

Assessing the Effects of Increasing Conjugation Length on Exciton Diffusion: From Small Molecules to the Polymeric Limit

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I. ABSORPTION AND EMISSION SPECTRA

A. Methods Comparison

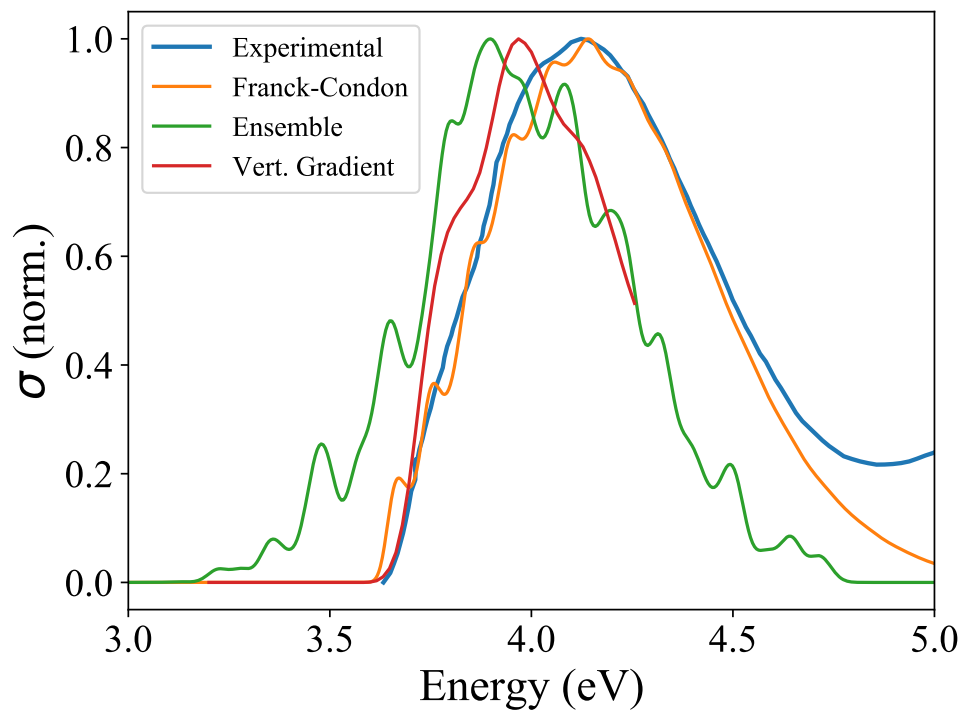


FIG. 1. Comparison between experimental and simulated absorption spectra of bithiophene using different methods.

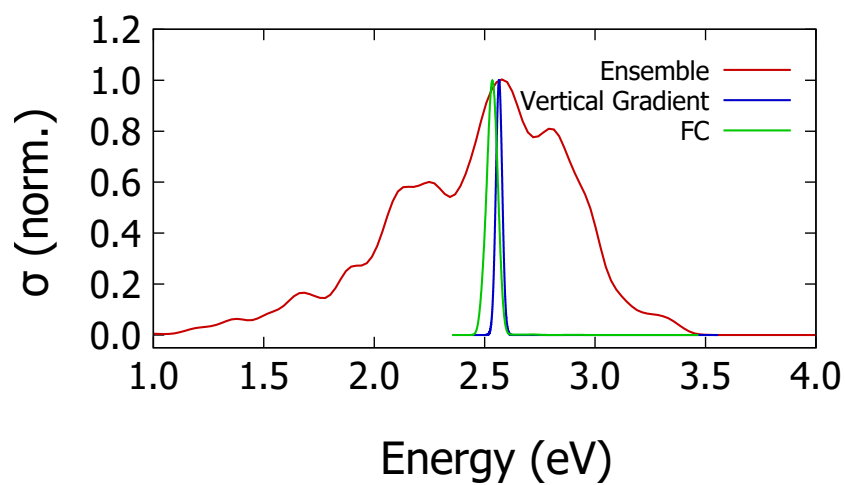


FIG. 2. Comparison between simulated absorption spectra of octothiophene using the nuclear ensemble method, the vertical gradient and Franck-Condon approximations.

