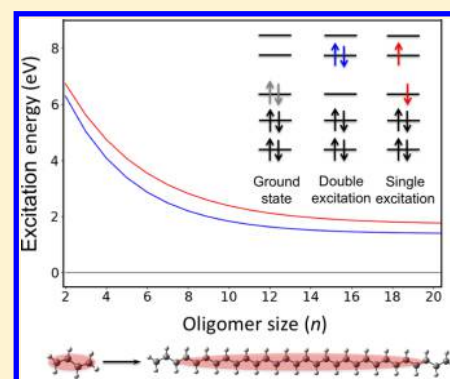


Single, Double Electronic Excitations and Exciton Effective Conjugation Lengths in π -Conjugated SystemsChristopher Sutton,^{†,||} Yang Yang,^{†,||} Du Zhang,[†] and Weitao Yang^{*,†,‡,§,||}[†]Department of Chemistry, Duke University, Durham, North Carolina 27708, United States[‡]Department of Physics, Duke University, Durham, North Carolina 27708, United States[§]Key Laboratory of Theoretical Chemistry of Environment School of Chemistry and Environment, South China Normal University, Guangzhou 510631, China

Supporting Information

ABSTRACT: The 2^1A_g and 1^1B_u excited states of two prototypical π -conjugated compounds, polyacetylene and polydiacetylene, are investigated with the recently developed particle–particle random phase approximation (pp-RPA) method combined with the B3LYP functional. The polymer-limit transition energies are estimated as 1.38 and 1.72 eV for the 2^1A_g and 1^1B_u states, respectively, from an extrapolation of the computed excitation energies of model oligomers. These values increase to 1.95 and 2.24 eV for the same transitions when ground-state structures with $\sim 33\%$ larger bond length alternation are adopted. Applying the pp-RPA to the vertical excitation energies in oligodiacetylene, the polymer-limit transition energies of the 2^1A_g and 1^1B_u states are computed to be 2.06 and 2.28 eV, respectively. These results are in good agreement with experimental values or theoretical best estimates, indicating that the pp-RPA method shows great promise for understanding many photophysical phenomena involving both single and double excitations.



Since the groundbreaking synthesis of the first conductive polymer polyacetylene,¹ numerous π -conjugated compounds have been incorporated as the active components in (opto)electronic devices.^{2–10} In nature, compounds that have a similar structure to polyacetylene are involved in various excited-state processes; for example, retinal serves as a photoreceptor that converts light to electrical signals, and carotenoids act as light-harvesting pigments.^{11–13} For these large symmetric π -conjugated systems, the first singlet excited state (2^1A_g) has significant double-excitation character and is optically dark using one-photon spectroscopic techniques,¹⁴ whereas the second singlet excited state (1^1B_u) is optically bright and corresponds to a one-particle excitation.

π -Conjugated compounds that have significant double-excitation character in the lowest excited states are used in a number of applications (e.g., see recent reviews^{15,16}) such as biological imaging,^{17–20} data storage,^{21,22} optical limiting,²³ up-converted lasing,²⁴ microfabrication,²⁵ and energy transfer in photosynthetic systems.^{11–13} Furthermore, a double-excitation state acts as a key intermediate state in singlet fission,^{26,27} which shows promise in boosting the overall efficiency in conventional photovoltaic cells.^{28,29} Therefore, an accurate computational determination of the electronic excited states in these materials is crucial for understanding both biological processes and emerging technologies.

From a theoretical perspective, the description of excited states with significant double excitation character^{30–37} is beyond the capabilities of conventional single-reference

theories such as configuration interaction singles (CIS), time-dependent density functional theory (TD-DFT) within the adiabatic approximation, and the Bethe–Salpeter equation based on the Green’s function quasi-particle energies (GW-BSE). Previously, vertical 2^1A_g excitation energies from adiabatic TD-DFT and CIS were overestimated for polyenes (oligomers of the infinite polymer polyacetylene), leading to a qualitatively incorrect energy ordering of the lowest excited states.^{38,39} To go beyond these limitations of TD-DFT, approaches such as dressed TD-DFT,^{40–42} which requires a postcalculation correction, and spin-flip TD-DFT (SF-TD-DFT)^{40,43–45} have been applied to calculate the vertical energies of the smallest polyenes with $n = 2–5$.^{45,46} To date, the highest accuracies in computed excitation states have mostly been obtained using multireference wave function methods that include both static and dynamic correlation (e.g., multireference second-order perturbation theory).^{30,47,48} Unfortunately, the computational cost of these approaches rapidly increases with a growing size of the active space to account for the growing multireference character of the ground state, which prohibits their application to large molecular systems.

