10.1071/CH16187_AC

Australian Journal of Chemistry 2016, 69(9), 960-968

Supplementary Material to: Electronic and Optical Properties of the Narrowest Armchair Graphene Nanoribbons Studied by Density Functional Methods

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I. EXPECTATION VALUE OF THE TOTAL SPIN-SQUARED OPERATOR $\langle \hat{S}^2 \rangle$

In spin-unrestricted Kohn-Sham density functional theory (KS-DFT), the spatial parts of α- and β-spin orbitals may be different. For simplicity, we refer to the spatial parts of α- and β-spin orbitals as α- and β-orbitals (ϕ^α and ϕ^β). Both α- and β-orbitals form an orthogonal set, respectively, but α- and β-orbitals are, in general, not orthogonal to each other:

$$\langle \phi_i^\alpha | \phi_j^\alpha \rangle = \delta_{ij} \quad \text{and} \quad \langle \phi_i^\beta | \phi_j^\beta \rangle = \delta_{ij} \tag{1}$$

$$\langle \phi_i^\alpha | \phi_j^\beta \rangle \neq \delta_{ij} \tag{2}$$

In this formalism, the Kohn-Sham (KS) Hamiltonian $\hat{H}_s$ commutes with the total spin projection operator $\hat{S}_z$, but may not commute with the total spin-squared operator $\hat{S}^2$. As a result, the KS ground-state wavefunction may not be an eigenfunction of $\hat{S}^2$. Instead, the expectation value of $\hat{S}^2$ can be calculated as [assuming that the number of α-orbitals (N_α) $\geq$ the number of β-orbitals (N_β)]:

$$\langle \hat{S}^2 \rangle = S(S+1) + N_\beta - \sum_{i=1}^{N_\alpha} \sum_{j=1}^{N_\beta} |\langle \phi_i^\alpha | \phi_j^\beta \rangle|^2, \tag{3}$$

where $S = (N_\alpha - N_\beta)/2$, the eigenvalue of $\hat{S}_z$, can be 0 (singlet), 1/2 (doublet), 1 (triplet), 3/2 (quartet), and so on [1, 2]. Note that the expression takes exactly the same form as the one in spin-unrestricted Hartree-Fock (HF) theory, except it is now evaluated with spin-unrestricted KS orbitals, rather than spin-unrestricted HF orbitals. If α- and β-orbitals are the same, the sum of the last two terms in Eq. (3) is zero, yielding the exact value $S(S+1)$ (i.e., the eigenvalue of $\hat{S}^2$). Otherwise, the deviation from the exact value $S(S+1)$ is always positive [2, 3], and the KS wavefunction is spin contaminated (i.e., spin symmetry is broken).

TABLE S1. Singlet-triplet energy gap E_{ST} [in eV] of n-PP as a function of the chain length, calculated using KS-DFT with various density functionals. For comparison, the experimental data [4–6] are taken from the literature.

n	LDA	PBE	BLYP	PBE0	B3LYP	ωB97	ωB97X	Expt
1	4.23	3.90	3.87	3.84	3.88	3.83	3.88	3.67 [4]
2	3.03	2.86	2.83	2.97	2.95	3.12	3.14	2.94 [5]
3	2.54	2.42	2.39	2.59	2.57	2.79	2.82	2.54 [6]
4	2.29	2.20	2.18	2.45	2.41	2.73	2.75	
5	2.15	2.07	2.05	2.37	2.32	2.68	2.70	
6	2.06	1.99	1.97	2.34	2.28	2.70	2.72	
7	2.00	1.94	1.92	2.32	2.26	2.67	2.69	
8	1.95	1.91	1.89	2.31	2.25	2.67	2.69	
9	1.92	1.88	1.87	2.30	2.24	2.67	2.69	
10	1.90	1.87	1.85	2.30	2.24	2.69	2.71	
11	1.89	1.85	1.84	2.30	2.24	2.67	2.69	
12	1.88	1.85	1.83	2.30	2.24	2.69	2.71	
13	1.87	1.84	1.83	2.30	2.24	2.67	2.69	
14	1.86	1.83	1.82	2.30	2.24	2.69	2.71	
15	1.86	1.83	1.82	2.30	2.24	2.67	2.69	
16	1.85	1.83	1.82	2.30	2.24	2.69	2.71	
17	1.85	1.83	1.82	2.30	2.24	2.67	2.69	
18	1.85	1.83	1.81	2.30	2.24	2.69	2.69	
19	1.85	1.82	1.81	2.30	2.24	2.67	2.69	
20	1.84	1.82	1.81	2.30	2.24	2.69	2.71	

TABLE S2. Vertical ionization potential IP(1) [in eV] for the lowest singlet state of n-PP as a function of the chain length, calculated using KS-DFT with various density functionals. For comparison, the experimental data [7] are taken from the literature.

