Project Title:

Development of new long-range corrected density functional theory and its applications

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１． Background and purpose of the project, relationship of the project with other projects

DFT is a quantum chemical methods that can be broadly applied to calculations of chemical properties of real systems, such as nanomaterials and biomolecules, but many studies have reported that DFT provides poor results for molecular systems. To overcome disadvantages of DFT, long-range corrected (LC) DFT was proposed by focusing on the lack of correct long-range exchange interactions of DFT, and has been reported to solve a variety of problems of DFT, such as underestimated reaction barrier heights, isomerization energies, charge-transfer excitation energies, and oscillator strengths.

Optimally tuned (OT) LC-DFT whose range separation parameter (μ) is optimized to each system with Koopmans' theorem generates the correct orbital energies and predicts well the electronic transition energies corresponding to absorption spectra. Although many theoretical studies have applied a range of DFT functionals to generate vibrationally resolved fluorescence (FL) spectra of various organic molecules, it has been reported that it is difficult for DFT functionals to provide the accurate FL peak positions and relative intensities simultaneously. Even though B3LYP-D3BJ provided the emission peak of an exciplex system in agreement with the experimental data, the intensities of the emission peaks corresponding to charge transfer were too low. M06 showed red-shifted peaks with different relative intensities. In the case of range-separated hybrids, such as ωB97XD and CAM-B3LYP, many studies have recommended them as theoretical methods with a high priority for calculating vibrationally resolved

spectrum, but they generally lead to a blue shift.

In this project, OT-LC-DFT satisfying Koopmans' theorem and several DFT functionals (B3LYP, CAM-B3LYP, and ωB97XD) will be applied to time-dependent (TD) DFT and Franck-Condon Herzberg-Teller (FCHT) calculations to assess the applicability of theoretical methods to the FL spectra of various chemical systems, such as carbon nano bands (CNBs) using the experimental absorption and fluorescence spectra (Fig 1). In addition, in order to investigate the detection mechanism and its structures of tetraphenylethene-based (TPE) florescent probe with aggregation-induced emission (AIE) behavior for Hg^{2+} ion, we applied OT-LC-DFT method.

２． Specific usage status of the system and calculation method

In this project, we used 76.6% of bwmpc (2,255,759.7 hour) for this project and other researches which will be submitted to publications.

３． Result

The absorption and fluorescence spectra of 12-CNB were calculated using various LC functionals and the B3LYP functional and compared with the experimental ones. The LC functionals, such as LC-BLYP (μ=0.47), ωB97XD, CAM-B3LYP, and OT-LC-BLYP with a basis set lacking a diffuse function, 6-31G(d,p), showed entirely blue-shifted peaks in the calculated absorption and vibrationally resolved fluorescence spectra compared to the experimental ones, whereas B3LYP showed red-shifted peaks.

The addition of a diffuse function to the 6-31G(d,p) basis set [6-31+G(d,p)] resulted in a shift of the

absorption and fluorescence peaks calculated using all the tested DFT functionals to longer wavelengths. As a result, the absorption and fluorescence peaks of B3LYP/6-31+G(d,p) were further from the experimental ones, but peak positions from the LC functionals were closer to the experimental ones. In particular, OT-LC-BLYP/6-31+G(d,p) reproduced the peak positions closest to the experimental spectrum among all the functionals tested.
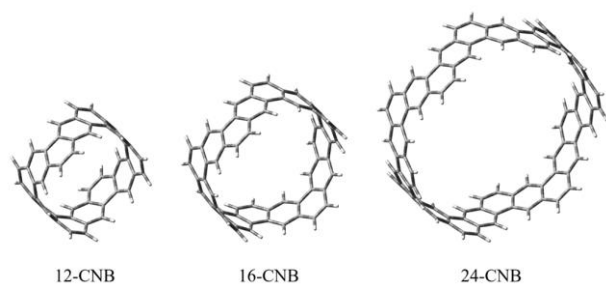

Fig 1. Optimized CNB structures (12-CNB, 16-CNB, and 24-CNB)

Transferring the basis set from double zeta [6-31+G(d,p)] to triple zeta [6-311+G(d,p)] made no significant difference in the calculated absorption spectrum but shifted the fluorescence spectra to longer wavelengths in all the DFT functionals tested. As a result, the fluorescence peaks of B3LYP/6-311+G(d,p) were more red-shifted compared to the experimental ones, which shows that the addition of a diffuse function and triple zeta worsens the performance of B3LYP on the prediction of those of 12-CNB. On the other hand, the fluorescence peaks of the LC functionals with 6-311+G(d,p) were much closer to the experimental ones than 6-31+G(d,p). The fluorescence peak positions of 12-CNB calculated using CAM-B3LYP/6-311+G(d,p) were close to the experimental ones, but the relative intensities of the peaks did not match the experimental ones. OT-LC-BLYP/6-311+G(d,p), however, provided the closest fluorescence spectra to the experimental ones among all the functionals tested in terms of the peak position and relative intensity.

