Supplementary Material for:

Calculation of Raman parameters of real-size zigzag (n, 0) single-walled carbon nanotubes using finite-size models

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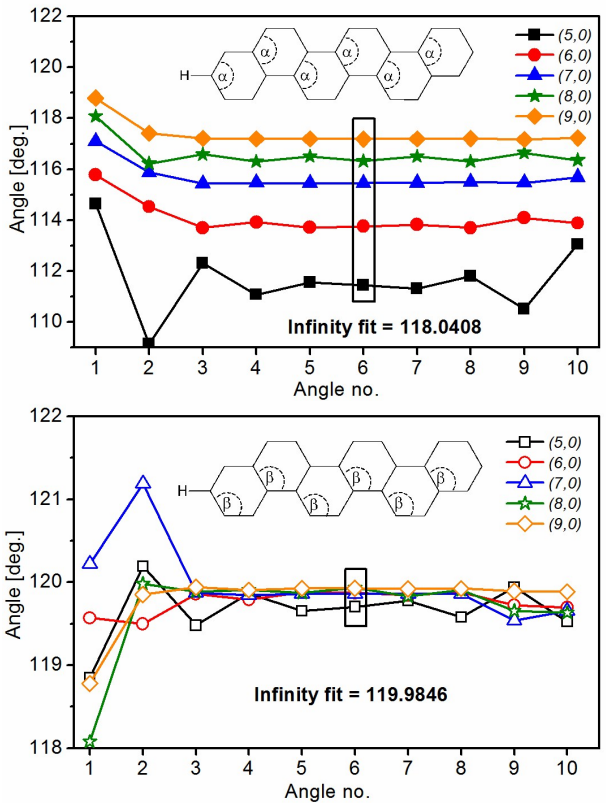


Fig. S1 Bond angle patterns of two types of angles along the SWCNT tube axis: (left) from α_1 to α_{10}, and (right) from β_1 to β_{10} along the tube. Pristine 10-units long zigzag (n, 0) SWCNTs with increasing diameter (n = 5 - 9) were inspected. Lines connecting the points are provided to show trends. Extrapolation of the angles to an infinitely wide SWCNT is indicated by the "Infinity fit" value.

