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A conceptually improved TD-DFT approach for predicting the maximum absorption wavelength of cyanine dyes

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ABSTRACT

Cyanine dyes have found valuable applications in modern bioresearch because of their biocompatibility, high molar absorptivity and moderate fluorescence quantum yield. Of special value for sensing and labeling applications is the fact they can cover a very large spectral range (from blue to infra-red). To design and select the most appropriate dyes for a given application the computational prediction of the absorption wavelength (prior to the costly chemical synthesis) serves as a valuable guidance. However, predicting absorption and emission wavelengths of such compounds remains a challenging task. Herein, we report a fast and highly accurate computational approach which allows the prediction of the maximum absorption wavelength for a wide range of cyanine dyes, including symmetrical and unsymmetrical, trimethine and pentamethine cyanine dyes but also unusual imino-based analogues. In addition to the vertical excitation energy (calculated from time-dependent density functional theory), the approach makes use of a novel correction term that is based on the ground-state zero-point vibrational energy (ZPVE). The correction term is statistically significant (*F*-test), and it reduces the average error and maximal error of the prediction by a factor of two. We anticipate that the concept of including the ZPVE into the calculation of the maximum absorption wavelength can be used also for other families of dyes to improve their predictability.

1. Introduction

Dyes are molecules that display light absorption in the long-wavelength region and thereby give raise to color perception [1]. Of particular interest in modern bioresearch are dyes capable of emitting a fluorescent signal upon excitation with a single (or multiple) photon(s). Fluorescence arises when the relaxation corresponding to the transition of an electron from the first singlet excited state (S_1) to the singlet electronic ground-state (S_0) occurs via photon emission. Since the discovery of the first natural fluorophore in 1845 [2], numerous fluorescent small molecules have been engineered that cover a very broad spectral range (from blue to infra-red) [3]. Among them, cyanine dyes have found valuable applications (*e.g.*, for optical data storage, proteomic, labeling of biomolecules) [4]. They generically consist of a conjugated system based on a polymethine chain linking two nitrogen-containing heterocycles (*e.g.*, indoles, benzothiazoles) [5].

We have recently introduced a new class of dyes differing from the well known cyanine dyes by one or two C → N substitutions within the polymethine chain (Fig. 1) [6,7]. While the potential of polymethine cyanine dyes for labeling purposes is now well-established [8], the possible use of their imino analogues for either sensing malondialdehyde (MDA) or alkylating DNA/RNA nucleobases has also been recently demonstrated [7].

Depending on the process or metabolite that needs to be sensed, fluorescent molecules absorbing and emitting in specific regions of the spectrum are necessary. Therefore, understanding and tuning the spectroscopic properties of cyanine dyes remains of vital interest. The prediction of spectroscopic properties from numerical calculations provides valuable input in this regard; *e.g.*, the computational appraisal of the absorption wavelength prior to the costly chemical synthesis may serve as guidance for the design and selection of the most appropriate dyes for a given application.

Absorption wavelengths of dyes have been calculated by various approaches ranging from simplistic π-electron models and semi-empirical all-valence-electron methods to computationally intensive *ab initio* model chemistries (for a concise overview, see reference [9]). In recent years time-dependent density functional theory (TD-DFT) [10] has increasingly been used [9,11–20] to fill the gap between the semi-empirical and high-level *ab initio*

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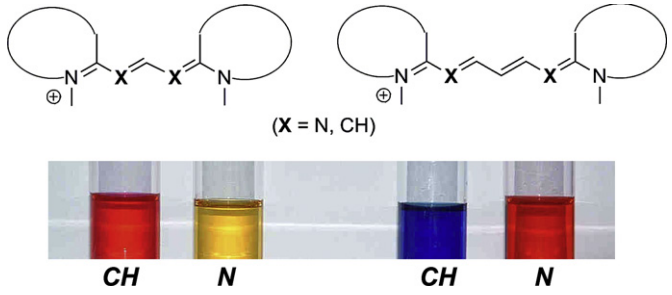


Fig. 1. General structure of polymethine (X=CH) and polyimine (X=N) cyanine dyes covering a spectral range from blue to red. Pictures of selected dyes in solution (DMSO) are also given for illustration. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

methods, *i.e.*, TD-DFT is a first-principles method that overcomes short-comings of the former methods (*e.g.*, electron correlation) and yet it is still applicable to much larger systems (about 100 second-row atoms) than the latter [9].

