

Choosing a Functional for Computing Absorption and Fluorescence Band Shapes with TD-DFT

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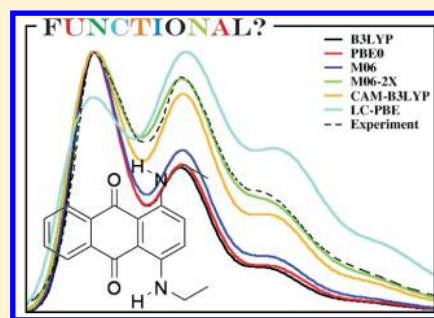
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S Supporting Information

ABSTRACT: The band shapes corresponding to both the absorption and emission spectra of a set of 20 representative conjugated molecules, including recently synthesized structures, have been simulated with a Time-Dependent Density Functional Theory model including diffuse atomic orbitals and accounting for bulk solvent effects. Six hybrid functionals, including two range-separated hybrids (B3LYP, PBE0, M06, M06-2X, CAM-B3LYP, and LC-PBE) have been assessed in light of the experimental band shapes obtained for these conjugated compounds. Basis set and integration grid effects have also been evaluated. It turned out that all tested functionals but LC-PBE reproduce the main experimental features for both absorption and fluorescence, though the average errors are significantly larger for the latter phenomena. No single functional stands out as the most accurate for all aspects, but B3LYP yields the smallest mean absolute deviation. On the other hand, M06-2X could be a valuable compromise for excited-states as it reproduces the 0–0 energies and also gives reasonable band shapes. The typical mean absolute deviations between the relative positions of the experimental and theoretical peaks in the vibrationally resolved spectra are ca. 100 cm⁻¹ for absorption and 250 cm⁻¹ for emission. In the same time, the relative intensities of the different maxima are reproduced by TD-DFT with a ca. 10–15% accuracy.



1. INTRODUCTION

The extension of Density Functional Theory (DFT) to the time-dependent domain, namely Time-Dependent Density Functional Theory (TD-DFT), originally proposed by Runge and Gross in 1984,¹ has become a very popular approach for modeling the energies, structures, and properties of electronically excited-states (ES). This success is related to the development in 1995 of the linear-response (LR) TD-DFT formalism by Casida² and the efficient implementations of the TD-DFT equations.^{3–6} One can find a large series of reviews, books, special issues, or perspective articles related to both fundamental and applied aspects of TD-DFT.^{7–29} Though TD-DFT is formally an exact theory, it is based on the adiabatic approximation (frequency independence) and also requires the selection of an exchange-correlation functional (XCF), both limiting its accuracy. During the past decade, the selection of an adequate XCF for modeling ES properties has been the subject of several benchmarks performed on a wide panel of systems.^{30–51} Though several general conclusions have been obtained, e.g., the superiority of hybrid functionals compared to pure XCF as well as the need of range-separated hybrids to describe charge transfer states, the “best” XCF for TD-DFT is not yet the subject of a large consensus. Indeed, there is a specific difficulty to TD-DFT benchmarks making the applied

protocol a possible issue: it is not straightforward to have reliable reference values. Indeed, on the one hand, accurate wave function approaches (e.g., MR-CI, CAS-PT2...) are not applicable on large molecules due to their unfavorable scaling with molecular size, and, on the other hand, optical spectra of industrially meaningful compounds are often measured in condensed phase making the accurate simulation of environmental effects a necessary prerequisite to XCF testing.

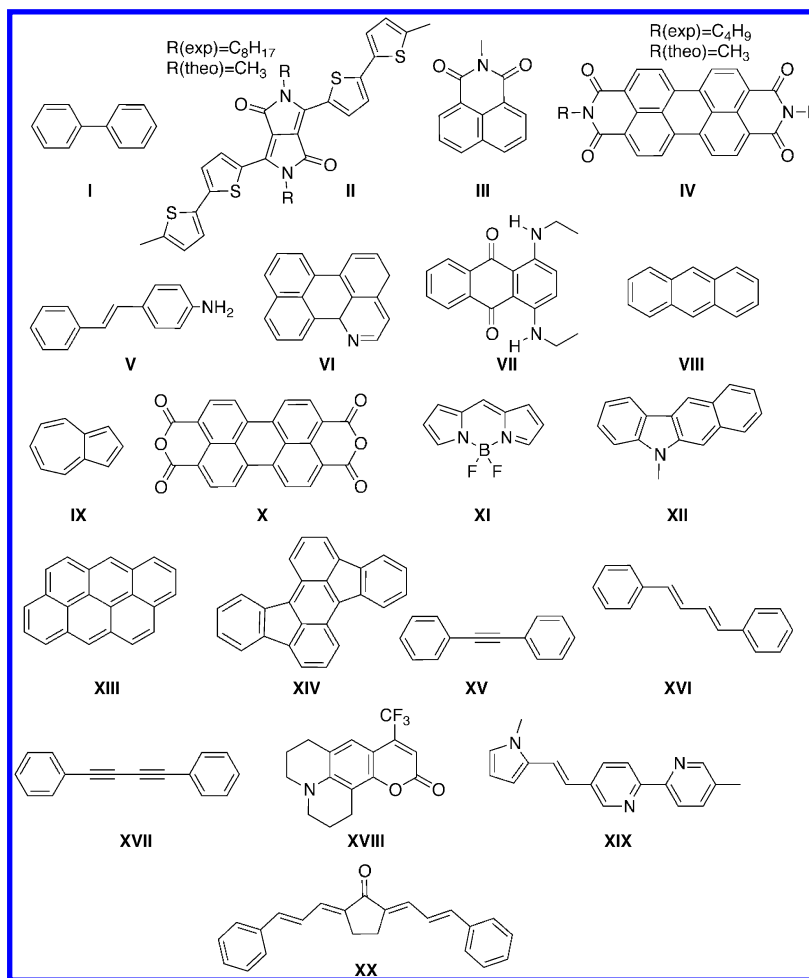
Today, a large majority of TD-DFT applications are (still) performed within the so-called vertical approximation. In this framework one estimates the ES energies (and related properties) using the optimal ground-state (GS) geometry, without exploring the ES potential energy surface. This approximation has the advantage to allow calculations on very large systems, as a “single-point” TD-DFT calculation is performed. However, comparing vertical transition energies to experimental measurements of λ_{max} is not a well-grounded approach.^{49–51} If one wishes to obtain more meaningful theory/experiment comparisons, one should compute the 0–0 energies and/or the band shapes. Both require the determination of the vibrational normal modes of the ES and therefore

