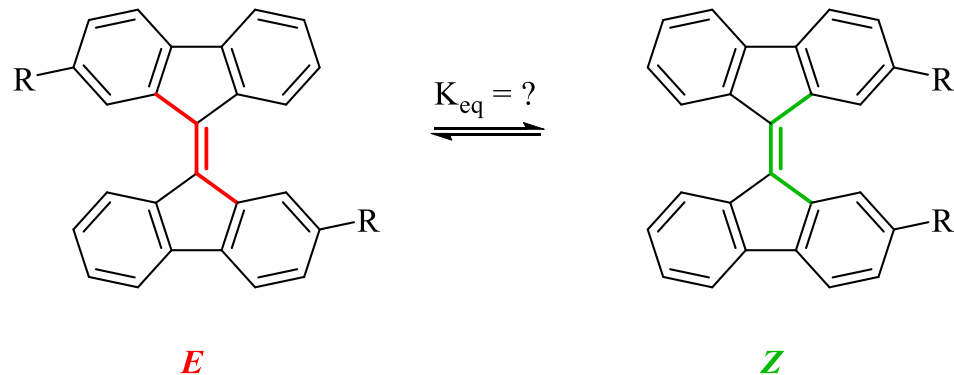


Probing London Dispersion in Solution with 2,2'-Substituted-9,9'-Bifluorenylidenes

Seminar talk presented by
Finn Wilming

August 7th, 2020

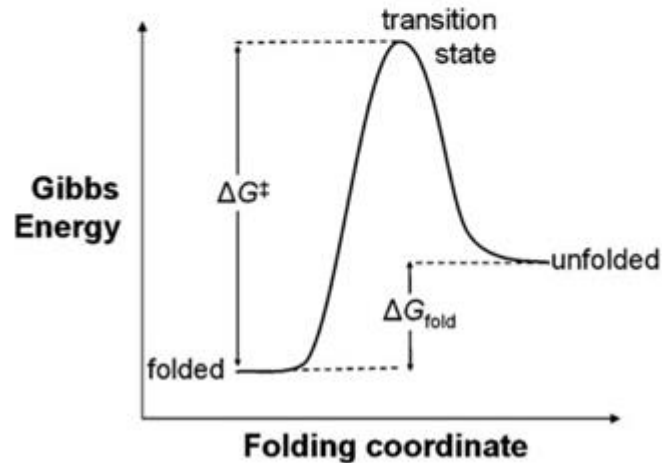
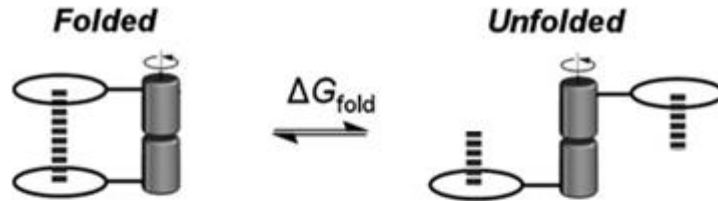
*Institute of Organic Chemistry
Justus-Liebig University Giessen*



Key Questions:

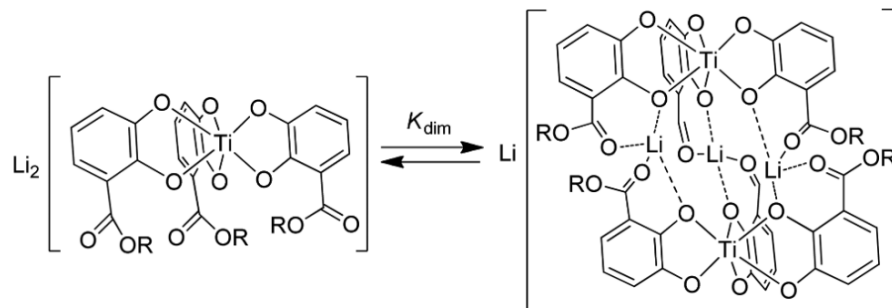
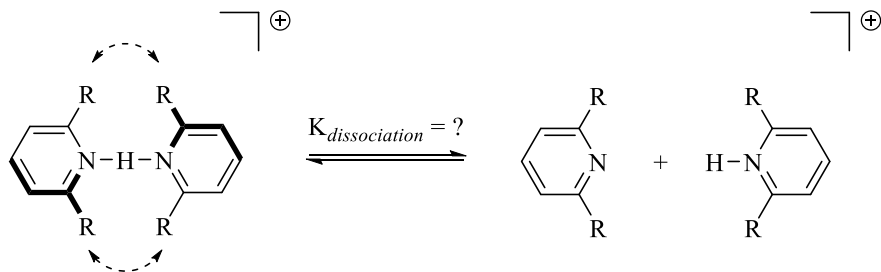
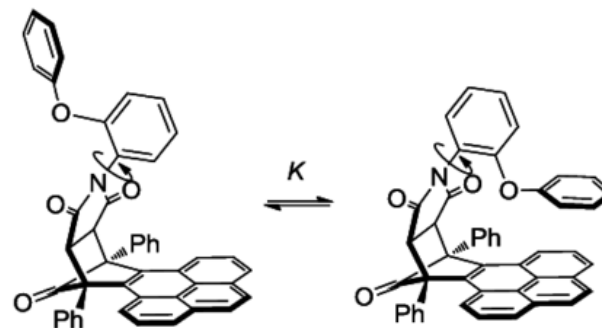
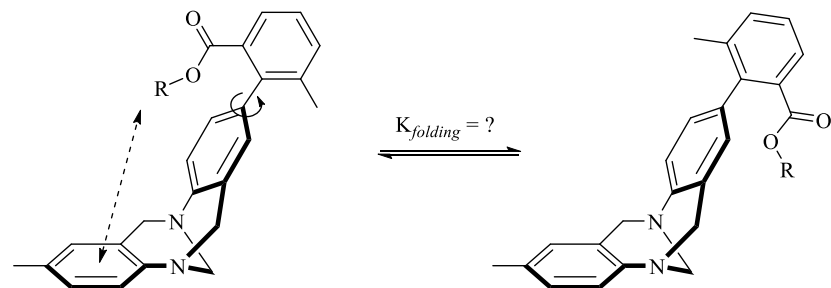


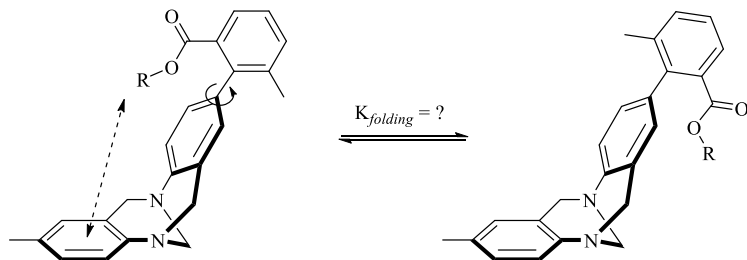
- What is a molecular balance for noncovalent interactions?
- Which molecular balances have been used to quantify London dispersion interactions in solution?
- What is the solvophobic effect?
- How can 2,2'-substituted-9,9'-Bifluorenylidenes improve our knowledge on London dispersion in solution?



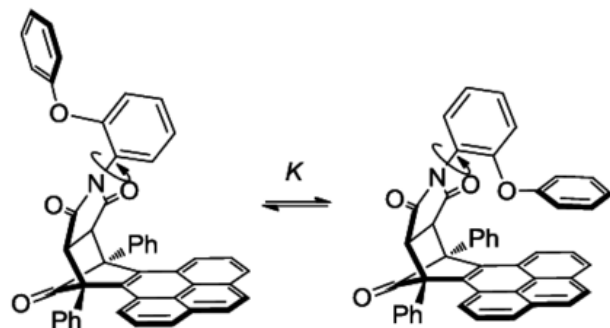
- Molecular machine
- Two experimentally distinguishable states called „**Folded**“ and „**Unfolded**“.
- Allows us to probe microscopic phenomena like noncovalent interactions.
- **Folded**: noncovalent interaction „**on**“.
- **Unfolded**: noncovalent interaction „**off**“.

Part 2 – Molecular balances used to measure noncovalent interactions





„Wilcox Balance“

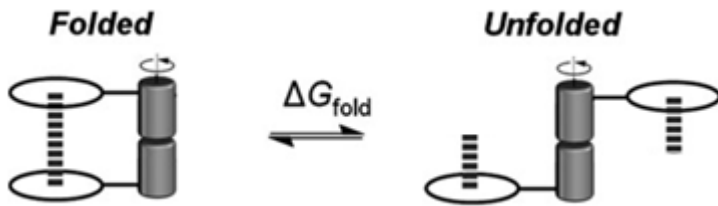


„Shimizu Balance“

- Molecular torsion balances
- Bond rotation is slow due to steric hindrance.
- Rotamers have distinguishable ^1H -NMR signals.
- Folded/unfolded equilibrium is influenced by several different intra- and intermolecular interactions.

