Charge transfer and vibrational structure of sp-hybridized carbon atomic wires probed by surface enhanced Raman spectroscopy

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SUPPORTING INFORMATION

Figure S1. Simulated Raman spectra of neutral diphenyl-polyynes of increasing chain lengths (from PhPy4 to PhPy12) from PBE1PBE/cc-pVTZ calculations (scaled frequency values, see text for details). The DFT computed intensities have been normalized. The effect of different relative orientations of the two phenyl planes is also considered.

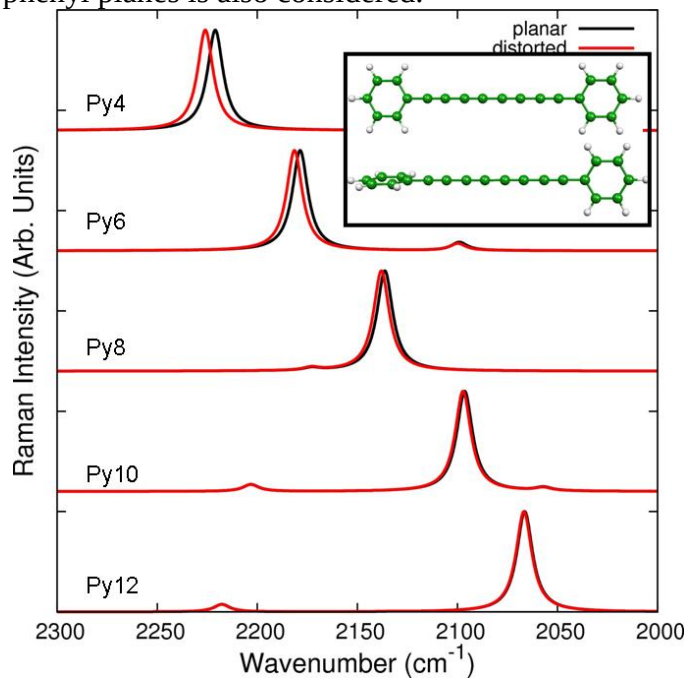

Figure S2 DFT computed (PBE1PBE/cc-pVTZ) values of (a) unscaled ECC frequency, (b) Raman scattering activity of diphenyl polyynes as a function of chain length (N is equal to the number of sp C atoms in the chains) for different charged states. Values for hydrogen-capped polyynes are reported for comparison.