In this work, we examine the particle–particle random phase approximation (pp-RPA) for the excited-state properties of the polyenes and oligodiacetylenes, which are oligomers of the two

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prototypical π -conjugated polymers polyacetylene and polydiacetylene, respectively (Figure 1). The pp-RPA was originally

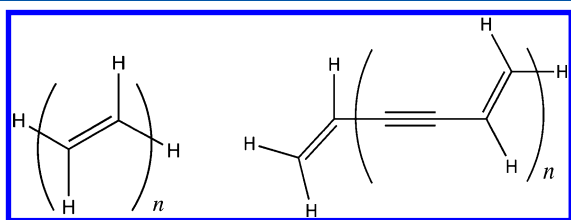


Figure 1. Molecular structures of the linear π -conjugated of *trans*-polyenes (left) ranging in size from $n = 2$ –20 (i.e., C_4H_6 to $C_{40}H_{42}$) and *trans*-oligodiacetylenes (right) from $n = 1$ –8 (i.e., C_6H_6 to $C_{34}H_{20}$) are considered in this study.

formulated as a correlation energy functional and can achieve an accuracy that is comparable to or higher than standard (semi)local or hybrid DFT functionals and the particle-hole (ph) RPA for a variety of computed properties.^{49–51} The pp-RPA has also been employed as an excited-state method. It can be viewed as an analog to the well-known particle-hole random phase approximation (ph-RPA) and TD-DFT,^{52–54} where instead of using the electron–hole density response the pp-RPA approach can be formulated in terms of the linear response of the pairing matrix to a time-dependent pairing field.⁵⁵ As an excited-state method,^{55–57} the pp-RPA shows a high accuracy for two-electron (double),^{56–58} charge-transfer,⁵⁹ and Rydberg excitations.⁶⁰

The pp-RPA can describe both single and double transitions on the same footing as the ground state. Starting from a double-ionized ($N - 2$)-electron reference, where N is the number of electrons for the system of interest, a two-electron addition mostly to the lowest unoccupied orbital leads to the singlet ground state (S_0) of the N -electron system (Figure 2).

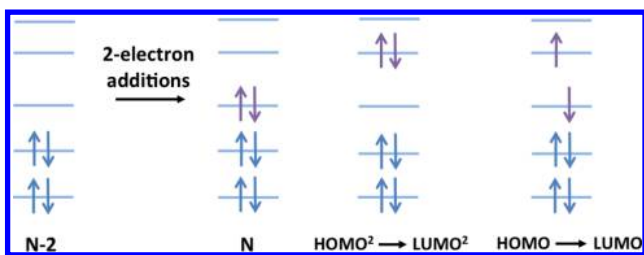


Figure 2. Diagram of two-electron additions starting from an ($N - 2$)-electron reference state, which results in the N -electron ground state and both two-electron ($HOMO^2 \rightarrow LUMO^2$) and one-electron ($HOMO \rightarrow LUMO$) excitations computed using the pp-RPA method. For simplicity, the second configuration for the $HOMO \rightarrow LUMO$ transition with opposite α and β spatial orbital occupation is not shown.

Other two-electron additions result in higher energy states. These higher states can be singly excited states, doubly excited states, or a mixture of both. Taking the difference between the two-electron addition energies leads to excitation energies of the N -electron system. In polyene, a main component to the 2^1A_g state is a two-electron addition to the LUMO+1 orbital of the ($N - 2$)-electron reference (labeled as a $HOMO^2 \rightarrow LUMO^2$ transition of the N -electron system in Figure 2); a main component of the 1^1B_u state is a two-electron addition to the LUMO and LUMO+1 (labeled as a $HOMO \rightarrow LUMO$ transition of the N -electron system in Figure 2).

