## **SUPPORTING INFORMATION**

## Benchmarking TD-DFT against vibrationally-resolved absorption spectra at room temperature: 7-aminocoumarin molecules as test cases.

Francesco Muniz-Miranda,<sup>a</sup> Alfonso Pedone, <sup>\*,a</sup> Giulia Battistelli, <sup>b</sup> Marco Montalti, <sup>b</sup> Julien Bloino, <sup>\*c</sup> Vincenzo Barone.<sup>d</sup>

(a) Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia, viaG. Campi 183, Modena, 41125, Italy.

(b) Dipartimento "G. Ciamician", Università di Bologna, 40126 Bologna, Italy.

(c) Consiglio Nazionale delle Ricerche, Istituto di Chimica dei Composti OrganoMetallici (ICCOM-CNR), UOS di Pisa, Area della Ricerca, via G. Moruzzi 1, I-56124 Pisa, Italy
(d) Scuola Normale Superiore di Pisa, Piazza dei Cavalieri 7, Pisa, 56126 Italy.



Figure S1. Kohn-Sham HOMOs and LUMOs of the investigated 7-aminocoumarin molecules.



**Figure S2.** Computed  $\omega$ B97X spectra of C450 and C480 in methyl-cyclohexane (upper panels) and acetonitrile (lower panels). The normal case numbers represent the excited normal modes and the superscripts the number of quanta involved in the excitation (they are omitted if just one normal mode is excited by just one quantum). Computed spectra in methyl-cyclohexane of C450 and C480 are shifted by +44 and -3 nm, respectively, in order to obtain the best match with the maxima of the experimental spectra. The computed spectra in acetonitrile are shifted by the same amounts. These spectra have been computed at zero temperature.





**Figure S3.** Normal modes of the  $S_1$  electronic state of C307 in methylciclohexane, at the  $\omega$ B97x level of theory



Figure S4. Normal modes of the  $S_1$  electronic state of C460 in methylciclohexane, at the  $\omega$ B97x level of theory.

## Analysis of the vibronic band-shapes at the ωB97X and LC-PBE levels for C307

In order to understand the differences between the LC-PBE and  $\omega$ B97X band-shapes for C307, a first step is the analysis of the Duschinsky transformation, and in particular the Duschinky matrix. The latter obtained at the AH|FC level is graphically depicted in **Figure S5**. The matrices are rather similar with the  $\omega$ B97X one slightly more compact than the LC-PBE one, which means a lesser mode mixing upon the electronic transition for the former. Indeed, if the mode mixing is ignored (model AS|FC), the  $\omega$ B97X band-shape, shown in **Figure S6**, is nearly unaltered, while the LC-PBE one is more impacted, with the relative intensity of the lower-energy band strongly enhanced. As a result the representation of the potential energy surfaces, and so the mode mixing, is not the main reason for the lower performance of  $\omega$ B97X in the case of C307.



**Figure S5**: Graphical representation of the Duschinsky matrix of C307 at the AH|FC level computed with the LC-PBE (left) and  $\omega$ B97X (right) functionals in methylcyclohexane. Each square corresponds to a squared element of the Duschinsky matrix, J(i,k)<sup>2</sup>. The value of gray is chosen to match the magnitude of the term (0: white, 1: black).



**Figure S6**: Vibronic spectra of C307 at the AH|FC (solid lines) and AS|FC (dashed lines) levels with the LC-PBE and  $\omega$ B97X functionals, compared to experiment, simulated at T=300K in methylcyclohexane. Gaussian distributions with half-widths at half-maximum of 405 cm<sup>-1</sup> were used to simulate the broadening observed experimentally.

At variance, the shift vectors obtained at the AH|FC level with the two methods and represented in **Figure S7** show significant discrepancies, in particular with the lower-energy modes. Since the shift vectors are directly related to the difference in geometries between the two states involved in the electronic transition, a comparison of their shape hints at a stronger distortion at the  $\omega$ B97X level. In order to analyze the effects of the various contributions of the data used for the simulation of the vibronic band-shape, two hybrid schemes have been employed. In "HybFreq", the basis are the LC-PBE data but the frequencies are those obtained with  $\omega$ B97X, so the electronic transition energy, the geometries and the normal modes remain those from LC-PBE. In "HybGeom", the starting point are the  $\omega$ B97X data but the geometries are those from the LC-PBE calculations. Thus, the difference

between the two hybrid schemes are the electronic transition energies and the normal modes. As expected from the similarity of the Duschinsky matrix, the two band-shapes, shown in **Figure S8**, are very similar, with the main difference being the shift of the overall band. Moreover, the correction of the geometries (HybGeom) is sufficient to improve significantly the agreement of the  $\omega$ B97X bandshape with its experimental counterpart.



**Figure S7**: Graphical representation of the shift vector of C307 at the AH|FC level computed with the LC-PBE (left) and  $\omega$ B97X (right) functionals in methylcyclohexane. Positive displacements are shown in clear blue and negative displacements in bright red. Mass weighted displacements along each normal coordinate are given in atomic units (m<sub>e</sub> represents the atomic unit of mass).



**Figure S8**: Vibronic spectra of C307 at the AH|FC level with the LC-PBE and  $\omega$ B97X functionals, compared to experiment, simulated at T=300K in methylcyclohexane. "HybFreq" and "HybGeom" are hybrid models combining data from both functionals. See text for details. Gaussian distributions with half-widths at half-maximum of 405 cm<sup>-1</sup> were used to simulate the broadening observed experimentally.