Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Material: Design of J-aggregates-like oligomers built from squaraine dyes exhibiting transparency in the visible regime and high fluorescence quantum yield in the NIR region

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Table S1: Comparison of experimental[1] and theoretical absorption maxima for J-aggregates formed by squaraine dyes in toluene solvent.

	$\lambda_{max}(exp)^1$		$\lambda_{max}(theor)$	
	nm	(eV)	nm	(eV)
dSQA	690	(1.80)	625	(1.98)
dSQB	747	(1.66)	681	(1.82)
tSQA	714	(1.74)	652	(1.90)
tSQB	773	(1.60)	707	(1.75)
tetSQA			662	(1.87)
tetSQB			719	(1.72)

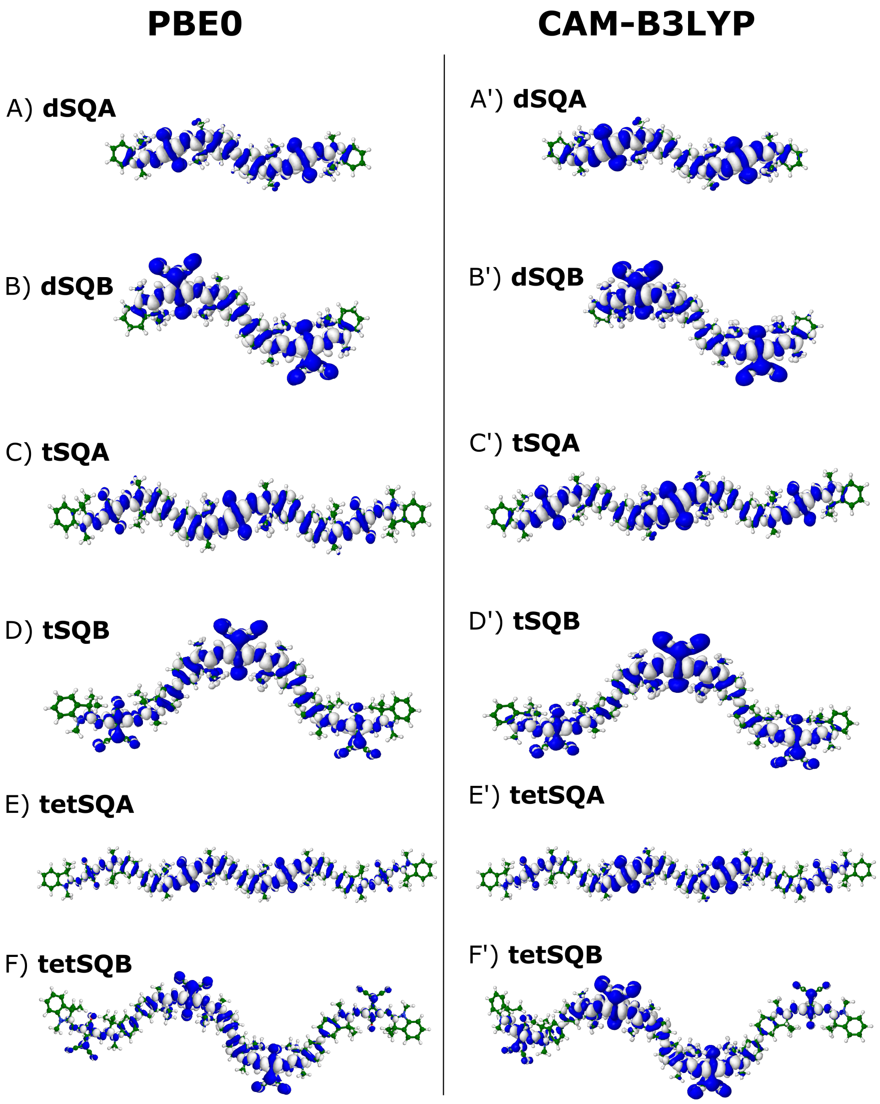


Figure S1: Comparison of calculated electron density difference (EDD) between first excited (S_1) and ground (S_0) state for squaraine J-aggregates in toluene solvent, for functionals PBE0/def2-SVP and CAM-B3LYP/def2-SVP in Multiwfn 3.6 software program.[2] Blue/white regions label the loss/gain of electronic charge during the transition.

