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TD-DFT Accuracy in Determining Excited-state Structures and Fluorescence Spectra of Firefly Emitter

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Abstract We analyzed the excited-state structures and emission spectra of firefly emitter, the anionic keto form of firefly oxyluciferin(keto-1), determined by the time dependent-density functional theory(TD-DFT) approach. The analysis is based on a direct comparison with the highly correlated CASSCF(MS-CASPT2) *ab initio* approach. 49 DFT functionals were considered and applied to the study. Among the tested functionals, mPW3PBE, B3PW91 and B3P86 give the best performance for ground-state geometry, absorption spectrum, excited-state geometry and emission spectrum.

Keywords Firefly; Time dependent-density functional theory(TD-DFT); Benchmarking; Keto-1; Excited state; Emission spectrum

1 Introduction

Firefly bioluminescence has become a ubiquitous tool for tagging and observing gene expression, protein-protein interactions, disease progression, and constructing recombinant whole-cell biosensors[1,2]. The accepted chemical mechanism of firefly bioluminescence involves the reaction of *D*-luciferin, (*S*)-2-(6-hydroxy-2-benzothiazolyl)-2-thizaoline-4-carboxylic acid, adenosine triphosphate(ATP) and O_2 to give the anionic keto form of firefly oxyluciferin(keto-1), 2-(6′-hydroxybenzothiazol-2-yl)-4-hydroxythiazole, which has been assumed to be the emitter in a singlet excited state[3,4]. As the excited state of the keto-1 decays to the ground state, multicolor light of it from green(*ca.* 530 nm) to red(*ca.* 635 nm) is emitted under the action of different luciferases[5,6]. However, many details of the chemical origin of the multicolor bioluminescence are ambiguous and challenge both theory and experiment.

Several authors have tried to clarify the bioluminescence phenomenon, with computational methodologies, *via* studying the excited-state structure and properties of keto-1[7—18]. However, despite of the good contribution to the literature, some aspects of these studies call for more investigation. Nowadays, *ab initio* methods allow for accurately determining a large set of properties for molecular systems in their ground state. On the contrary, the calculations of excited-state properties, including emission phenomena are still a challenge, because they require the nontrivial task of an accurate determination of excited-state structures[19]. On the one hand, fast and cheap purposely tailored semiempirical approaches lack consistency when applied to families of bioluminescence molecules[20]. On the other hand, more reliable theoretical tools, such as CASPT2[7—9] and SACCI[10,11], are too expensive to include implicit and/or explicit solvent models and luciferase models in the calculation which are crucial in the multicolor bioluminescence. Therefore, a new strategy with similar reliability and lower computational cost is needed.

Another theoretical approach, density functional theory(DFT) is popular, by which one can calculate the electronic spectra of a medium with organic and biological molecules large to *ca.* 200 atoms[21—24] within a realistic timeframe. Furthermore, the current accuracy to cost ratio is significantly lower than that of sophisticated post-Hatree-Fock approaches. Some authors have used this characteristic to include implicit/explicit solvation models and luciferase models in their studies of multicolor bioluminescence[14,15]. However, both *in vacuo* and in solvent phase DFT studies did not provide convincing proof for their reliability in the computation of multicolor bioluminescence systems, because it is difficult to be aware of which functional is best for the system or property of interest.

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The aim of this article is the systematic investigation of the excited state structures and fluorescent properties by unravelling specific behaviors of time dependent-density functional theory(TD-DFT) methods. We intended to focus on some aspects not explored by other theoretical studies. A TD-DFT benchmarking study was performed for the calculation of the excited state structure and emission spectrum. To this end, we have compared the results obtained *in vacuo* by 49 density functionals with the result obtained from a MS-CASPT2//CASSCF state of the art approach[7]. A strategy with similar accuracy to these states of the art methods but with lower computational cost was developed.

