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# Resonance Raman Spectroscopy of the $T_1$ Triplet Excited State of Oligothiophenes

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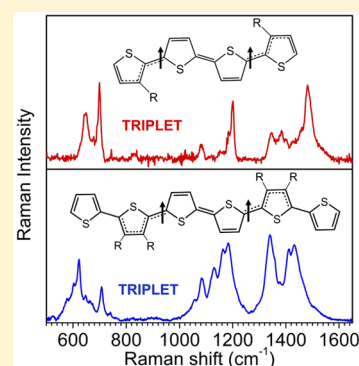
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## S Supporting Information

**ABSTRACT:** The characterization of triplet excited states is essential for research on organic photovoltaics and singlet fission. We report resonance Raman spectra of two triplet oligothiophenes with *n*-alkyl substituents, a tetramer and hexamer. The spectra of the triplets are more complex than the ground state, and we find that density functional theory calculations are a useful starting point for characterizing the bands. The spectra of triplet tetrathiophene and hexathiophene differ significantly from one another. This observation is consistent with a  $T_1$  excitation that is delocalized over at least five rings in long oligomers. Bands in the 500–800  $\text{cm}^{-1}$  region are greatly diminished for an aggregated sample of hexathiophene, likely caused by fast electronic dephasing. These experiments highlight the potential of resonance Raman spectroscopy to unequivocally detect and characterize triplets in thiophene materials. The vibrational spectra can also serve as rigorous standards for evaluating computational methods for excited-state molecules.



Triplet excited states (triplets) of conjugated organic molecules play major roles in applications that utilize these materials. For organic light-emitting diodes (OLEDs), the harvesting of triplet excitons was an important advancement.<sup>1–6</sup> For organic photovoltaics (OPVs), triplet excitons have been linked to deleterious charge recombination.<sup>7–10</sup> However, the relatively long lifetimes and transport distances of triplets could be beneficial for advanced solar cells.<sup>3,11,12</sup> Any advantages of triplets must be considered in view of their mechanism of generation. Triplets can be formed pairwise, and with high efficiency, via singlet fission.<sup>13</sup> The theoretical energy conversion efficiency of a bilayer solar cell that harvests pairs of excitons from singlet fission exceeds 40%, a substantial improvement over the ~30% limit for a single-threshold solar cell.<sup>14,15</sup>

The various connections of triplets to the performance of OLEDs, OPVs, and other organic electronic devices motivate fundamental research on excited states of conjugated molecules. The bonding pattern and spatial extent of an excited state are key characteristics<sup>16–21</sup> that are intimately related to the energy and mobility of an exciton within a material. Excited states of thiophene polymers and oligomers have been widely researched, partly because of the many applications of these molecules.<sup>22–35</sup> Despite significant advances in our understanding of oligo- and polythiophene triplets, fundamental aspects remain unclear, including their spatial delocalization. Reported sizes of triplet excited states of oligo- and polythiophenes have ranged from one ring<sup>25,36–40</sup> to four rings or more.<sup>26,29,41</sup> Additionally, reports of singlet fission in

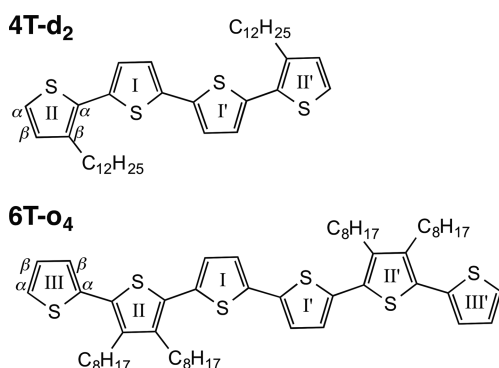
thiophene chains inspire further studies of triplets in these systems.<sup>42–44</sup>

Vibrational spectroscopy can be a powerful probe of molecular structure in both ground and excited electronic states. Vibrational spectra of ground-state thiophene oligomers and polymers in neutral and cationic states have been widely reported, and only a subset can be cited here.<sup>45–53</sup> Infrared and Raman spectra were reported previously for photoexcited thiophene molecules, but without definitive assignment to a triplet excited state.<sup>51,54–59</sup> Only recently were broadened vibrational bands assigned to triplet excitons in polythiophene, using femtosecond stimulated Raman spectroscopy.<sup>60,61</sup> Given the lack of resolved vibrational data for the triplets, we have acquired and analyzed resonance Raman spectra of two alkyl-functionalized oligothiophenes in their lowest triplet ( $T_1$ ) excited state. The spectra are markedly different from those of the ground state. The unique Raman signatures may prove to be useful for monitoring triplets in complex systems, such as the bulk heterojunctions of OPVs. A comparison of the experimental spectra with results from density functional theory (DFT) calculations here yields some insights into the bonding pattern and delocalization of the  $T_1$  excited state of these oligomers.