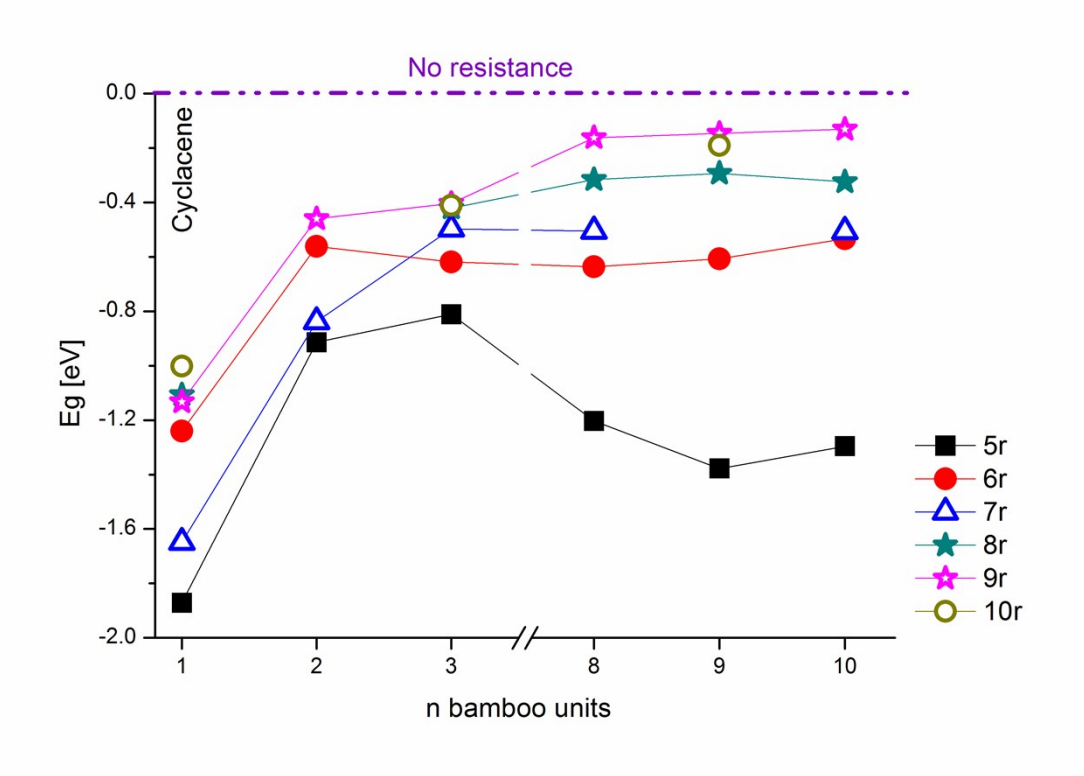


Fig. S2. Sensitivity of E_g to (n, 0) SWCNT size (diameter and length)

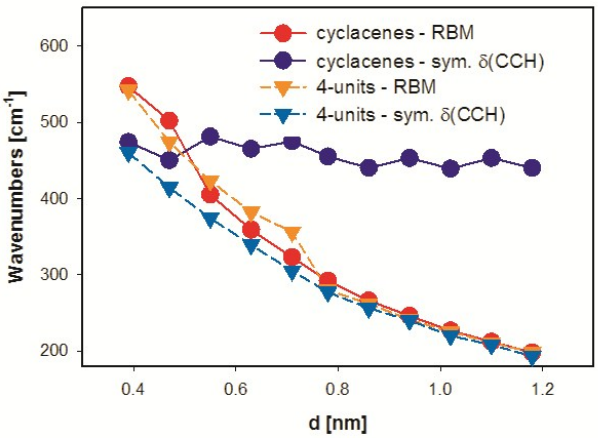


Fig. S3 Calculated RBM and δ(CCH) wagging vibrations (cm^{-1}) and the dependency on increasing diameters *d* (nm) in cyclacenes and SWCN consisting of 4 bamboo units, respectively.

