Supporting Information for

Insight into the Excited State Electronic and Structural Properties of the Organic Photovoltaic Electron Donor Polymer Poly(thieno[3,4-b]thiophene benzodithiophene) by Means of *ab Initio* and Density Functional Theory

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Testing of the freezing scheme

In testing the freezing of occupied and molecular orbitals, the $(PTB1)_1$ S_1 transition energy was computed systematically using the 18 freezing schemes depicted in Figure S1 below. The results show for a given percentage of frozen occupied orbitals in the range from 70% to 90% that increasing the percentage of frozen virtual orbitals up to 50% increases the S_1 transition energies of $(PTB1)_1$ by at most ~ 0.2 eV. In total, the S_1 excitation energy increases only by less than 0.4 eV over the whole range of freezing schemes. This quite modest dependence of the excitation energies in the range of our freezing schemes lets us expect that the overall error in the computed transition energies of $(PTB1)_5$ using the 60% frozen occupied and 50% frozen virtual scheme should not exceed 0.3 to 0.4 eV.

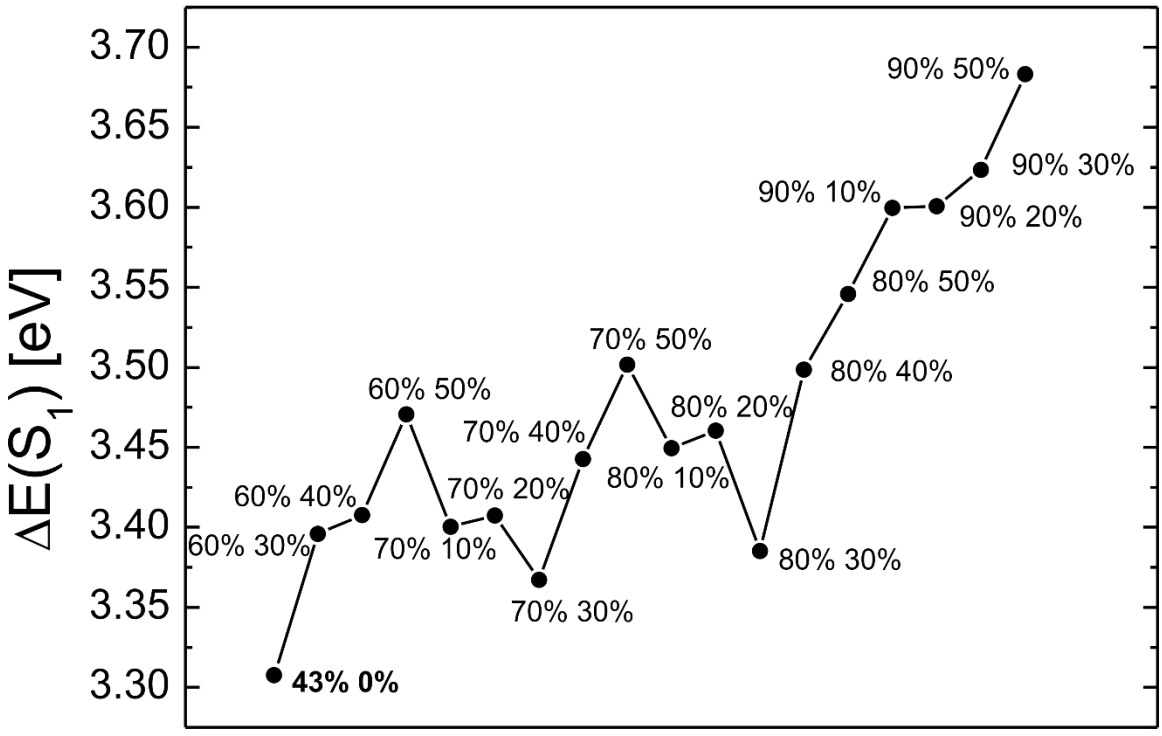

Figure S1. ADC(2)/SV-SVP testing of freezing schemes for the first excitation energy $\Delta E(S_1)$ of $(PTB1)_1$. Notation for each pair of percentage is: first number - percentage of lowest energy frozen occupied orbitals (%); second number - percentage of highest energy frozen virtual orbitals (%). For $(PTB1)_1$ the freezing of only the core orbitals (standard freezing) corresponds to (43%, 0 %).