Molecular structures of the *n*-alkyl substituted tetrathiophene and hexathiophene probed in this study are shown in Chart 1.

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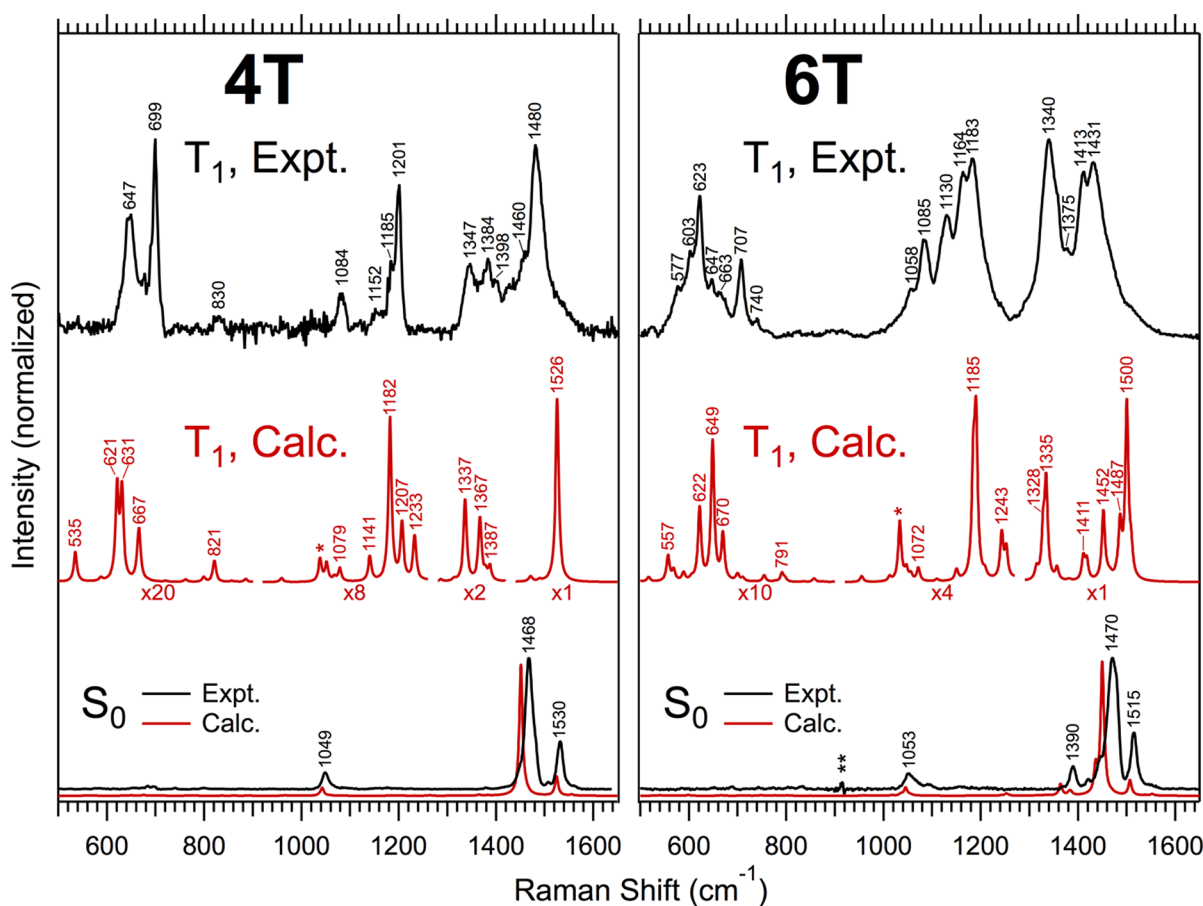
**Chart 1.** Didodecyl Tetrathiphene (4T-d<sub>2</sub>) and Tetraoctyl Hexathiophene (6T-o<sub>4</sub>)