The pp-RPA excitation energies are computed using QM⁴D⁶¹ as a post-DFT calculation on top of the ($N - 2$)-electron reference orbitals that are generated from a single-point calculation in Gaussian 09⁶² (with the same choice of functional and basis set). To improve the computational efficiency of the pp-RPA calculations for an examination of various structures, basis sets, and functionals, an active-space orbital truncation scheme is used.⁶³ The size of the truncated (active) orbital space is increased to reproduce the excitation energies from the full pp-RPA method to within 0.01 eV for the larger oligomers (see Table S1 of the Supporting Information).⁶⁴

As has been shown for the smallest polyenes,⁵⁶ the transition energies computed with the pp-RPA display a dependence on the DFT functional of the reference state. This is because the pp-RPA is in essence a linear response TD-DFT with pairing fields for estimating $N \pm 2$ excitations. Therefore, just as the conventional particle-hole TD-DFT excitation energies depend on the choice of the DFT reference with which the density matrix linear response is performed, the pp-RPA excitation energies also depend on the reference state with which the pairing matrix linear response is performed. To understand the impact of the functional choice on the excitation energies for longer polyenes, the pp-RPA energies are computed using PBE, B3LYP, and CAM-B3LYP references (Table S2).⁶⁴ A qualitatively correct ordering of $2^1A_g < 1^1B_u$ is obtained for all three functionals; however, the excited-state energies for the $2A_g$ ($1B_u$) state computed from a PBE reference are ca. 0.4 to 0.6 (0.2 to 0.3) eV lower compared with the B3LYP reference. In contrast, the excited-state energies are 0.4 to 0.7 (0.2 to 0.3) eV higher using the CAM-B3LYP reference for the 2^1A_g (1^1B_u) state compared with B3LYP. These results indicate that a larger amount of HF exchange in the reference functional increases the computed excitation energies (Table S2). The increase in the excitation energies is partly attributed to a larger energy difference between the LUMO and LUMO+1 reference orbitals of the ($N - 2$)-electron system (Figure S1), which are involved in both of the 2^1A_g and 1^1B_u transitions. The dependence of the excitation energy on the choice of the reference functional follows a similar trend to what is observed in other post-DFT approaches such as GW-BSE (i.e., neutral excitation calculation on top of reference orbitals generated with DFT) for polyenes with $n = 2$ –4.⁶⁵ The highest accuracies compared with the experimental and theoretical benchmark values are obtained using the reference orbitals computed with B3LYP. Therefore, the pp-RPA with B3LYP will be used for the remainder of the discussion.

We begin with a comparison of excited-state energies computed with the pp-RPA (using a complete active space) with the available results from wave-function-based methods for butadiene ($n = 2$). Benchmark values of 6.41 and 6.21 eV for the 2^1A_g and 1^1B_u states, respectively, were reported using equation-of-motion coupled-cluster theory with singles, doubles, triples, and quintets with a complete basis set extrapolation (EOM-CCSDTQ/CBS) with the experimental geometry (Table S3).⁶⁶ Using the same experimental geometry, the pp-RPA/B3LYP/cc-pVDZ computed 2^1A_g (6.66 eV) and 1^1B_u (6.92 eV) excitation energies are 0.25 and 0.71 eV larger than the reference EOM-CCSDTQ/CBS values (Table S3). When the basis set is increased to aug-cc-pVDZ, the errors in the excitation energies computed using pp-RPA/B3LYP for the 2^1A_g (6.46 eV) and 1^1B_u (6.60 eV) states are reduced to 0.05 and 0.39 eV (Table S3).

Focusing on the 2^1A_g state, single-reference EOM-CCSD overestimates the vertical excitation energies by 1.28 eV with the 6-31G** basis set (7.69 eV)⁶⁷ and 1.24 eV with cc-pVDZ (7.65 eV).⁶⁶ Increasing the basis set size reduces the error to 0.84 eV for EOM-CCSD/cc-pV6Z (7.25 eV) and 0.65 eV for EOM-CCSD/aug-cc-pVDZ (7.06 eV).⁶⁶ The decrease in the energy overestimation with a larger basis set is attributed to the unphysical mixing of Rydberg-like and valence double excited states.^{48,68} The electron correlation necessary to describe the 2^1A_g state can instead be accurately treated by including full triples in the EOM-CC formalism; however, EOM-CCSDT/cc-pVDZ (6.83 eV) and EOM-CCSDT/aug-cc-pVDZ (6.58 eV) both overestimate the excitation energy of the 2^1A_g state by 0.42 and 0.17 eV, respectively.⁶⁶ These results indicate that pp-RPA/B3LYP/aug-cc-pVDZ achieves a similar accuracy to EOM-CCSDT/aug-cc-pVDZ for the excitation energy of the 2^1A_g state. The relatively good performance of the pp-RPA at a much lower computational cost for the 2^1A_g state is attributed to the explicit treatment of the valence double-excitation component and incorporation of correlation effects through the exchange-correlation potential. However, we note that EOM-CC has the advantage of achieving potentially higher accuracies through an inclusion of higher order operators.

