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Published in:
Organic Chemistry Frontiers

DOI:
[10.1039/c9qo00259f](https://doi.org/10.1039/c9qo00259f)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2019

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Shi, J., Izquierdo, M. A., Oh, S., Park, S. Y., Milian-Medina, B., Roca-Sanjuan, D., & Gierschner, J. (2019). Inverted energy gap law for the nonradiative decay in fluorescent floppy molecules: larger fluorescence quantum yields for smaller energy gaps. *Organic Chemistry Frontiers*, 6(12), 1948-1954. <https://doi.org/10.1039/c9qo00259f>

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RESEARCH ARTICLE

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Inverted energy gap law for the nonradiative decay in fluorescent floppy molecules: larger fluorescence quantum yields for smaller energy gaps†

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A data survey on experimental fluorescence quantum yields of (multi)substituted dicyano-distyrylbenzenes in fluid solution evidences that non-radiative decay increases with the Franck–Condon energy (E_{FC}), being opposite to the conventional energy gap law. Quantum-chemistry indicates that this is controlled by access to the conical intersection (CI) following the Bell–Evans–Polanyi principle as a first-step approximation for this family of molecules; the variations in E_{FC} among the different compounds are found to be decisive, while those of E_{CI} are estimated to be weaker or even enhancing the effect. The current findings may have significant consequences for the design of molecules for organic solid state emitters.

Received 18th February 2019,

Accepted 18th April 2019

DOI: 10.1039/c9qo00259f

rsc.li/frontiers-organic

1. Introduction

Emissive organic molecules and (nano-)materials play a central role in modern materials, life and analytical science as light-emitting diodes, sensors, lasers, smart multi-responsive materials, photoswitches, bioprobes and -markers *etc.*^{1–17} In particular, special emphasis has been given to molecules which are ‘dark’ in fluid solution, but become ‘bright’ in solid/frozen solution and in the aggregated state. This long-known phenomenon^{17–22} has received a new drive in its now popular (however ambiguous)²³ term ‘aggregation induced emission’ (AIE);²⁴ a physically sound, phenomenological term might simply be ‘solid state luminescence enhancement’ (SLE).²³

Crucial for all applications of fluorescent molecules (as SLE-active compounds) in materials science, as well as in life and analytical science is the understanding or even prediction

of the non-/emissive character of molecules in fluid solution; indeed, the unbiased pre-synthesis computational design of novel innovative materials is seen as a pillar of future molecular/materials science. In fact, the advancement of quantum-chemical methods and computational resources in the last two decades now allows for predictive determination of crucial properties of organic emitters such as geometry, electronic structure, absorption and emission color, absorption strength, and spectral shapes, as well as the fluorescence rate constant k_F .

However, the prediction of fluorescence efficiency, expressed by the fluorescence quantum yield Φ_F is still a major challenge. This is because the calculation of Φ_F requires not only k_F , but the knowledge of the non-radiative decay pathways which occur after photoexcitation from the (singlet) ground state S_0 to the Franck Condon (FC) point on the S_1 potential hypersurface. In the absence of efficient intersystem crossing and of bimolecular photochemical loss pathways, Φ_F reads:

$$\Phi_F = \frac{k_F}{k_F + k_{nr}} \quad (1)$$

where k_{nr} is the non-radiative deactivation rate through $S_1 \rightarrow S_0$ internal conversion. Hence, low Φ_F can have two sources, a low k_F or a large k_{nr} . Low k_F are directly associated with a small oscillator strength f of the emitting state as k_F scales with f (Strickler–Berg relation; *vide infra*). Small f are for instance observed in molecules with a symmetry-forbidden $S_1 \rightarrow S_0$ transition or possible intramolecular charge-transfer (ICT) contributions of the latter.