The substituents impart solubility in the selected solvents chlorobenzene (for 4T-d<sub>2</sub>) and tetrahydrofuran (THF, for 6T-o<sub>4</sub>). Resonance Raman spectra of transient species were collected with a modified optical microscope and two beams focused on a fast-flowing, deoxygenated solution of oligothiophene in a capillary. When excited with a 420 nm quasi-continuous-wave (cw) pump, the triplet quantum yields from

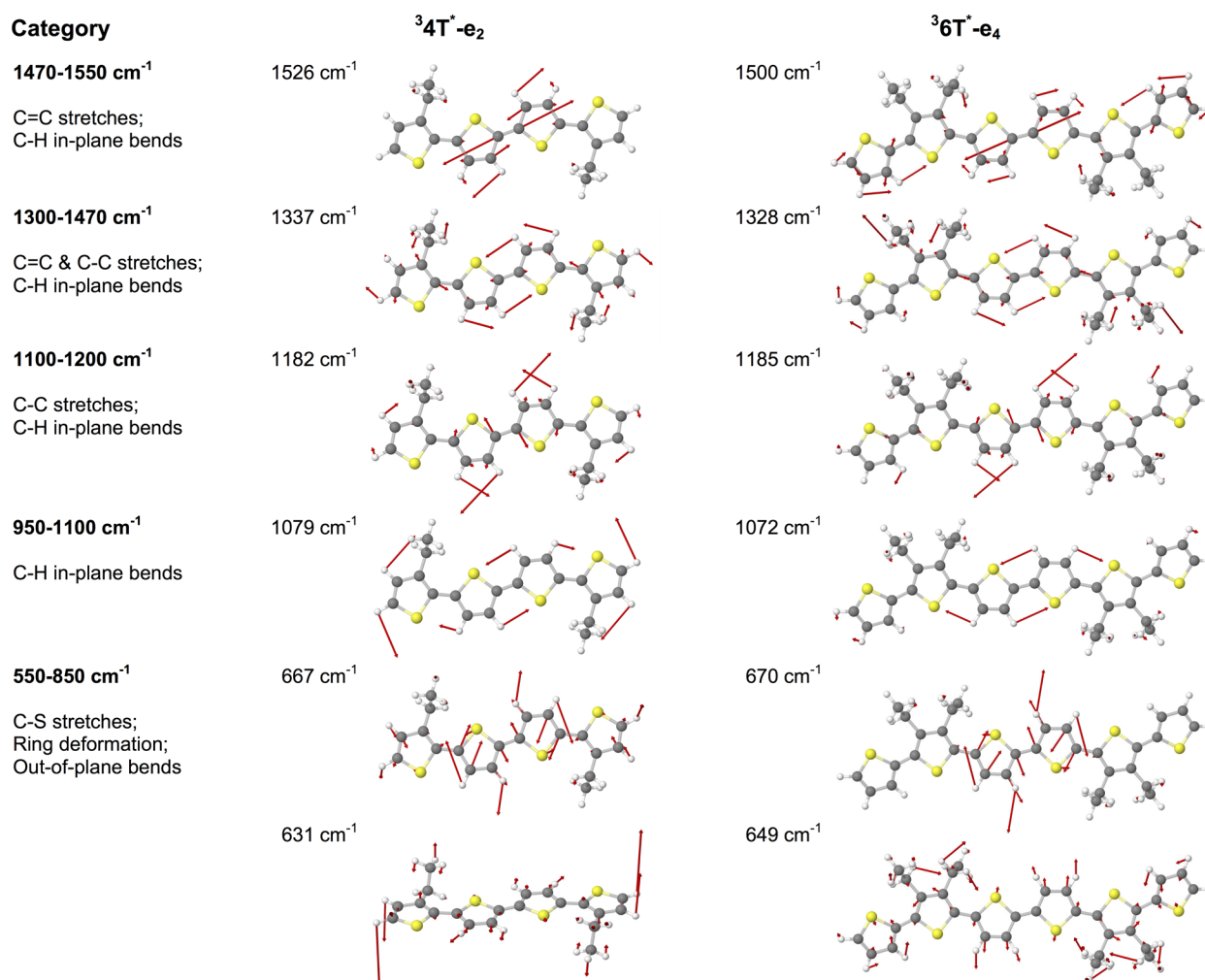
intersystem crossing are expected to exceed 50%, as reported previously for unsubstituted tetra- and hexathiophene.<sup>24</sup> A 647.09 nm cw probe was selected for near-resonance with the T<sub>1</sub> → T<sub>n</sub> transitions, and the narrow line width of this source optimized the resolution of the Raman bands. The time delay between pump and probe was 5 μs (solvated monomers) or 1 μs (aggregate), selected via the solution flow rate and the micrometer separation between pump and probe foci.