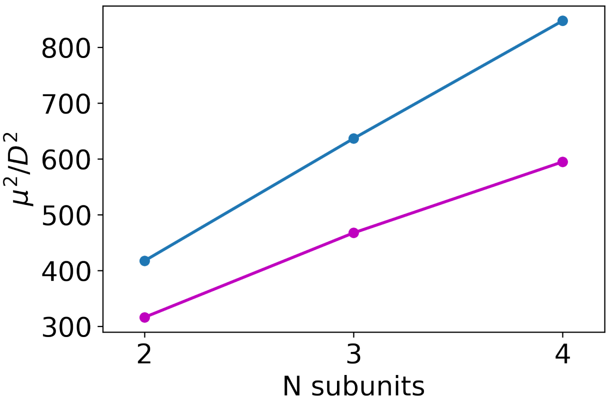


Figure S2: The calculated squared transition dipole moments (μ^2=dipole strength) for SQA (blue) and SQB (violet) J-aggregates in toluene solvent as a function of the number of subunits N.

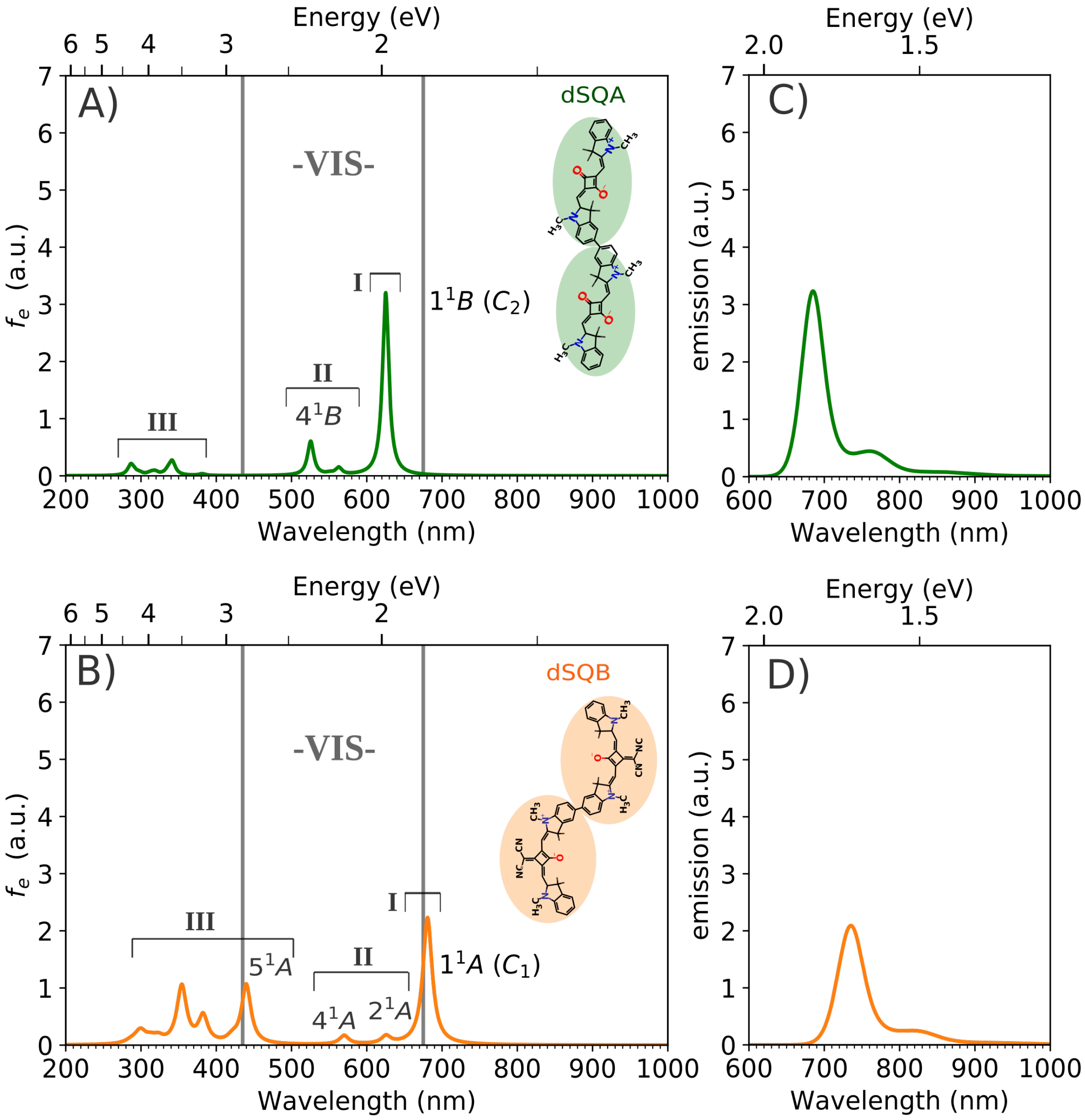


Figure S3: TD-DFT absorption spectra of J-aggregates forming dimers in toluene solvent: A) dSQA (green) built from squaraine dyes with the central squaric acid ring and oxygen atoms, and B) dSQB (orange) built from squaraine dyes with the central squaric acid ring substituted with the dicyanovinylene group. Transitions are divided into groups I, II, and III. The most intense transitions (I) are labeled according to symmetry point groups. f_e labels oscillator strengths. The visible regime (VIS) is shown within gray lines. HOMO-LUMO gaps are 2.35 eV for dSQA and 2.22 eV for dSQB J-aggregates. Comparison between emission spectra of C) dSQA and D) dSQB J-aggregates in toluene solvent (cf. Computational). Notice that monomer subunits forming J-aggregates are covalently bound (1.5Å).

