Exploring the Photophysical Properties and Self-Assembly of a Spiropyran/Merocyanine Amphiphile in Different Solvents

V. Savchenko, O. Guskova

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Outline

- **Introduction**
- Spiropyrans – another example of photoresponsive molecules and molecular switches. SP and MC isomers
- Photoresponsive amphiphiles. What we think we know, how do they work?

- **Research questions**

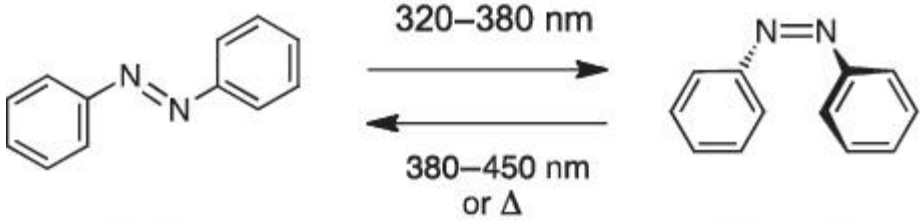
- **Details of experiments and simulations (will be provided on each slide)**

- **Results**
- Comparison and explanation of the experimental results
- What is the most stable isomer in water SP or MC? Why?
- Which micellar shape is the most probable for the amphiphile in water?
- Thermodynamics of solvation
- Bonus: Assemblies in water. What to expect if solution concentration goes above CMC?

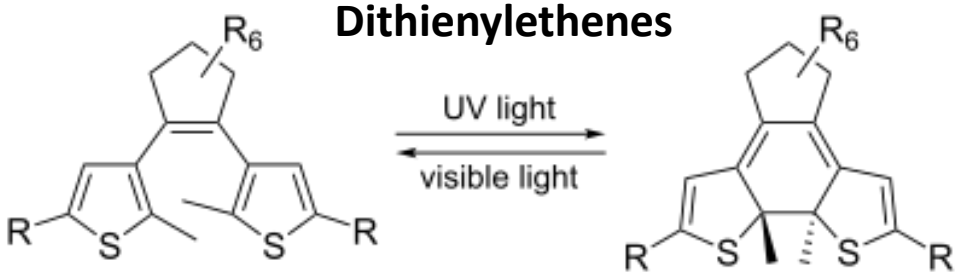
- **Conclusions**

Spiropyrans – another example of molecular switches

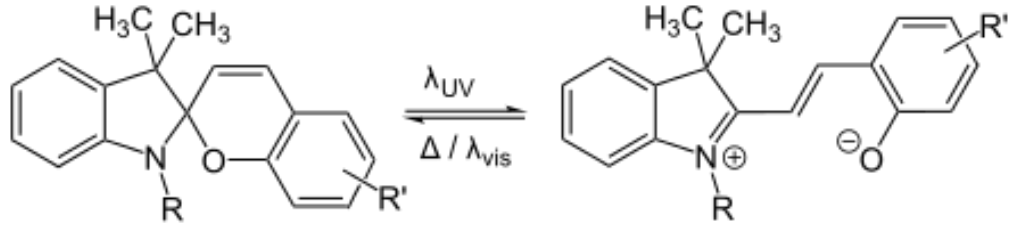
Azobenzene



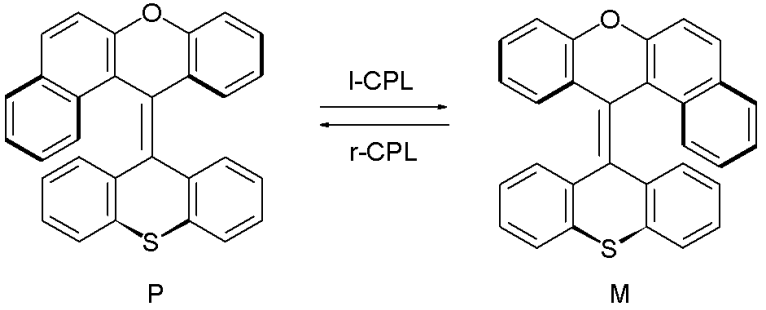
Dithienylethenes



Spiropyrans

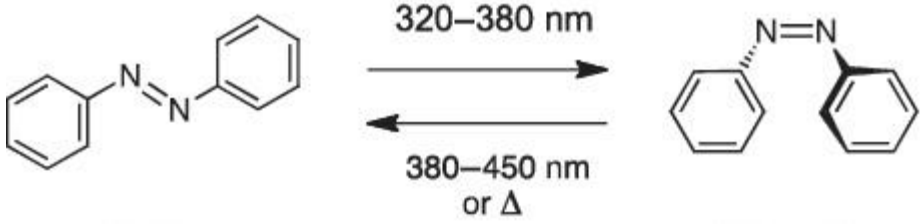


Chiroptical molecular switches



Spiropyrans – another example of molecular switches

Azobenzene



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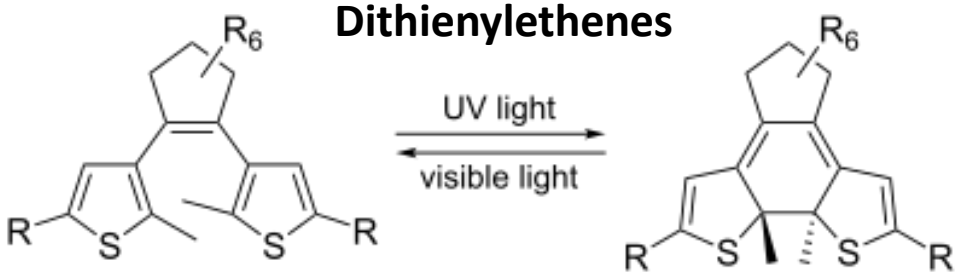
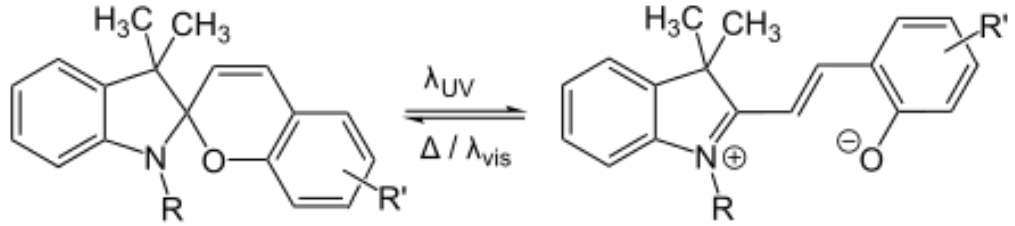
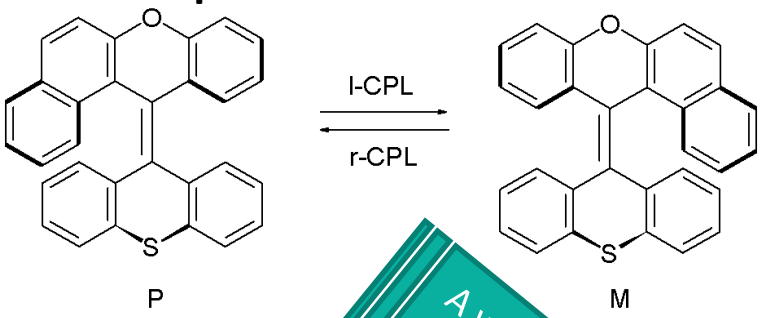