The experimental Raman spectra of the oligothiophenes in their lowest triplet excited state, <sup>3</sup>4T\*-d<sub>2</sub> and <sup>3</sup>6T\*-o<sub>4</sub>, are shown in Figure 1 along with the corresponding ground-state spectra. The triplet spectra are distinguished from those of the ground state by a much greater distribution of prominent bands. Furthermore, the spectra of <sup>3</sup>4T\*-d<sub>2</sub> and <sup>3</sup>6T\*-o<sub>4</sub> differ significantly from one another, whereas the ground-state spectra are similar. The assignment to a triplet excited state, rather than a cation, was supported by the disappearance of the transient hexathiophene spectrum at 5 μs for an oxygen-saturated solution. The spectrum was also greatly diminished at a time delay of 20 μs, consistent with an assignment to <sup>3</sup>6T\*-o<sub>4</sub> (see Supporting Information).

We employed unrestricted DFT calculations on model triplet oligothiophenes with ethyl substituents (<sup>3</sup>4T\*-e<sub>2</sub> and <sup>3</sup>6T\*-e<sub>4</sub>)



**Figure 1.** Resonance Raman spectra of triplet tetrathiphene <sup>3</sup>4T\*-d<sub>2</sub> (black trace, top left) and hexathiophene <sup>3</sup>6T\*-o<sub>4</sub> (black trace, top right) in deoxygenated chlorobenzene and THF, respectively. DFT-calculated spectra (UB3LYP/6-31G(d)) of model triplet molecules with ethyl substituents, <sup>3</sup>4T\*-e<sub>2</sub> and <sup>3</sup>6T\*-e<sub>4</sub>, are shown as red traces in the middle of each panel. To aid comparison with the experimental spectra, the frequency axes of the calculated spectra are scaled by 0.9614, and the intensities are scaled in various spectral regions as indicated below the baseline. Single asterisks mark calculated bands that are substituent-localized and not expected to be resonantly enhanced in the experimental spectra. Corresponding experimental and calculated spectra for the ground state are shown for 4T-d<sub>2</sub>/4T-e<sub>2</sub> (black/red traces; bottom left) and 6T-o<sub>4</sub>/6T-e<sub>4</sub> (black/red traces; bottom right). A double asterisk (\*\*) marks an artifact from solvent subtraction.



**Figure 2.** Categories and examples of vibrational normal modes for model triplet oligothiophenes  $^34T^*-e_2$  and  $^36T^*-e_4$ , based on DFT calculations (UB3LYP/6-31G(d); frequencies scaled  $\times 0.9614$ ).

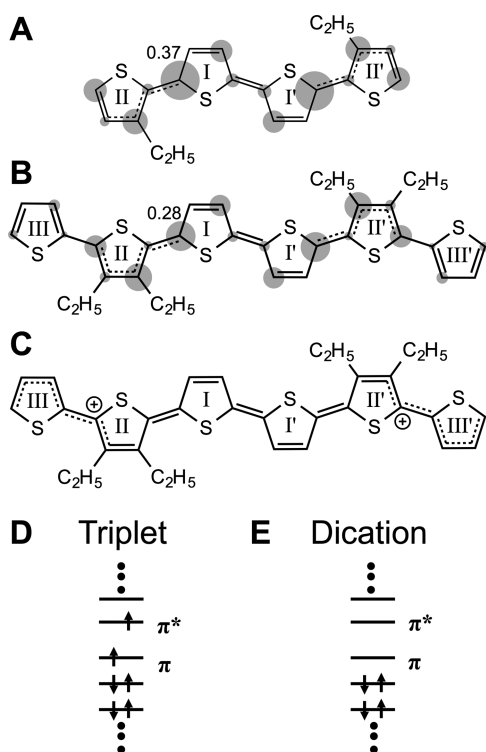
to gain insights into the unique experimental spectra. The present calculations do not take into account factors that determine resonance Raman intensities, such as mode-specific displacements in the resonant electronic state. Despite this limitation, the overall calculated profiles resemble the experimental spectra, particularly after scaling intensities in sections (Figure 1). The similarities prompted us to organize the bands of the triplet oligothiophenes in groups, according to the vibrational character from DFT normal-mode analysis. Representative normal modes with  $A_g$  symmetry in the  $C_i$  point group are illustrated for each category in Figure 2. Normal modes with frequencies 1100–1550  $\text{cm}^{-1}$  consist of CC stretches coupled with C—H in-plane (IP) bends. Within that spectral range, modes with frequencies 1470–1550  $\text{cm}^{-1}$ , 1300–1470  $\text{cm}^{-1}$ , and 1100–1200  $\text{cm}^{-1}$  involve primarily the stretches of double bonds, mixed bond orders, and single bonds, respectively. Bands in the 950–1100  $\text{cm}^{-1}$  region are associated with normal modes that are predominantly C—H IP bends. Strong vibrational bands with frequencies in the 550–850  $\text{cm}^{-1}$  range are assigned to ring deformation/breathing in combination with C—S stretches. Modes with out-of-plane (OOP) motions may also contribute to this spectral region (vide infra).

