UV/Vis spectra of Poly(L-glutamic acid) featuring photochromic azobenzene side chain

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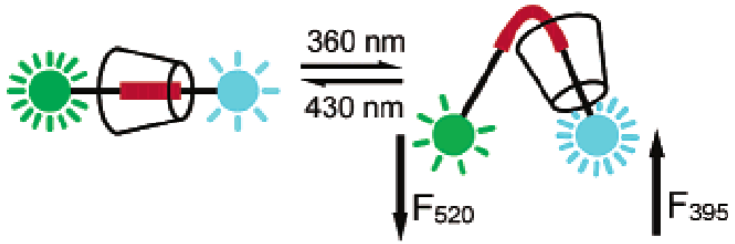
France

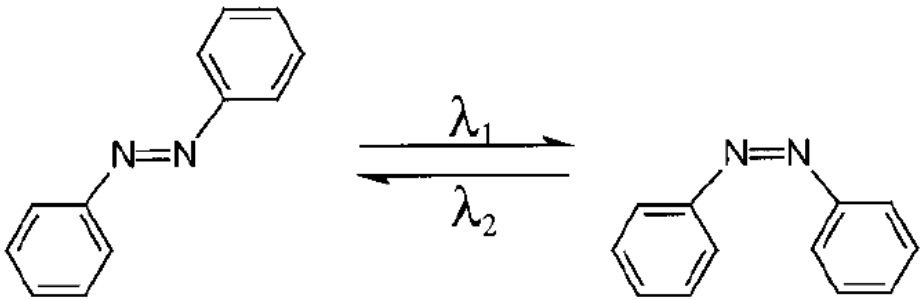
September 28, 2007

Industrial and technological applications of azobenzene (AB) derivatives

- 'Absorption' dyes: 60-70% of the world production[1]



Reversible photochromic isomerization: TAB ⇌ CAB



[1] Zollinger, H. In *Color Chemisrty, Syntheses, Properties and Applications of Organic Dyes and Pigments*; Wiley-VCH, Weinheim, 3 ed., 2003.

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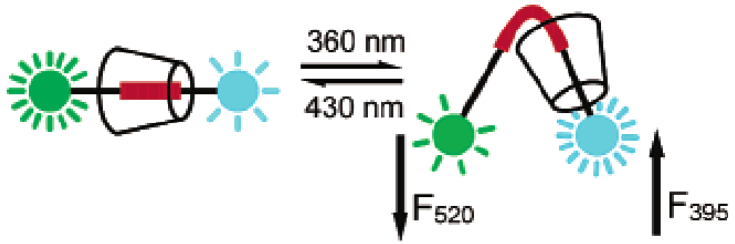
- Media storage devices[2]
- Molecular motors[3]



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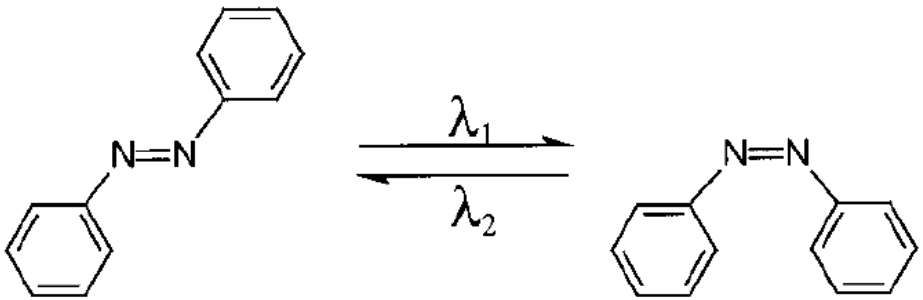

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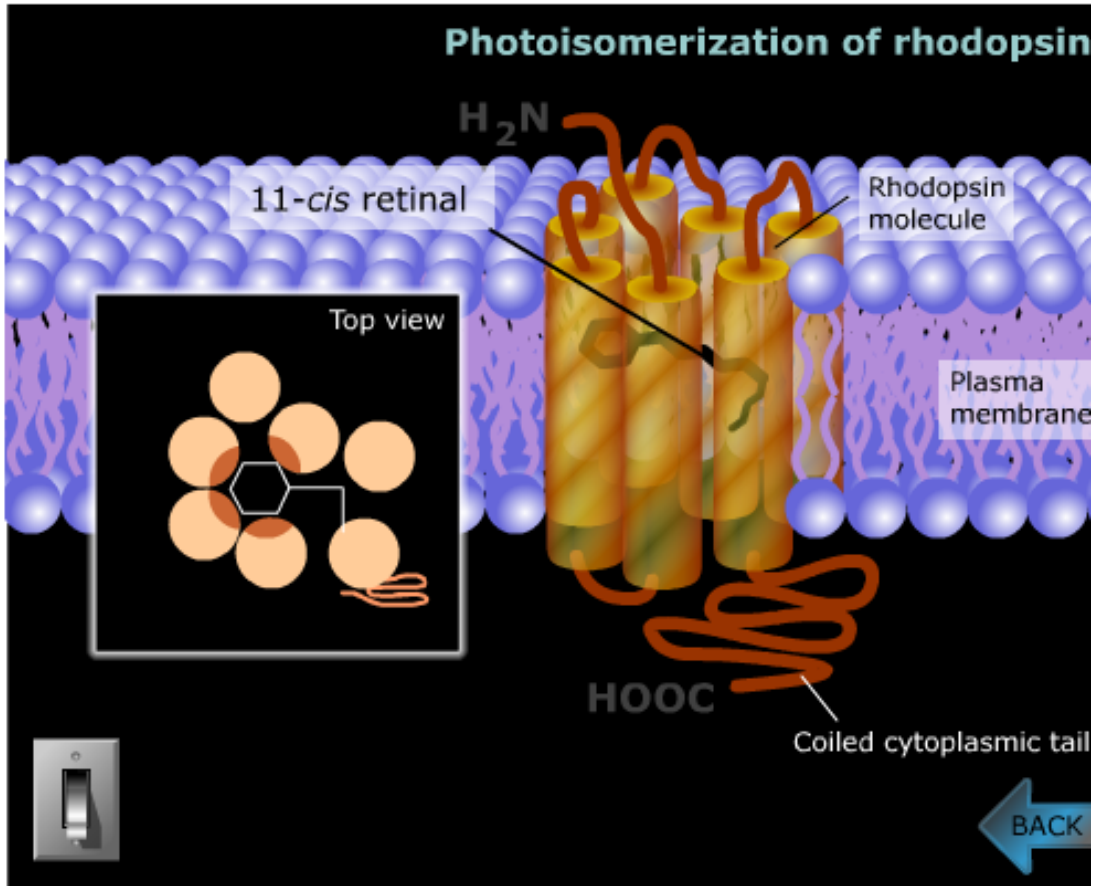
- light energy $\rightleftharpoons$ mechanical energy