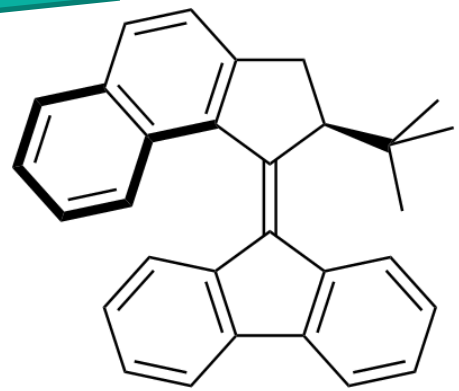
Spiropyrans



Chiroptical molecular switches



A way to molecular motors



Spiropyran (SP) and merocyanine (MC) isomers

SP

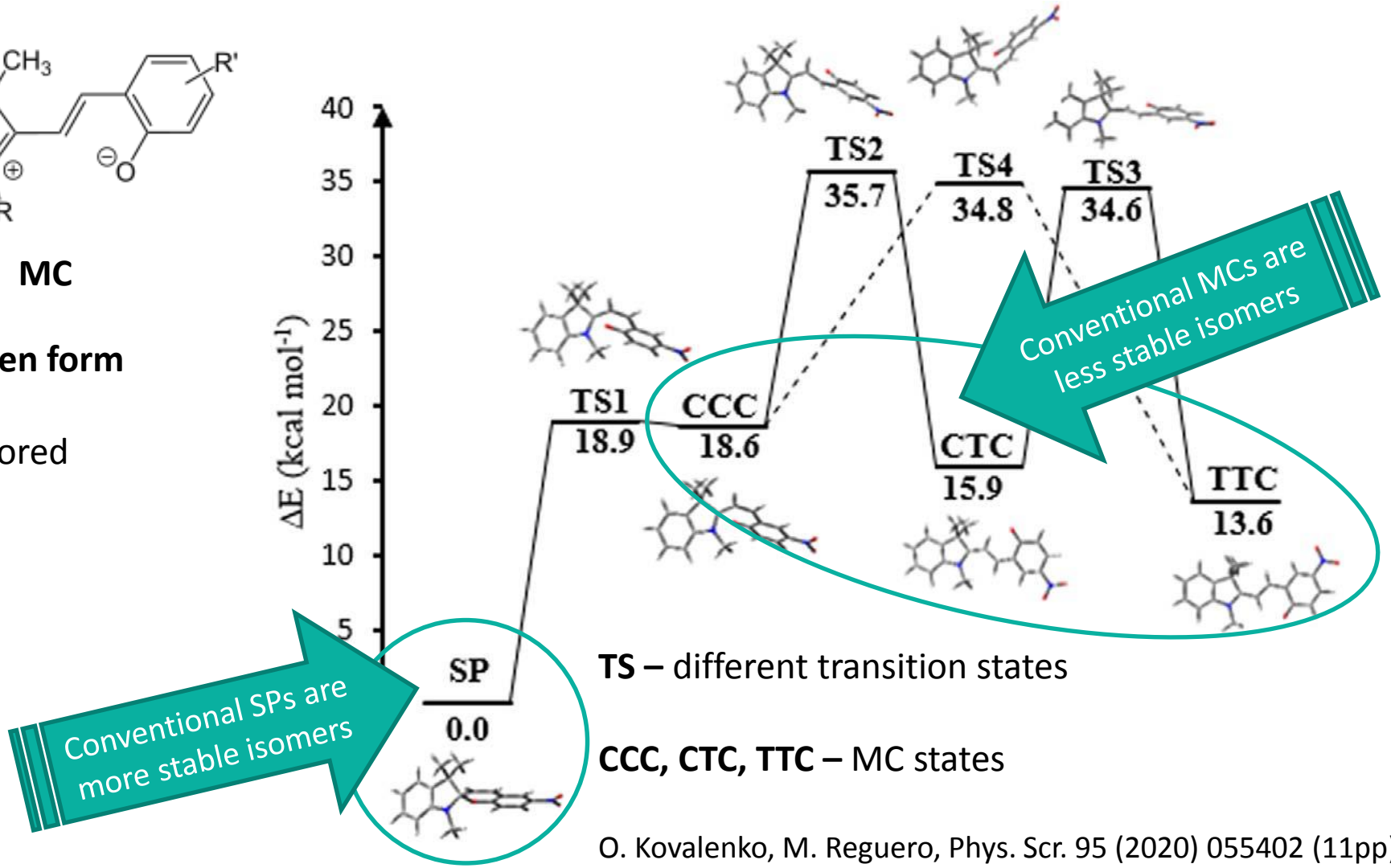
Closed form

colorless

MC

Open form

colored

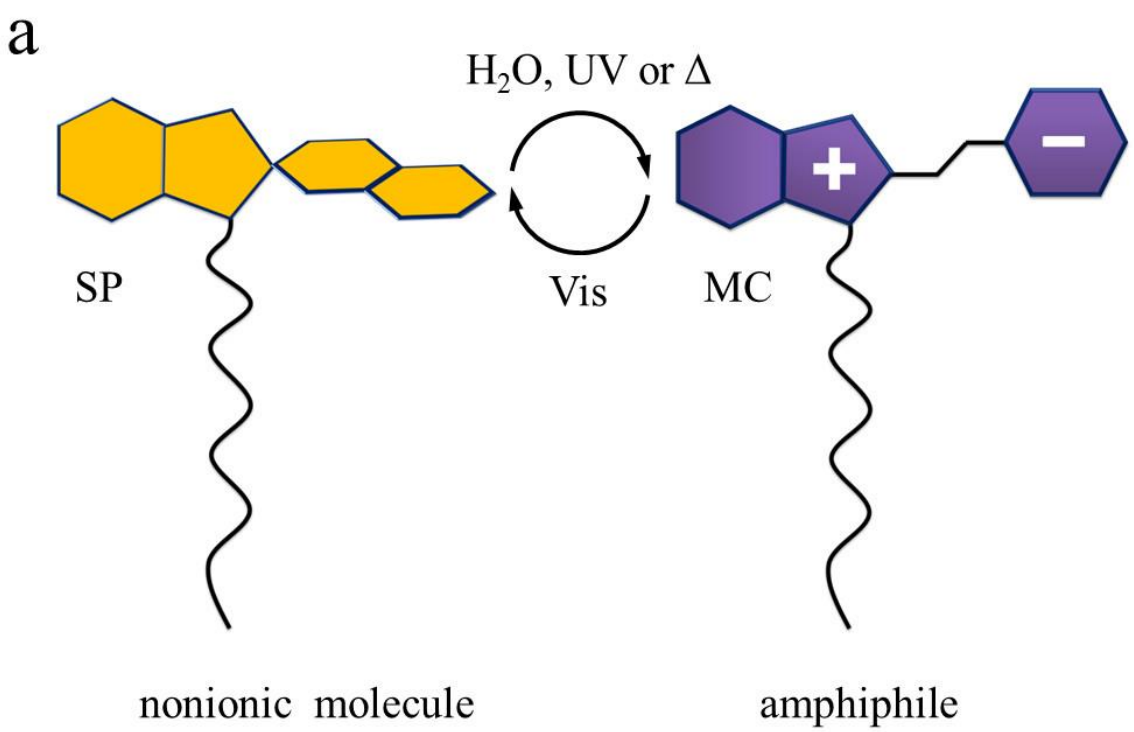


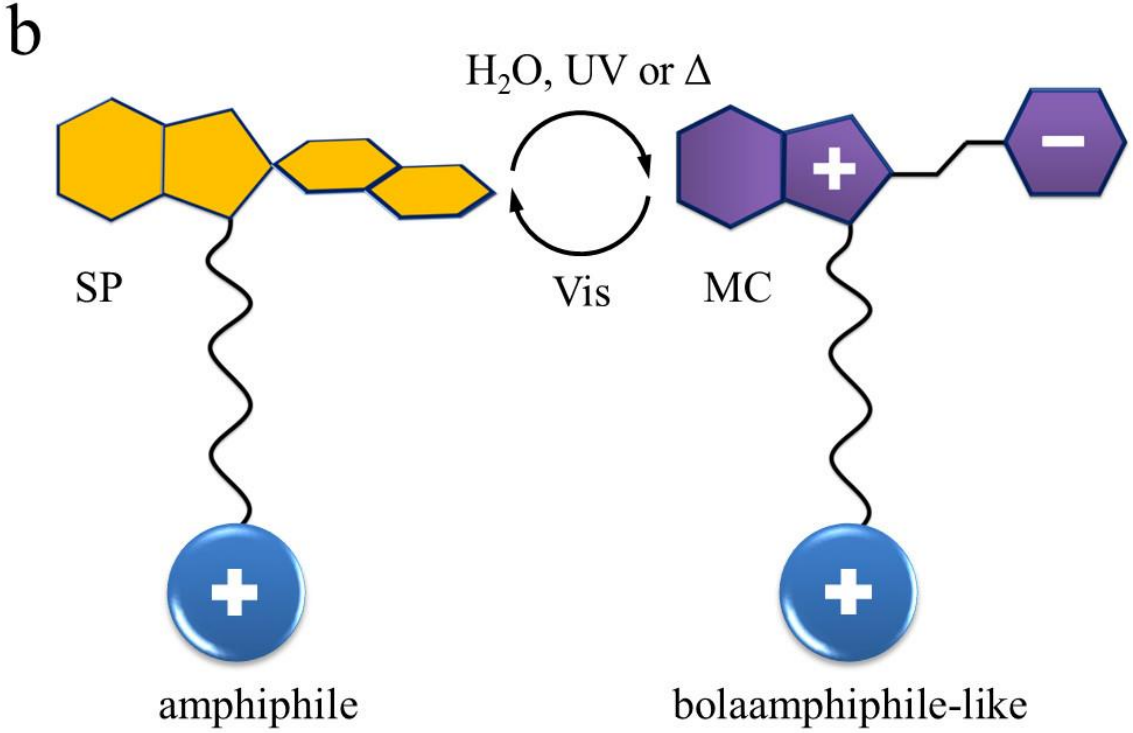
TS – different transition states

CCC, CTC, TTC – MC states

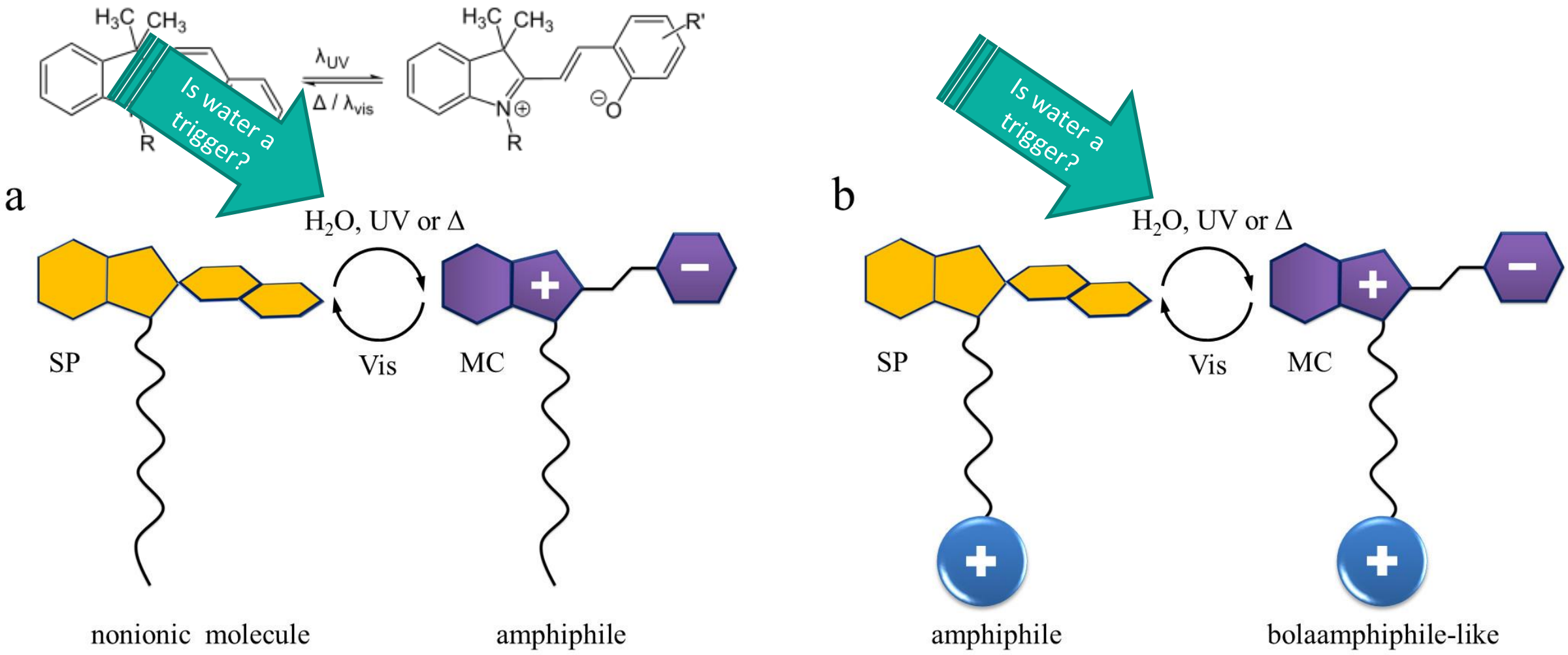
O. Kovalenko, M. Reguero, Phys. Scr. 95 (2020) 055402 (11pp)

How to make SP amphiphilic? Some thoughts about structures





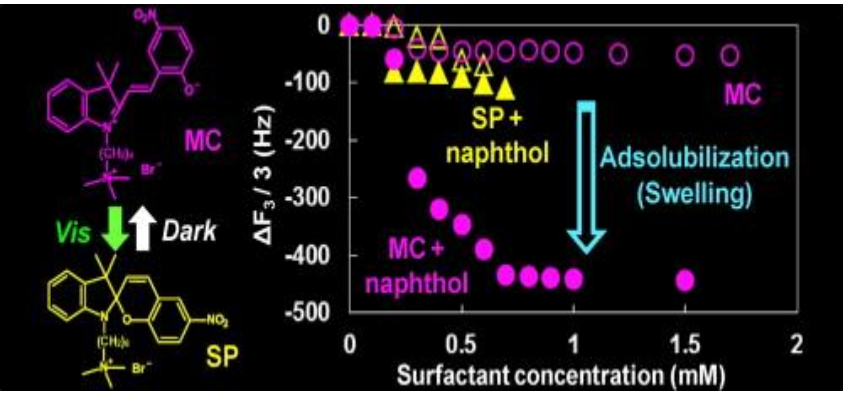
How to make SP amphiphilic? Some thoughts about structures



SP amphiphiles that have found their applications