n	LDA	PBE	BLYP	PBE0	B3LYP	ωB97	ωB97X	Expt
1	9.29	9.00	8.76	9.08	9.01	9.11	9.11	9.25 [7]
2	7.80	7.57	7.31	7.77	7.65	8.01	7.96	8.38 [7]
3	7.12	6.91	6.64	7.18	7.04	7.56	7.50	8.04 [7]
4	6.72	6.52	6.25	6.84	6.69	7.35	7.28	7.80 [7]
5	6.45	6.26	5.99	6.63	6.46	7.24	7.16	7.68 [7]
6	6.25	6.06	5.79	6.47	6.30	7.19	7.10	7.62 [7]
7	6.10	5.92	5.64	6.36	6.17	7.16	7.07	
8	5.98	5.80	5.53	6.27	6.08	7.15	7.05	
9	5.88	5.70	5.43	6.19	6.00	7.14	7.04	
10	5.80	5.62	5.35	6.13	5.93	7.14	7.04	
11	5.73	5.55	5.28	6.08	5.87	7.14	7.04	
12	5.67	5.49	5.22	6.04	5.83	7.14	7.04	
13	5.62	5.44	5.17	6.00	5.78	7.14	7.04	
14	5.57	5.39	5.12	5.96	5.75	7.14	7.04	
15	5.53	5.35	5.08	5.93	5.71	7.14	7.04	
16	5.49	5.32	5.04	5.90	5.68	7.14	7.04	
17	5.46	5.28	5.01	5.88	5.66	7.14	7.04	
18	5.43	5.25	4.98	5.85	5.63	7.14	7.04	
19	5.40	5.23	4.95	5.83	5.61	7.14	7.04	
20	5.38	5.20	4.93	5.82	5.59	7.14	7.04	

TABLE S3. Vertical ionization potential IP(2) [in eV] for the lowest singlet state of n-PP as a function of the chain length, calculated using KS-DFT with various density functionals. For comparison, the experimental data [7] are taken from the literature.

n	LDA	PBE	BLYP	PBE0	B3LYP	ωB97	ωB97X	Expt
1	6.12	5.93	5.65	7.02	6.69	9.44	9.22	9.25 [7]
2	5.44	5.25	4.98	6.20	5.90	8.44	8.24	8.38 [7]
3	5.17	4.98	4.71	5.85	5.58	8.03	7.84	8.04 [7]
4	5.03	4.84	4.57	5.69	5.41	7.81	7.65	7.80 [7]
5	4.95	4.76	4.49	5.58	5.33	7.70	7.51	7.68 [7]
6	4.90	4.73	4.46	5.52	5.25	7.62	7.43	7.62 [7]
7	4.84	4.68	4.41	5.50	5.22	7.56	7.40	
8	4.84	4.65	4.38	5.47	5.20	7.54	7.35	
9	4.82	4.65	4.38	5.44	5.17	7.51	7.35	
10	4.79	4.63	4.35	5.41	5.17	7.48	7.32	
11	4.79	4.63	4.35	5.41	5.14	7.48	7.29	
12	4.79	4.63	4.35	5.39	5.14	7.48	7.29	
13	4.79	4.60	4.33	5.39	5.12	7.46	7.29	
14	4.76	4.60	4.33	5.39	5.12	7.46	7.27	
15	4.76	4.60	4.33	5.39	5.12	7.46	7.27	
16	4.76	4.60	4.33	5.39	5.12	7.46	7.27	
17	4.76	4.60	4.33	5.36	5.12	7.43	7.27	
18	4.76	4.60	4.33	5.36	5.12	7.43	7.27	
19	4.76	4.60	4.33	5.36	5.12	7.43	7.27	
20	4.76	4.60	4.33	5.36	5.09	7.43	7.27	

TABLE S4. Vertical electron affinity EA(1) [in eV] for the lowest singlet state of n-PP as a function of the chain length, calculated using KS-DFT with various density functionals. For comparison, the experimental data: Expt1 (vertical EA) [8, 9] and Expt2 (adiabatic EA) [10, 11], are taken from the literature.

n	LDA	PBE	BLYP	PBE0	B3LYP	ωB97	ωB97X	Expt1	Expt2
1	-2.16	-2.21	-2.41	-2.26	-2.31	-2.30	-2.32	-1.13 [8]	-1.12 [10]
2	-0.52	-0.62	-0.84	-0.74	-0.80	-0.97	-0.97	-0.30 [9]	-0.17 [11]
3	0.23	0.12	-0.12	-0.07	-0.12	-0.42	-0.42		0.39 [11]
4	0.68	0.55	0.31	0.32	0.28	-0.15	-0.14		0.66 [11]
5	0.98	0.84	0.59	0.57	0.53	0.00	0.02		
6	1.20	1.06	0.80	0.75	0.71	0.09	0.11		
7	1.37	1.22	0.96	0.88	0.85	0.14	0.16		
8	1.50	1.35	1.09	0.99	0.96	0.17	0.19		
9	1.61	1.45	1.19	1.07	1.05	0.18	0.22		
10	1.70	1.54	1.28	1.14	1.12	0.20	0.23		
11	1.77	1.62	1.36	1.20	1.18	0.20	0.24		
12	1.84	1.68	1.42	1.25	1.23	0.21	0.24		
13	1.90	1.74	1.47	1.29	1.28	0.21	0.25		
14	1.95	1.79	1.52	1.33	1.32	0.22	0.25		
15	1.99	1.83	1.57	1.36	1.36	0.22	0.25		
16	2.03	1.87	1.61	1.39	1.39	0.22	0.25		
17	2.07	1.90	1.64	1.42	1.42	0.22	0.26		
18	2.10	1.94	1.67	1.44	1.44	0.22	0.26		
19	2.13	1.97	1.70	1.47	1.47	0.22	0.26		
20	2.16	1.99	1.73	1.49	1.49	0.22	0.26		