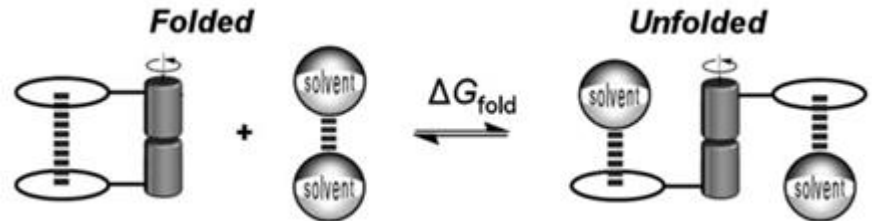


Gas phase:



- Folded state is stabilized through:
 - Balance-Balance interactions
- Unfolded state is not stabilized

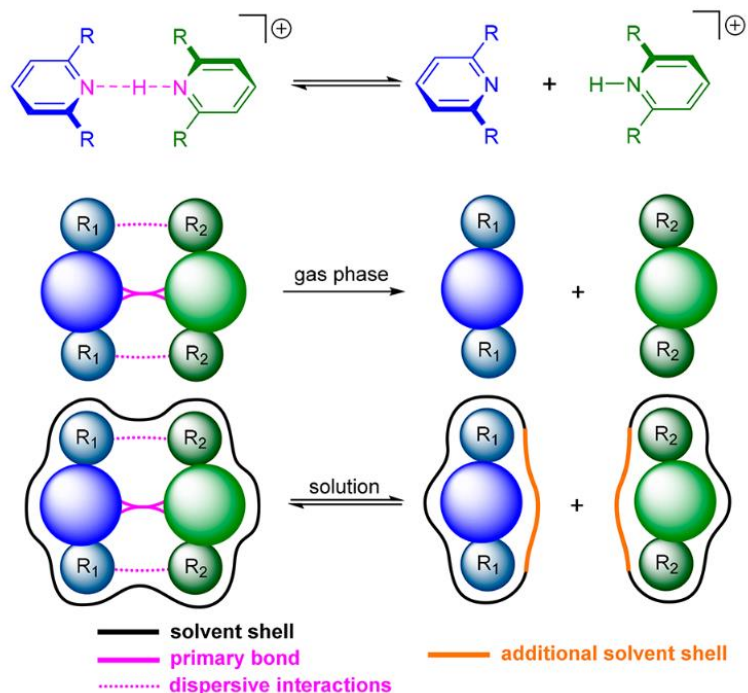
In solution:



- Folded state is stabilized through:
 - Balance-Balance interactions
 - Balance solvents shell
- Unfolded state is stabilized through:
 - Larger balance solvents shell



Molecular balances in solution are influenced by the solvophobic effect.

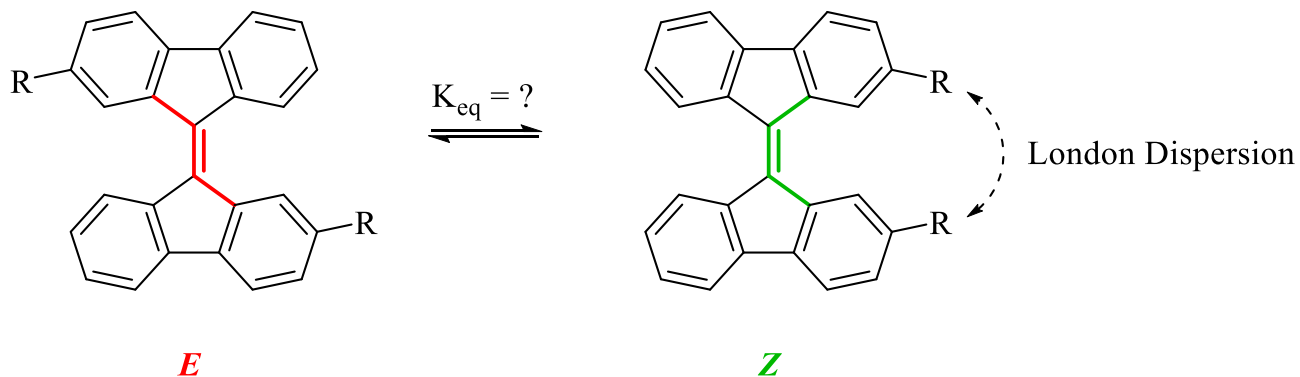


- Dimerization balance
- Monomer/dimer equilibrium is influenced by choice of substituent
- Equilibrium can be probed in gas and liquid phase.
- London dispersion is attenuated in DCM solutions by 70%.



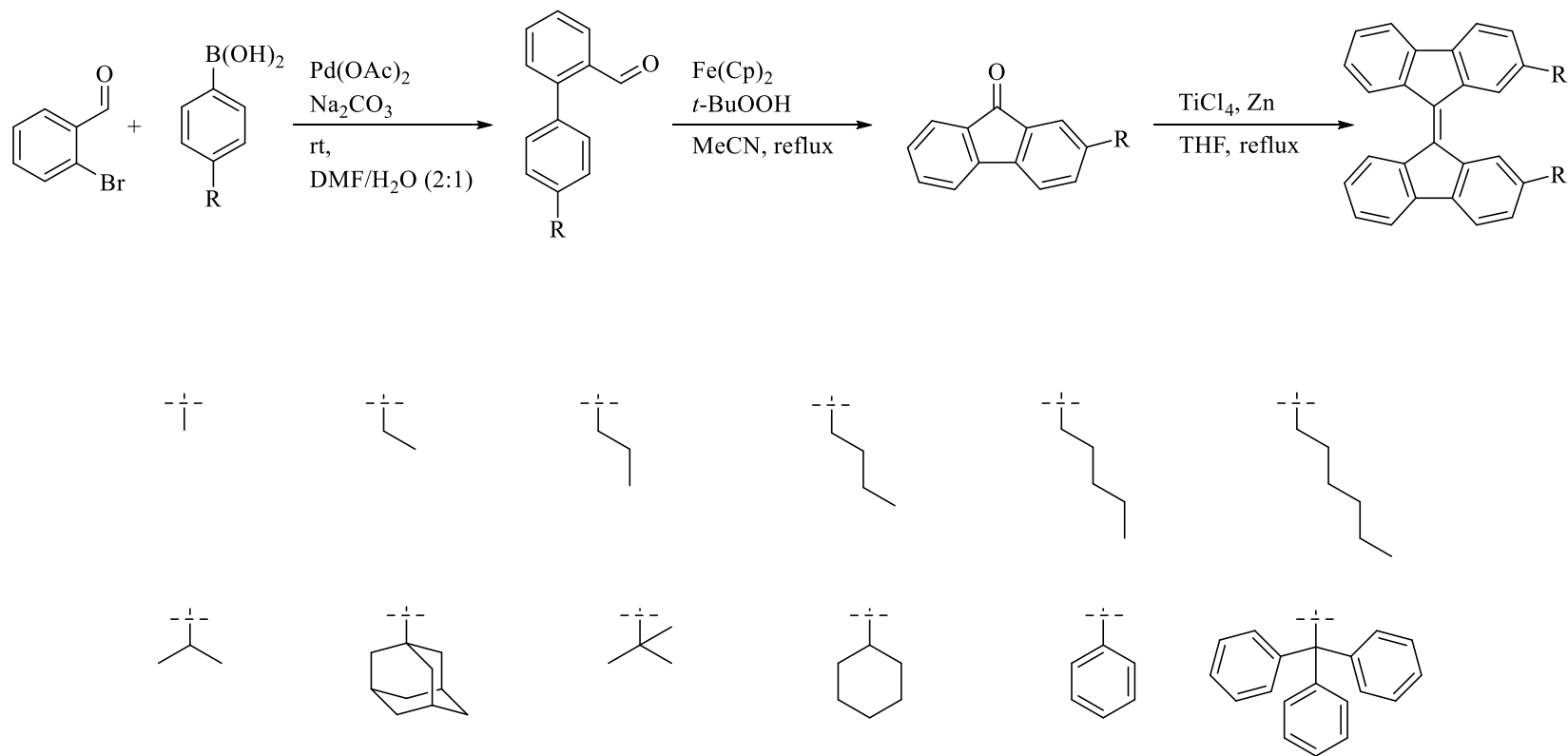
Why is this important?

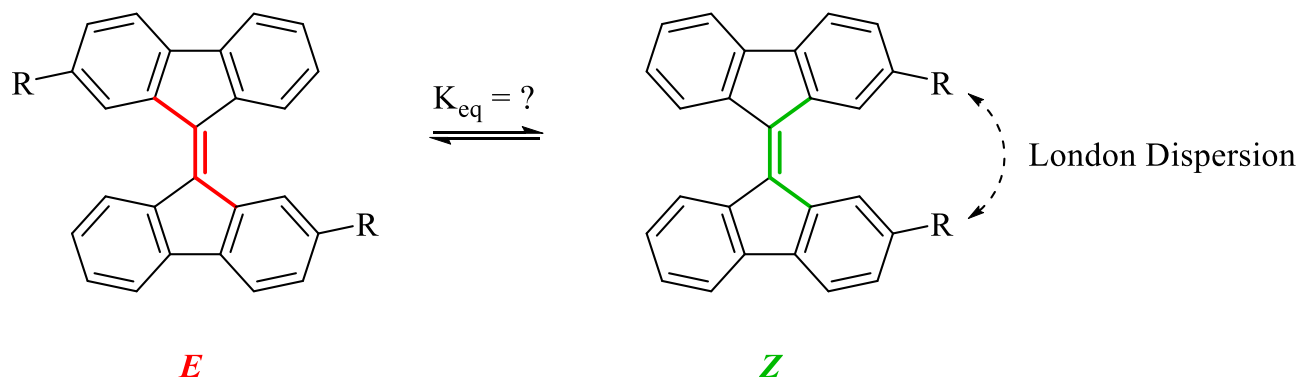
- ➔ London dispersion was generally ignored for centuries because of its „weakness“ in contrast to other noncovalent interactions.
- ➔ A better understanding of London dispersion in solution could allow us to make better predictions on how to apply it in fields like catalysis, reaction design etc.