for a controllable change of the physicochemical properties of the micellar solutions, e.g. adsolubilization

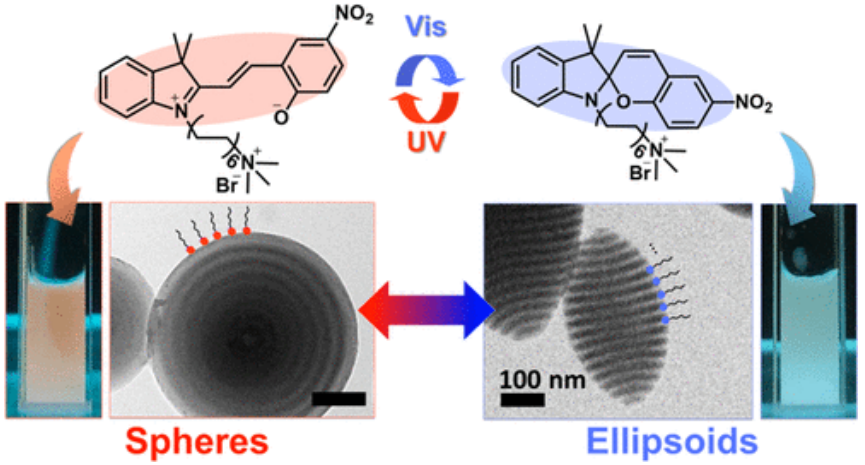
(long alkyl chain between the head and SP C12)



Sakai et al. *Colloids Surf. A* 2012, 410, 119

for the construction of the reversible shape and color-changing block copolymer particles

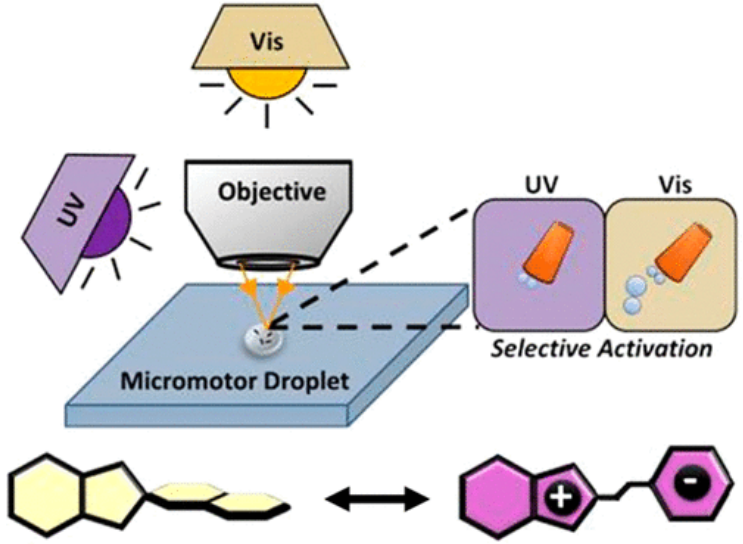
(long alkyl chain between the head and SP C12)



Kim et al. *J. Am. Chem. Soc.* 2021, 143, 33, 13333

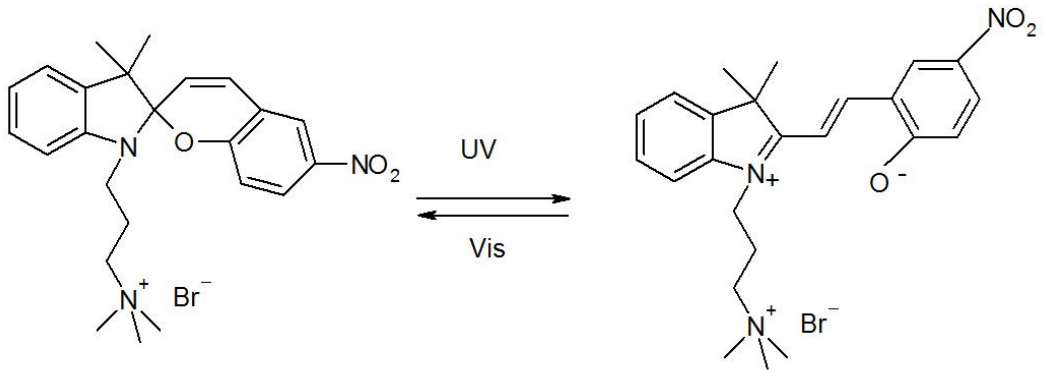
for the spatiotemporal control of bubble-propelled micromotors

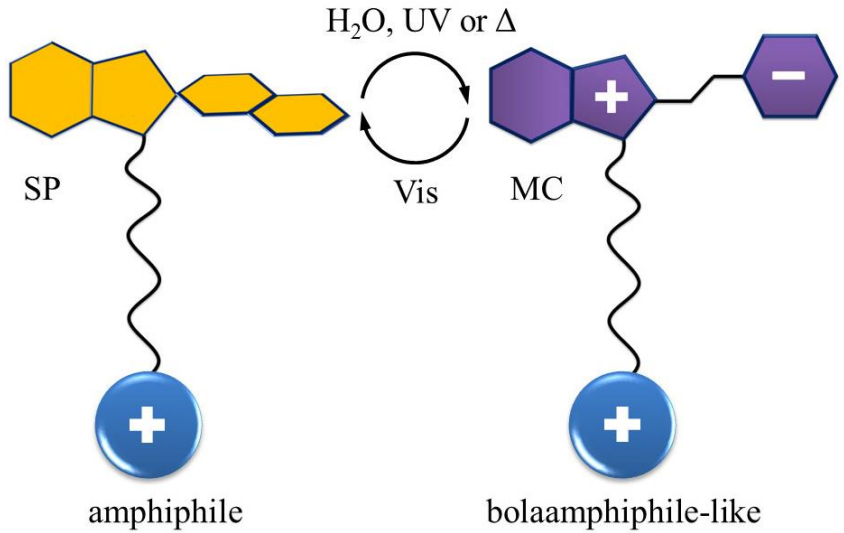
(SP is a head of the surfactant, C1, C8 and C18 are studied)