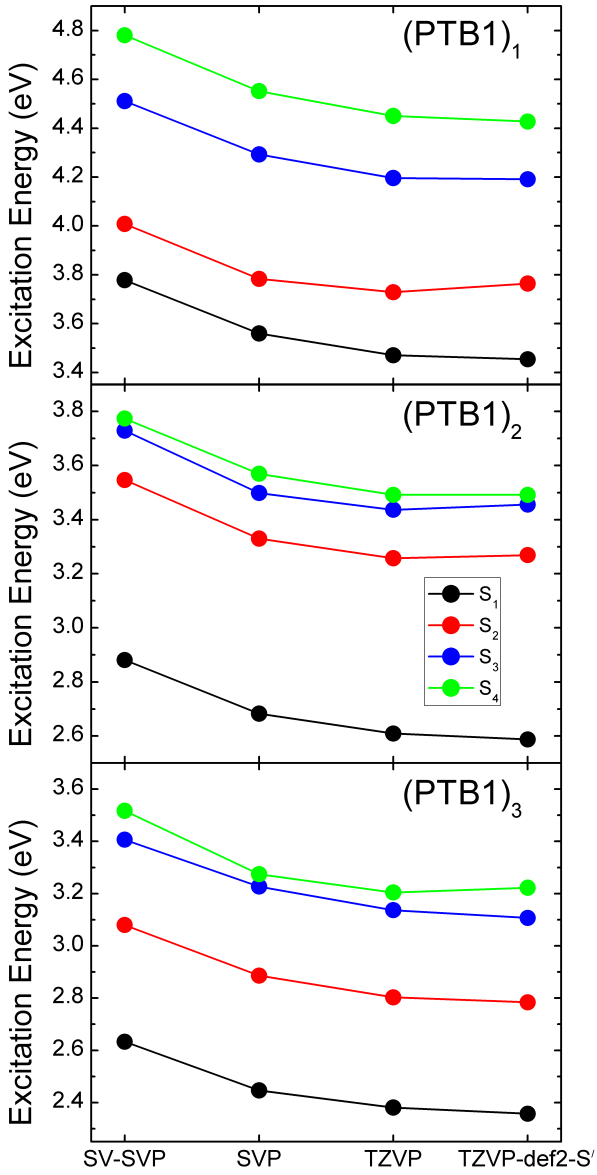

Figure S2. PTB1 (*n*=1-3) ADC(2) excitation energies ΔE (eV) as function of the type of basis set using the SV-SVP/PBE optimized geometry for each oligomer. TZVP-def2-S$^{/}$ contains the TZVP basis set for the C and H atoms and the def2-TZVP basis set for sulfur, which includes polarization functions (2d/1f).