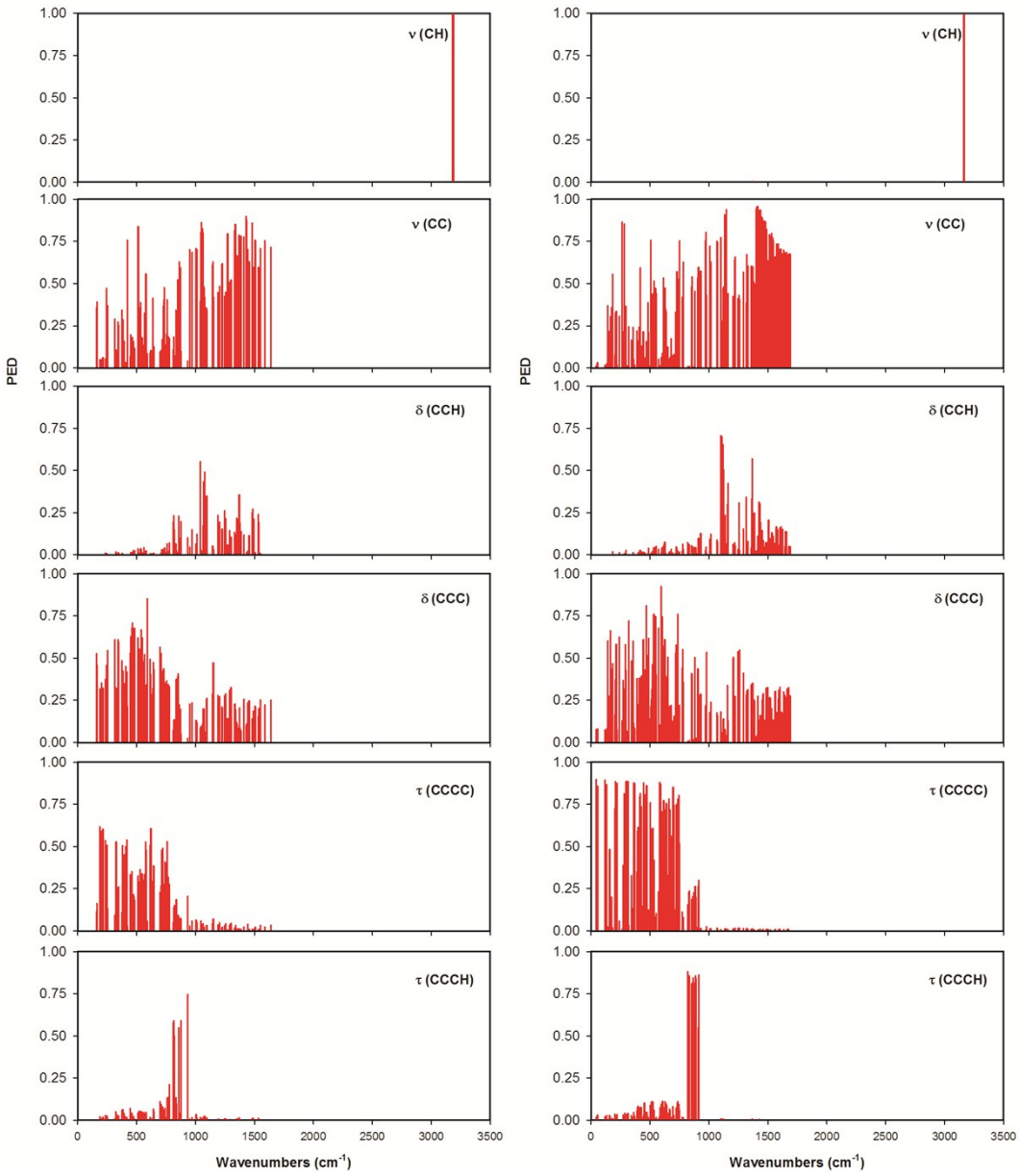


Fig. S4 Calculated B3LYP/6-31G* relative potential energy distribution (PED) of internal coordinates for selected stretching (ν), bending (δ), and torsion (τ) vibrations up to 3500 cm^{-1}. PED was calculated for (5, 0) SWCNT (left) and (12, 0) SWCNT (right). Both tubes consist of 4 "bamboo" units.