Checklist:

1. Synthesis
2. E/Z Isomer distinguishable
3. Isomerization (kinetics)
4. What is influencing the equilibrium?

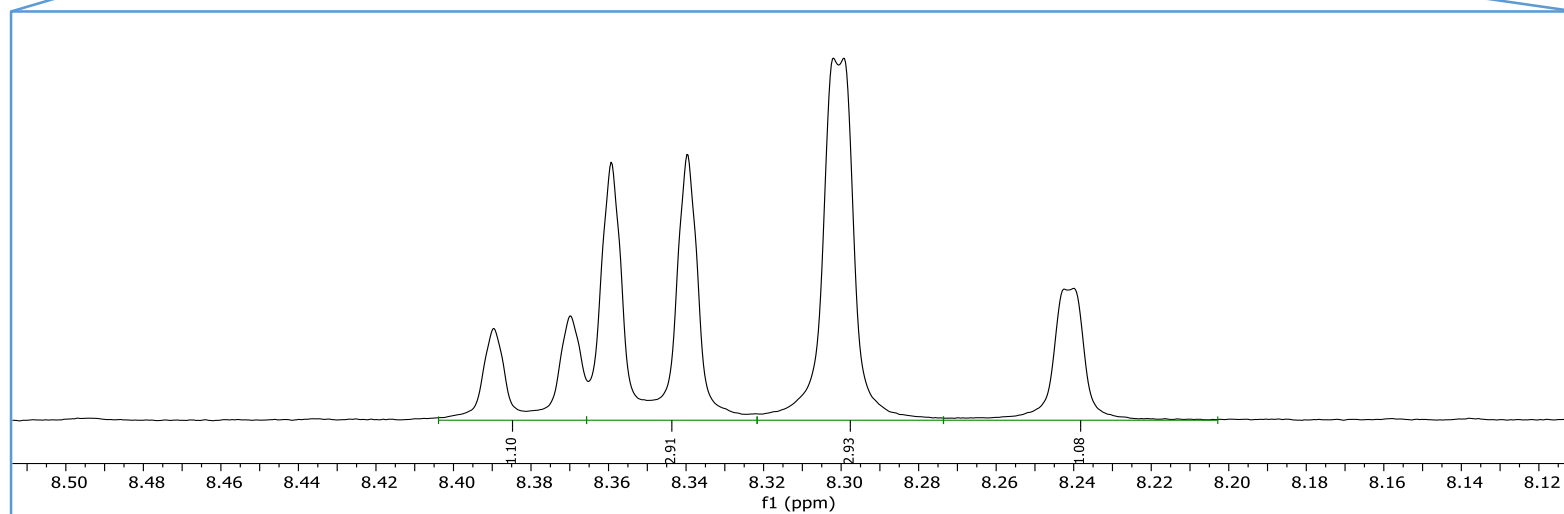
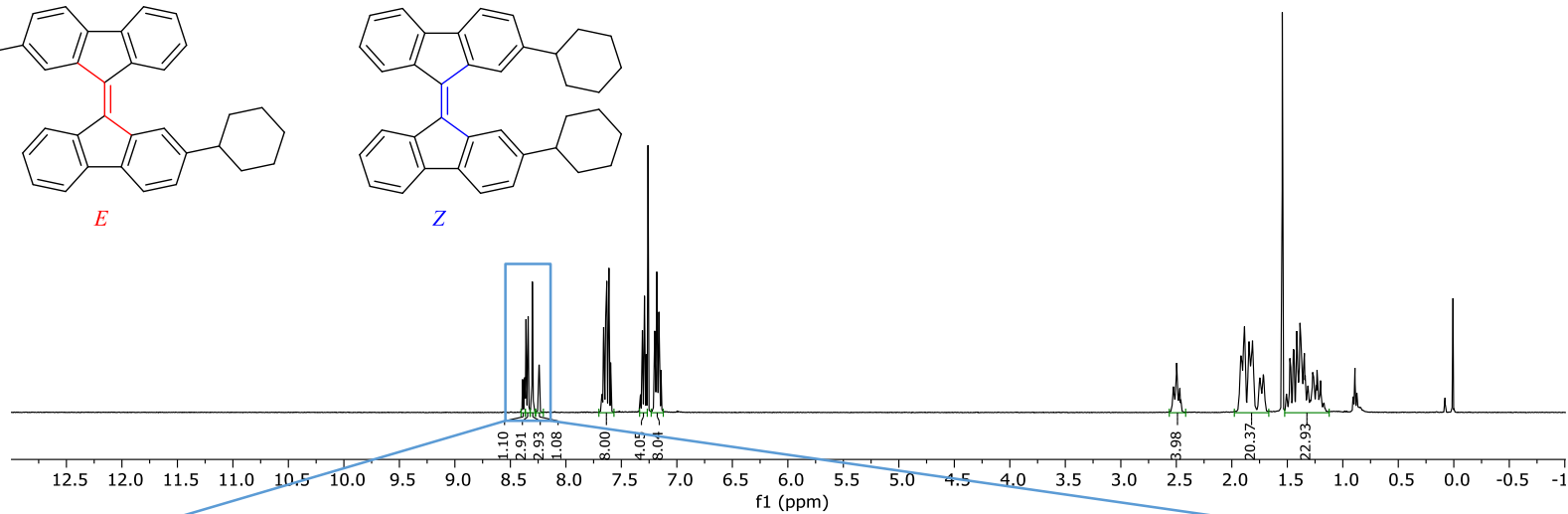
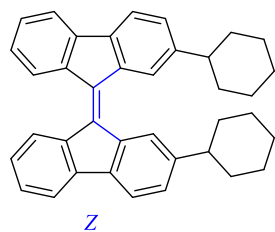
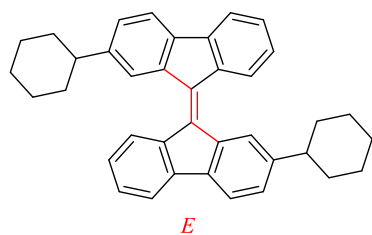


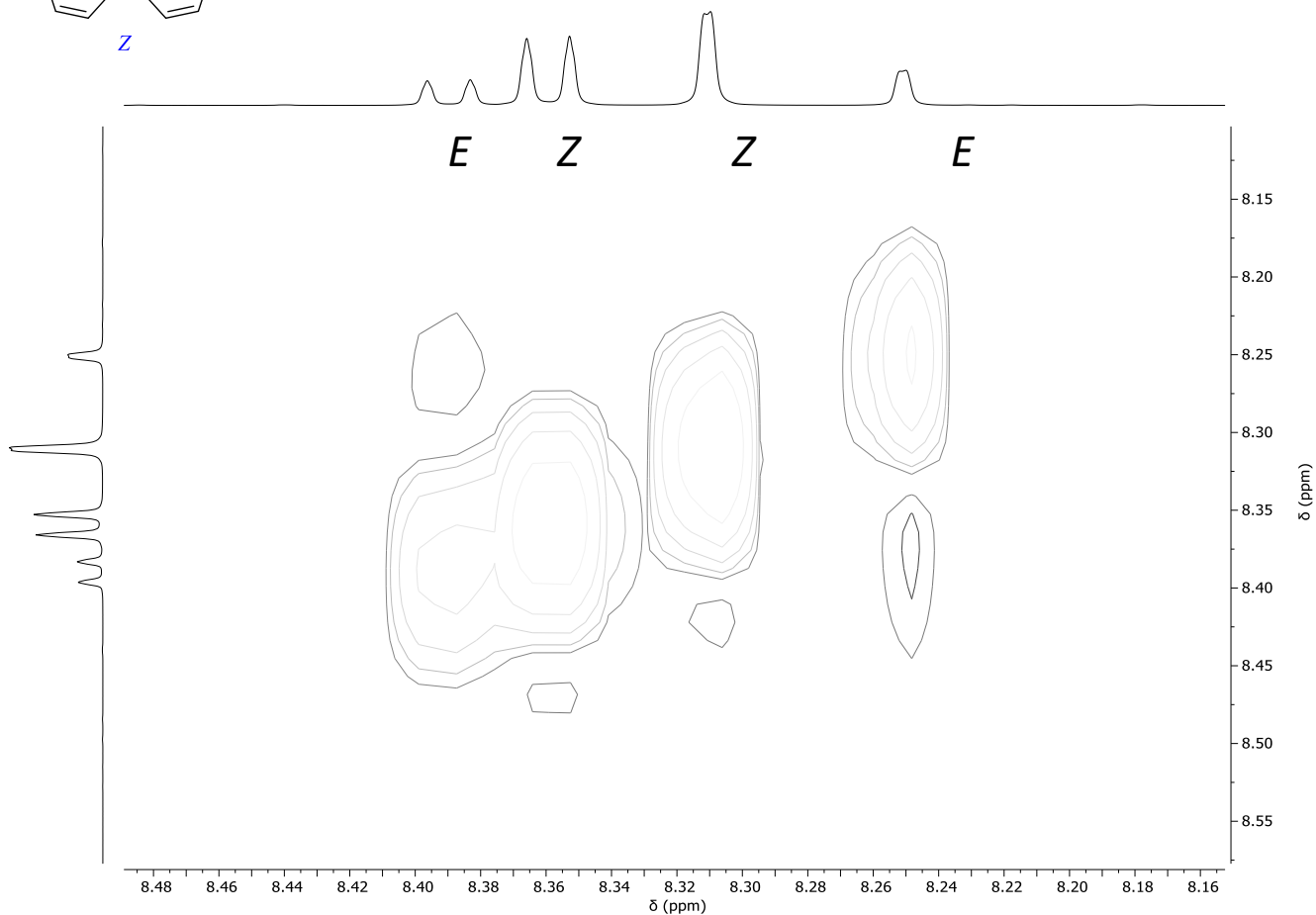
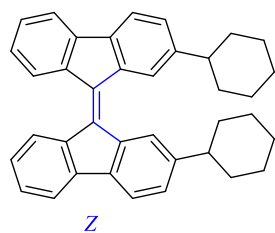
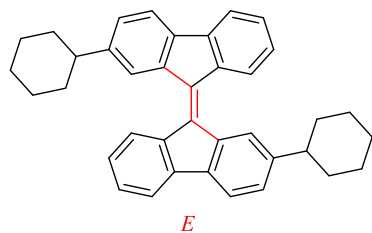


