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Design of new functionalized materials by tuning the photochemical properties of organic dyes

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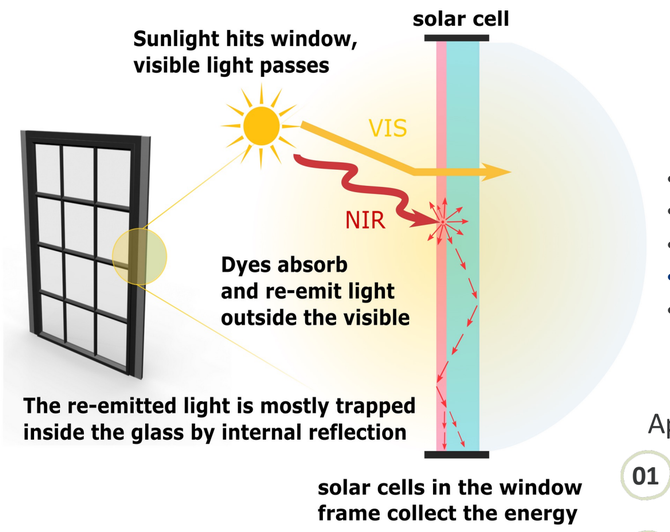
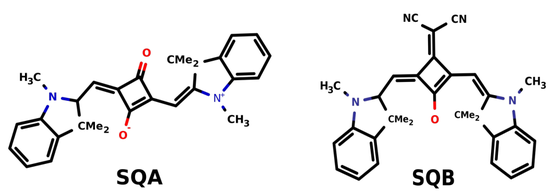
INTRODUCTION & AIM

TLSC transparent luminescent solar concentrator



SQUARAINE DYE - ACTIVE COMPONENT



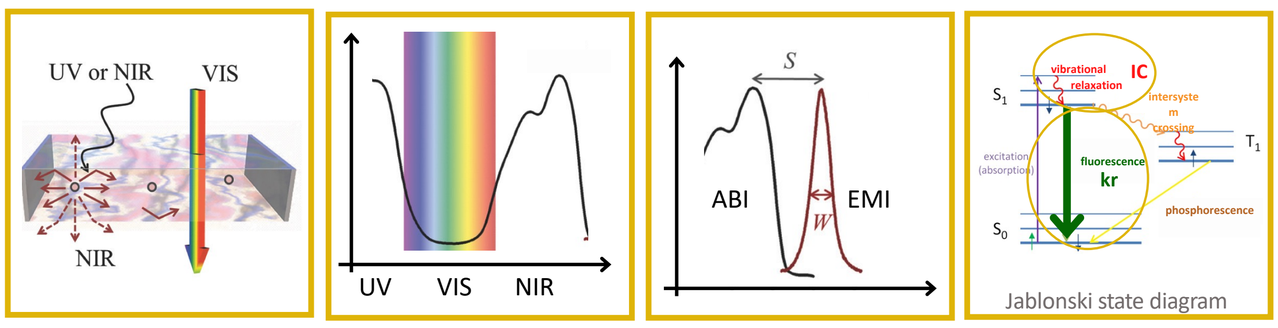
- central squaric-acid ring with two indoline groups
- planar molecules & DAD structure arrangement
- strong absorption & emission
- **Photostable**
- The most intensive absorption band appears as a result of the HOMO-LUMO transition from the ground to the first excited state

Application:

01 photoconducting materials
02 photovoltaic cells
03 DSSC
04 non-linear optics
05 bioimaging
06 fluorescent probes

AIM is to study the influence of the structural changes on the photochemical properties of squaraine dyes.

wavelength selectivity | optimal band-gap | narrow EMI, separated emission & absorption | high fluorescence QY