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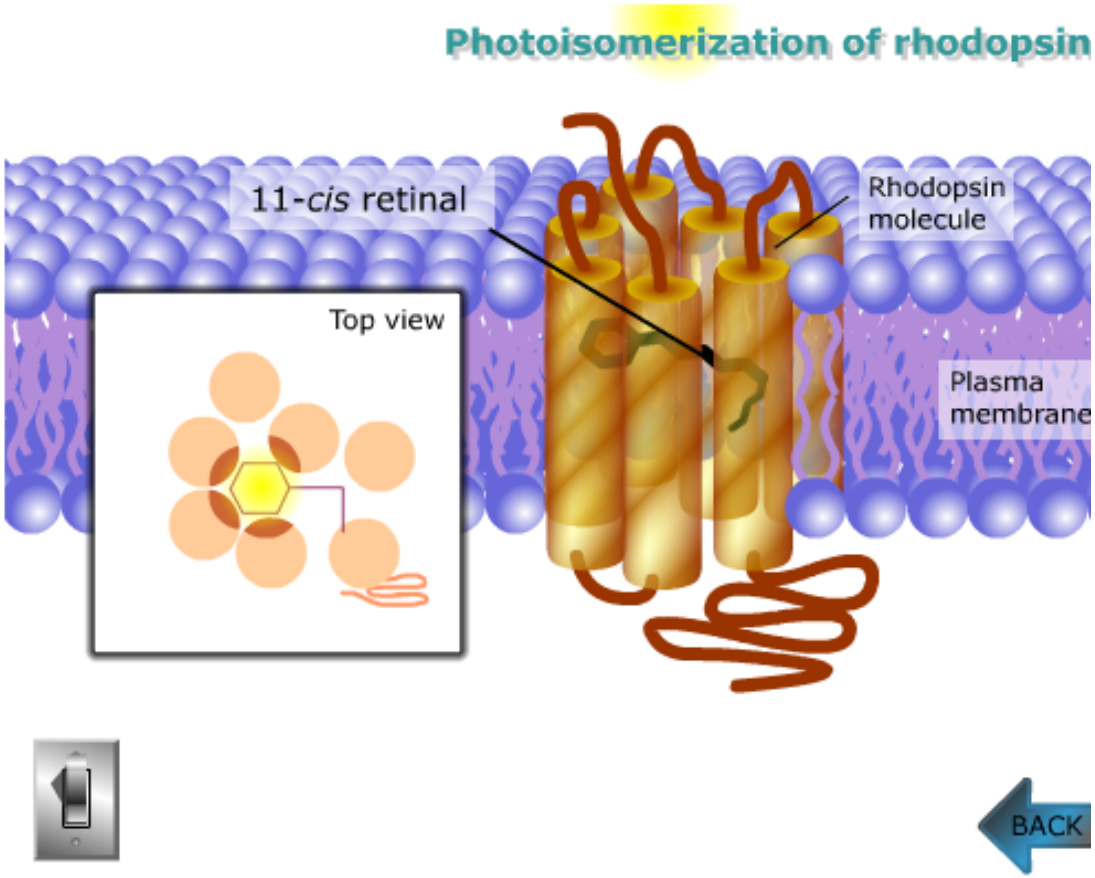

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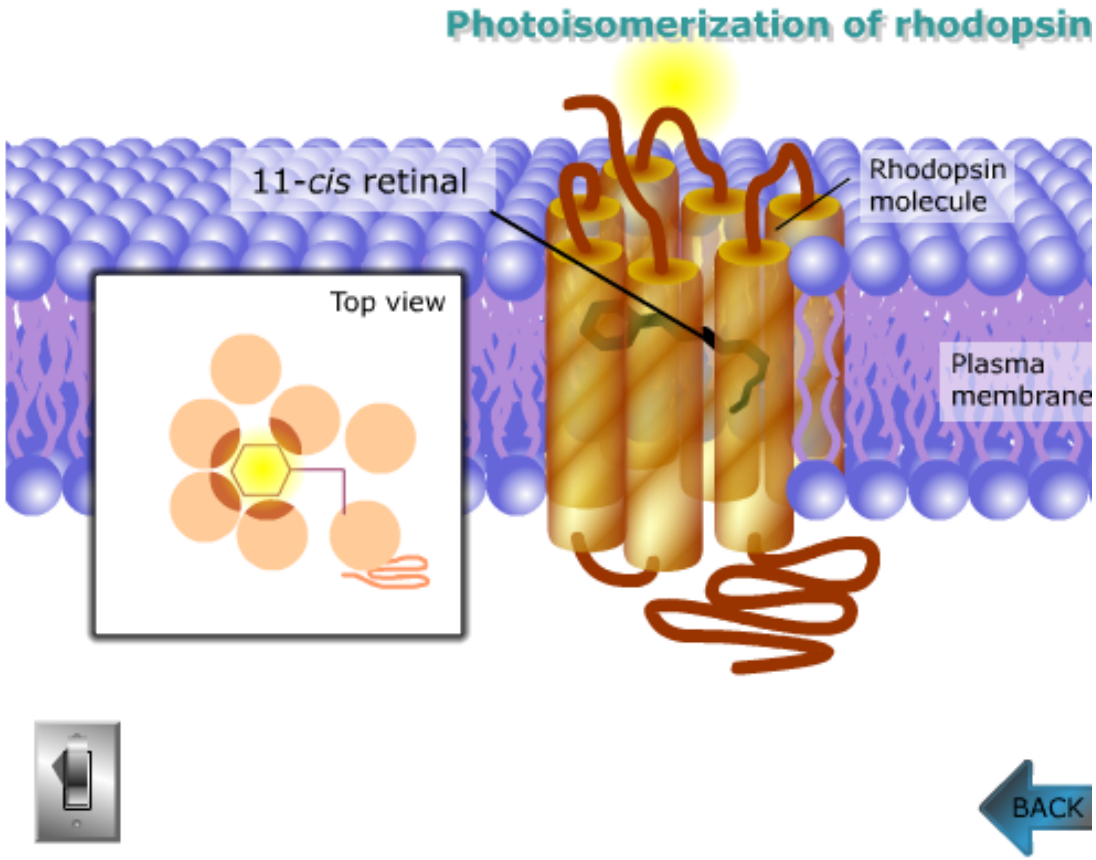

