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Comparison of LC-TDDFT and ADC(2) Methods in Computations of Bright and Charge Transfer States in Stacked Oligothiophenes

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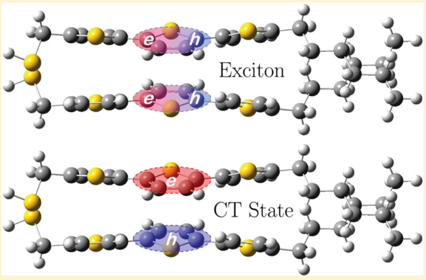
ABSTRACT: Long-range corrected time-dependent density functional theory (LC-TDDFT) has been applied to compute singlet vertical electronic excitations of oligothiophene molecules and their dimers and compared with the algebraic diagrammatic construction method to second order [ADC(2)], a wave function-based polarization propagator method. The excitation energies obtained from both methods agree to each other excellently. In particular, energetics of charge transfer states is concertedly reproduced. The linear response (LR) and the state specific (SS) approaches have been evaluated to appraise solvent effect on excited states. Benchmarked by the reference wave function method, the necessity of the SS treatment is justified in the prediction of charge transfer (CT) states under the TDDFT framework.



1. INTRODUCTION

Conjugated oligomers and their derivatives found in a variety of photovoltaic and optical applications[1−5] have been intensively studied both theoretically and experimentally;[6−9] this is attributed to their interesting and sophisticated electronic excited-state structures. Accurate and efficient excited-state modeling and simulations of conjugated molecules form an important research field of organic semiconductor materials.[9−14] The complexity of electronic structure in these π-conjugated systems is attributed to strong electron correlations, electron−phonon couplings and conformational disorder. Concerning the importance of molecular electronic properties, great efforts have been made for developing adequate and numerically feasible quantum-chemical methodologies. In past decades, such theories and techniques have been well-developed in terms of static properties based on ground-state electronic structures. Understanding and interpreting optoelectronic properties of molecular systems call for the necessity of computing electronic excitations. However, present quantum-chemical techniques for excited-state calculations are not as mature as those for ground states, not only because of the numerically difficult solution of time-dependent Schrödinger equation for a large light-driven molecular system but also due to a variety of competing interactions presented in these materials.

Let us briefly overview some of these factors frequently emerging when comparing the results of theoretical calculations with the experimental data commonly obtained for a solid state material or a solution. Perhaps, at the moment the most challenging but very important task of electronic structure calculations is the correct description of the energetics of electronic states that have different nature. We recall that the low dimensionality and low-dielectric constants of organic conjugated materials signify electronic many-body interactions appearing as pronounced excitonic effects, where the electron−hole binding energy is significant and nonperturbative. These corrections are not the same for other excitations such as $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ origins.[15,16] The other illustrative examples are $\pi \rightarrow \pi^*$ states of odd and even symmetries in conjugated polyenes (where electronic correlations can change the state ordering)[17] and interplay of ligand−ligand $\pi \rightarrow \pi^*$ and metal-to-ligand charge transfer excitations in organo-metallic complexes and quantum dots.[18−20] The presence of solvent or solid state dielectric environment adds another layer of complexity. A new class of intermolecular charge transfer (CT) excitations appears between molecules/fragments[21,22] weakly bound by electrostatic and/or dispersive interactions in the ground state (in which calculation is a nontrivial task for electronic structure theory by itself[23]). Identifying a correct energetic alignment between intermolecular CT states and intramolecular $\pi \rightarrow \pi^*$ states is an important computational goal in view of plethora of optoelectronic applications dealing with the rate of light-to-electric energy conversion and vise versa.[24] Here, inclusion of dielectric environment effects is necessary for an accurate assessment of stabilization energies presumably different for these excitations. Finally, dynamic (e.g., electron−phonon interactions) and static (e.g., conformations) disorders are unavoidably presented in experimental measurements but are very difficult to account for in simulations.[25−29]

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One way to address the arduous challenges outlined above is careful benchmarking between "low accuracy/low cost" techniques and "high precision/high cost" methods, which is frequently nontrivial since results obtained for small molecules cannot be readily extrapolated to the world of large systems. Nowadays, most commonly used methodologies toward electronic excitations are either built on explicit computation of electronic wave functions or count on the approximate map between energy and driven molecular electron density (i.e., time dependent density functional theory, TDDFT). Due to the historical independence of development paths for these two family of methodologies, their comparisons and mutually enriching interactions have been frequently underexploited, particularly, in the arena of complex electronic excitations that determine optoelectronic functionalities of technologically important materials.