TABLE S5. Vertical electron affinity EA(2) [in eV] for the lowest singlet state of n-PP as a function of the chain length, calculated using KS-DFT with various density functionals. For comparison, the experimental data: Expt1 (vertical EA) [8, 9] and Expt2 (adiabatic EA) [10, 11], are taken from the literature.

n	LDA	PBE	BLYP	PBE0	B3LYP	ωB97	ωB97X	Expt1	Expt2
1	-5.17	-5.14	-5.33	-4.27	-4.52	-2.04	-2.23	-1.13 [8]	-1.12 [10]
2	-2.83	-2.86	-3.10	-2.29	-2.50	-0.57	-0.71	-0.30 [9]	-0.17 [11]
3	-1.69	-1.77	-2.01	-1.36	-1.55	0.05	-0.08		0.39 [11]
4	-0.98	-1.09	-1.33	-0.82	-0.98	0.35	0.24		0.66 [11]
5	-0.49	-0.60	-0.84	-0.44	-0.57	0.52	0.44		
6	-0.14	-0.24	-0.49	-0.16	-0.30	0.60	0.52		
7	0.16	0.03	-0.22	0.03	-0.08	0.65	0.57		
8	0.38	0.24	0.00	0.19	0.11	0.68	0.60		
9	0.57	0.44	0.19	0.33	0.24	0.68	0.63		
10	0.73	0.60	0.33	0.44	0.38	0.71	0.63		
11	0.87	0.71	0.46	0.54	0.49	0.71	0.63		
12	0.98	0.84	0.57	0.63	0.57	0.71	0.63		
13	1.09	0.93	0.68	0.71	0.65	0.71	0.63		
14	1.17	1.03	0.76	0.76	0.71	0.71	0.63		
15	1.25	1.12	0.84	0.82	0.79	0.71	0.63		
16	1.33	1.17	0.93	0.87	0.84	0.71	0.63		
17	1.39	1.25	0.98	0.93	0.90	0.71	0.63		
18	1.44	1.31	1.03	0.98	0.95	0.71	0.63		
19	1.50	1.36	1.09	1.01	0.98	0.71	0.65		
20	1.55	1.39	1.14	1.06	1.03	0.71	0.65		

TABLE S6. Vertical electron affinity EA(3) [in eV] for the lowest singlet state of n-PP as a function of the chain length, calculated using KS-DFT with various density functionals. For comparison, the experimental data: Expt1 (vertical EA) [8, 9] and Expt2 (adiabatic EA) [10, 11], are taken from the literature.

n	LDA	PBE	BLYP	PBE0	B3LYP	ωB97	ωB97X	Expt1	Expt2
1	0.84	0.73	0.52	-0.24	-0.11	-2.56	-2.39	-1.13 [8]	-1.12 [10]
2	1.80	1.63	1.41	0.79	0.90	-1.33	-1.22	-0.30 [9]	-0.17 [11]
3	2.15	2.01	1.77	1.22	1.31	-0.84	-0.73		0.39 [11]
4	2.37	2.20	1.96	1.47	1.52	-0.57	-0.46		0.66 [11]
5	2.48	2.31	2.07	1.61	1.66	-0.41	-0.30		
6	2.56	2.39	2.12	1.69	1.74	-0.33	-0.22		
7	2.61	2.45	2.18	1.74	1.80	-0.24	-0.14		
8	2.64	2.48	2.23	1.80	1.85	-0.19	-0.08		
9	2.67	2.50	2.26	1.82	1.88	-0.16	-0.05		
10	2.69	2.53	2.26	1.85	1.90	-0.14	-0.03		
11	2.72	2.56	2.29	1.88	1.90	-0.11	0.00		
12	2.72	2.56	2.29	1.88	1.93	-0.08	0.00		
13	2.75	2.59	2.31	1.90	1.93	-0.08	0.03		
14	2.75	2.59	2.31	1.90	1.96	-0.08	0.03		
15	2.78	2.59	2.31	1.93	1.96	-0.05	0.03		
16	2.78	2.59	2.34	1.93	1.96	-0.05	0.05		
17	2.78	2.61	2.34	1.93	1.96	-0.05	0.05		
18	2.78	2.61	2.34	1.93	1.99	-0.05	0.05		
19	2.78	2.61	2.34	1.93	1.99	-0.03	0.05		
20	2.80	2.61	2.34	1.96	1.99	-0.03	0.08		