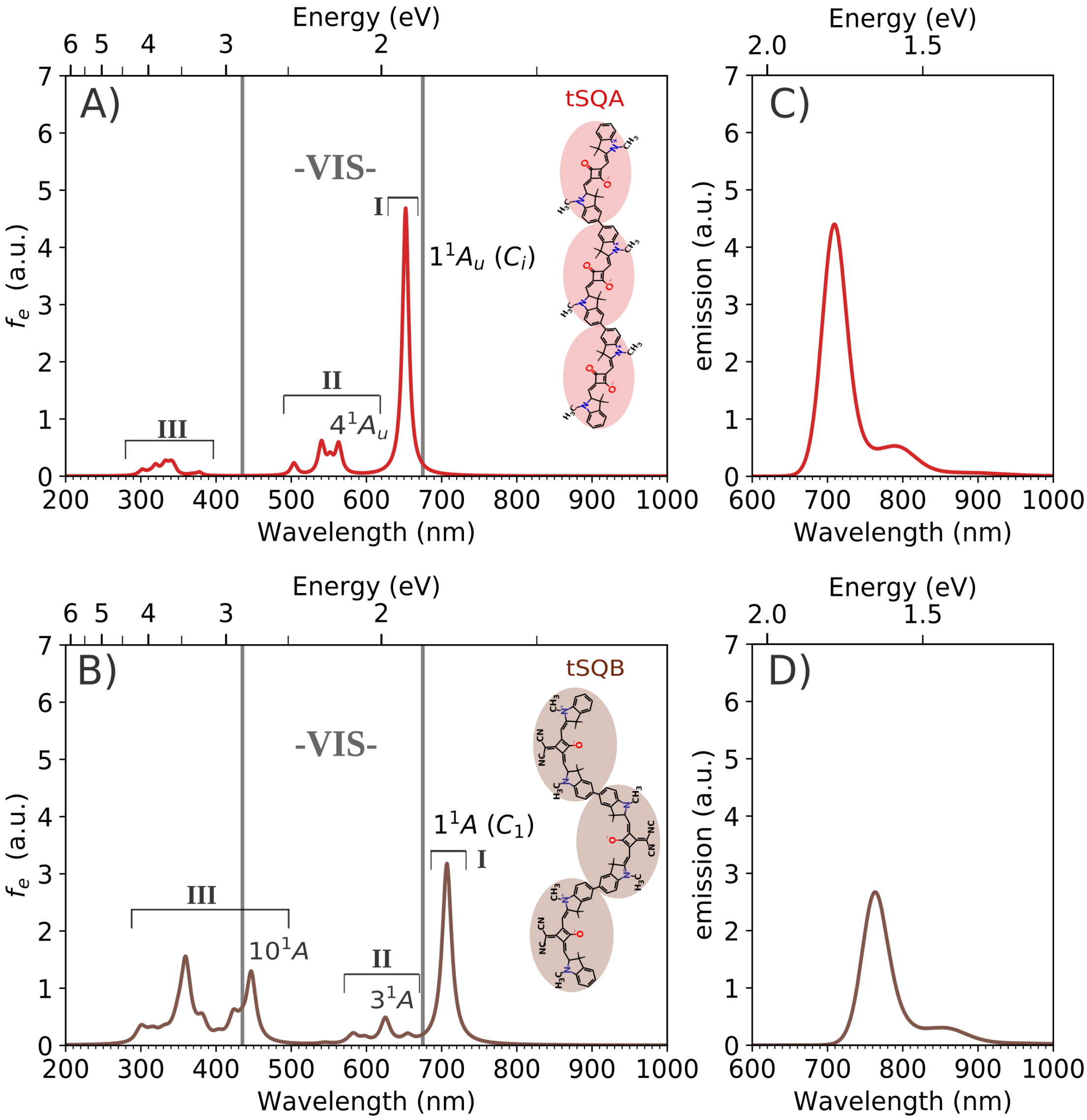


Figure S4: TD-DFT absorption spectra of J-aggregates forming trimers in toluene solvent: A) tSQA (red) built from squaraine dyes with the central squaric acid ring and oxygen atoms, and B) tSQB (brown) built from squaraine dyes with the central squaric acid ring substituted with the dicyanovinylene group. Transitions are divided into groups I, II, and III. The most intense transitions (I) are labeled according