## 4P055

# Optical and geometrical properties of oligomers of poly-*para*-phenylene vinylene (PPV) and poly-*para*-phenylene (PP): A SAC-CI study

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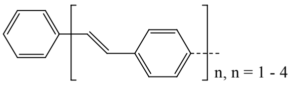
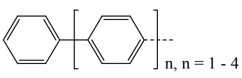
The optical and geometrical properties of the oligomers of poly-*para*-phenylene vinylene and poly-*para*-phenylene which are frequently used as an active layer for polymer-based light-emitting diode (LED) have been investigated by the SAC-CI *SD-R* method. The excitation energies for the lowest singlet and triplet excited states of PPVn and PPn consisting of 1 - 4 repeat units are calculated with planar $C_{2h}$ symmetry constrained for PPVn and with non-planar $D_2$ and planar $D_{2h}$ symmetry for PPn. The doubly excited state, $2^1A_g$, of PPV1 was studied by SAC-CI general-*R* method considering up to quadruple excitation operators.[1] The SAC-CI geometry optimization was performed for PPV1, PPV2, PP1 and PP2. For all these calculations double-zeta basis set due to Huzinaga/Dunning plus one polarization function [4s2p1d/2s] was adopted.



Poly-*para*-phenylene vinylene (PPVn)



Poly-*para*-phenylene (PPn)

The transition energies were calculated accurately; maximum deviation from experimental results lies within 0.2 eV. The chain length dependence of transition energies for both singlet and triplet excitations was reproduced correctly as displayed in figures 1 and 2, respectively, although earlier TDDFT (for $S_0 \rightarrow S_1$) and MRSDCI (for $S_0 \rightarrow T_1$) calculations failed to reproduce it. The triplet state is predicted at lower energy (~1.0-1.5 eV for PPVn and ~0.9-1.7 eV for PPn) than the singlet state which indicates localized triplet state with large exchange energy. The present SAC-CI emission energy also produced correct chain length dependence as shown in Fig. 3. The failure of TDDFT is also apparent from this figure as the chain length increases. The singlet excitation energies of PPn have been compared with experimental and TDDFT results in Fig. 4. The transition energy is almost proportional to 1/n. For planar case, the excitation energies of PPn decreases more rapidly as the chain length increases. In planar case, the π-electrons are more delocalized over the oligomers length than the non-planar case as a consequence the singlet and triplet states are more stabilized.

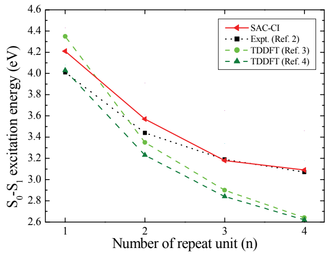


Fig. 1 Singlet excitation in PPVn.

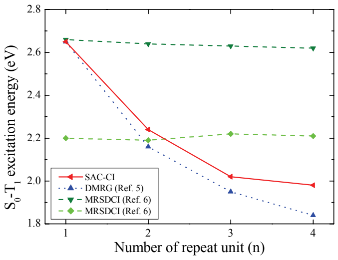


Fig. 2 Triplet excitations in PPVn.

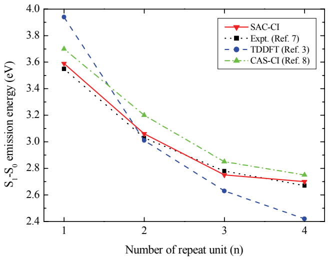


Fig. 3 Emission spectra of PPVn.

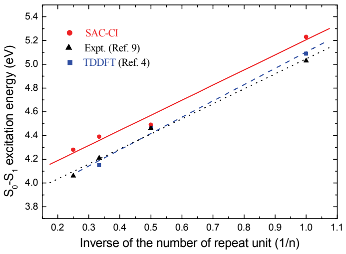


Fig. 4 Singlet excitations in PPn.

Zero-point energy correction to the excitation energy was estimated as -0.07 eV for PPV1 and -0.16 eV for PP1; theoretical value approaches to experimental value with this correction. For calculating zero-point energy correction, ground-state and lowest excited-state harmonic frequencies were calculated by using Hartree-Fock and CIS level of theories, respectively. As in most π-conjugated systems in PPVn and PPn, the $S_1$ state mainly corresponds to a single excitation from HOMO to LUMO.

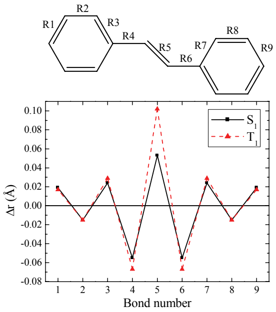


Fig. 5 Geometry changes in PPV1.

For PPV1, the doubly excited $2^1A_g$ state transition energy of 4.99 eV agrees very well with the experimental value of 4.84 eV.[10] Contrary to the previous theoretical reports we predict this $2^1A_g$ state above the $1^1B_u$ state.[11]

The change in bond length for lowest singlet and triplet states of PPV1 and PP2 have shown in figures 5 and 6, respectively. For PPV1, the increase in the central vinylene C=C bond length is of the order of 0.05 Å and 0.10 Å for singlet and triplet, respectively and the decrease in C-C vinyl bond length is of the order of 0.05 Å and 0.07 Å, respectively. In case of PP2, the maximum increase of the C=C bond length is about 0.04 Å for both singlet and triplet states and the decrease in C-C bond length is around 0.04 Å. Comparatively larger geometry relaxation is obtained for triplet state. Geometry relaxation is localized mainly in the central part of the molecule.

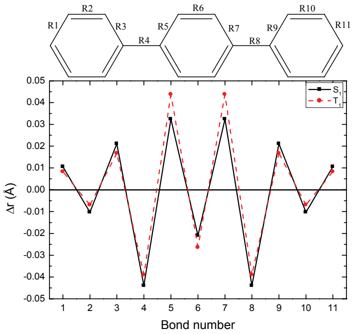
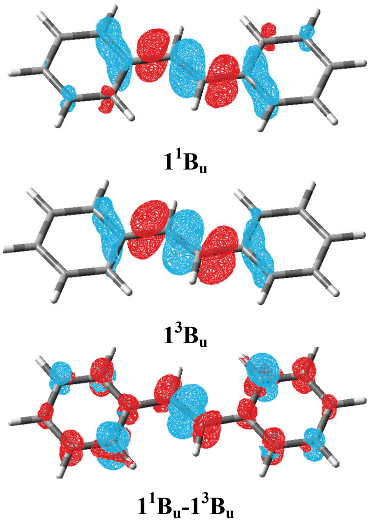


Fig. 6 Geometry changes in PP2



$1^1B_u$

$1^3B_u$

$1^1B_u$-$1^3B_u$

Fig. 7 Electron density difference in PPV1.

Light - decrement, Dark - increment
interval=0.003 (for $^1A_g$-$^1B_u$, $^3B_u$),
and interval=0.001 (for $^1B_u$-$^3B_u$)

The SAC-CI electron density difference between the ground and singlet/triplet excited state is calculated and the geometrical changes are discussed in detail using electrostatic force theory. The electron density difference in PPV1 is shown in Fig. 7. The electron density in the σ-bond region increases and that in the π-bond region decreases in general. The change in electron density due to excitation in the triplet state is more pronounced than the singlet state as it is apparent from Fig. 7. This is the reason behind the larger change of bond length in the triplet state than in the singlet state. From this study, we can say that the SAC-CI method is useful for investigating the electronic spectra and excited state geometries of the oligomers of poly-*para*-phenylene vinylene (PPV) and poly-*para*-phenylene (PP).

## Reference

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