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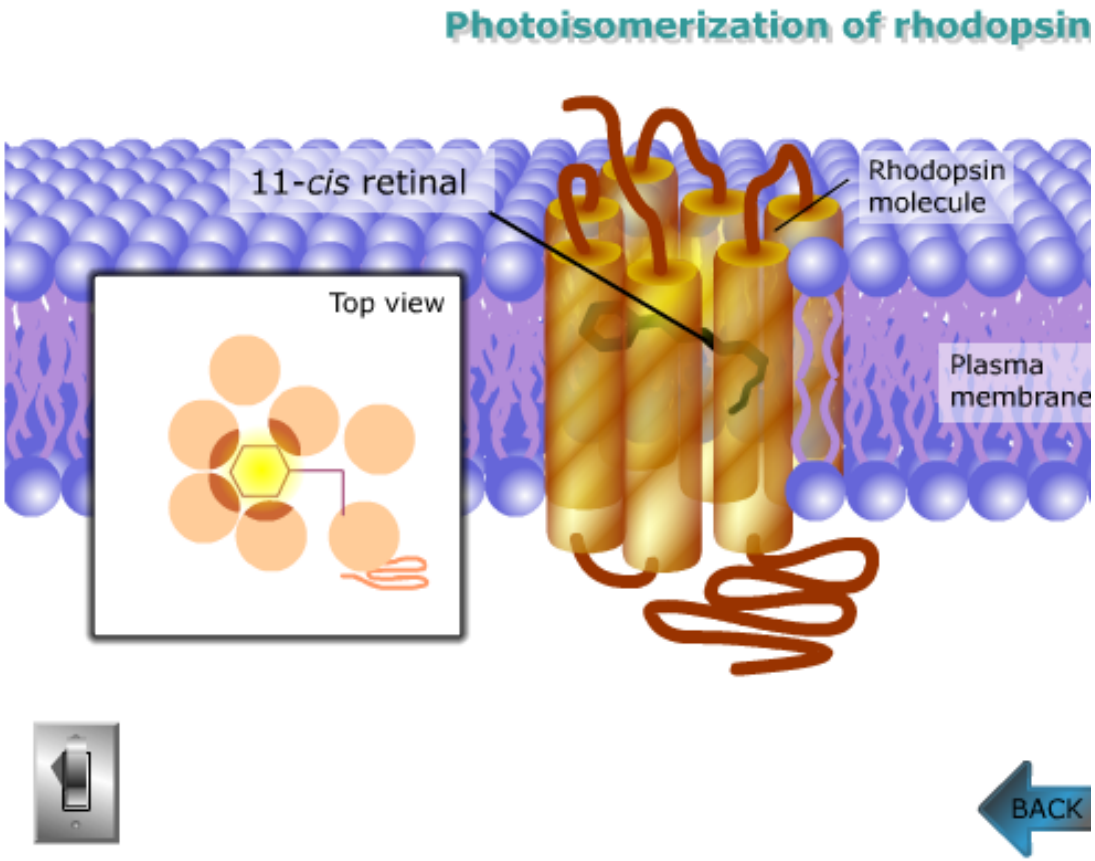

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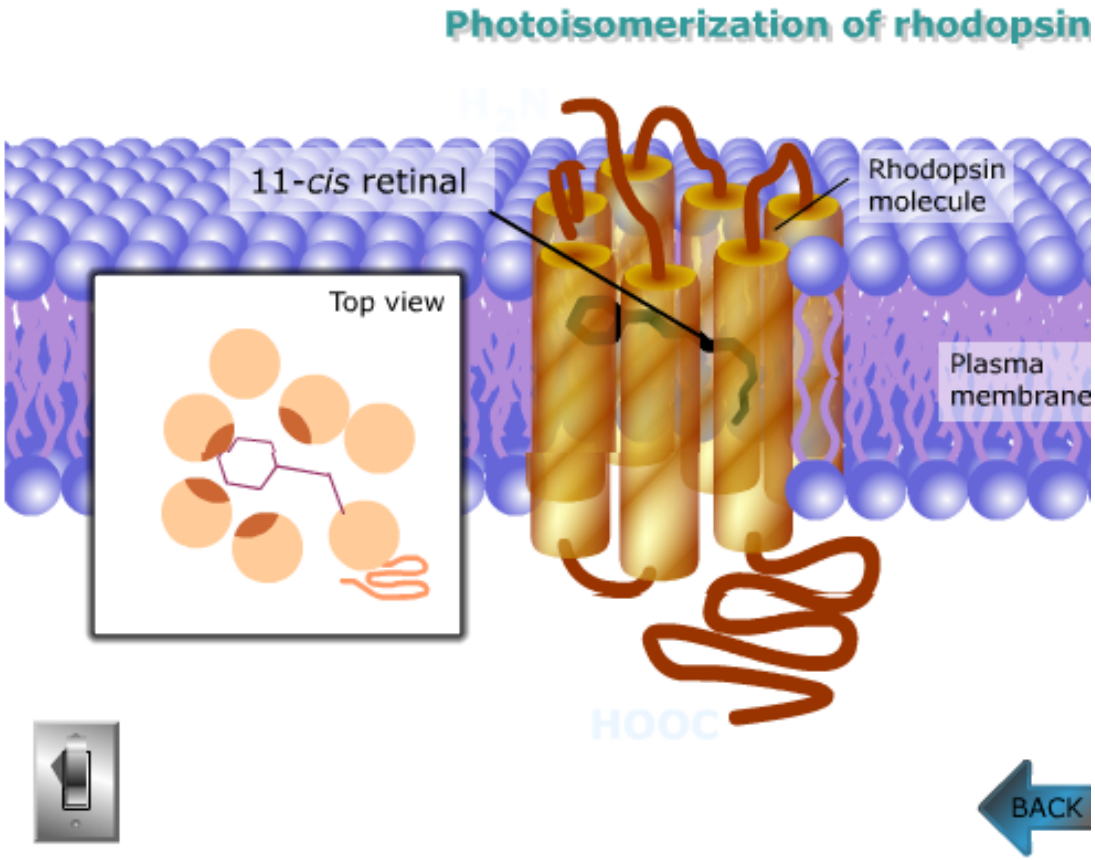

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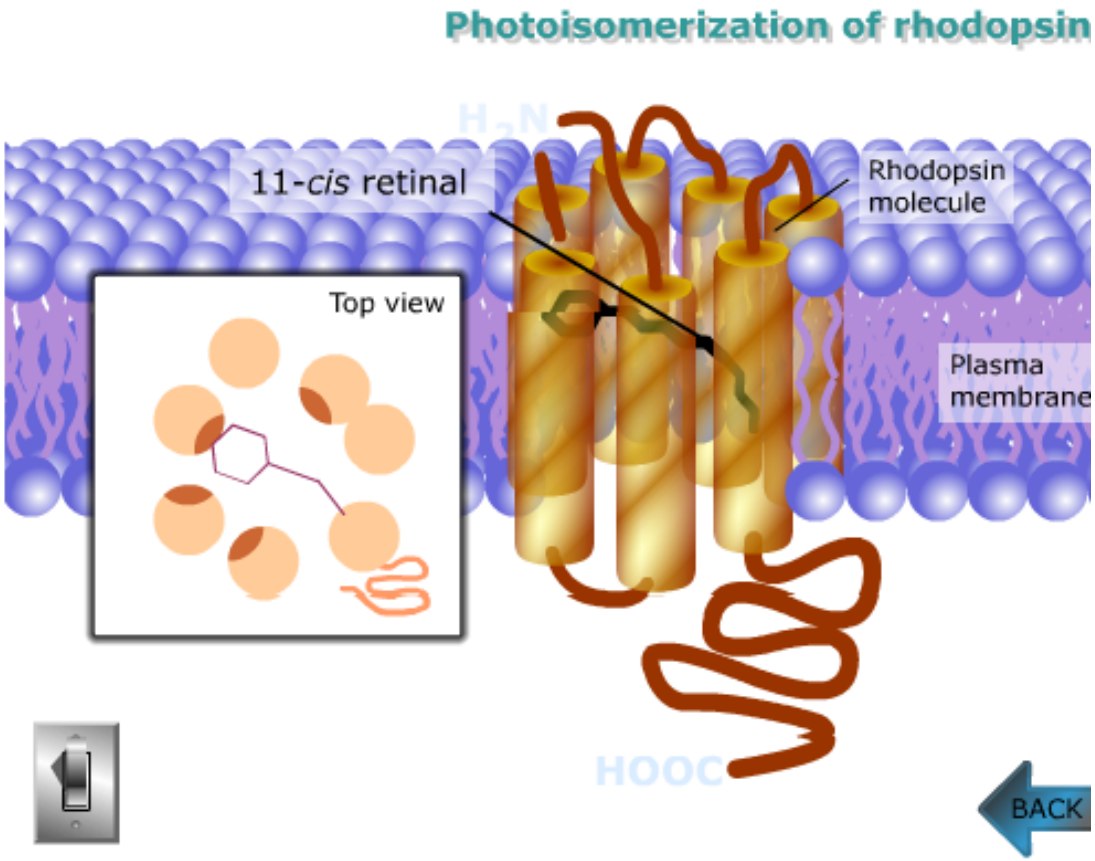