Despite considerable efforts in TD-DFT, the accurate prediction of maximum absorption wavelengths from computations remains, however, a challenging task. There are several reasons for this. Beside the Hamiltonian approximations (*e.g.*, exchange correlation functional, basis set, treatment of solvent) the calculations usually differ also conceptually from the experiment, *i.e.*, a discrete value for the vertical excitation energy of a ground-state minimum-energy structure is calculated (ΔE_v), whereas the reported value of the experiment corresponds to the energy value of the absorption maximum (ΔE_{max}) which depends on the virbonic structure of the dye; see also discussion by Champagne et al. [14].

Herein, we report the development of an optimized approach for predicting with high accuracy the maximum absorption wavelength of polymethine cyanine dyes as well as that of their imino analogues. As a first test, we use a linear scaling approach [14] that estimates the maximum absorption wavelength ΔE_{max} solely from the TD-DFT-calculated ΔE_v. We then propose a conceptual refinement of the standard approach by introducing an empirical correction term that is based on the zero-point vibrational energy. The statistical significance of the ZPVE-based correction is verified (*F*-test), and the portability of this methodological development to other families of dyes is discussed.

2. Material and methods

Compounds **1**–**14** were synthesized following experimental procedures previously reported by us [6,7] and others [21]. Ultraviolet absorption spectra of analytically pure samples were recorded on a V-670 UV/VIS spectrophotometer from JASCO in a 10 mm pathlength cuvette.

3. Theory and calculations

We build on a linear scaling approach [14]: ΔE_{max}, is obtained from the TD-DFT-based ΔE_v through an empirical equation:

$$\Delta E_{max} = \alpha \Delta E_v + \beta, \quad (1)$$

where α and β are two parameters that are fitted from a series of dyes with known experimental maximum absorption wavelengths. We used the cyanine dyes of Table 1 for which ΔE_{max} has been measured under the same experimental conditions, *i.e.*, same solvent (DMSO), counter ion, and temperature [6,7].

Variants of Eq. (1) are known where additional terms for solvent effects are included [15,16], or where the absorption wavelengths of maximal intensity is calculated based on multiple QSAR descriptors [22]. In this work we propose the following extension of Eq. (1):

$$\Delta E_{max} = \alpha \Delta E_v + \beta + \gamma(\mathrm{ZPVE}/n_{DOF} - \delta)^2, \quad (2)$$

with ZPVE the zero-point vibrational energy (in the harmonic approximation) [23], n_{DOF} the number of vibrational degrees of freedom (3*N*-6 for non-linear molecules, with *N* the number of atoms), and γ, δ are two additional parameters to be fitted.

Several methods of calculating ΔE_v were tested to fit Eq. (1), the "best" method (highest R^2 and Q^2, see below) was then used to fit Eq. (2). The minimum-energy structure was calculated on the B3LYP/6-31G* level of theory either in the gas phase or in solution (using the PCM solvation model [24]); in both cases a tight minimization was performed and the localization of the stationary points was verified with a frequency calculation that yielded ZPVE. Two different functionals, B3LYP [25,26] and PBE0 [27] (also named PBE1PBE [28]), in combination with three different basis sets, 6-31G*, 6-311G*, and 6-311+G**, were then used to determine the vertical excitation energy ΔE_v by a single-point TD-DFT calculation (with and without solvation model) [29]. All calculations were carried out with the program Gaussian09 [28].

For each prediction model we calculated the squared correlation coefficient, R^2, between the calculated and experimental ΔE_{max} values, as well as the leave-one-out cross-validated R^2, named Q^2; the former parameter is a measure of the goodness-of-fit, the latter of the goodness-of-prediction [30].

When two models are compared that are based on different equations (with a different number of parameters, such as Eq. (1), Eq. (2) and variants of the latter; see section Results and Discussion), an increase in R^2 when going from the smaller, nested equation to the larger equation does not always indicate a statistically significant improvement of the model. We therefore performed a likelihood-ratio test (*F*-test) [31]. Under the null hypothesis that the larger model does not fit the data better than the smaller, nested model, the value

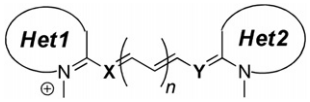
$$F = \left[\left(R_l^2 - R_s^2\right)\Big/\left(1 - R_l^2\right)\right]\Big/[(p_l - p_s)/(N - p_l)], \quad (3)$$

will have a *F*-distribution with $p_l - p_s$ numerator and $N - p_l$ denominator degrees of freedom. R_l^2 is the correlation coefficient for the model with the larger number of parameters (p_l); R_s^2 and p_s are the respective quantities of model with the simpler, nested equation. *N* is the number of data points available for the fit. To reject the null hypothesis, the value of Eq. (3) needs to be greater than the value of the *F*-distribution for some desired false-rejection probability (*P* value). For the comparison of the fits with Eq. (2) and Eq. (1), for example, the value of the *F*-distribution (two numerator and ten denominator degrees of freedom) is 4.10 for the critical *P* value of 0.05.