Moo et al. *ACS Nano* 2016, 10, 3, 3543

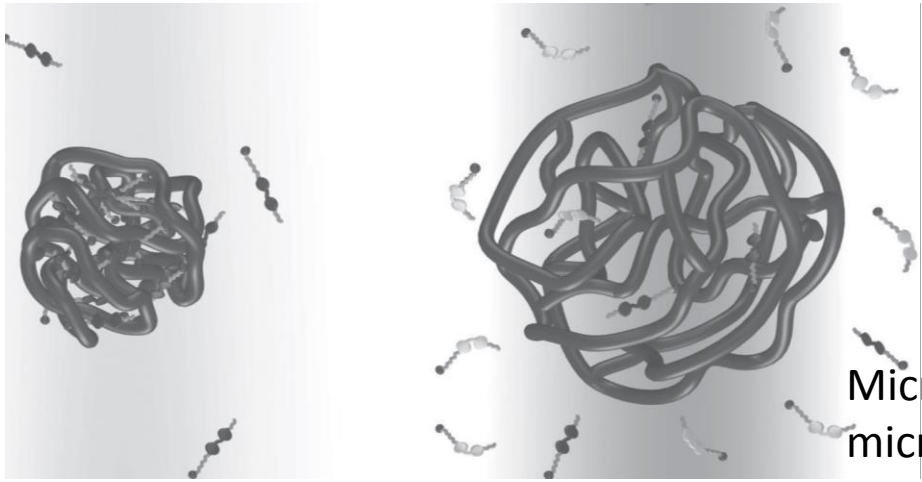
Object of the study: why do we need it?





Properties:

- positively charged head (microgel's compatible)
- the shortest C3 (propyl) chain between the head and the SP part
- the counterion is Br^{-1}
- is soluble in water, acetonitrile, chloroform, DMSO, ethanol
- optical properties are measured for the solution concentration below CMC



Microgel's particle = micropump

Zakrevskyy et al. *Adv. Funct. Mater*. 2012, 22, 23, 5000

The SPs showed negligible toxic effects on the cells up to millimolar concentrations. Fagan et al. *Front. Chem*. 2021, 9, 720087

Research questions

- can we reproduce/prove/explain in the simulations **MC isomer is appearing in water upon SP dissolution**?

- which self-assembling morphologies can be predicted for this amphiphile?

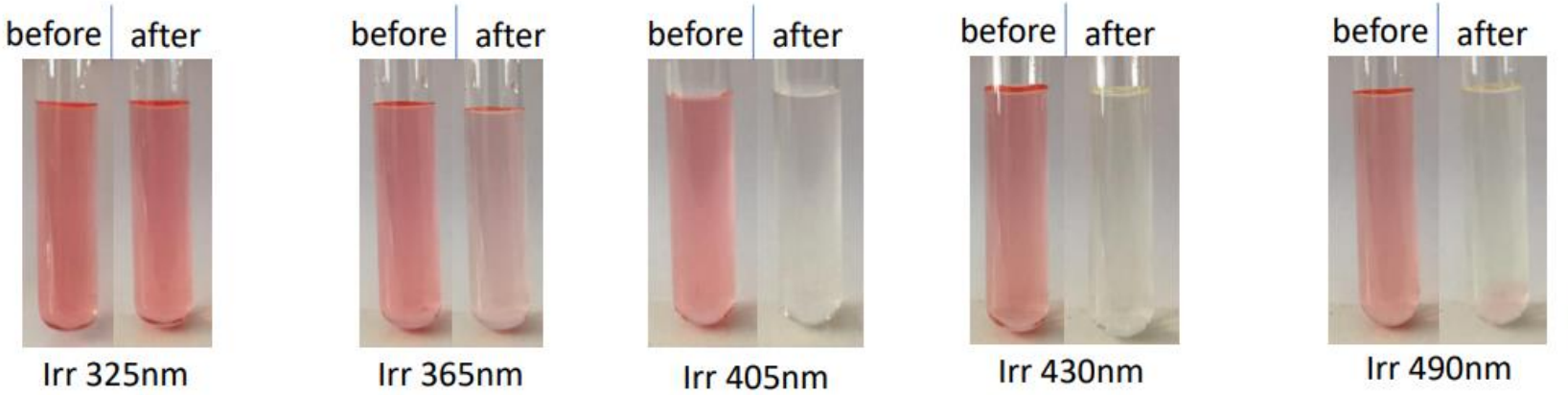
- what is the behavior of SP/MC in other solvents?

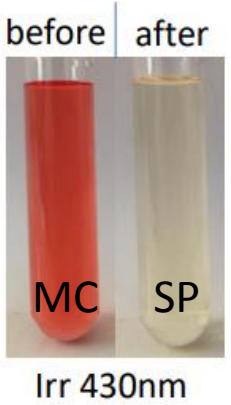
- what happens in aqueous solution at a concentration above CMC?

Experimental results. Aqueous systems

0,1mM Spiropyran water solution

fresh prepared → irradiated with different wavelength 5min





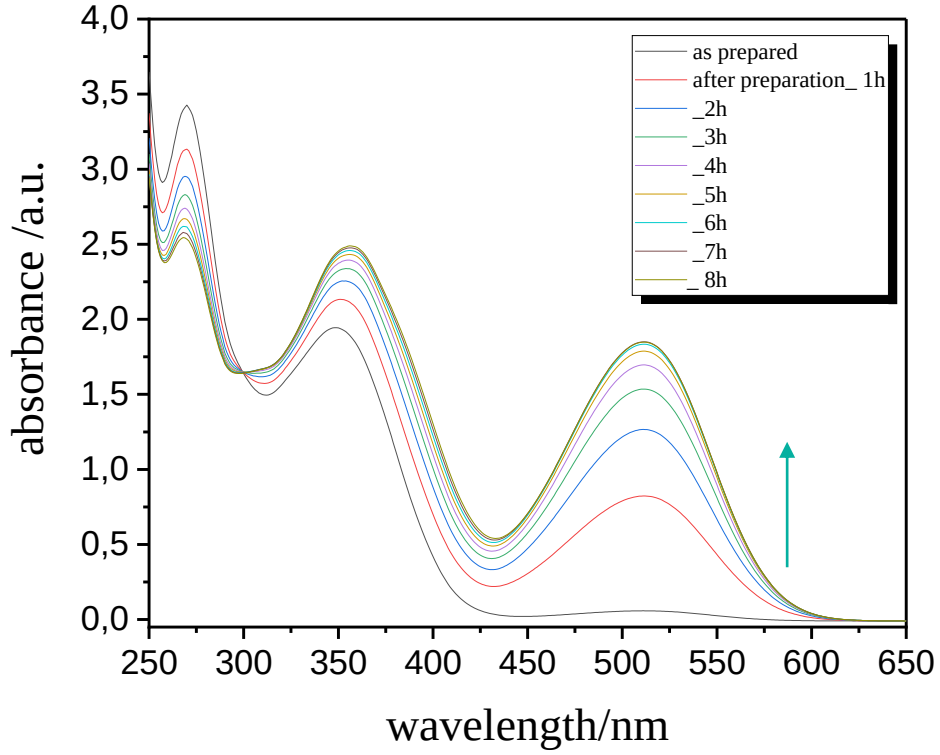
24h relaxed in yellow light lab

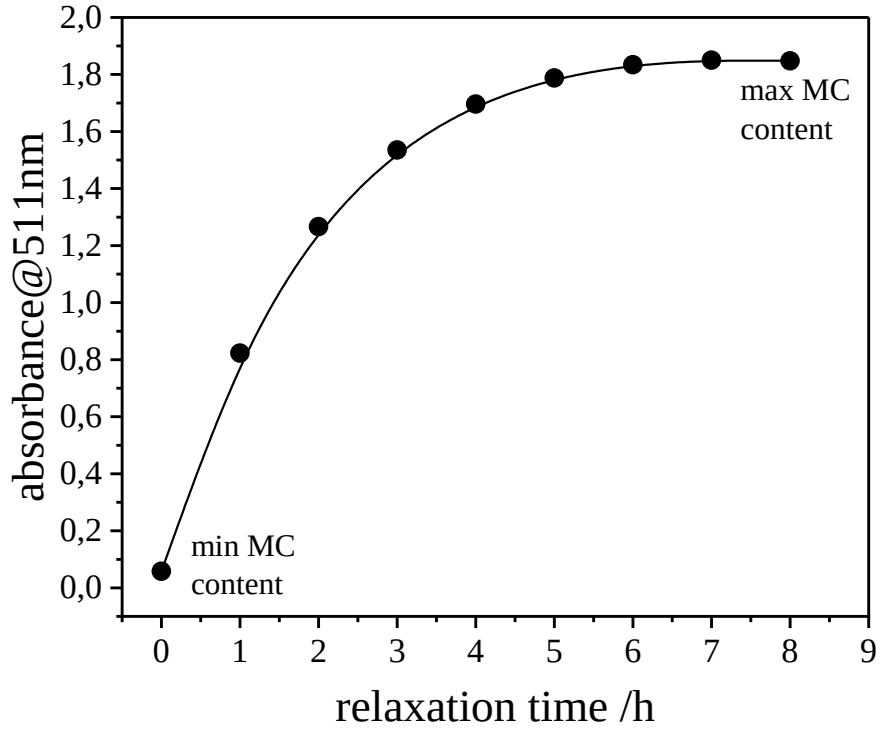
More yellow because of starting colour i.e. more MC content