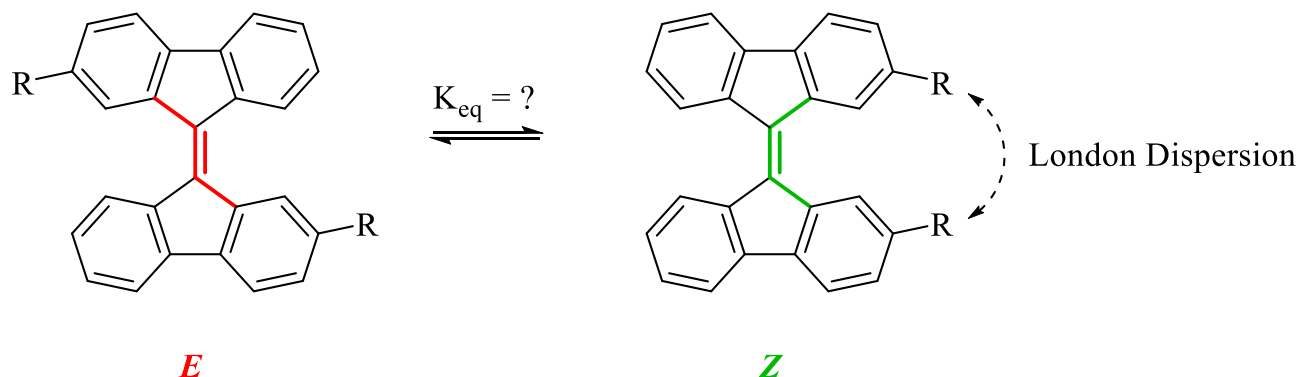
Checklist:

1. **Synthesis**
2. E/Z Isomer distinguishable
3. Isomerization (kinetics)
4. What is influencing the equilibrium?

Part 3 – Bifluorenylidenes as Molecular Balances for London Dispersion



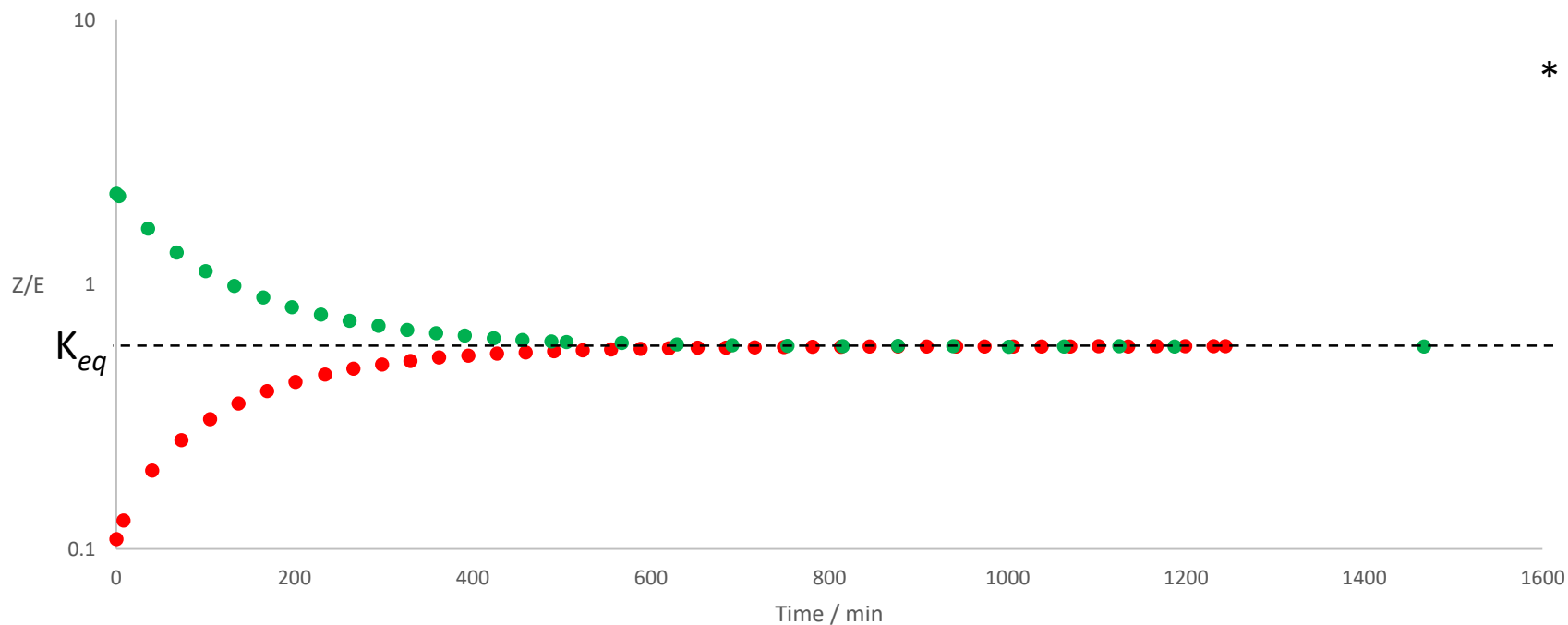
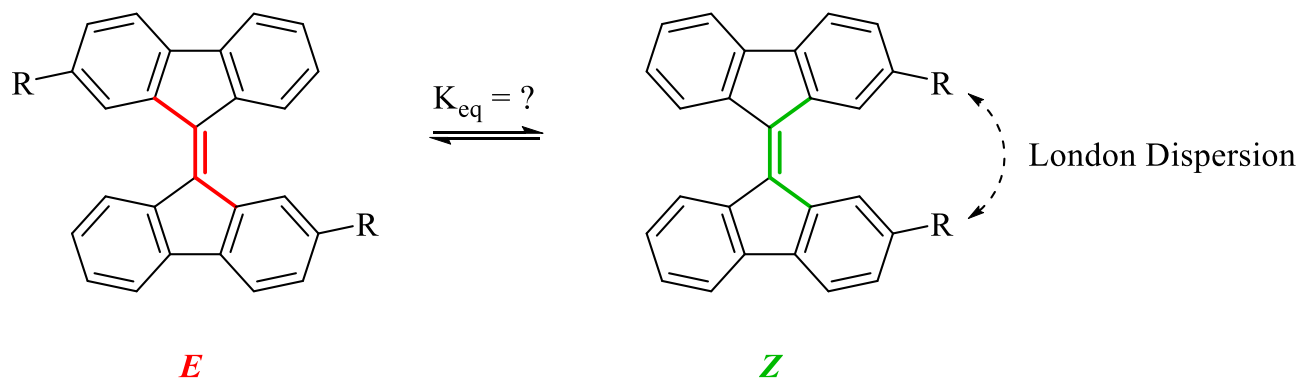




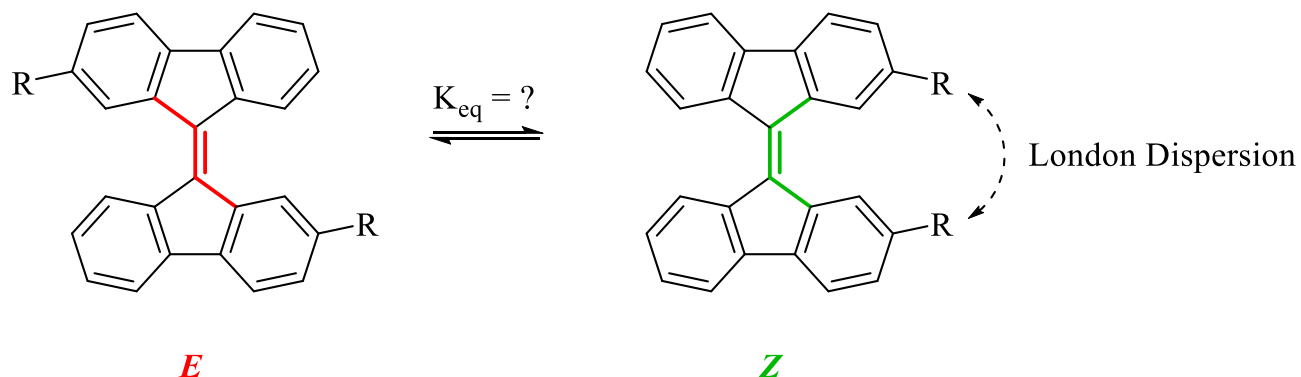
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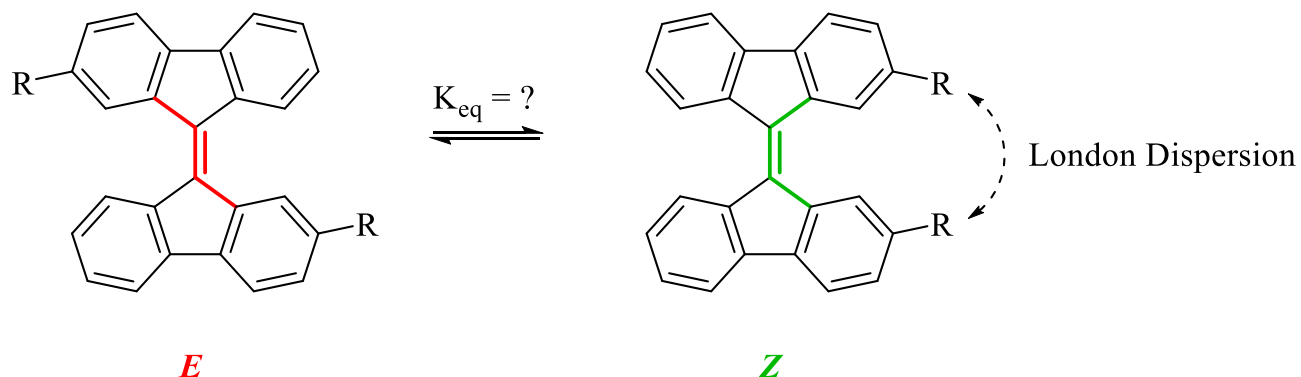


*Equilibration was performed in benzene d6 at 333K.