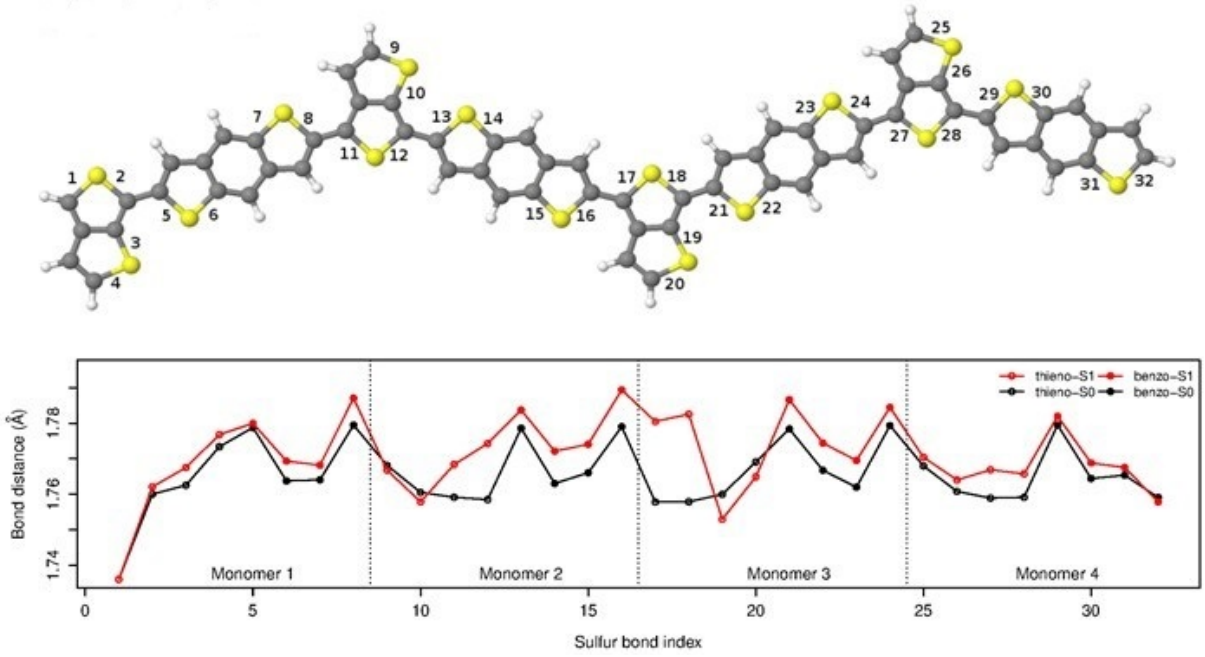

Figure S3. Computed carbon-sulfur bond distances for the optimized structures of the S_0 and S_1 states of the PTB1 tetramer using the MP2 and ADC(2)/SV-SVP methods.