In this manuscript, we compared the accuracy and efficiency of the TDDFT method relying on two long-range corrected (LC) functional kernels with those of the ADC(2) approach, regarding excited-state properties of several conjugated molecular systems, including chemically functionalized thiophene oligomers and their dimers. The CT excitations have been investigated using the linear response (LR) and the state-specific (SS) approaches within the TDDFT framework and evaluated by the reference wave function-based method. Satisfactory agreement on vertical electronic excitations has been achieved between the efficient TDDFT-based carefully selected hybrid LC functionals and the accurate wave function method.

2. OVERVIEW OF COMPUTATIONAL METHODOLOGIES

We start with a brief overview of underlying excited-state methodologies. Within wave function-based methods, elaborate approaches evolved from coupled-cluster (CC) method are important in quantum-chemical calculations of excited states in molecular system, such as the coupled-cluster linear response (CCLR) approach,[30,31] the equation-of-motion coupled-cluster (EOM-CC) approach,[32−34] and the CC-related symmetry adapted cluster configuration interaction (SAC−CI) method.[35]

Beside the widely used CC and CI (configuration interaction)[36] approaches, electron propagator approaches based on the many-body Green's function formalism are also prevalent techniques in calculations of electronic excited states in molecular environments, by expressing linear response functions in terms of polarization propagators.[37] The second-order polarization propagator approximation (SOPPA)[38] and the algebraic-diagrammatic construction (ADC) approach[39−43] are examples of such methods. In particular, the ADC approach to the polarization propagator, allows for partial summation of the diagrammatic perturbation expansion of the polarization propagator (transition function) up to different orders of the perturbation theory. In the further developed ADC(2) (ADC at the second-order perturbation level),[41] benefited from the so-called ADC intermediate state representation, excited-state wave functions can be explicitly calculated, which makes it a "true" wave function method. It gives similar results in comparison to the approximate coupled-cluster method to second order (CC2).[44−46] A systematic benchmark investigation on the capabilities of the CC2 method can be found in ref 47, and for exampe, CC2 calculations on the optical properties of methylene-bridged oligofluorenes[48] and oligo-para-phenylenes have been performed in ref 49. The ADC(2) has, however, the advantage that the excited states are obtained as eigenvalues of a Hermitian matrix whereas in coupled-cluster response the excitation energies are obtained as eigenvalues of a non-Hermitian Jacobi matrix.[45] It has been shown in recent EOM-CC with singles and doubles (EOM-CCSD) and including noniterative triples [EOM-CCSD(T)] investigations on DNA nucleobases[50] and on stacked base pairs[51] that the ADC(2) method can reproduce electronic excitations very well, especially $\pi \rightarrow \pi^*$ excitations whereas $n \rightarrow \pi^*$ excitations are often found to be underestimated. Important for the present work is also the observation that the location of charge-transfer (CT) states is also quite well reproduced by ADC(2). Thus, the accuracy of the treatment (only a second order) is quite satisfactory, whereas the numerical expense [$O(N^5)$, N being the size of the basis set] is comparable to CC2. Additionally, the combination of the ADC(2) approach with the resolution-of-the-identity (RI) method[52] allows for efficient calculations on excited states with molecular sizes being relevant for π-conjugated oligomers.[53] In spite of these advantages, the CC2 and ADC(2) methods become increasingly or prohibitively expensive with molecular size especially for large molecular systems such as organic semiconductors.

TDDFT has become a very popular technique for the calculation of excited-state properties in the past decade benefiting from its efficient numerical implementations. The modest numerical cost [$O(N^2)$−$O(N^4)$, N being the size of the basis set] and the favorable accuracy makes TDDFT capable of excited-state calculations for a variety of molecular systems of medium to large size.[19,23,54,55] Since the reliability of TDDFT computation essentially relies on the choice of the exchange-correlation (XC) kernels, its results should be benchmarked either against experimental data or against accurate wave function-based computations. As an electron-density-based method, the time-dependent Kohn−Sham (KS) potential (which consists of the external time-dependent potential, the Hartree potential, and the XC potential) has been considered as a complicated density functional that can be approximated. Currently, the linear response TDDFT based on Casida formulation[56] and relying on the adiabatic approximation (i.e., neglect of memory effects in the functional kernel),[57] constitutes the most practical and commonly used formulation incorporated in a broad variety of electronic structure codes.

Choosing proper density functionals according to the system under investigation is essential for KS-DFT computations. Among generally used, there are three classes of approximations for the XC potential that have been derived for ground-state DFT. These include the local (spin-) density approximation (LDA),[58] the generalized gradient approximation (GGA), and a family of hybrid functionals incorporating a fraction of nonlocal Hartree−Fock exchange. The corresponding adiabatic approximations of LDA, GGA, and hybrids have been adopted in TDDFT and applied to a variety of molecular systems and types of electronic excitations. However, the asymptotic (nonlocal) property of $-1/r$ of the XC potential is absent in either LDA or GGA kernel due to their nature of its spatial locality. In conjugated systems of our interest, such spatial nonlocality feature of the functional becomes crucial because of the existence of delocalized π-electrons, their high polarizabilities, and the large molecular sizes. Particularly, calculations of CT excitations become problematic in LDA and GGA schemes since the matrix elements describing interactions between donor and acceptor orbitals quickly vanish at large distances, which leads to unphysical low-lying CT state