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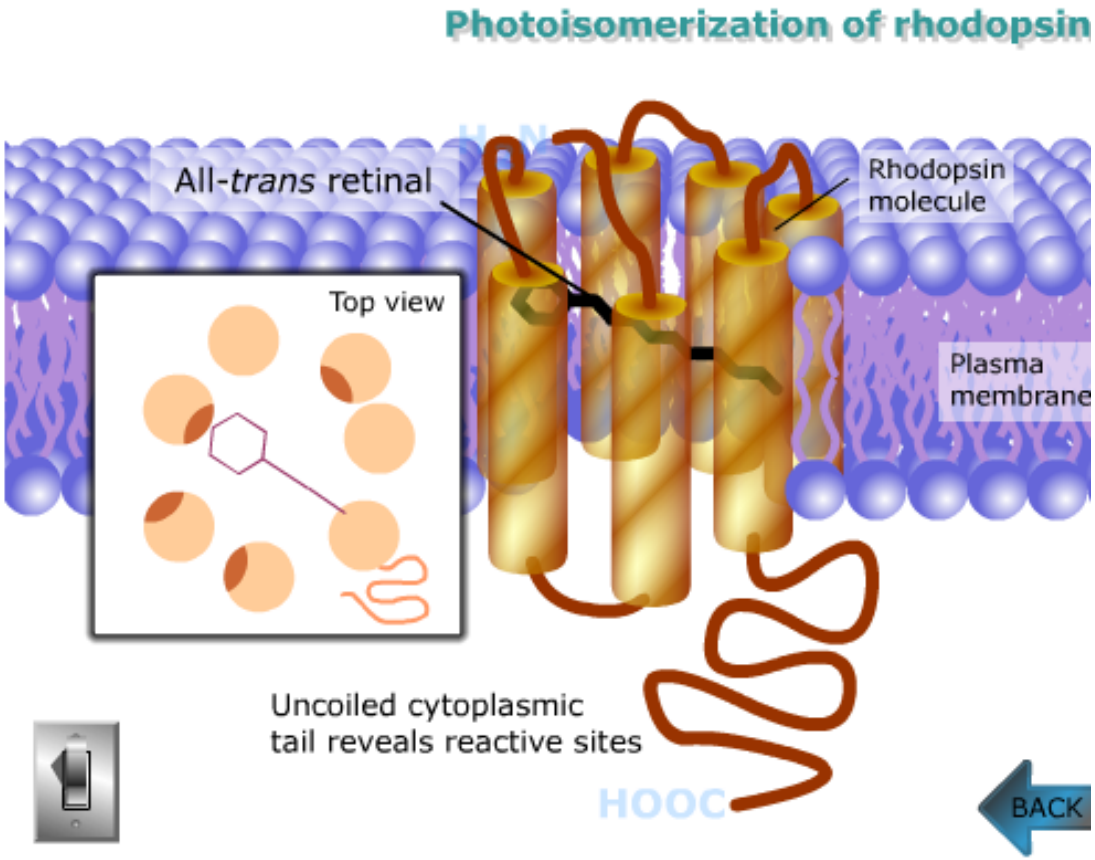

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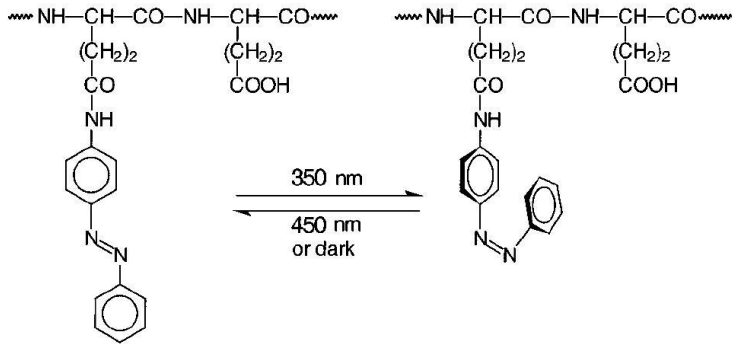
- Poly(L-glutamic acid) with AB side chains



- $n \longrightarrow \pi^\star$: 380–520 nm
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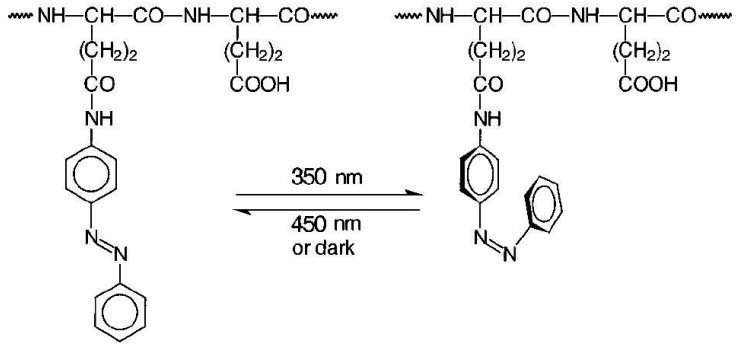