B. B3LYP Functional

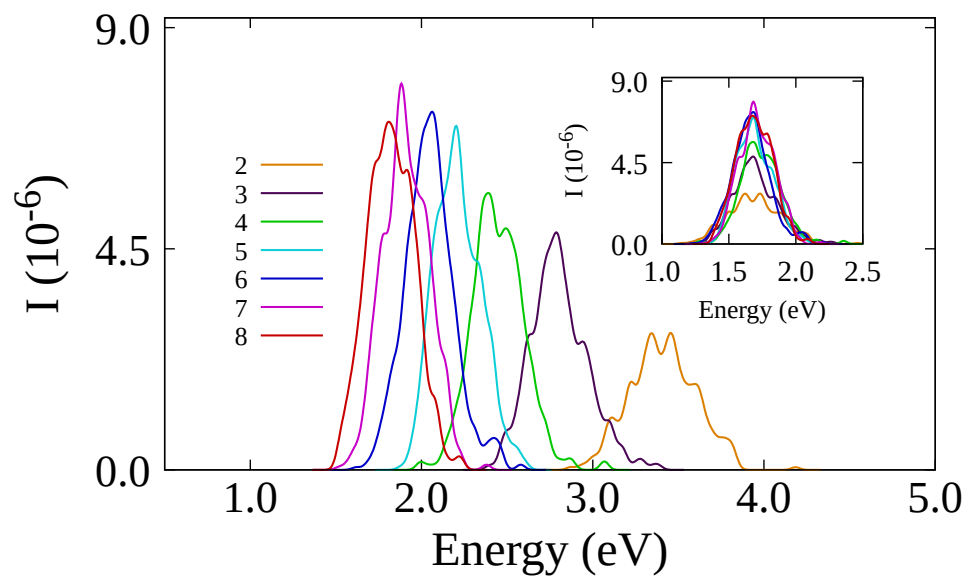


FIG. 3. Differential emission rate for the thiophene oligomer series. Inset shows the same spectra shifted to the polymeric emission peak.

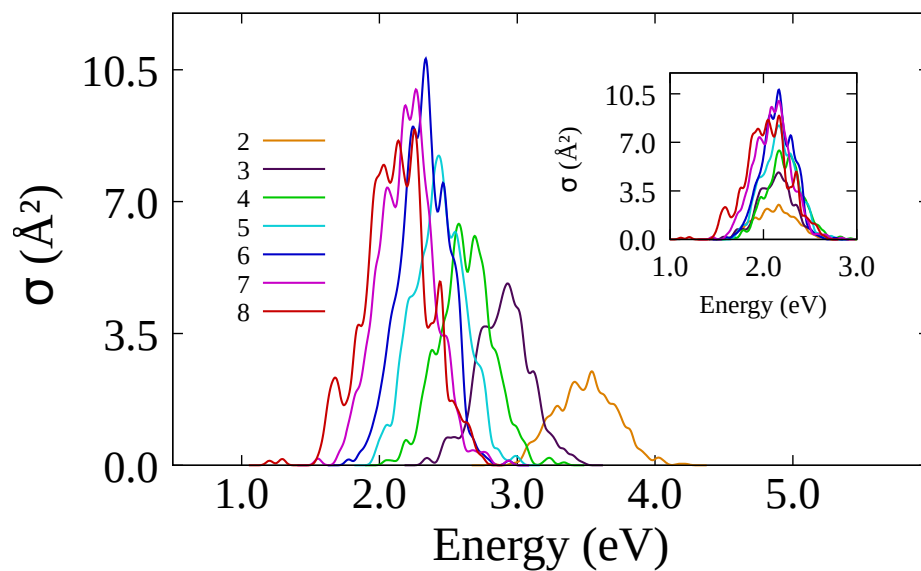


FIG. 4. Absorption cross section spectra for the p-phenylene vinylene oligomer series. Inset shows the same spectra shifted to the polymeric absorption peak.

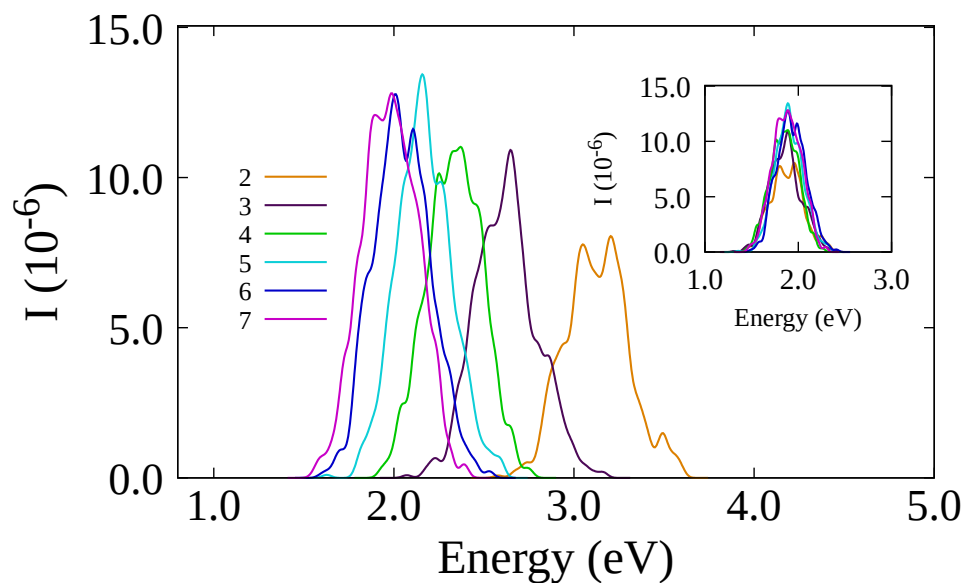


FIG. 5. Differential emission rate for the p-phenylene vinylene oligomer series. Inset shows the same spectra shifted to the polymeric emission peak.