For k_{nr} , the ‘energy gap law’ (EGL) is often evoked,¹⁹ which predicts an increase of k_{nr} with decreasing Franck–Condon E_{FC}

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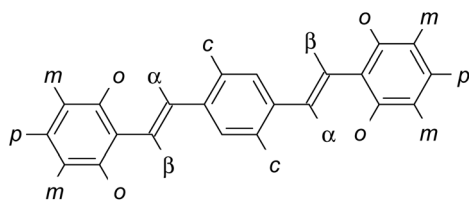
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†Electronic supplementary information (ESI) available. See DOI: 10.1039/c9qo00259f

between S_0 and S_1 . This is based on Fermi's golden rule, which associates the increase of k_{nr} at small E_{FC} with increased vibrational wavefunction overlap; this should particularly hold if the displacement of the S_1 equilibrium structure *vs.* that of S_0 is sufficiently small; *i.e.* for molecules with small geometrical reorganization. Thus, a typical application of the EGL are rigid systems as it was indeed observed for the nonradiative deactivation from the lowest triplet state of polycyclic aromatic hydrocarbons (PAHs);¹⁹ on the other side, deviations from the EGL are sometimes observed.^{25,26} Multi-mode two-state models based on Fermi's golden rule in a harmonic approximation were applied for such systems.²⁷

On the other hand, for floppy molecules, such approaches might become problematic, and detailed explanations of the non-radiative decay have to go beyond phenomenological terms such as the popular 'restriction of intramolecular rotation/motion' (RIR/RIM).²⁴ In fact, the current paradigm in photochemistry (however little acknowledged in the materials community)^{24,28} for ultrafast non-radiative deactivation from the excited state in floppy molecules involves a conical intersection (CI);^{20,29} from there, the molecules turn back to their initial ground state, and/or might undergo intramolecular photochemical reactions such as (partial) *trans-cis*-isomerization or cyclization.^{20,30} Prominent examples for the appearance of a CI are stilbenes^{20,30} (in particular tetraphenylethylene; TPE^{31,32}), diphenyldibenzofulvene,³³ tetraphenylsilole,³⁴ malononitriles,³⁵ indoline,³⁶ boron hydrides,^{37,38} DNA nucleobases,³⁹ cyanines and carotenoids;³⁰ furthermore, the appearance of a CI was also highlighted for the S_1 deactivation of rigid systems like PAHs.^{25,26} As the CI controls the competing pathways against fluorescence, the CI accessibility^{34,40} is considered as the most useful scenario to distinguish between non-/emissive materials. However, by now, it is not clear if and how this concept can be utilized to establish the desired predictive molecular design rule.

We recently performed a combined experimental-computational study on a prototype SLE material, that is distyrylbenzene (DSB) which carries cyano-functionalities in the vinylene units (DCS, see Scheme 1); the in-depth analysis elucidated all intra- *vs.* intermolecular contributions to SLE, disentangled electronic *vs.* geometrical effects, and quantified radiative *vs.* non-radiative pathways.²³ A cornerstone of the study was the comprehension of excited state non-radiative deactivation in fluid solution, which was estimated on the basis of a simplified quantum-chemical analysis to be operative *via* a CI. We



Scheme 1 Molecular structure of the DCS and BnPV compounds under study.

Table 1 Substitution patterns of the DCS compounds under study (Ph = phenyl, Cz = carbazole, R = alkyl). For the molecular structure, see Scheme 1; for references see Table S1 in the ESI

No.	α	β	c	o	m	p
1	CN					
2	CN					OC ₄ H ₉
3	CN		C ₆ H ₁₃			
4	CN		OCH ₃			
5	CN		OCH ₃			OC ₄ H ₉
6	CN				CF ₃	
7	CN		OCH ₃	OCH ₃		
8	CN				OC ₁₂ H ₂₅	OC ₁₂ H ₂₅
9	CN					CONHR
10	CN					N(C ₄ H ₉) ₂
11	CN		OCH ₃			N(CH ₃) ₂
12	CN					NPh ₂
13		CN				
14		CN	C ₆ H ₁₃			
15		CN	C ₆ H ₁₃	C ₆ H ₁₃	C ₆ H ₁₃	
16		CN	Ph			
17		CN			CF ₃	
18		CN				OC ₄ H ₉
19		CN	OCH ₃			
20		CN	OCH ₃	OCH ₃		
21		CN	OCH ₃			OC ₄ H ₉
22		CN	OC ₈ H ₁₇			OPh
23		CN	OC ₆ H ₁₃		CF ₃	
24		CN				CONHR
25		CN	Ph			NPh ₂
26		CN	OCH ₃			N(CH ₃) ₂
27		CN	NPh ₂		CF ₃	
28		CN	PhNPh ₂		OCH ₃	
29		CN	PhCz			OC ₆ H ₁₃
30		CN	PhCz		CH ₃	
31		CN	PhCz		CF ₃	
32		CN	CzR			CF ₃
33		CN	CzR		CF ₃	

concluded that the access to the CI could be decided by the FC energy E_{FC} compared to the CI energy E_{CI} , similar to results on PAHs;^{25,26} Thus, compounds with much lower E_{FC} than E_{CI} are much more emissive.