Checklist:

1. Synthesis
2. E/Z Isomer distinguishable
3. Isomerization (kinetics)
4. What is influencing the equilibrium?



Equilibrium might be influenced by:

- London dispersion
- Steric repulsion
- Solvophobic effects
- Dipolemoment

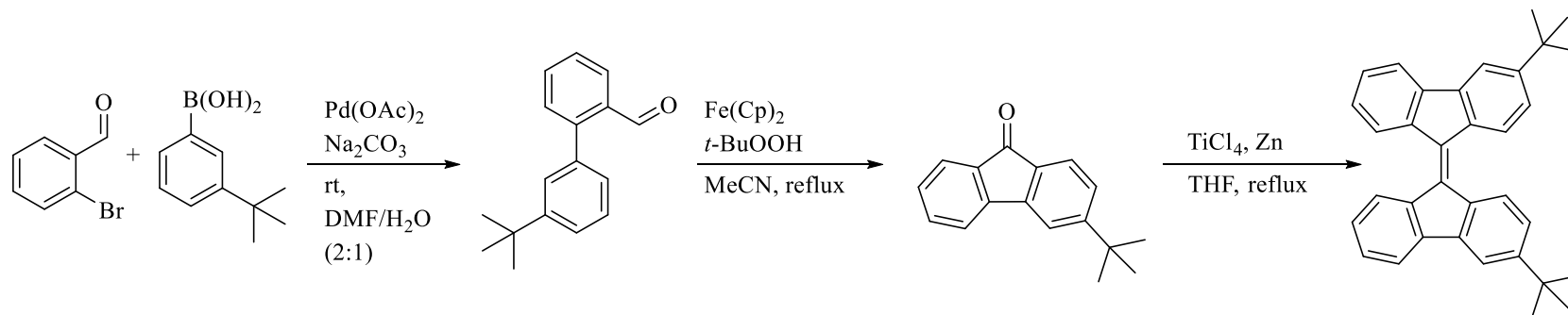
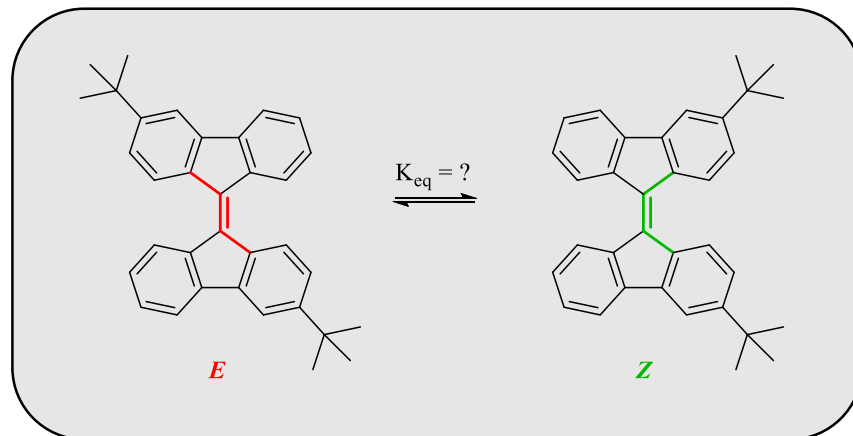


Can we **isolate** some of those **interactions experimentally**?



How can we design a Bifluorenylidene balance **only** dependent of difference in dipolemoment?

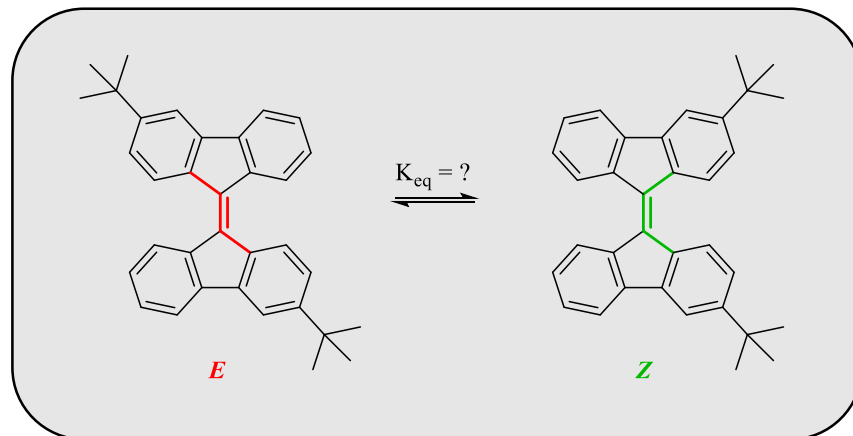
- No dispersive/repulsive interactions.
- No difference in solvent accessible surface.
- Difference in dipolemoment.





Solvent	E/Z ratio
CDCl ₃	50/50
Benzene d ₆	50/50
Nitrobenzene d ₅	50/50

Do 2,2' and 3,3' substituted Bifluorenylidenes have similar dipolemoments?



	3,3' <i>t</i> Bu	2,2' <i>t</i> Bu	2,2' Cy	2,2' <i>i</i> Pr	2,2' C ₂ H	2,2 Ph	*
$\vec{d}$ (E) (Debye)	0.36	0.46	0.57	0.41	0.74	0.02	
$\vec{d}$ (Z) (Debye)	0.85	0.96	1.25	0.91	1.55	0.17	



The influence of difference in dipolemoment on K_{eq} should be negligible!

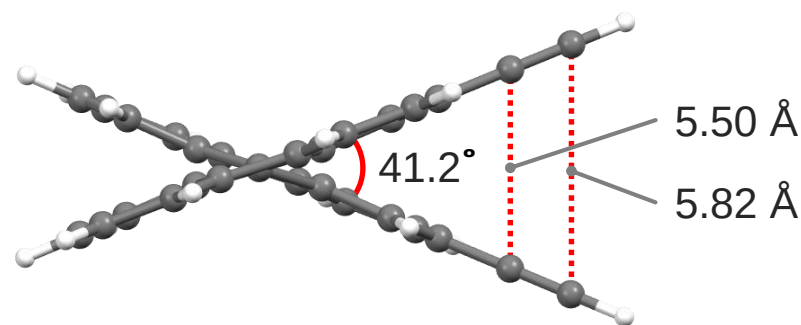
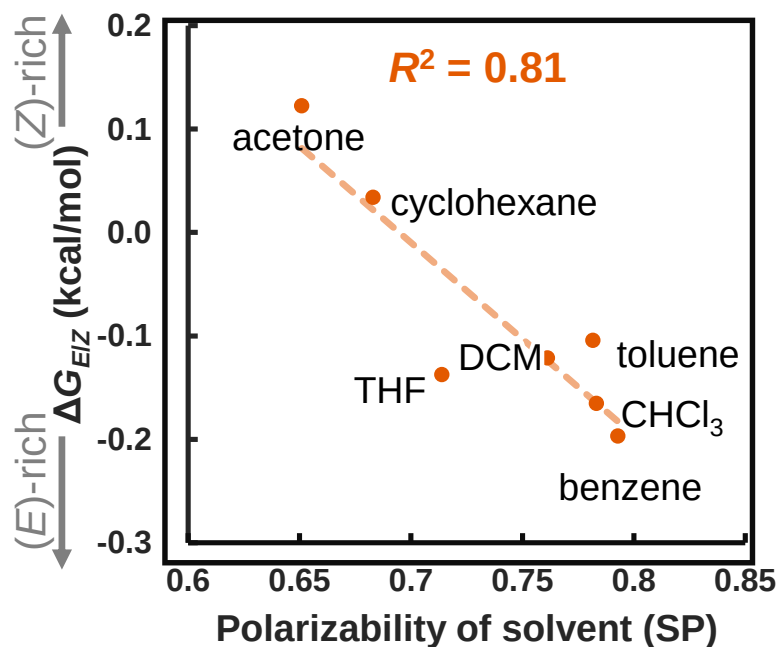
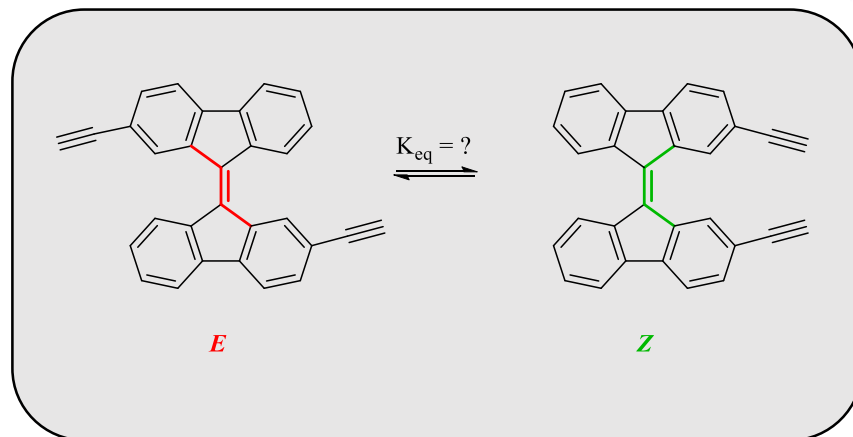
*All dipolemoments were computed using B3LYP(D3)/def2TZVP.