MC: colored
SP: colorless

Experimental results. Aqueous systems

Relaxation in dark

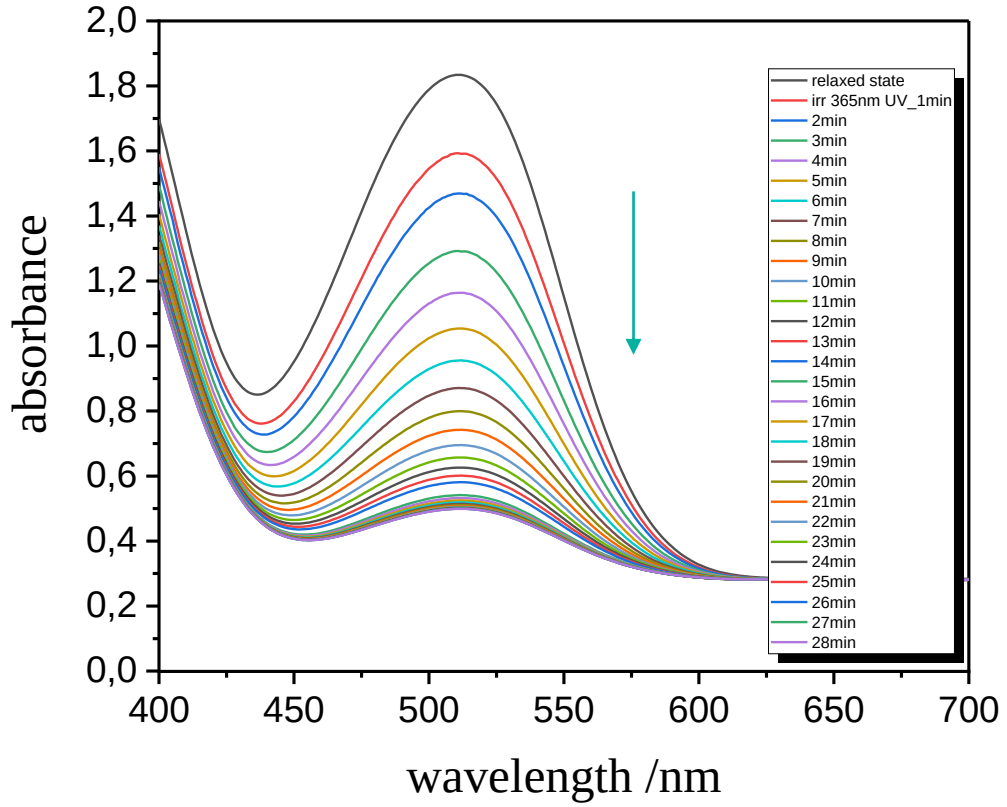


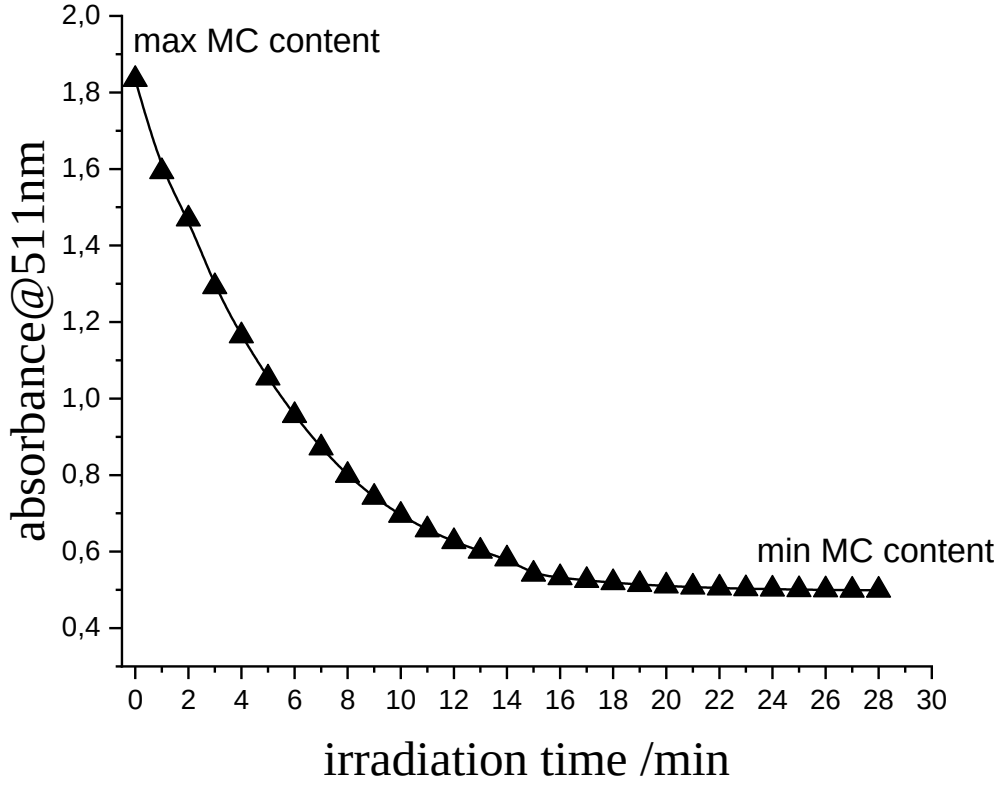


Sample dissolved in water and placed directly in the spectrometer

Experimental results. Aqueous systems

dark relaxed state to UV irradiated photostationary state

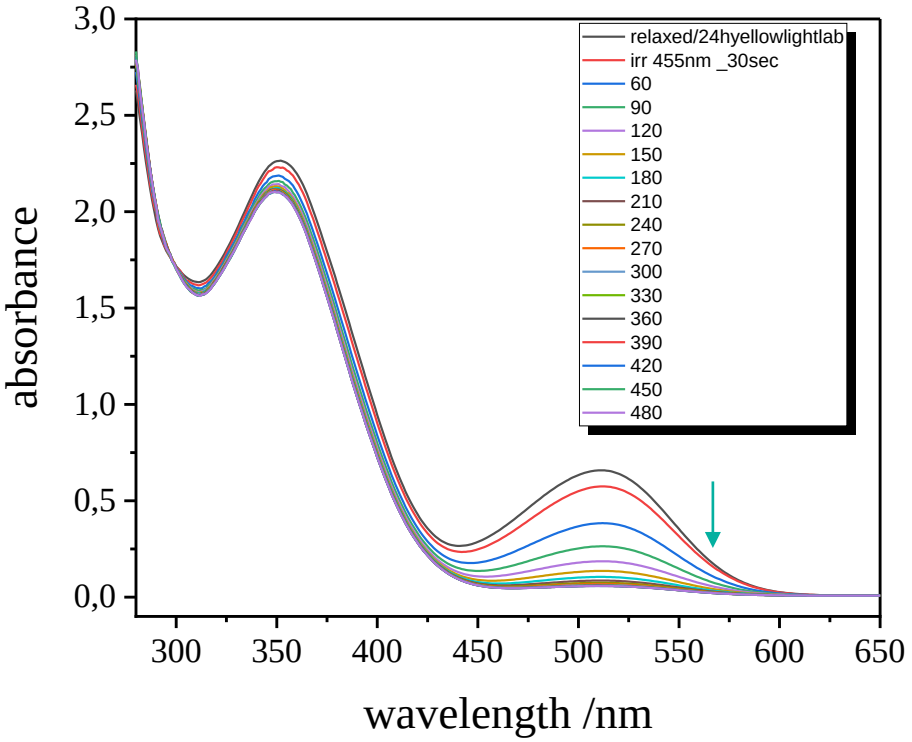


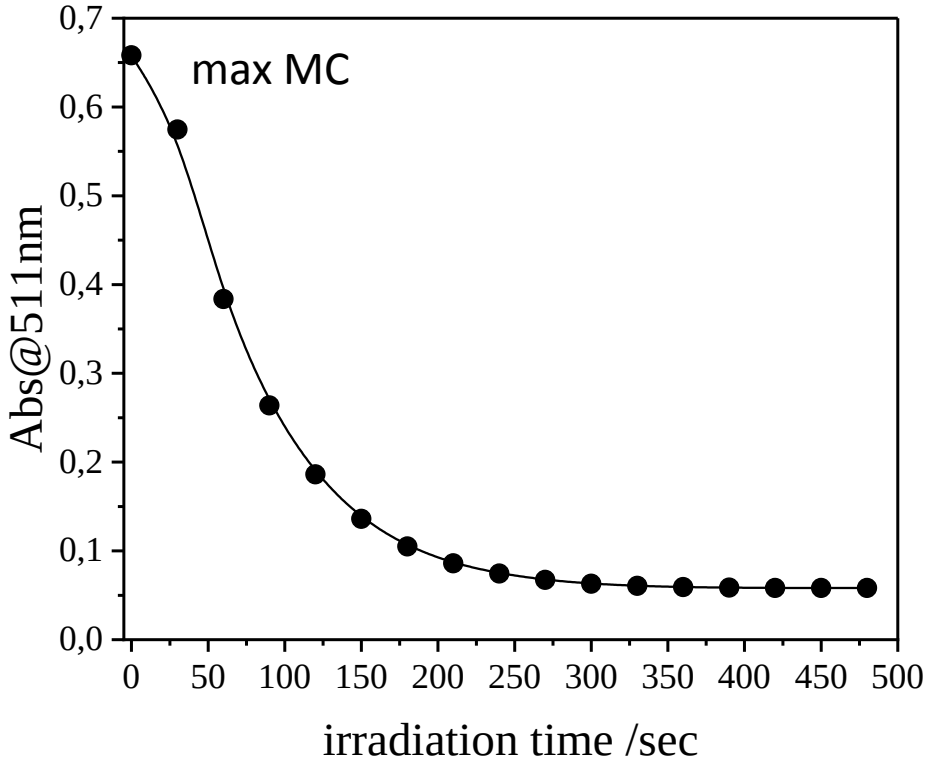


without taking out from spectrometer

Experimental results. Aqueous systems

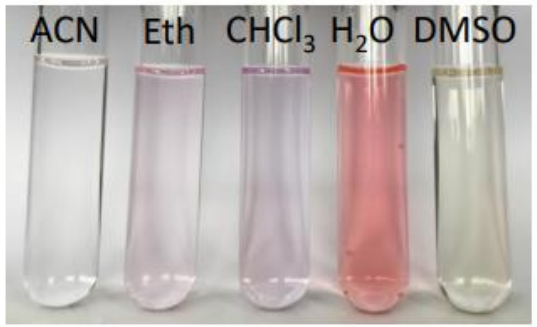
Relaxed state (24h yellow light lab) to blue (455nm) irradiated photostationary state, I=2mW/cm^2





