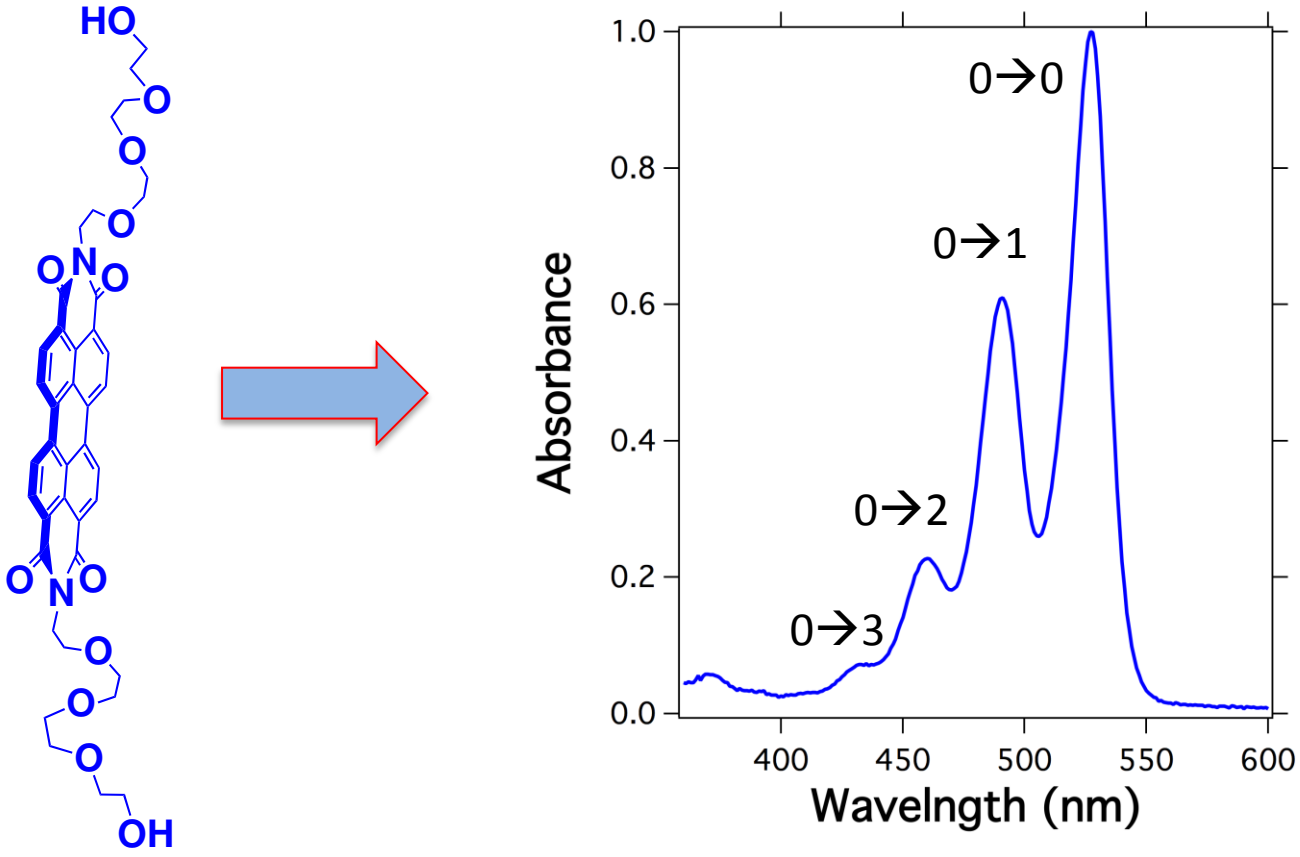
July 30, 2014

Motivation for Understanding π-Stacking

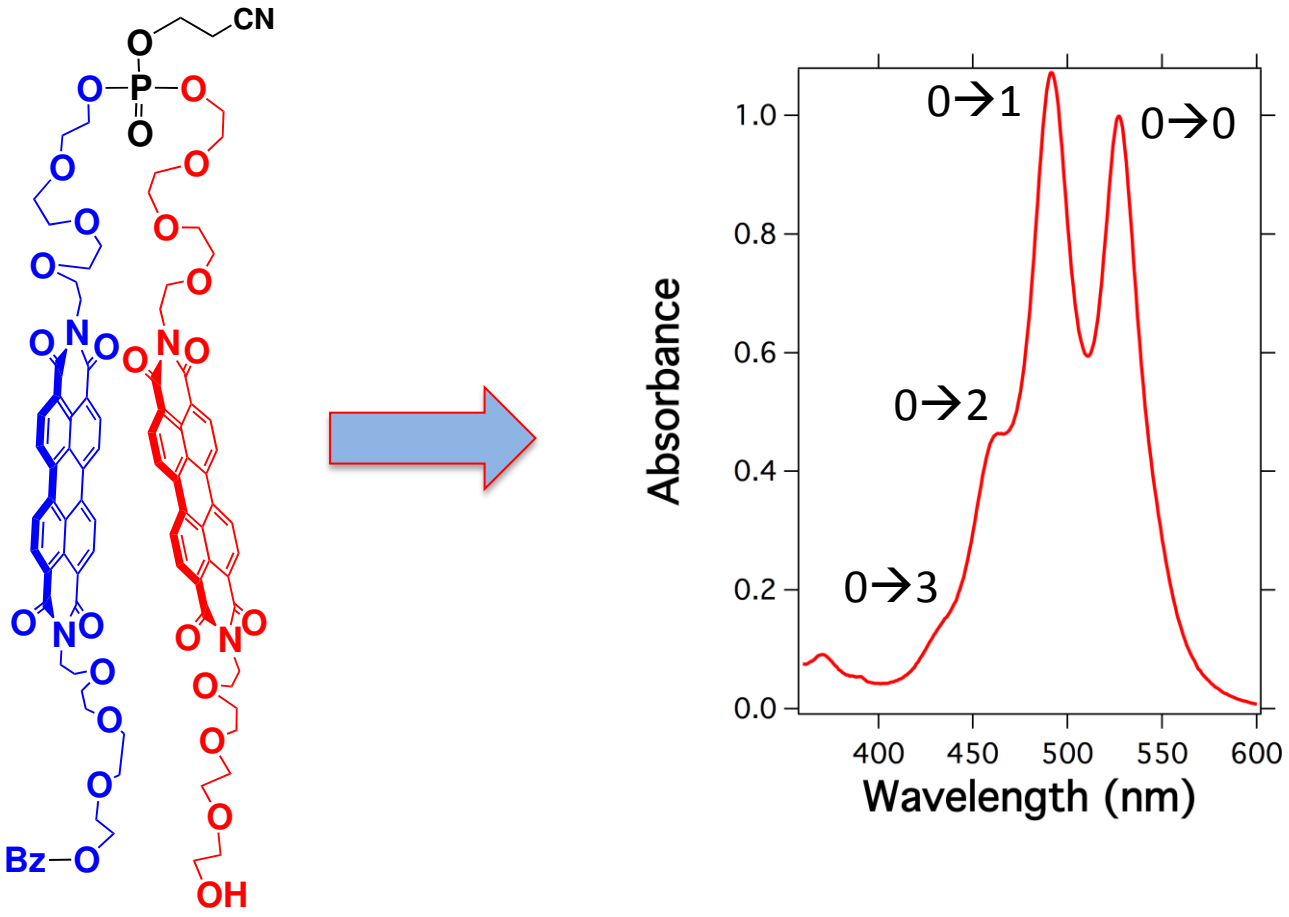
- Signature of π-stacking reveals intramolecular folding that involves conjugate structures.
  - Folding is the key mechanism that nature uses to create catalytic reaction centers, along with other functions.
- Signature of π-stacking also reveals molecular self-assembly intermolecularly?
  - Self-assembly generates diverse structures and thus imparts novel phenomena.