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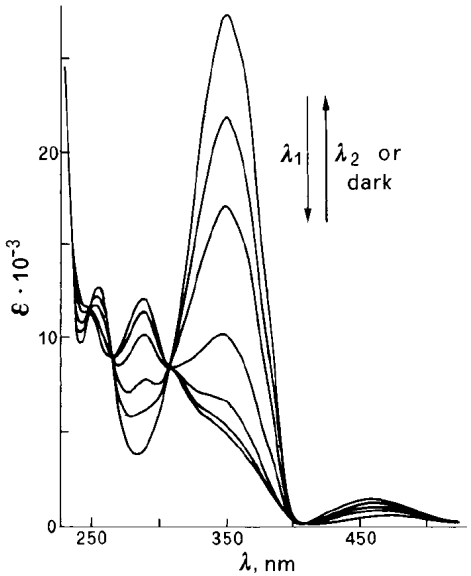
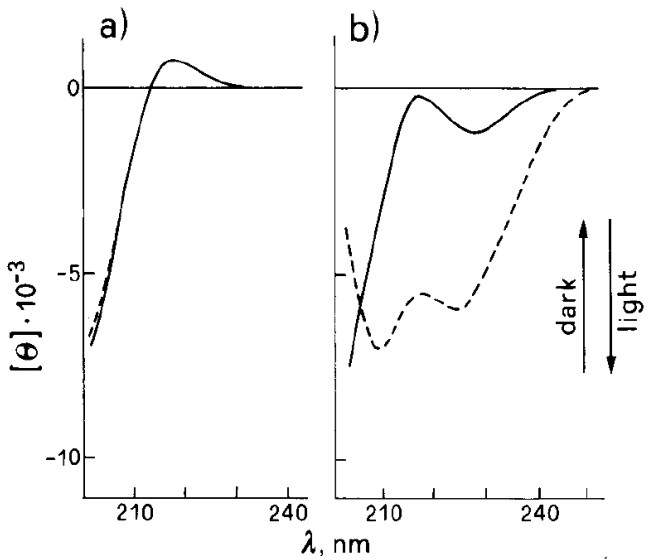
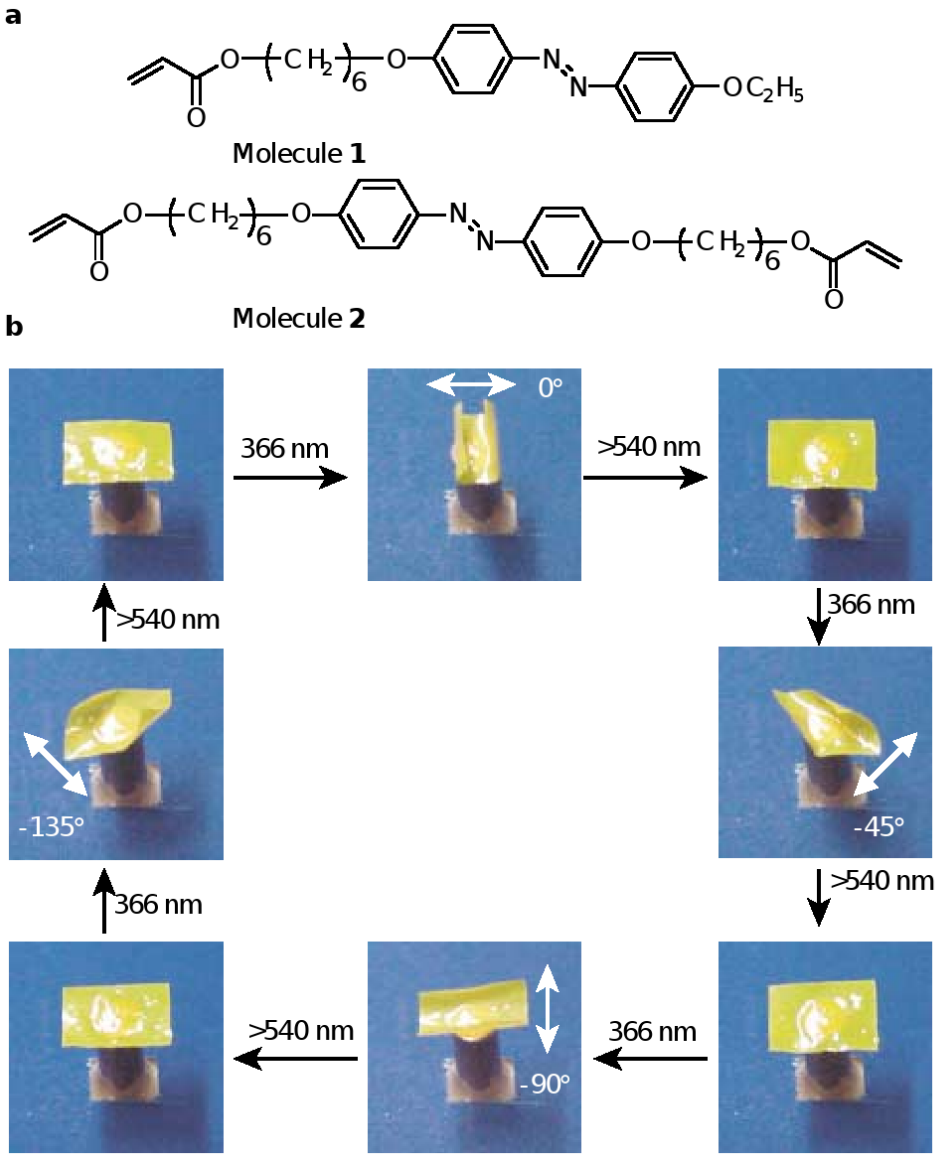
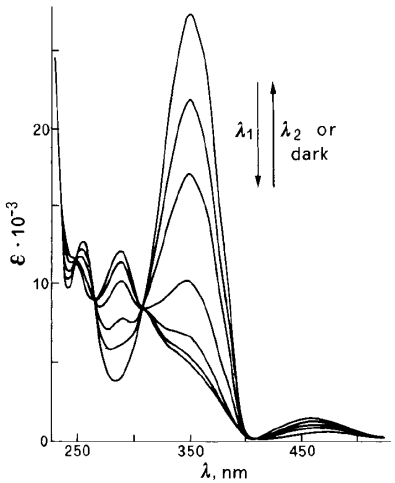




Yu, Y.; M. Makoto, M.; T. Ikeda, T. *Nature*, **2003**, *425*, 145.



UV/Vis spectra :TD-DFT calculation (GAUSSIAN 03[4])



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[4] Frisch et al. GAUSSIAN 03, Revision B.05, Gaussian Inc. Wallingford, CT (2004).
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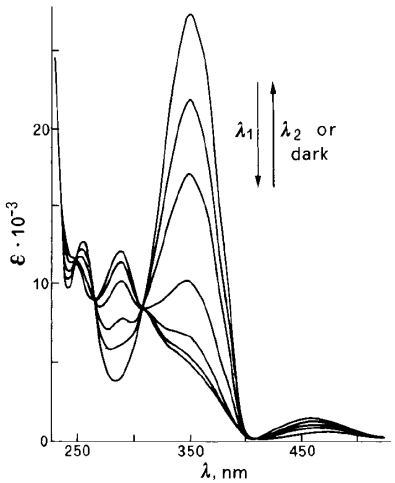

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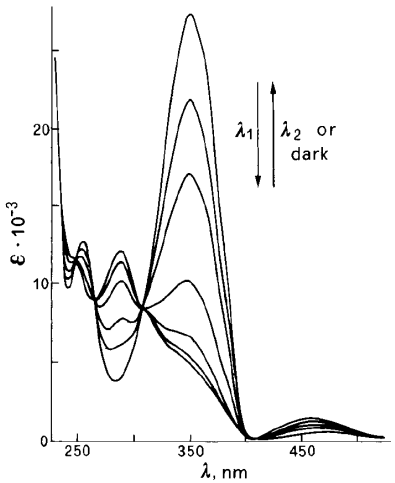

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- Force Field: Amber *ff99*
- Protonated form of GLU
- N and C-*terminus*: NME and ACE group