C. CAM-B3LYP Functional

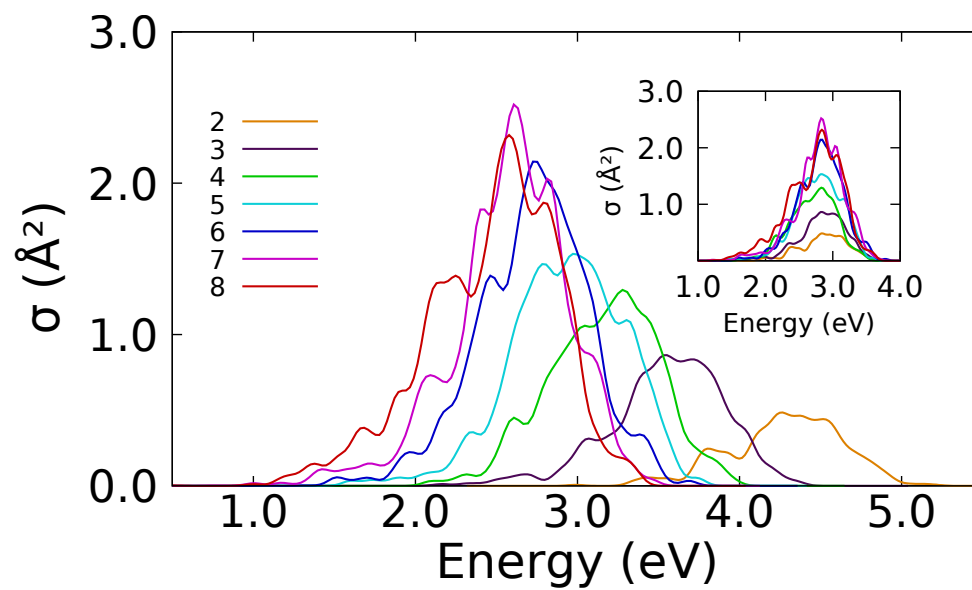


FIG. 6. Absorption cross section spectra for the thiophene oligomer series. Inset shows the same spectra shifted to the polymeric absorption peak.

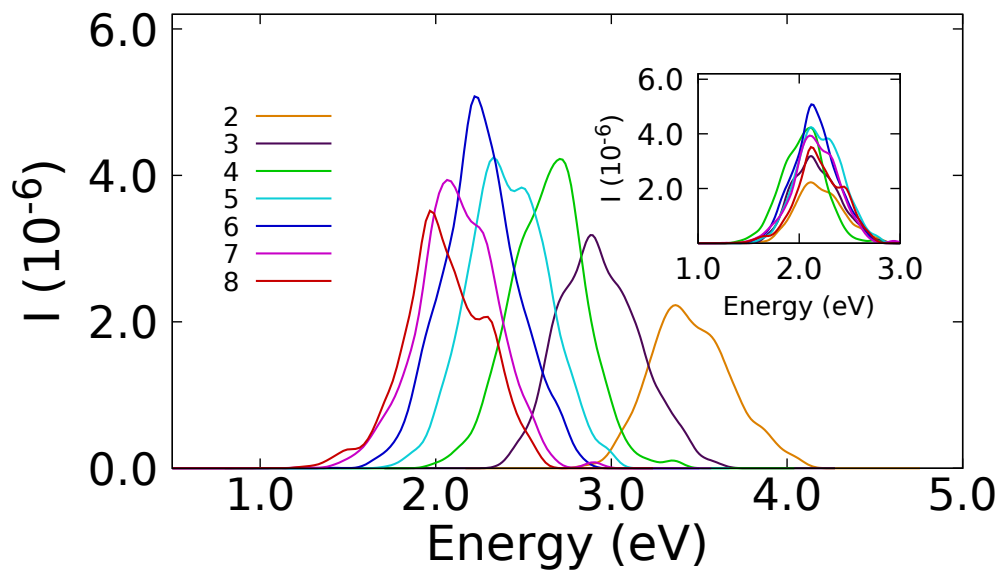


FIG. 7. Differential emission rate for the thiophene oligomer series. Inset shows the same spectra shifted to the polymeric emission peak.