However, it remained an open question at this moment how generic this concept is, and in particular, whether a general correlation between E_{FC} and Φ_F can be established. For this reason, in the current work, we surveyed and collected a broad library of DCS compounds for which Φ_F in fluid solution are known; see Scheme 1 and Table 1. Comparison is done with DSB oligomers (*i.e.* not bearing the cyano motif); reasons for the largely differing behavior of DSB and DCS compounds are elucidated *inter alia* with the help of quantum-chemical methods, to draft the conditions for the unprecedented 'inverted energy gap law' observed in the DCS family.

2. Results and discussion

DSB-type oligomers: floppy molecules following the EGL

In a first step, to provide a reference point for the DCS family, we examine DSB-type molecules which exhibit the identical molecular backbone but miss the cyano functionality in the

vinylene unit. To access a larger range of Franck–Condon energies E_{FC} , while keeping the structural motif, we chose homologues of DSB, *i.e.* oligophenylenevinyls with varying number of repetition units, carrying *t*-butyl groups in the *meta*-positions of the terminal rings (BnPv, see inset of Fig. 1). For the BnPv series, both fluorescence quantum yields Φ_F and lifetimes τ_F were measured;⁴¹ here, τ_F relates to the rates as:

$$\tau_F = (k_F + k_{nr})^{-1}. \quad (2)$$

This allows for the extraction of the experimental rates from eqn (1) and (2). As seen in Fig. 1, with increasing n and thus decreasing E_{FC} ,⁴² Φ_F decreases due to the significant increase of k_{nr} despite an increase of k_F .⁴¹ This behavior is expected from the EGL, and evidences that this rule is also applicable to floppy molecules in specific cases like *n*PVs. It has to be emphasized however that the smallest oligomer ($n = 1$; stilbene), *i.e.* with the largest E_{FC} , shows very effective non-radiative decay and thus a low Φ_F in solution; that is contrary to the EGL. This is attributed to the lability of the double bond in stilbene in the first excited state S_1 as confirmed by time-dependent density functional calculations (TD-DFT);⁴³ in fact, for $n > 1$, the length of the double bonds r_{DB} in S_1 is quite short with about 1.37 Å, while for $n = 1$ it is significantly elongated with $r_{DB} = 1.41$ Å. Therefore, stilbene deactivates effectively *via* a CI,^{20,30} while higher homologues are brightly emissive.⁴¹ The multi-reference quantum-chemical treatment of the CI for stilbene and DSB indeed corroborates this result, as will be shown elsewhere.⁴⁴

Survey of experimental data for DCS compounds

In a second step, we screened all those DCS compounds found in literature for which Φ_F and E_{FC} in fluid solution had been determined experimentally;⁴⁵ here, E_{FC} was extracted as the maxima of the lowest energy absorption band. The literature search gave a library of 12 α -compounds, *i.e.* with the cyano-group in the inner position of the vinylene unit (no. 1–12 in Table 1) and 21 β -compounds (cyano-group in the outer posi-

tion; 13–33); this comprises (multiple) substitutions with positive/negative mesomeric and/or inductive effects ($\pm M$, $\pm I$). Plotting Φ_F against E_{FC} in Fig. 2, a clear correlation is observed, if some outliers are omitted (*i.e.* compounds 10, 11, 27) which will be discussed further down; thus, the experimental data indeed suggests that lowering of E_{FC} systematically enhances the emissivity of the compounds.