Challenge: prediction of fluorescence QY NIR - high QY dye

Radiative decay rate

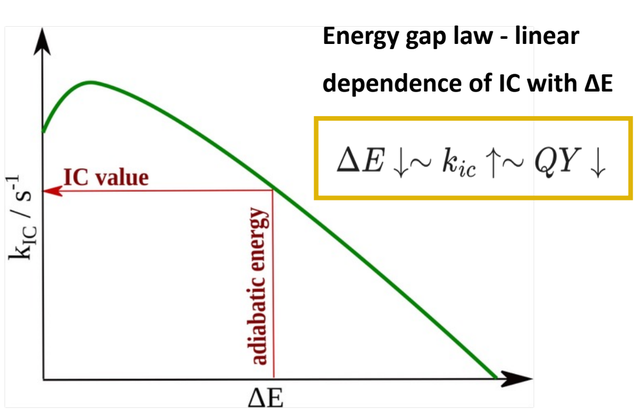
- integration of the emission spectrum

$$k_r = \int_0^\infty \sigma_{em}(\omega)d\omega$$

IC rate - form energies of excited and ground state

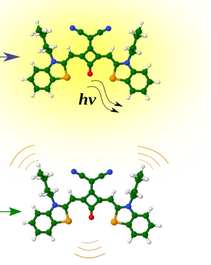
- inverse Fourier transform:

$$k_{ic}(\Delta E) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt \quad e^{i\Delta Et}\tilde{f}(t)\tilde{k}_{ic}(t)$$



$$\Delta E \downarrow \sim k_{ic} \uparrow \sim QY \downarrow$$

$$QY = \frac{k_r}{k_r + k_{nr}}$$



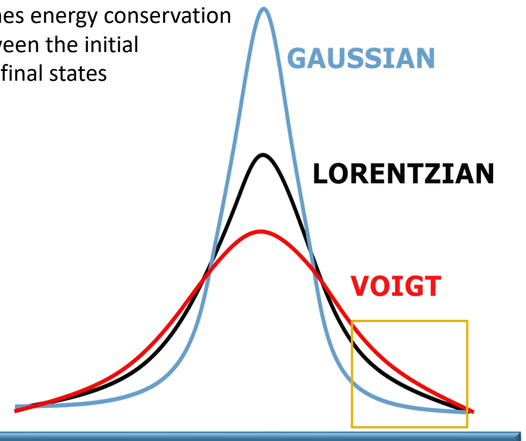
I) Harmonic models

Adiabatic Hessian and Vertical Hessian include:

- displacement
- frequency change
- Duschinsky rotation

II) Broadening function *δ(. . .)*

defines energy conservation between the initial and final states



COMPUTATIONAL

Structural and optical properties are calculated with DFT and TD-DFT within the Gaussian16 program, with PBE0 functional and def2-SVP AO basis set. Solvent effect is included implicitly via the PCM continuum model.
Radiative and IC rates are calculated with FCclasses 3 program developed by J.Cerzero and F.Santoro