to symmetry point groups. f_e labels oscillator strengths. The visible regime (VIS) is shown within gray lines. HOMO-LUMO gaps are 2.29 eV for tSQA and 2.15 eV for tSQB J-aggregates. Comparison between emission spectra of C) tSQA and D) tSQB J-aggregates in toluene solvent (cf. Computational). Notice that monomer subunits forming J-aggregates are covalently bound (1.5Å).

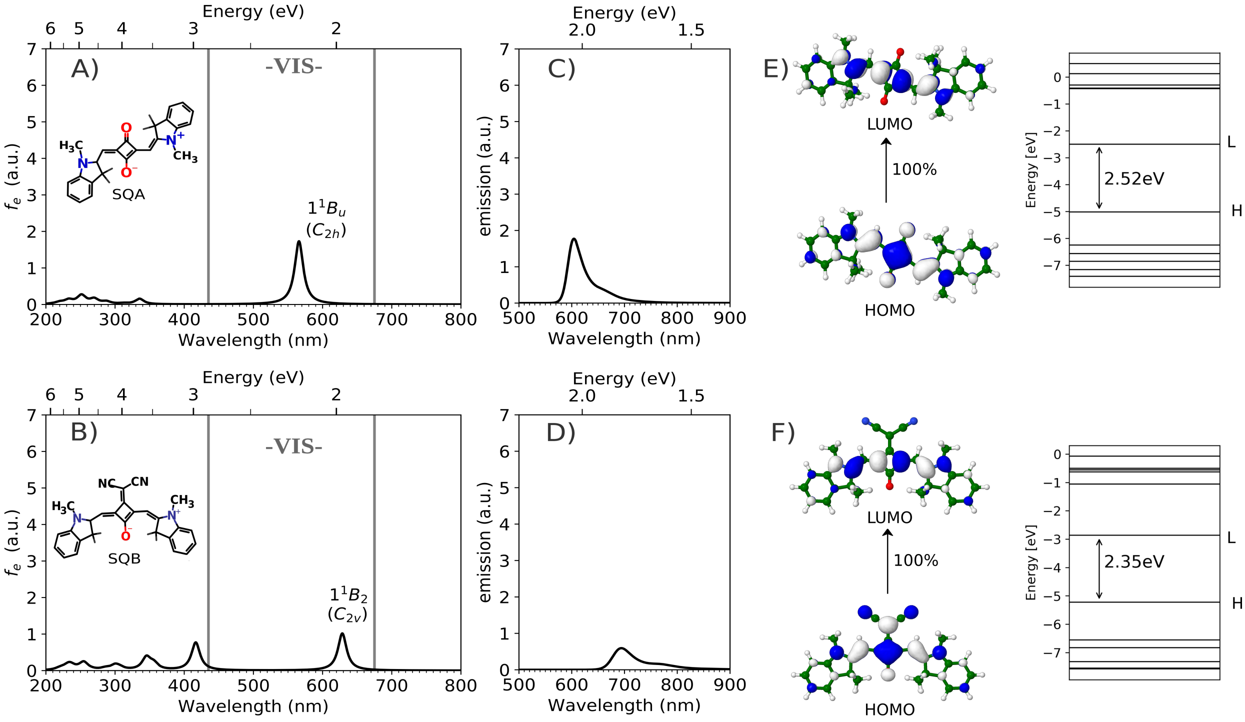
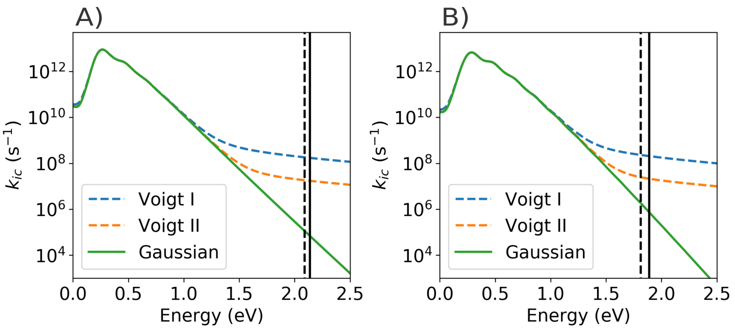