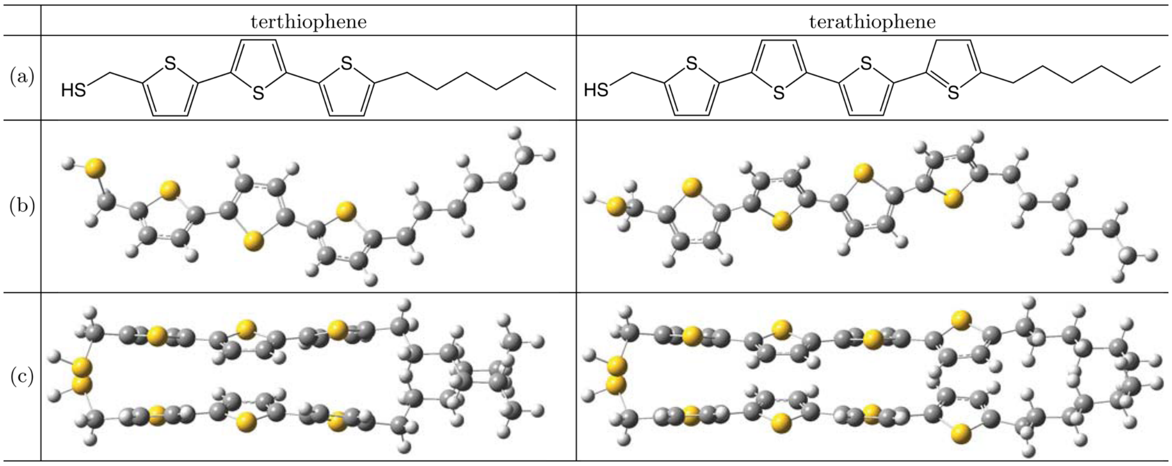

Figure 1. (a) Structural formula of chemically functionalized terthiophene and terathiophene. (b) Ground-state molecular structures and (c) dimer geometries optimized at TDDFT/ωB97XD/6-31G* level.

energies.[59−61] Popular hybrid functionals in which the asymptotic feature is considered via introduction of a constant moderate fraction of the orbital exchange (e.g., 20% in B3LYP and 25% in PBE1) are often also unsatisfactory in large polarizable systems[62] and for CT transitions.[60,61] It should be noticed that in the limit of analogous methods with 100% Hartree−Fock exchange, that is, time-dependent Hartree−Fock (TDHF) and configuration interaction singles (CIS) techniques, there is a strong overestimation of energies of both singlet intramolecular and CT excitations.[63] This is partly due to the lack of dielectric screening for orbital exchange, explicitly addressed in the Bethe-Salpeter framework.[64] These drawbacks provided strong impetus toward the development of LC scheme, which has been successfully applied to a number of hybrid XC functionals, such as CAM-B3LYP,[65] LC-ωPBE,[66,67] and ωB97X.[68] In the LC approach, the $1/r$ term of the XC potential is treated by the error function (erf) as $\mathrm{erfc}(\mu r)/r + \mathrm{erf}(\mu r)/r$, in which the XC potential at short-range and long-range are both well approximated by the first and second terms, respectively. Consequently, the fraction of the HF exchange in the XC functional a varies for different ranges. The optimal choice of the range-separation parameter μ, however, was found to be system-dependent and currently remains an active area of research.[69] Such LC hybrid functionals have been justified for the excited-state calculation of large conjugated molecules, particularly alleviating the problem of CT excitations.[59,68] In addition, long-range corrections to XC kernels are essential to predict physically correct spatial localization of electronic excitations in conjugated molecules. It has been suggested that LC-ωPBE (a = 0−100)[66] accurately describes localized excitations in charged oligomers, whereas both LC-ωPBE and CAM-B3LYP (a = 19−65) work well for excited states in neutral molecules.

In the consideration of van der Waals forces between atoms and molecules, which are important especially in large molecules and aggregates, long-range dispersion corrections on DFT/TDDFT approaches become necessary in favor of higher accuracy of simulations on molecular structures and energetics. The dominant approach at present to account for dispersive interactions is adding empirical dispersion correction energy to the KS-DFT potential. Prevailing empirical models, such as the Petersson−Frisch disperion (PFD) model[70] and Grimme's DFT-D2 and DFT-D3 methods,[71,72] have been tested in combination with a number of XC functionals for their accuracy in the description of dispersive interactions. In particular, dispersion correction methods are highly suggested for structure optimizations and calculations of interaction energies in large molecular systems.