RESULTS & DISCUSSION

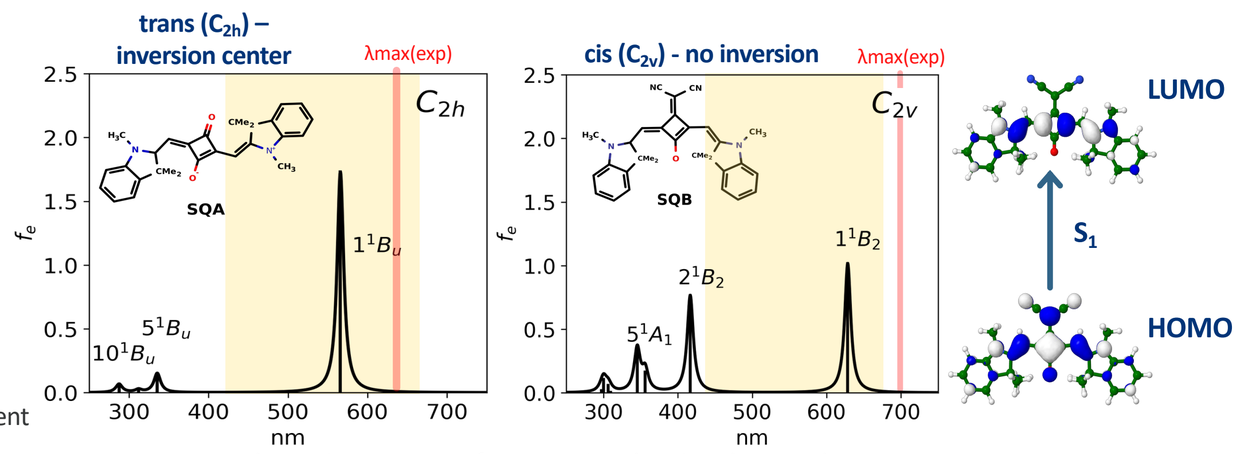
DESIGN REQUIREMENTS

- Shift in NIR
- Transparency in VIS

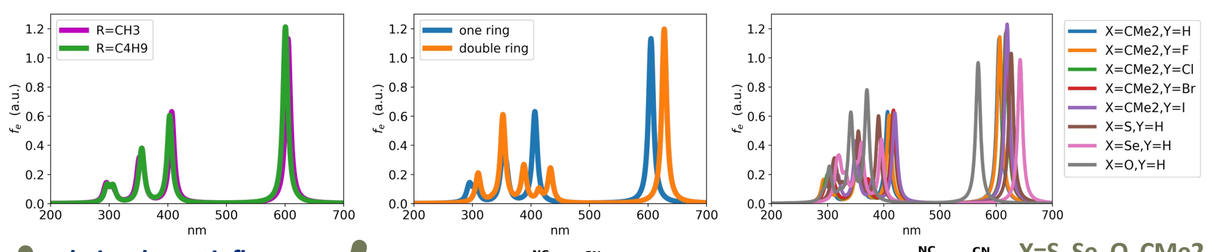
Trans-squaraines, because of the inversion, have symmetry-forbidden transitions (dark), which are in the case of cis-squaraines, allowed (bright).

Absorption spectrum of SQA molecule has a strong and intensive S1 peak. Due to the C2h symmetry and dark transitions, the SQA structure has a transparency window in the visible region of the spectrum.

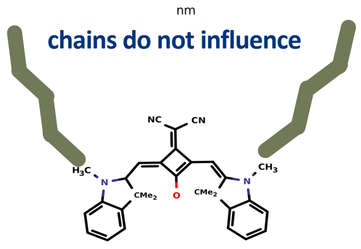
Problem: Absorption maximum is BLUE shifted



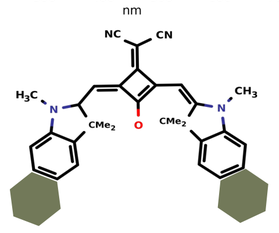
TDDFT absorption spectrum for squaraine dyes in toluene solvent



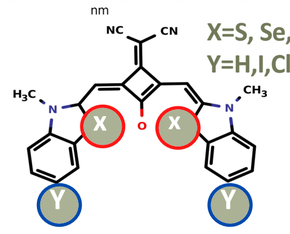
chains do not influence



addition of rings shifts absorption to red (due to the enlargement of the system)

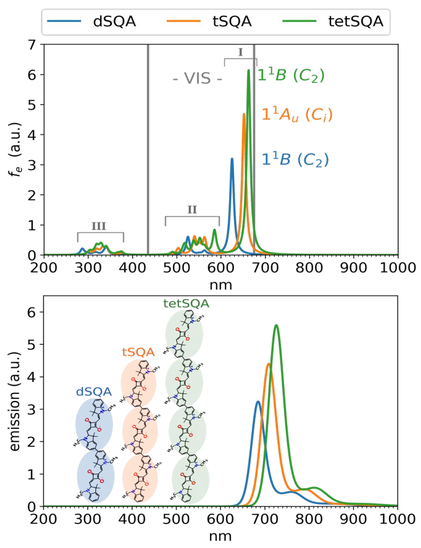


X=S, Se, O, CMe2
Y=H,I,Cl,Br,F



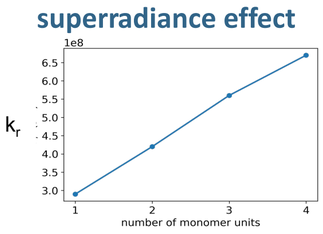
substitution of Y does not have influence, with X shifts spectrum (selenium most in the NIR)

Substitution near the active center have strongest influence



TDDFT absorption & emission spectrum for J-aggregates in toluene solvent

superradiance effect



toluene	QY(exp)/%	QY(theor)/%
dSQA	82	77
tSQA	85	96
tetSQA	-	92

J-AGGREGATES

- **shift in NIR**
- **optimal emission & Stokes shift**
- **large QY**

= good TLSC candidates

CONCLUSION & FUTURE PERSPECTIVES

- The inversion center has a profound influence on the optical properties of SQ dyes
- Substitution of squaraine dyes with different atoms and groups should be further investigated, with an accent on reliable QY prediction
- Due to their excitonic nature and the superradiance effect, J-aggregates can be used as TLSC luminophores. SQA is more efficient than SQB

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