4. Results and discussion

It has been noted previously that the use of a solvation model can improve significantly the agreement between experimental ΔE_{max} and predicted values from Eq. (1) [14]. When a pure gas phase method, *i.e.*, both geometry optimization and single-point calculation are carried out in gas phase (see values in parentheses of Table 2), is compared with a method where the latter step is carried out with the PCM solvation model, the correlation coefficient R^2 and the leave-one-out cross-validated correlation coefficient Q^2 increase by about 20%. When both steps are carried out in solution, R^2 and Q^2 further increase; the effect is, however, smaller. Improvement is also possible when the functional B3LYP is replaced by PBE0 [15]. Furthermore, increasing the basis set from 6-31G* to

Table 1
Absorption properties of cyanine dyes from experiments and calculations, and zero-point vibration energy per vibrational degree of freedom. Chemical structures of compounds **1**–**14** are shown in the Supplementary data.



						Experiment		Calculation	
Compound	Het1	Het2	X	Y	*n*	λ_{max} (nm)	ΔE_{max} (eV)	ΔE_v[a] (eV)	ZPVE/n_{DOF}[b] (10^{-2} eV)
1	Benzothiazole	Benzothiazole	N	N	0	412	3.00	3.13	7.40
2	Quinoline	Quinoline	N	N	0	424	2.92	3.16	7.81
3	Naphtobenzothiazole	Naphtobenzothiazole	N	N	0	460	2.69	2.81	7.32
4	Benzothiazole	3,3-dimethylindole	N	CH	0	469	2.64	2.86	7.84
5	Benzothiazole	Benzothiazole	N	N	1	512	2.42	2.66	7.42
6	Quinoline	Quinoline	N	N	1	520	2.38	2.67	7.79
7	Benzothiazole	3,3-dimethylindole	CH	CH	0	542	2.29	2.63	7.90
8	Naphtobenzothiazole	Naphtobenzothiazole	N	N	1	557	2.23	2.44	7.34
9	Benzothiazole	Benzothiazole	CH	CH	0	562	2.21	2.58	7.57
10	Benzothiazole	3,3-dimethylindole	N	CH	1	579	2.14	2.51	7.82
11	Naphtobenzothiazole	Naphtobenzothiazole	CH	CH	0	592	2.09	2.40	7.45
12	Benzothiazole	3,3-dimethylindole	CH	CH	1	643	1.93	2.31	7.88
13	Benzothiazole	Benzothiazole	CH	CH	1	660	1.88	2.29	7.58
14	Naphtobenzothiazole	Naphtobenzothiazole	CH	CH	1	683	1.82	2.15	7.46

[a] PBE0(PCM)/6-311++G**//B3LYP(PCM)/6-31G*.
[b] B3LYP(PCM)/6-31G*.

6-311G* increases R^2 and Q^2, but 6-311G* and 6-311++G** yield essentially identical results. The highest goodness-of-fit and goodness-of-prediction are obtained for the method PBE0/6-311++G**(PCM)//B3LYP/6-31G*(PCM) (Fig. 2a). With this model the error in the prediction of ΔE_{max} ranges from −0.07 to +0.12 eV (−28 to +21 nm), the root-means-square error is 0.06 eV (15 nm).

The quality of the prediction with Eq. (1) (correlation coefficient $R^2 = 0.968$, maximal error = 0.12 eV) is notably worse than previously reported for analogous polymethine cyanine dyes ($R^2 = 0.988$, maximal error = 0.04 eV) [14]. In this study, however, we used a much more heterogeneous data set for the fitting of Eq. (1) including mono- and di-imino dyes. Especially di-imino derivatives show large deviations between prediction and experiment as indicated by the arrows in Fig. 2a. Thus for this heterogeneous set the simple linear scaling approach of Eq. (1) fails to reproduce the experimental order of the ΔE_{max} values.

