SUPPORTING INFORMATION: Disentangling vibronic and solvent broadening effects in the absorption spectra of coumarin derivatives for dyes sensitized solar cells

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S.1 Validation of the computational protocols

Evaluation of the limitations of harmonic models comparing AH and VH results

Given the larger temperature effect in nkx-2753 compared with the other dyes, we investigate a possible failure of the harmonic approximation for this molecule. To that end, we simulate the vibronic spectra using the AH model with normal modes in both Cartesian (AH-Cart) and internal (AH-int, the one utilized through this study) coordinates, and using the Vertical Hessian (VH) model in Cartesian coordinates. The simulations at 0 and 300 K are shown in Figure S1 and they show that, at room temperature, AH-Cart model predicts a spectrum larger than the ones obtained with AH-int and VH models, which closely resemble each other. This behavior normally indicates a partial failure of Cartesian coordinates to describe large displacements of normal modes between GS and ES minima.¹ . For all the other molecules, both AH-Cart and AH-int give practically the same results. Given the similar structure of nkx-2586 and nkx-2753, the larger temperature effect for nkx-2753 might indicate an overestimation of the displacement between GS and ES minima in that molecule. Moreover, the prediction of such a large vibrational broadening should further be checked including anharmonic effects not considered in the present work.



Figure S1 – Computed vibrationaly resolved absorption spectra for nkx-2753 in EtOH at 0K and 300K using (TD)CAM-B3LYP PES and the Adiabatic Hessian model in Cartesian (AH-Cart) and internal (AH-int) coordinates and the Vertica Hessian (VH) model. In the latter 3 imaginary frequencies arise. Spectra convoluted with a Gaussian with HWHM=0.01 eV.



Figure S2 – Computed vibrationaly resolved absorption spectra for c343 in EtOH at 0K using the TI and TD formulations to compute the lineshape. A convergence of 0.998 was achieved for the TI calculation using $N_{Max}^I = 10^9$ (see ref. 2 for details). The TD was performed with a correlation function evaluated from -1 ps to 1 ps, with a timestep of 0.24 fs. Spectra convoluted with a Gaussian with HWHM=0.01 eV.

S.2 HOMO-LUMO orbitals for all the transitions

Table S1 – Contour plots (isovalue=0.02) for the HOMO and LUMO orbitals of all the dyes computed at CAM-B3LYP/6-31G(d) level. Note that all the spectroscopic trantions treated in this work correspond to $H \rightarrow L$ ones.

Dye	НОМО	LUMO
c343		
nkx-2311		
nkx-2398		
nkx-2586		
nkx-2753		

S.3 Different protomers for c343

Figure S3 of this SI shows the two most stable protomers of c343 and their relative internal energy according to PBE0/6-31G(d) calculations in EtOH.



Figure S3 – Protonation isomers of C343 investigated and their relative energy. The enthalpy and free energy of the reaction at 298 K are: $\Delta H^0 = -6.1 \text{ kcal mol}^{-1}$ and $\Delta G^0 = -5.5 \text{ kcal mol}^{-1}$. Both CAM-B3LYP/6-31G(d) and PBE0/6-31G(d) provide the same results.

S.4 On the analysis on the effect of CT character on the PBE0 results

As discussed in the main text, PBE0 simulations deliver vibronic shapes of similar size for all the studied dyes (see also Figures S7 and S8). The larger progressions observed with CAM-B3LYP are related with C=C stretching modes, and they result from the bond length alternation in the conjugated chain from the ground to the excited state, which is connected to the $\pi \rightarrow \pi^*$ transition. In the case of PBE0, such bond order alternation is notably reduced and, consequently, the C=C progression is limited to only the first overtone, which eventually results in much narrower lineshapes. The differences between either the GS or the ES PES predicted by the two functionals can be conveniently monitored considering the Franck-Condon integral between their ground vibrational states (FC^{GS}₀₀(PBE0,CAM) and FC^{ES}₀₀(PBE0,CAM), see Table S2. In all the systems, FC^{GS}₀₀ integrals are larger than FC^{ES}₀₀ ones. Concretely, FC^{GS}₀₀ is above ~0.9 for all dyes, with the notable exception of nkx-2753, for which it drops to 0.80, pointing out a significant difference between the GS minimum computed with PBE0 and CAM-B3LYP. Regarding FC^{ES}₀₀ the values lie well below 0.9 for all the dyes, highlighting significant differences between the ES PES predicted by PBE0 and CAM-B3LYP, that increase for larger dyes.

Let us describe now the differences revealed by the FC integrals more in detail. We

Table S2 – Franck-Condon integrals (FC) between vibrational ground states for the optimized structures computed at PBE0 and CAM-B3LYP functionals. The integrals for both the ground state (GS) and excited state (ES).