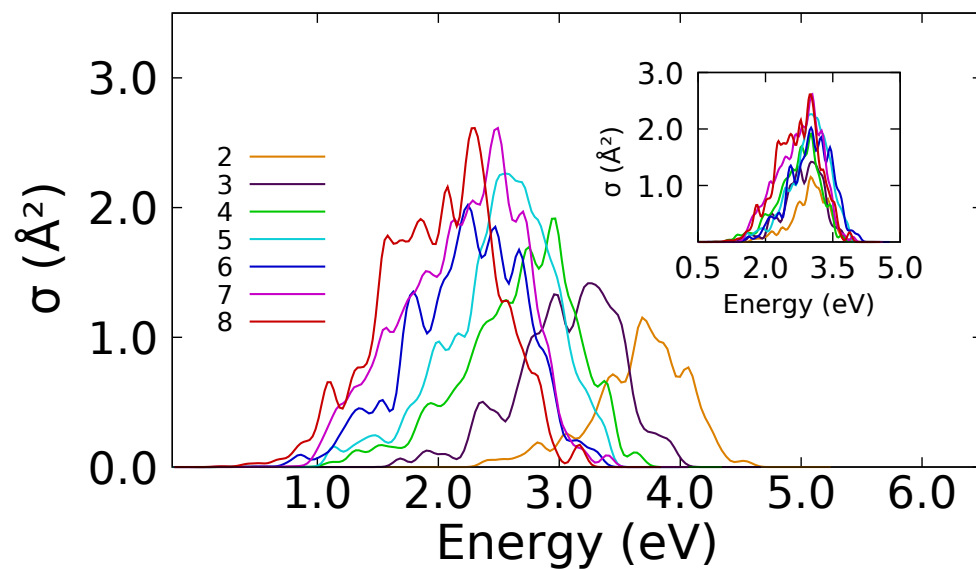


FIG. 8. Absorption cross section spectra for the p-phenylene vinylene oligomer series. Inset shows the same spectra shifted to the polymeric absorption peak.

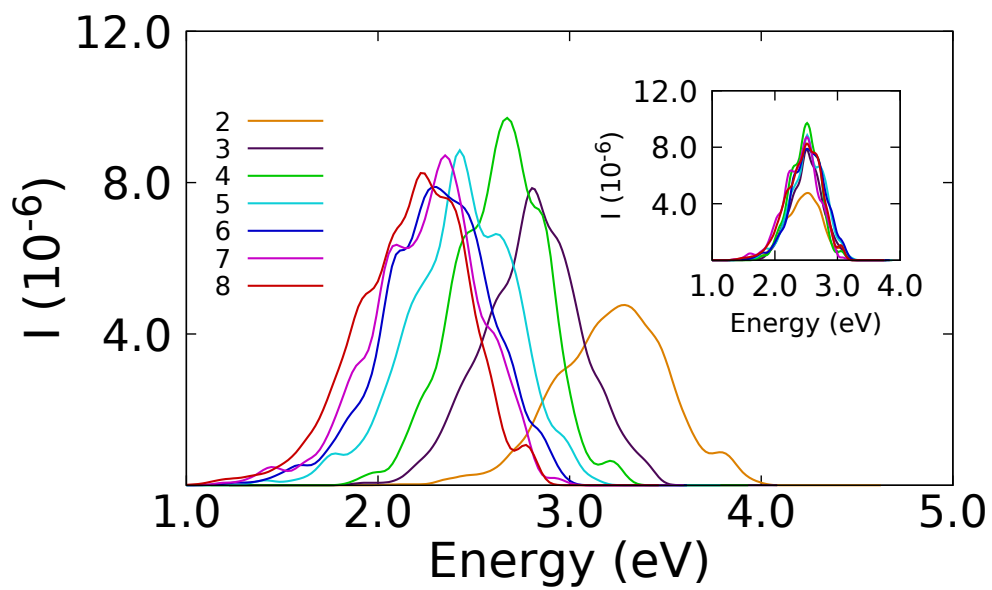


FIG. 9. Differential emission rate for the p-phenylene vinylene oligomer series. Inset shows the same spectra shifted to the polymeric emission peak.

Polymer	Functional	
	B3LYP	CAM-B3LYP
Oligothiophene Absorption	0.19 eV	0.34 eV
Oligothiophene Emission	0.21 eV	0.22 eV
OPV Absorption	0.20 eV	0.43 eV
OPV Emission	0.16 eV	0.26 eV

TABLE I. Average standard deviation for absorption and emission spectra of both thiophene and OPV oligomer series.