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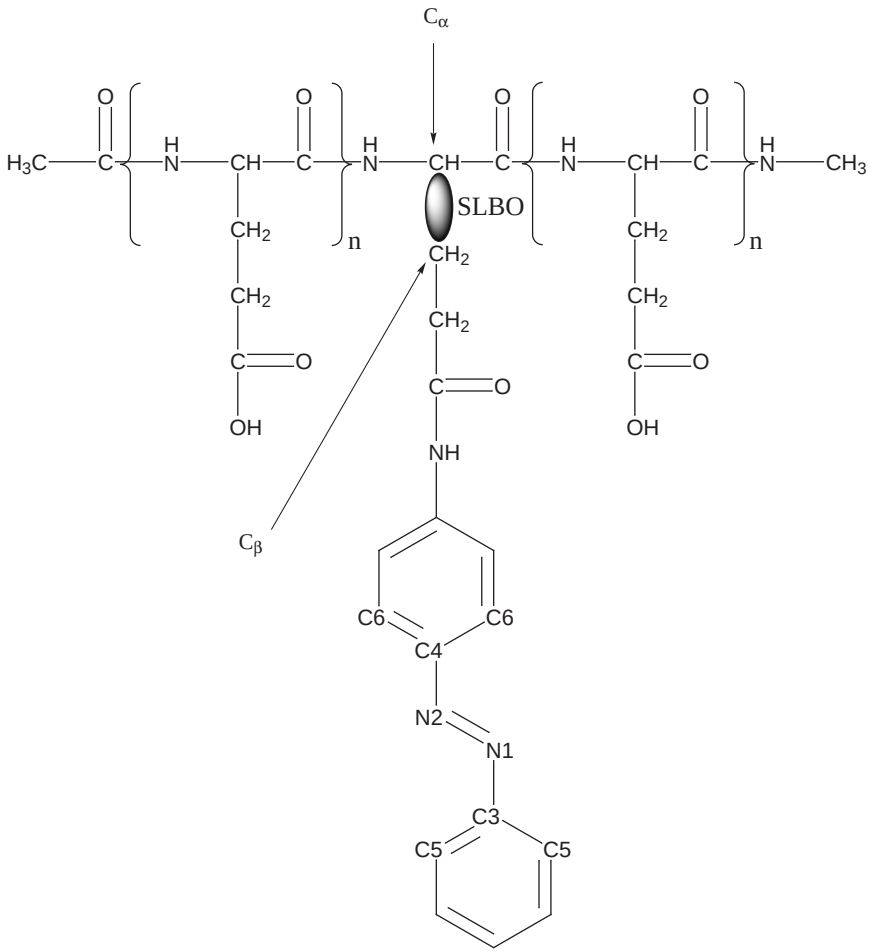
LSCF/MM calculation

- Local Self-Consistent Field[7,8]

QM/MM partition



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  - Constraint optimization of the WF:

$$\mathbf{F}\cdot\mathbf{C} = \underbrace{\mathbf{S}\cdot\mathbf{C}\cdot\mathbf{E}}_{\text{variational}} + \underbrace{\mathbf{S}\cdot\mathbf{L}\cdot\mathbf{\Lambda}}_{\text{frozen}}$$

  - QM/MM frontier $\Longleftrightarrow$ *Strictly Localized Bond Orbital* (SLBO)
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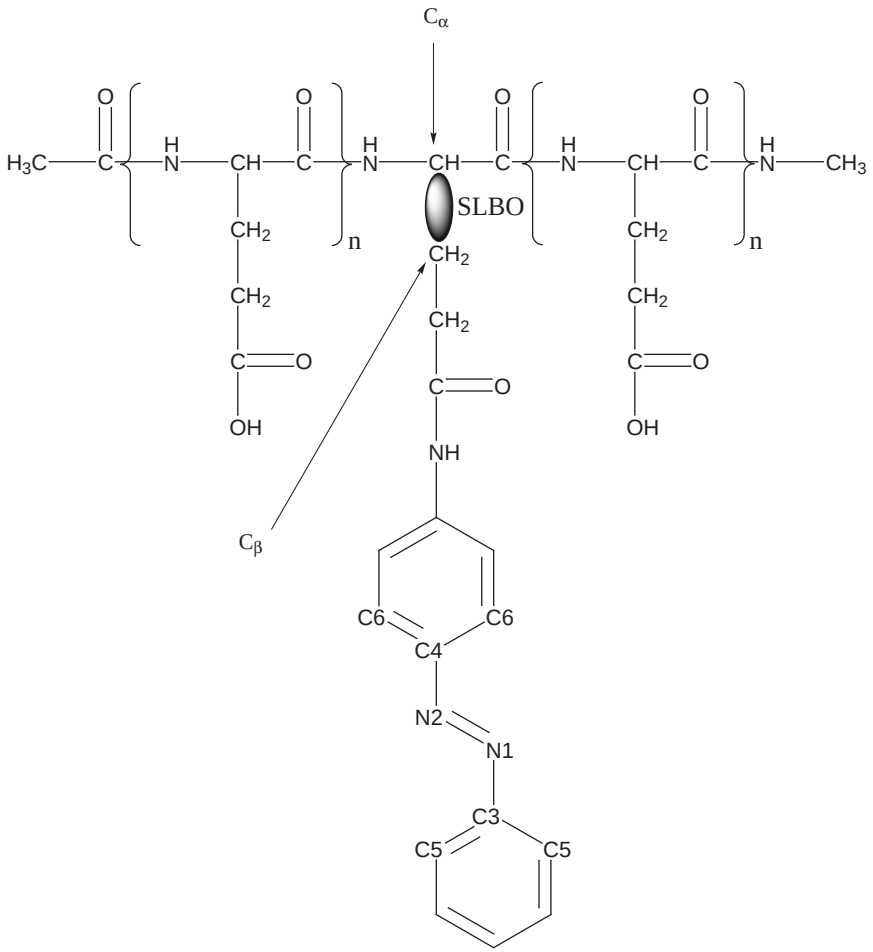

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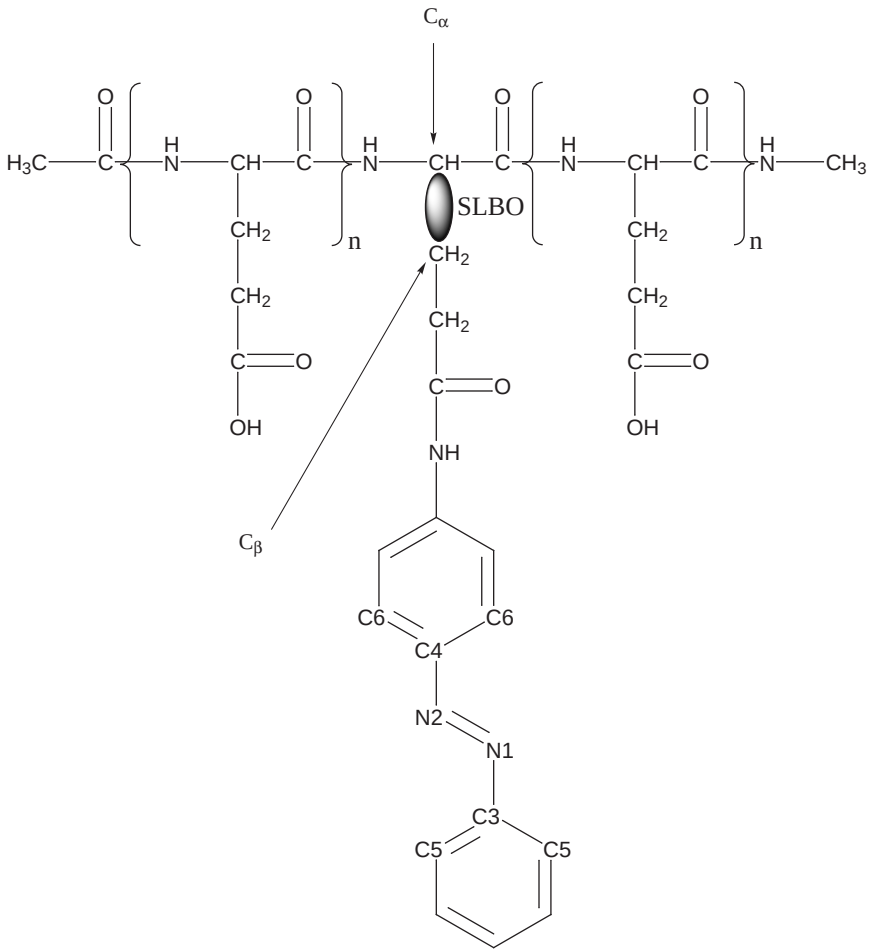