The relatively complex spectra of  $^34T^*-d_2$  and  $^36T^*-o_4$  compared with those of the ground state molecules reflect

the more complex bonding structure of the triplet excited states. The ground state Raman spectra show a weak dependence upon chain length because the characteristics of the active vibrational modes are conserved.<sup>48,49,62,63</sup> However, the broad frequency distribution of the CC stretching modes in the triplet excited state reflects variation of the CC bonding pattern from one thiophene ring to the next. For many linked aromatic systems including poly- or oligothiophenes, experimental and theoretical studies indicate that single and double bonds of low-lying excited states are reversed relative to the ground state.<sup>25,60,61,64–71</sup> A quinoidal structure forms upon excitation of linked thiophene rings, whereby double bonds are found between  $C_\alpha=C_\alpha$  and  $C_\beta=C_\beta$ , rather than  $C_\alpha=C_\beta$  of the ground state. On the basis of DFT calculations (Figure 3A,B), the quinoidal region is confined to the two central rings and the spin density inherent to the triplet state is primarily distributed over four rings. These results agree with those from prior DFT calculations<sup>34</sup> and from semiempirical extended Hubbard calculations.<sup>41</sup> We propose that the localized quinoidal region and the distributed unpaired electron density disrupt the regular bonding pattern of the ground state and give rise to the relatively complex vibrational spectra of triplet tetra- and hexathiophene.

Unlike the similar ground-state spectra, we find significant differences between the triplet spectra of tetrathiophene and





**Figure 3.** Valence bond structures of the triplets (A)  ${}^34T^*-e_2$  and (B)  ${}^36T^*-e_4$ , based on DFT calculations (UB3LYP/6-31G(d)). The region with reversed bond order (quinoidal region) is identified where differences between a CC bond length of the triplet differs from the corresponding bond of the ground state by  $>0.030$  Å. Single/dashed (---) lines are drawn where neighboring CC bond lengths differ by  $\leq 0.025$  Å. Shaded circles, each with diameter proportional to the calculated spin density centered at the carbon atom, are shown for values  $>0.06$ . The location of maximum spin density for each oligomer is labeled with the numerical value. (C) Valence bond structure of the  $6T-e_4$  dication, based upon DFT calculation (UB3LYP/6-31G(d)). The quinoidal region and single/dashed bonds are drawn using the same criteria as for the triplets. Molecular orbital electronic configurations of the (D) triplet and (E) dication states.

hexathiophene. The DFT calculations point to possible origins of these differences. First, in the ethylenic region, there is a  $50\text{ cm}^{-1}$  experimental downshift for the strongest  $\text{C}=\text{C}$  Raman-active mode of  ${}^36T^*-o_4$  compared with  ${}^34T^*-d_2$ . The calculation for tetrathiophene indicates one strong ethylenic band at  $1526\text{ cm}^{-1}$ , attributed to  $\text{C}=\text{C}$  stretches in the central quinoidal region. Similarly, the strong  $1500\text{ cm}^{-1}$  band of hexathiophene is assigned to a mode with significant  $\text{C}=\text{C}$  motion in the center of the chain; however, substantial  $\text{C}_\alpha=\text{C}_\beta$  stretching in the outer rings are also part of the motion (Figure 2). In the case of ground-state conjugated oligomers, vibrational frequencies of ethylenic modes are often correlated with extent of delocalization. Similar relationships may also apply here in the case of  ${}^36T^*-o_4$  versus  ${}^34T^*-d_2$ , but additional experiments and computations for a series of triplet oligomers would be necessary before generalizing. Second, we notice that there are more bands in the low-frequency region for the longer oligomer. This region includes ring deformations and hydrogen OOP motions. The greater number of bands for hexathiophene is likely a consequence of the additional ring deformation modes for this molecule. Additionally, the outer rings of triplet  ${}^36T^*-e_4$  are calculated to have dihedral angles of  $20\text{--}25^\circ$ ; for the  $C_i$  point group of the twisted molecule, the OOP motions