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Scheme 1. Representation of the Investigated Molecules



the numerical or analytic calculation of the TD-DFT Hessian. Due to the joint increase of computing power and implementation of TD-DFT derivatives in several widely available codes,^{32,52–55} a series of studies going beyond the vertical approximation have appeared recently.^{30,38,41,49–51,56–85} This has led to a quite thorough series of 0–0 benchmarks where accurate experimental gas-phase 0–0 values (for small molecules) or measured absorption/fluorescence crossing points (for large compounds) have been compared to 0–0 TD-DFT estimates obtained with several XCF.^{30,38,41,49–51,81} Several procedures and molecular sets have been used to perform these 0–0 TD-DFT simulations, so that there is probably no need of discussing them in the present paper (A summary of the results of these works can be found in one of our previous publications, see ref 51.). However, there are much fewer works that have been focused on the accurate description of band shapes for a large set of diverse compounds, and this paper aims to fill this gap. To simulate the topology of the bands, one needs not only to compute the vibrational signatures of both GS and ES but also to determine the Franck–Condon factors (vibronic) coupling these two states. Although there exist several specific benchmarks (one or two molecules with several functionals of vice versa) performed for vibronic shapes,^{49,59–63,65,66,70,73,75,77–79,82,86} the most significant investigation to date remains, to the best of our knowledge, the 2004 study of Dierksen and Grimme.⁴⁹ These authors investigated the absorption spectra of 43 organic

molecules (both closed-shell and radical species, mainly aromatic derivatives) using three XCF (BP86, B3LYP, and BH&HLYP). At that time, solvent models for the TD-DFT geometrical derivatives were not available, and the authors performed their investigation in gas phase and focused their work on absorption spectra (no emission spectra are reported in ref 49.). Dierksen and Grimme concluded that “no universal amount of EXX seems to exist that gives a uniformly good description for all systems and states. Nevertheless an inclusion of about 30–40% of EXX in the functional is found empirically to yield in most cases simulated spectra that compare very well with those from experiment”. Since that time, not only TD-DFT gradients became available in combination with continuum models,⁵³ such as the Polarizable Continuum Model (PCM),⁸⁷ but also more “modern” functionals have appeared, such as the M06 Minnesota series⁸⁸ and range-separated hybrids.^{89–93} They obviously deserve an adequate assessment in the framework of vibronic simulations. Indeed, while several recent works have indicated that these new advancements are beneficial for mimicking experimental spectra, others pointed out that the standard B3LYP scheme remains the most appropriate, that is, conflicting conclusions have been reached. For instance, for aza-BODIPY and anthraquinone dyes,^{73,82} we found that the BMK⁹⁴ and ω B97X-D XCF,⁹⁵ respectively, provide very realistic band shapes, though standard hybrids, e.g. B3LYP or PBE0, remained reasonably satisfying. For the challenging dithiophene case, Stendardo et al. found that the

Table 1. List of Solvents Used and Experimental References

molecule	solvent	ref	molecule	solvent	ref	molecule	solvent	ref
I	cyclohexane	111	VIII	gas	109	XV	ethanol	111
II	dichloromethane	121	IX	cyclohexane	114	XVI	hexane	111
III	dioxane	116	X	dimethylsulfoxide	113	XVII	ethanol	111
IV	dimethylformamide	122	XI	methanol	117	XVIII	methylpentane	118
V	hexane	112	XII	ethanol	110	XIX	hexane	119
VI	acetonitrile	120	XIII	benzene	110	XX	cyclohexane	115
VII	cyclohexane	123	XIV	benzene	110			

vibrational structure was accurately reproduced by PBE0 and CAM-B3LYP, whereas other tested functionals (BLYP, B3LYP, and BHLYP) provided a poorer match with experiment.⁷⁹ On the contrary, for the small and rigid phenylacetylene, B3LYP was reported to be more accurate than both LC-BLYP and CAM-B3LYP (for vibronic couplings).⁷⁸ Santoro and co-workers have adopted PBE0 to compute vibrationally resolved spectra of several systems, including anthracene, coumarin, porphyrin, pyrazine, and uracil:^{59–62,84} in combination with the 6-31G(d) basis set, they obtained a reasonably accurate reproduction of the experimental data in most cases. However, as stated by the authors themselves, the goal of these investigations was to develop and validate efficient vibronic approaches, rather than benchmarking XCF. Obviously, additional investigation(s) using modern XCF to simulate vibronic shapes of a large set of compounds would be welcome to reach general conclusions, and this paper is in this vein of research.

Here, we investigate the shape of the absorption and emission spectra of the molecules depicted in Scheme 1. We have tried to select “real-life” molecules, including one anthraquinoidic dye that is of industrial importance, one coumarin and one BODIPY that stand as two of the most efficient emitters, and a member of the diketopyrrolopyrrole family that has become increasingly popular in solar cell applications. Several of the dyes sketched in Scheme 1 have been synthesized during the past decade. Note that, at the exception of XVIII, the states investigated here are mainly localized valence excited-state and do not present a strong charge-transfer character. To allow meaningful comparisons of band shapes with experiment, we have selected molecules presenting a significant structure in their optical spectra (i.e., we eliminated bell-shaped spectra) and tried to consider systems for which both absorption and emission spectra are experimentally known.

2. METHODOLOGY

The general methodological framework applied here follows our recent ref 51, and we only briefly summarize the protocol. All calculations have been performed with the Gaussian09.A02 revision,⁹⁶ using six functionals: B3LYP,^{97,98} PBE0,^{99,100} M06,⁸⁸ M06-2X,⁸⁸ CAM-B3LYP,⁹⁰ and LC-PBE^{101,102} that have been shown to be effective in recent TD-DFT benchmarks.^{36,38,40,42,46,51,103,104} We underline that the selected LC-PBE implementation uses an attenuation parameter of 0.47 corresponding to the 2007 parametrization,¹⁰² rather than the original 2001 value of 0.33.¹⁰¹ Several atomic basis sets (BS) have been tested (see below), and it was shown that 6-31+G(d) is sufficient for our purposes, and this diffuse containing basis set was applied in the following except when noted. We have also mainly used the Euler-Maclaurin integration “fine” grid constituted of 75 radial and 302 angular points. In the few

cases, where convergence could not be achieved with this “fine” grid, a tighter (99,590) “ultra fine” grid has been applied. Of course, for a given molecule, the same grid was systematically used for both GS and ES. The influence of the integration grid can be potentially significant¹⁰⁵ and has also been studied (see below). The GS and ES geometries have been determined with the Berny-GEDIIS algorithm,¹⁰⁶ using a 1×10^{-5} a.u. threshold for the rms force (tight keyword in Gaussian). To ensure a valid description of the geometric and vibrational features, we used an energy convergence threshold of at least 1×10^{-9} a.u. The force minimizations have been performed thanks to the analytical DFT and TD-DFT gradients available for the GS and ES, respectively.^{30,52,53,107} The GS and ES vibrational frequencies have been computed using analytical and numerical derivatives, respectively. For modeling solvent effects, we have used the PCM scheme,⁸⁷ in combination with cavities obtained by selecting the G09 defaults (VDW cavities based on UFF radii scaled by 1.1). Discussions of the relationships between the PCM parameters and the computed ES properties can be found elsewhere.^{75,108} We have applied the LR-PCM model, the only one available for TD-DFT derivatives, using the equilibrium limit that corresponds to a relaxed solvent and is an adequate choice for determining vibrational signatures. We have used the same solvents as in the experiment (see Table 1).^{109–123}