Correlation of the non-radiative rate with the FC energy

Although the correlation of Φ_F with E_{FC} is significant as seen in Fig. 2, a rather broad scattering of data points is observed. The most obvious reason arises from the fact that Φ_F depends not only on k_{nr} but equally on k_F , see eqn (1). The latter can largely vary even in the same family of compounds; in fact, for DCS compounds k_F is in the range of *ca.* 5×10^6 s⁻¹ to 5×10^8 s⁻¹; *i.e.* varying by two orders of magnitude;²³ see ESI.† To eliminate the effect of k_F , the non-radiative rate k_{nr} instead of Φ_F should be plotted against E_{FC} . As mentioned above, k_{nr} is attainable *via* eqn (2) by measuring additionally τ_F which is typically done by time-correlated single photon counting (TCSPC); this however becomes imprecise for low emissive compounds as τ_F is here in the lower ps range, *i.e.* below the typical width of the instrumental response function. Therefore, even if TCSPC data for τ_F were obtained experimentally for several DCS compounds, they are often little reliable for low-emissive compounds. For this reason, and to provide a complete dataset, we calculate k_F from the steady-state spectra; here, k_F is readily obtained *via* a simplified version of the Strickler–Berg equation:²³

$$k_{F,SB} = 4.34 \times 10^7 [\text{s}^{-1} \text{eV}^{-2}] \frac{E_{F,vert}^3}{E_{A,vert}} f \quad (3)$$

where $E_{F,vert}$ and $E_{A,vert}$ are the vertical absorption (FC) energies for emission and absorption, respectively, and f is the oscillator strength of the emitting state; all these quantities can be calculated straightforward by TD-DFT.⁴³ In fact, the calculated

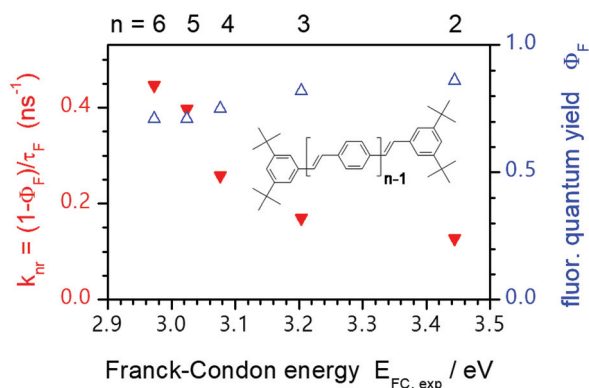


Fig. 1 Correlation of experimental fluorescence quantum yields Φ_F and non-radiative rates k_{nr} *via* eqn (1) and (2) for BnPv oligomers vs. their Franck–Condon energies E_{FC} as extracted as the maxima of the lowest energy absorption band.⁴¹

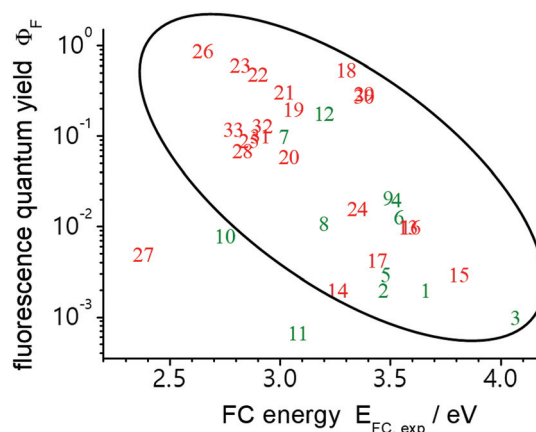


Fig. 2 Correlation of experimentally observed quantum yields Φ_F vs. their Franck–Condon energies E_{FC} ; α -isomers are indexed in green, β -isomers in red.

values for k_F from eqn (3) typically compare quite well with experiment, *i.e.* obtained *via* eqs. (1) and (2).²³

Fig. 3 plots k_{nr} as obtained from eqn (1) and (3) against E_{FC} . In order to be consistent in the approach, we use here E_{FC} as obtained as vertical absorption energies from TD-DFT; the latter correlate well with experiment;²³ see ESI.† Indeed, the correlation between k_{nr} and E_{FC} is much better than that of Φ_F vs. E_{FC} ; it should be stressed in this context that the k_{nr} values span more than four orders of magnitude. We further emphasize that the experimentally observed increase of the non-radiative deactivation with the FC energy is contrary to the EGL; the current finding might be thus termed as ‘inverted energy gap law’.