3. COMPUTATIONAL DETAILS

Oligothiophenes and their derivatives have been attracting extensive attentions recently for their potential applications in molecular optoelectronics.[73] UV−vis and fluorescent spectra of oligothiophenes will be reported in ref 74. In this work, two thiolated oligothiophene derivatives (terthiophene and tetrathiophene) of different conjugation lengths have been studied as examples of conjugated molecules as shown in Figure 1. In addition, we have considered their dimers in parallel orientation maximizing interchain $\pi \rightarrow \pi$ overlaps (Figure 1c), which is expected in the ordered assemblies (e.g., on the gold surface owing the presence of thiol termination known of effective binding to the metal). Vertical electronic excitations in vacuum and in dichloromethane solution have been computed for both molecular monomers and dimers. The monomer calculations allow us to analyze intramolecular excitonic states, whereas the dimer results address appearing intermolecular CT excitations.

In the DFT/TDDFT computations, we have selected range-corrected ωB97XD[75] (a = 22−100) and CAM-B3LYP[65,76] (a = 19−65) functionals for both ground-state optimizations and excited-state calculations. In addition to the presence of LC modifications, being important for $\pi \rightarrow \pi^*$ excitations and charge transfer transitions, the ωB97XD functional, by construction, is able to describe weak dispersive interactions emerging due to interoligomer $\pi \rightarrow \pi$ overlaps, which bind the monomers into a dimer. The CAM-B3LYP functional overcomes the deficiencies of the B3LYP functional, such as CT excitations, by adopting the Coulomb-attenuating method as the LC modification. Considering the stacked π-conjugations in the dimers, the dispersion corrections empirically approximated by the DFT-D method[77] have been applied to the CAM-B3LYP calculations to calibrate the optimized ground-state structures and excited-state energies. All DFT and TDDFT computations have been conducted with the Gaussian 09 computational package[78] using the 6-31G* basis set. In TDDFT computations, the ground-state geometries have been optimized at levels of ωB97XD/6-31G* and CAM-B3LYP/6-31G* with dispersion, in the gas-phase and solvent

Table 1. Excitation Energies and Oscillator Strengths of Thiolated Terthiophene (a) and Terathiophene (b) Monomers in Vacuum and in Dichloromethane Solution, Tabulated in the Top and Bottom Panels of Each Molecule, Respectively, Computed by ADC(2) Method and Linear Response LC-TDDFT

	(a) thiolated terthiophene							
	ADC(2)/SV(P)		ADC(2)/TZVP		CAM-B3LYP		ωB97XD	
mode	Ω (eV)	*f*	Ω (eV)	*f*	Ω (eV)	*f*	Ω (eV)	*f*
1	4.106	1.236	3.967	1.149	3.677	1.071	3.807	1.082
2	5.012	0.004	4.828	0.003	4.804	0.000	4.866	0.000
3	5.281	0.021	5.134	0.022	5.226	0.002	5.326	0.007
4	5.372	0.032	5.233	0.030	5.272	0.006	5.388	0.006
1	4.016	1.270	3.879	1.185	3.527	1.174	3.649	1.186
2	4.981	0.003	4.795	0.002	4.711	0.001	4.765	0.001
3	5.215	0.015	5.064	0.016	5.184	0.001	5.286	0.010
4	5.324	0.037	5.164	0.016	5.225	0.007	5.333	0.004
	(b) thiolated tetrathiophene							
	ADC(2)/SV(P)		ADC(2)/TZVP		CAM-B3LYP		ωB97XD	
mode	Ω (eV)	*f*	Ω (eV)	*f*	Ω (eV)	*f*	Ω (eV)	*f*
1	3.808	1.659	3.680	1.550	3.377	1.479	3.536	1.495
2	4.665	0.005	4.488	0.004	4.319	0.001	4.422	0.004
3	4.901	0.006	4.739	0.008	4.816	0.002	5.018	0.059
4	5.071	0.060	4.896	0.058	4.979	0.063	5.127	0.002
1	3.731	1.686	3.604	1.579	3.232	1.585	3.386	1.604
2	4.580	0.007	4.410	0.006	4.177	0.001	4.274	0.005
3	4.884	0.004	4.710	0.005	4.771	0.001	4.972	0.083
4	5.056	0.075	4.880	0.074	4.940	0.090	5.085	0.002

environments. The optimized structures obtained from ωB97XD/6-31G* computations without solvent have been further used for ADC(2) calculations of singlet excited states. The latter approach, for its favorable performance-to-cost ratio, has been used as a wave function-method benchmark for the TDDFT counterpart. Two polarized basis sets, the split valence polarization [SV(P)] and the triple-zeta valence polarization (TZVP), have been used in the ADC(2) computations, since both sets provide reliable description of chemical bonding effects.[79,80] In all ADC(2) calculations, the core orbitals have been frozen. To make possible dimer computations with a larger basis set TZVP, the head and the tail groups (thiol group and alkane chain) of the oligothiophenes are described by the SV basis set, whereas the conjugated thiophene chains are associated with the TZVP basis set. All ADC(2) calculations have been performed with the Turbomole program suite.[81]

