Supporting information:
Semiconductor-to-Metal Transition in Carbon-Atom Wires Driven by sp^2 Conjugated Endgroups

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***Table S1**: Numerical values of the DFT computed values of BLA in A (defined as the difference between the average values of sp-hybridized CC bond lengths of alternated longer and shorter bonds in CAWs)*

n	BPh[n] neutral	BPh[n] Cation	BPh[n] anion	Ph[n]	H[n]	Naph[n]	Cor[n]	tBuPh(n)	Mes(n)	O=Ph(n)	O=Cor(n)
2	0.1413	0.1019	0.1047	0.1427	0.1597	0.1404	0.1401	0.0408	0.0341	0.0556	0.0990
3	0.1315	0.0933	0.0939	0.1326	0.1459	0.1307	0.1304	0.0361	0.0288	0.0483	0.0924
4	0.1250	0.0880	0.0875	0.1259	0.1370	0.1243	0.1240	0.0325	0.0257	0.0437	0.0893
5	0.1204	0.0845	0.0837	0.1213	0.1311	0.1198	0.1195	//	//	0.0412	0.0880
6	0.1170	0.0822	0.0814	0.1178	0.1267	0.1165	0.1162	//	//	0.0388	0.0882

***Table S2**: Numerical values of the DFT computed values of HOMO-LUMO gap in eV*

n	BPh[n]	Ph[n]	H[n]	Naph[n]	Cor[n]	tBuPh(n)	Mes(n)	O=Ph(n)	O=Cor(n)
2	3.95	4.31	6.88	3.74	3.40	2.76	3.03	2.16	0.83
3	3.71	3.94	5.56	3.55	3.29	2.35	2.61	1.91	0.71
4	3.50	3.62	4.76	3.37	3.16	2.09	2.30	1.71	0.61

5	3.31	3.36	4.22	3.21	3.03	//	//	1.54	0.53
6	3.16	3.13	3.82	3.06	2.91	//	//	1.41	0.45

***Table S3**: Numerical values of the DFT computed values of ECC wavenumber in cm^{-1}*

n	BPh[n] neutral	BPh[n] cation	BPh[n] anion	Ph[n]	H[n]	Naph[n]	Cor[n]	tBuPh (n)	Mes(n)	O=Ph(n)	O=Cor(n)
2	2330	2231	2208	2337	//	2323	2321	2167	2175	2163	2170
3	2289	2179	2163	2296	2333	2284	2282	2030	2033	2033	2059
4	2239	2102	2113	2247	2294	2234	2232	1993	2006	1976	1995
5	2195	2038	2069	2202	2243	2191	2189	//	//	1882	1921
6	2154	1981	2029	2160	2204	2150	2148	//	//	1812	1871

Charge Transfer effects

Eion = ionization potential (IP) – Electron affinity (EA)

Eion is the work required for the formation of charged species in the two possible case of charge-transfer of one electron from the Ag to the polyynes (Ag+/polyyne-) or from the polyynes to the Ag (Ag-/polyyne+)
The lower values of Eion so determined is relative to the most probable process and reveals again that charge transfer occurs predominantly from the Ag nanoparticle to the polyynes, as already mentioned in the text. The values of IP and EA of polyynes have been calculated respectively as the energy difference between the +1 and the neutral polyynes (AIP – Adiabatic Ionization Potential) and as the energy difference between the -1 and the neutral polyynes (AEA – Adiabatic electron Affinity) while the experimental values of 4.6 eV (IP) and -1.30 eV (EA) have been used for the Ag [JPCC].

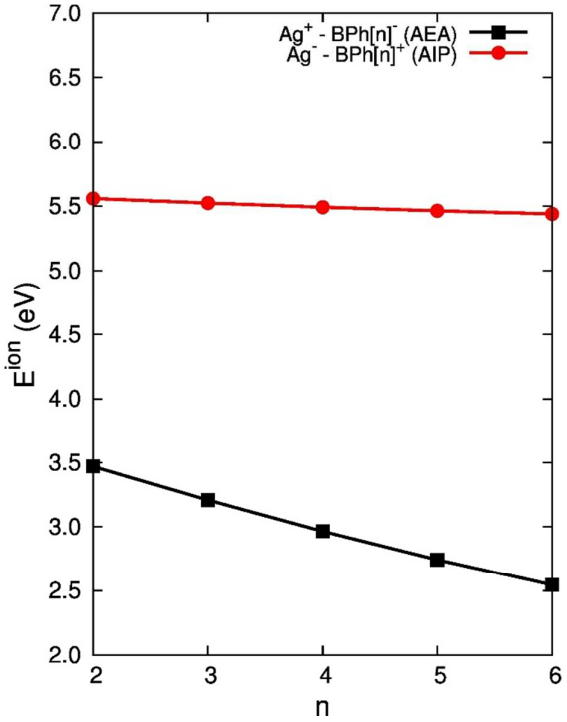

***Figure S1**: Plot of the Eion values computed for BPh[n] CAWs*

***Table S4**: DFT computed values of AIP and AEA in eV computed for BPh[n] CAWs*

n	AIP (eV)	AEA (eV)
2	6.86	-1.13
3	6.82	-1.39
4	6.79	-1.64
5	6.76	-1.86
6	6.73	-2.06