Nevertheless, residual data point dispersion is still observed. An anticipated possible (and probable) reason is related with the uncertainties in the (non-trivial) experimental determination of Φ_F .⁴⁵ On the other hand, there are also potential physical sources for the dispersion of k_{nr} . In fact, molecules with ICT character of the emitting state are prone to solvent effects as the solvent polarity may change the characteristics of the state,^{46,47} *e.g.* through the twisted ICT (TICT) mechanism.⁴⁸ As the cyano group is present as an effective acceptor in all DCS compounds, additional strong donor groups (in particular amino functionalities) promote partial ICT. Thus, solvent effects are expected to be important for compounds 10–12 in the α -series, and 25–27 in the β -series (labeled with an asterisk in Fig. 3). As the determination is typically done in solvents with non-negligible polarities (tetrahydrofuran, dichloromethane *etc.*), this might in particular explain strong outliers like 10, 11, 27. Furthermore, varying solvent viscosities (in combination with varying steric demands of the substituents) might significantly influence the access to the CI, as it was intensively discussed for stilbenes in the past.⁴⁷

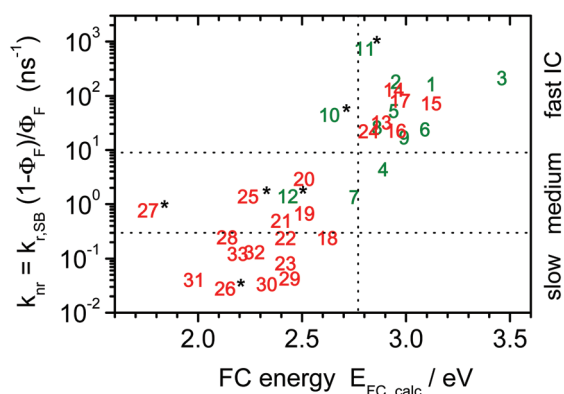


Fig. 3 Correlation of the non-radiative rate constants $k_{nr} = k_r (1 - \Phi_F) / \Phi_F$ vs. their calculated Franck–Condon energies E_{FC} ; here, k_r was calculated *via* eqn (3). The vertical line denotes the TD-DFT-calculated CI energy, approximated to be constant; horizontal lines indicate approximate boundaries for slow/medium/fast internal conversion; α -isomers are indexed in green, β -isomers in red. Asterisks indicate ICT compounds, see text.

CI treatment

The significant correlation of k_{nr} vs. E_{FC} as observed in the experimental dataset can be understood within the CI framework which we have recently applied to DCS compounds.²³ There, we showed that positional isomers of DCS compounds exhibit an intriguing behavior: while α -compounds are practically non-fluorescent in fluid solution, most β -compounds are highly emissive. This is a striking example for the limitations of the ‘RIR/RIM concept’, as the local environment of the floppy vinylic unit is the same, *i.e.* exhibiting the identical cyano-stilbene motif. In fact, Fermi’s Golden Rule based approaches cannot deal with this issue.⁴⁹ The proper description of the non-radiative decay demands a CI, reached by a progressive rotation around one double bond (θ_{DB}), or upon combining rotation and pyramidalization of one carbon atom.^{35,36} This was back then tested by rather facile TD-DFT calculations assisted by a multi-configurational wave-function analysis.²³ For the FC region, TD-DFT provides energies in reasonable agreement with the experimental values. For the CI region, E_{CI} of both α and β isomers were found to be identical at this level of theory, see Fig. 4;²³ while it is true that TD-DFT is conceptually wrong due to the adiabatic approximation to the exchange kernel and generally fails,⁵⁰ its energy was assumed to be a less decisive descriptor compared to the FC energy. Multi-reference methods, *i.e.* CASSCF/CASPT2, also support the hypothesis of using E_{FC} as main descriptor in the studied systems; as detailed elsewhere.⁴⁴

The multi-configurational wavefunction analysis at the CI indicates a localized character of the frontier molecular orbitals (MOs), where the LCAO coefficients⁵¹ of the highest occupied and lowest unoccupied MOs, *i.e.* HOMO and LUMO, are essentially located in the α and β C-atoms, respectively, see Fig. 4. This was proposed as a reason that could explain in