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UV/Vis spectra

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  - $n \longrightarrow \pi^\star$: $\simeq$ 40 nm red-shifted
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- TAB $\leftrightharpoons$ CAB
  - $n \longrightarrow \pi^\star$:
    - Gas-phase: -2 nm (Exp: -19 $\longrightarrow$ -15 nm)
    - Ethanol: -10 nm (Exp: -10 $\longrightarrow$ +6 nm)
  - $\pi \longrightarrow \pi^\star$:
    - Gas-phase: -35 nm (Exp: -38 $\longrightarrow$ -35 nm)
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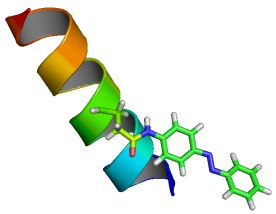
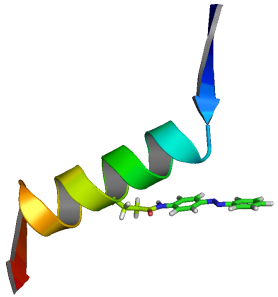
QM/MM geometries of the Poly(L-glutamic acid) with TAB side chain

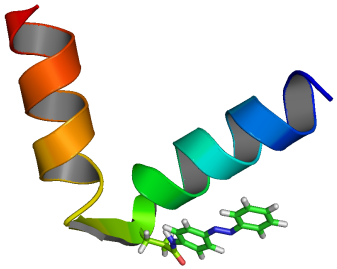
- α-containing structures



α-helix



β-α-β



α-β-α

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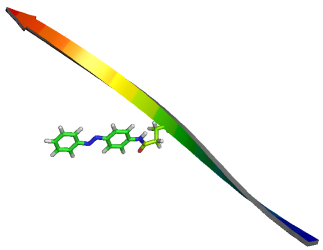
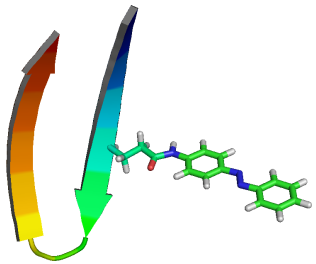
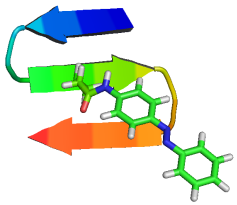


