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A simple method for calibration of hybrid exchange–correlation functionals for precise calculations of fluorescence wavelengths of dibenzoylmethanatoboron difluoride exciplexes with benzene, alkylbenzenes and pyridine

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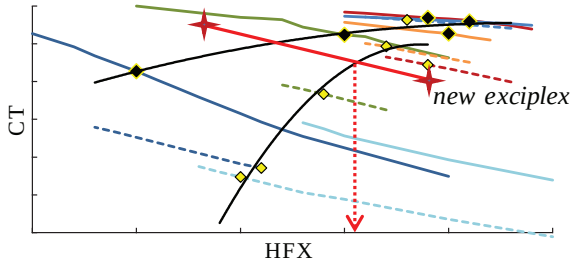
A simple approach to precise calculation of fluorescence wavelengths of charge-transfer exciplexes formed by dibenzoylmethanatoboron difluoride ($DBMBF_2$) with benzene, alkylbenzenes and pyridine by varying the percentage of Hartree–Fock exchange energy (HFX) in the hybrid BHHLYP exchange–correlation functional is proposed. A correlation revealed between the optimal HFX parameter and the degree of charge transfer (CT) in the exciplexes provides a basis for the pre-assessment of the required HFX parameter in the BHHLYP functional from the calculated CT value in an exciplex of interest.



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The development of theoretical approximations to the description of excited states and electronic transitions in molecules has remained one of the main tasks of theoretical and quantum chemistry for decades. The development of the density functional theory (DFT) and especially the time-dependent density functional theory (TDDFT) has become a breakthrough in theoretical methods for calculating molecular excited states and allowed researchers to predict physicochemical and photophysical properties of typical chemical molecules with sufficient accuracy at a reasonable computational cost.[1–4] Today DFT and TDDFT are the most widely used methods in quantum chemical calculations, successfully predicting the most important properties of molecules, such as structures, potential energies and energy barriers of chemical reactions, complexation energies, vibrational frequencies, absorption spectra of molecules and their complexes, though in many cases giving wrong results for emission spectra of complex compounds,[5,6] especially for charge-transfer and Rydberg states.

A summary of TDDFT possibilities in calculations of molecular properties important for photochemistry was provided in monograph[7] and reviews.[8–17] The key factor in TDDFT calculations of transition energies is the proper choice of an exchange–correlation functional, for which one can use multiple benchmarks of exact theoretical or experimental data.[18–28]

New functionals of different quality[29] are usually developed either for description of specific properties or for certain classes of compounds; their recent versions often include variation of the percentage of Hartree–Fock exact exchange (HFX),[30] density correction,[31] partial involvement of second-order perturbation theory (PT2) correlation energy,[32] *etc*. However, novel functionals are often inapplicable to large molecules because of high computational cost; they are not included into available software packages, and, therefore, cannot be used by many researchers. This necessitates the development of simple approaches based on conventionally available functionals.

The description of properties of charge-transfer exciplexes is one of the problems highly important for photochemistry. It is known that the wavelength of exciplex fluorescence (corresponding to the $S_1 \rightarrow S_0$ transition energy at the equilibrium geometry of the S_1 state) calculated within the TDDFT approach with conventional hybrid generalized gradient approximation (GGA) functionals strongly depends on the percentage of Hartree–Fock exchange energy in the total exchange energy, partially taking into account the long-range component of the energy of electron correlation. As was previously shown for dibenzoylmethanatoboron difluoride ($DBMBF_2$) exciplexes with a series of aromatic hydrocarbons, fluorescence wavelengths λ calculated by TDDFT using hybrid functionals with low HFX, such as PBE0 (HFX = 0.25), were overestimated, whereas they were strongly underestimated in the post-Hartree–Fock configuration interaction singles (CIS) method (HFX = 1).[33] The BHHLYP functional (HFX = 0.5), provided a better agreement between calculated and experimental λ values for the series of exciplexes studied by Valat,[34] but the λ values had still remained underestimated. For example, for the $DBMBF_2$–benzene exciplex, calculations with the BHHLYP functional gave λ(calc) = 391 nm, whereas λ(exp) = 427 nm.[33] On the basis of the observed regularity, we could suppose that, by varying

HFX in the functional, one can adjust the calculated λ value in a relatively wide range. This will give an HFX parameter at which the calculated λ value best approximates the experimental data.

The proposed simple approach may be helpful, for example, in calculations of large charge-transfer exciplexes important for organic electronics, fluorescence band shapes due to molecular vibrations, and in many other cases when the computational cost is important. Previously, when using the TDDFT method, due to significant difference between calculated and experimental λ values, the maximum of the calculated absorption band was shifted along the λ scale until the calculated and experimental maxima coincided.[35] The use of a calibrated functional, well reproducing the experimental λ value, would make this procedure unnecessary and the fitted functionals might also be applied to systems of interest at a low computational cost.

The goal of this work was to calibrate the standard BHHLYP[36] exchange–correlation functional by varying the percentage of Hartree–Fock exchange energy (HFX) using examples of $DBMBF_2$ exciplexes with benzene, toluene, *p*-xylene and other alkyl benzenes, and also with pyridine as benchmarks to accurately describe the fluorescence wavelengths of these systems.