TABLE S7. Fundamental gap $E_g(1)$ [in eV] for the lowest singlet state of n-PP as a function of the chain length, calculated using KS-DFT with various density functionals. For comparison, the experimental data: Expt1 (vertical IP − vertical EA) [7–9] and Expt2 (vertical IP − adiabatic EA) [7, 10, 11], are taken from the literature.

n	LDA	PBE	BLYP	PBE0	B3LYP	ωB97	ωB97X	Expt1	Expt2
1	11.45	11.21	11.17	11.34	11.32	11.41	11.43	10.38 [7, 8]	10.37 [7, 10]
2	8.32	8.19	8.15	8.51	8.45	8.97	8.94	8.68 [7, 9]	8.55 [7, 11]
3	6.89	6.80	6.77	7.24	7.16	7.98	7.92		7.65 [7, 11]
4	6.04	5.97	5.94	6.52	6.42	7.49	7.42		7.14 [7, 11]
5	5.47	5.41	5.39	6.05	5.93	7.24	7.15		
6	5.05	5.01	4.99	5.72	5.58	7.10	6.99		
7	4.74	4.70	4.68	5.47	5.32	7.02	6.91		
8	4.48	4.45	4.44	5.28	5.12	6.98	6.86		
9	4.28	4.25	4.23	5.13	4.95	6.96	6.83		
10	4.11	4.08	4.07	4.99	4.81	6.94	6.81		
11	3.96	3.94	3.92	4.89	4.69	6.93	6.80		
12	3.83	3.81	3.80	4.79	4.59	6.93	6.79		
13	3.72	3.70	3.69	4.71	4.50	6.92	6.79		
14	3.63	3.61	3.60	4.63	4.43	6.92	6.79		
15	3.54	3.52	3.51	4.57	4.36	6.92	6.79		
16	3.46	3.45	3.44	4.51	4.29	6.92	6.78		
17	3.39	3.38	3.37	4.46	4.24	6.92	6.78		
18	3.33	3.32	3.31	4.41	4.19	6.92	6.78		
19	3.27	3.26	3.25	4.37	4.14	6.92	6.78		
20	3.22	3.21	3.20	4.33	4.10	6.92	6.78		

TABLE S8. Fundamental gap $E_g(2)$ [in eV] for the lowest singlet state of n-PP as a function of the chain length, calculated using KS-DFT with various density functionals. For comparison, the experimental data: Expt1 (vertical IP − vertical EA) [7–9] and Expt2 (vertical IP − adiabatic EA) [7, 10, 11], are taken from the literature.

n	LDA	PBE	BLYP	PBE0	B3LYP	ωB97	ωB97X	Expt1	Expt2
1	11.29	11.07	10.99	11.29	11.21	11.48	11.46	10.38 [7, 8]	10.37 [7, 10]
2	8.27	8.11	8.08	8.49	8.41	9.01	8.95	8.68 [7, 9]	8.55 [7, 11]
3	6.86	6.75	6.72	7.21	7.13	7.97	7.92		7.65 [7, 11]
4	6.01	5.93	5.90	6.50	6.39	7.46	7.40		7.14 [7, 11]
5	5.44	5.36	5.33	6.01	5.90	7.18	7.07		
6	5.03	4.98	4.95	5.69	5.55	7.02	6.91		
7	4.68	4.65	4.63	5.47	5.31	6.91	6.83		
8	4.46	4.41	4.38	5.28	5.09	6.86	6.75		
9	4.24	4.22	4.19	5.12	4.93	6.83	6.72		
10	4.05	4.03	4.03	4.98	4.79	6.78	6.69		
11	3.92	3.92	3.89	4.87	4.65	6.78	6.67		
12	3.81	3.78	3.78	4.76	4.57	6.78	6.67		
13	3.70	3.67	3.65	4.68	4.46	6.75	6.67		
14	3.59	3.56	3.56	4.63	4.41	6.75	6.64		
15	3.51	3.48	3.48	4.57	4.33	6.75	6.64		
16	3.43	3.43	3.40	4.52	4.27	6.75	6.64		
17	3.37	3.35	3.35	4.44	4.22	6.72	6.64		
18	3.32	3.29	3.29	4.38	4.16	6.72	6.64		
19	3.27	3.24	3.24	4.35	4.14	6.72	6.61		
20	3.21	3.21	3.18	4.30	4.05	6.72	6.61		

TABLE S9. Fundamental gap $E_g(3)$ [in eV] for the lowest singlet state of n-PP as a function of the chain length, calculated using KS-DFT with various density functionals. For comparison, the experimental data: Expt1 (vertical IP − vertical EA) [7–9] and Expt2 (vertical IP − adiabatic EA) [7, 10, 11], are taken from the literature.