A Free Molecule



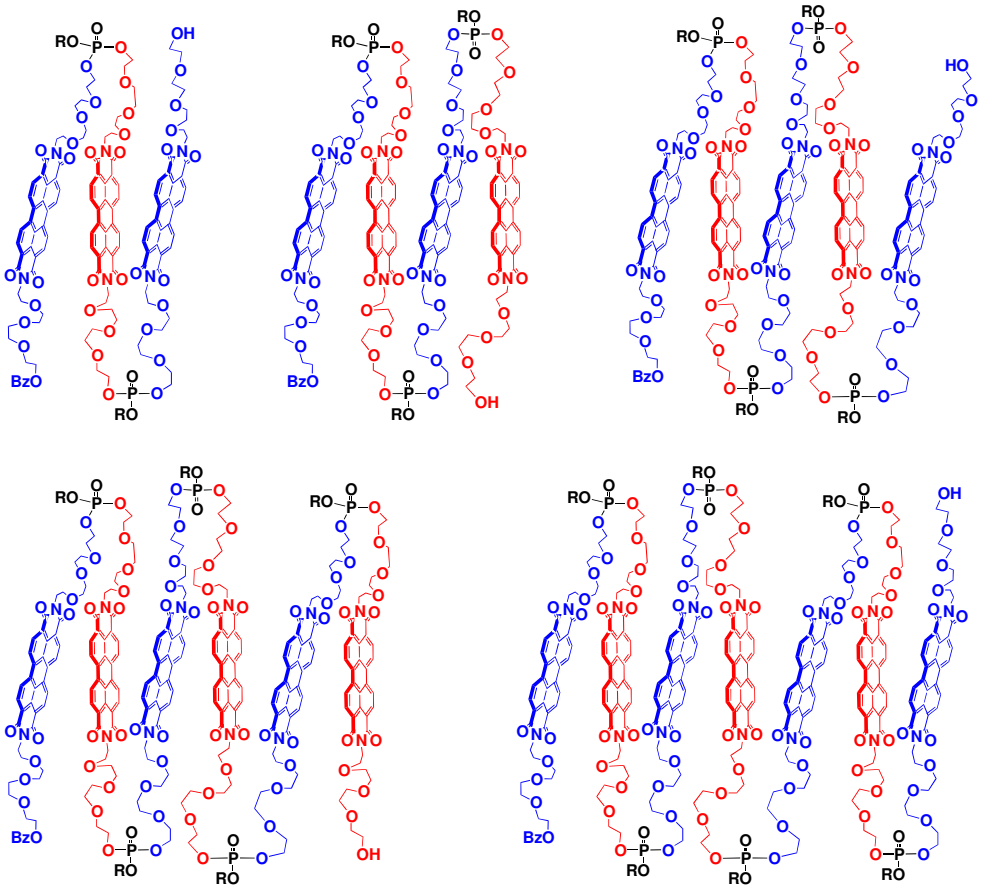
Gives absorption spectrum with A(0→0) >> A(0→1) >>A(0→2) etc.
A progressively reduction in intensity as wavelength decreases.

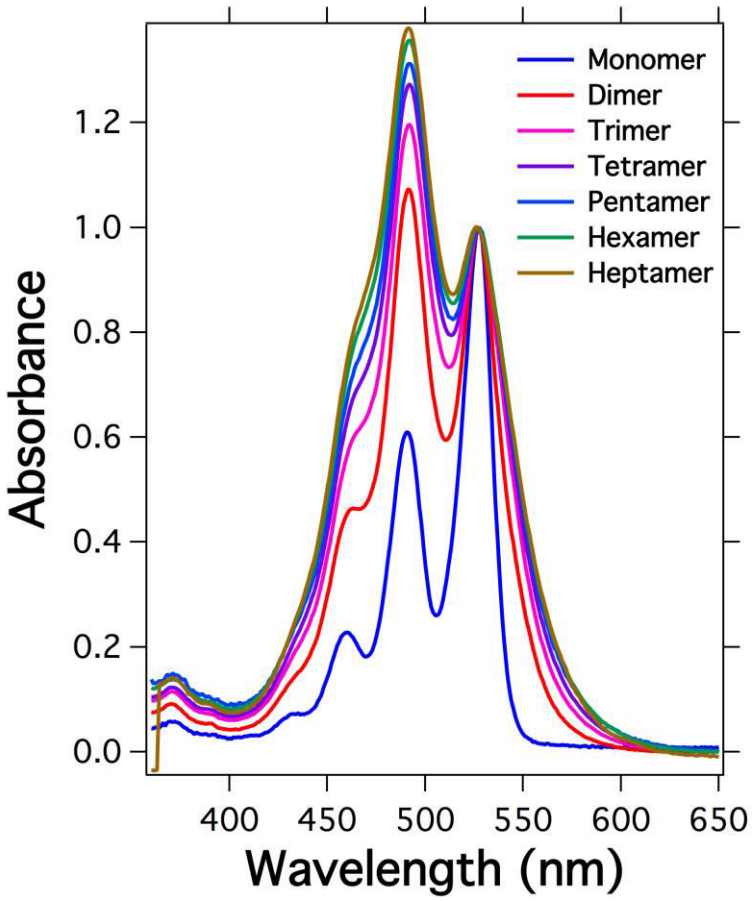
A Stacked Dimer



Yields a dramatic intensity reversal: A(0→0) < A(0→1, a signature of π-stacking.

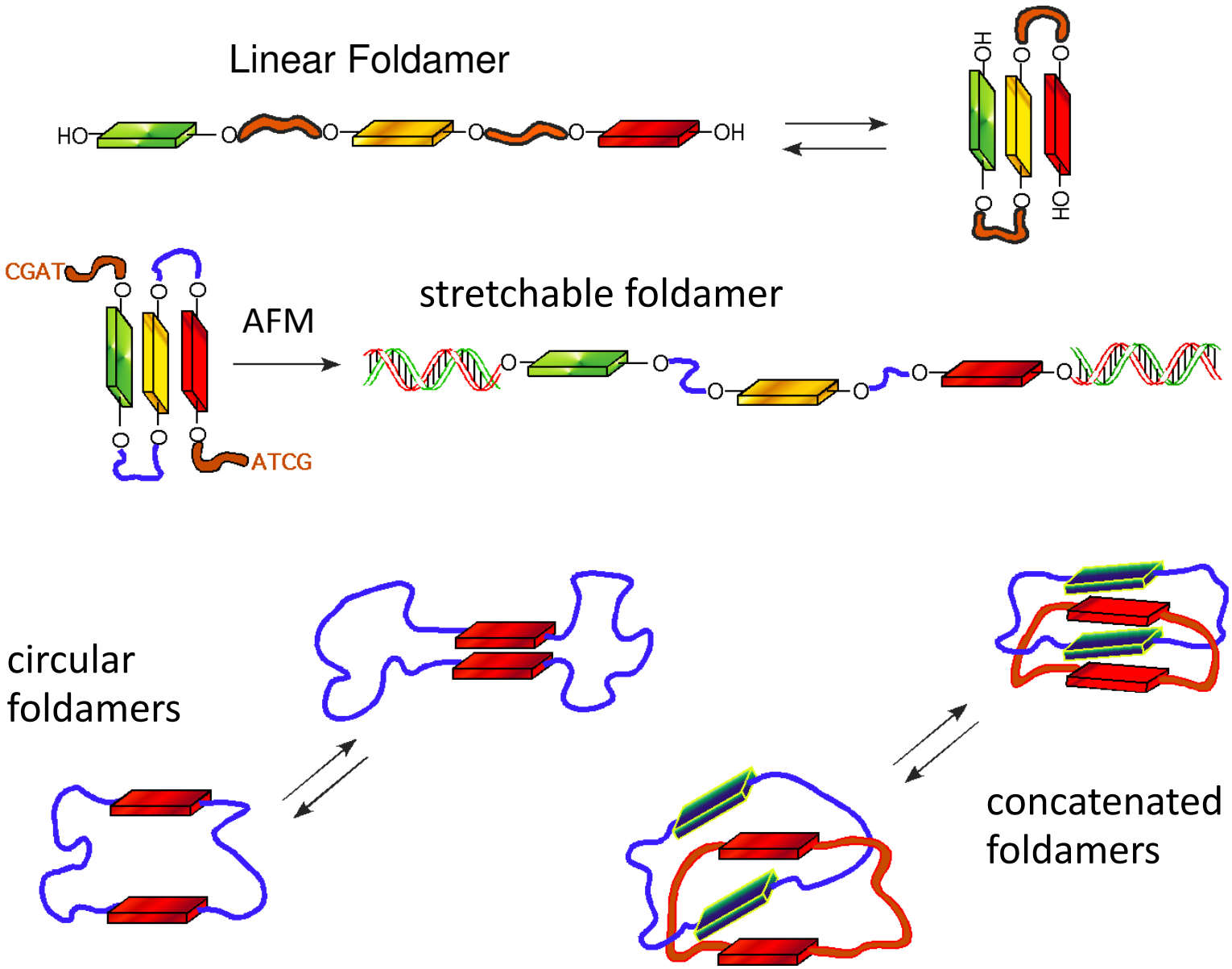
How about Stacked Trimer, Tetramer, Pentamer, Hexamer, Heptamer





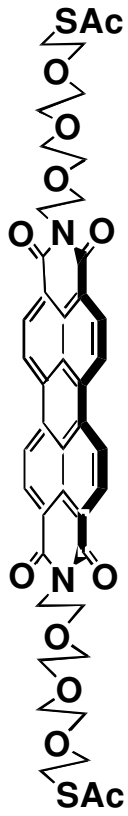
Universal Signature: The ratio A(0→1)/A(0→0) gradually increases as the stack grows longer.

