Supporting Information

Morphology and Optical Response of Carbon Nanotubes Functionalized by Conjugated Polymers

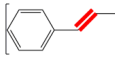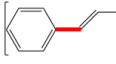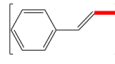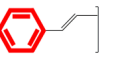Al'ona Furmanchuk[†§], Jerzy Leszczynski[§], Sergei Tretiak[†], Svetlana V. Kilina[‡*]

[†]*Theoretical Division and Center for Integrated Nanothechnology,*
Los Alamos National Laboratory, Los Alamos, NM 87545
[§]*Department of Chemistry and Biochemistry,*
Jackson State University, Jackson, MS 39217
[‡]*Department of Chemistry and Biochemistry,*
North Dakota State University, Fargo, ND 58108
**corresponding author*
e-mail: svetlana.kilina@ndsu.edu

Table S1. Average values of structural parameters (all units are Å) of isolated linear PPV oligomer compared with PPV oligomers in PPV/SWCNT hybrids. SWNT-PPV binding energy (E/unit) and energy per unit of PPV required for an oligomer bending[+] (E_{bend}/unit), both in eV. Data based on MM3 force field optimization.

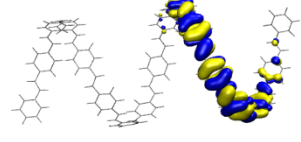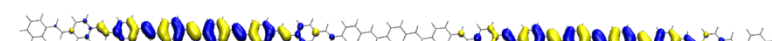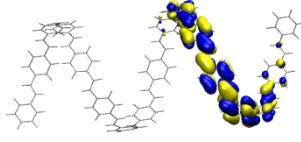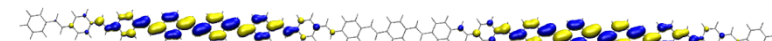| structure	wrapping angle (°)					BLA[*]	PPV-SWNT distance	E/unit (eV)	E_{bend}/unit[+] (eV)
Isolated linear PPV oligomer									
17 units	-	1.3444	1.4515	1.4515	1.3999	0.1072	-		-
PPV/(6,5) SWCNT composites									
A9	0.98	1.3443	1.4516	1.4514	1.3997	0.1072	3.33	-0.38	
A8	5.25	1.3442	1.4518	1.4510	1.3998	0.1072	3.34	-0.36	0.02
A7	19.91	1.3485	1.4595	1.4594	1.4027	0.1109	3.31	-0.32	0.05
A6	27.93	1.3436	1.4497	1.4502	1.3993	0.1063	3.43	-0.29	0.08
A5	42.82	1.3465	1.4546	1.4550	1.4012	0.1083	3.27	-0.15	0.23
A4	48.77	1.3437	1.4504	1.4498	1.3994	0.1064	3.46	-0.13	0.23
A3	56.03	1.3440	1.4501	1.4502	1.3994	0.1061	3.40	-0.07	0.31
A2	70.28	1.3431	1.4483	1.4482	1.3985	0.1051	3.53	0.16	0.39
A1	75.83	1.3438	1.4503	1.4503	1.3990	0.1065	3.54	-0.02	0.34
PPV/(8,0) SWCNT composites									
B8	0.20	1.3444	1.4517	1.4517	1.3998	0.1072	3.32	-0.36	
B7	7.23	1.3438	1.4502	1.4512	1.3996	0.1069	3.33	-0.35	0.02
B6	9.98	1.3443	1.4515	1.4515	1.3997	0.1072	3.33	-0.35	
B5	11.24	1.3439	1.4505	1.4509	1.3995	0.1068	3.26	-0.34	0.02
B4	19.66	1.3480	1.4584	1.4585	1.4023	0.1105	3.29	-0.31	0.06
B3	34.37	1.3422	1.4471	1.4469	1.3981	0.1048	3.40	-0.20	0.16
B2	58.60	1.3458	1.4532	1.4533	1.4003	0.1075	3.28	0.02	0.38
B1	72.77	1.3442	1.4508	1.4504	1.3991	0.1064	3.61	0.10	0.43
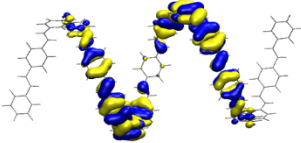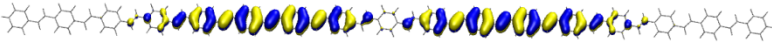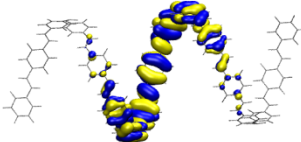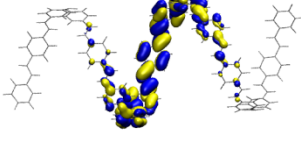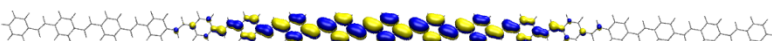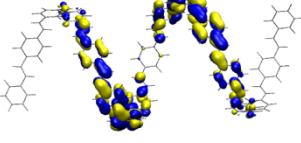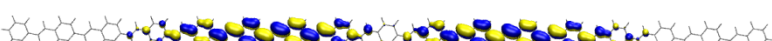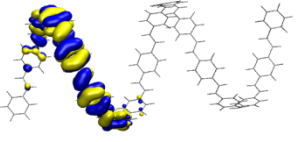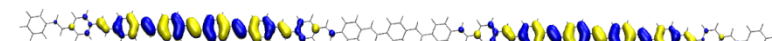
[*]BLA stands for bond length alternation. It is defined as difference between average value of single bonds and double bond length in carbon-carbon chains connected benzene rings of PPV oligomers.
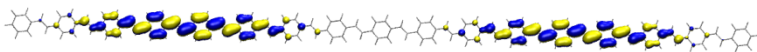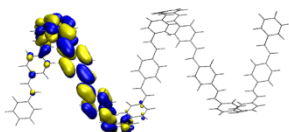
[+]Energy difference was found between the coiled oligomer and the same length linear fully optimized PPV.