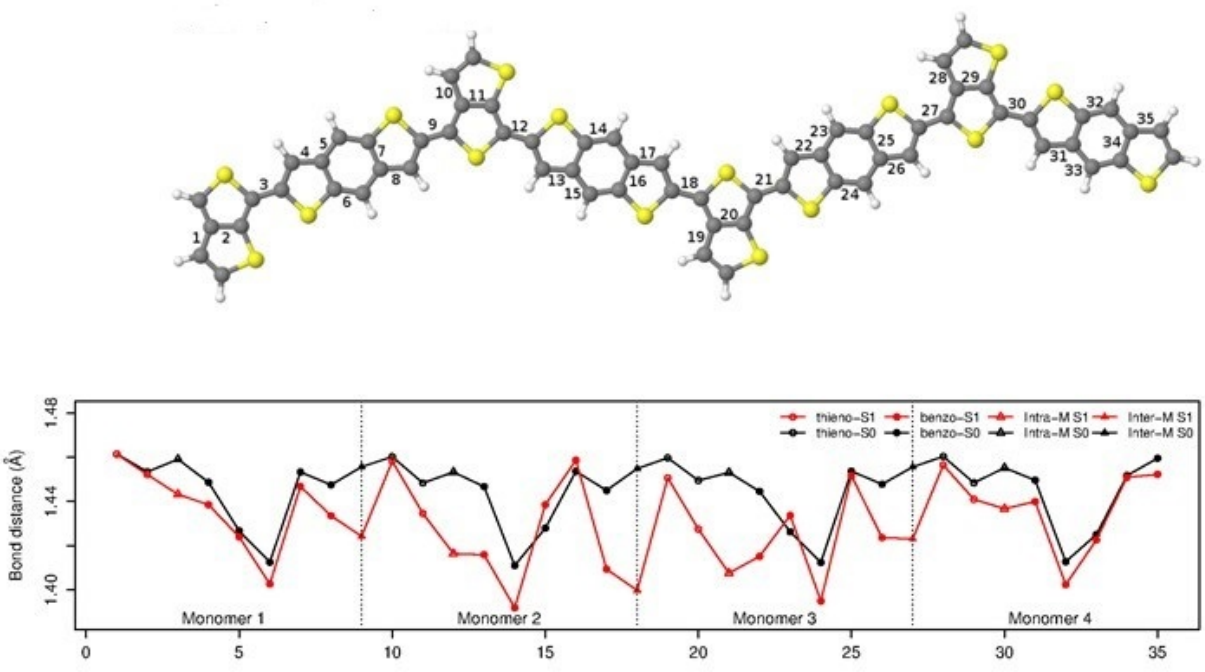

Figure S4. Computed single carbon-carbon bond distances for the optimized structures of the S_0 and S_1 states of the PTB1 tetramer using the MP2 and ADC(2)/SV-SVP methods.

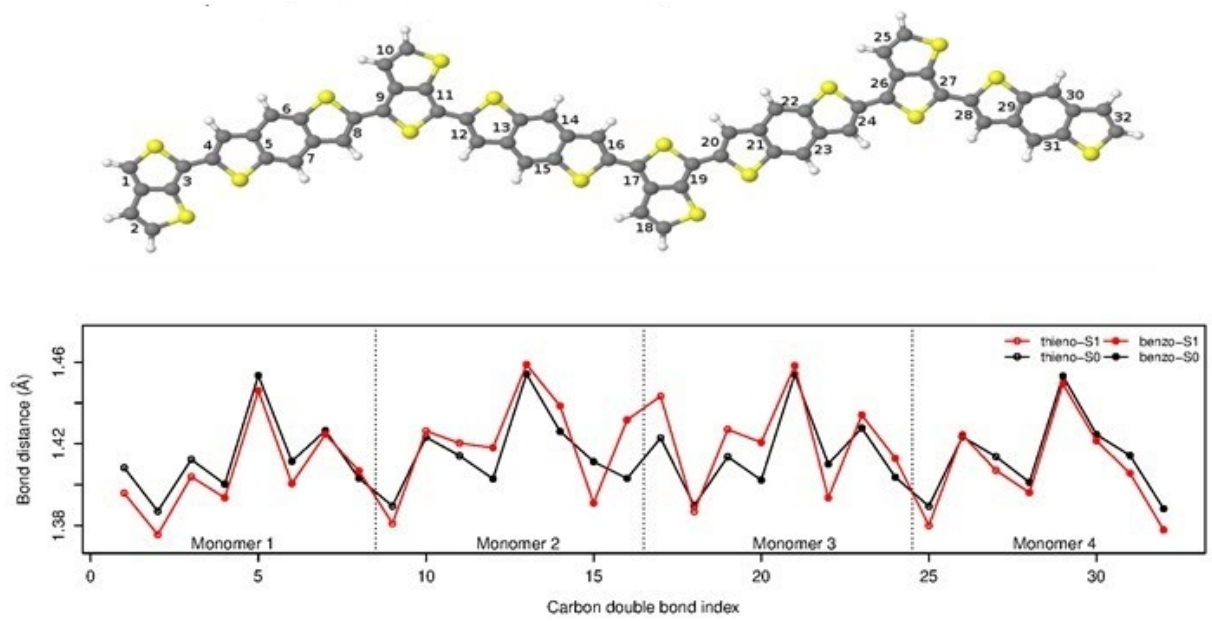

Figure S5: Computed double carbon-carbon bond distances for the optimized structures of the S_0 and S_1 states of the PTB1 tetramer using the MP2 and ADC(2)/SV-SVP methods.