n	LDA	PBE	BLYP	PBE0	B3LYP	ωB97	ωB97X	Expt1	Expt2
1	5.28	5.20	5.14	7.27	6.80	12.00	11.62	10.38 [7, 8]	10.37 [7, 10]
2	3.65	3.62	3.56	5.41	5.01	9.77	9.47	8.68 [7, 9]	8.55 [7, 11]
3	3.02	2.97	2.94	4.63	4.27	8.87	8.57		7.65 [7, 11]
4	2.67	2.64	2.61	4.22	3.89	8.38	8.11		7.14 [7, 11]
5	2.48	2.45	2.42	3.97	3.67	8.11	7.81		
6	2.34	2.34	2.34	3.84	3.51	7.95	7.65		
7	2.23	2.23	2.23	3.76	3.43	7.81	7.54		
8	2.20	2.18	2.15	3.67	3.35	7.73	7.43		
9	2.15	2.15	2.12	3.62	3.29	7.67	7.40		
10	2.10	2.10	2.10	3.56	3.27	7.62	7.35		
11	2.07	2.07	2.07	3.54	3.24	7.59	7.29		
12	2.07	2.07	2.07	3.51	3.21	7.56	7.29		
13	2.04	2.01	2.01	3.48	3.18	7.54	7.27		
14	2.01	2.01	2.01	3.48	3.16	7.54	7.24		
15	1.99	2.01	2.01	3.46	3.16	7.51	7.24		
16	1.99	2.01	1.99	3.46	3.16	7.51	7.21		
17	1.99	1.99	1.99	3.43	3.16	7.48	7.21		
18	1.99	1.99	1.99	3.43	3.13	7.48	7.21		
19	1.99	1.99	1.99	3.43	3.13	7.46	7.21		
20	1.96	1.99	1.99	3.40	3.10	7.46	7.18		

TABLE S10. Optical gap E_{opt} [in eV] for the lowest singlet state of n-PP as a function of the chain length, calculated using TDDFT with various density functionals. For comparison, the experimental data [12, 13] and SAC-CI data [13] are taken from the literature.

n	LDA	PBE	BLYP	PBE0	B3LYP	ωB97	ωB97X	Expt	SAC-CI
1	7.29	7.22	7.15	7.49	7.39	7.58	7.56	6.20 [12]	
2	4.51	4.45	4.40	4.86	4.75	5.26	5.22	5.03 [13]	5.09 [13]
3	3.68	3.64	3.60	4.12	4.01	4.68	4.63	4.46 [13]	4.33 [13]
4	3.21	3.18	3.14	3.72	3.61	4.38	4.32	4.21 [13]	3.90 [13]
5	2.90	2.88	2.85	3.48	3.35	4.21	4.15	4.06 [13]	3.63 [13]
6	2.68	2.67	2.64	3.32	3.19	4.10	4.03	4.01 [13]	
7	2.53	2.52	2.50	3.21	3.08	4.03	3.96		
8	2.42	2.41	2.38	3.13	2.99	3.98	3.91		
9	2.33	2.32	2.31	3.07	2.94	3.94	3.87		
10	2.26	2.26	2.25	3.03	2.89	3.91	3.84		
11	2.21	2.21	2.20	2.99	2.86	3.91	3.83		
12	2.17	2.17	2.16	2.97	2.83	3.88	3.81		
13	2.14	2.14	2.13	2.95	2.81	3.86	3.79		
14	2.11	2.11	2.10	2.93	2.79	3.84	3.78		
15	2.09	2.09	2.08	2.92	2.78	3.84	3.76		
16	2.07	2.07	2.06	2.90	2.77	3.83	3.75		
17	2.05	2.05	2.04	2.90	2.76	3.82	3.74		
18	2.04	2.04	2.03	2.89	2.75	3.81	3.74		
19	2.03	2.03	2.02	2.88	2.74	3.81	3.74		
20	2.01	2.02	2.01	2.88	2.74	3.80	3.73		

TABLE S11. Exciton binding energy $E_b(1)$ [in eV] for the lowest singlet state of n-PP as a function of the chain length, calculated using KS-DFT and TDDFT with various density functionals. For comparison, the experimental data: Expt1 [(vertical IP − vertical EA) − E_{opt}] [7–9, 12, 13] and Expt2 [(vertical IP − adiabatic EA) − E_{opt}] [7, 10–13], are taken from the literature.

n	LDA	PBE	BLYP	PBE0	B3LYP	ωB97	ωB97X	Expt1	Expt2
1	4.16	3.99	4.02	3.85	3.93	3.83	3.87	4.18 [7, 8, 12]	4.17 [7, 10, 12]
2	3.81	3.74	3.76	3.65	3.70	3.71	3.72	3.65 [7, 9, 13]	3.52 [7, 11, 13]
3	3.21	3.15	3.16	3.12	3.15	3.30	3.29		3.19 [7, 11, 13]
4	2.83	2.79	2.80	2.80	2.81	3.11	3.09		2.93 [7, 11, 13]
5	2.57	2.54	2.54	2.57	2.57	3.03	3.00		
6	2.37	2.34	3.35	2.41	2.39	3.00	2.96		
7	2.21	2.18	2.18	2.27	2.25	2.99	2.95		
8	2.07	2.04	2.05	2.15	2.12	3.00	2.95		
9	1.95	1,92	1.93	2.06	2.02	3.01	2.96		
10	1.84	1.82	1.82	1.97	1.92	3.03	2.97		
11	1.75	1.73	1.73	1.89	1.84	3.02	2.97		
12	1.66	1.64	1.64	1.82	1.76	3.04	2.98		
13	1.59	1.57	1.57	1.76	1.70	3.06	3.00		
14	1.52	1.50	1.50	1.70	1.63	3.08	3.01		
15	1.45	1.44	1.44	1.65	1.58	3.08	3.02		
16	1.40	1.38	1.38	1.61	1.53	3.09	3.03		
17	1.34	1.33	1.32	1.56	1.48	3.10	3.04		
18	1.29	1.28	1.28	1.52	1.44	3.10	3.04		
19	1.25	1.23	1.23	1.49	1.40	3.11	3.04		
20	1.21	1.19	1.18	1.45	1.36	3.11	3.05		