Dye	FC(GS)	FC(ES)
C343	0.98	0.82
nkx-2311	0.92	0.80
nkx-2398	0.95	0.86
nkx-2586	0.89	0.73
nkx-2753	0.80	0.73

first focus on the low FC_{00}^{GS} value for nkx-2753; this actually reports significant differences between C=C (and C-C) bond lengths along the conjugated chain, with C=C being significantly shorter for the CAM-B3LYP minimum. Such difference is smaller for nkx-2586, despite the structural similarity with nkx-2753, suggesting that for nkx-2753, either CAM-B3LYP or PBE0 are providing erroneous results, which we will discuss later. The smaller values for FC_{00}^{ES} are also related to differences between C=C and C-C bond lengths along the conjugated chain, with C=C being larger, in this case, for CAM-B3LYP. Interestingly, the geometrical differences between ES minima can be explained resorting to the well known limitations of standard hybrid GGAs to describe charge transfer (CT) states.³ In order to better understand the different results obtained with the two functionals, we performed the CT analysis proposed by Le Bahers, Adamo and Ciofini⁴ with the CT program by Jacquemin.⁵ In this model, the CT character is described in terms the difference density from the initial to the final state, through the definition of three parameters: the amount of charge transfered Q_{CT}, computed as the integral of the positive part of the density), the displacement of the charge D_{CT} , obtained by the distance between the barycenters of the negative and positive regions, and the dispersion index (H_x, H_y, H_z) accounting for the spread of each region.⁴ Large values of Q_{CT} and D_{CT} indicate a high CT character, and it is also relevant that both negative and positive density regions do not overlap excessively, which is approximately achieved when $D_{CT} > H_{\xi}$ (being ξ the axis connecting the barycenters). The picture arising from the CT analysis is illustrated in Figure S4 (the actual parameters are reported in Table 1 in the main text) showing that the CT character increases with the size of the dye, i.e., it is higher for the dyes with larger conjugated chain (nkx-2586 ad nkx-2753) and, consequently, the change of dipole moment is also larger. Moreover, for all the dyes the CT character decreases significantly from the FC geometry to the ES minimum. Taking into account that hybrid GGAs (such as PBE0) incorrectly over-stabilize states with CT character, such spurious over-stabilization will depend on the conformation, thus introducing a bias on the ES PES that affect the position of the minimum on the PES. As a consequence, the bond order alternation from GS to ES is remarkably lower for PBE0 and, consequently, the vibrational progressions associated to the C=C stretching modes is reduced. Compared with the experiments,^{6–9} CAM-B3LYP vibrational broadening are in much better agreement, thus supporting the adequacy of this functional over PBE0.



Figure S4 – Baricenters of the positive (i.e. electronic charge increment, orange) and negative (i.e. electronic charge depletion, blue) parts of the difference of GS and ES densities ($\rho_{ES} - \rho_{GS}$), as defined by the CT model by Le Bahers, Adamo and Ciofini, using CAM-B3LYP (left) and PBE0 (right). The results at both the GS minimum (solid balls) and ES minimum (semi-transparent balls) are shown.

S.5 Comparison of spectra in gas-phase and EtOH according to PBE0 and CAM-B3LYP predictions

In general, the spectra computed in gas phase (GP) and ethanol (EtOH) are quite similar, both with PBE0 (Figures S7 and S8) and CAM-B3LYP (Figures S5 and S6) functionals. Going into further details, it is observed that for the smaller dyes (c343 and nkx-2398), GP spectra are slightly larger than EtOH ones, for both PBE0 and CAM-B3LYP. On the other hand, for the larger dyes (nkx-2586 and nkx-2753), the EtOH spectrum is larger than the GP one, and this is again observed with both functionals, although for CAM-B3LYP the differences seem to be more noticeable. For the intemediate-sized dye, nkx-2311, both EtOH spectrum is only slightly larger that GP one. These effects are more evident at 300 K, but they are already appreciable at 0 K.



Figure S5 – Computed vibrationaly resolved absorption spectra for the 5 coumarins under study at 0K in gas phase (top) and in EtOH (bottom), using the CAM-B3LYP functional. Spectra convoluted with a Gaussian with HWHM=0.02 eV.



Figure S6 – Computed vibrationaly resolved absorption spectra for the 5 coumarins under study at 300K in gas phase (top) and in EtOH (bottom), using the CAM-B3LYP functional. Spectra convoluted with a Gaussian with HWHM=0.02 eV.



Figure S7 – Computed vibrationaly resolved absorption spectra for the 5 coumarins under study at 0K in gas phase (top) and in EtOH (bottom), using the PBE0 functional. Spectra convoluted with a Gaussian with HWHM=0.02 eV.



Figure S8 – Computed vibrationaly resolved absorption spectra for the 5 coumarins under study at 300K in gas phase (top) and in EtOH (bottom), using the PBE0 functional. Spectra convoluted with a Gaussian with HWHM=0.02 eV.

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