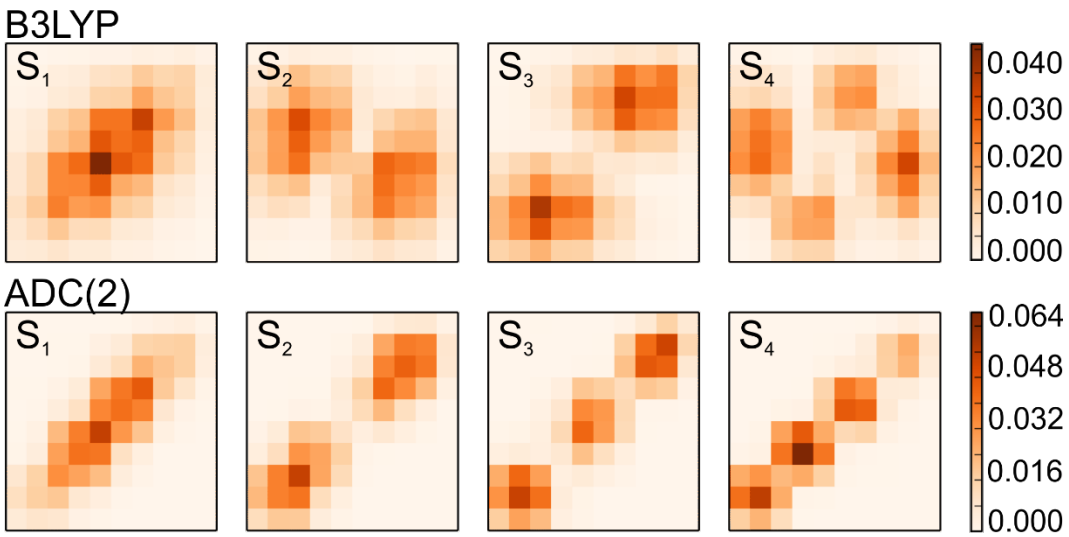

Figure S6: $(PTB1)_5$ Ω_{AB}^{α} plots of the first four electronic transitions (S_1 to S_4) employing ADC(2), B3LYP and the SV-SVP basis set. The vertical axis indicates the position of the hole and the horizontal axis the position of the electron. Each square of the plot represents either a benzodithiophene or a thienothiophene subunit. The square in the lowest leftmost corner corresponds to the electron rich benzodithiophene moiety and in the highest rightmost corner to the electron deficient thienothiophene. The shades represent the probability values according to the scale on the right of each panel.

Figure S7: $(PTB1)_4$ ground (S_0) and excited ($_{S1}$) optimized geometries using the SV-SVP basis set.

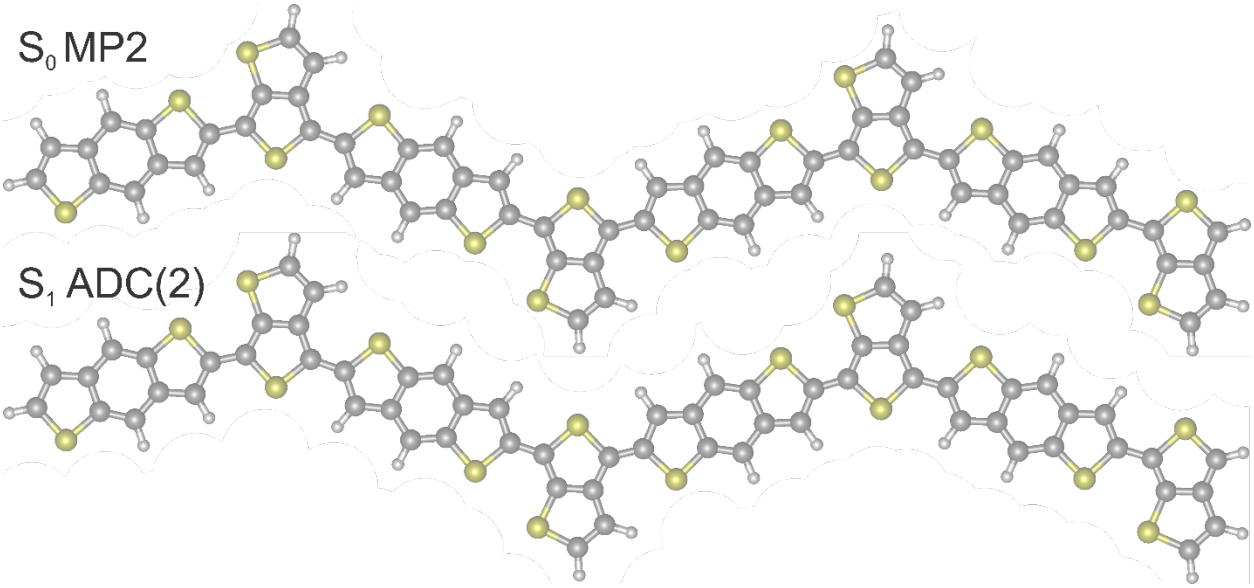

Table S1. $(PTB1)_1$ excitation character and transition energy ΔE (eV) using the SV-SVP, SVP, TZVP and TZVP-def2-S$^{/}$ basis sets and standard freezing.