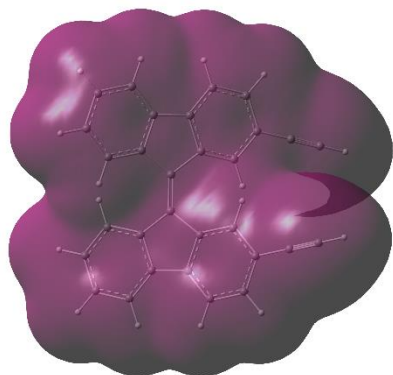
Part 3 – Bifluorenylidenes as Molecular Balances for London Dispersion



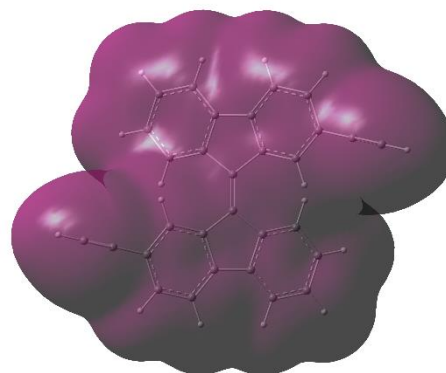
How can we design a Bifluorenylidene balance **only** dependent of solvophobic effects?

- No dispersive/repulsive interactions.
- Difference in solvent accessible surface.





$$\Delta S = 0.00 \text{ \AA}^2$$



isosurface of
electron density
at 0.0001

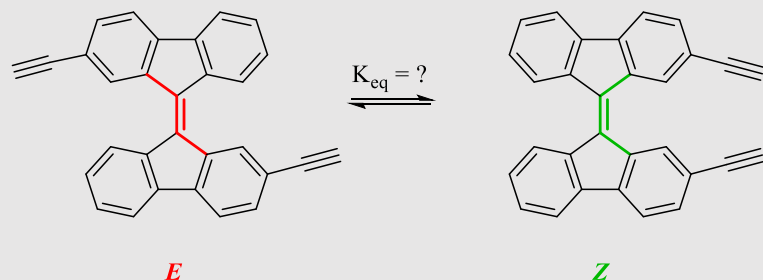
$$\Delta S = 2.55 \text{ \AA}^2$$



We can use those values to estimate the influence of solvophobicity on our other balances.



Can we use those values to calculate the influence of solvophobicity on our other balances?



$$K_{eq} \text{ (benzene d6, 298 K)} = 0.72$$

$$\Delta G_{E/Z} = -0.194 \text{ kcal/mol}$$

$$\Delta S = 2.55 \text{ Å}^2$$

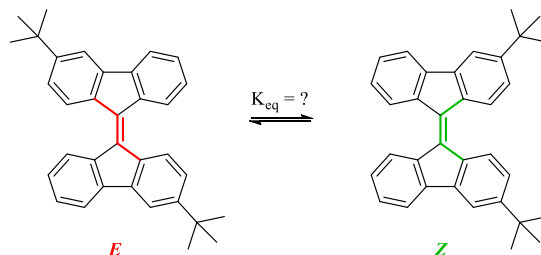
$$E_{solv} = -0.076 \text{ kcal/mol Å}^2$$

Assumptions:

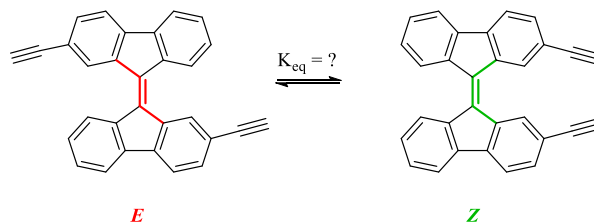
1. K_{eq} of this system is primarily influenced by solvophobic effects.
2. Every part of the solvent accessible surface is treated equally.



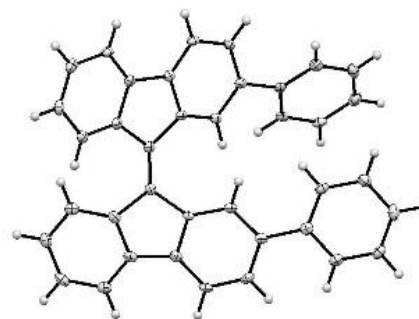
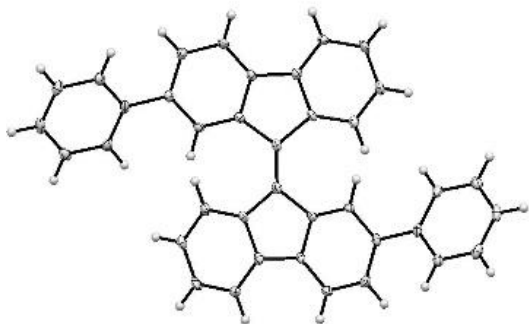
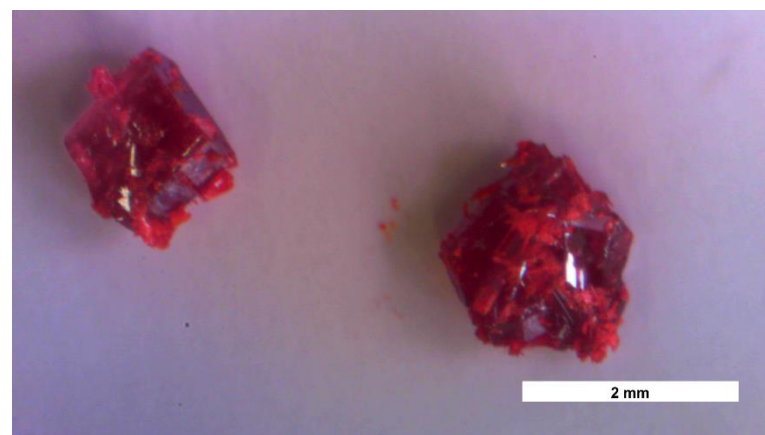
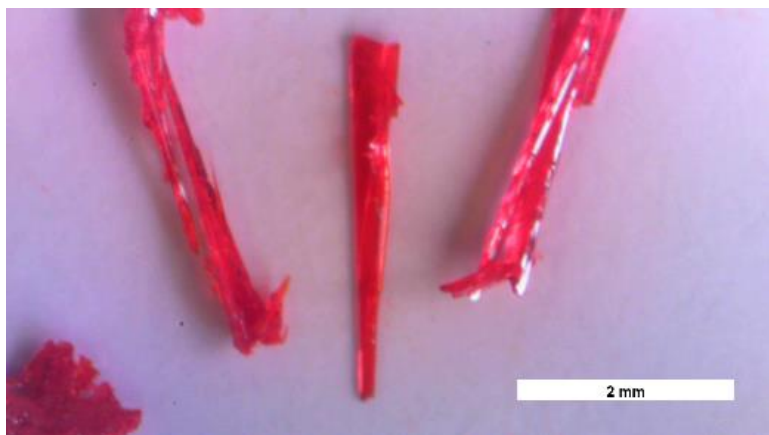
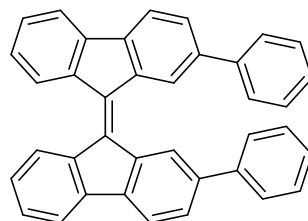
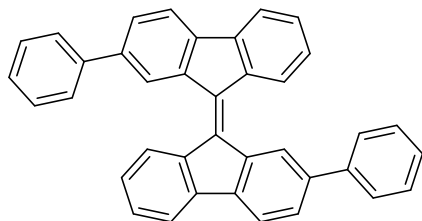
- Experimental results suggest that difference in dipolemoment is not influencing the *E/Z* equilibrium of 2,2'-substituted-9,9'-Bifluorenylidenes.