Solvent effects have been accounted for by using basic continuum models, in which the solvent is described as a continuum dielectric with a cavity that hosts the solute. An efficient conductor-like polarizable continuum model (C-PCM)[82] as implemented in the Gaussian package[78] has been employed in the TDDFT calculations. Here, the solvent effects on excited states have been obtained within the linear response (LR) regime in which the variations of Hartree and XC potentials can be linearly expanded with respect to the variation of the time-dependent ground-state density. However, the LR model being valid in the limit of weak external perturbation may be inadequate to describe polarizable electronic excitations in solutions. Here, the description of fast relaxation of the solvent electronic polarization is determined by its dielectric constant at optical frequency.[83] Limited to the continuum solvation models, the energy change due to the coupling between the solute excited state and the solvent polarization, in the LR approach, is classically described by the transition density and the solvent reaction field related to the transition density itself. The response of solvent reaction field to the change of solute charge distribution due to excitation is not actually expressed quantum mechanically. The state specific (SS) approach overcomes the deficiency of the LR method by allowing the solvation reaction field to adopt the changes in the solute wave function due to excitations.[83,84] The energy correction due to the fast electronic relaxation of the solvent, becomes state-dependent. By construction, the SS approach is more reliable than its LR counterpart, particularly for excited electronic states with charge distributions being significantly different from these of the ground state. Therefore, in the highly polarized scenario (i.e., polar solvent and/or CT excitations of solute), the SS approach is preferable since the significant effect of electric dipole variation is explicitly accounted for in the SS framework. Thereby, the SS treatment as implemented in the Gaussian 09 package[78] has been performed for calculating electronic states of dimers and compared to the LR counterpart.

In the ADC(2) counterpart, solvent effect has been simulated by conductor-like screening model (COSMO), which is also a continuum model and similar to C-PCM approach.[85] It has been recently extended for ADC(2)[86] using a state-specific approach. The COSMO calculations were performed with a Turbomole[81] development version.

4. RESULTS AND DISCUSSION

The calculated lowest four vertical excitation energies and their oscillator strengths in the two oligothiophenes are tabulated in Table 1. As in the usual case of organic semiconductors, only the lowest (band gap) state is optically allowed (bright), whereas the other three states are dipolar forbidden (dark), and

Table 2. Excitation Energies, Ω, Oscillator Strengths, *f*, and Charge Transfer Characters, CT, of Thiolated Terthiophene Dimer, in Vacuum (Top) and in Dichloromethane Solution (Bottom), Calculated by ADC(2) Method and LC-TDDFT Using the LR and the SS Approaches

	thiolated terthiophene dimer														
	ADC(2)/SV(P)			ADC(2)/TZVP			CAM-B3LYP/LR			ωB97XD/LR			ωB97XD/SS	
mode	Ω (eV)	*f*	CT	Ω (eV)	*f*	CT	Ω (eV)	*f*	CT	Ω (eV)	*f*	CT	Ω (eV)	*f*
1	3.736	0.002	0.171	3.595	0.002	0.196	3.401	0.001	0.162	3.522	0.002	0.098		
2	4.019	1.917	0.123	3.876	1.695	0.135	3.706	1.538	0.182	3.816	1.797	0.064		
3	4.387	0.252	0.876	4.208	0.244	0.862	4.186	0.345	0.807	4.362	0.110	0.928		
4	4.461	0.000	0.828	4.296	0.000	0.802	4.228	0.000	0.828	4.411	0.000	0.893		
1	3.700	0.002	0.159	3.553	0.002	0.182	3.358	0.002	0.154	3.488	0.003	0.089	3.516	0.003
2	3.924	2.101	0.084	3.779	1.870	0.096	3.592	1.904	0.126	3.696	2.123	0.044	3.807	1.811
3	4.370	0.178	0.915	4.186	0.176	0.903	4.149	0.274	0.865	4.351	0.081	0.948	4.069	0.216
4	4.449	0.000	0.840	4.276	0.000	0.816	4.207	0.000	0.837	4.403	0.001	0.904	4.069	0.216

have vanishing effect on the optical absorbance so that the comparison of oscillator strengths of dark states is not meaningful. Good agreement for excitation energies has been obtained for both oligothiophene monomers in the gas phase. The energetic difference of the brightest state (the lowest excitation) between TDDFT/ωB97XD/6-31G* and ADC(2)/TZVP is less than 0.2 eV, while the discrepancy between TDDFT/CAM-B3LYP/6-31G* and ADC(2)/TZVP is about 0.3 eV. Energies of the dark states are systematically shifted to the blue in both methods used. Similar consistency is observed for red shifts of 0.3 eV in the two levels of TDDFT and the two levels [SV(P) and TZVP] of ADC(2) calculations, with respect to an increase of the conjugation length. Finally, we observe a remarkable agreement for the oscillator strengths of the lowest state suggesting similar distribution of transition charges giving rise to the same transition dipole moments calculated by various approaches. These results demonstrate an adequate description of excited states in large π-conjugated systems under the TDDFT framework employing LC density functionals with low computational expense.