This general rule applies to all foldable oligomers and polymers



Free Monomer Signature

(Free molecules are those not interacting with itself typically found in dilute solutions)



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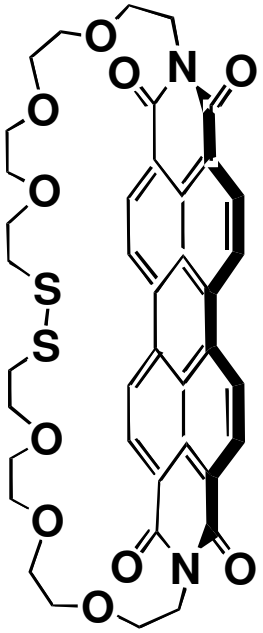
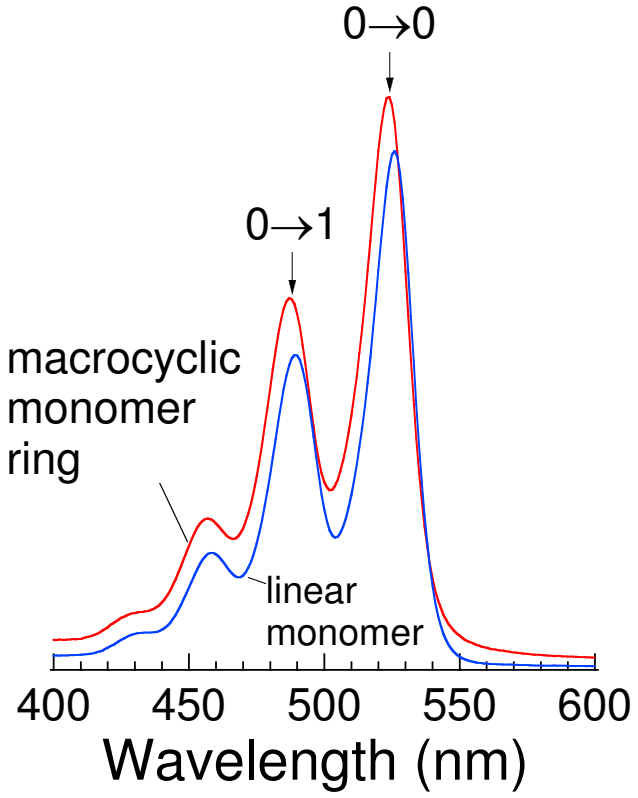
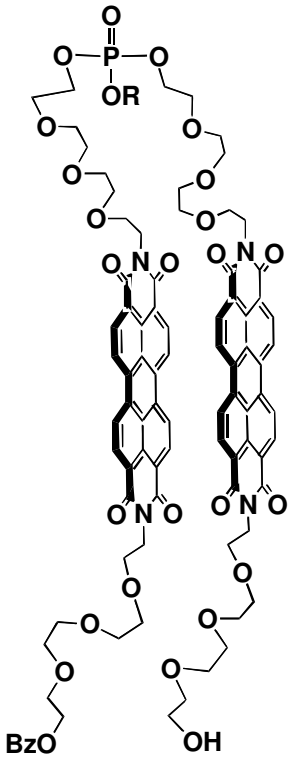




Free monomers, cyclic or not, have the same absorption pattern.

Stacked Dimer Signature



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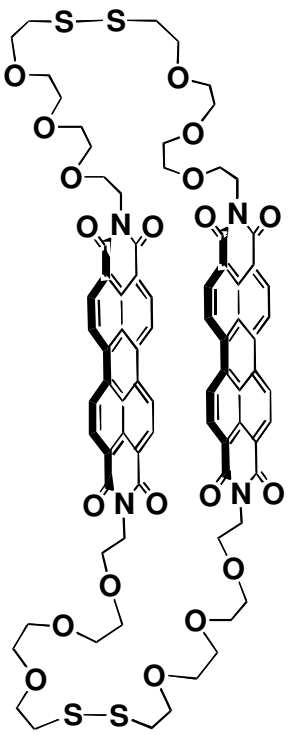
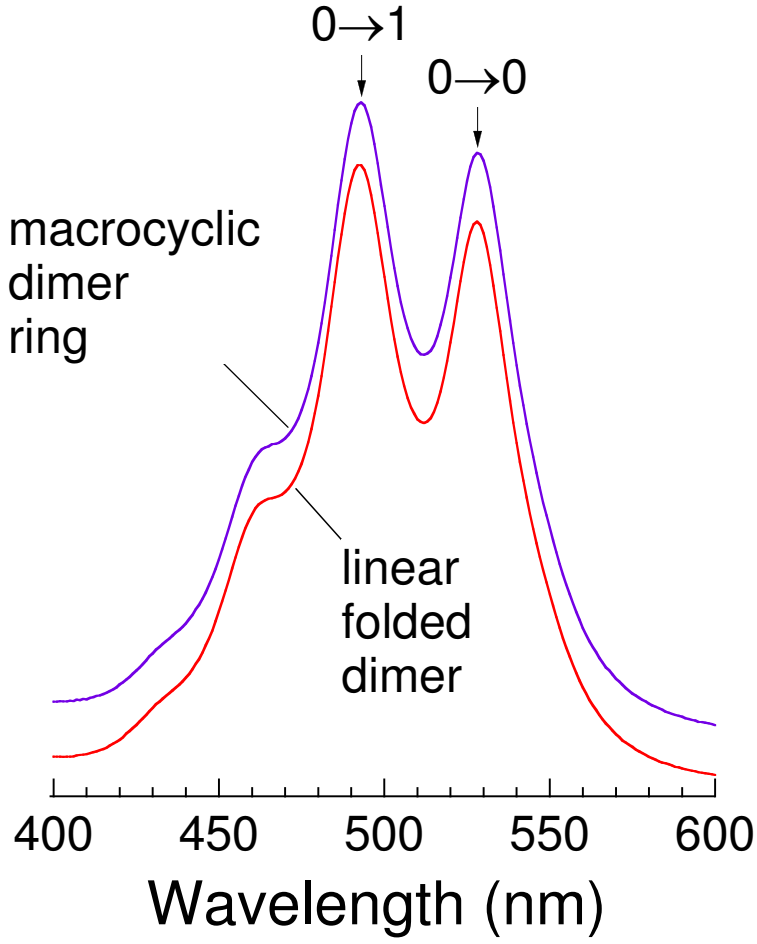
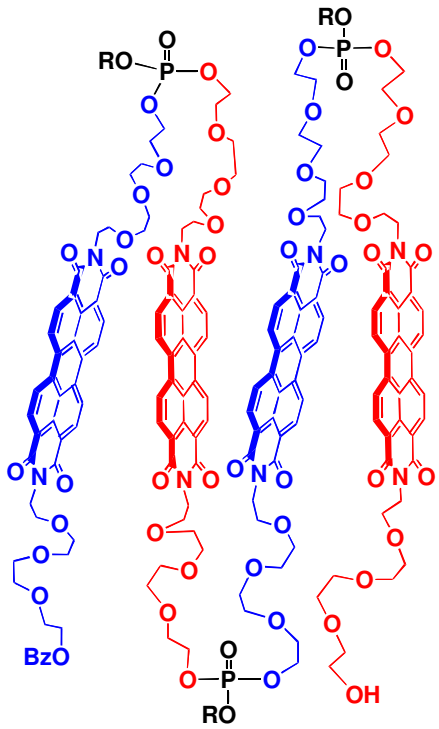