We note significant differences in the zero-point vibrational energy (ZPVE) among the studied dyes. Since its value depends strongly on the number of atoms, the comparison of the ZPVE between molecules with different number of atoms is not very informative. Normalization (*i.e.*, division) by the number of degrees of freedom (n_{DOF}) allows, however, the identification of changes in the distribution of normal mode frequencies. Such changes may influence the "sharp" vibrational coupling of cyanine dyes with the solvent [32]; thereby alternate the strength of the solute–solvent interaction (*e.g.*, change the solvation contribution to the free energy values in the Marcus model [33]) and slightly shift the absorption maximum. The vertical excitation energy ΔE_v (calculated from an energy-minimized structure with an implicit solvation model) does not capture such solvent coupling effects.

The ZPVE is also of relevance in terms of vibronic contributions (when calculating ΔE_{max} from ΔE_v). For cyanine dyes the band with the highest intensity corresponds to a transition between the vibrational ground states of S_0 ($v'' = 0$) and S_1 ($v' = 0$) [34]. Consider for the moment a (0,0)-transition (Fig. 3) of a hypothetical molecular model system with n_{DOF} identical harmonic vibrations of frequency ν and ZPVE = ½ n_{DOF} $h\nu$. The frequency does not change upon excitation, but the vibration's equilibrium geometry in the excited state, r_e', differs slightly from that in the ground-state, r_e'', where the difference in reduced (dimensionless) coordinates is denoted by d. Since it is $\Delta E_{max} = D_o$ and $\Delta E_v = D_o + n_{DOF}$ ½ $h\nu$ d^2 (see Fig. 3) we find $\Delta E_{max} = \Delta E_v - \text{ZPVE}\ d^2$, where the last term, ZPVE d^2, is the vibrational reorganization energy [33]. For systems with large n_{DOF} the value d should be smaller than for systems with small n_{DOF} because for large molecules the relative geometric change per degree of freedom is smaller upon excitation than for small molecules. If we assume that the total geometric change in reduced coordinates is constant among dyes of the same family (*i.e.*, $n_{DOF}\ d^2 = \text{const}$), we have

$$\Delta E_{max} - \Delta E_v \propto \text{ZPVE}/n_{DOF}, \quad (4)$$

i.e., the difference between the maximum absorption energy and the vertical excitation energy is proportional to ZPVE/n_{DOF}. Eq. (4) is, of course, a drastically oversimplified representation for realistic molecular systems; but it may reflect to some extent relevant information when comparing different members of dyes from the same family (*e.g.*, cyanine dyes) relative to each other. Using the

Table 2
The correlation coefficient R^2 for the fit of the experimental ΔE_{max} data using Eq. (1) and different methods of calculating ΔE_v. The leave-one-out cross-validated correlation coefficient Q^2 is shown in italics. For selective cases the single-point TD-DFT calculations were carried out without solvation model (see values in parentheses). The best result is marked in bold.

Geometry	Functional	Basis set		
		6-31G*	6-311G*	6-311++G**
Gas phase	B3LYP	0.925 (0.776)	0.935	0.937
		0.903 (0.717)	*0.915*	*0.918*
	PBE0	0.953 (0.843)	0.960	0.962
		0.937 (0.802)	*0.946*	*0.948*
Solution	B3LYP	0.935	0.944	0.946
		0.916	*0.926*	*0.929*
	PBE0	0.960	0.967	**0.968**
		0.947	*0.955*	***0.956***

