Electronic Supplementary Information

Carbon nanobuds based on carbon nanotube caps: A first-principles study

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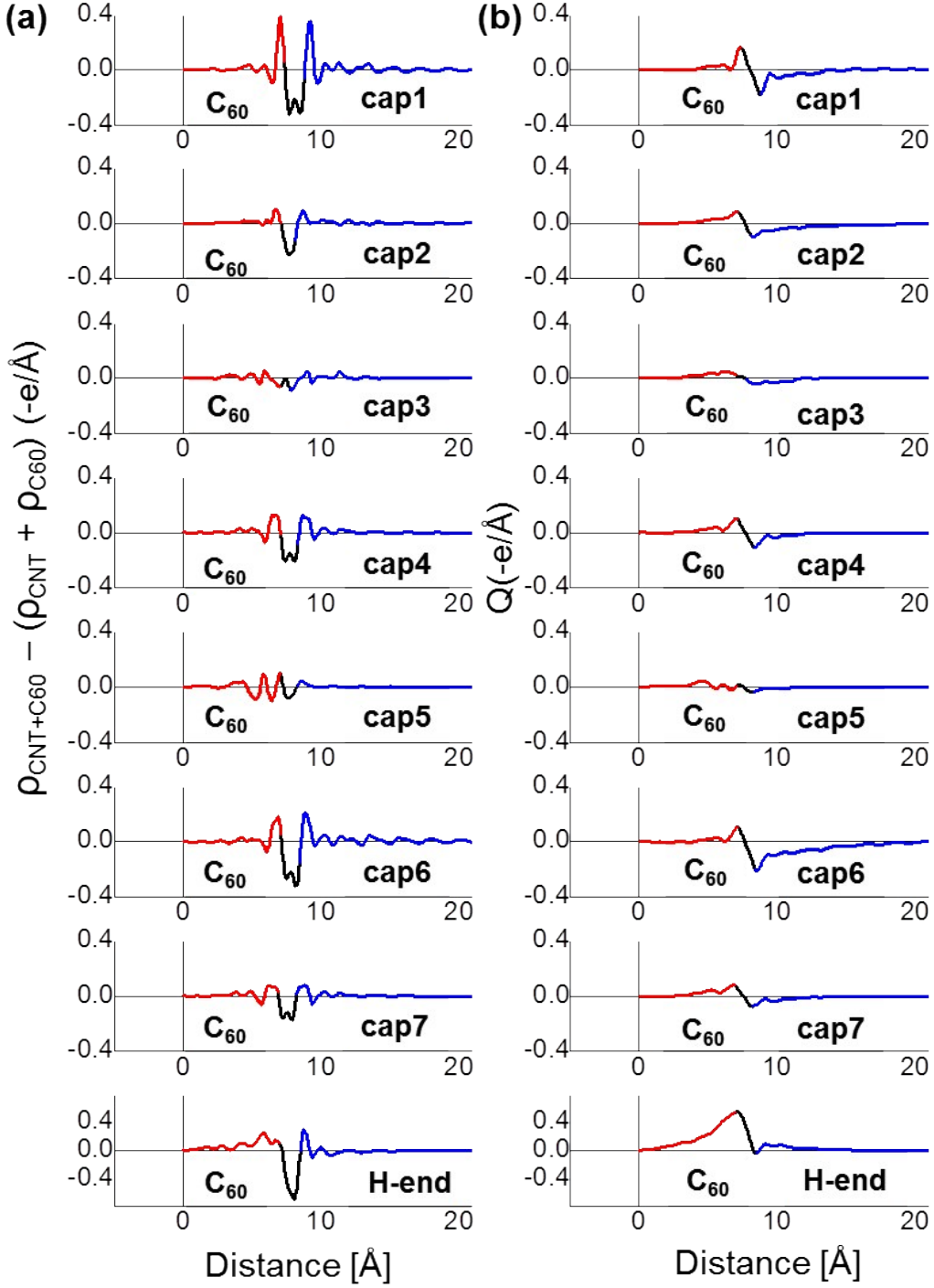† E-mail address: y.h.him@kaist.ac.kr

Figure S1: (a) Plane-averaged charge density differences at the C_{60}|CNT contacts $\Delta\rho = \rho_{C_{60}+CNT} - (\rho_{C_{60}} + \rho_{CNT})$ and (b) integrated plane-averaged charge density differences $Q(z) = \int_0^z \Delta\rho(z')dz'$ for the cycloaddition-bonded (carbon nanobuds) CNBs based on (10,0) CNT **cap** and **H-end** models (see Fig. 1). Red, black, and blue colors represent the C_{60}, bonding, and CNT area. A positive (negative) Q indicates a right-to-left (left-to-right) electron transfer. It is generally found that the C_{60}-CNT interfaces in the **cap**-based CNB models are characterized by small balanced charge redistributions that result in the net charge accumulation in C_{60} and CNT near the bonding region as well as the cycloaddition bonds and

the corresponding charge depletion in the center of cycloaddition bond (See also Fig. 2). Note the much bigger charge redistribution at the at the C_{60}|CNT interfaces in the **H-end** model compared with those in the **cap** models.