As expected, the presence of dichloromethane solvent accounted by C-PCM and COSMO models in LR-TDDFT and ADC(2) computations, respectively, results in red-shifts of the excitation energies (positive solvatochromism) and slight increases of the oscillator strengths of the brightest states (Table 1). The computational results can be compared to the experimental data, providing absorption maxima in dichloromethane to be at 369 nm (3.36 eV) and 402 nm (3.08 eV) for terthiophene and tetrathiophene, respectively.[74] The LC-TDDFT predictions of the lowest state excitation energy for each oligomer are higher compared to the respective experimental values, which is a typical case for the use of functionals with a significant fraction of the orbital exchange. Benchmarked by the experimental data, larger fraction $a = 22-100$ of the HF exchange in the ωB97XD functional results in larger overestimate of 0.3 eV compared to the overestimate of 0.2 eV of the CAM-B3LYP functional with a smaller fraction $a = 19-65$. When comparing ADC(2) with TDDFT results for excitation energies of the lowest state, we first notice smaller solvatochromic shifts observed in ADC(2) calculations (about 0.1 eV) compared to the TDDFT counterpart (about 0.15 eV). Nevertheless, the results in the solution display close agreement of the TDDFT and ADC(2) approaches, but not as good as what is obtained in the gas phase. It is worth mentioning that the lowest vertical excitations in solution computed with the SS-TDDFT approach show much smaller solvent shifts compared to their LR-TDDFT counterparts due to the weak electrostatic potential of the solute. In principle, because all the excited states of the monomers are not highly polarized and have very small permanent state dipole moments, the SS treatment does not effect the order of the excitations, albeit it makes slightly better agreement with the result of the wave function method. Overall, being gauged by the ADC(2)/TZVP method, the LC-TDDFT approach is testified to be reliable for such conjugated oligomers in the estimations of excited-state energies (with discrepancies less than 0.25 and 0.4 eV for ωB97XD and CAM-B3LYP, respectively), oscillator strengths and solvatochromic shifts. This result justifies the reliability of the TDDFT approach coupled with range-corrected functionals for the simulation of electronic excitations in large molecular systems with delocalized π-conjugation.

Analogous computations of electronic excitations have been performed for the oligothiophene dimers. It is noticeable that TDDFT computations using the CAM-B3LYP functional without dispersion correction fail to simulate the intermolecular interactions of π-conjugation, although they yield analogous monomer structures as the ωB97XD functional does. By taking into account the van der Waals interactions, computations with dispersion-corrected CAM-B3LYP/6-31G* and ωB97XD/6-31G* (including empirical dispersion by construction) provide similar optimized dimer structures in which the interchain interactions of $\pi-\pi$ stacking have been properly reproduced.

The dimer results of vertical excitations are tabulated in Tables 2 and 3. In addition, the underlying distribution of a calculated excitonic wave function has been characterized by the two-dimensional contour plot of the transition density matrix for a given excited state.[12,87] Here, the diagonal elements reflect changes of the electronic density due to electronic excitation and the off-diagonal extent of the plot is relevant to a distance between photoexcited electron and hole, thus quantifying the exciton size. We compared the transition density matrices for the lowest four electronic states obtained from TDDFT and ADC(2) methods for terthiophene dimer using their contour plots shown in Figure 2. Similar transition patterns have been recognized for the other dimer and for all higher energy excitations. In the dimer case, each plot can be roughly interpreted as 2×2 matrix, where the diagonal blocks correspond to intramolecular character of the excitation (i.e., when both an electron and a hole reside on the same monomer) whereas off-diagonal quadrants signify its CT character (i.e., when both an electron and a hole reside on different monomers). By averaging over the respective matrix