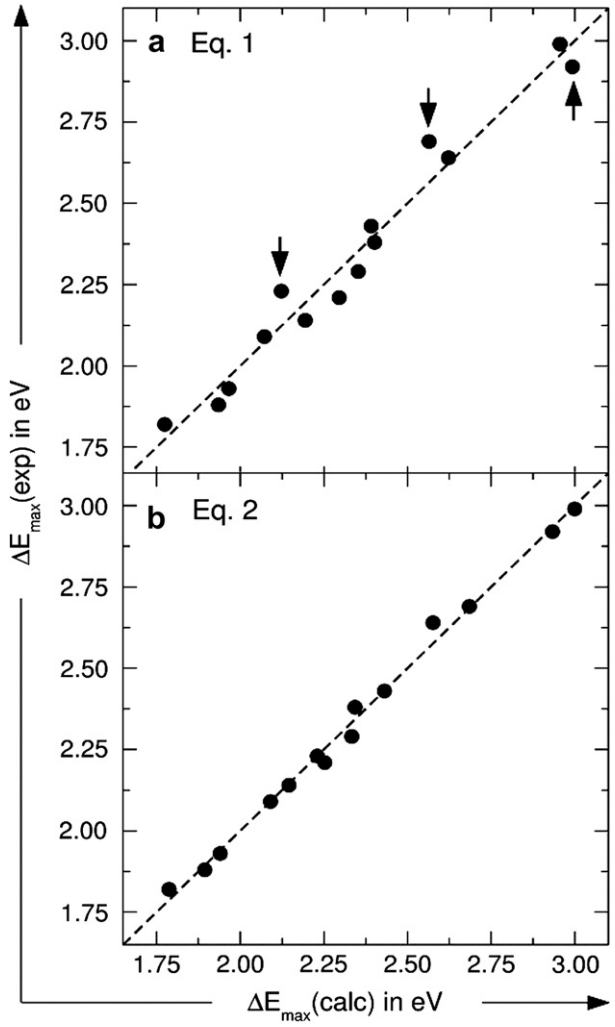


Fig. 2. Plot of calculated and experimental ΔE_{max} values for cyanine dyes of Table 1 using Eq. (1) (a) and Eq. (2) (b). The fitted parameters are $\alpha = 1.2104$, $\beta = -0.8334$ eV for Eq. (1), and $\alpha = 1.1985$, $\beta = -0.8687$ eV, $\gamma = 1.2771 \times 10^4$ (eV)$^{-2}$, and $\delta = 7.7045 \times 10^{-2}$ eV, for Eq. (2), respectively. The value of δ is close to the value of $ZPVE/n_{DOF}$ averaged over all dyes ($<ZPVE/n_{DOF}> = 7.6113 \times 10^{-2}$ eV). The arrows in a) indicate di-imino derivates with large deviations between experiment and prediction using Eq. (1).

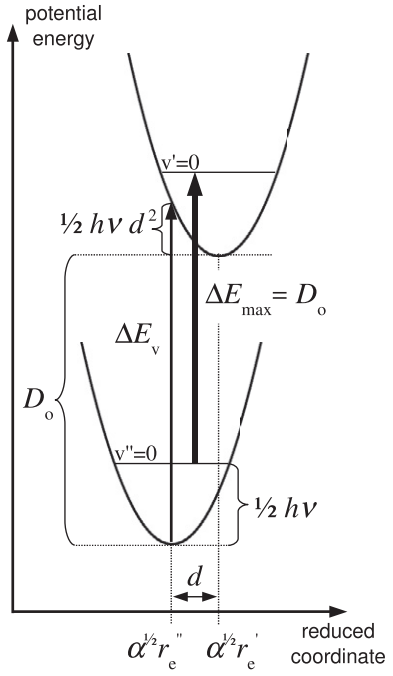


Fig. 3. Schematic representation of the potential energy surfaces of the ground-state, S_0, and the first excited state, S_1 (for $n_{DOF} = 1$). The value ΔE_v (thin arrow) corresponds to the potential energy difference between S_1 and S_0 at the equilibrium geometry of the ground-state (r_e''). Note that ΔE_v is a purely theoretical quantity (which has no experimental equivalence); it corresponds to the vertical electronic transition energy traditionally calculated in quantum chemical calculations, *e.g.*, single-point TD-DFT calculations. For fluorescent molecules such as cyanine dyes the equilibrium geometry of S_1 (r_e') differs only slightly from that of S_0 [34], so that the most intensive transition occurs between $v'' = 0$ and $v' = 0$. When the vibrational frequency ν is identical in S_0 and S_1 the excitation energy for the most probable $S_0 \rightarrow S_1$ transition, ΔE_{max} (bold arrow), corresponds to D_o (the energy difference between the minima of the two potential energy surfaces). Thus, the difference $\Delta E_{max} - \Delta E_v$ depends on the zero-point vibrational energy, ZPVE = ½ $h\nu$, and the difference between r_e' and r_e'' in reduced coordinates, $d = \alpha^{1/2} r_e'' - \alpha^{1/2} r_e'$ (with $\alpha = 4\pi^2 \mu\nu/h$; h the Planck constant and μ the reduced mass of the vibration).

calculated ZPVE values of the studied dyes the hypothetical frequency $\nu = (2/h)\,ZPVE/n_{DOF}$ ranges between 1180 and 1273 cm^{-1}. Interestingly this is within the typical frequency span of vibrations that get excited upon $S_0 \rightarrow S_1$ transitions in cyanine dyes (1200 ± 200 cm^{-1} [35]).