Natural Transition Orbitals (NTOs) analysis of four lowest excited states of differently coiled PPV oligomers has been done in order to check effect of coiling angle. The coiling angles in isolated oligomers chosen in correspondence with wrapping angles observed in PPV/SWNT hybrids. The same length linear oligomers have also been generated for every coiled one (see Table S2, S3). This way, shape and position of electron and hole orbitals will be independent of conjugation length.

Oligomers similar to A2- and B2-like hybrid structures were chosen, since their spectra revealed significant shift and broadening in the first absorption bands comparing to linear PPV analogs. Degeneracy of NTOs is detected for these oligomers. Therefore, two dominant pairs of NTOs were always used to characterize the first four single-particle transitions. All NTOs of isolated coiled oligomers revealed π - π^* character of excitations that is also typical for the linear oligomers. It is interesting to see that localization of transition orbitals of the first state in A2-like and B2-like oligomers is always similar to corresponding orbitals of the linear oligomer. Therefore, coiling results only in change of intensity of corresponding peaks in Figure 4. States S_2 and S_3 in A2-like oligomer represented by change in localization of orbitals. In state S_2 electron and hole in both HOTO $\rightarrow$ LUTO and HOTO -1 $\rightarrow$ LUTO +1 excitations are loosing half portion of orbitals comparing with corresponding orbitals of linear oligomer. In state S_3 only HOTO -1 $\rightarrow$ LUTO +1 excitation reduced by half, while central symmetry is lost for HOTO $\rightarrow$ LUTO excitation. The S_4 state is slightly similar to S_2 except remained part of the orbital is significantly shifted to the very end of coiled oligomer. Therefore, we may conclude that change of the NTOs' symmetry results in increase of oscillator strength of corresponding transition band. Except for state S_2, The first four states keeps distribution of orbitals similar to linear oligomers. The HOTO $\rightarrow$ LUTO excitation of S_2 state are reflected in significant reduction of electron delocalization and change of symmetry for the hole orbital.

Table S2. The electron and hole NTOs for the four lowest excited states in isolated A2-like coiled PPV oligomer and linear one of the same length. The overall length of each oligomer is 17 units. The population of each orbital is given above its picture. Position (eV) and intensity (arb.u.) of each excitation is listed.