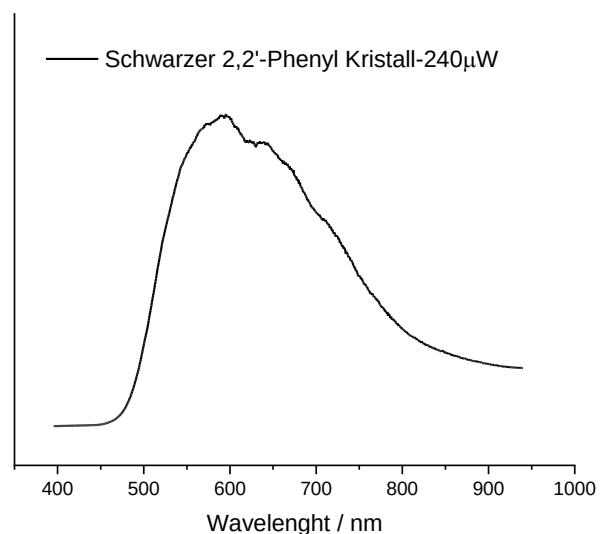
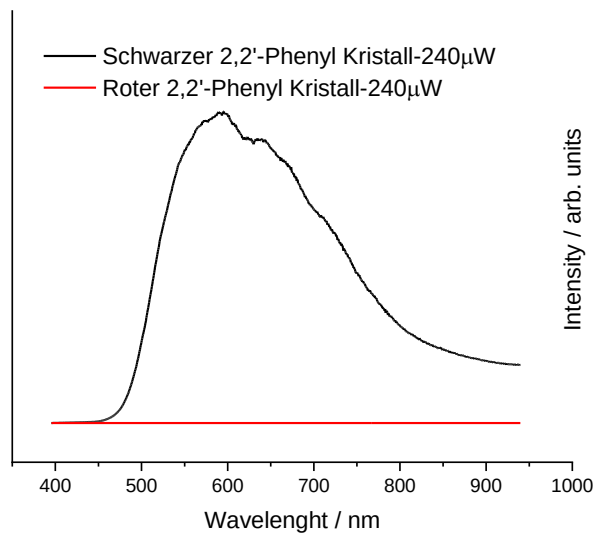
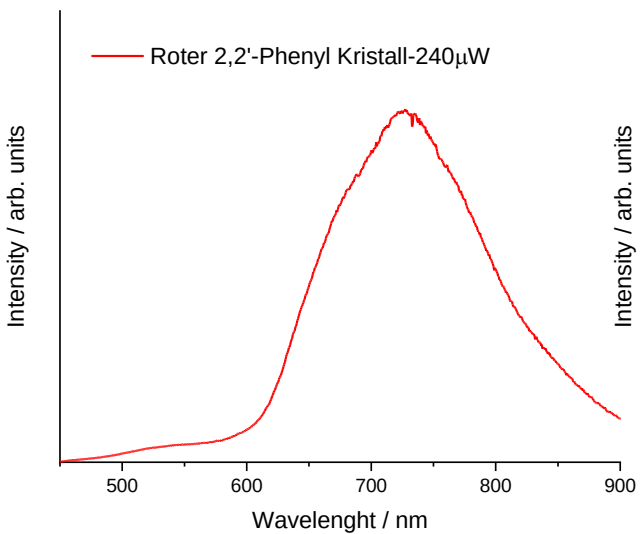
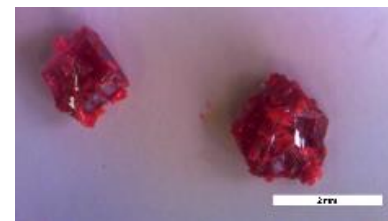
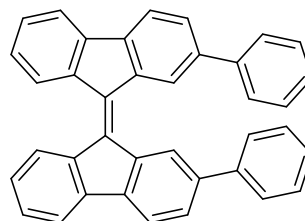
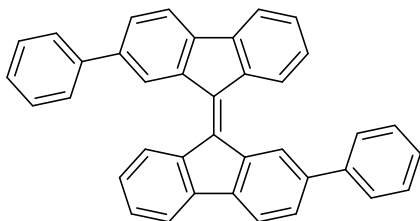


- 2,2'-Diethynyl-9,9'-bifluorenylidene can therefore be used to probe solvophobic effects.

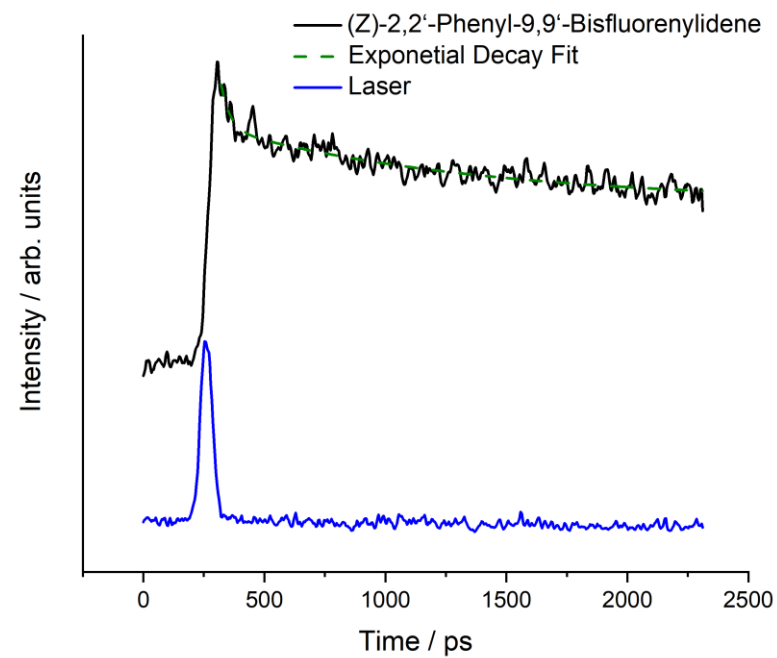
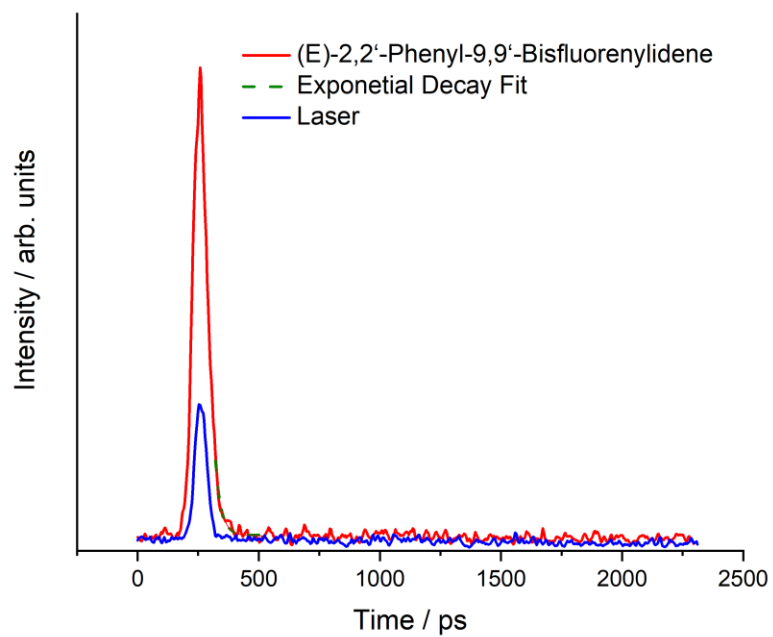
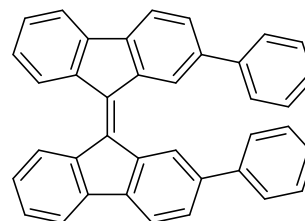
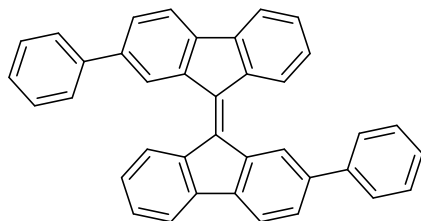


- Experimentally derived E_{disp} values could be obtained through this pathway.
Can we reproduce the 70 % attenuation in DCM solutions?

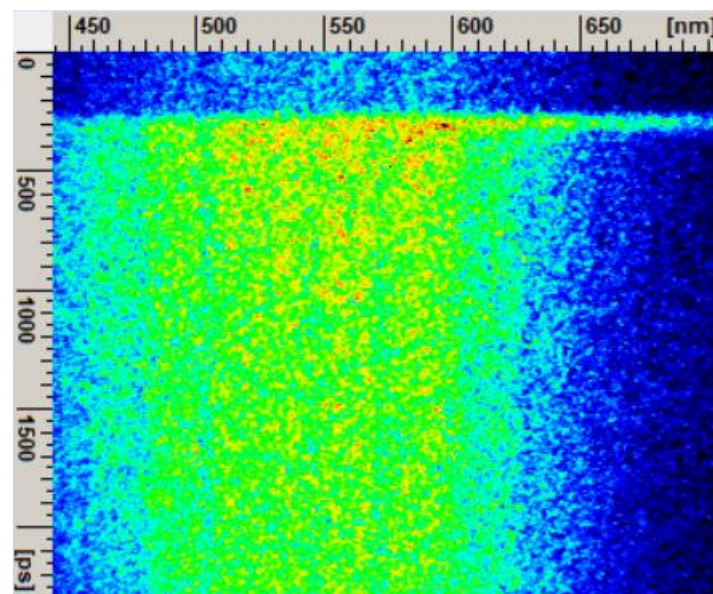
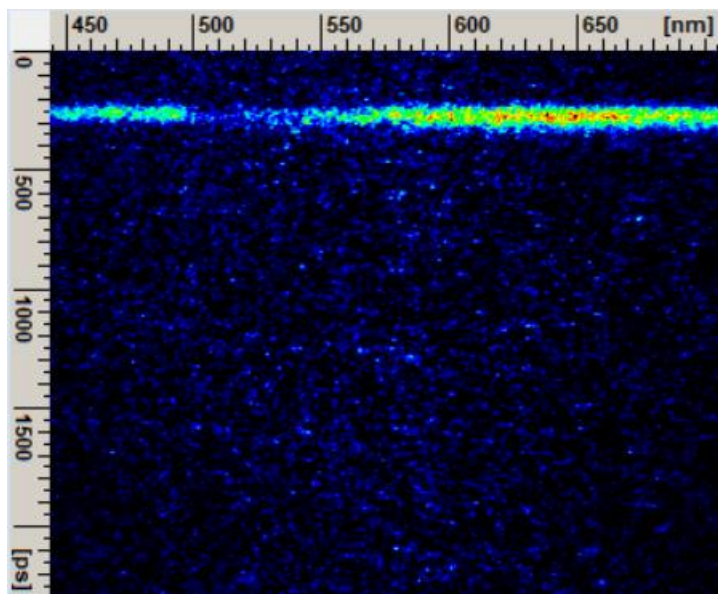
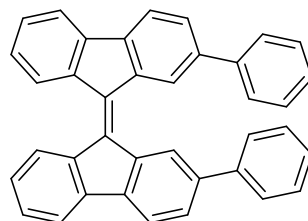
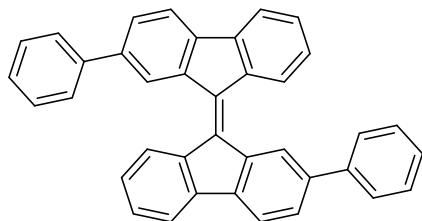