are totally symmetric and corresponding bands in the experimental spectrum of  ${}^36T^*-o_4$  may be resonantly enhanced. By contrast, calculations of  ${}^34T^*-e_2$  show less than  $2^\circ$  dihedral angles between rings; for the limiting  $C_{2h}$  point group of the flatter molecule, the OOP modes are nontotally symmetric and resonance enhancement is unlikely for these bands in the experimental spectrum of  ${}^34T^*-d_2$ .

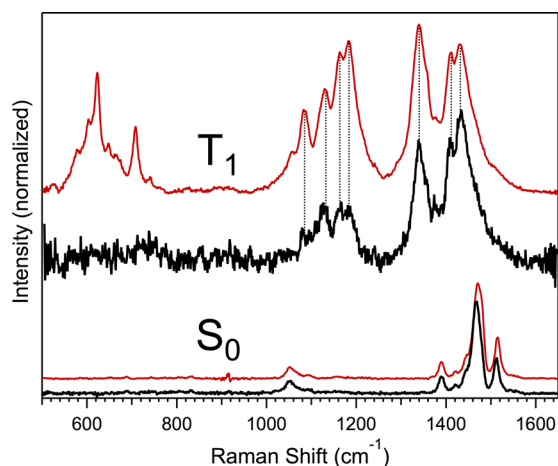
Given the substantial differences between the resonance Raman spectra of the tetramer and hexamer, we infer that a fully extended  $T_1$  state of a long oligomer, or polythiophene, is not adequately described by four thiophene rings; five or more rings are necessary. Consistent with this viewpoint, the zero-field splittings (D values) from EPR experiments were found to decrease for triplet hexathiophene relative to tetrathiophene, reflecting expansion of spin density beyond four rings when available.<sup>26,41</sup> Furthermore, measurements on a series of soluble thiophene polymers indicated that the  $T_1$  energy decreases as the effective conjugation length increases to six thiophene units.<sup>29</sup>

We note a striking resemblance between resonance Raman spectra of the triplets, and previously reported spectra of oligothiophene dications.<sup>46,48,72</sup> Similarly, quinoidal-like oligothiophenes formed by the attachment of electron acceptors at the termini have spectral features in common with the  $T_1$  state.<sup>73,74</sup> The similarities include numerous bands in the  $1100\text{--}1550\text{ cm}^{-1}$  region that are significantly enhanced compared with ground-state oligothiophenes that have all aromatic rings.<sup>48,72–74</sup> The dications for short oligomers are described by a bipolaron structure, which has a quinoidal region bordered on each side by positive charge centers.<sup>46,52,75,76</sup> Results from DFT calculations (Figure 3) show that the dication and the  $T_1$  states of the hexamer share some structural features. Furthermore, the molecular orbital configuration diagrams highlight that the unoccupied  $\pi$  orbital of the dication, or two singly occupied  $\pi$  and  $\pi^*$  molecular orbitals of the triplet, have an equivalent effect on the overall bond order.