II. REORGANIZATION ENERGY

A. B3LYP

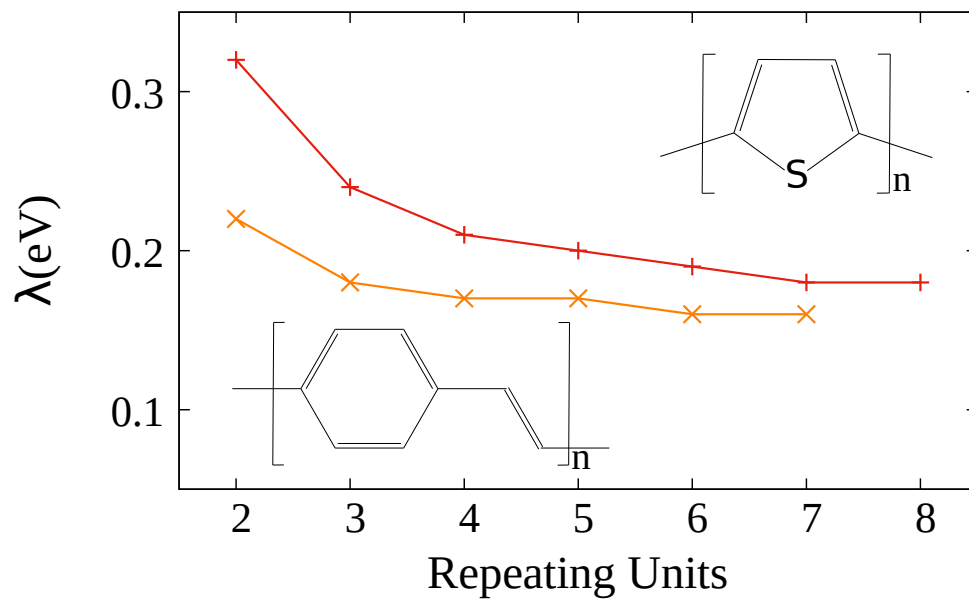


FIG. 10. Progression of reorganization energy as a function of the number of repeating units for the thiophene (red) and PPV (orange) oligomer series.

B. CAM-B3LYP

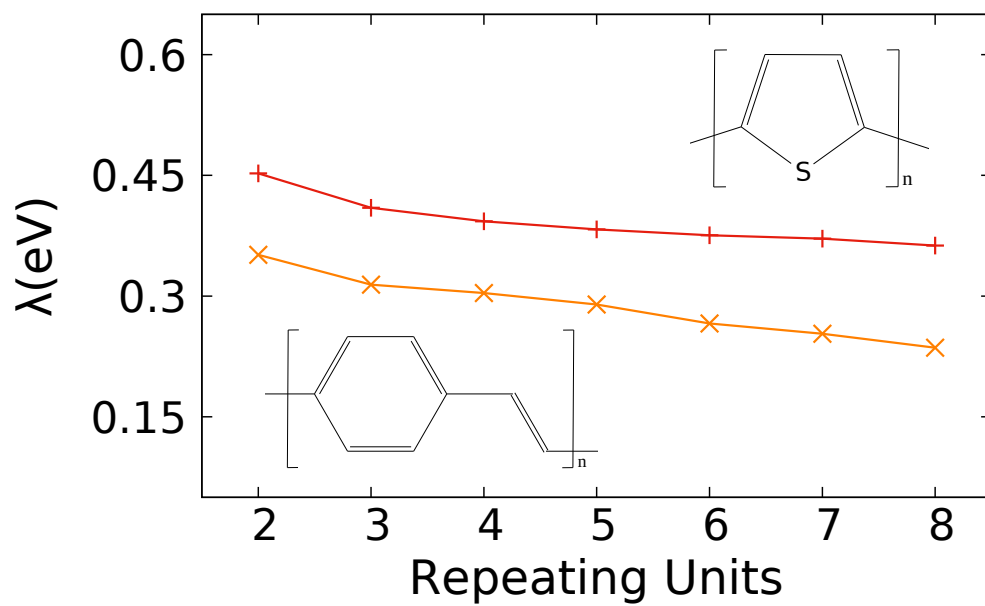


FIG. 11. Progression of reorganization energy as a function of the number of repeating units for the thiophene (red) and PPV (orange) oligomer series.