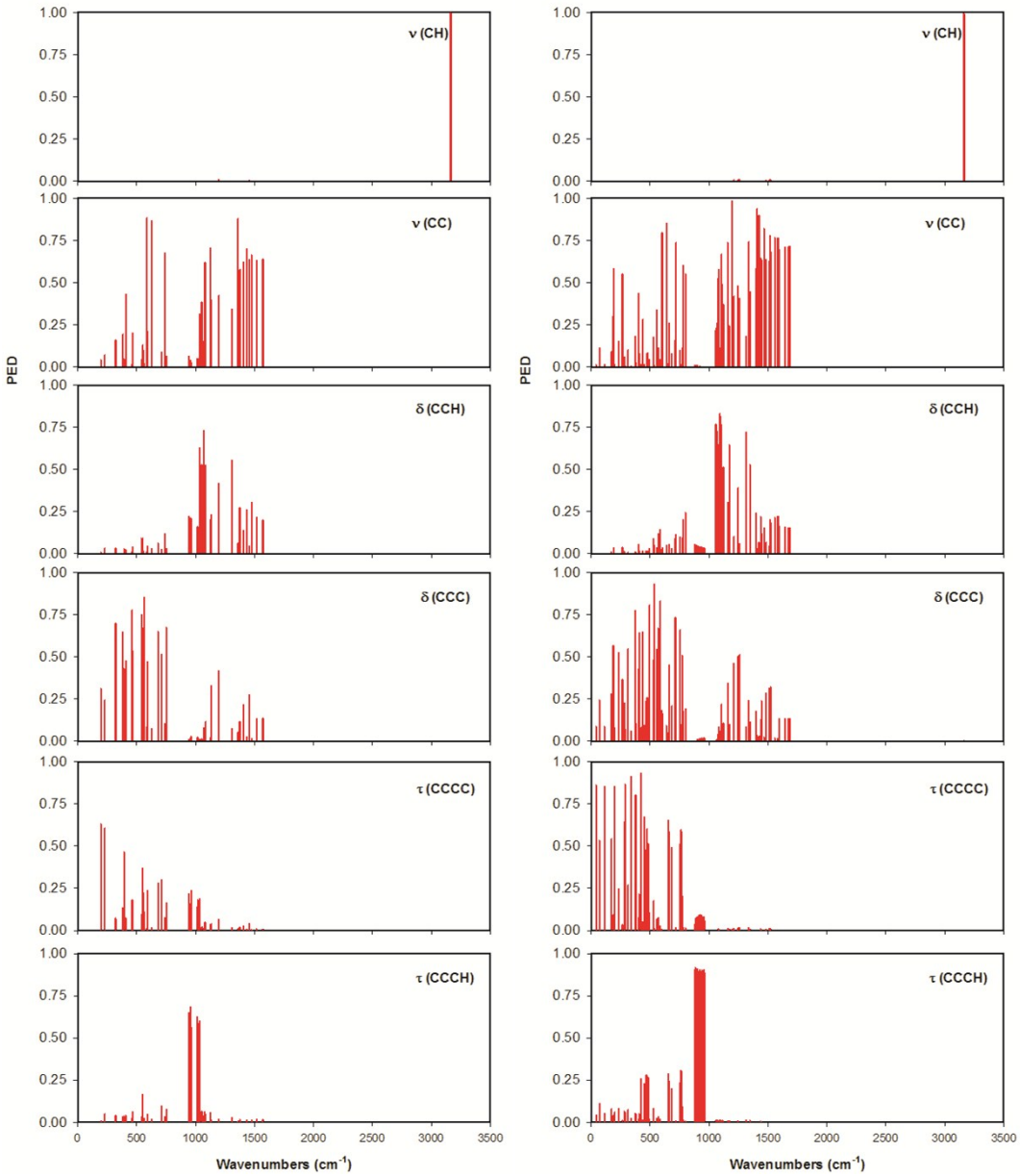


Figure S5. Calculated B3LYP/6-31G* relative potential energy distribution (PED) of internal coordinates for selected stretching (ν), bending (δ), and torsion (τ) vibrations up to 3500 cm^{-1}. PED was calculated for (5, 0) cyclacene (left) and (12, 0) cyclacene (right).

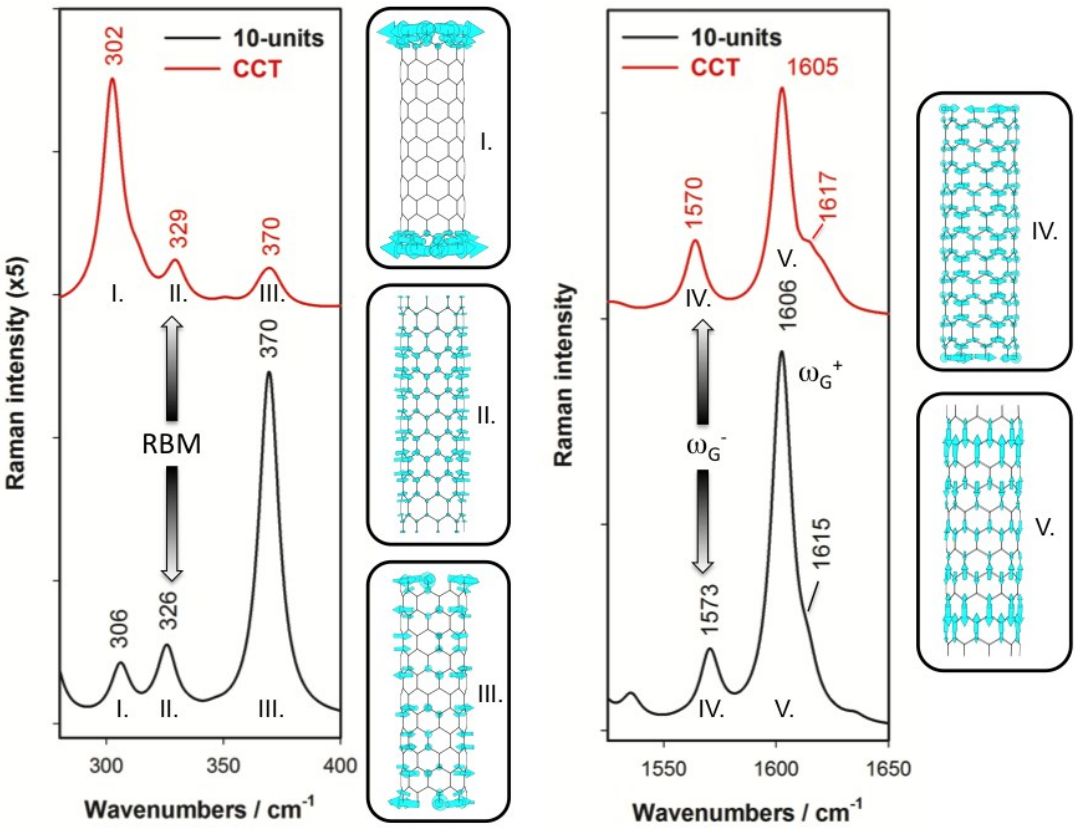
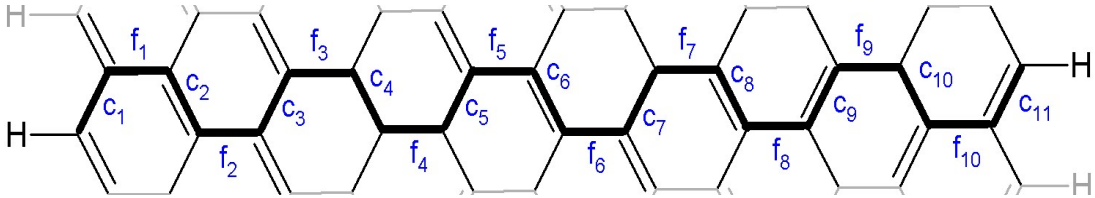