For larger oligomers, results are compared using two different sets of all-*trans* geometries that were previously optimized using MP2/aug-cc-pVDZ⁶⁹ and a tuned-hybrid PBEh* functional with 45.73% Hartree–Fock exchange (PBEh*/6-311G)⁷⁰ to understand the impact of geometries on the excited-state energies of polyenes. The geometries optimized with the PBEh* functional converge to a bond length alternation (BLA) of 0.08 Å with increasing oligomer length, whereas the MP2 geometries converge to a smaller BLA value of 0.06 Å. In comparison, the experimental BLA values from NMR and X-ray spectroscopy are 0.08⁷¹ and 0.104 Å,⁷² respectively. In terms of the basis set dependence of the pp-RPA-computed excited-state energies, we observe that an increase in the basis set size from cc-pVDZ to either cc-pVTZ or aug-cc-pVDZ does not significantly affect the pp-RPA-computed excitation energies for the 2^1A_g state for polyenes with $n > 2$ (Table S4); therefore, cc-pVDZ basis set is used for the remainder of this discussion, and the excitation energies were generated using the truncated active space.

Multireference Møller–Plesset perturbation (MRMP) theory results have been reported for polyenes with $n = 3–5$ and allows for a comparison to a high-level wave-function-based method for these oligomers.³⁰ Using the MP2/aug-cc-pVDZ geometry, the pp-RPA/B3LYP/cc-pVDZ excitation energies for the 2^1A_g and 1^1B_u states are -0.21 and $+0.37$ eV, respectively, relative to the MRMP values for polyene with $n = 3$. A difference of -0.52 eV for polyene with $n = 4$ and -0.33 eV for $n = 5$ is observed in MRMP and pp-RPA/B3LYP vertical excitation energies of the 2^1A_g states. In contrast, for the 1^1B_u state, pp-RPA/B3LYP overestimates MRMP by 0.07 eV for polyenes with $n = 4$ and 5 (Figure 3). Using the PBEh* geometry, the errors are -0.21 and $+0.12$ eV for the 2^1A_g and 1^1B_u states for polyene with $n = 4$ (which is the only coinciding oligomer size published using PBEh*). MRMP using complete active space configuration interaction reference functions (CASCI-MRMP) provides the best computational estimates of excitation energies for longer polyenes with $n = 6–14$.⁷³ For the 1^1B_u state, the pp-RPA excitation energies at the MP2-optimized geometries are on average 0.48 eV lower than the CASCI-MRMP values (computed using ground-state struc-

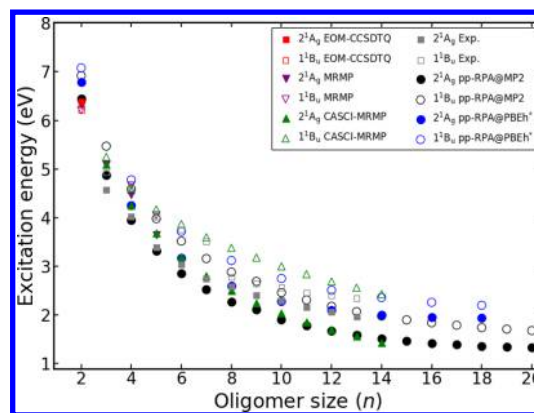


Figure 3. Vertical excitation energies (eV) from pp-RPA B3LYP/cc-pVDZ for polyenes with $n = 2–20$ for ground-state structures optimized using MP2/aug-cc-pVDZ⁶⁹ (black circles) and PBEh*/6-311G⁷⁰ (blue circles) compared with EOM-CCSDTQ/CBS (red squares),⁶⁶ MRMP (purple triangles),³⁰ CASCI-MRMP (green triangles),⁷³ and experimental values^{34,81} (gray squares) for the 1^1B_u (open) and 2^1A_g (filled) states.

tures optimized using MP2/cc-pVDZ); in contrast, a better agreement is found for the 2^1A_g state of polyenes with $n \geq 9$, with an average difference of 0.08 eV for those oligomer sizes (Figure 3).