III. EMISSION LIFETIMES, DIPOLE MOMENTS AND EXCITONIC COUPLINGS

A. CAM-B3LYP

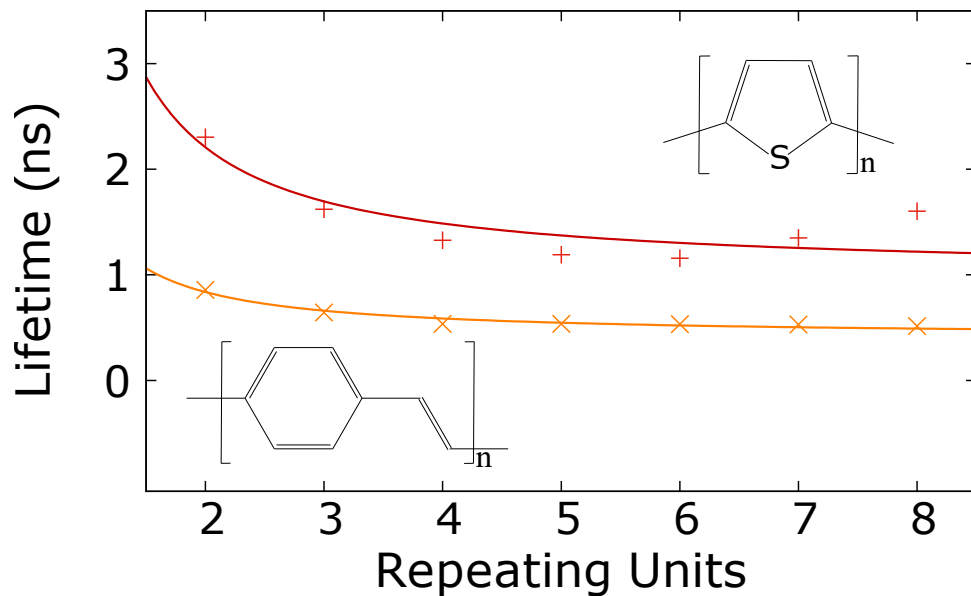


FIG. 12. Radiative lifetimes as a function of repeating units for both oligomer series. Curves correspond to exponential fits to the data.

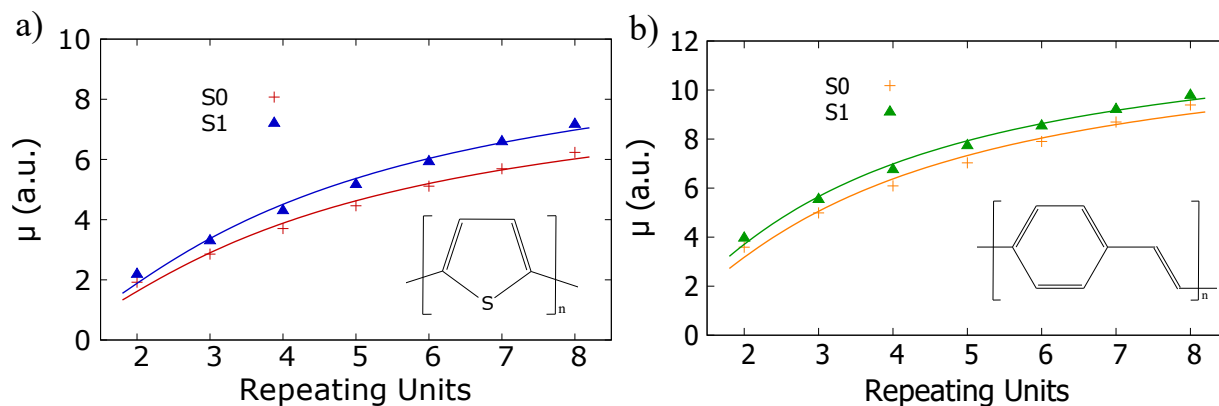


FIG. 13. Transition dipole moments from the S_0 and S_1 states as a function of the number of repeating units for the thiophene (a) and phenylene vinylene (b) oligomer series. Curves correspond to fits to the data.

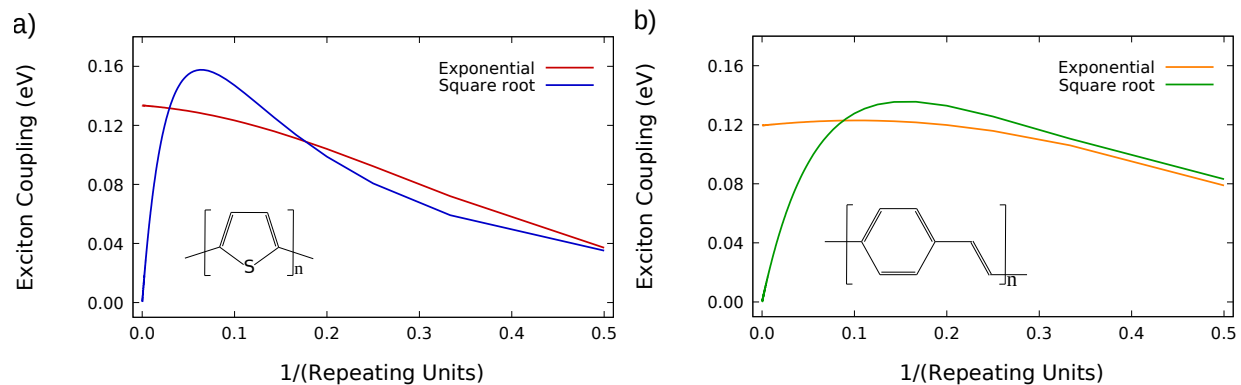


FIG. 14. Exciton coupling for a) oligothiophenes and b) OPVs as a function of the inverse number of repeating units using the corrected point dipole approximation coupled to both a square root and exponential dependence for transition dipole moments.