TABLE S12. Exciton binding energy $E_b(2)$ [in eV] for the lowest singlet state of n-PP as a function of the chain length, calculated using KS-DFT and TDDFT with various density functionals. For comparison, the experimental data: Expt1 [(vertical IP − vertical EA) − E_{opt}] [7–9, 12, 13] and Expt2 [(vertical IP − adiabatic EA) − E_{opt}] [7, 10–13], are taken from the literature.

n	LDA	PBE	BLYP	PBE0	B3LYP	ωB97	ωB97X	Expt1	Expt2
1	4.00	3.85	3.85	3.80	3.82	3.91	3.89	4.18 [7, 8, 12]	4.17 [7, 10, 12]
2	3.77	3.66	3.69	3.63	3.65	3.75	3.73	3.65 [7, 9, 13]	3.52 [7, 11, 13]
3	3.17	3.10	3.12	3.09	3.12	3.29	3.29		3.19 [7, 11, 13]
4	2.81	2.75	2.76	2.78	2.79	3.07	3.08		2.93 [7, 11, 13]
5	2.54	2.48	2.48	2.54	2.55	2.97	2.93		
6	2.35	2.31	2.31	2.37	2.36	2.92	2.88		
7	2.15	2.13	2.13	2.26	2.23	2.88	2.87		
8	2.05	2.00	2.00	2.15	2.09	2.88	2.84		
9	1.91	1.89	1.88	2.05	1.99	2.89	2.85		
10	1.79	1.77	1.78	1.95	1.90	2.86	2.86		
11	1.71	1.71	1.70	1.88	1.80	2.87	2.83		
12	1.64	1.61	1.62	1.79	1.74	2.89	2.86		
13	1.56	1.54	1.52	1.73	1.65	2.88	2.87		
14	1.48	1.45	1.47	1.70	1.62	2.91	2.86		
15	1.42	1.39	1.41	1.65	1.55	2.91	2.88		
16	1.36	1.36	1.34	1.61	1.51	2.92	2.89		
17	1.32	1.29	1.30	1.54	1.46	2.90	2.90		
18	1.28	1.25	1.26	1.49	1.41	2.91	2.90		
19	1.24	1.21	1.22	1.47	1.39	2.91	2.87		
20	1.20	1.19	1.17	1.42	1.32	2.92	2.88		

TABLE S13. Exciton binding energy $E_b(3)$ [in eV] for the lowest singlet state of n-PP as a function of the chain length, calculated using KS-DFT and TDDFT with various density functionals. For comparison, the experimental data: Expt1 [(vertical IP − vertical EA) − E_{opt}] [7–9, 12, 13] and Expt2 [(vertical IP − adiabatic EA) − E_{opt}] [7, 10–13], are taken from the literature.

n	LDA	PBE	BLYP	PBE0	B3LYP	ωB97	ωB97X	Expt1	Expt2
1	-2.01	-2.02	-2.00	-0.23	-0.58	4.42	4.06	4.18 [7, 8, 12]	4.17 [7, 10, 12]
2	-0.86	-0.83	-0.83	0.56	0.25	4.51	4.25	3.65 [7, 9, 13]	3.52 [7, 11, 13]
3	-0.66	-0.68	-0.66	0.50	0.26	4.19	3.94		3.19 [7, 11, 13]
4	-0.54	-0.54	-0.53	0.50	0.29	4.00	3.79		2.93 [7, 11, 13]
5	-0.42	-0.43	-0.43	0.50	0.32	3.90	3.66		
6	-0.34	-0.33	-0.30	0.52	0.32	3.84	3.61		
7	-0.30	-0.29	-0.27	0.55	0.35	3.78	3.58		
8	-0.21	-0.23	-0.23	0.55	0.35	3.75	3.52		
9	-0.18	-0.17	-0.19	0.55	0.36	3.73	3.53		
10	-0.17	-0.16	-0.15	0.54	0.37	3.71	3.51		
11	-0.14	-0.14	-0.13	0.54	0.38	3.68	3.46		
12	-0.10	-0.10	-0.09	0.54	0.38	3.68	3.48		
13	-0.10	-0.12	-0.11	0.54	0.37	3.67	3.47		
14	-0.09	-0.10	-0.09	0.55	0.36	3.70	3.46		
15	-0.10	-0.08	-0.06	0.54	0.38	3.67	3.47		
16	-0.08	-0.06	-0.07	0.55	0.39	3.68	3.46		
17	-0.06	-0.07	-0.06	0.53	0.40	3.66	3.47		
18	-0.05	-0.05	-0.04	0.54	0.38	3.67	3.47		
19	-0.04	-0.05	-0.03	0.55	0.39	3.65	3.47		
20	-0.05	-0.04	-0.03	0.53	0.37	3.65	3.45		