Starting from the harmonic vibrational spectra of the GS and ES determined with Gaussian09, the vibrationally resolved spectra were computed using the FCclasses program.^{59,61,62} The reported spectra have been simulated using a convoluting Gaussian functions presenting a half width at half-maximum (HWHM) that has been adjusted to allow meaningful comparisons with experiments (typical value: 0.04 eV). A maximal number of 25 overtones for each mode and 20 combination bands on each pair of modes were included in the calculation. The maximum number of integrals to be computed for each class was set to 10^6 except when the obtained FC factor was too small (see discussion in 3.2). Indeed, FCclasses is one of the most effective codes for computing vibrationally resolved spectra: it allows obtaining a converged spectra for a relatively modest computing time. FCclasses uses the Franck–Condon approximation^{124,125} and selects only relevant vibronic contributions. Here it is mostly applied within the harmonic approximation for both initial and final states. In fact, different harmonic models are possible, namely the vertical and adiabatic schemes (VH and AH in ref 84). These two schemes provide the same description of the PES of the initial state but differ for its final counterpart. In VH, the PES of the final state is built only from the initial state data, i.e. the expansion of the PES of final state is performed around the equilibrium geometry of the initial state. In contrast, in the AH approximation that we used here, one expands the PES of the final state around its equilibrium geometry. A complete comparison between these

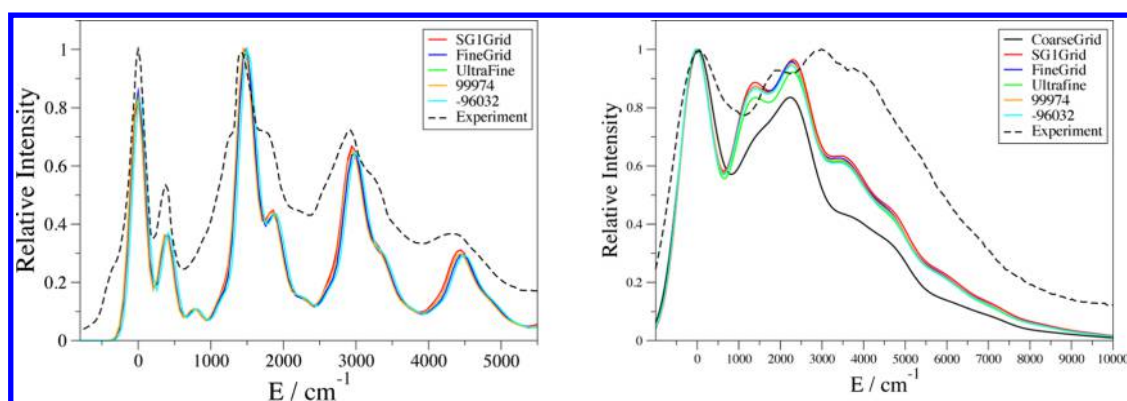


Figure 1. Left: comparison of the experimental¹⁰⁹ and computed absorption spectra for **VIII**. Right: comparison of the experimental¹¹¹ and computed fluorescence spectra for **XV**. All calculations at the M06-2X/6-31+G(d) level.

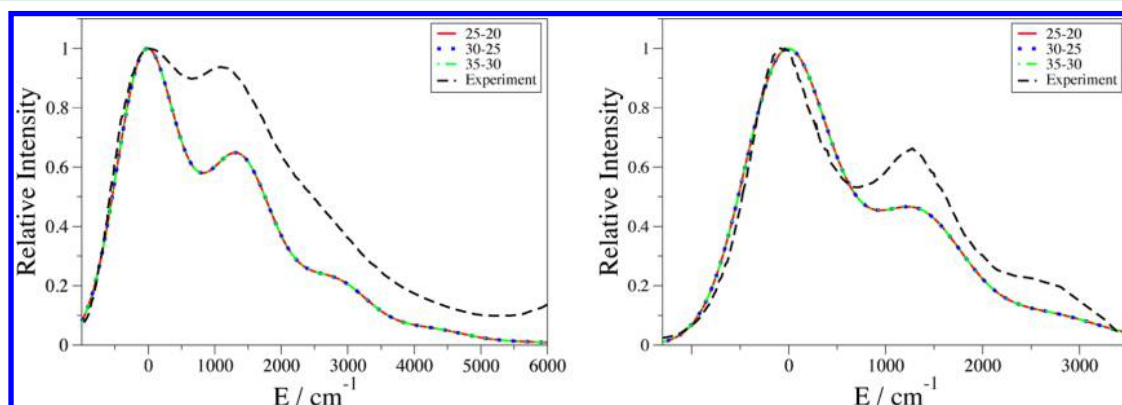


Figure 2. B3LYP/6-31+G(d) absorption (left) and emission (right) spectra computed for **III**. The maximal number of integrals has been set to 10^8 in each cases. The experimental curves taken from ref 116 are given as well.

two models has been performed recently,⁸⁴ and it was shown that the two schemes provide completely similar results.

As we do not aim to evaluate the performances of the six XCF in reproducing the 0–0 energies, we have systematically set the first (absorption or fluorescence) band to zero and evaluated both the relative intensities of all maxima and the energies of the following peaks in order to quantify the accuracy of each XCF. The fluorescence spectra were mirror-transformed to allow easy comparisons with the corresponding absorption. Note that in the following, the experimental fluorescence spectra measured in the wavelength scale have been transformed in line shapes by applying an intensity correction proportional to ω^2 ,¹²⁶ as this correction—that allows consistent theory/experiment comparisons—significantly affects the band shapes.¹²⁷ Other renormalization effects have been discussed recently by Santoro and co-workers¹²⁷ and have been shown to have a negligible impact. The experimental data have been taken in a series of publications (see Table 1).^{109–117,119–123} The “raw” data are listed in Section S-1 in the SI.

3. RESULTS

3.1. Integration Grids. In this first step, we have evaluated the interplay between the applied integral grids and the obtained vibronic spectra. Overall, we have found that the default Gaussian09 integration grid to be sufficient. This is illustrated in Figure 1 for the absorption of **VIII** and emission of **XV**,^{109,111} that are small enough to allow the application of very extended grids (the absorption of **XV** can be found in

Figure S-1 in the SI). We have used the M06-2X functional, that is known to be one of the most grid-sensitive XCF,¹⁰⁵ in combination with the 6-31+G(d) basis set. We have tested 6 increasingly accurate grids, namely, coarsegrid, SG1grid, finegrid, ultrafinegrid, and 99974 and –96032 grids (see the manual of ref 96 for details). From Figure 1, it is quite obvious that the very loose coarse grid is not adequate: it does not allow convergence of the ES calculations for **VIII** and is significantly off the results of larger grids for the fluorescence of **XV**. By contrast, all other tested grids provide similar estimates: the positions and the heights of all peaks are not only comparable to experiment but also unaffected by the selected grid. Apparently, even a rather small grid, e.g., the SG1grid, could provide a sufficient accuracy. Therefore, the default fine G09 grid is undoubtedly adequate for the purposes of the present study.