Continuous-wave photoluminescence (PL) spectra



Time dependant photoluminescence spectra

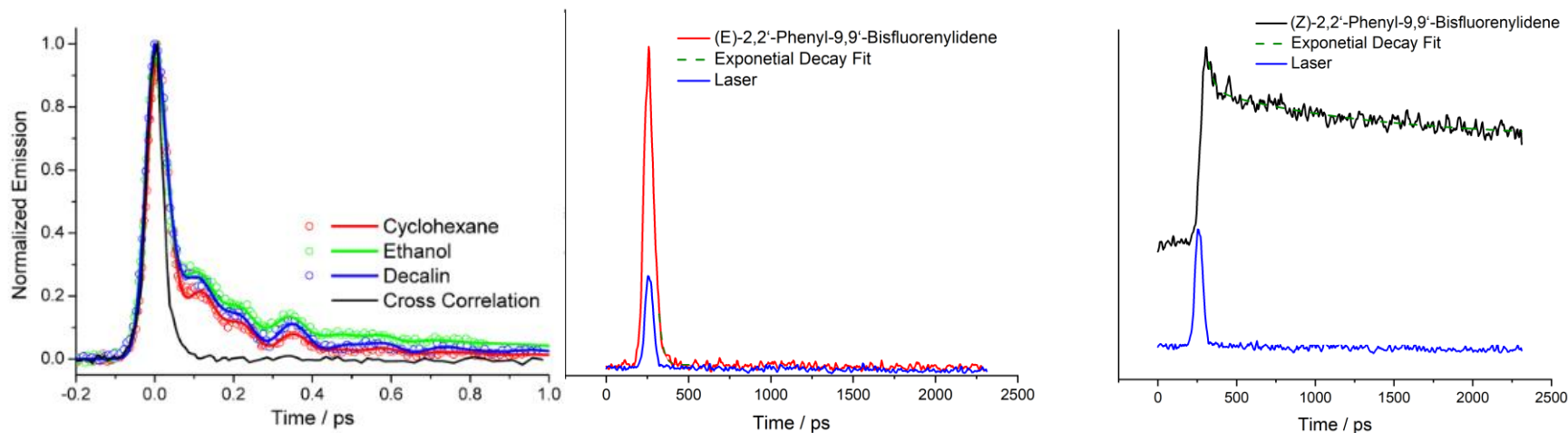


Time dependent photoluminescence spectra (3D)



But why?

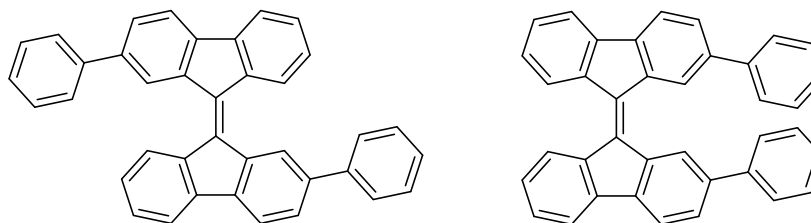
“The excited state dynamics of **9,9'-BF** were studied in detail through ultrafast time-resolved fluorescence and transient absorption in the visible and mid-IR regions. The primary relaxation step is extremely rapid (100 fs) and **involves population of an intermediate (dark) state** [...].



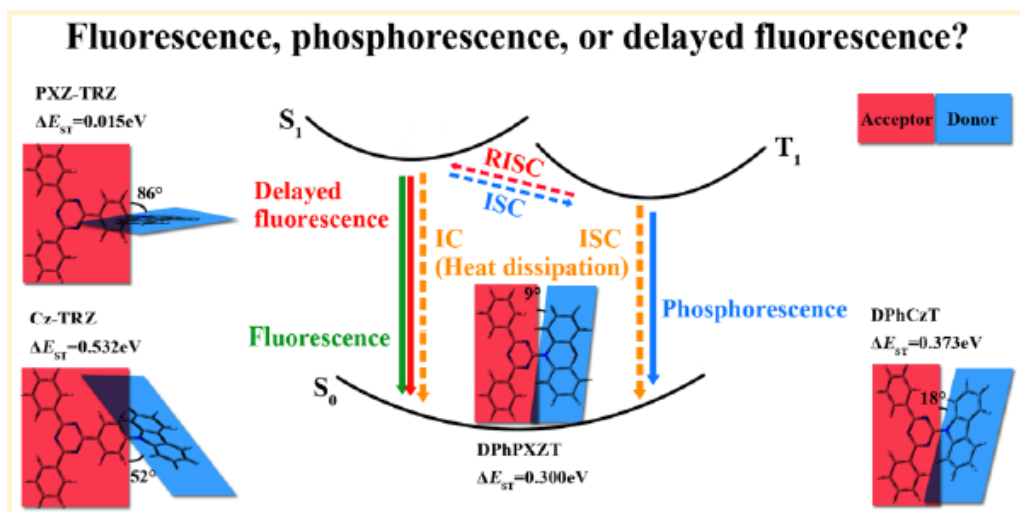
Z Isomer has different relaxation mechanism



➡ Z Isomer has different relaxation mechanism



Thermally activated delayed fluorescence (TADF) is a process through which a molecular species in a non-emitting excited state can incorporate surrounding thermal energy to change states and only then undergo light emission.





- Investigating the possible use of 2,2'-Ethynyl-9,9'-Bifluorenylidene as a molecular balance for solvophobic effects.
- Can we reproduce 70 % attenuation of London dispersion in DCM solutions?
- Are solvophobic effects temperature dependant?
- Performing computations on the excited state chemistry of (Z)-2,2'-Diphenyl-9,9'-bifluorenylidene.



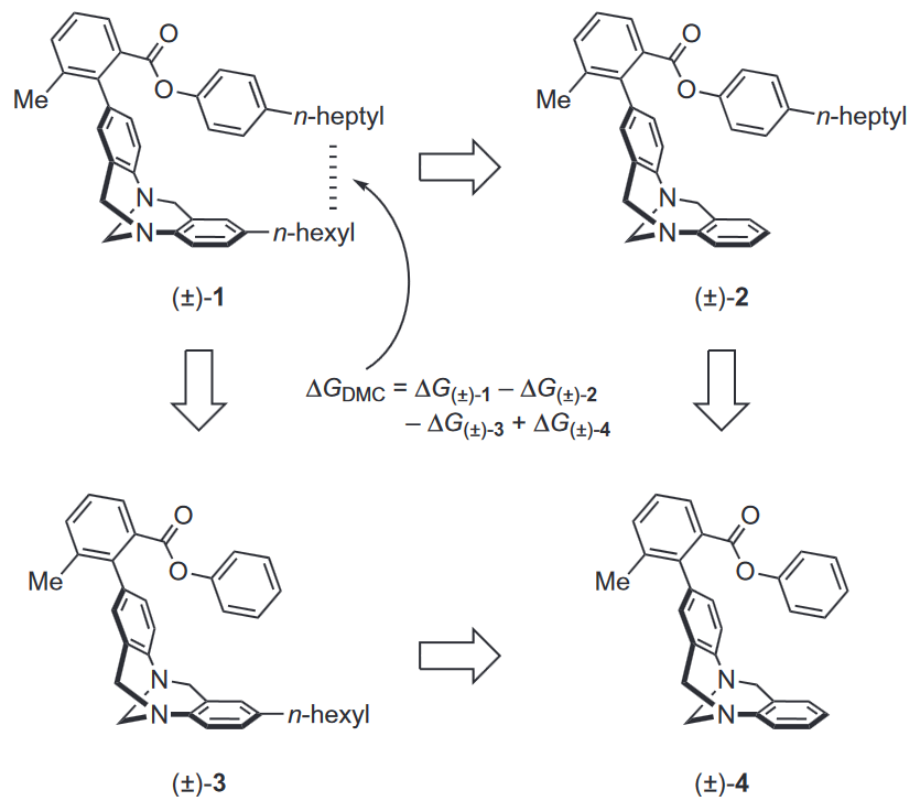
Prof. Dr. Peter R. Schreiner

Yu Ozawa

Lars, Bastian, Jan, Lukas and Dennis for Discussions.

Lab B201

PRS Group



- Double Mutant Cycle
- Approximation to isolate the n-hexyl/n-heptyl interactions.
- Assumptions:
 - Core Structure is not influenced by removal of alkyl chain.
 - Alkyl-alkyl and secondary interactions are additive.
- Secondary effects are „black box“