TABLE S14. Expectation value of the total spin-squared operator $\langle \hat{S}^2 \rangle$ for the lowest triplet state of n-PP as a function of the chain length, calculated using KS-DFT with various density functionals.

n	LDA	PBE	BLYP	PBE0	B3LYP	ωB97	ωB97X
1	2.0131	2.0301	2.0269	2.0724	2.0542	2.1037	2.0900
2	2.0065	2.0169	2.0157	2.0596	2.0415	2.1245	2.1000
3	2.0048	2.0130	2.0122	2.0552	2.0373	2.1407	2.1082
4	2.0037	2.0102	2.0096	2.0518	2.0337	2.1609	2.1231
5	2.0030	2.0083	2.0079	2.0518	2.0327	2.1791	2.1363
6	2.0024	2.0069	2.0066	2.0495	2.0307	2.1753	2.1332
7	2.0021	2.0059	2.0056	2.0494	2.0299	2.1887	2.1428
8	2.0018	2.0051	2.0049	2.0479	2.0287	2.1892	2.1433
9	2.0015	2.0045	2.0043	2.0482	2.0285	2.1901	2.1437
10	2.0014	2.0040	2.0039	2.0471	2.0279	2.1800	2.1362
11	2.0012	2.0036	2.0035	2.0478	2.0279	2.1904	2.1438
12	2.0011	2.0033	2.0032	2.0475	2.0275	2.1799	2.1363
13	2.0010	2.0031	2.0030	2.0476	2.0277	2.1901	2.1439
14	2.0010	2.0029	2.0028	2.0471	2.0275	2.1801	2.1362
15	2.0009	2.0027	2.0027	2.0476	2.0276	2.1901	2.1439
16	2.0008	2.0026	2.0026	2.0476	2.0274	2.1802	2.1364
17	2.0008	2.0025	2.0025	2.0476	2.0276	2.1901	2.1439
18	2.0008	2.0025	2.0024	2.0476	2.0276	2.1802	2.1439
19	2.0007	2.0024	2.0024	2.0476	2.0276	2.1901	2.1439
20	2.0007	2.0024	2.0024	2.0476	2.0276	2.1801	2.1365

TABLE S15. Expectation value of the total spin-squared operator $\langle \hat{S}^2 \rangle$ for the ground state of cationic n-PP as a function of the chain length, calculated using KS-DFT with various density functionals (at the ground-state geometry of neutral n-PP).

n	LDA	PBE	BLYP	PBE0	B3LYP	ωB97	ωB97X
1	0.7530	0.7567	0.7556	0.7661	0.7656	0.7842	0.7782
2	0.7520	0.7551	0.7545	0.7730	0.7652	0.8231	0.8051
3	0.7512	0.7532	0.7529	0.7691	0.7624	0.8242	0.8066
4	0.7508	0.7522	0.7520	0.7661	0.7602	0.8298	0.8106
5	0.7506	0.7516	0.7514	0.7635	0.7585	0.8313	0.8117
6	0.7505	0.7512	0.7511	0.7613	0.7572	0.8313	0.8115
7	0.7504	0.7510	0.7509	0.7595	0.7561	0.8304	0.8104
8	0.7503	0.7508	0.7507	0.7580	0.7552	0.8294	0.8092
9	0.7503	0.7507	0.7506	0.7569	0.7545	0.8285	0.8081
10	0.7502	0.7506	0.7505	0.7560	0.7539	0.8279	0.8073
11	0.7502	0.7505	0.7505	0.7553	0.7535	0.8274	0.8068
12	0.7502	0.7505	0.7504	0.7547	0.7532	0.8272	0.8064
13	0.7502	0.7504	0.7504	0.7543	0.7529	0.8271	0.8062
14	0.7502	0.7504	0.7503	0.7539	0.7526	0.8270	0.8060
15	0.7501	0.7503	0.7503	0.7536	0.7524	0.8269	0.8060
16	0.7501	0.7503	0.7503	0.7533	0.7523	0.8269	0.8059
17	0.7501	0.7503	0.7503	0.7531	0.7521	0.8269	0.8059
18	0.7501	0.7503	0.7503	0.7529	0.7520	0.8269	0.8059
19	0.7501	0.7503	0.7502	0.7527	0.7519	0.8269	0.8059
20	0.7501	0.7502	0.7502	0.7526	0.7518	0.8270	0.8059

TABLE S16. Expectation value of the total spin-squared operator $\langle \hat{S}^2 \rangle$ for the ground state of anionic n-PP as a function of the chain length, calculated using KS-DFT with various density functionals (at the ground-state geometry of neutral n-PP).