3.2. FC Convergence. It is important to ascertain the convergence of FC calculations. First of all, in the output of the FCclasses program,^{59,61,62} we have checked that the determinant of the transformation matrix is close to 1. The values can be found in the SI for both B3LYP and CAM-B3LYP, and the smallest determinant obtained is 0.991 (Table S-XXI). In the same time, FC_{00} , the overlap between the ground vibrational states of the initial and final states should exceed 10^{-4} , and the smallest value computed is 2 orders of magnitude larger (0.013 for **II** with CAM-B3LYP, see Table S-XXII). Only one borderline case could be detected: the emission of **I** (that goes from a twisted ground-state to a planar excited-state) and its has been removed from the statistics presented below to

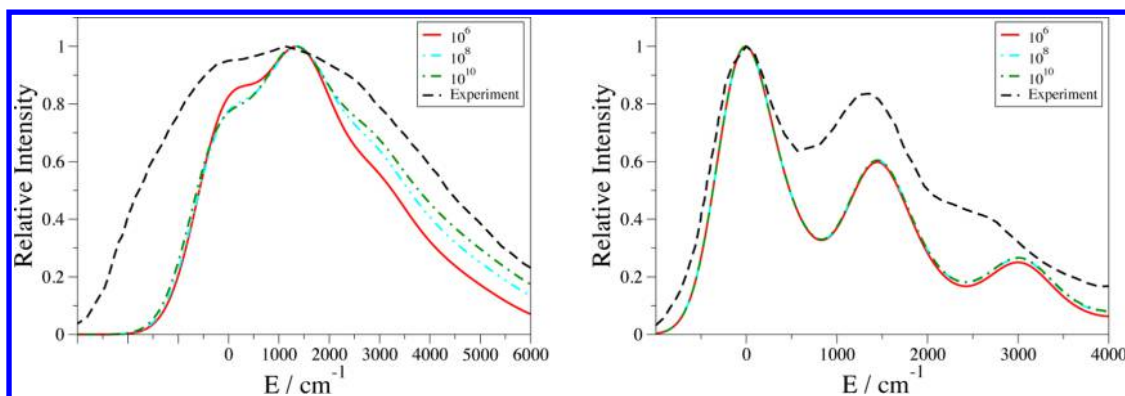


Figure 3. PBE0/6-31+G(d) absorption spectra computed for **V** (left) and **XII** (right), as a function of the maximal number of integrals used. The corresponding emission spectra can be found in the SI.

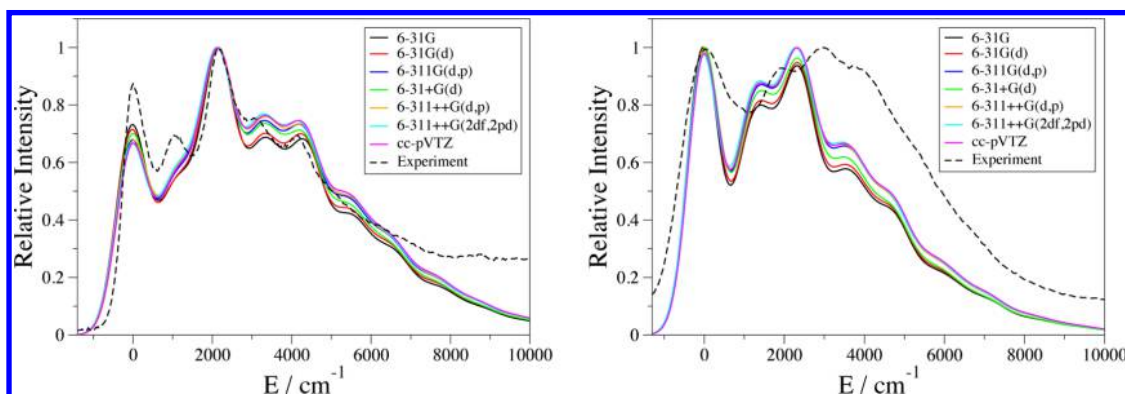


Figure 4. Comparison between CAM-B3LYP absorption (left) and emission (right) spectra of **XV** computed with several atomic basis sets and the fine integration grid. Experimental data taken in ref 111.

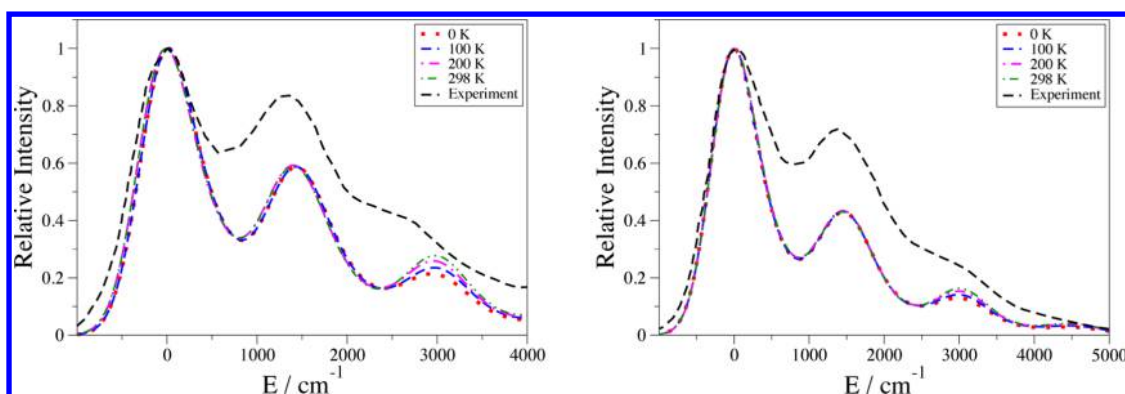


Figure 5. Absorption (left) and emission (right) spectra for **XII** computed at different temperature. The experimental spectra are taken in ref 110. All calculations at the B3LYP/6-31+G(d) level.

avoid pointless discussion. For all other molecules, there is no doubt that the FC calculations are meaningful.

In a second step, we have checked that the numbers of overtones (25) and combination bands (20) are sufficient. Two representative examples are shown in Figure 2. As can be seen, increasing these limits to larger values does not impact the simulated curves. This outcome seems to be general for the systems investigated herein, though of course, for very complex structures, more overtones and/or combination bands might become necessary.