Table 3. Excitation Energies, Ω, Oscillator Strengths, *f*, and Charge Transfer Characters, CT, of Thiolated Tetrathiophene Dimer, in Vacuum (Top) and in Dichloromethane Solution (Bottom), Calculated by ADC(2) Method and LC-TDDFT Using the LR and the SS Approaches

	thiolated tetrathiophene dimer																
	ADC(2)/SV(P)			ADC(2)/SV(P)[a]			ADC(2)/TZVP			CAM-B3LYP/LR			ωB97XD/LR			ωB97XD/SS	
mode	Ω (eV)	*f*	CT	Ω (eV)	*f*	CT	Ω (eV)	*f*	CT	Ω (eV)	*f*	CT	Ω (eV)	*f*	CT	Ω (eV)	*f*
1	3.406	0.000	0.223	3.389	0.000	0.238	3.268	0.000	0.247	3.092	0.000	0.200	3.245	0.000	0.131		
2	3.763	2.764	0.065	3.770	2.783	0.083	3.631	2.507	0.062	3.463	2.237	0.144	3.588	2.589	0.033		
3	4.051	0.151	0.940	4.013	0.219	0.921	3.877	0.123	0.942	3.882	0.393	0.845	4.088	0.073	0.958		
4	4.212	0.000	0.776	4.176	0.000	0.764	4.051	0.000	0.739	3.981	0.000	0.595	4.143	0.000	0.311		
1	3.383	0.000	0.209	3.384	0.000	0.209	3.243	0.000	0.231	3.163	0.071	0.073	3.261	0.054	0.065	3.291	0.020
2	3.671	2.914	0.048	3.671	2.907	0.047	3.538	2.658	0.046	3.349	2.818	0.044	3.453	2.954	0.015	3.570	2.663
3	4.046	0.101	0.958	4.045	0.099	0.959	3.867	0.084	0.959	3.754	0.063	0.826	4.011	0.009	0.717	3.752	0.023
4	4.197	0.000	0.791	4.200	0.000	0.791	4.035	0.000	0.756	3.817	0.010	0.896	4.100	0.001	0.888	3.752	0.023

[a] SV(P) basis set for thiophene chains with SV basis set on the head and tail groups.

elements of the transition density matrix, as specified in ref 87, the intermolecular CT character of every transition can be conveniently described by a single number recorded in Tables 2 and 3 for both TDDFT and ADC(2) approaches.

Parallel arrangement of the chains in a dimer corresponds to the H-aggregate configuration.[88,89] Subsequently, the lowest two electronic states of the dimer are roughly "negative" and "positive" superpositions of the monomeric wave functions, where the lowest state is optically forbidden and the second state gains all oscillator strength from the pair. The splitting of the states (so-called Davydov's splitting) reflects the strength of intermolecular coupling.[90] Compared to the ideal aggregation case,[88] the center of the state pair in the dimer is red-shifted with respect to the monomer's lowest state energy, reflecting significant intermolecular π-orbital overlaps. Indeed, by examining plots in Figure 2 (the first and the second columns), we observe that the first two excitations have mostly intramolecular character (diagonal blocks) being strongly delocalized over both monomers as expected from the aggregate states. In addition, strong intermolecular π-orbital overlaps introduce a weak CT flavor to both states (at about 5–20% CT character depending on the state and the method as shown in Tables 2 and 3). Similar to the monomer case, under the LC-TDDFT framework, the ωB97XD/6-31G* computation precisely reproduced the excitation energies of the Davydov's state pair for both dimers in the gas phase as compared to the results of the ADC(2)/TZVP method, with differences less than 0.1 eV, whereas the CAM-B3LYP/6-31G* approach yields slightly small numbers.

The other two excited states obtained in the LC-TDDFT simulations have strong intermolecular CT nature as evidenced by Figure 2 (the third and the forth columns) with up to 90% CT character (see Tables 2 and 3). The existence of such excitations has been confirmed in the ADC(2) computations. Such low-energy CT states in the homodimers are somewhat unexpected but they are not uncommon.[91,92]

Regarding dielectric environment effects, LR- and SS-TDDFT results on dimer excitations in solution are collected in Table 2 and 3 together with ADC(2) data using different basis sets. As already noticed in the comparisons for excitations of monomers, LR-TDDFT simulation provides very satisfactory agreement with the COSMO-ADC(2) treatment including the CT excitations as well. In addition, considering the large electric dipole of CT states, followed by significant response of the solvent, the SS approach becomes desirable in such computations. Indeed, polar solvent environment provides about 0.3 eV of additional stabilization energy for CT transitions within the SS treatment. Notably, the transition energies of the lowest two ("non-polar") states calculated using the SS-TDDFT approach are shifted to the blue by about 0.1 eV compared to the LR-TDDFT results and become practically isoenergetic with the respected transition energies calculated in the gas phase. Stated equivalently, the solvation potential correction (being negative for $\pi \rightarrow \pi^*$ transition) is underestimated in the LR approach, for the highly polarized case. This fact agrees well with the theoretical analysis on the difference of treating fast solvent relaxation between SS and LR approaches. It is worth to mention that solvent shifts for the CT transitions computed at the ADC(2) level are significantly smaller than the SS-TDDFT results but are comparable for non-CT states.