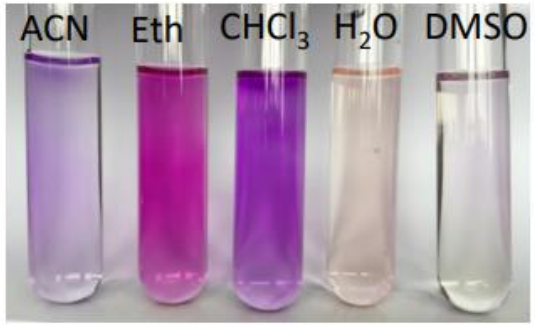
Experimental results. Organic solvents

0,1mM Spiropyran in different solvents



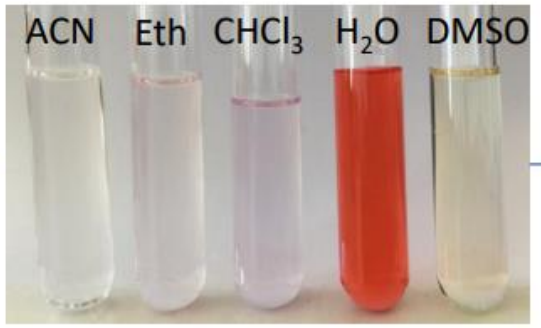
5min after preparation

Irr 365nm



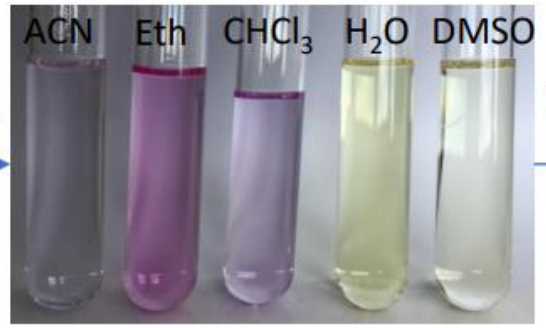
Photostationary state

48h in yellow light lab



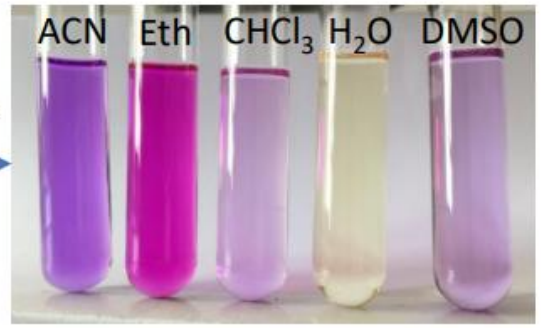
Relaxed state

Exposed to sunlight 1h



1h sunlight

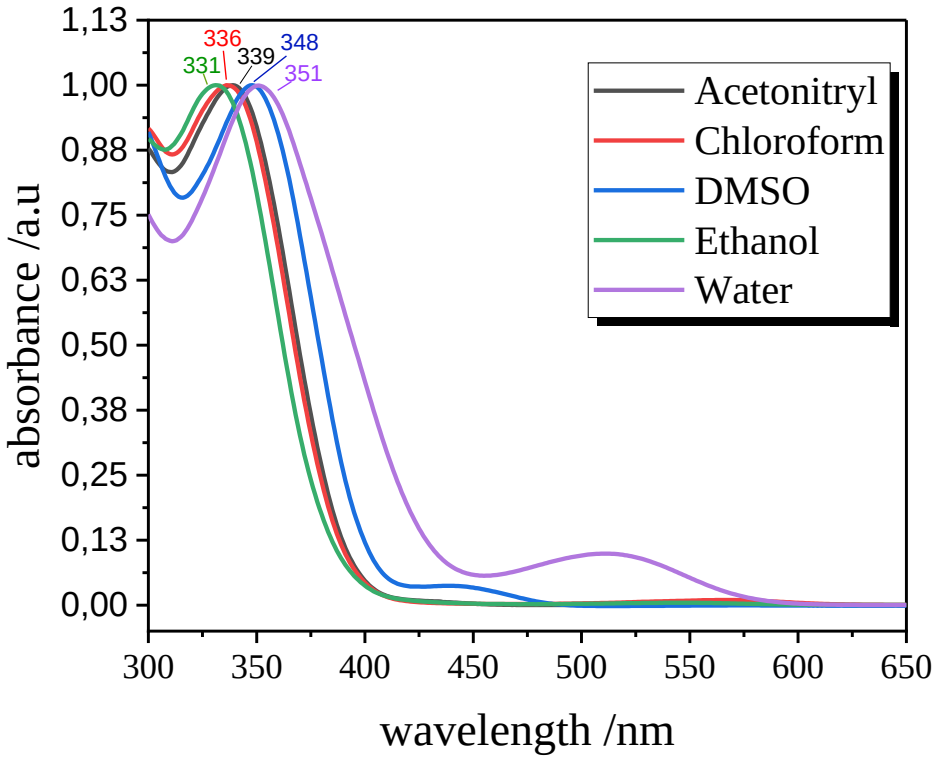
Irr 405nm



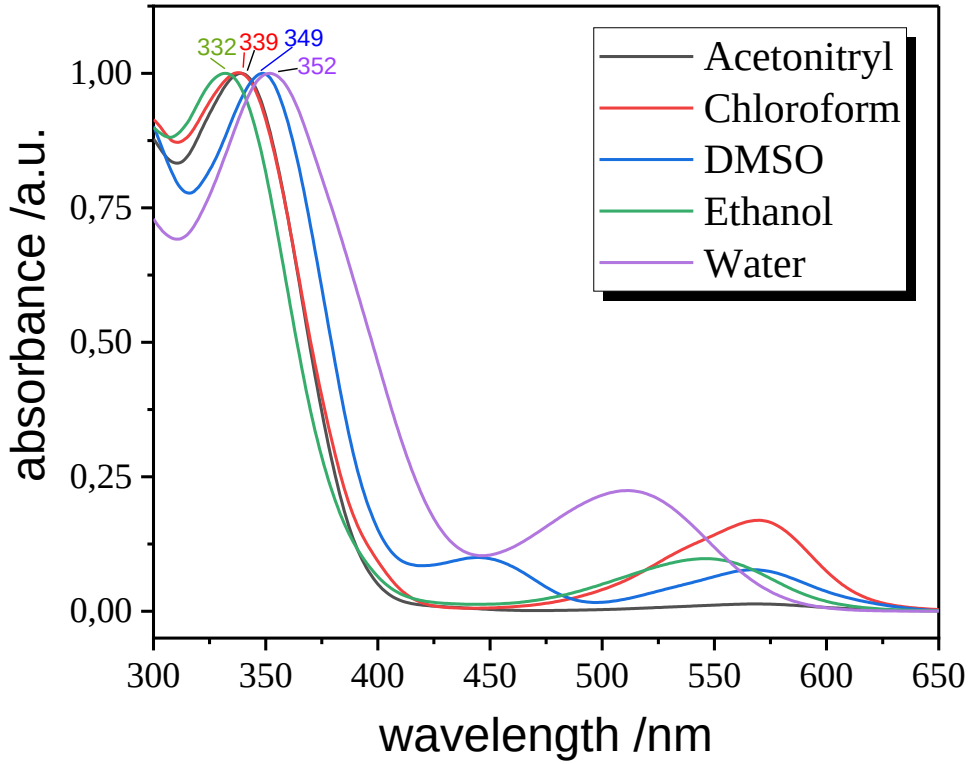
Photostationary state

PSS of a reversible photochemical reaction is the equilibrium chemical composition under a specific kind of electromagnetic irradiation.