Linear folded dimer or macrocyclic dimer has the same pattern

Stacked Tetramer Signature



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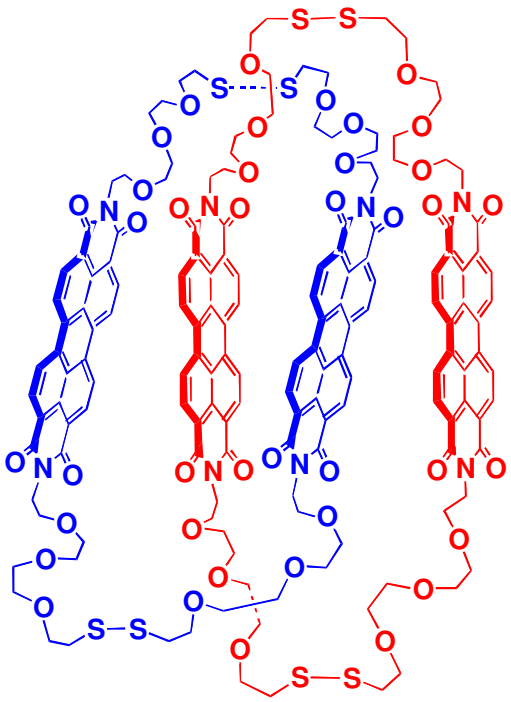
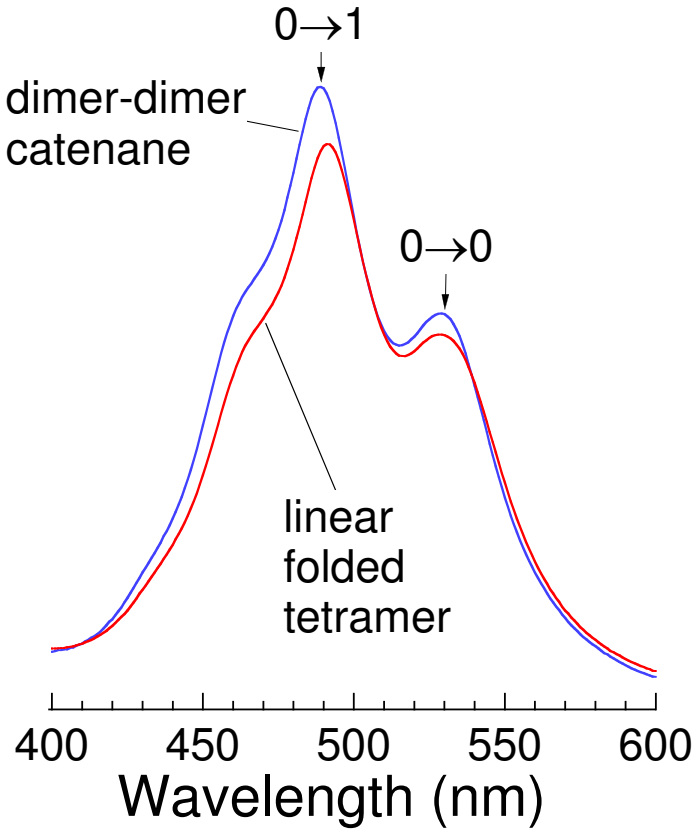
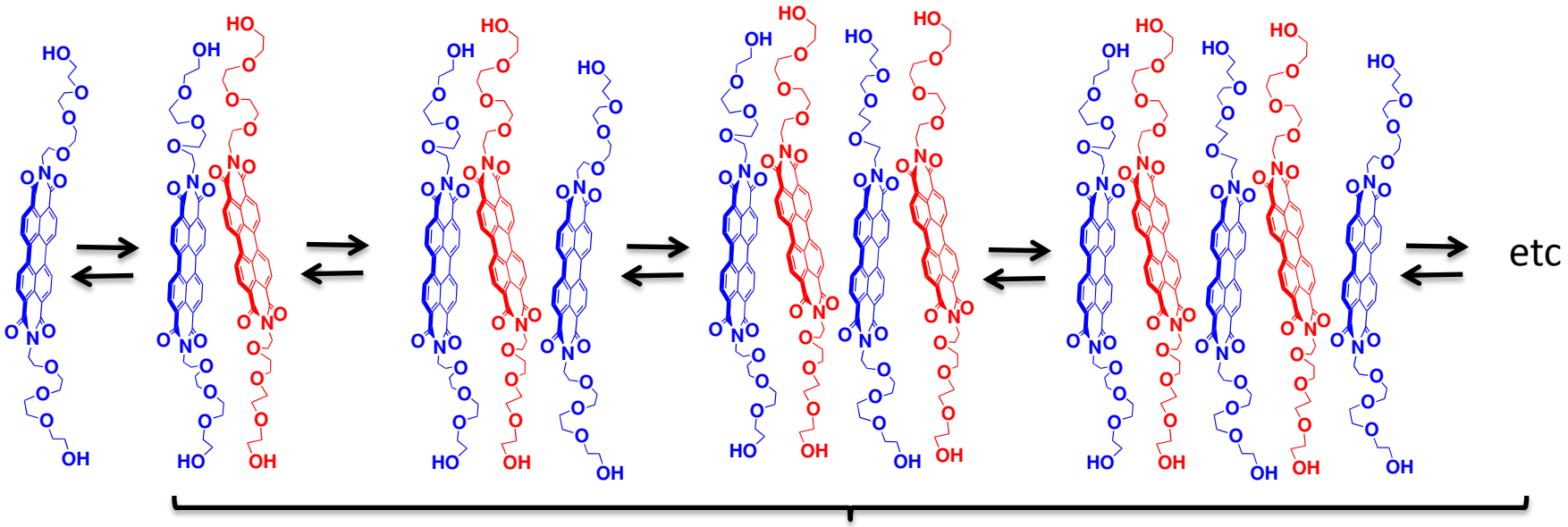




Linear folded tetramer and concatenated tetramer have the same characteristics.

How about Dynamic Stacking



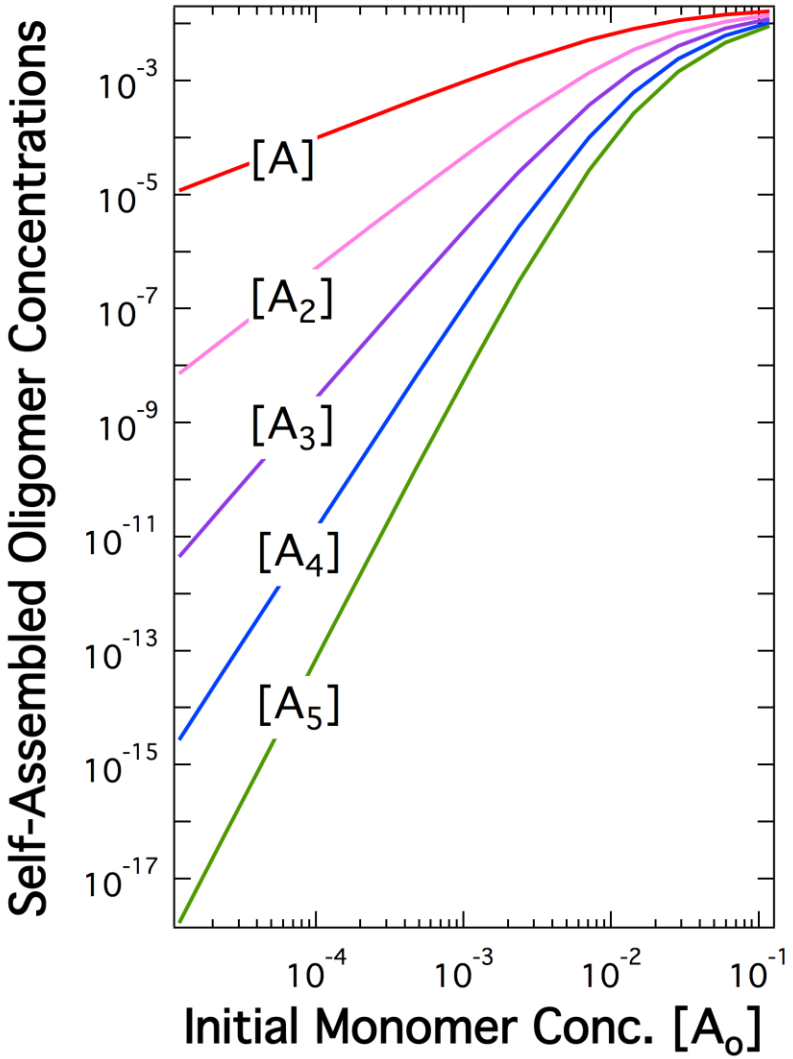
In solution, molecular self-Assembly is dynamic

Distribution of Self-Assembled Oligomers

Factors Driven Assembly:

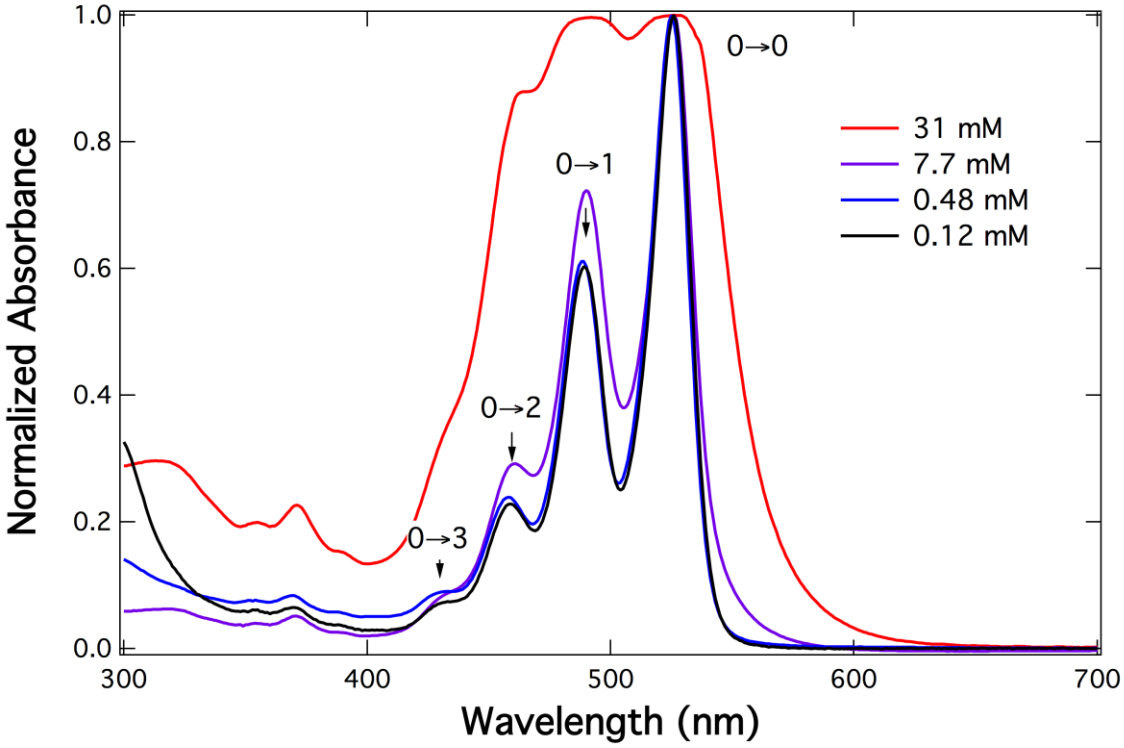
- **Solvent**
- **Temperature**
- **Concentration**

When solvent and temperature are fixed, concentration of the molecule becomes the major factor that drives the formation of self-assembled dimer, trimer, tetramer, pentamer, and etc. The resulting distribution pattern of the self-assembled oligomers is shown here.



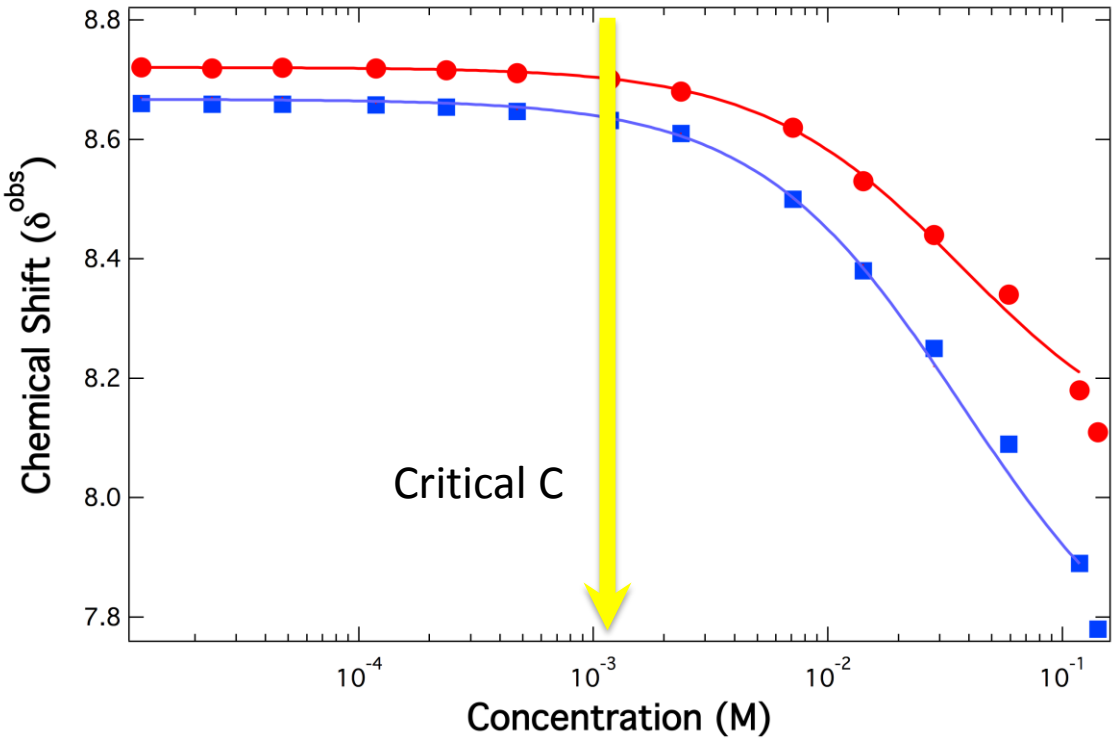
The Observed Absorbance Is the Sum of Individual Contributions by All Oligomers

$A^{obs} = A^{monomer} \times [monomer]\% + A^{dimer} \times [dimer]\% + A^{trimer} \times [trimer]\% + A^{tetramer} \times [tetramer]\% + etc$

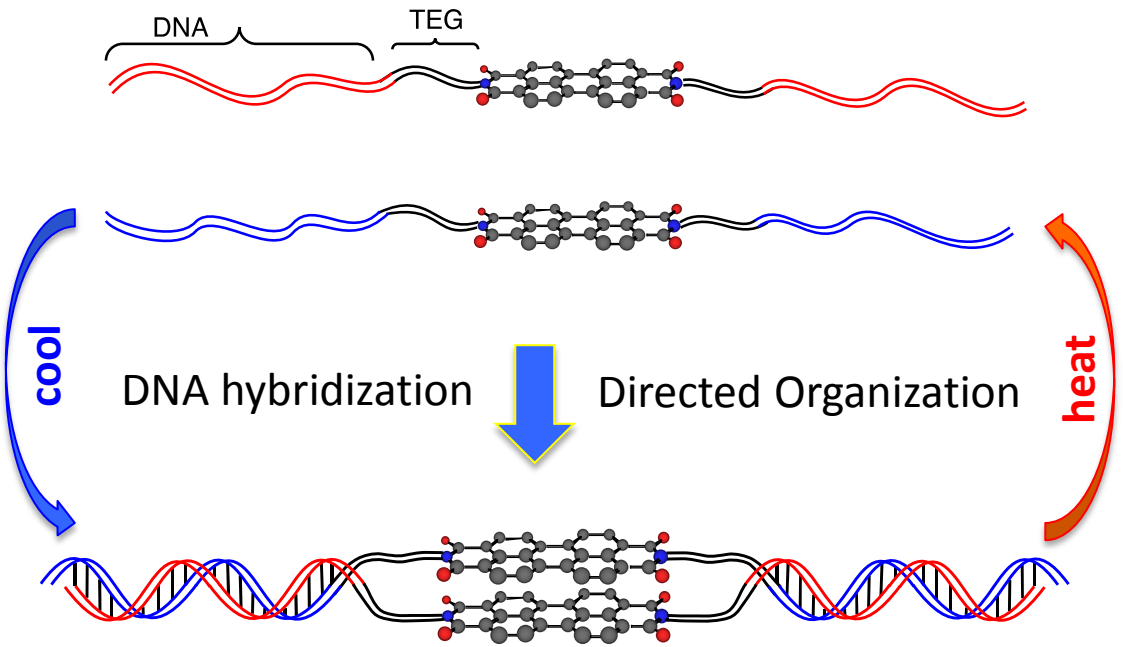


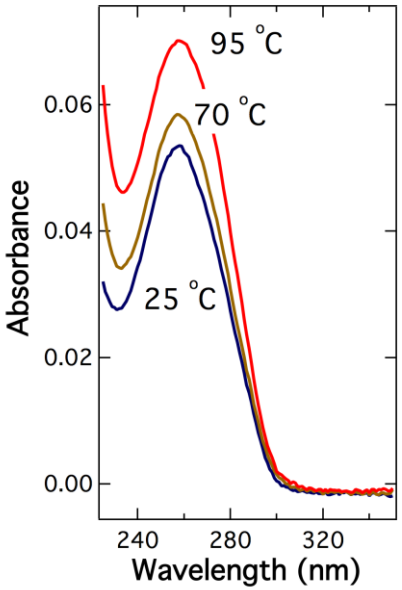
There Is a Critical Concentration for Molecules to Self-Assemble