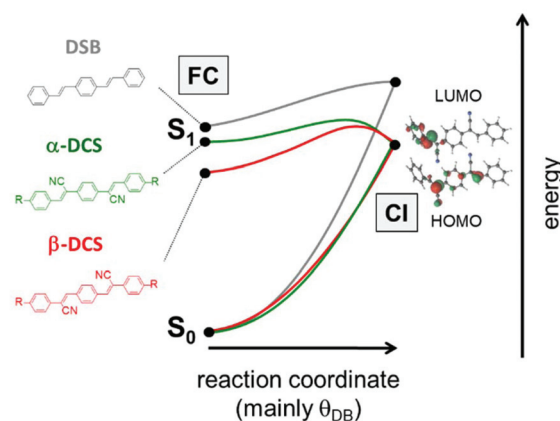


Fig. 4 Schematic potential energy surfaces for S_0 and S_1 α DBDCS (green) and β DBDCS (red) and DSB (grey) as a function of one double bond torsion θ_{DB} , starting from the Franck–Condon (FC; left) region ($\theta_{DB} = 180^\circ$) to the conical intersection (CI; right) at $\theta_{DB} = 90^\circ$; due to the underlying TD-DFT approach, the description of the CI region is only approximate (see text). Contour plots of the dominant MOs were obtained with the CASSCF method.²³

part the major role of the E_{FC} descriptor. It should be noted that the electronic situation at the CI gives further rise to a pronounced ICT character; this results in equal importance of internal conversion and inter-system crossing processes in the non-radiative decay path as it provokes a degeneracy of the lowest triplet state T_1 with S_1 and S_0 at the CI.²³

Assuming the CI energy and its dynamics as a minor-order descriptor, the access to the CI is expected to be mainly determined by the energy of the FC point E_{FC} , following the Bell–Evans–Polanyi principle (based on Hammond’s postulate), that is here a decrease of the activation barrier with increasing E_{FC} .⁵² The decisive difference between the luminescent β -isomers vs. the non-luminescent α -isomers is thus the lower FC energy of the β -compounds, $\Delta E_{FC}(\beta-\alpha) \approx -0.25$ eV, see Fig. 4. This stabilization is in part due to a less twisted geometry (-0.05 eV), but mainly due to an electronic effect, *i.e.* ‘enhanced resonance stabilization’ (ERS); the latter is caused by the enlarged number of zwitterionic resonance structures in the β - vs. the α -isomers.²³

Although, in a general view and according to the results, the predominance of the FC energy seems to be a good approximation in the studied systems, there are some specific cases for which regiospecific effects play a role (*e.g.* the meta-effect in stilbenes);⁴⁶ for instance, the β -compound **17** is lower emissive than its α -counterpart **6** (with anyway low Φ_F), going against the general trend. This is indeed reproduced by multi-configurational quantum chemistry which correctly describes the CI region; details are discussed in a separate paper.⁴⁴

The inverted energy gap law

The quantum-chemical study revealed that low FC energies within the DCS family inhibit the effective access to the CI through the high activation barrier, which rationalizes the experimentally observed ‘inverted energy gap law’. As we have seen in the beginning, this is contrary to the observation of DSB homologues $BnPV$ (without the presence of the cyano functionality) which follow the conventional energy gap law for $n > 1$; that is the increase of non-radiative decay with decreasing FC energy, *i.e.* with increasing chainlength n ; see Fig. 1.⁴¹ We emphasize that both DCS and $BnPV$ systems are ‘floppy’ due to the low energy torsional motions around the single bonds. The difference between the two systems is twofold; on the one hand, the presence of the acceptor strength of the cyano group stabilizes a zwitterionic structure which leads to a decrease of the CI energy;^{35,44} on the other hand, the DCS compounds exhibit significantly larger geometrical distortion in the S_1 state which arises from the sterical demand of the cyano group.^{22,53,54} Although this stress is somewhat released in S_1 compared to S_0 , the DCS compounds do not planarize in S_1 and reveal a longer bond length of the vinyl double bonds ($r_{DB} \approx 1.40$ Å) compared to DSB (1.38 Å).²³ Thus, similar to the case in stilbene,²⁰ the lability of r_{DB} in DCS opens the path towards the CI, while in DSB, the double bond twist becomes energetically costly, impeding an effective access to the CI, see Fig. 4. This further indicates that the hypothesis of the predominance of the FC descriptor vs. poss-

ible effects in the crossing region is only applicable to molecules in the same family (DCS isomers) but not to DSB due to the missing cyano-functionality, being decisive for k_{nr} .