We tried to include possible solvent coupling effects and vibronic contributions into the calculation of ΔE_{max} by complementing Eq. (1) with an empirical $ZPVE/n_{DOF}$-based correction term (Eq. (2)). The improvement of the prediction with Eq. (2) in comparison to Eq. (1) is obvious (Fig. 2b). R^2 and Q^2 increase from 0.968 to 0.994 and from 0.956 to 0.989, respectively. The error in the prediction of ΔE_{max} ranges now from −0.04 to +0.06 eV (−10 to +12 nm), the root-mean-square error is 0.03 eV (7 nm). Thus, both the maximal and root-mean-square error drop by a factor of two in comparison with the best model of Eq. (1). The model based on Eq. (2) yields also the correct order of ΔE_{max} values for the set of studied cyanine dyes; an exception is the couple **8** and **9** for which the experimental ΔE_{max} differs by less than 0.02 eV (*i.e.*, the difference is smaller than the root-mean-square error of the model).

When we compare the models of Eq. (2) and Eq. (1) in a likelihood-ratio test under the null hypothesis that Eq. (2) does not fit the data better than Eq. (1), we find an F value of 21.3. This is much larger than the value of the F-distribution (4.10) for a critical false-rejection probability of 0.05. In fact, the null hypothesis can be rejected with a certainty of 99.97% (P value $= 2.48 \times 10^{-4}$). This underlines the statistical significance of the correction term in Eq. (2).

We tested also a linear form of the correction term (γ [ZPVE/n_{DOF}] with only one additional parameter to fit) and a cubic form (γ [ZPVE/n_{DOF}] + δ [ZPVE/n_{DOF}]^2 + ε [ZPVE/n_{DOF}]^3, *i.e.*, a third-order polynomial with three additional parameters). The former fits the data notably worse ($R^2 = 0.985$ and $Q^2 = 0.978$) than the quadratic form (Eq. (2)), the latter fits marginally better ($R^2 = 0.995$, $Q^2 = 0.989$). When comparing the models of the quadratic correction term and the nested, linear term in a likelihood-ratio test, we find an F value of 14.3 which corresponds to a P value of 0.004 (one numerator and ten denominator degrees of freedom). The null hypothesis (*i.e.*, the quadratic correction term does not fit the data better than the linear correction term) can be rejected with a certainty of 99.6%. The comparison of the models of the cubic correction term and the nested, quadratic term, yields, however, an F value of only 1.2 which corresponds to a P value of 0.302 (one numerator and nine denominator degrees of freedom). This is six times larger than the critical false-rejection probability of 0.05. The quadratic form of the correction term is therefore sufficient to describe the dependence of ΔE_{max} on $ZPVE/n_{DOF}$.

5. Conclusions

A more accurate TD-DFT prediction of the maximum absorption wavelength of symmetrical or unsymmetrical cyanine dyes is possible by introducing a correction term that potentially accounts for vibronic contributions and solvent coupling effects. Interestingly, with this correction term the prediction is also successful for "unusual" cyanine dyes that contain one or two imino linkage(s) within their polymethine chain. The maximal error in the prediction is 12 nm with correction term, instead of 28 nm without correction term; the improvement of the agreement (between prediction and experiment) is statistically significant. The correction term is based on the zero-point vibrational energy (ZPVE) normalized by the number of vibrational degrees of freedom. With the aid of a simplified model system it was shown that the correction term possibly accounts for the conceptual difference between the maximum absorption energy (as obtained from experiments, see ΔE_{max} in Fig. 3) and the vertical excitation energy (as obtained from quantum chemical calculations, ΔE_v). The model is not limited to cyanine dyes but it is generally applicable to dyes with a dominant (0,0)-transition. For dyes with larger geometric changes upon excitation (*i.e.*, for dyes where the most favorable transition leads to a vibrationally excited S_1. state) the difference between ΔE_{max} and ΔE_v also depends on ZPVE: the energy for the most probable transition corresponds to the zero-point corrected vertical transition energy (Franck–Condon principle); the normalization of ZPVE by $3N$-6 could be less important though. We anticipate therefore that ZVPE-based correction terms can be used also for many families of dyes to improve the prediction of their maximum absorption wavelengths. The investigation of the theoretical basis of the correction term, especially its quadratic nature (*e.g.*, anharmonicity effects) is subject to future studies.

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Appendix. Supplementary data

Supplementary data related to this article can be found online at doi:10.1016/j.dyepig.2010.12.001.

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