Two mismatches between the calculated and experimental spectra point to shortcomings of the unrestricted DFT calculations. First, if the strongest high-frequency ethylenic band of each experimental spectrum is correctly assigned to the central  $\text{C}_\alpha=\text{C}_\alpha$  stretch, then the scaled frequencies are too high by  $46\text{ cm}^{-1}$  ( $1526 - 1480\text{ cm}^{-1}$ ) for the tetramer, and  $69\text{ cm}^{-1}$  ( $1500 - 1431\text{ cm}^{-1}$ ) for the hexamer. The differences suggest that the biradical and the central quinoidal region are more overlapped than calculated by DFT. More radical-like character in the center would lower the frequency of the  $\text{C}_\alpha=\text{C}_\alpha$  stretch. Second, the calculations yield only a  $26\text{ cm}^{-1}$  downshift for the frequency of the central  $\text{C}_\alpha=\text{C}_\alpha$  stretch from tetramer to hexamer ( $1526 - 1500\text{ cm}^{-1}$ ), whereas the experimental downshift is almost two times larger ( $1480 - 1431\text{ cm}^{-1}$ ). DFT calculations with different functionals or basis sets did not improve the comparison with experimental findings. In general, these mismatches indicate that the unrestricted DFT calculations do not treat the delocalization of the  $T_1$  state along the conjugated chain with sufficient veracity to determine the vibrational structure at the same level as for the ground state. Higher level computations of the triplet electronic structure are necessary to predict the vibrational spectra of the excited states. A recent study demonstrated that the CC2 method (approximate coupled cluster, with single and double excitations) excelled in simulating the phosphorescence spectrum of bithiophene.<sup>77</sup> Coupled-cluster methods and

advances in parallel algorithms now allow the calculation of triplet state properties for large molecules such as  $\beta$ -carotene.<sup>78</sup> Also, multireference methods are known to improve calculated energies of triplet excited states, relative to single-determinant methods.<sup>79</sup> We note that resolved vibrational spectra of excited-states, such as those reported here, are valuable data for evaluating various computational techniques for excited-states.

We also probed the triplet excited state of 6T-o<sub>4</sub> in a self-assembled aggregate. These aggregates can be considered a proxy for thiophene molecules in other solid-state systems, including those within OPVs. The off-resonance Raman spectra of aggregated and solvated 6T-o<sub>4</sub> in the ground state are nearly identical, with only slight differences in band frequencies that are likely related to small changes in molecular geometry upon aggregation (Figure 4). The resonance Raman spectra of



**Figure 4.** Raman spectra of the  $T_1$  and  $S_0$  states of aggregated 6T-o<sub>4</sub> in 5:95 (v/v) THF:water (black). The spectra of the monomer in THF (red) are reproduced from Figure 1. All spectra were acquired with a 647.09 nm probe.

solvated and aggregated 6T-o<sub>4</sub> in the triplet excited state have band positions that are close in frequency, however the intensity profiles differ substantially (Figure 4). Bands of the aggregate have decreased intensity toward lower frequencies, in comparison with the solvated hexamer. In particular, the prominent Raman bands between 550 and 750  $\text{cm}^{-1}$  for the solvated molecule are not observed above the noise of the aggregate spectrum. The loss of these bands could be caused by increased homogeneous broadening (faster electronic dephasing) for the aggregate, which tends to attenuate resonance Raman scattering of low frequency bands more than high frequency bands.<sup>80</sup> Faster dephasing for the aggregate is reasonable for two reasons: (1) the resonant  $T_n$  state is almost certainly more delocalized than for the fully solvated hexathiophene<sup>81</sup> and (2) the  $T_n$  state can couple to intermolecular charge-transfer states.

The results described above comprise the first report and analysis of resolved vibrational spectra of oligothiophene triplet excited states. The Raman spectra differ greatly from the ground state, but are similar to those of dications. Substantial differences between the experimental resonance Raman spectra of  $^34\text{T}^*\text{-d}_2$  and  $^36\text{T}^*\text{-o}_4$  are the basis for our conclusion that the vibrational structure of the fully extended triplet excited state requires at least five rings for its description. The pattern of bands for the experimental spectra resembles predictions from DFT, which indicates that these efficient calculations are a

useful starting point for describing the triplet excited-state structure and normal modes of vibration. However, more advanced computations, including those that treat mode-specific displacements in a resonant electronic state, are clearly necessary for full assignment of resonance Raman bands of triplet oligothiophenes. In general, the comparison of simulated and experimental vibrational spectra can be a rigorous approach for evaluating computational methods for excited states. The spectral features of the  $T_1$  state are largely maintained for an aggregate, and this finding suggests that spectra recorded for solvated species will be relevant for studies of the triplet state in oligo-/polythiophene films, or bulk heterojunctions.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.5b01410.

Experimental details (sample preparation, absorption spectra, description of pump–probe Raman microscope and flow system); data workup for Raman spectra; confirmation of  $T_1$  state; vibrational mode assignments for  $S_0$  and  $T_1$  states; calculated spin density distribution and bond lengths in the  $T_1$  state; and exploration of different DFT methods. (PDF)

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### Notes

The authors declare no competing financial interest.

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