β-sheet

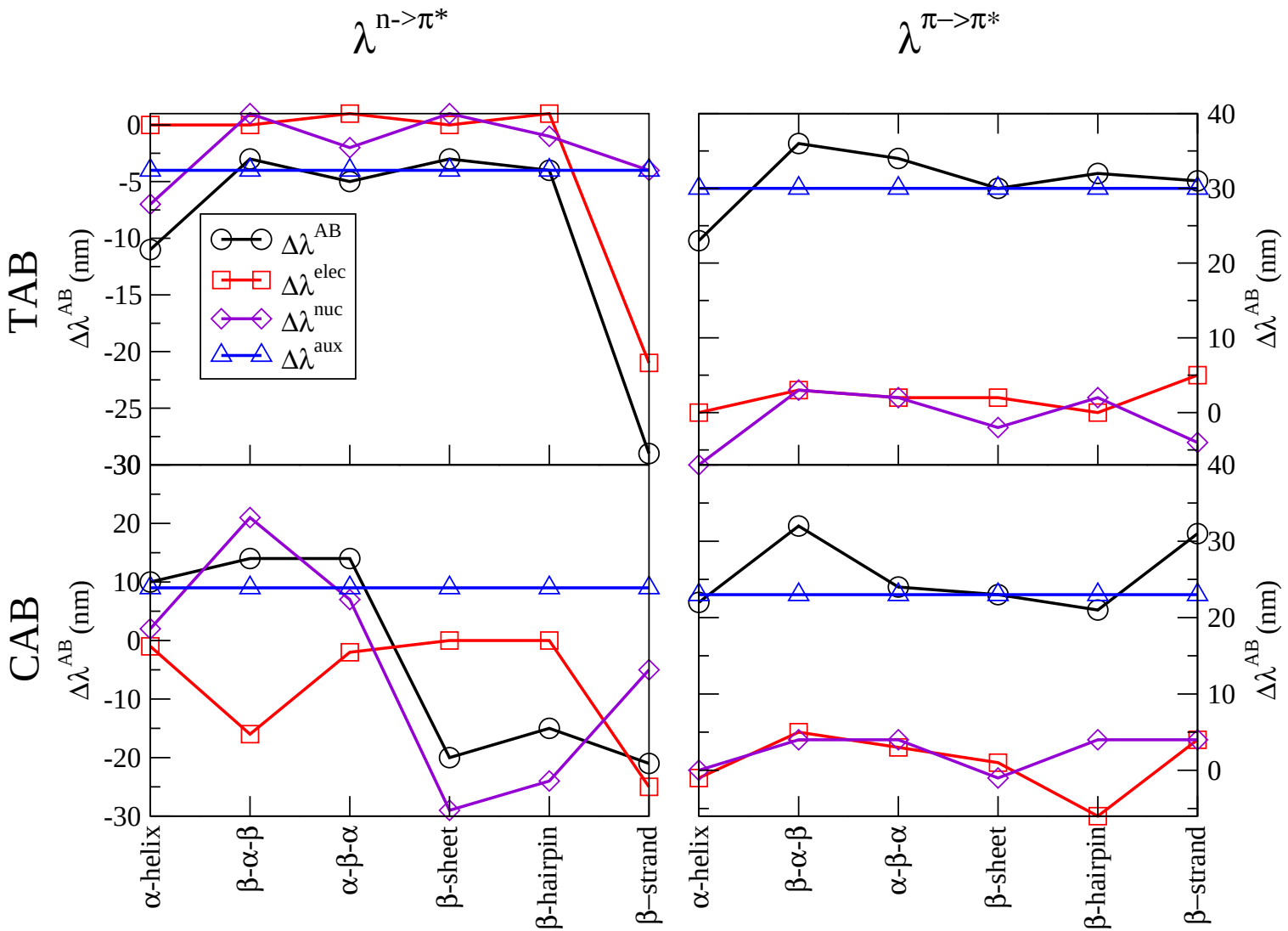


β-hairpin



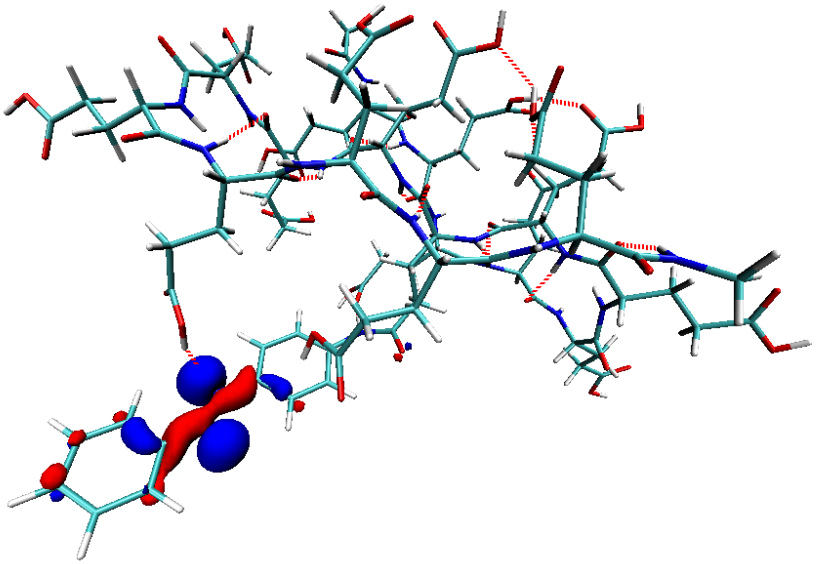
β-strand

$$\Delta\lambda^{\mathrm{AB}} = \Delta\lambda^{\mathrm{elec}} + \Delta\lambda^{\mathrm{nuc}} + \Delta\lambda^{\mathrm{aux}}$$

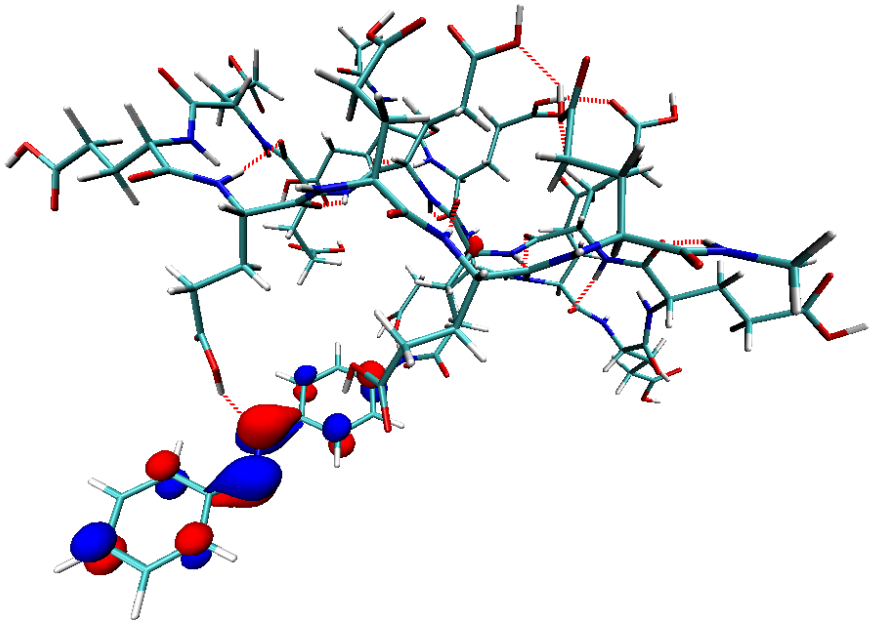


Frontier orbitals involved in the $n \longrightarrow \pi^\star$ transition

n non-bonding orbital



$\pi^\star$ anti-bonding orbital



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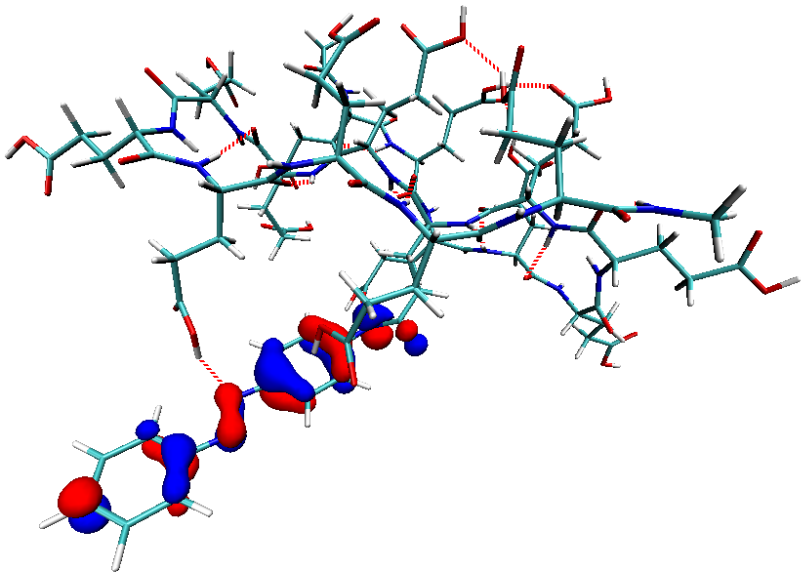

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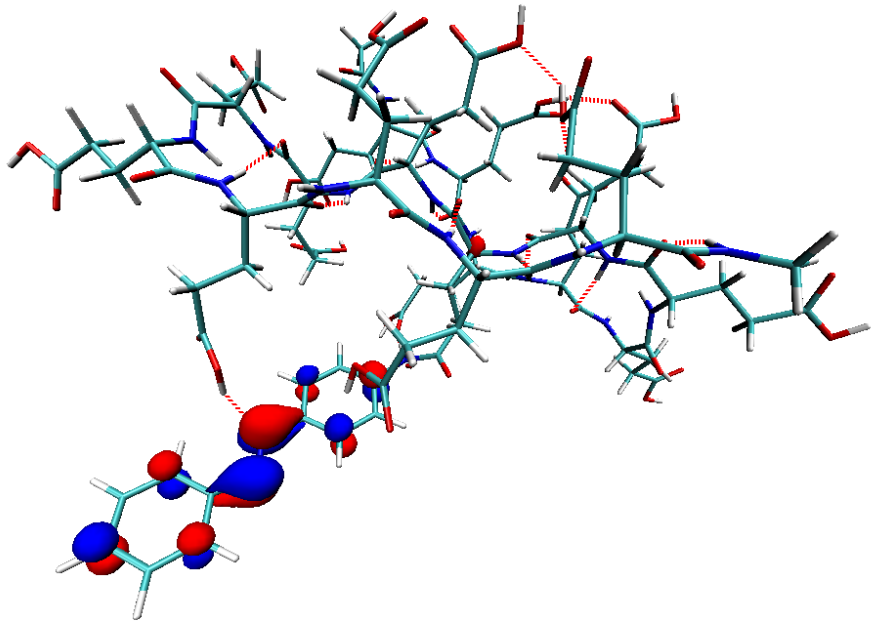

Conclusions

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Outlooks

- Adding some AB groups at the MM level
- Dynamical behaviour of the AB photoisomerization

Namur, Belgium

- Denis Jacquemin & Julien Preat

- Eric Perpète

PhD & Boss, Nancy

- Yohann Moreau & Nicolas Ferré

- Xavier Assfeld