State	Character % (SV-SVP/SVP/TZVP/ TZVP-def2-S$^{/}$)
S_1-2^1A'	(93.6/91.8/92.0/93.5)(HOMO → LUMO)
S_2-3^1A'	(64.6/72.1/70.8/68.5)(HOMO-1→LUMO)
S_3-4^1A'	(48.0/47.3/50.2/55.3)(HOMO→LUMO+1)
S_4-5^1A'	(33.7/37.9/31.5/32.5)(HOMO-2→LUMO) + (26.5/27.9/30.9/29.8)(HOMO→LUMO+2)

State	ΔE(SV-SVP)	ΔE(SVP)	ΔE(TZVP)	ΔE(TZVP-def2-S$^{/}$)
S_1-2^1A'	3.779	3.559	3.471	3.454
S_2-3^1A'	4.008	3.783	3.728	3.764
S_3-4^1A'	4.511	4.292	4.197	4.191
S_4-5^1A'	4.781	4.552	4.450	4.427

Table S2. $(PTB1)_2$ excitation character and transition energy ΔE (eV) using the SV-SVP, SVP, TZVP and TZVP-def2-S$'$ basis sets and standard freezing.

State	Character % (SV-SVP/SVP/TZVP/ TZVP-def2-S$'$)
S_1-2^1A'	(92.9/91.9/91.9/92.8)(HOMO → LUMO)
S_2-3^1A'	(65.9/56.5/61.6/69.7)(HOMO-1→LUMO)
S_3-4^1A'	(51.2/48.0/52.7/34.7)(HOMO-3→LUMO)
S_4-5^1A'	(68.2/28.1/37.0/24.9)(HOMO→LUMO+1)+(8.4/35.5/31.1/16.4)(HOMO-2→LUMO)

State	ΔE(SV-SVP)	ΔE(SVP)	ΔE(TZVP)	ΔE(TZVP-def2-S$'$)
S_1-2^1A'	2.881	2.683	2.609	2.588
S_2-3^1A'	3.546	3.330	3.257	3.269
S_3-4^1A'	3.729	3.498	3.437	3.456
S_4-5^1A'	3.773	3.570	3.491	3.491

Table S3. $(PTB1)_3$ excitation character and transition energy ΔE (eV) using the SV-SVP, SVP, TZVP and TZVP-def2-S′ basis sets and standard freezing.

State	Character % (SV-SVP/SVP/TZVP/ TZVP-def2-S′)
S_1-2^1A'	(83.9/83.6/83.8/84.7)(HOMO → LUMO)
S_2-3^1A'	(45.7/46.4/45.0/44.4)(HOMO-1→LUMO)+(44.1/42.6/44.2/45.9)(HOMO→LUMO+1)
S_3-4^1A'	(33.7/29.5/33.2/36.1)(HOMO-1→LUMO)+(36.2/32.3/34.4/35.8)(HOMO→LUMO+1)
S_4-5^1A'	(38.0/28.9/34.3/40.8)(HOMO-2→LUMO)+(19.5/22.4/20.4/14.6)(HOMO-4→LUMO)

State	ΔE(SV-SVP)	ΔE(SVP)	ΔE(TZVP)	ΔE(TZVP-def2-S′)
S_1-2^1A'	2.633	2.446	2.380	2.357
S_2-3^1A'	3.080	2.885	2.803	2.783
S_3-4^1A'	3.407	3.227	3.137	3.107
S_4-5^1A'	3.517	3.274	3.205	3.222