On top of that the computed FC factor should be large to obtain valid convoluted spectra. For the majority of molecules, using 10^6 integrals is sufficient to obtain a FC factor larger than

0.9. This value is known to be sufficient to obtain converged spectra.^{59,61,62} This is illustrated in the right panel of Figure 3 for **XII**. The selection of 10^6 (FC=0.955), 10^8 (FC=0.989), and 10^{10} (FC=0.998) integrals yields nearly exactly the same band shapes, with only a very slight increase of the height of the third peak. On the contrary for **V** (left panel of Figure 3), the FC factor is only 0.715 with 10^6 integrals, and the shape evolves when using 10^8 (FC=0.860) and 10^{10} (FC=0.934) integrals. As can be seen in the SI, the trends are similar for the emission of these two compounds (Figure S-2). In the following, we have used 10^6 integrals, except for the molecules for which this threshold did not allow reaching a 0.9 FC factor for all XCF. In these cases, we used 10^{10} , 10^{11} , or even 10^{12} integrals. A list of

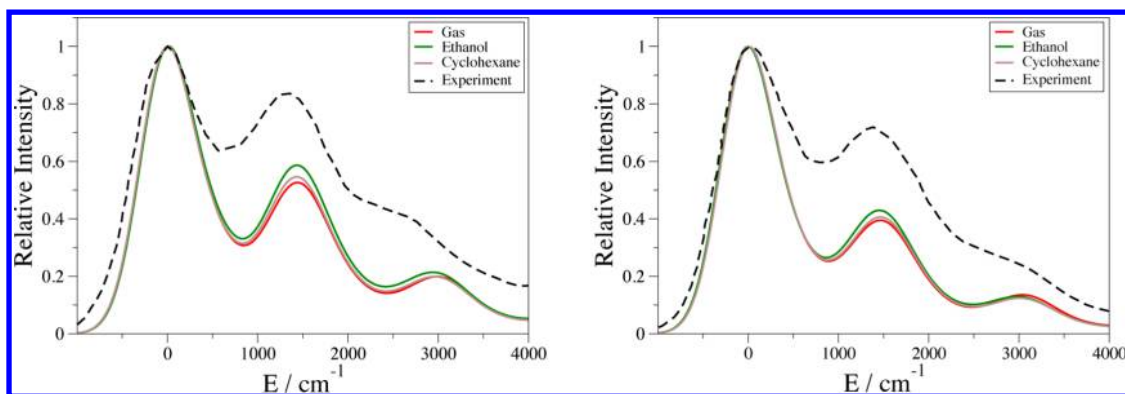


Figure 6. B3LYP/6-31+G(d) absorption (left) and emission (right) spectra of **XII** with several environmental effects. CAM-B3LYP results can be found in the SI. Experimental spectra from ref 110.

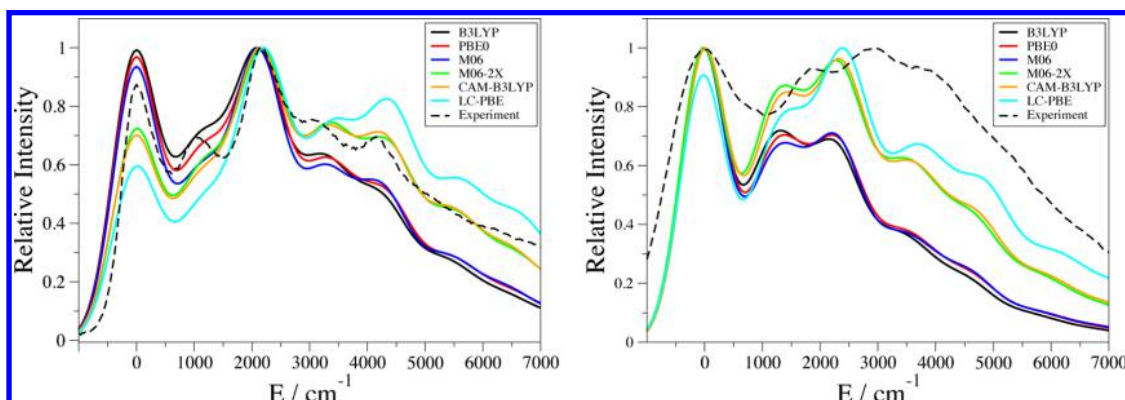


Figure 7. Absorption (left) and emission (right) spectra of **XV** computed with several XCF. Experimental data taken in ref 111.

all FC factors can be found in the SI. Even with 10^{12} integrals, a few molecules did not reach the 0.9 FC limit (see the SI), and these cases were not considered in section 3.7 presented later in the paper, though we have still provided graphical representations.

3.3. Basis Set Effects. Of course, the selected integral grid is not the only parameter that might influence the computed spectra, the applied BS might also play an important role in TD-DFT calculations. As always with BS choice, a compromise between accuracy and computational effort is looked for, but, in this benchmark, we want to be close enough to basis set convergence, so that the conclusions regarding the relative accuracies of each XCF should not be affected by the 6-31+G(d) selection. In Figure 4, we compare the absorption and emission of **XV** using the CAM-B3LYP XCF in conjunction with several Pople's and Dunning's BS.^{128–133} As can be seen, theoretical vibronic spectra are almost unaffected by the BS and even with a simple and quick 6-31G calculation they are close to convergence for both absorption and emission. Going beyond 6-31+G(d), for instance using the much larger 6-311++G(2df,2pd) and cc-pVTZ (that yield identical results), does not affect the position of the different peaks and only changes the relative intensities by a trifling amount. For the emission of **I**, several BS have been tested (Figure S-3 in the SI), and 6-31+G(d) results are alike in their 6-311++G(d,p) counterpart. For **XI**, comparisons between the absorption and fluorescence spectra computed with 6-31+G(d) and 6-311++G(d,p) BS for the six XCF can be found in the SI (Figure S-4), and no significant difference between the two BS can be detected.

3.4. Temperature Effects. We have also assessed the impact of temperature on the simulated band shapes. In Figure 5, we present the absorption and emission spectra of **XII** simulated at 0, 100, 200, and 298 K, the latter being the experimental temperature. As can be seen, the shape of the spectra slightly changes with the temperature. Indeed, when going from 0 to 298 K, the relative position of the third maxima (the most affected) goes from 2935 cm^{-1} to 2968 cm^{-1} for the absorption and from 2968 cm^{-1} to 3000 cm^{-1} for the emission, that is variations of less than 1%. At the same time, the height of these third peaks slightly increases by +0.063 and +0.034 (normalized units) for absorption and fluorescence, respectively. A similar investigation performed with CAM-B3LYP for **III** is shown in Figure S-5 in the SI, and the influence of the temperature is completely negligible in that second case. In the following, we have systematically carried out the FC simulations using the experimental temperature, except in the cases where convergence problems prevented meaningful calculations at room temperature.