A detailed comparison between the excitation energies obtained from the pp-RPA and computational benchmark values for the 2^1A_g and 1^1B_u states of polyene with $n = 2$ is discussed above; therefore, a comparison between the pp-RPA vertical excitation energies and experimental values will focus on polyenes with $n = 3–7$ using the MP2-optimized geometries. Results for polyenes with $n = 4$ and 6 will be discussed using the PBEh*-optimized geometries. For polyene with $n = 3$, the pp-RPA/B3LYP vertical excitation energy underestimates by 0.54 eV the experimental value for the 1^1B_u state (4.93 eV) determined from gas-phase measurements⁷⁴ and UV–visible absorption spectra.^{75,76} For the 2^1A_g state of polyene with $n = 3$, the experimental value of 4.57 eV (determined from resonance enhanced multiphoton ionization spectroscopy) is overestimated by 0.31 eV using pp-RPA/B3LYP. Experimental vertical transition energies have been estimated from room-temperature absorption and emission spectra in solution for polyene derivatives with $n = 4–7$.³⁴ For polyene with $n = 4$, the pp-RPA/B3LYP excitation energies at the MP2 geometry underestimate the experimental values of 4.60 and 4.02 eV by 0.01 and 0.07 eV for the 1^1B_u and 2^1A_g states, respectively. Additional experimental results for polyene with $n = 4$ from gas-phase and solution-based optical measurements indicate that the 1^1B_u state energy is in the range of 4.38 to 4.41 eV.^{36,74,77,78} Taking these values instead, pp-RPA excitation energies using the MP2 geometries give slightly larger errors of ca. 0.2 eV. The pp-RPA/B3LYP vertical excitation underestimates an experimental value for the 2^1A_g state by 0.15 eV.⁷⁹ In comparison with the vertical transition energies from ref 34 for oligomer sizes $n = 5–7$, the error in the pp-RPA/B3LYP excitation energy (using the MP2-optimized geometry) for the 1^1B_u (2^1A_g) state increases with system size: 0.04 eV (0.07 eV) for polyene with $n = 5$; 0.23 eV (0.18 eV) for $n = 6$; and 0.35 eV (0.22 eV) for $n = 7$. The opposite trend is observed using the PBEh* geometries, where the ppRPA/B3LYP energy is 0.18 eV (0.24 eV) higher in energy compared with the experimental value for the 1^1B_u

(2^1A_g) state of polyene with $n = 4$, which decreases to a difference of 0.03 eV (0.13 eV) for the 1^1B_u (2^1A_g) state of polyene with $n = 6$. The better comparison with experiment in the vertical transition energies obtained using the PBEh* geometries is attributed to BLA values that compare well to experiment for larger oligomers.

Spectroscopic data are not available for polyenes with $n \geq 8$. Instead, the 1^1B_u and 2^1A_g vertical excitation energies are estimated by Gaussian decomposition of room-temperature solution-based electronic absorption spectra of carotenoids (i.e., methylated polyene derivatives) for polyenes with $n = 8$ –13.⁸⁰ The vertical excitation energies of the 2^1A_g state are taken as is from ref 81. For vertical transition energies of the 1^1B_u state, a correction to the experimental values was suggested in ref 81 to account for the effects of the solvent and substitutional groups, which are neglected in this discussion. The pp-RPA underestimates the experimental excitation energies for polyenes with $n = 8$ –13 by 0.29 to 0.39 eV for the 2^1A_g state using the MP2 geometries. For the 1^1B_u state, the pp-RPA overestimates the experimental value by 0.10 eV for $n = 8$ but underestimates the $n = 13$ result by 0.27 eV. In contrast, a decrease in the error with an increase in oligomer size from $n = 8$ (+0.34 eV) to $n = 12$ (+0.11 eV) is observed for the pp-RPA excitation energies using the PBEh* structures. The decreasing error compared with experiment for the 1^1B_u state with increasing system size is consistent with what was observed comparing the vertical excitation energies in ref 79 for the smaller oligomers. For the 2^1A_g state, an absolute energy difference of <0.04 eV between experiment and the pp-RPA/B3LYP excitation energy is observed for polyenes with $n = 8, 10$, and 12 using the PBEh* geometry (which are the only oligomer lengths with reported PBEh* structures).