Figure S6. Comparison of selected Raman active bands (e.g. RBMI - II., ω_G^- - IV., and ω_G^+ - V.) obtained by the CCT transfer with characteristics calculated fully DFT for the 10-units long (9, 0) SWCNT. Illustrations of corresponding vibrations are also displayed. Bands II., IV. and V. correspond to RBM, ω_G^- and ω_G^+ vibrational modes discussed thoroughly in the main text.

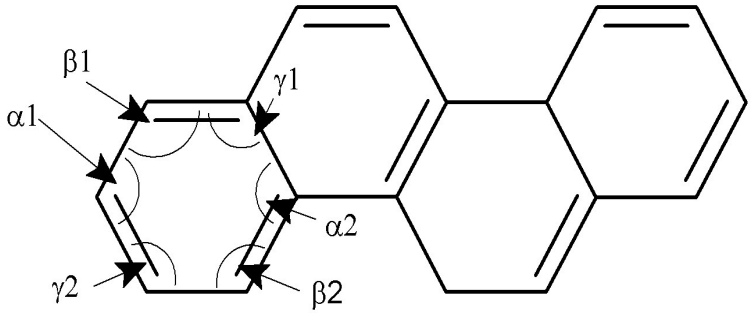
Tab. S1. Calculated two types (*c* and *f*) of CC bond lengths along the axis of (n, 0) SWCNT formed by 10 bamboo units.



model	c1	c2	c3	c4	c5	c6	c7	c8	c9	c10	c11
(5, 0)	1.42957	1.45292	1.45946	1.45928	1.45797	1.45745	1.45797	1.45928	1.45946	1.45292	1.42957
(6, 0)	1.42166	1.43862	1.44119	1.44265	1.44333	1.44353	1.44333	1.44265	1.44119	1.43862	1.42166
(7, 0)	1.42497	1.43504	1.43541	1.43575	1.43575	1.43574	1.43557	1.43524	1.43342	1.42987	1.41979
(8, 0)	1.41771	1.42657	1.43137	1.43272	1.43366	1.43361	1.43367	1.43287	1.43194	1.42894	1.41628
(9, 0)	1.41514	1.42559	1.42781	1.42896	1.42932	1.4294	1.42932	1.42896	1.42781	1.42559	1.41514
(10, 0)	1.41249	1.42429	1.42701	1.42835	1.42878	1.42878	1.42878	1.42701	1.42429	1.41249	

model	f1	f2	f3	f4	f5	f6	f7	f8	f9	f10
(5, 0)	1.42508	1.4016	1.39873	1.40024	1.40166	1.40166	1.40024	1.39873	1.4016	1.42508
(6, 0)	1.43426	1.42176	1.41725	1.41535	1.41454	1.41454	1.41535	1.41725	1.42176	1.43426
(7, 0)	1.43875	1.42304	1.42164	1.42065	1.42057	1.42056	1.42076	1.42192	1.42285	1.44611
(8, 0)	1.44026	1.42496	1.42207	1.41919	1.42021	1.41845	1.42118	1.42028	1.42818	1.4373
(9, 0)	1.44308	1.42931	1.42673	1.42576	1.42537	1.42537	1.42576	1.42673	1.42931	1.44308
(10, 0)	1.44321	1.42812	1.42487	1.42341	1.42347	1.42341	1.42487	1.42812	1.44321	

Tab. S2. Calculated two types (*c* and *f*) of CCC angles along the axis of (n, 0) SWCNT formed by 10 bamboo units.