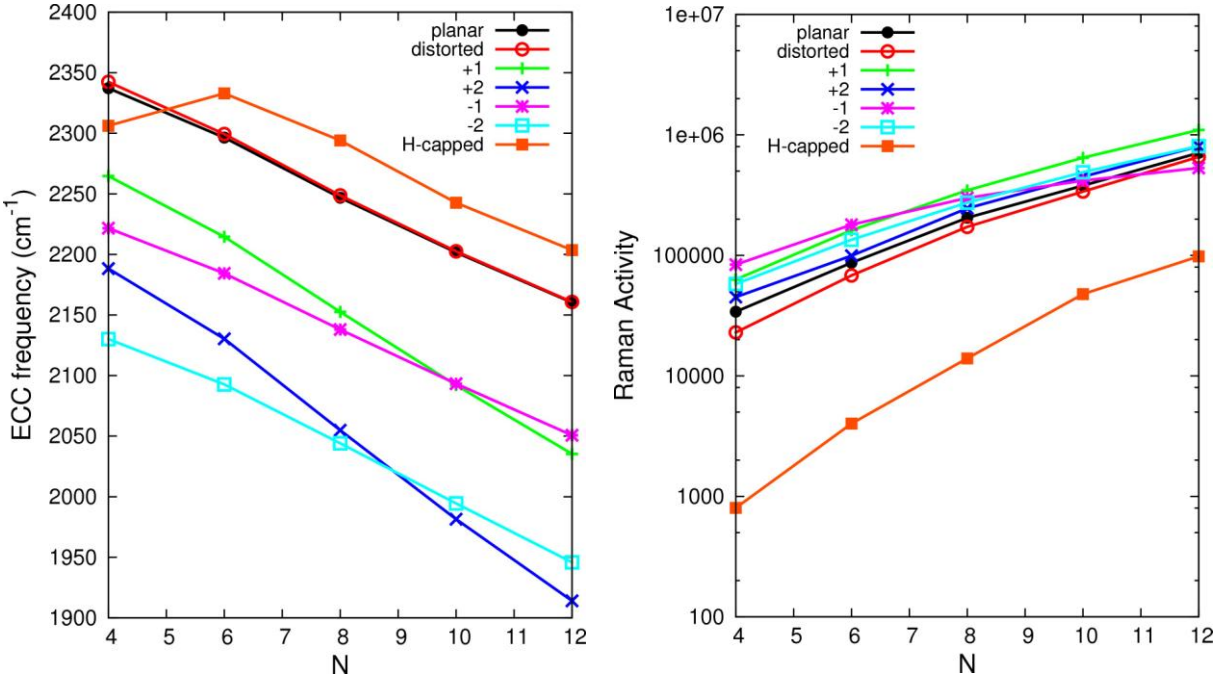

Table S1. Computed PBE1PBE/cc-pVTZ values of average bond length alternation (A), ECC wavenumbers (cm^{-1}) (unscaled values), Raman scattering activity (A^4/amu) for diphenyl polyynes of different chain lengths and charge states.

BLA (A)						
	neutral/planar	neutral/distorted	Charged +1	charged -1	charged +2	charged -2
Ph-C4-Ph	0.14270	0.14380	0.092683	0.096777	0.048611	0.056287
Ph-C6-Ph	0.13260	0.13300	0.086254	0.088462	0.044200	0.050100
Ph-C8-Ph	0.12590	0.12620	0.082500	0.084100	0.041800	0.047200
Ph-C10-Ph	0.12130	0.12140	0.080200	0.081800	0.040800	0.045800
Ph-C12-Ph	0.11780	0.11780	0.078700	0.080500	0.040400	0.045200

ECC Mode Wavenumber (cm^{-1})						
	neutral/planar	neutral/distorted	Charged +1	charged -1	charged +2	charged -2
Ph-C4-Ph	2337	2342	2265	2222	2188	2130
Ph-C6-Ph	2296	2299	2215	2184	2130	2093
Ph-C8-Ph	2247	2249	2153	2138	2055	2044
Ph-C10-Ph	2202	2203	2092	2093	1981	1994
Ph-C12-Ph	2160	2161	2035	2051	1914	1946

ECC Mode Raman Activity (A^4/amu)						
	neutral/planar	neutral/distorted	Charged +1	charged -1	charged +2	charged -2
Ph-C4-Ph	34090	22977	63018	83754	45031	57948
Ph-C6-Ph	86910	68188	161875	179567	99486	134859
Ph-C8-Ph	205083	172480	346368	299998	245996	274251
Ph-C10-Ph	379236	339120	647010	417681	450182	490239
Ph-C12-Ph	709946	656285	1097793	530761	804856	807283

Table S2. Computed PBE1PBE/cc-pVTZ values of vertical ionization potentials (VIP) and electron affinities (VEA) and their adiabatic counterparts (AIP, AEA) for diphenyl polyynes of different chain lengths – see text for details. Values are in eV. These data are plotted below to show more clearly the trends observed for increasing chain lengths (N is equal to the number of sp C atoms in the chains).

	AIP	VIP	AEA	VEA
Ph-C4-Ph	7.366	7.483	-0.695	-0.551
Ph-C6-Ph	7.242	7.359	-1.094	-0.957
Ph-C8-Ph	7.149	7.273	-1.428	-1.298
Ph-C10-Ph	7.072	7.192	-1.712	-1.588
Ph-C12-Ph	7.008	7.128	-1.955	-1.834