A2-like coiled oligomer	Linear oligomer
S_1: 2.6 eV (0.8)	2.8 eV (11.7)
hole	
21.56%	21.36%

| 33.10% | 31.83% |

electron

| 33.10% | 31.83% |

| 21.56% | 21.36% |

S_2: 2.7 eV (0.1)	2.9 eV (0.0)
hole	
27.26%	27.23%

| 27.56% | 27.25% |

electron

| 27.56% | 27.25% |

| 27.26% | 27.23% |

S$_3$: 2.8 eV (0.2)	3.0 eV (1.1)
hole	
23.58%	22.62%
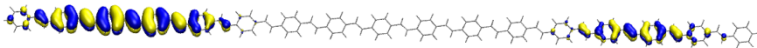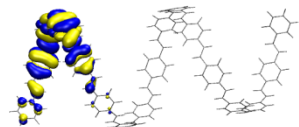
23.84%	24.08%
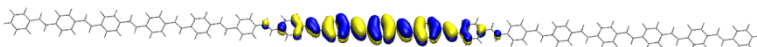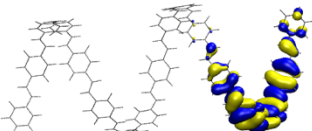
electron	
23.84%	24.08%
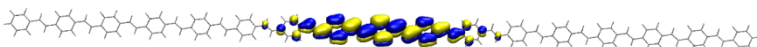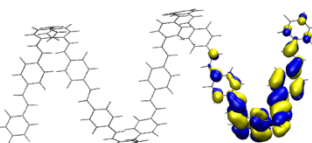
23.58%	22.62%
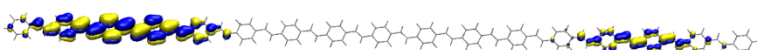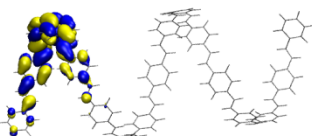
S$_4$: 3.0 eV (3.6)	3.1 eV (0.0)
hole	
21.94%	20.32%
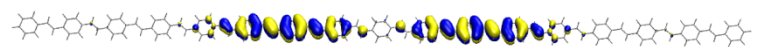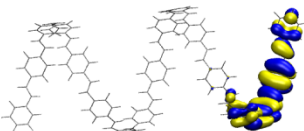
22.06%	20.69%
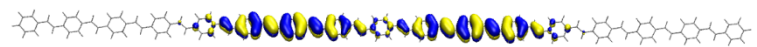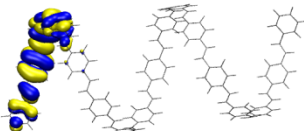
electron	
22.06%	20.69%
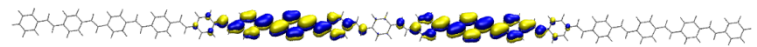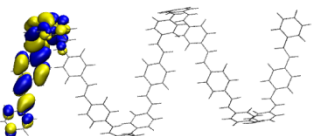
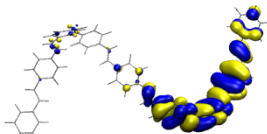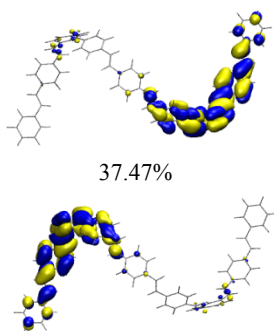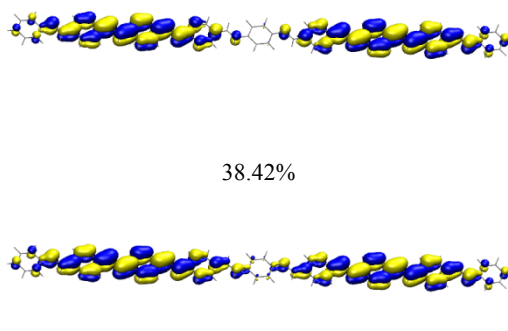|	20.32%
21.94%	
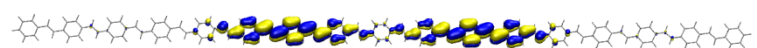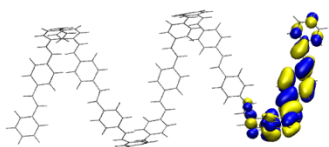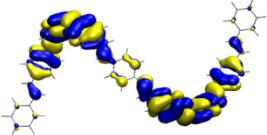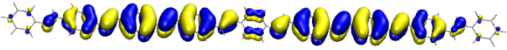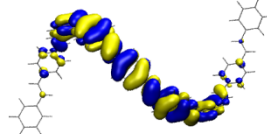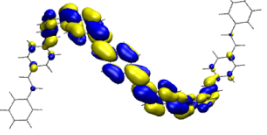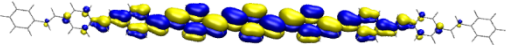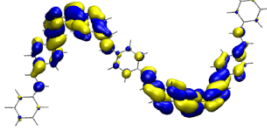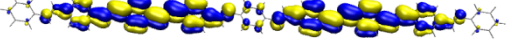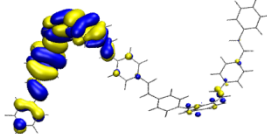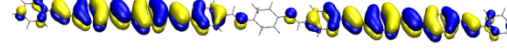
Table S3. The electron and hole NTOs for the four lowest excited states in isolated B2-like coiled PPV oligomer and linear one of the same length. The overall length of each oligomer is 9 units. The population of each orbital is given above its picture. Position (eV) and intensity (arb.u.) of each excitation is listed.