	(5, 0) (Angles)							(6, 0) (Angles)			
No.	**α1**	**α2**	**β1**	**β2**	**γ1**	**γ2**	**No.**	**α1**	**α2**	**β1**	**β2**
1	114.64	109.13	118.85	120.19	120.19	118.85	1	115.78	114.52	119.57	119.50
2	113.05	110.51	119.53	119.94	119.94	119.53	2	113.88	114.09	119.70	119.73
3	112.31	111.08	119.48	119.87	119.87	119.48	3	113.70	113.92	119.86	119.79
4	111.79	111.31	119.58	119.78	119.78	119.58	4	113.70	113.82	119.88	119.84
5	111.56	111.44	119.65	119.71	119.71	119.65	5	113.72	113.76	119.88	119.87
6	111.44	111.56	119.71	119.65	119.65	119.71	6	113.76	113.72	119.87	119.88
7	111.31	111.79	119.78	119.58	119.58	119.78	7	113.82	113.70	119.84	119.88
8	111.08	112.31	119.87	119.48	119.48	119.87	8	113.92	113.70	119.79	119.86
9	110.51	113.05	119.94	119.53	119.53	119.94	9	114.09	113.88	119.73	119.70
10	109.13	114.64	120.19	118.85	118.85	120.19	10	114.52	115.78	119.50	119.57

	(7, 0) (Angles)					(8, 0) (Angles)			
No.	**α1**	**α2**	**β1**	**β2**	**No.**	**α1**	**α2**	**β1**	**β2**
1	117.10	115.88	120.22	121.19	1	118.08	116.23	118.08	119.98
2	115.56	115.50	119.36	119.50	2	116.45	116.11	120.15	120.03
3	115.43	115.47	119.87	119.85	3	116.59	116.31	119.89	119.91
4	115.49	115.48	119.86	119.85	4	116.53	116.32	119.97	119.97
5	115.45	115.45	119.86	119.86	5	116.50	116.32	119.87	119.93
6	115.46	115.46	119.86	119.86	6	116.52	116.34	119.94	119.95
7	115.46	115.50	119.86	119.86	7	116.51	116.31	119.83	119.91
8	115.47	115.52	119.84	119.89	8	116.61	116.34	119.91	119.96
9	115.47	115.68	119.54	119.66	9	116.64	116.36	119.66	119.63
10	114.60	115.69	121.00	119.57	10	117.27	117.96	119.70	119.55

	(9, 0) (Angles)					(10, 0) (Angles)			
No.	**α1**	**α2**	**β1**	**β2**	**No.**	**α1**	**α2**	**β1**	**β2**
1	118.79	117.41	118.78	11.85	1	119.35	117.90	118.81	119.90
2	117.23	117.17	119.89	119.89	2	117.74	117.67	119.91	119.93
3	117.22	117.19	119.94	119.90	3	117.71	117.69	119.96	119.93
4	117.20	117.19	119.93	119.92	4	117.70	117.69	119.95	119.95
5	117.19	117.19	119.93	119.93	5	117.69	117.69	119.95	119.95
6	117.19	117.19	119.93	119.93	6	117.69	117.69	119.95	119.95
7	117.19	117.20	119.92	119.93	7	117.69	117.70	119.95	119.95
8	117.19	117.22	119.90	119.94	8	117.69	117.71	119.93	119.96
9	117.17	117.23	119.89	119.89	9	117.67	117.74	119.93	119.91
10	117.41	118.79	119.85	118.78	10	117.90	119.35	119.90	118.81

Tab. S3. Cyclacene HOMO, LUMO and E_g parameters (in eV)