An important consideration is the variation in the nature of the excited states with the oligomer size. For $n = 2$, an analysis of the eigenvectors from the pp-RPA calculation indicates that the 1^1B_u state corresponds to an almost pure HOMO \rightarrow LUMO transition, whereas the 2^1A_g state transition is described by a combination of a two-particle HOMO² \rightarrow LUMO² transition and a one-particle HOMO \rightarrow LUMO+1 transition (Table S5). In comparison, a one-particle HOMO-1 \rightarrow LUMO component has been shown to contribute to the 2^1A_g excitation from the EOM-CCSDTQ/CBS.⁶⁶ This component is not present here because only transitions originating from the HOMO are described by the current implementation of the pp-RPA. The HOMO-1 \rightarrow LUMO transition can be computed in the pp-RPA formalism starting from a non-ground-state ($N - 2$)-electron reference; however, this procedure would introduce a large error in the pp-RPA estimate for the 2^1A_g state transition because the orbital relaxation of the ground state $N - 2$ reference will be missing and is important in describing the HOMO² \rightarrow LUMO² transition. In addition, previous results have shown that transitions with a minor non-HOMO excitation character can still be estimated well by the pp-RPA values.⁵⁶

For the 2^1A_g states of polyenes with $n = 2$ –20, the double-excitation (HOMO² \rightarrow LUMO²) component accounts for ~40% of the overall transitions, whereas the contribution from the HOMO \rightarrow LUMO+1 transition decreases from 50% for polyene with $n = 2$ to 36% for polyene with $n \geq 6$. For the 1^1B_u state, the HOMO \rightarrow LUMO transition (93%) dominates the vertical transition for polyene with $n = 2$, which decreases to <50% for $n = 20$; a one-particle HOMO \rightarrow LUMO+2

transition becomes an important component of the vertical 1^1B_u excitations of polyenes with $n > 9$ (Table S5).

From an extrapolation of pp-RPA calculations of MP2-optimized oligomers using the effective conjugation length model (ECL),⁸² the 2^1A_g and 1^1B_u excited-state energies are 1.38 and 1.72 eV, respectively, with a saturation of about $n = 18$ (Figure 4). From the extrapolation based on results

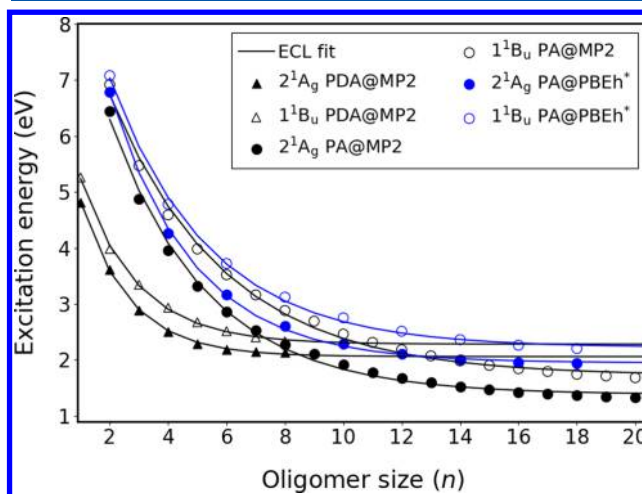


Figure 4. Excitation energies (eV) of the 2^1A_g and 1^1B_u states as a function of increasing oligomer size (n) for *trans*-polyenes (PA) optimized using MP2/aug-cc-pVDZ⁶⁹ (black circles) and PBEh*/6-311G⁷⁰ (blue circles) and *trans*-oligodiacylenes (PDA, black triangles). The excitation energies were extrapolated to the infinite polymer using the effective conjugation length (ECL) model.

computed using the PBEh* geometries, the excitation energies in the polymer limit are slightly higher with 1.95 and 2.24 eV for the 2^1A_g and 1^1B_u state, respectively. This is attributed to the larger BLA for PBEh* geometries. However, despite the geometry and energy differences, a similar ECL value of about $n = 18$ is also obtained with the PBEh* geometries, indicating a similar exciton delocalization length. In comparison, experimental polymer-limit energies range from 1.6 to 2.0 eV for the 1^1B_u state,^{83–85} which are similar to the extrapolated value from the excitation energies of substituted polyenes (1.8 eV).^{86,87}

The bulk excited states of polyacetylene have been previously investigated using GW-BSE under periodic boundary conditions, which estimated the dipole-allowed (i.e., 1^1B_u) and dipole-forbidden (i.e., 2^1A_g) states to be 1.7 and 1.8 eV, respectively.⁸⁸ This qualitatively incorrect state ordering of $2^1A_g > 1^1B_u$ for GW-BSE is attributed to the absence of the double-excitation component of the 2^1A_g state, which leads to an overestimation of the $1^1A_g \rightarrow 2^1A_g$ transition energy. In terms of the exciton delocalization length, a value of 50 Å was determined from GW-BSE,⁸⁸ which compares well to the value of $n = 18$ obtained from a similar saturation in the pp-RPA excitation energies for both MP2 and PBEh* geometries.