B2-like coiled oligomer	Linear oligomer
S₁: 2.8 eV (1.3)	2.8 eV (6.1)

S_1:   2.8 eV (1.3)   2.8 eV (6.1)

hole

24.11%   24.12%

51.95%   52.07%

electron

51.95%   52.07%

24.11%   24.12%

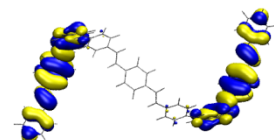S_2:   3.0 eV (1.8)   3.1 eV (0.0)

hole

37.47%   38.42%

39.89%   39.02%
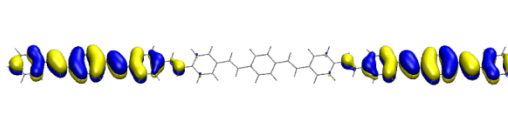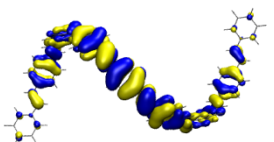

electron

39.02%

39.89%

37.47%   38.42%

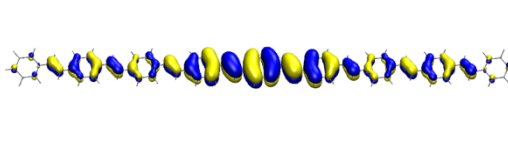| S₃: | 3.3 eV (2.8) | 3.3 eV (0.5) |

hole

28.62%   28.65%
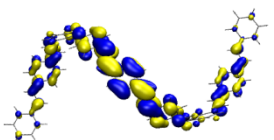

32.00%   31.87%
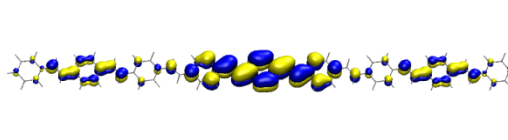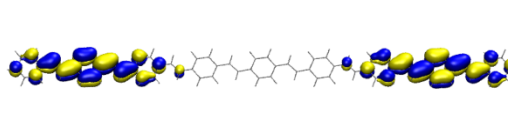

electron

32.00%   31.87%

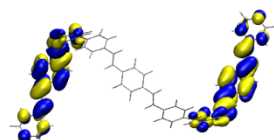28.62%   28.65%

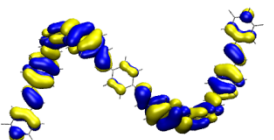| S₄: | 3.5 eV (0.3) | 3.6 eV (0.0) |

hole

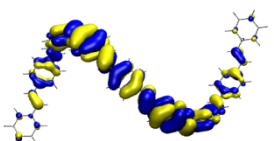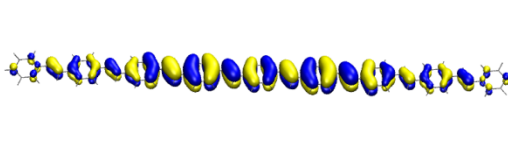24.60%   24.43%
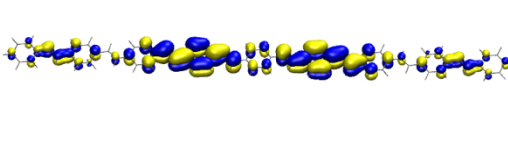

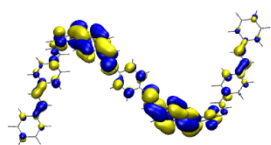
27.25%   26.39%

electron

                                          26.39%

27.25%

24.60%   24.43%