3.5. Impact of the Solvent. As mentioned in the methodological section, we have systematically included solvent effects during our simulations. For **XII** we present in Figure 6 the absorption and emission spectra calculated in gas phase, cyclohexane, and ethanol (see section S-6 in the SI for other examples). Although the impact of the solvent is detectable, it remains relatively small compared to the theory-experiment discrepancies. With the PCM model specific solute–solvent interactions, such as hydrogen bonds (HB), are generally not properly taken into account. For this reason, we have mainly selected aprotic solvent here but (due to experimental

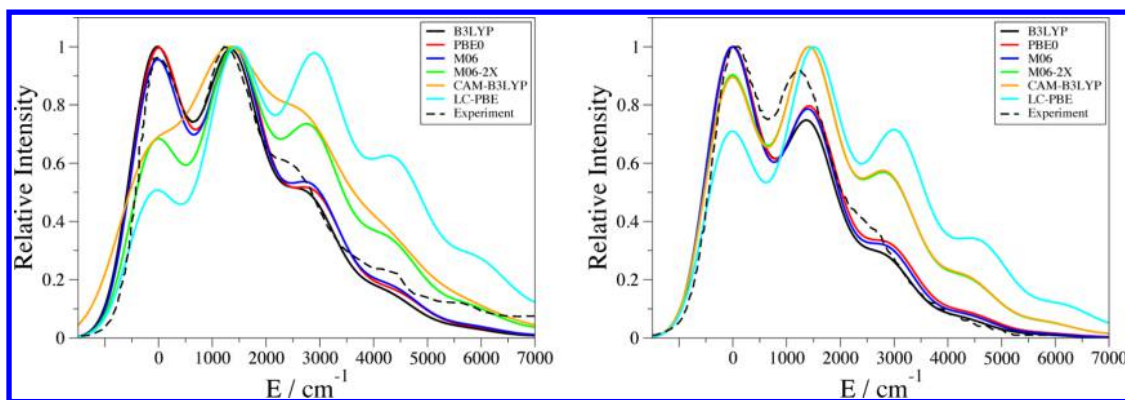


Figure 8. Absorption (left) and emission (right) spectra of VI computed with several XCF. Experimental data taken in ref 120.

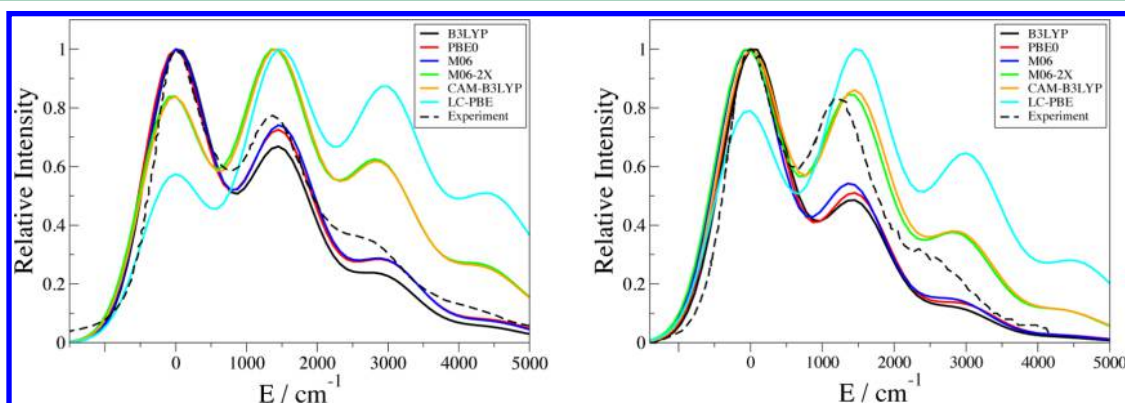


Figure 9. Absorption (left) and emission (right) spectra of IV computed with several XCF. Experimental data taken in ref 122.

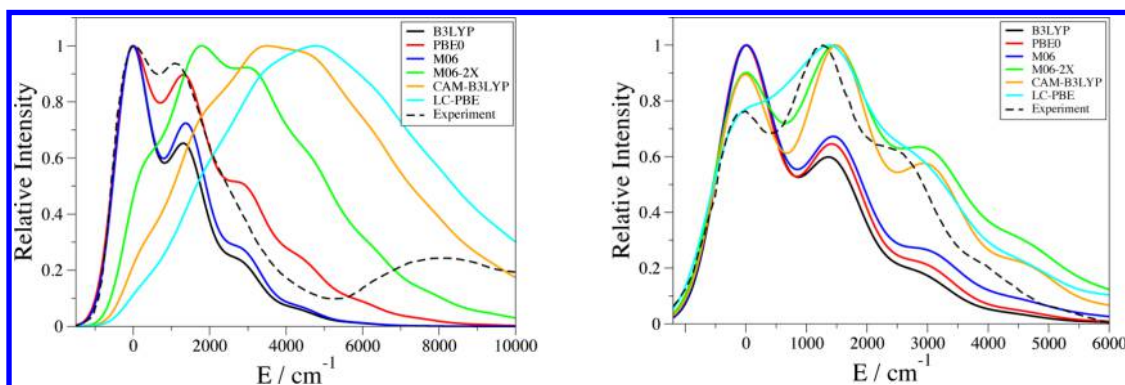


Figure 10. Absorption of II (left) and emission of XIX (right) spectra computed with several XCF. Experimental data taken in refs 121 and 119, respectively.

limitations) for four molecules: XI, XII, XV, and XVII. The two latter are hydrocarbons, so that absolutely no significant HB interactions can be expected. As it is planar, XII behaves similarly, the lone pair of the nitrogen atom being part of the π -conjugated path so that ethanol cannot form HB with XII. Eventually for XI the nitrogen lone pairs are in the π -system like in XII and the fluoroborate group is a template absolutely not implied in the ES of BODIPY dyes so that eventual methanol-fluorine HB do not impact the optical signatures.^{82,134} Therefore, we are confident that the PCM model is adequate for all molecules investigated herein.

3.6. Case Studies. In this section, we discuss a number of selected examples representative of all theory/experiment comparisons. A full list of figures for all molecules can be found in section S-7 in the SI. We start with two “classical”

molecules, namely XV (see Figure 7) and VI (see Figure 8). In both cases, one can split the six XCF in three groups, the first includes B3LYP, PBE0, and M06, three global hybrids presenting 20–27% of exact exchange; the second includes M06-2X and CAM-B3LYP that are known to behave relatively similarly in the TD-DFT framework;⁵¹ the third is LC-PBE and possesses a rapidly growing exact exchange ratio. Within a group, the variations of predicted band shapes are rather small but for the M06-2X and CAM-B3LYP absorption of VI. For VI, LC-PBE is clearly the least satisfying of the six XCF, and it also underrates significantly the intensity of the first absorption band of XV. For this latter compound, the intensities provided by the first group of XCF are too small at higher energy, and this finding holds for both absorption and fluorescence. The members of the second group are more satisfying though they

Table 2. Statistical Analysis Obtained from a Comparison of the Theoretical and the Experimental Absorption Spectra^a

XCF	positions						intensities					
	MSE	MUE	RMS	SD	max(+)	max(-)	MSE	MUE	RMS	SD	max(+)	max(-)
B3LYP	30	94	155	153	238	-806	-0.07	0.12	0.16	0.15	0.34	-0.38
PBE0	63	117	175	166	334	-806	-0.07	0.11	0.15	0.14	0.34	-0.36
M06	83	95	120	87	302	-69	-0.07	0.11	0.16	0.14	0.35	-0.35
M06-2X	83	106	142	117	472	-90	-0.01	0.11	0.14	0.14	0.32	-0.31
CAM-B3LYP	88	108	144	115	472	-121	-0.01	0.13	0.17	0.17	0.62	-0.33
LC-PBE	172	182	219	137	553	-180	0.01	0.22	0.27	0.27	0.55	-0.45

^aLeft: relative positions of the bands (in cm^{-1}). Right: relative intensities of the main peaks (arb. units, most intense band set to 1).