Experimental results. Organic solvents

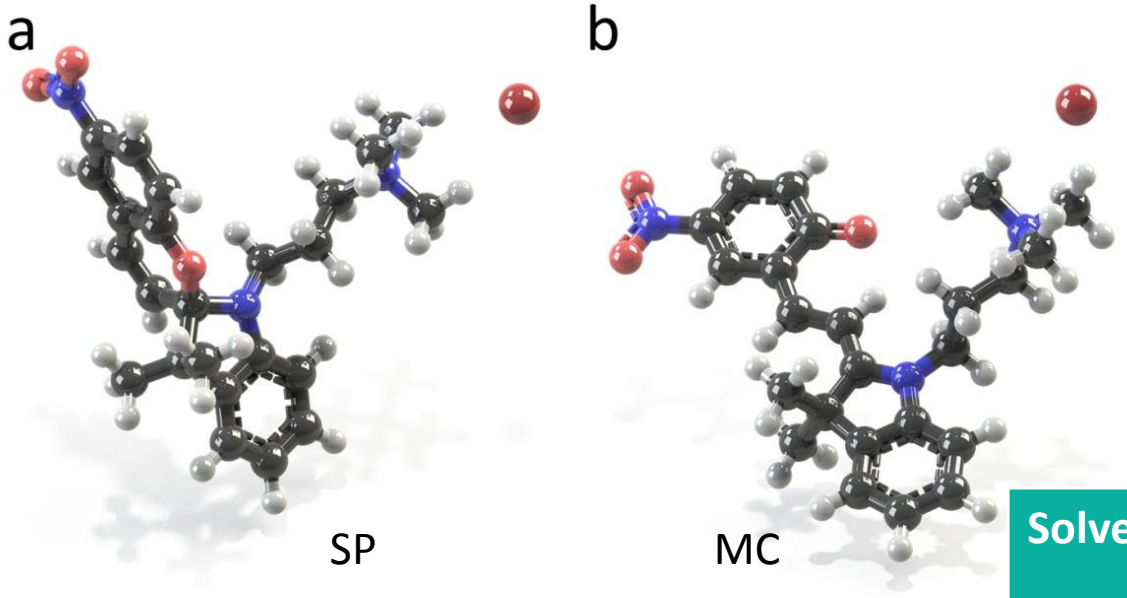


Normalized absorption spectra of 0,1mM SP before irradiation: sample dissolved in appropriate solvent and measured after one hour standing in yellow light lab



Normalized absorption spectra of 0,1mM SP after irradiation: samples irradiated with UV light until photostationary state achieved

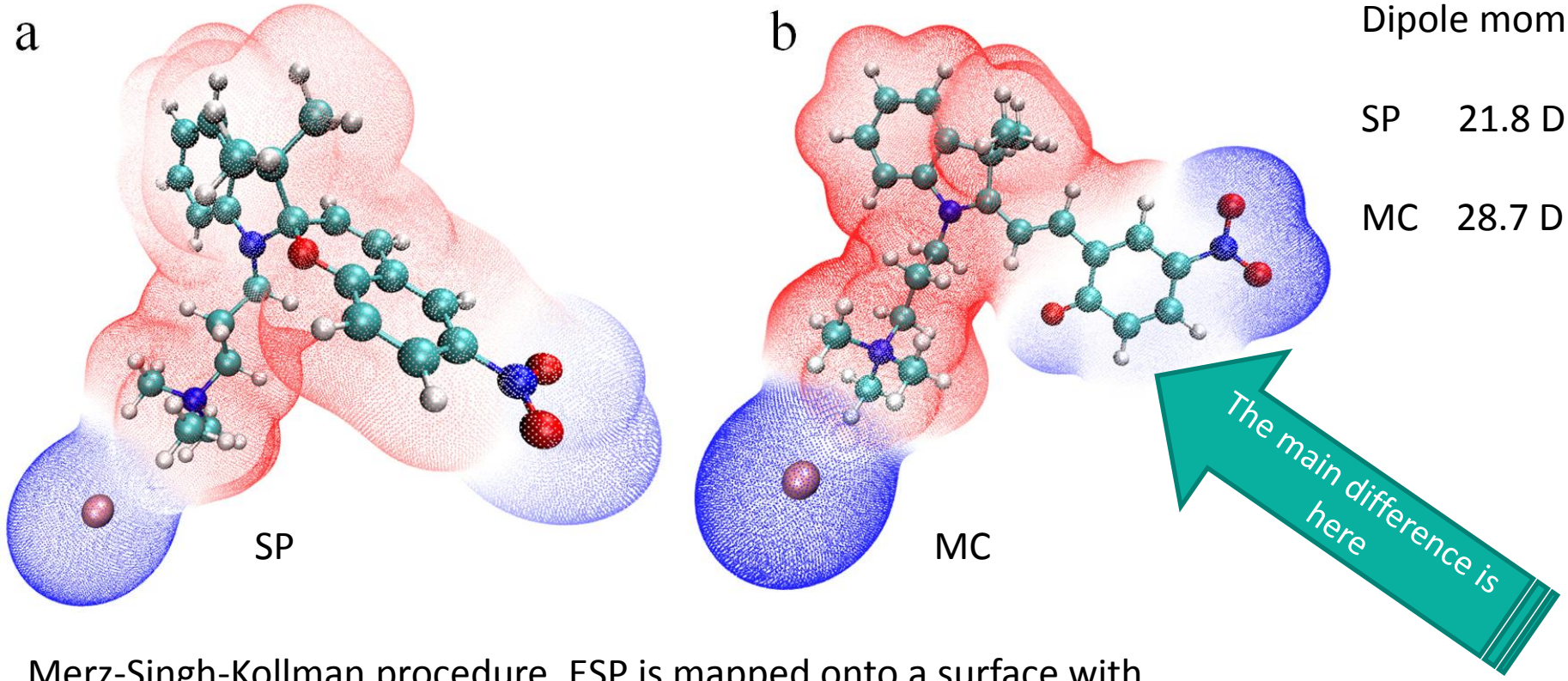
Simulation results. Molecular geometries. Relative energies



B3LYP/DGDZVP, IEFPCM/UFF solvent
Gaussian 09 Rev. A01

Solvent	ε	MC (reference)	SP ΔE [kJ mol^{-1}]
Chloroform	4.7	0	+58.0
Ethanol	24.9	0	+67.5
Acetonitrile	35.7	0	+68.8
DMSO	46.8	0	+68.8
Water	**78.4**	**0**	**+70.2**

Simulation results. ESP and dipole moments.



Dipole moments μ [D]