A similar analysis was applied to oligodiacylene (oligomers of polydiacylene) to estimate the bulk polymer values for the 2^1A_g and 1^1B_u states, which are predicted to be 2.06 and 2.28 eV, respectively, with a saturation of these excited states of about $n = 8$ (Figure 4, Table S7). The $2^1A_g < 1^1B_u$ state ordering obtained from the pp-RPA excited-state energies is consistent with experimental two-photon measurements of

polydiacetylene.^{89–91} The computed 1^1B_u state in the polymer limit agrees well with the previous estimates of the optical gap as 2.5 ($n = 8$)⁹² and 2.25 eV ($n = 10$)⁹³ based on the extrapolation of the experimentally observed electronic transitions of oligodiacetylene. The slightly longer exciton delocalization length for polyacetylene ($n = 18$) compared with polydiacetylene ($n = 8$) is consistent with the qualitative trend expected from the larger band dispersion along the backbone of polyacetylene^{88,94} compared with polydiacetylene.⁹⁵

An analysis of the eigenvectors from the pp-RPA calculation on the oligodiacetylenes with $n = 1$ indicates that the excitation to the 1^1B_u state corresponds to a mostly a one-electron HOMO \rightarrow LUMO transition (86%), whereas the excitation to the 2^1A_g state is described by an almost equal combination of a two-particle HOMO² \rightarrow LUMO² (ca. 40%) transition and a one-particle HOMO \rightarrow LUMO+1 transition (ca. 40%); see Table S5. Although the evolution of the eigenvectors of the 2^1A_g transition for the various sized oligodiacetylenes is qualitatively similar to polyene, the HOMO \rightarrow LUMO component accounts for ca. 70% of the 1^1B_u vertical transition for all oligodiacetylenes, which is in contrast with what is computed for polyene.

Several conclusions can be derived from the examination of the lowest excited states of all-*trans* conjugated π -systems using pp-RPA. For polyenes, the pp-RPA excitation energies for the 1^1B_u states are in good agreement with experiment and previously reported results from high-level wave function methods. Moreover, the excitation energies of the challenging 2^1A_g states are also accurately predicted. The correct relative energy ordering ($2^1A_g < 1^1B_u$) is obtained using the pp-RPA, in contrast with results reported using other commonly used methods such as TD-DFT, EOM-CCSD, and GW-BSE.

The computational efficiency of pp-RPA allows for the calculation of the excitation energies of large oligomers and an analysis of the exciton delocalization based on a saturation of the excited-state energies as a function of increasing oligomer length. For polyacetylene, the extrapolated values from MP2 geometries yield vertical excitation energies in the polymer limit, which are 1.38 and 1.72 eV for the 2^1A_g and 1^1B_u states, respectively. At the PBEh* geometries, the excitation energies are 1.95 eV and 2.24 eV for the 2^1A_g and 1^1B_u states, which are slightly higher than the results from MP2 geometries because of a decrease in the bond-length alternation. For both MP2 and PBEh* geometries, an ECL value of about $n = 18$ is obtained, indicating a similar excited-state delocalization (estimated from a saturation in the excited-state energies with increasing oligomer length). To examine the effect of the bonding type on the exciton delocalization length, the properties of polydiacetylene in the polymer limit are extrapolated from MP2 geometries. Using the ECL model, the exciton delocalization length for polydiacetylene is predicted to be $n = 8$ for both the 2^1A_g and 1^1B_u states, which corresponds to an energy of 2.06 and 2.28 eV, respectively. The slightly reduced exciton delocalization length for polydiacetylene compared with polyacetylene is attributed to the differences in the bonding nature between the oligomers for these two systems and is consistent with the picture obtained from comparing the computed band dispersions for these two π -conjugated systems.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.8b01366.

Computed excitation energies and fitting parameters corresponding to Figures 3 and 4 as well as the basis set and functional dependence of the excited-state energies. (PDF)

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Notes

The authors declare no competing financial interest.

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