IV. SPECTRA IN THE POLYMERIC LIMIT

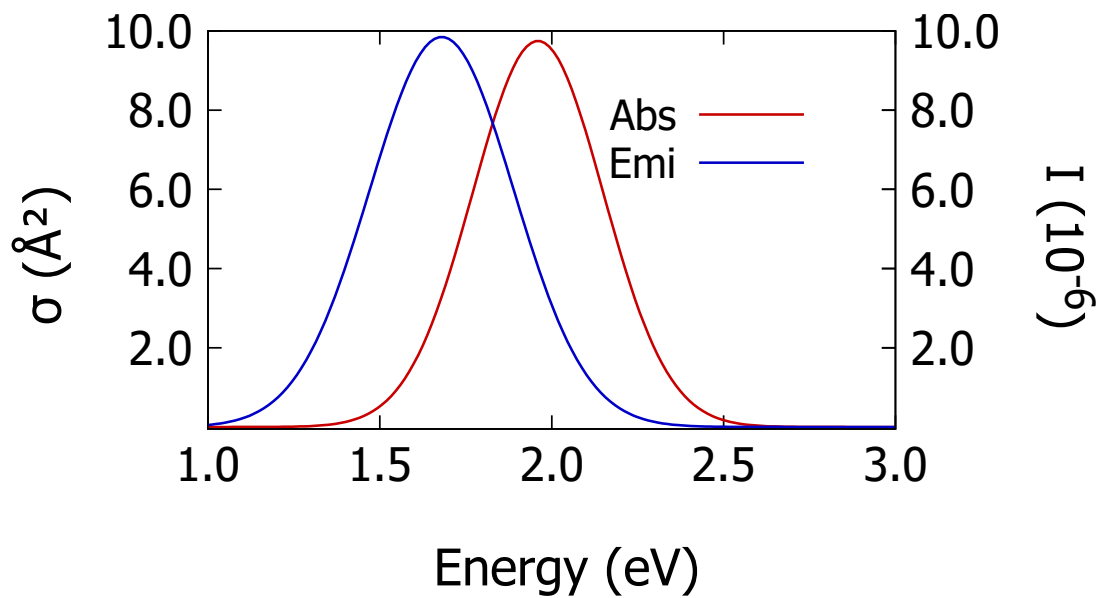


FIG. 15. Absorption cross-section and differential emission rate for the thiophene polymeric limit obtained with B3LYP.

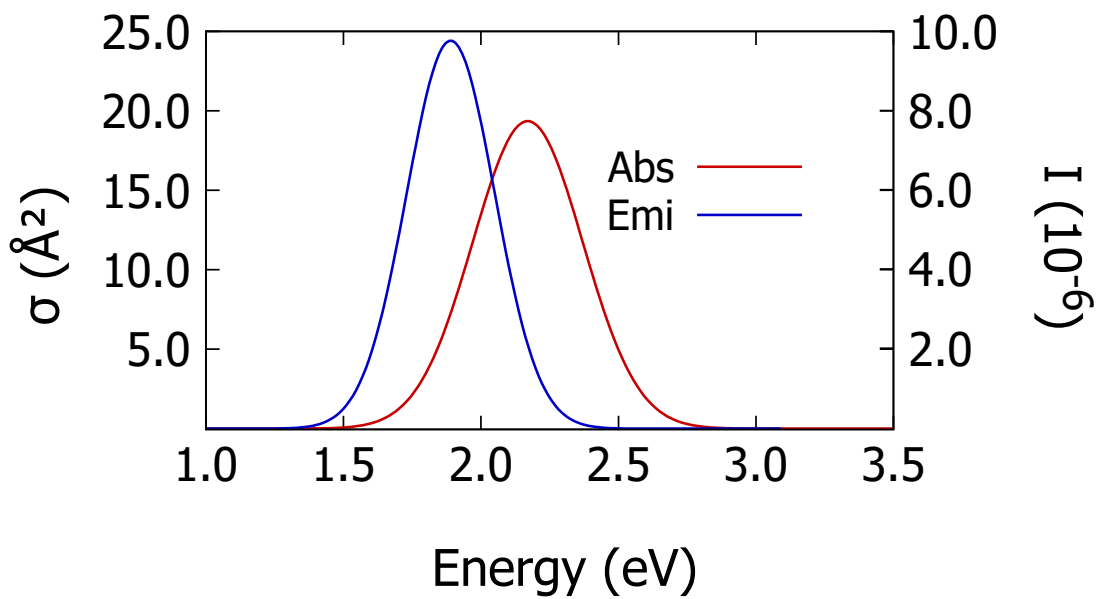


FIG. 16. Absorption cross-section and differential emission rate for the p-phenylene vinylene polymeric limit obtained with B3LYP.