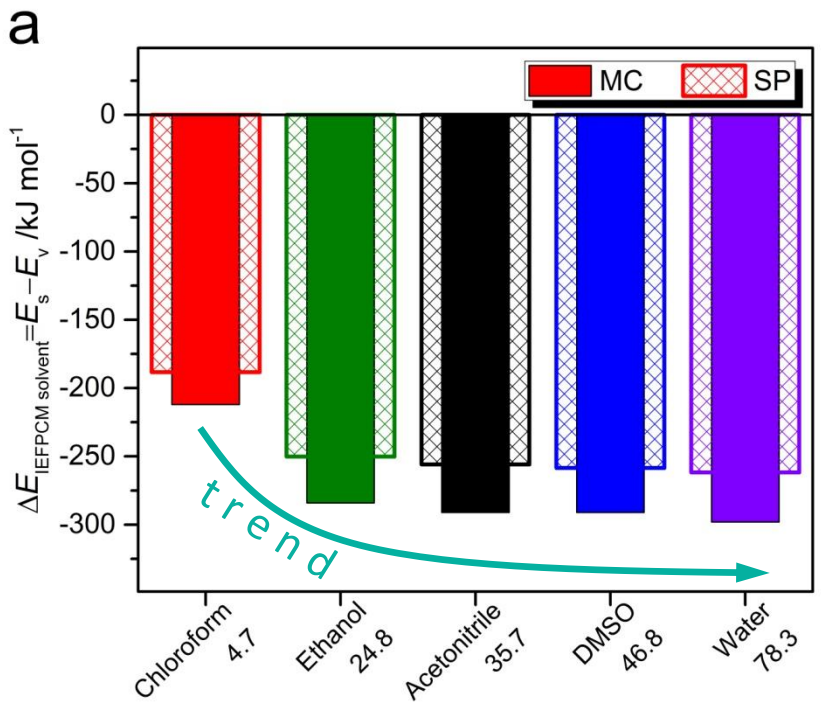
SP 21.8 D

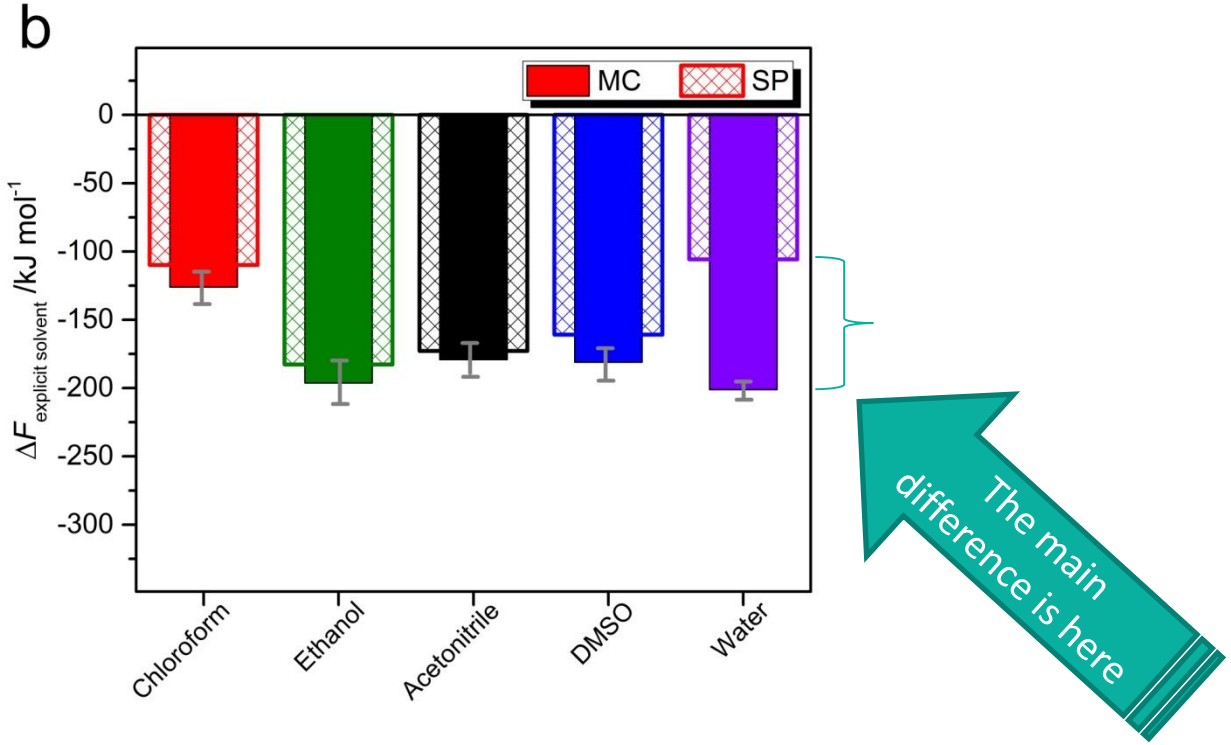
MC 28.7 D

Merz-Singh-Kollman procedure, ESP is mapped onto a surface with an electron density isovalue of 0.02 au

Illustration: Multiwfn, Version 3.8 and VMD, Version 1.9.3.

Simulation results. Thermodynamics of SP/MC cation solvation





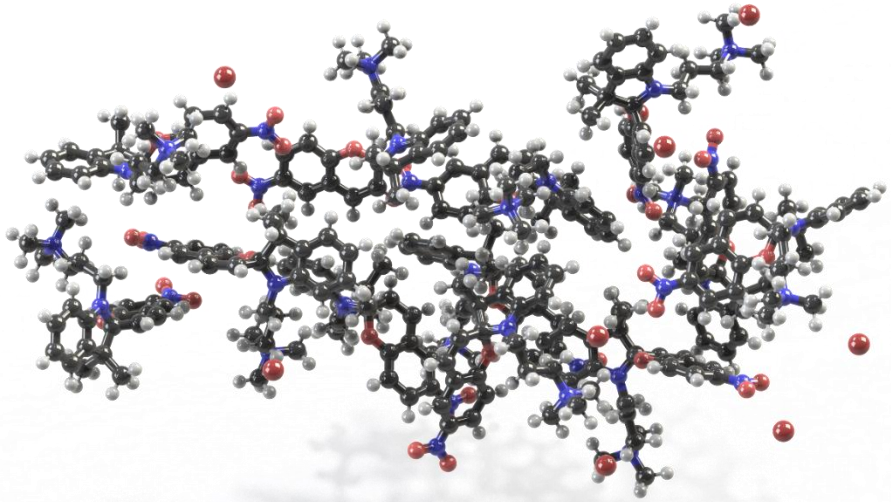
Implicit solvation, B3LYP/DGDZVP, IEFPCM/UFF solvent

Explicit solvation, Materials Studio, Thermodynamic Integration (21 λ values), UFF, NVT (averaged values of the Helmholtz free energy), *T*=298 K, 3 independent MD runs

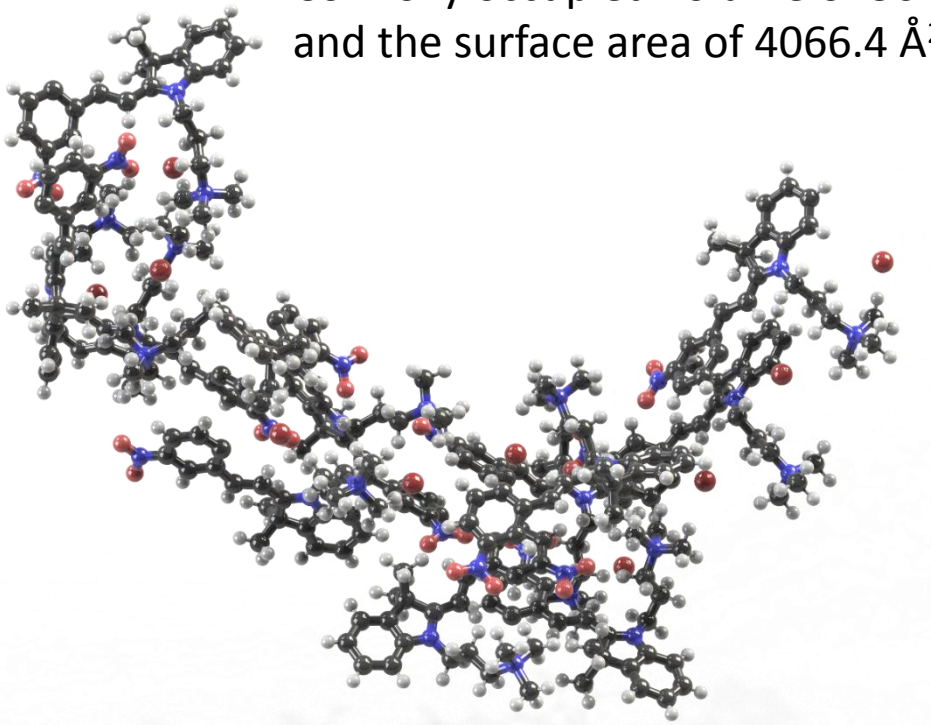
MC is preferably hydrated, numerous hydrogen bonds with water. E.g. pyran oxygen of MC has three HBs on average, ℓ_{HB}=1.94±0.06 Å
Oxygen in SP structure is not connected to water (sterics, weaker donor)

Simulation results. *P* values. Assemblies in water (*C*=0.4mM)

SP Connolly occupied volume of 5201.3 Å^3 and the surface area of 4238.0 Å^2



MC Connolly occupied volume of 5621.3 Å^3 and the surface area of 4066.4 Å^2



SP ***P*=0.95**

MC ***P*=0.97**

Both SP and MC are prone to form **lamellar structures** or **bilayer vesicles**

P is Israelachvili's critical packing parameter. $P = {}^{v}/_{\ell a_0}$ SASA values are used to define *v* and a_0

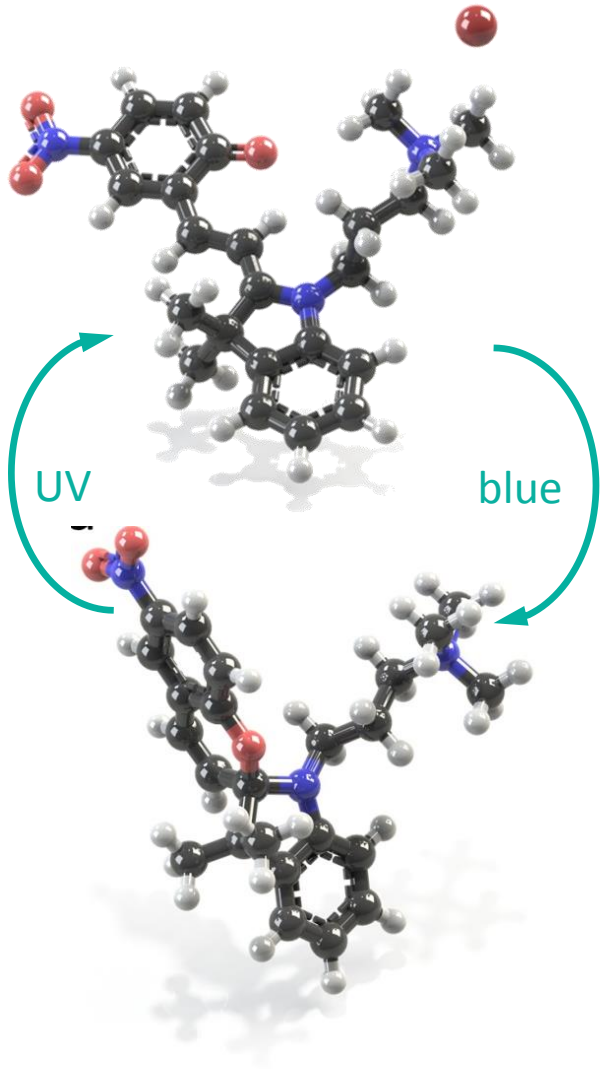
Conclusions

○ MC isomer is spontaneously appearing in water. Simulations explain that it is more stable in water, has larger dipole moment, the free energy of hydration is noticeably lower as compared to SP.

○ Experiments show the isomerization from SP to MC in water without UV stimulus. UV converts SP to MC as well, blue light transforms MC to SP.

○ Calculated optical spectra for MC in water coincide with experimental data. Spectrum for SP reproduces only a band at shorter wavelength.

○ Israelachvili's packing parameter predicts lamellar ordering in the solutions above CMC. MD simulations of 0.4 mM solution show the formation of the elongated layers.



Acknowledgements

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for computational resources

for informational support