Cyclacene Size	HOMO	LUMO	E_g	Lit.[a]
(4, 0)	-4.897	-1.465	-3.433	-3.43
(5, 0)	-4.32	-2.45	-1.87	-1.87
(6, 0)	-3.809	-2.571	-1.238	-1.24
(7, 0)	-4.063	-2.415	-1.648	-1.65
(8, 0)	-3.895	-2.788	-1.107	-1.11
(9, 0)	-3.923	-2.791	-1.133	-1.13
(10, 0)	-3.929	-2.928	-1.001	-1.00
(11, 0)	-3.697	-3.255	-0.442	-0.82
(12, 0)	-3.939	-3.027	-0.912	-0.91
(14, 0)	-3.936	-3.099	-0.837	-0.84

a) BLYP/6-31G* result from ref. [1]

Tab. S4. HOMO, LUMO and Eg (in eV) for selected SWCNTs of different length

CNT length (units)	HOMO	LUMO	E_g
	(5, 0) SWCNT		
1	-4.320	-2.450	-1.871, -1.87[a]
2	-3.674	-2.760	-0.914
3	-3.516	-2.704	-0.811
8	-4.011	-2.807	-1.203
9	-4.335	-2.957	-1.378
10	-4.450	-3.154	-1.296
	(6, 0) SWCNT		
1	-	-	-1.24[a]
2	-3.102	-2.542	-0.561
3	-3.362	-2.743	-0.619
8	-3.856	-3.220	-0.636
9	-3.885	-3.278	-0.607
10	-3.860	-3.327	-0.533
	(7, 0) SWCNT		
1	-4.063	-2.415	-1.649, -1.65[a]
2	-3.760	-2.923	-0.838
3	-3.660	-3.163	-0.497
8	-3.775	-3.270	-0.505
9	0.000	0.000	0.000
10	-3.794	-3.288	-0.506
	(8, 0) SWCNT		
1	-3.895	-2.788	-1.107, -1.11[a]
2	0.000	0.000	0.000
3	-3.702	-3.281	-0.421
8	-3.766	-3.449	-0.316
9	-3.730	-3.437	-0.293
10	-3.769	-3.445	-0.324
	(9, 0) SWCNT		
1	-3.923	-2.791	-1.133, -1.13[a]
2	-3.711	-3.251	-0.460
3	-3.729	-3.325	-0.404
8	-3.718	-3.556	-0.162
9	-3.722	-3.576	-0.146
10	-3.725	-3.594	-0.131
	(10, 0) SWCNT		
1	-3.929	-2.928	-1.001, -1.00[a]
2	0.000	0.000	0.000
3	-3.782	-3.371	-0.411
8	0.000	0.000	0.000
9	-3.732	-3.541	-0.191

a) B3LYP/6-31G* results for cyclacenes from ref. [1]

Table S5. Comparison of RBM values in (n,0) zigzag SWCNTs and cyclacenes modeled calculated using finite models (B3LYP/6-31G*), empirical formulas and periodic calculations.

Type	*d* (nm)	CASTEP	Empirical (Eqn.1)	Cyclacene	4-units	6-units	10-units	Lit.[c]
(5,0)	0.39		584	547	542	541	535	602
(6,0)	0.47	507	488	502	474	468	462	492, 457
(7,0)	0.55	416	420	405	423	417	412	425, 410, 401
(8,0)	0.63	368	370	359	382	367	363	370, 363
(9,0)	0.71	324	330	323	356	330	329[a]	318, 327, 239
(10,0)	0.78	302	298	292	280	302	294[a]	294, 296, 287
(11,0)	0.86	272	272	266	262	280	270[a]	266
(12,0)	0.94	251	251	246	241	263	247[a]	241
(13,0)	1.02	239	232	227	225	226	243[a]	
(14,0)	1.10	219	216	212	211	207	214[a]	208
(15,0)	1.18	205	202	198	194		198[a]	175
RMSD[b]			4	8	16	8	5	

CASTEP: periodic calculation on SWCNTs of infinite size; Empirical: RBM obtained using the equation 1; Cyclacene: RBM calculated at the B3LYP/6-31G(d) level for a cyclacene ring; 4-units, 6-units, 10-units: RBM calculated at the B3LYP/6-31G* level for SWCNT comprising 4, 6 or 10 bamboo units. Data for the 6-units long (15, 0) SWCNT were not accessible due to high computational demands; [a]Values were obtained by the CCT transfer; [b]RMSD obtained without data for (5, 0) and (6, 0) tubes; [c]values taken from Ref. [2-6]

References

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