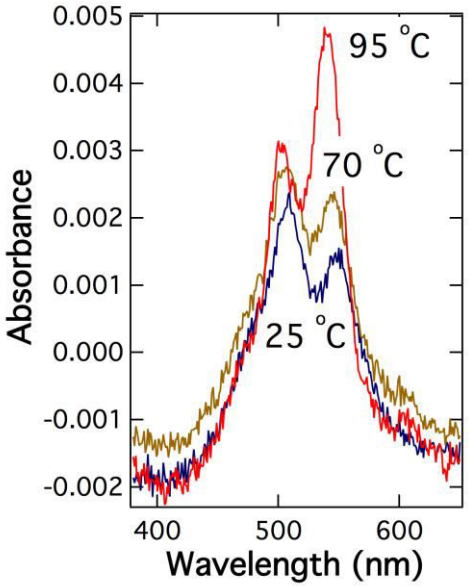
Measured physical properties such as absorbance values or NMR chemical shifts can be used to monitor the dynamic self-assembly. Here the aromatic proton chemical shifts reveal a critical concentration (~1mM), below which molecules are free and above which molecules are actively self-assembling.



DNA Duplex Organized Stacking

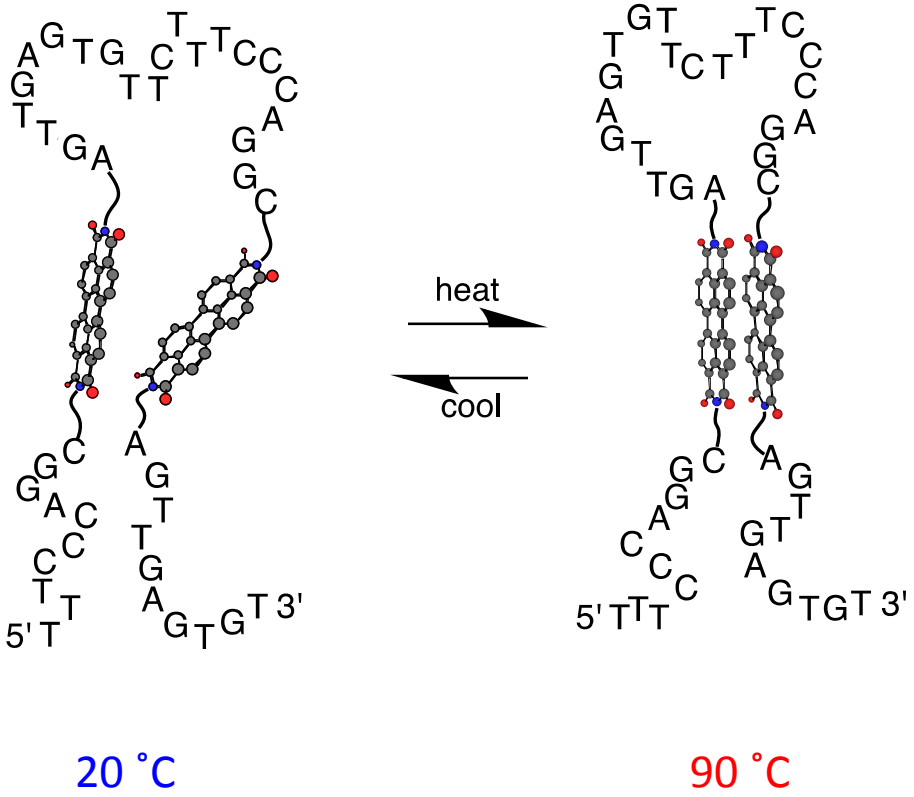


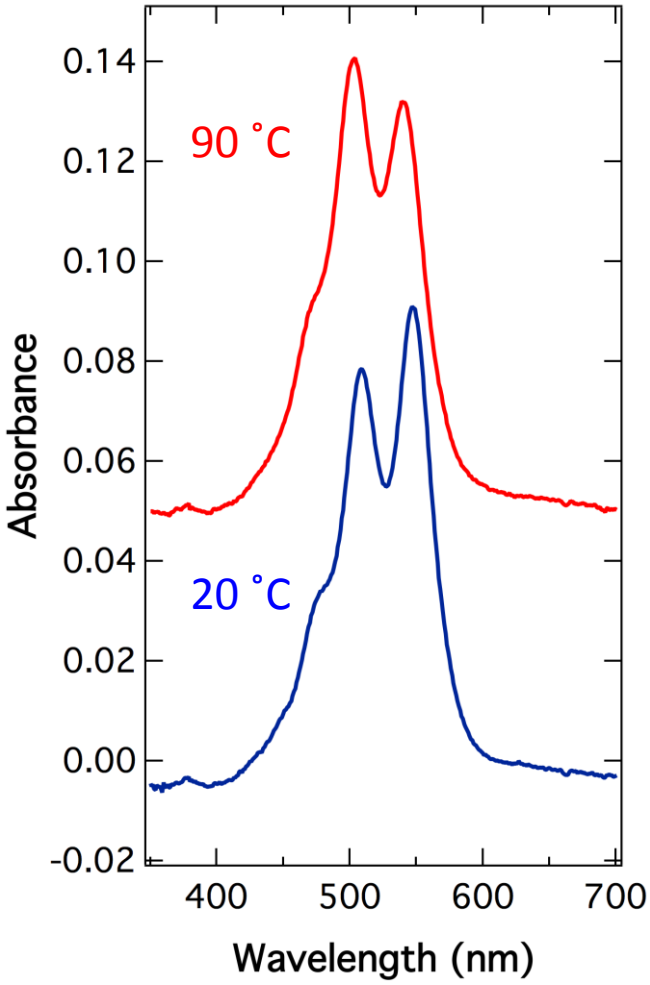




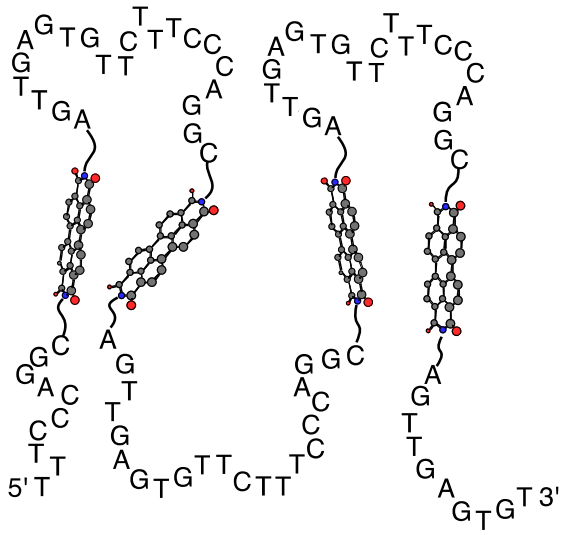
DNA duplex melting or formation (top right) is validated by the π-stacking signature of perylene (bottom right).

Synthetic and Biological Hybrid: DNA-linked Perylene Dimer





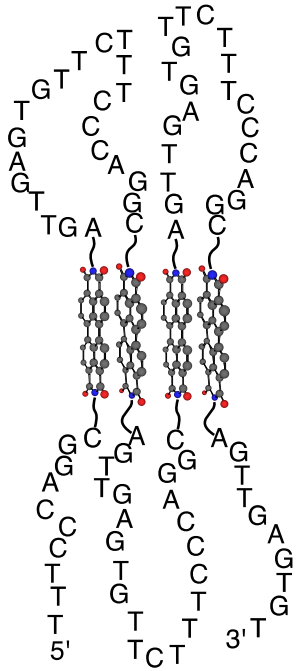
Synthetic and Biological Hybrid: DNA-linked Perylene Tetramer