Table 3. Statistical Analysis Obtained from a Comparison of the Theoretical and the Experimental Fluorescence Spectra^a

XCF	positions						intensities					
	MSE	MUE	RMS	SD	max(+)	max(-)	MSE	MUE	RMS	SD	max(+)	max(-)
B3LYP	80	225	291	286	531	-722	-0.09	0.16	0.22	0.20	0.55	-0.45
PBE0	115	263	316	301	531	-726	-0.07	0.16	0.21	0.20	0.61	-0.42
M06	110	244	298	283	531	-726	-0.07	0.16	0.21	0.20	0.67	-0.36
M06-2X	106	262	310	300	497	-674	0.00	0.07	0.12	0.12	0.36	-0.30
CAM-B3LYP	129	242	287	262	446	-623	0.01	0.07	0.12	0.12	0.38	-0.32
LC-PBE	229	351	391	326	644	-571	0.04	0.12	0.17	0.17	0.39	-0.29

^aSee the caption of Table 2 for more details.

undershoot the height of the first absorption peak. For **XV**, the positions of the emission maxima are less accurately reproduced by TD-DFT than their absorption counterparts (irrespective of the XCF), and this holds in many cases (see the next section). For **VI**, B3LYP, PBE0, and M06 are close to the experimental spot, whereas the three other functionals are less satisfying, illustrating that two relatively similar aromatic compounds might yield different conclusions regarding the “best” XCF.

Let us now focus on three recently investigated dyes, namely **IV** (see Figure 9), **II** (see left panel of Figure 10 and the SI), and **XIX** (see right panel Figure 10). For the absorption of the perylene, **IV**, the XCF of the first group are clearly more accurate, functionals with large share of exact exchange inverting the relative intensities of the two first peaks. For the emission, all functionals but LC-PBE are rather satisfying though they all slightly overestimate the position of the second and third bands. For the intensity of the second maximum, members of the first (second) group provide too small (accurate) estimates. For the absorption spectra of the diketopyrrolopyrrole, **II**, a molecule for which FC convergence could be problematic (see the SI), there is more contrast between the results of the different XCF, but PBE0 significantly outperforms the other hybrid XCF. Indeed, the two range-separated hybrid functionals do not restore the correct shapes, whereas B3LYP and M06 significantly underestimate the intensity of the second band. For the emission of **II** (see the SI), the three XCF of the first group nicely reproduce the experimental trends. Eventually for the emission of **XIX**, the three functionals of the first group are not satisfying, whereas, for once, LC-PBE is close to the experimental data (but in that latter case, the FC factor is far from convergence, so this outcome could be fortuitous).

3.7. Statistical Analysis. To have a general view of the relative performances of the six benchmarked XCF, a statistical analysis is provided in Table 2 and Table 3, for absorption and fluorescence, respectively (a table with joint phenomena is available in the SI). In these tables, we report the mean signed error (MSE, theory-experiment), mean unsigned error (MUE), root means square deviation (RMS), and standard deviation

(SD) as well as the maximum discrepancies for both relative positions and height of the peaks. We recall that the first band was set to 0.0 cm^{-1} in both theory and experiment and is consequently removed from the statistics for the positions but not for the relative intensities (see the SI for statistics including this initial band). As stated previously, only the cases for which the FC factor exceeds 0.9 have been included in the statistics. We do not analyze in detail, all vibrational terms for all molecules and XCF. Indeed, while for some molecules, e.g. simple hydrocarbons, this analysis is pertinent as only a few vibrations significantly contribute to the total spectra, in most cases, the number of individual contributions (stick spectra) is too large to allow chemically intuitive interpretations. Detailed analysis for anthraquinones, coumarins, BODIPY, and other structures can also be found elsewhere.^{60,61,73,77,79,82,127,134}

Let us start by analyzing the relative positions of the absorption peaks. We note that the MSE is positive for all functionals, indicating that the experimental separations between the different absorption bands tend to be overestimated by TD-DFT, an outcome that is probably partially related to the harmonic approximation used to compute the vibrational modes of both GS and ES (see below). Clearly, LC-PBE provides less accurate positions than the five other XCF, that all yield relatively similar error patterns, but for a very small MSE with B3LYP. The smallest RMS, SD, and extreme deviations are obtained with M06, whereas B3LYP's and M06's MUE are the only one below the 100 cm^{-1} threshold. The MUE of the relative absorption intensities indicate that the typical deviations are of the order of 10%–15%, M06-2X being the most accurate. Again, LC-PBE is relatively poor on peak's height with deviations typically exceeding 20%.

As can be seen in Table 3, the computed errors on the position of the fluorescence maxima are significantly larger than for absorption, e.g., the MUE of M06 increases from 95 cm^{-1} to 244 cm^{-1} . Note that for fluorescence, Santoro reported that the accuracy of the intensities in the stick spectrum to be more sensitive to the accuracy (ν^3 dependency) than their absorption counterpart, which in turn could affect after convolution the positions of the bands.^{59,61,62} The fact that all XCF but LC-PBE

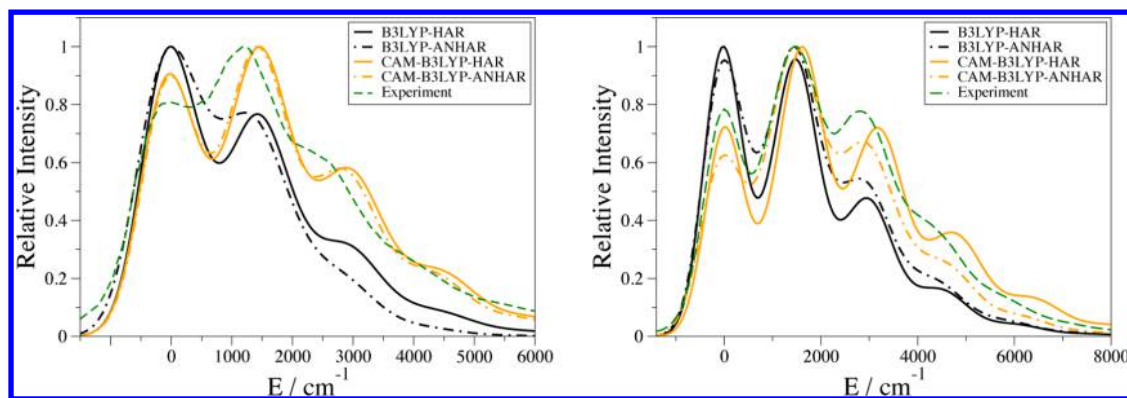


Figure 11. Harmonic and anharmonic emission spectra of **III** (left) and emission of **XVI** (right) spectra computed with B3LYP and CAM-B3LYP. Experimental data taken in refs 116 and 111, respectively.

provide rather similar deviations is conserved for our six XCF set. B3LYP yields the smallest MUE, whereas CAM-B3LYP provides the smallest SD. Contrary to what is found for the relative positions of the peaks, the error patterns for intensities are similar for both absorption and emission with average absolute deviations below 10% for both M06-2X and CAM-B3LYP.