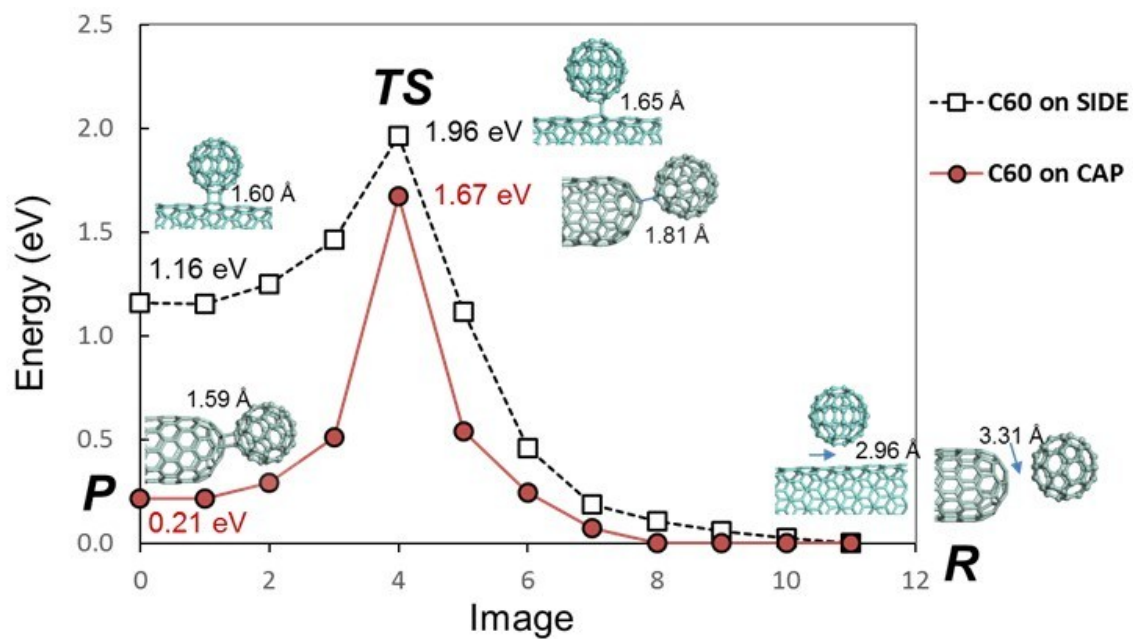
Figure S2: Minimum-energy path for the formation of C_{60}-**cap4** (66) configuration calculated within the spin-unpolarized DFT-D3 scheme. The *R*, *TS*, and *P* symbols denote the reactant, transition states, and product, respectively. The energy of the reactant was set to zero.