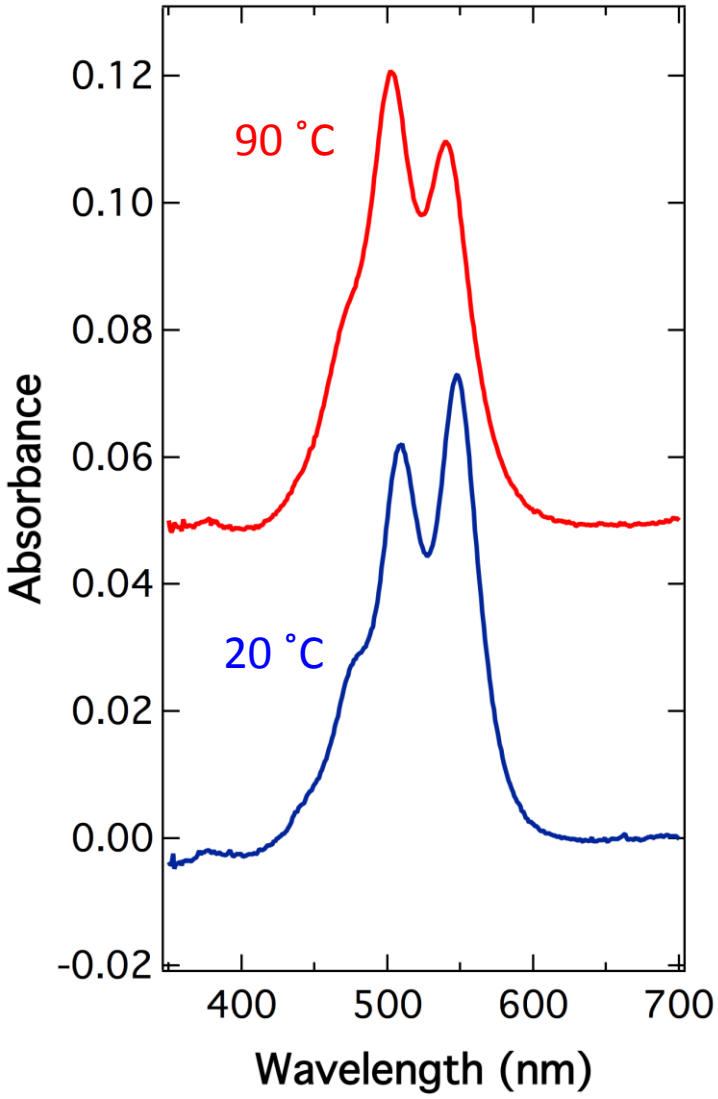
20 ˚C

heat

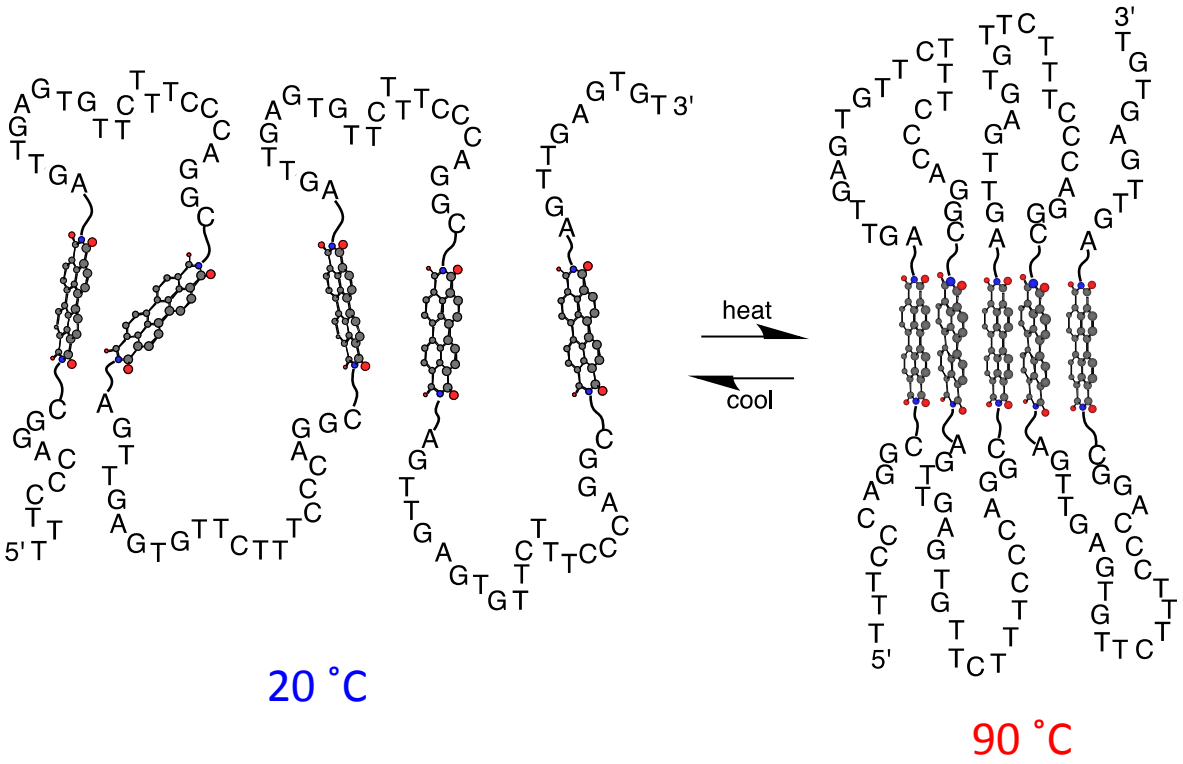
cool

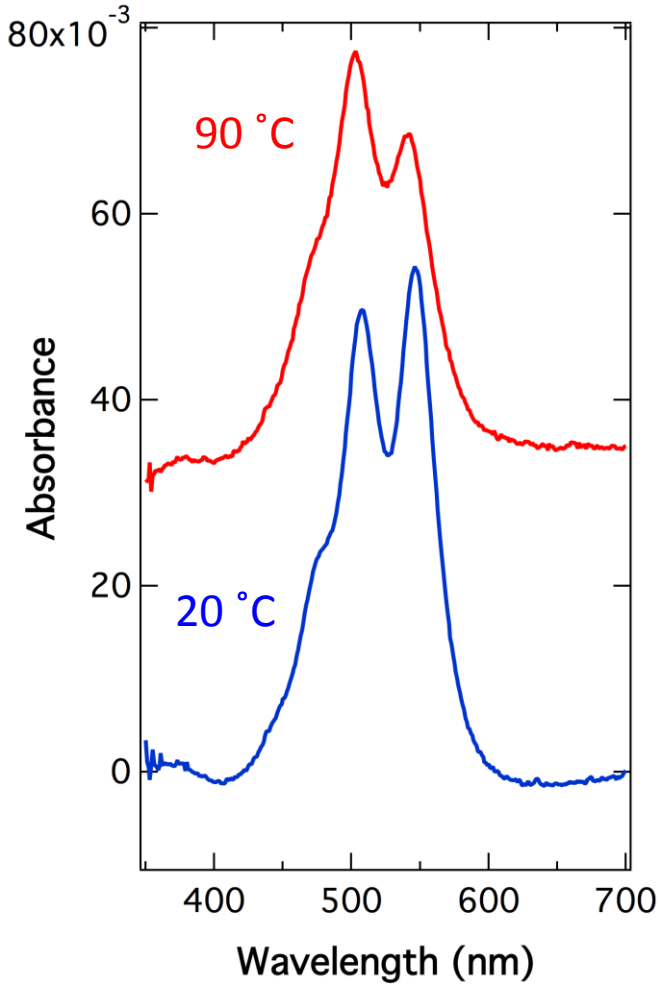


90 ˚C



Synthetic and Biological Hybrid: DNA-linked Perylene Pentamer





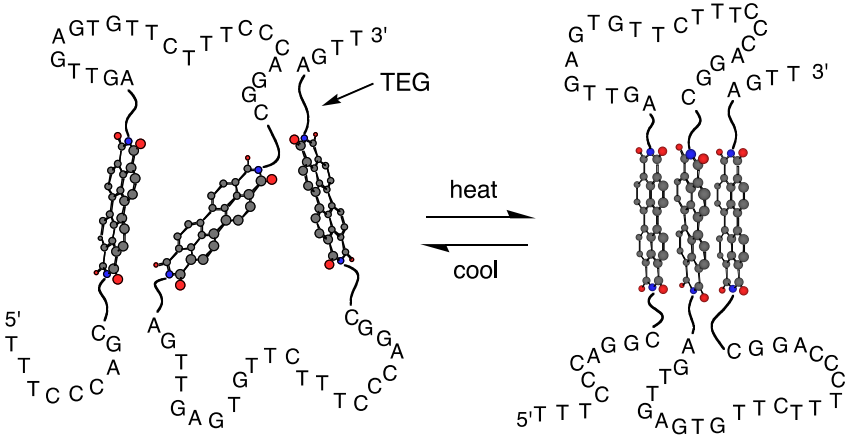
The Empirical Rule Observed

- Perylene stacking comes from two contributions: intermolecular interactions between π-orbitals and hydrophobic interactions.
- Experimental results reveal that hydrophobic effects and π-π stacking do not weaken, perhaps even strengthen, as temperature rises.