2 Computational Methods

All DFT and TD-DFT calculations have been carried out with the Gaussian 09 program[25], using 49 density functionals in the DFT benchmarking, including (i) 11 generalized gradient approximation(GGA, in which the density functional depends on density and its reduced gradient): B97D[26], BPBE[27,28], BPW91[27,29], HCTH[30—32], HCTH93[30—32], HCTH147[30—32], HCTH407[30—32], mPWLYP[33,34], mPWPBE[28,34], mPWPW91[29,34], OLYP[33,35,36]; (ii) 5 meta GGA(in which the functional also depends kinetic energy density): BB95[27,37], M06L[38], mPWB95[34,37], τHCTH[39], VSXC[40]; (iii) 21 hybrid GGA(a combination of GGA with Hartree-Fock exchange): B1LYP[27,33], B3LYP[27,33], B3P86[27,41], B3PW91[27,29], B98[42], B971[30], B972[43], BHandH[44], BHandHLYP[33,44], HSEh1PBE[45], MPW1K[34,46], mPW1LYP[33,34], mPW1PBE[28,34], mPW1PW91[34,42], MPW3LYP[33,34,47], mPW3PBE[28,34], O3LYP[33,35,36], PBE[28], PBE1PBE[28], τHCTHhyb[39], X3LYP[48]; (iv) 8 hybrid meta GGA(a combination of meta GGA with Hartree-Fock exchange): B1B95[27,37], BB1K[27,37,49], BMK[50], M06[51], M06HF[52], M062X[51], MPWB1K[34,37,47], MPW1B95[34,37,47]. In addition we studied 4 long-range corrected functionals, CAM-B3LYP[53], ωB97[54], ωB97X[54] and ωB97XD[55]. Diffuse functions, which often are critical in predicting excited states, as well as *d*-type polarization functions augmented the 6-31G split-valence basis set to yield 6-31+G(*d*). The larger basis sets, which include 6-31+G(*d,p*), 6-31++G(*d,p*), 6-311+G(*d*), 6-311+G(*d,p*) and 6-311++G(*d, p*) have been tested with B3LYP functional and showed no improvement in the excited geometry optimization and emission spectrum(see Table 1). We appraised the qualities of the selected functionals *via* comparing TD-DFT results to MS-CASPT2 reference values as reported in ref.[7].

Table 1 TD B3LYP computed excited geometrical parmeters(R_1—R_{18}, nm), emission spectra(λ_{em}, nm) and oscillator strengths(f) of keto-1

Method	6-31+G(*d*)	6-31+G(*d,p*)	6-31++G(*d,p*)	6-311+G(*d*)	6-311+G(*d,p*)	6-311++G(*d,p*)
R_1	0.1233	0.1233	0.1233	0.1226	0.1226	0.1226
R_2	0.1374	0.1374	0.1374	0.1372	0.1372	0.1372
R_3	0.1318	0.1318	0.1318	0.1314	0.1314	0.1314
R_4	0.1439	0.1439	0.1439	0.1437	0.1437	0.1437
R_5	0.1317	0.1317	0.1316	0.1313	0.1313	0.1312
R_6	0.1397	0.1397	0.1397	0.1395	0.1395	0.1395
R_7	0.1412	0.1412	0.1412	0.1410	0.1410	0.1410
R_8	0.1387	0.1387	0.1387	0.1384	0.1384	0.1384
R_9	0.1448	0.1448	0.1448	0.1446	0.1446	0.1446
R_{10}	0.1266	0.1266	0.1266	0.1259	0.1259	0.1259
R_{11}	0.1462	0.1462	0.1462	0.1460	0.1460	0.1460
R_{12}	0.1408	0.1408	0.1408	0.1405	0.1405	0.1405
R_{13}	0.1411	0.1411	0.1411	0.1407	0.1407	0.1407
R_{14}	0.1743	0.1743	0.1743	0.1741	0.1741	0.1742
R_{15}	0.1779	0.1779	0.1779	0.1778	0.1778	0.1778
R_{16}	0.1791	0.1791	0.1791	0.1790	0.1790	0.1790
R_{17}	0.1828	0.1827	0.1827	0.1826	0.1826	0.1826
R_{18}	0.1552	0.1552	0.1551	0.1550	0.1550	0.1550
λ_{em}	555.22	555.30	555.42	555.35	555.00	555.03
f	0.4576	0.4579	0.4602	0.4450	0.4463	0.4475

3 Results and Discussion

3.1 Excited-state Structures by TD-DFT and CASSCF

The molecule considered for the present study is keto-1 originally selected by the reference of Liu *et al.*[7](see Fig.1). To the best of our knowledge, no general and extensive tests on geometries have been carried out. Table S1(see the Electronic Supplementary Material of this paper) reports the variations of structural parameters with respect to CASSCF values.