We performed a series of calculations for $DBMBF_2$ exciplexes with the selected alkylbenzenes and pyridine in the gas phase (to compare with experimental data[34]) and in a solvent within a conductor-like polarizable continuum (CPCM) model (cyclohexane, to compare with experimental data[37]) with varying HFX and, for each complex, chose the value of HFX at which the calculated fluorescence wavelength λ (or $S_1 \rightarrow S_0$ transition energy E) best approximates the experimental one.[34,37] The calculation procedure is described in Online Supplementary Materials.

The results of calculations compared with the experimental data are presented in Table S1. A similar variation of HFX for the $DBMBF_2$–benzene exciplex was performed for the PBE0 functional in the vicinity of the standard value HFX = 0.25; the optimized HFX values for both functionals were very close to each other (see Table S2).The results of calculations demonstrate that the HFX value in a suitable hybrid functional (BHHLYP or PBE0) can be fitted to accurately reproduce the experimental value of E or λ for a corresponding exciplex (see Figure S1). At the same time, as shown in Figure S1, the fitted HFX value in a functional for one system appears inapplicable to another system, even for chemically related systems, such as alkylbenzenes.

To understand the reasons for such a difference, we studied the relationship between the HFX value in the optimized functional and the value of charge transfer (CT) in the exciplex, calculated as the sum of Mulliken charges on atoms transferred from the donor (alkylbenzene or pyridine) to the acceptor ($DBMBF_2$) molecule. The results obtained (Figure 1) demonstrate the following two interesting features.

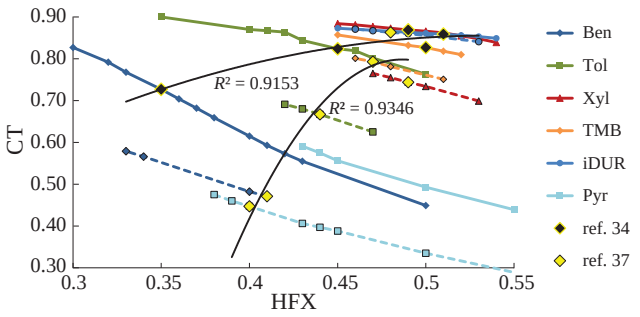

Figure 1 CT–HFX correlations for benzene (Ben), toluene (Tol), *p*-xylene (Xyl), 1,3,5-trimethylbenzene (TMB), isodurene (iDUR) and pyridine (Pyr). Gas phase calculations are shown by solid lines. Calculations with CPCM are shown by dashed lines with framed points. Quadratic approximation by points chosen by the experimental data in the text above are shown by solid black lines ($y = -50.572x^2 + 49.226x - 11.181$, $R^2 = 0.9346$, yellow rhombs,[37] and $y = -3.7407x^2 + 4.0063x - 0.2173$, $R^2 = 0.9153$, black rhombs[34]).

First, we found close-to-linear CT–HFX correlations with smooth changes in the geometry of the complexes upon varying HFX for each system.

Second, we could observe clear correlations between the values of HFX in the optimized functional, best reproducing λ value in the experimental fluorescence spectrum, and the calculated CT value in the corresponding exciplexes throughout the whole series (yellow and black rhombs in Figure 1) and built two quadratic approximations for two series of experimental data[34,37] (solid black lines in Figure 1).

Note that the results of our previous calculations performed for exciplexes formed at an interface between a hole-transporting layer of *N*,*N*′-bis(naphthalen-1-yl)-*N*,*N*′-diphenylbenzidine (α-NPD) and an electron transporting layer of bis(2-methyl-8-quinolinato)(4-phenylphenolato)aluminum (BAlq) in OLEDs,[38] also demonstrated that the standard BHHLYP functional with HFX = 0.5 well described the experimental energy of the $S_1 \rightarrow S_0$ transition for four different mutual orientations of molecules in exciplexes with CT = 0.92–0.98. Combining this fact with the observation made in this work, where the standard BHHLYP functional with HFX = 0.5 gave results very close to the experimental data for the exciplexes with CT about 0.8–0.9, we suggested that the value of the HFX parameter in the functional best approximating the experimental data can be assessed by the value of CT in the exciplex and the correlations found in this work may also be used for other charge-transfer exciplexes formed by molecules chemically different from those explored in this work. This suggestion well agrees with the fact that the main contribution to the bonding energy in CT exciplexes is made by Coulomb interactions,[38] for which charge transfer is quite important.

Therefore, to assess the HFX value in an exchange–correlation functional, at which the experimental fluorescence wavelength for a chosen exciplex can be reproduced with a good precision, one can take a quadratic HFX–CT correlation built by a desired set of experimental data (in the gas phase or in cyclohexane, see Figure 1), plot a linear HFX–CT correlation for a new exciplex of interest by two points calculated with the standard functional and one other value of HFX, and find the required HFX value at the point of intersection of the newly built HFX–CT straight line and a quadratic correlation in Figure 1. Using this value, the fluorescence wavelength of the new exciplex will be calculated with a reasonably high precision within acceptable time.

Thus, we have shown a possibility of fitting the percentage of Hartree–Fock exchange in the hybrid exchange–correlation BHHLYP functional to properly consider the long-range electron interactions in calculations of CT exciplexes. The proposed approach is rather simple and economical and may be used in precise calculations of wavelengths and energies of $S_1 \rightarrow S_0$ transitions in fluorescence spectra of large charge-transfer exciplexes, widely used, for example, in organic electronics, where ‘exact’ quantum-chemical methods of higher level are inapplicable. A similar study using the PBE0 functional (HFX = 0.25) and exciplexes with a lower degree of charge transfer is planned for the nearest future.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2024.01.040.

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