3. Conclusions

In conclusion, our study on variously substituted DCS compounds gives a striking experimental example for the occurrence of an ‘inverted energy gap law’, *i.e.* the increase of non-radiative decay with the FC energy E_{FC} . This increase is rationalized as a first-step approximation by the decrease of the activation barrier on the deactivation path towards the conical intersection (CI) following the Bell–Evans–Polanyi principle; here, the variation of the CI energy between the different compounds is approximated to be much less pronounced than the variation in E_{FC} or even operating in the same direction. This allows indeed for qualitative predictions on emissive floppy DCS compounds by a simple rule, $E_{FC} < E_{CI}$, being a first example where a relatively complex photophysical concept is used for simple predictive molecular design. We emphasize, that our energetic argument might hold as all compounds of the DCS family display the identical cyano-stilbene motif, which is the operative unit for structural change on the path towards the CI.

Particularly high-emissive DCS compounds in solution are expected by cyano-substitution in the β -position (to make use of the ERS effect), combined with multi-substitution by strong donor (*e.g.* amino) groups in the central ring and the *para*-position of the terminal rings to achieve large bathochromic shifts *via* a push–pull effect; at the same time, strong sterical demands (*e.g.* by *ortho*-substitution) have to be avoided as they impose twists which shift the spectra hypsochromically. On the contrary, particularly low-emissive compounds are anticipated when utilizing the α -DCS motif adding such sterical demanding, however electronically ‘innocent’ groups (such as branched alkyl chains) in the *ortho*-positions. We expect that similar considerations hold for DCS-related families of stilbenoid compounds with other substituents than $-CN$ in the vinylene unit, which exhibit sterical demands (and a mesomeric effect) like, for instance, $-SO_2CF_3$.^{22,55}

Nevertheless, although the *qualitative* predictive power for multi-substituted DCS compounds was clearly evidenced, it should be stressed that *quantitative* statements on molecules’ emissivity are limited to compounds where specific solute–solvent interactions (polarity and viscosity) are of (very) minor importance; this concerns in particular chromophores without polar or push–pull functionalities. For the latter compounds, quantitative predictions of Φ_F would require an exhaustive theoretical treatment of the CI including specific solute–solvent interactions by (multi-reference) quantum mechanics/molecular mechanics (QM/MM)-based approaches;^{56,57} this is still out of reach for fast materials screening.

We emphasize that the current findings can be crucial for the design of SLE-active compounds for luminescent organic solids. In general, solid environments (*i.e.* solid or frozen solu-

tions, as well as aggregated molecules in films, nanoparticles or crystals) suppress large amplitude motions, which restricts the access to the CI (RACI mechanism) and give rise to SLE.^{33,34,58} This however depends critically on the environment (for instance when embedded in polymers with substantial free volume)²³ as well as on the sterical demands of side chains attached to the molecular backbone, which may allow for residual large amplitude motions. Thus, by the right choice of substitution pattern, virtually low emissive DCS molecules become highly emissive in molecular solids under trap-free conditions,⁵ *i.e.* in single crystals, even for H-aggregates.^{6,23} Even more, highly luminescent H-aggregates can be realized in polycrystalline thin films if high structural integrity and small exciton coupling is ensured by proper molecular design.^{59,60}

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The work in Madrid and Valencia was supported by the Spanish Ministerio de Economía y Competitividad (MINECO-FEDER project CTQ2017-87054); the work in Madrid was further supported by for the Centers of Excellence in R&D program of the MINECO (SEV-2016-0686) and by the Campus of International Excellence (CEI) UAM + CSIC. The work at Seoul National University was supported in parts by the Creative Research Initiative Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT & Future Planning (MSIP; Grant No. 2009-0081571 [RIAM0417-20170011] and by Basic Science Research Program through the NRF funded by the Ministry of Science, ICT and Future Planning (Grant No. 2017R1E1A1A01075372 [RIAM0417-20190019]). D. R.-S. acknowledges the “Ramón y Cajal” grant (RYC-2015-19234) of the MINECO. This work is also part of a European Joint Doctorate (EJD) in Theoretical Chemistry and Computational Modelling (TCCM), financed by the European Commission (ITN-EJD-642294-TCCM). J. S. acknowledges a grant of the Chinese Scholarship Council (CSC).

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