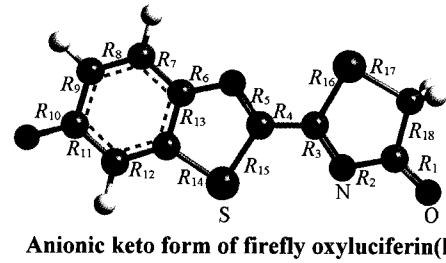

Fig.1 Anionic keto form of firefly oxyluciferin(keto-1)

As shown in Table S1(see the Electronic Supplementary Material of this paper), the root-mean-square deviation(RMS) between the CASSCF and TD-DFT results was from 0.0012 nm(B1B95 and MPW1B95) to 0.0038 nm(mPWLYP).

For B3P86, B3PW91, B972, BHandHLYP, HSEh1PBE, MPW1K, mPW1PBE, mPW1PW91, mPW3PBE, PBE1PBE, B1B95, BB1K, M06, MPWB1K and MPW1B95, they presented low RMS, which provided an excellent agreement with the reference value(RMS≤0.0015 nm). In more details, for the functionals(RMS≤0.0015 nm), the central C—C bond(R_4) is described with deviations from 0.1% to 0.7%. MPW1K and BB1K gives the best performances(–0.0002 nm), and the worst result comes from B972(0.001 nm). For C—N bonds, the best agreement is provided by MPW1B95(R_3) and HSEh1PBE(R_5) calculations(0 nm for R_3 and 0.0011 nm for R_5, corresponding to 0% and 0.8% deviations, respectively). The worst one is obtained with B3PW91 and BHandHLYP(0.0005 nm for R_3 and 0.0018 nm for R_5, 0.4% and 1.4%, respectively). For C—S bonds(R_{15} and R_{16}), the optimal description is obtained with HSEh1PBE(R_{15}) and B972(R_{16})(0.0001 and 0.0001 nm, *ca.* 0% and 0%, respectively). In summary, we can conclude that the excited state structures of keto-1 are not accurately estimated by GGA, meta GGA and long-range corrected functionals. Finally, it should be noted that the popular B3LYP functional, also used in the field of researches, presents the excited geometrical parameters significantly different from the reference va- lue(RMS of 0.0017 nm).

3.2 Emission Spectra by TD-DFT and MS-CASPT2

We reported the emission spectra for keto-1 predicted *via* the functionals in Table S1(RMS≤0.0015 nm). And the deviations are no more than 30 nm compared with MS-CASPT2 results and no more than 10 nm compared with experiment values listed in Table 2. The three best density functionals are mPW3PBE, B3PW91 and B3P86(552.8, 552.5 and 551.7 nm, respectively) compared with both MS-CASPT2 and experiment values. In more details, the order is mPW3PBE, B3PW91, B3P86, B972, HSEh1PBE, M06, PBE1PBE, mPW1PBE, mPW1PW91, B1B95. From this point of view, from which we conclude that mPW3PBE, B3PW91 and B3P86 can be used safely in the study of the excited-state geometry and emission spectrum of keto-1, for the results calculated with these functionals are very similar to those obtained with a state of the art methodology.