Figure S5: TD-DFT absorption spectra of monomer squaraine dyes in toluene solvent: A) SQA squaraine dye with the central squaric acid ring and oxygen atoms, and B) SQB squaraine dye with the central squaric acid ring substituted with the dicyanovinylene group. The most intense transitions (I) are labeled according to symmetry point groups. f_e labels oscillator strengths. The visible regime (VIS) is shown within gray lines. Comparison between emission spectra of C) SQA and D) SQB in toluene solvent (cf. Computational). HOMO and LUMO molecular orbitals involved in excitations within the first excited state together with the energies of Kohn-Sham orbitals and HOMO-LUMO gap are shown for E) SQA and F) SQB squaraine dyes. Both monomers have the first excited state with a bright π-π^* character within the VIS regime which is separated from higher excited states. Therefore no mixing of states nor breaking of Born-Oppenheimer approximation occurs.



C)

Squaraine	Broad. f	k_{ic} (s^{-1})	k_{nr} (s^{-1})
		VH	Exp.
SQA	Voigt I	$1.7*10^{8}$	$2.3*10^{8}$
	Voigt II	$1.7*10^{7}$	
	Gauss	$7.0*10^{4}$	
SQB	Voigt I	$2.1*10^{8}$	$7.2*10^{7}$
	Voigt II	$2.1*10^{7}$	
	Gauss	$6.9*10^{5}$	

Figure S6: IC rate vs. adiabatic energy profiles (VH model) for: A) SQA, and B) SQB squaraines in toluene solvent. The broadening functions are a Gaussian ($\mathrm{HWHM_G} = 0.02$ eV), Voigt I ($\mathrm{HWHM_G} = 0.02$ eV, $\mathrm{HWHM_L} = 0.001$ eV) and Voigt II ($\mathrm{HWHM_G} = 0.02$ eV, $\mathrm{HWHM_L} = 0.0001$ eV). The solid black line marks the adiabatic energy and dashed black line vertical emission energy. C) IC rates squaraine dyes calculated within vertical hessian model (VH) in toluene solvent (at 300K) using FCclasses3 program. k_{nr} labels the experimental non-radiative rate taken from Ref.[1] Internal conversion rates k_{ic} for monomers show larger dependence on different broadening in comparison with J-aggregates.