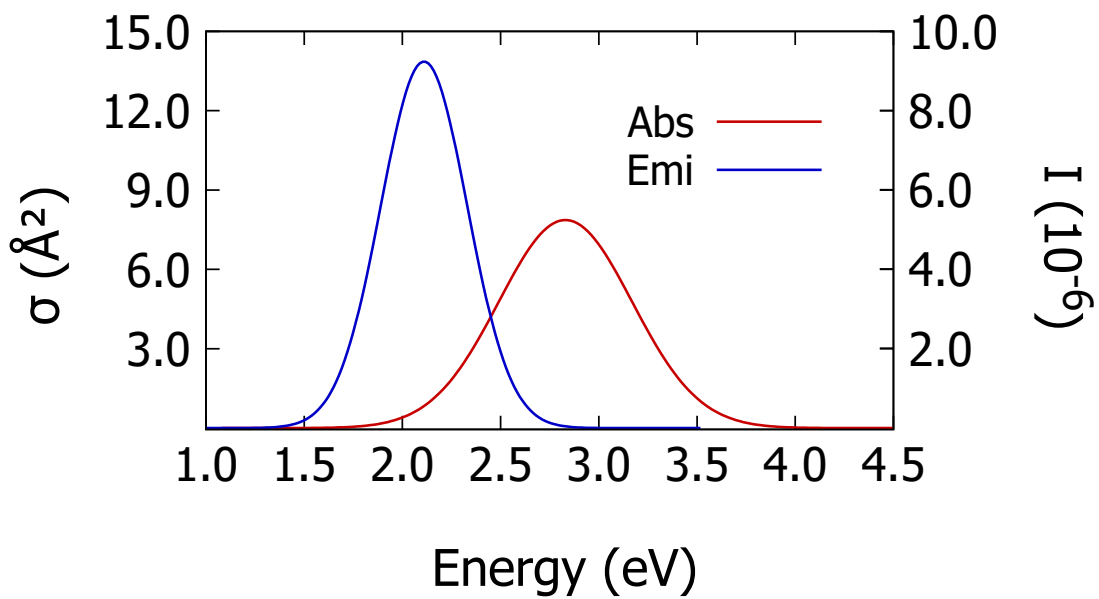


FIG. 17. Absorption cross-section and differential emission rate for the thiophene polymeric limit obtained with CAM-B3LYP.

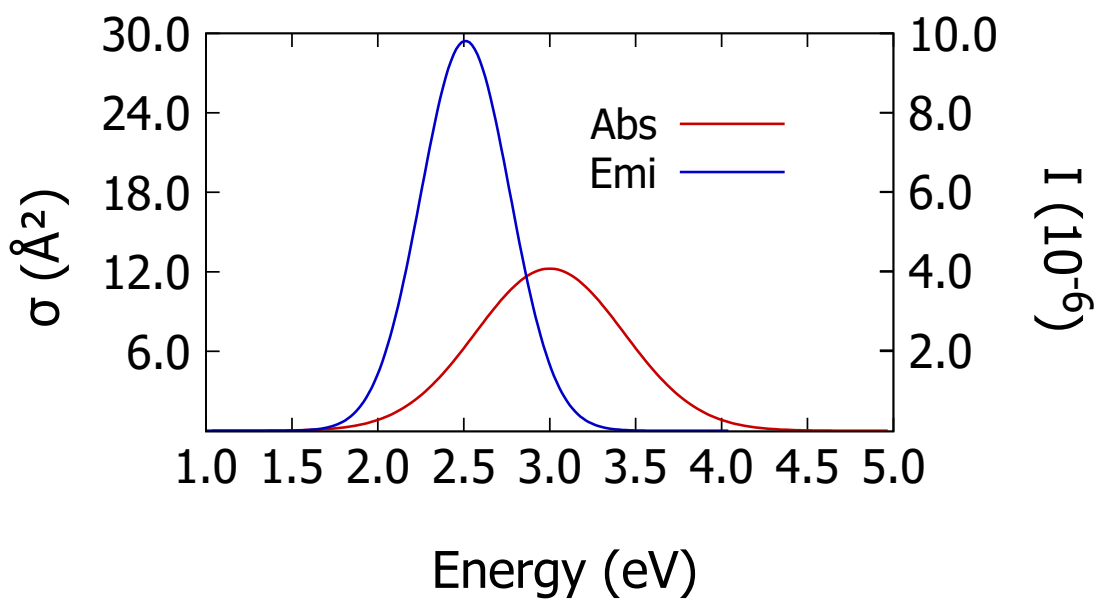


FIG. 18. Absorption cross-section and differential emission rate for the p-phenylene vinylene polymeric limit obtained with CAM-B3LYP.