Table 2 Emission spectra, λ_{max}, and oscillator strengths(f), predicted for keto-1

Method	λ_{max}/nm	f	Method	λ_{max}/nm	f
MS-CASPT2[7]	563.6	—	mPW1PW91	534.4	0.5054
B3P86	551.7	0.4466	mPW3PBE	552.8	0.4478
B3PW91	552.5	0.4492	PBE1PBE	534.9	0.5039
B972	546.9	0.4637	B1B95	533.3	0.5144
HSEh1PBE	542.4	0.4791	M06	538.8	0.4908
mPW1PBE	534.4	0.5043	Expt.[56,57]	545	—

3.3 Ground-sate Structures and Properties

After the analysis of excited-state properties and structures, it is interesting to briefly investigate ground-state optimized structures. The ground state geometrical parameters are reported in Table S2(see the Electronic Supplementary Material of this paper). Label of bonds is referred to excited-state structure. The RMS between CASSCF and DFT results was from 0.0006 nm(BHandHLYP) to 0.0032 nm(mPWLYP). Among B3P86, B3PW91, B972, BHandHLYP, HSEh1PBE, MPW1K, mPW1PBE, mPW1PW91, mPW3PBE, PBE1PBE, B1B95, BB1K, M06, MPWB1K, MPW1B95, the top ranked functionals for the excited-state structures also presented low RMS for ground-state geometries(RMS≤0.0013nm). The results suggest that the fuctionals which could precisely predict the excited-state structures and emission spectra, are sufficient to precisely predict the ground-state structures and absorption spectra. The others were not considered.

The C—C bond length between the benzothiazole and thiazoline fragments(R_4) are overestimated with the reference value, and it holds for all functionals. Differences for all functionals are less than 0.0011 nm. MPWB1K provides the best agreement with the reference value(0.0003 nm, *ca.* 0.2%). As in the ground state, C—N bonds are generally overestimated with deviations from 0.0008 nm to 0.0022 nm for R_3 and 0 to 0.001 nm for R_5. For C—S bond lengths, the best agreement is obtained with BHandHLYP(0 nm) and B3P86(0 nm) for R_{15} and R_{16}, respectively. And the worst one is obtained with MPWB1K(–0.0015 and –0.0022 nm, 0.8% and 1.2% for R_{15} and R_{16}, respectively). We can conclude that the functionals are the top ranked functionals for the excited-state structures, on average, reproducible results for ground-state geometries in comparison to CASSCF results.

Finally, Table 3 reports the absorption spectra obtained with different functionals. mPW3PBE, B3P86 and B3PW91 give the best agreement with MS-CASPT2 values, with the difference less than 0.9 nm. The worst result(475.1 nm) is provided by mPW1PW91. All the maximum absorption λ_{max}(nm)

Table 3 Absorption spectra, λ_{max}, and oscillator strengths(f), predicted for keto-1

Method	λ_{max}/nm	f	Method	λ_{max}/nm	f
MS-CASPT2[7]	486.21	—	mPW1PW91	475.1	0.6881
B3P86	484.6	0.6324	mPW3PBE	485.9	0.6322
B3PW91	485.4	0.6350	PBE1PBE	475.8	0.6856
B972	481.4	0.6513	B1B95	475.7	0.6944
HSEh1PBE	478.1	0.6654	M06	481.8	0.6569
mPW1PBE	475.2	0.6867			

are less than 12 nm compared to MS-CASPT2 values. In principle, a TD-DFT method can yield the exact absorption spectra for keto-1.

4 Conclusions

We have performed a study on the performances of several TD-DFT functionals in describing excited-state geometries and emission spectra for the anionic keto form of firefly oxyluciferin and compared them with CASSCF(MS-CASPT2) data in the literature[7]. It shows that the excited-state structures of keto-1 are not accurately estimated by GGA, meta GGA and long-range corrected functionals. Among the tested methods, mPW3PBE, B3PW91 and B3P86 give a qualitatively good description of excitation energies and excited-state structures. For keto-1, the central C—C, C—N, and C—S bond lengths are overestimated by the three best density functionals, with respect to CASSCF, which is known to provide accurate results[7]. Finally, mPW3PBE, B3PW91 and B3P86 also give the best performance for ground-state geometries and absorption spectra.

Electronic Supplementary Material

Supplementary material is available in the online version of this article at http://dx.doi.org/10.1007/s40242-013-3050-6.

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