Overall the SS-TDDFT results imply that the lowest CT transition are energetically very close to the low-energy

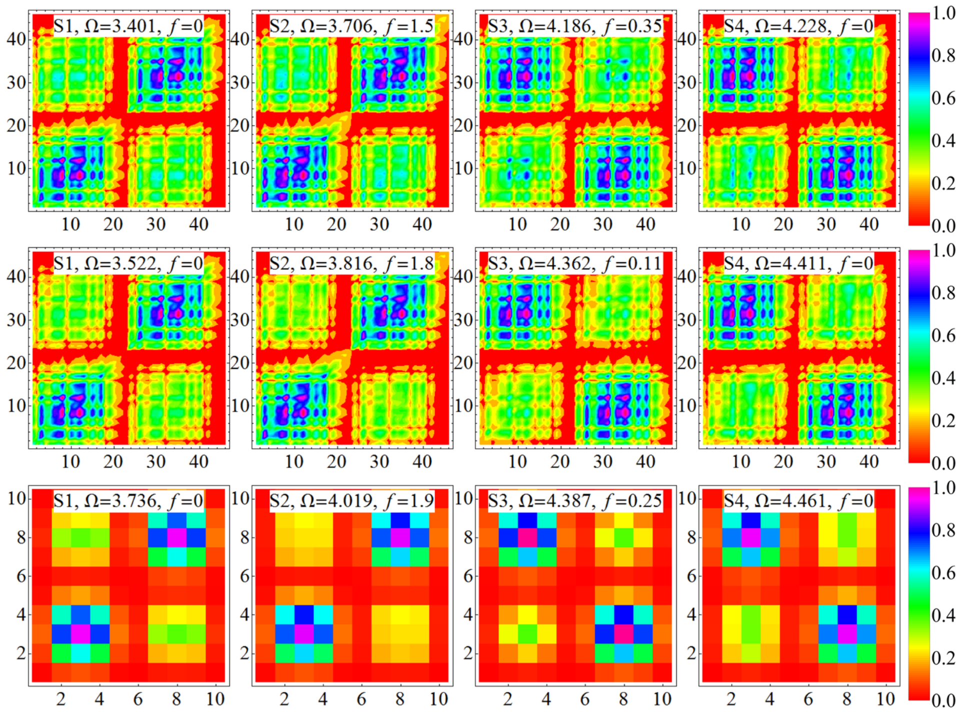

Figure 2. Lowest four electronic excitations of thiolated terthiophene dimer in vacuum given by the contour plots of the transition density matrices from the ground state to excited states, obtained from TDDFT/ωB97XD/6-31G* (top), TDDFT/CAM-B3LYP/6-31G* (middle), and ADC(2)/SV(P) calculations (bottom). The axis labels in the LC-TDDFT cases represent indices of non-hydrogen atoms from thiol group to alkane group in the dimer (oligomer 1:1–23, oligomer 2:24–46). In case of the ADC(2) analysis, the axes represent oligomer segments numbered in the order oligomer 1: alkane chain (1), three thiophenes (2–4), thiol group (5); oligomer 2: alkane chain (6), three thiophenes (7–9), thiol group (10). The inset of each plot shows the index of electronic mode, excitation energy Ω, oscillator strength *f* and charge transfer character CT.

excitonic states in the dimers. This possibly suggests an overlapping Frenkel exciton and charge transfer band of electronic transitions in the ordered oligothiophene assemblies, which could affect photoexcited state dynamics and have specific spectroscopic signatures.[74]

5. CONCLUSIONS

In this work, we have assessed the capability of the TDDFT approach based on the LC functionals (ωB97XD and CAM-B3LYP) with empirical dispersion corrections and the 6-31G* basis set in calculating electronic excitations in large conjugated molecular systems of oligothiophenes. The LC-TDDFT results have been carefully compared to the wave function-based method ADC(2) paired with the SV(P) and TZVP basis sets. Our analysis has shown that the LC functionals work very well in the estimation of absorption spectra of individual conjugated oligomers (monomers), whereas dispersion corrections are necessary for the simulation of intermolecular interactions in their aggregates (dimers). Excellent agreement on absolute values of transition energies as well as the dependence of excitation energies on the conjugation length has been reached between the LC-TDDFT and the ADC(2) methodologies. The solvation effects have been investigated under the TDDFT framework by both linear response (LR) and state-specific (SS) approaches, and the ADC(2) technique relying on COSMO methodology. Similar solvatochromic shifts have been predicted by both TDDFT and ADC(2) methods. The necessity of the SS method in comparison to the LR approach is demonstrated for the low-lying intermolecular CT states of dimers. Our results have shown a significant stabilization of CT transition energies suggesting a complex interplay of excitonic and CT transitions in the low-energy region for aggregated oligothiophenes. Therefore, benchmarked by the ADC(2) method, the presented LC-TDDFT approach is justified to be both accurate and efficient in the calculation of electronic excited states in the molecular family of oligothiophene.

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Notes

The authors declare no competing financial interest.

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