Let us now briefly analyze the most significant outliers obtained with the M06-2X functional: **XIV** and **XVIII** for absorption and **XIII** and **XV** for emission. The stick spectra are represented in Figure S-24 in the SI. For the absorption cases, many individual transitions do contribute to the total spectra, and the situation is easier to analyze for fluorescence. Indeed, for **XV**, the two main GS vibrations are modes 38 and 56, that respectively correspond to the stretching of the central single bonds and of the triple bond. Obviously, describing correctly such triple bond vibration remains a challenge for DFT. For **XIII**, the main contribution originates from a 1418 cm^{-1} elongation vibration of the CC bonds of the aromatic structure, and the description can be slightly improved by including anharmonic corrections (see the next section).

In the SI (Tables S-XXVII to S-XXX), one can find a statistical analysis obtained by separating the hydrocarbons and heteroatomic compounds of Scheme 1. For both the relative positions and intensities of the absorption peaks, these two subsets behave rather similarly, e.g., the M06-2X MUE for absorption are 105 (107) cm^{-1} and 0.09 (0.13) for the first (second) subgroup. For fluorescence, the variations are more significant. Indeed, the position errors obtained for the heteroatomic systems are significantly smaller than their hydrocarbon counterparts. In all cases, LC-PBE remains the least accurate, and the position of the emission maxima are harder to predict than the absorption peaks. In Tables S-XXXI and S-XXXII, we provide an analysis including only the two first peaks, and though the errors are, as expected, smaller than in Table 2 and Table 3, the trends are similar than those discussed above.

In short, all tested functionals, except LC-PBE, provide satisfying spectra with respect to experiment, and more accurate descriptions are almost systematically achieved for absorption than fluorescence. As already noted for the 0–0 energies,⁵¹ B3LYP, PBE0, and M06 provide very similar trends, and the same holds for M06-2X and CAM-B3LYP. This is related to the amount of exact exchange included in each functional. It is certainly difficult to pinpoint univocally a preferred functional, but our choice will be M06-2X that is reasonably accurate for all

positions, the best of the set for relative intensities and is also known to provide 0–0 energies nicely correlating with experiment.⁵¹ Of course, this study also demonstrates that the standard B3LYP is not to be discarded and can often offer reliable spectral shapes; it actually yields the smallest MSE and MUE for the relative positions of both absorption and fluorescence bands.

3.8. Further Discussion: Anharmonicity. The harmonic approximation can be considered as a source of significant errors. While the computation of anharmonic ES vibrations is practically impossible (but for very small molecules), anharmonic GS frequencies can be obtained through numerical differentiation of the analytic harmonic GS frequencies.¹³⁵ This therefore allows for correction of the vibronic shapes computed for emission,^{136,137} using harmonic ES vibrations but anharmonic GS data. This procedure has been applied for both **III** and **XVI** (see Figure 11). For the former, the anharmonic vibrational corrections are rather small, and, consequently, the errors performed when using harmonic data are only slightly decreased when anharmonicity is taken into account. On the contrary, for **XVI**, anharmonic corrections improve the description in a significant way, and this is especially noticeable for the third band with CAM-B3LYP: both its position and intensity are significantly better matching experiment once anharmonicity is accounted for. For **XIII**, one of the most significant outliers (see above), we also performed anharmonic simulations with the B3LYP functional (see the SI), and the position of the maximum at ca. 2500 cm^{-1} in the emission spectra is improved with anharmonic corrections.

4. CONCLUSIONS AND OUTLOOK

We have determined the vibrational spectra of both the ground and the first excited states of 20 conjugated molecules, including recently designed dyes, using six hybrid functionals and the (LR-)TD-DFT approach. Our protocol systematically uses diffuse orbitals and accounts for bulk solvent effects through a continuum approach. From these data, the vibrationally resolved absorption and emission spectra have been obtained and compared to experiment. The impact of the DFT integration grid was found to be negligible provided a very loose grid is not selected. Additionally, we have shown that 6-31+G(d), that was already found to be adequate for computing 0–0 energies,⁵¹ provides optical spectra close to basis set convergence and therefore allows meaningful benchmarks of DFT functionals. By investigating several cases, it was found that the obtained accuracy was significantly system dependent,

confirming Dierksen and Grimme's findings.⁴⁹ For instance, the topologies are often reasonably reproduced by most functionals for fused aromatic systems, but they all fail to provide an accurate estimate of the shoulder height in BODIPY. In that latter case, the six tested functionals severely underrate the intensity of the hallmark BODIPY shoulder. For the relative position of the absorption and emission peaks, the errors are typically 100 cm⁻¹ and 250 cm⁻¹, respectively, whereas the relative intensities are estimated with a 10–15% accuracy. All functionals provide relatively similar error patterns except for LC-PBE that yields larger deviations and is consequently not recommended for computing vibronic shapes. B3LYP provides the smallest MSE and MUE for the position of absorption and emission peaks but is not the most efficient in terms of RMS or largest deviations. In view of our recent 0–0 work,⁵¹ and the present investigation, M06-2X could probably be viewed as a reasonable compromise between a satisfying average accuracy and relatively limited problematic cases.

While vibronic shapes are an indication of the accuracy of the computed GS and ES geometries and can therefore be viewed as an indirect measurement of TD-DFT's accuracy for ES structures, they also depend on other approximations such as the use of harmonic vibrational signatures. In other words, they cannot be viewed as a fully satisfying metric for benchmarking XCF for ES bond lengths and valence angles. Despite recent efforts aiming at finding the most adequate XCF for ES structures,^{30,56,69,138–143} additional works using high-level wave function references, e.g., CAS-PT2, EOM-CCSD, or SAC-CI, would be welcome, and we have started working in this direction.^{144,145}

■ ASSOCIATED CONTENT

■ Supporting Information

List of “raw” results for all peaks. Impact of the integration grid on the absorption spectra of XV. Impact of the number of integrals for two fluorescence cases, FC₀₀ parameters for both B3LYP and CAM-B3LYP, FC factors for all functionals. Comparison between 6-31+G(d) and 6-311++G(d,p) absorption and fluorescence spectra (six functionals) for XI. Additional temperature study for III. Spectra for molecules not shown in the paper. Additional (joint absorption and emission, hydrocarbon or non-hydrocarbon subgroups) statistical analysis. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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