In an examination of OT-LC-BLYP/6-311+G(d,p) for calculations of the absorption and fluorescence spectra of 16-CNB and 24-CNB,

OT-LC-BLYP/6-311+G(d,p) also reproduced the experimental absorption and fluorescence spectra with high accuracy in terms of both the peak position and intensity, in that LC-DFT can calculate effectively the electron hole pair interaction between occupied and unoccupied molecular orbitals related to electron transition, which is significant in the excited state geometry relaxations (Fig 2).
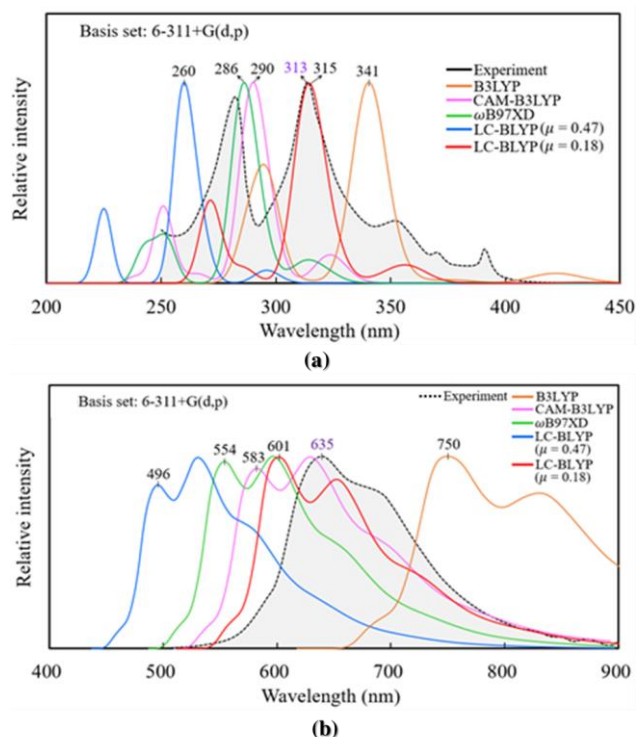
Fig 2. (a) Absorption (HWHM=750cm^{-1}) and **(b)** vibrationally resolved fluorescence (HWHM=200 cm^{-1}) spectra of 12-CNB with TD-DFT calculations using 6-311+G(d,p)

Then, to understand the photophysical properties of TPE-BTA and TPE-BTA-2Hg^{2+} at the molecular level, theoretical studies of their electronic structures were carried out using DFT calculations. To find the binding site of two Hg^{2+} to TPE-BTA, we performed geometry optimizations of the predicted several conformations of TPE-BTA-2Hg^{2+} and calculated their binding energies. The calculated UV spectrum of TPE-BTA-2Hg^{2+} was found to be consistent with those obtained experimentally with regard to both the UV absorbance patterns. To obtain fluorescence spectra of both TPE-BTA and TPE-BTA-2Hg^{2+}, geometry optimizations of the S$_1$ state of both TPE-BTA and TPE-BTA-2Hg^{2+} were performed

using TD-DFT, which provided the fluorescence peak of TPE-BTA-$2Hg^{2+}$ over two times stronger than that of TPE-BTA (Fig. 3) as shown in the experimental spectra of TPE-BTA and TPE-BTA-$2Hg^{2+}$. Furthermore, the peak positions of the experimental fluorescence spectra of TPE-BTA and TPE-BTA-$2Hg^{2+}$ are shown to be also reproduced successfully.
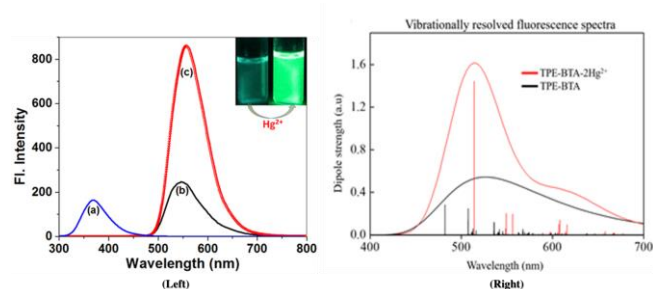
Fig 3. (Left) Fluorescence (a) excitation and (b) emission spectra of 0.1 μM of TPE-BTA in a 0.2 M HEPES buffer solution containing 2 vol% of THF/water (fw = 70%, pH 7.4), and (c) emission spectrum of TPE-BTA after reacting with 5 μM of Hg^{2+}. Inset: Corresponding photographic images of TPE-BTA and Hg2+-TPE-BTA-Hg^{2+} under UV□lamp. (Right) Vibrationally resolved ($S_1 \rightarrow S_0$, HWHM=1300cm^{-1}) fluorescence spectra of TPE-BTA and TPE-BTA-$2Hg^{2+}$ calculated using FCHT calculations.