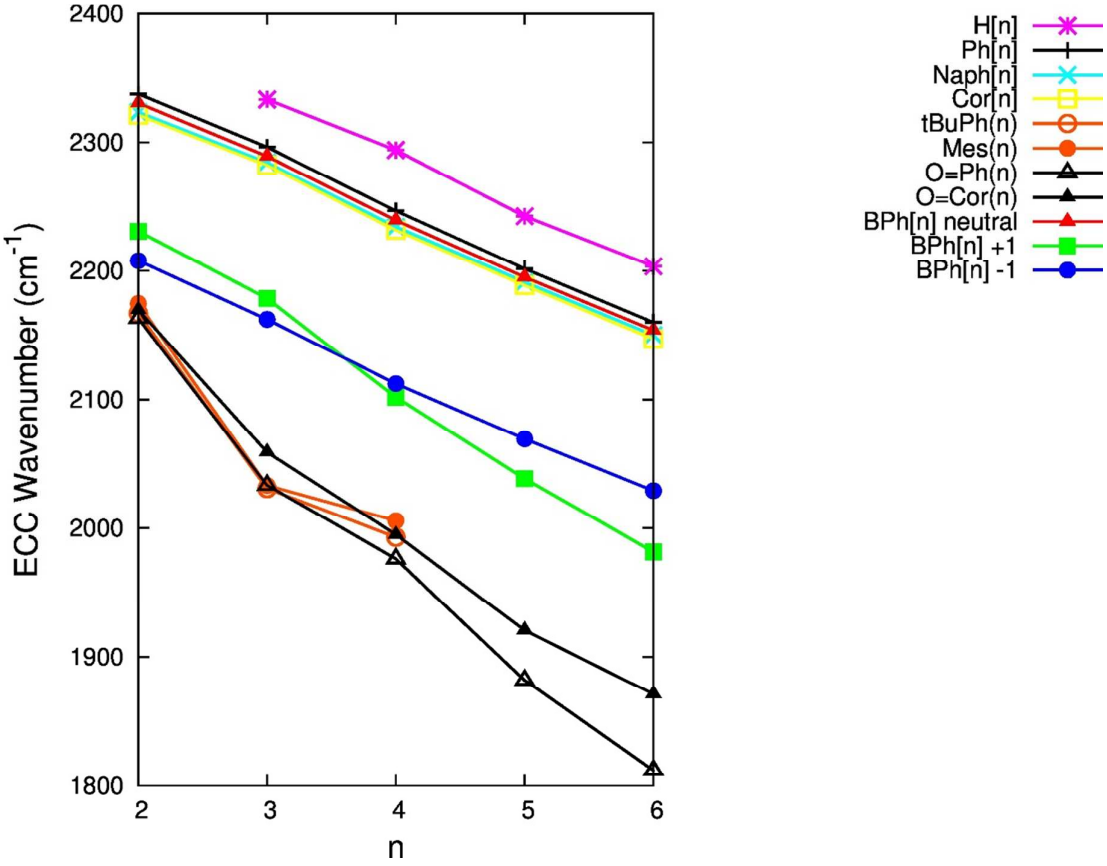

***Figure S2**: Plot of the DFT computed values of ECC wavenumber (in cm^{-1}) of the CAWs reported in Figure 1 of the paper.*

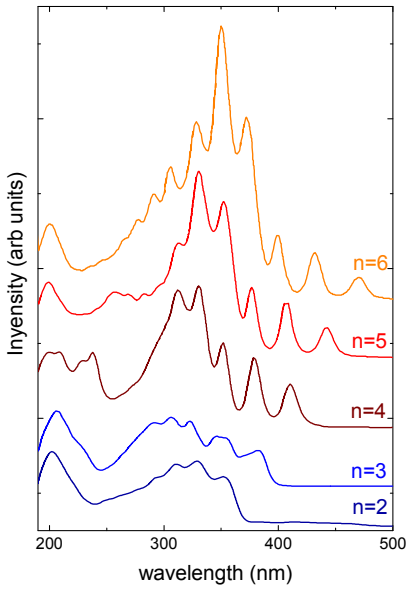

***Figure S3**: UV-vis absorption spectra of BPh[n] as a function of wire length*

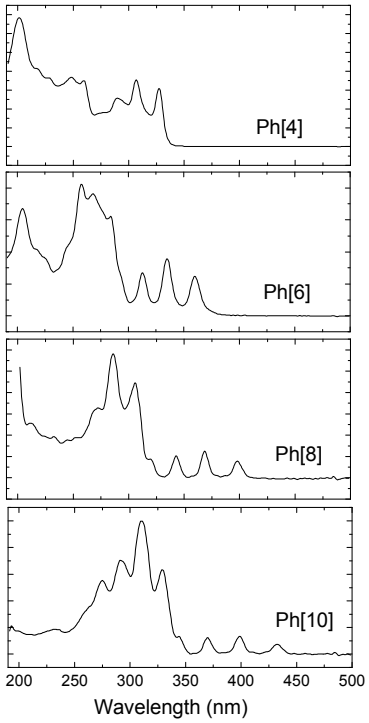

***Figure S4**: UV-vis absorption spectra of Ph[n] as a function of wire length. Adapted from Ref. 55*