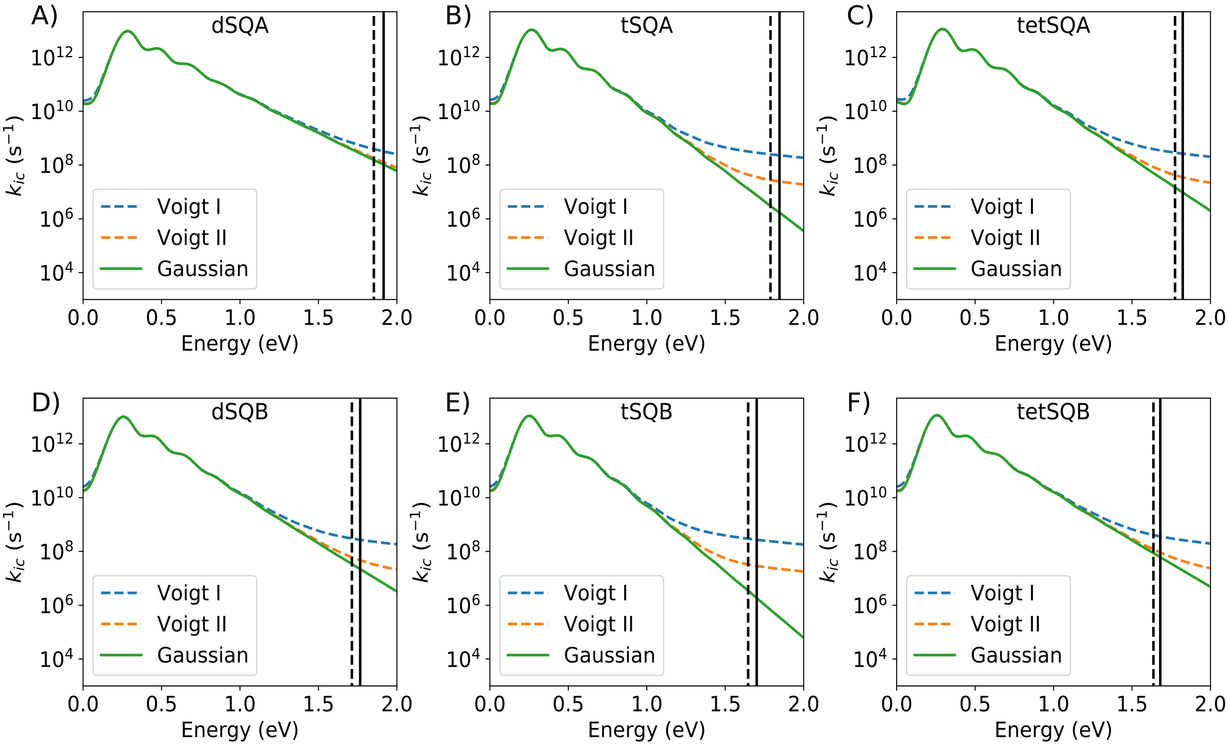


Figure S7: k_{ic} rates vs. emission energy (VH model) for: A) dSQA, B)tSQA, C) tetSQA, D) dSQB, E) tSQB and F) tetSQB J-aggregates in toluene solvent for different broadening functions: Voigt I ($\mathrm{HWHM_G}$ = 0.02 eV and $\mathrm{HWHM_L}$ = 0.001 eV), Voigt II ($\mathrm{HWHM_G}$ = 0.02 eV and $\mathrm{HWHM_L}$ = 0.0001 eV) and Gaussian ($\mathrm{HWHM_G}$ = 0.02 eV). The solid black line marks the adiabatic emission energy and the dashed black line vertical emission energy. The broadening has been described in the Computational part and has been investigated in Ref.[3]

Table S2: Parameters for scaling relations obtained from DFT and TD-DFT calculations for SQA and SQB monomers in toluene solvent.

	N_v	S(1)	$\lvert\vec{\tau}(1)\rvert$ $[Bohr^{-1}]$	$\Delta\epsilon(1)$ $[eV]$	ω_{eff} $[cm^{-1}]$	J_{ge} $[cm^{-1}]$
SQA	174	0.006	1.39	2.09	1579	-881
SQB	186	0.009	1.24	1.81	1568	-645

N_v labels the number of vibrational modes, S the average Huang-Rhys factor, $|\vec{\tau}|$ the non-adiabatic coupling vector, and $\Delta\epsilon$ excitation energy. The effective vibrational mode ω_{eff} corresponds to the C-C stretch vibration. $S(1)$, $|\vec{\tau}(1)|$, and $\Delta\epsilon(1)$ are monomer values, as indicated in brackets. The excitonic couplings J_{ge} are determined from calculations of Davydov splitting for dSQA and dSQB.

The following expression for internal conversion rate[4] k_{ic} is used:

$$k_{\text{ic}} = u_{\text{ic}} \sqrt{\frac{\pi}{2}} |\vec{\tau}(1)|^2 \left[1 + 2\frac{J_{ge}}{\Delta\epsilon(1)} \cos\left(\frac{\pi}{N+1}\right)\right]^{-2} \frac{1}{\sqrt{X}} \exp\left(-X \left[\log\left(\frac{NX}{N_v S(1)}\right) - 1\right] - \frac{N_v S(1)}{N}\right) \quad (1)$$

where electronic excitation is:

$$X = \frac{\Delta\epsilon(1)}{\omega_{\text{eff}}} + 2\frac{J_{ge}}{\omega_{\text{eff}}} \cos\left(\frac{\pi}{N+1}\right) \quad (2)$$

N is the number of monomer units in J-aggregate, and the factor for the conversion of atomic units in s^{-1} is $u_{\text{ic}} = 4.13 \times 10^{16}$ s^{-1}.

References

[1] H. Ceymann, A. Rosspeintner, M. H. Schreck, C. Mützel, A. Stoy, E. Vauthey, and C. Lambert. *Phys. Chem. Chem. Phys.*, 2016, **18**, 16404.

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[4] A. Humeniuk, R. Mitrić, and V. Bonačić-Koutecký. *The Journal of Physical Chemistry A*, 2020, **124**, 10143–1015.