The S_0 state structure of TPE-BTA-$2Hg^{2+}$ shows binding with Hg^{2+} ions makes the central C=C bond length shortened (1.364 Å) and two phenyl rings and two S atoms of thiophenes gather to Hg^{2+} ions. However, the photo excitation of TPE-BTA-$2Hg^{2+}$ leads the structural changes, such as lengthening of the central C=C bond (1.459 Å) and gathering of two phenyl rings and two S atoms of thiophenes to Hg^{2+} ions. Noticeably, the dihedral angle of the central C=C (C1-C2-C3-C4) twists (increases) to become 51.6° from 19.5° by the geometry optimization in the S_1 state. Twisting of the dihedral angle of the C=C is shown to occur also even in the photo excitation of TPE-BTA (Fig 4A and B), but it does less than in the excited state of TPE-BTA-$2Hg^{2+}$. Binding with Hg^{2+} seems to result in not only twisting of the C=C, but also structural restriction in

the excited state, which may explain stronger intensity of fluorescence emission of TPE-BTA-$2Hg^{2+}$.
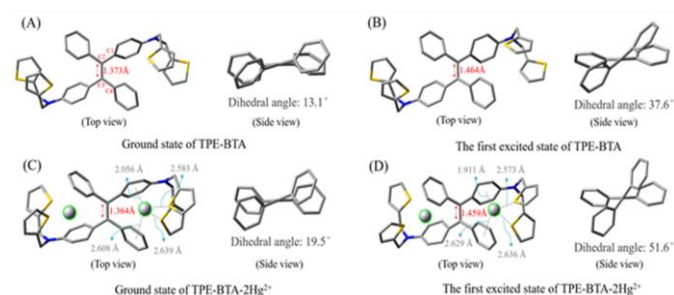
Fig 4. (A, C) The optimized structures of TPE-BTA and TPE-BTA-$2Hg^{2+}$ in the ground (S_0) state show that two thiophene rings are perpendicular to the phenyl ring, while two BTA molecules of TPE-BTA are situated with a staggered form to each other. Moreover, the Hg^{2+} ion in TPE-BTA-$2Hg^{2+}$ is coordinated to two S atoms and two phenyl rings. Top and side views show the distances (between Hg^{2+} and S atoms or phenyl rings) and C1-C2-C3-C4 dihedral angle. (B, D) The optimized structures of TPE-BTA and TPE-BTA-$2Hg^{2+}$ in the first excited (S_1) state.

4. Conclusion

In this project, optimally tuned (OT) long-range corrected (LC) density functional theory (DFT) is shown to successfully reproduce the experimental UV-vis absorption spectra as well as fluorescence spectra without referring to the empirical information specially on carbon nano bands. In the calculations of reproducing vibrationally resolved fluorescence spectra, large basis set size is preferred in a viewpoint of correct reproduction of the position of the peaks. Then, in the fluorescence spectrum calculations of TPE-BTA and TPE-BTA-$2Hg^{2+}$ for exploring the excited state structures to detect Hg^{2+} ion, it is shown that OT-LC-DFT is an aidful quantum chemical computation tool.

5. Schedule and prospect for the future

6. If no job was executed, specify the reason.

Fiscal Year 2021 List of Publications Resulting from the Use of the supercomputer

[Paper accepted by a journal]

1. "Koopmans-Type Theorem in Kohn–Sham Theory with Optimally Tuned Long-Range Corrected (LC) Functionals" Kimihiko Hirao,* Han-Seok Bae, Jong-Won Song, and Bun Chan, *J. Phys. Chem. A* **125**, 3489 (2021).[DOI:10.1021/acs.jpca.1c01593]

2. "Assessment of long-range corrected density functional theory on the absorption and vibrationally resolved fluorescence spectrum of carbon nanobelts" Dae-Hwan Ahn and Jong-Won Song,* J. Compt. Chem. **42**, 505 (2021) [DOI:10.1002/jcc.26473].

3. "Tetraphenylethene-based fluorescent probe with aggregation-induced emission behavior for Hg^{2+} detection and its application" Muthusamy Selvaraja, Kanagaraj Rajalakshmia, Daehwan Ahn, Su-Jin Yun, Yun-Sik Nam, Yeonhee Lee, Jong-Won Song,* and Kang-Bong Lee* Anal. Chim. Acta. **1148**, 238178 (2021) [DOI:10.1016/j.aca.2020.12.0].

[Conference Proceedings]

[Oral presentation]

[Poster presentation]

[Others (Book, Press release, etc.)]