

Mini review on squaraines

in preparation of master thesis work

Maximilian Jeindl

1 Structure

Anilino squaraines, see basic structure in fig. 1, have a symmetric structure with an aniline on either side of a squaric acid. The structure electronically is of D-A-D type, with the anilines being donators and the central core being of acceptor type. R here can be either an isobutyl in the case of squaraine with isobutyl sidechains (SQIB) or an alkyl chain of variable length n, leading to for example n-butyl chains as nBSQ or n-octyl chains as nOSQ. [1]

2 Modeling

2.1 Kasha theory

The Kasha model is based entirely on Coulomb coupling between neighboring chromophores, derived from the molecular transition dipole moment interaction. The coupling can be negative or positive (or neutral?) depending on orientation of the aggregates. J-aggregates have negative coupling and are usually associated with relative orientation side-by-side. H-aggregates on the other hand have positive coupling and are orientated head-to-tail.[Introduction][2] These classifications are based just on coulombic intermolecular coupling within Frenkel exciton theory. Within Frenkel excitation theory molecular aggregate photophysics usually use the point-dipole approximation for Coulomb coupling between molecules.[2][Kasha]

$$J = \frac{\boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_2 - 3(\boldsymbol{\mu}_1 \cdot \hat{R})(\boldsymbol{\mu}_2 \cdot \hat{R})}{4\pi\epsilon R^3} \quad (1)$$

Here μ is the corresponding dipole moment for the $S_0 \rightarrow S_1$ transition of a molecule. The displacement vectors and the transition dipole moment of the molecules can be simplified by relative positions with an angle θ between the direction of one transition dipole moment and the relative position vector to the other molecule. At $\theta_{crit} = 54.7^\circ$ there is no coupling, for smaller angles coupling is negative (J-aggregate) and larger angles positive (H-aggregate).[2][Kasha]

$$J = \frac{\mu^2 (1 - 3 \cos^2 \theta)}{4\pi\epsilon R^3} \quad (2)$$

The Coulomb coupling leads to two delocalized excited states split by $2|J_C|$. The in-phase, symmetric, state is shifted by J_C and the out-of-phase state is shifted by $-J_C$. While the in-phase state shows an enhanced transition dipole moment the out-of-phase state is optically dark due to the cancellation

of the transition dipole moments. The energy diagram for J and H aggregates can be seen in fig. [2][7073 fig 2]

Additional to the energy shifts of absorption the decay rate is also different for J- and H-aggregates. H-aggregates likely feature a fast intraband relaxation after absorption populating the low energy out-of-phase state, which due to symmetry forbids radiative coupling to the groundstate $|g_1 g_2 \rangle$. Meanwhile J-aggregates are radiatively coupled to the groundstate. Compared to the monomer the J-aggregate containing N-coupled molecules has a relaxation enhancement by a factor of N, which is called superradiance. This only concerns radiative decay rate and not total emission yield.[2]

Linear aggregates of N-coupled chromophores with a single molecule per unit cell can be described with the Frenkel exciton hamiltonian in eq. 3, as their delocalized excited states may be described as molecular excitons. There E_M is the monomer $S_0 \rightarrow S_1$ transition energy, D the gas-to-crystal frequency shift, typically negative as neighboring molecules stabilize an excited state via nonresonant interactions, $J_{m,n}$ is the resonant Coulomb coupling between molecules m and n. The states describe a single local excited state of the mth chromophore $|m\rangle \equiv |g_1, g_2, \dots, g_m, \dots, g_N\rangle$. [2]

$$H_{excitation} = E_M + D + \sum_{m,n} J_{m,n} |m\rangle \langle n| \quad (3)$$

2.2 Alkyl sidechains

An extended essential states model, based on Painelli's essential states model for DAD chromophores, is used to model the absorption spectra observed. The molecule has two degenerate states, the so called zwitterionic states, due to its symmetry, where the excitation is D^+A^-D and DA^-D^+ respectively for states $|Z_1\rangle$ and $|Z_2\rangle$. The zwitterionic states along with the neutral $|N\rangle$ DAD together are the essential states model. Compared to the neutral state $|Z_1\rangle$ and $|Z_2\rangle$ have a higher energy by μ_Z and they couple to it through $-t_Z$. [1]

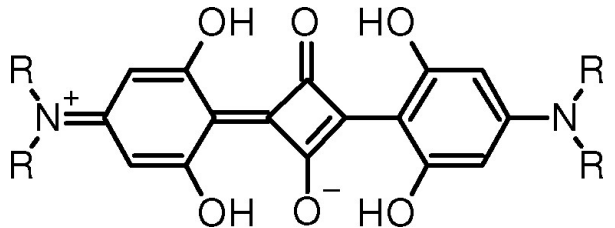


Figure 1: asdf[1]

References

- [1] F. Balzer, N. J. Hestand, J. Zablocki, G. Schnakenburg, A. Lützen, and M. Schiek, “Spotlight on charge-transfer excitons in crystalline textured n-alkyl anilino squaraine thin films,” *The Journal of Physical Chemistry C*, vol. 126, no. 32, pp. 13 802–13 813, 2022. DOI: [10.1021/acs.jpcc.2c03665](https://doi.org/10.1021/acs.jpcc.2c03665). eprint: <https://doi.org/10.1021/acs.jpcc.2c03665>. [Online]. Available: <https://doi.org/10.1021/acs.jpcc.2c03665>.
- [2] N. J. Hestand and F. C. Spano, “Expanded theory of h- and j-molecular aggregates: The effects of vibronic coupling and intermolecular charge transfer,” *Chemical Reviews*, vol. 118, no. 15, pp. 7069–7163, 2018, PMID: 29664617. DOI: [10.1021/acs.chemrev.7b00581](https://doi.org/10.1021/acs.chemrev.7b00581). eprint: <https://doi.org/10.1021/acs.chemrev.7b00581>. [Online]. Available: <https://doi.org/10.1021/acs.chemrev.7b00581>.