n	LDA	PBE	BLYP	PBE0	B3LYP	ωB97	ωB97X
1	0.7526	0.7556	0.7556	0.7595	0.7577	0.7709	0.7681
2	0.7515	0.7536	0.7535	0.7660	0.7612	0.7984	0.7882
3	0.7510	0.7527	0.7525	0.7652	0.7602	0.8073	0.7955
4	0.7507	0.7520	0.7518	0.7638	0.7591	0.8145	0.8010
5	0.7506	0.7515	0.7514	0.7622	0.7579	0.8174	0.8032
6	0.7504	0.7512	0.7511	0.7606	0.7568	0.8180	0.8035
7	0.7504	0.7510	0.7509	0.7591	0.7559	0.8174	0.8028
8	0.7503	0.7508	0.7507	0.7579	0.7551	0.8164	0.8017
9	0.7503	0.7507	0.7506	0.7568	0.7544	0.8154	0.8006
10	0.7502	0.7506	0.7506	0.7560	0.7539	0.8146	0.7997
11	0.7502	0.7505	0.7505	0.7553	0.7535	0.8140	0.7990
12	0.7502	0.7505	0.7504	0.7547	0.7531	0.8135	0.7984
13	0.7502	0.7504	0.7504	0.7543	0.7529	0.8133	0.7980
14	0.7502	0.7504	0.7504	0.7539	0.7526	0.8131	0.7978
15	0.7501	0.7504	0.7503	0.7536	0.7524	0.8129	0.7976
16	0.7501	0.7503	0.7503	0.7533	0.7523	0.8128	0.7975
17	0.7501	0.7503	0.7503	0.7531	0.7521	0.8128	0.7974
18	0.7501	0.7503	0.7503	0.7529	0.7520	0.8127	0.7973
19	0.7501	0.7503	0.7503	0.7527	0.7519	0.8127	0.7973
20	0.7501	0.7503	0.7502	0.7526	0.7518	0.8127	0.7973

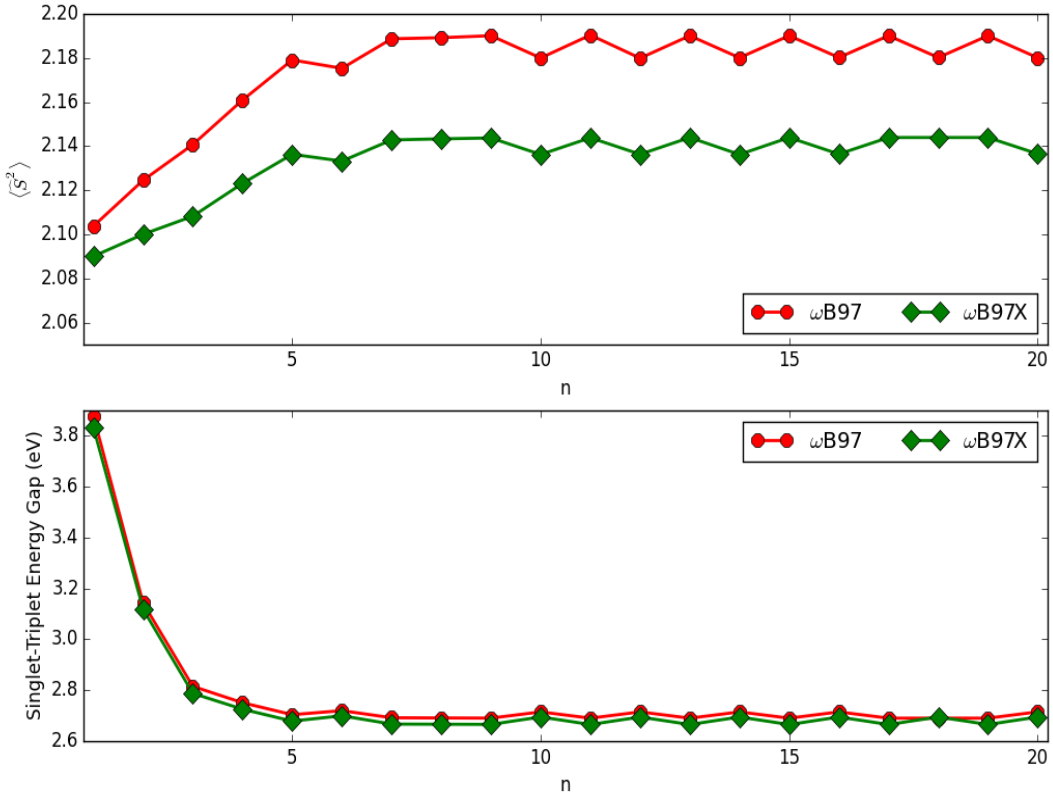

FIG. S1. Comparison of the singlet-triplet energy gap and expectation value of the total spin-squared operator $\langle \hat{S}^2 \rangle$ for the lowest triplet state of n-PP as a function of the chain length, calculated using KS-DFT with the ωB97 and ωB97X functionals.

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