The Origin of Thermophilic Folding Properties

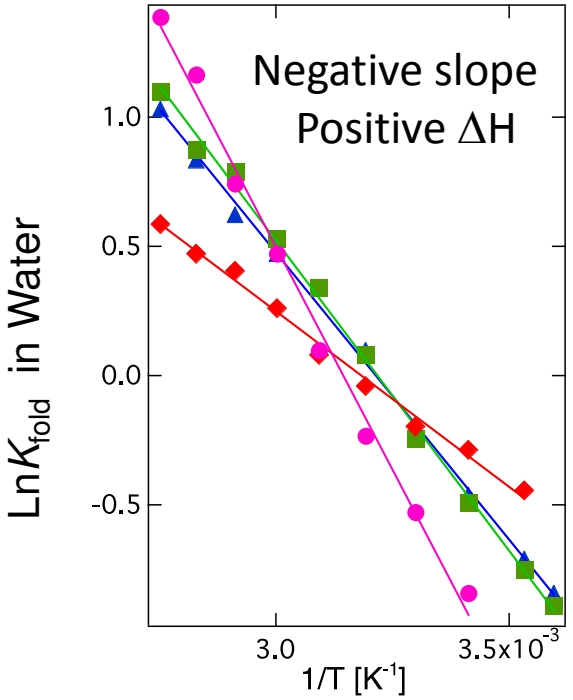
comes from the endothermic interactions among conjugate sheet-like structures.

Endothermic Folding



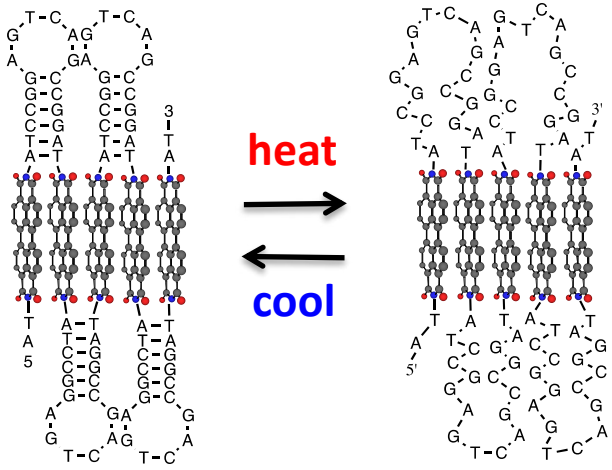
In Water

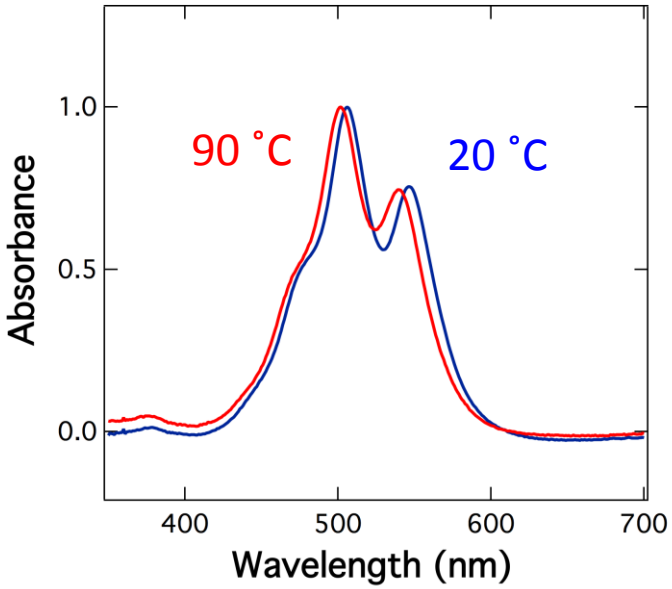
ΔS^o(cal/mol•K)	ΔH^o (kcal/mol)
8.64 ~ 15.4	2.72~6.88

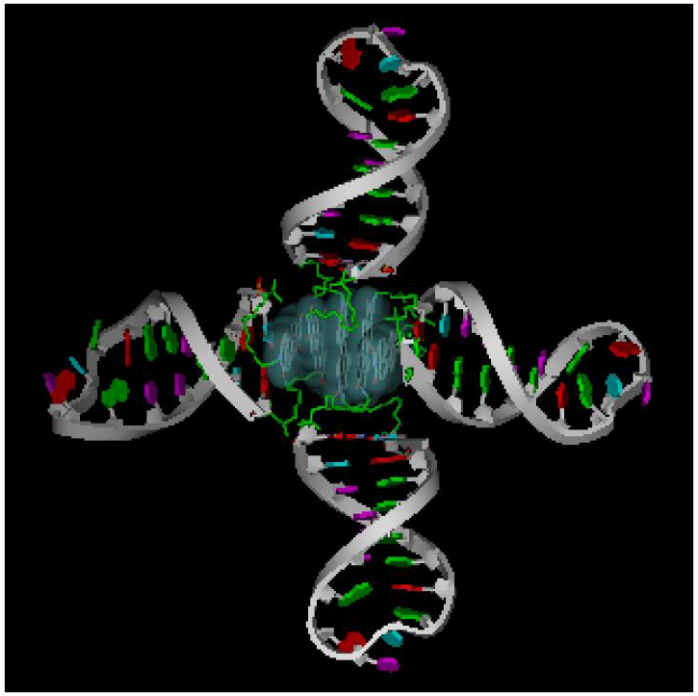


If a folding process is endothermic, then heat drives the molecule to fold, rather than unfold.

Hyperthermophilic Folded Hybrid Polymers







Introducing DNA stem loops between adjacent perylenes results in hyperthermophilic foldamer because hydrogen bonding stabilizes the structure at low temperature and π-stacking stabilizes the structure at high temperature.

Conclusions

Optical spectroscopies are powerful tools to reveal molecular interactions, thus enabling deciphering nature laws such the thermophilic folding in biological and synthetic hybrid polymers.

Acknowledgment: The author greatly acknowledges the support of National Science Foundation (CHE-1212429)

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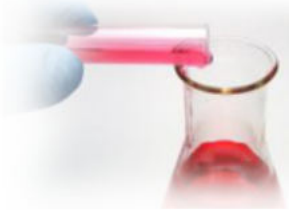

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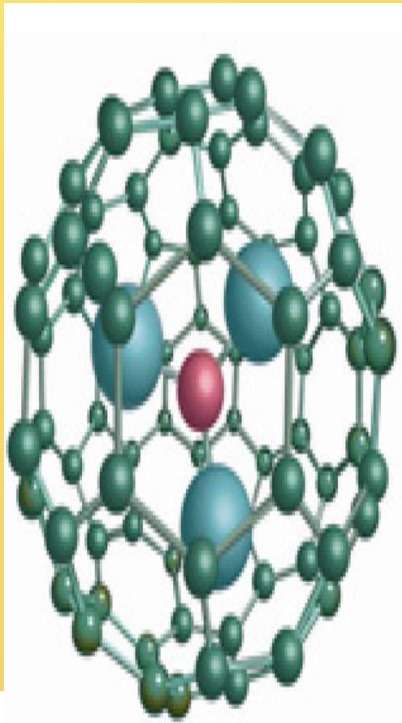

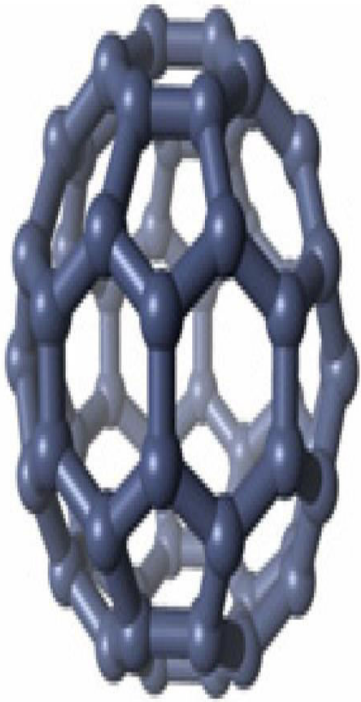

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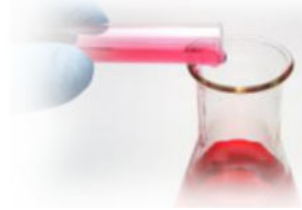

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