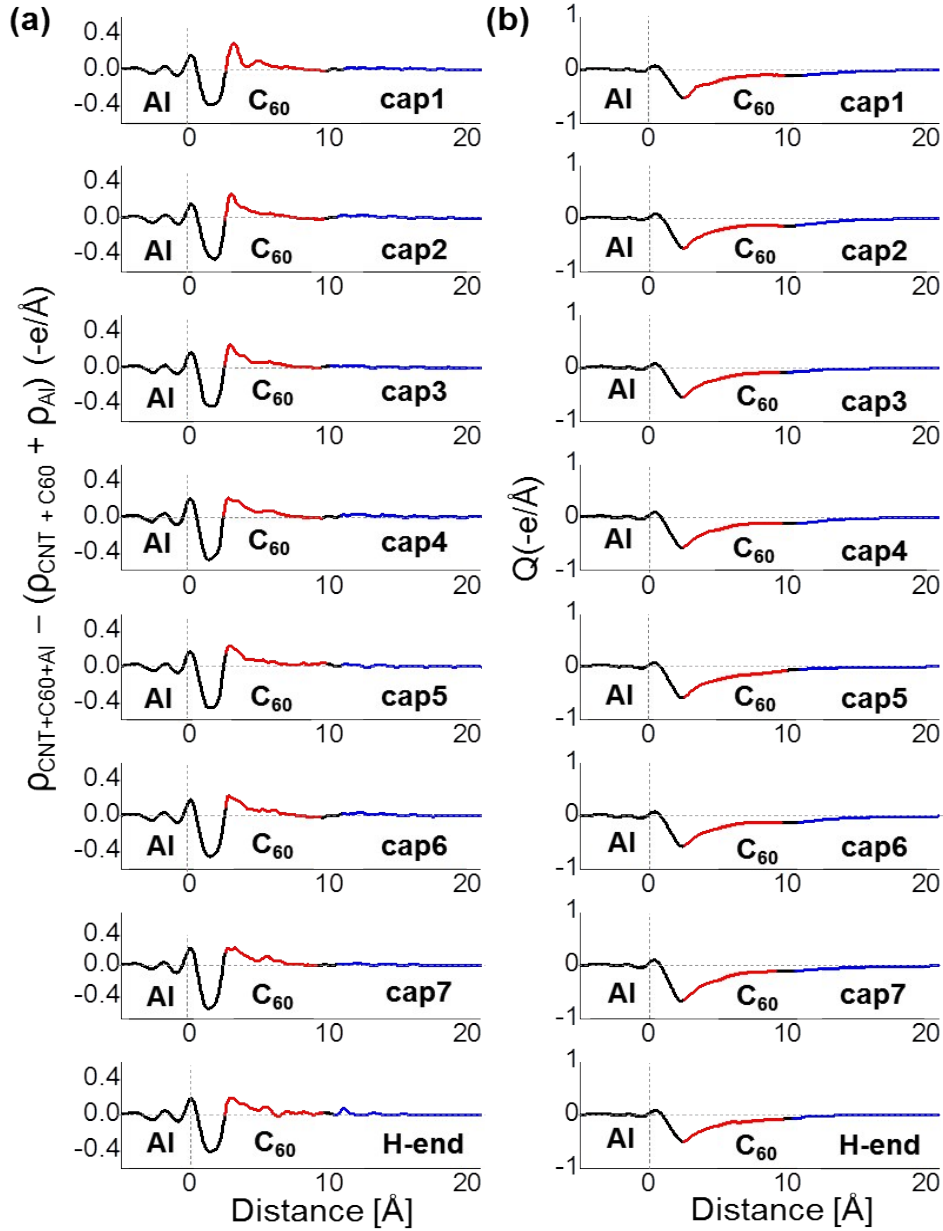
Figure S3: (a) Plane-averaged charge density differences $\Delta\rho = \rho_{Al+C60+CNT} - (\rho_{Al} + \rho_{C60+CNT})$ at the Al|C$_{60}$ contacts and (b) their integration for the C$_{60}$-CNT complexes sandwiched between Al(111) electrodes. The charge redistribution characteristics at the Al|C$_{60}$ contacts are almost uniform for all the CNT models *including the **H-end** model* and similar to those at Al-**cap** contacts reported in H. S. Kim *et al.*, MRS Commun., **2**, 91 (2012). The induced charge redistribution pattern at the Al-C$_{60}$ interface is characterized by a strong "push-back effect" originating from Pauli repulsion and a significant net charge transfer from Al to C$_{60}$ according to the highly electron-attracting nature of C60. Whereas the pushed-back electrons rapidly attenuate along the metal side, a significantly long-ranged net charge transfer is induced along the C60+CNT direction. .
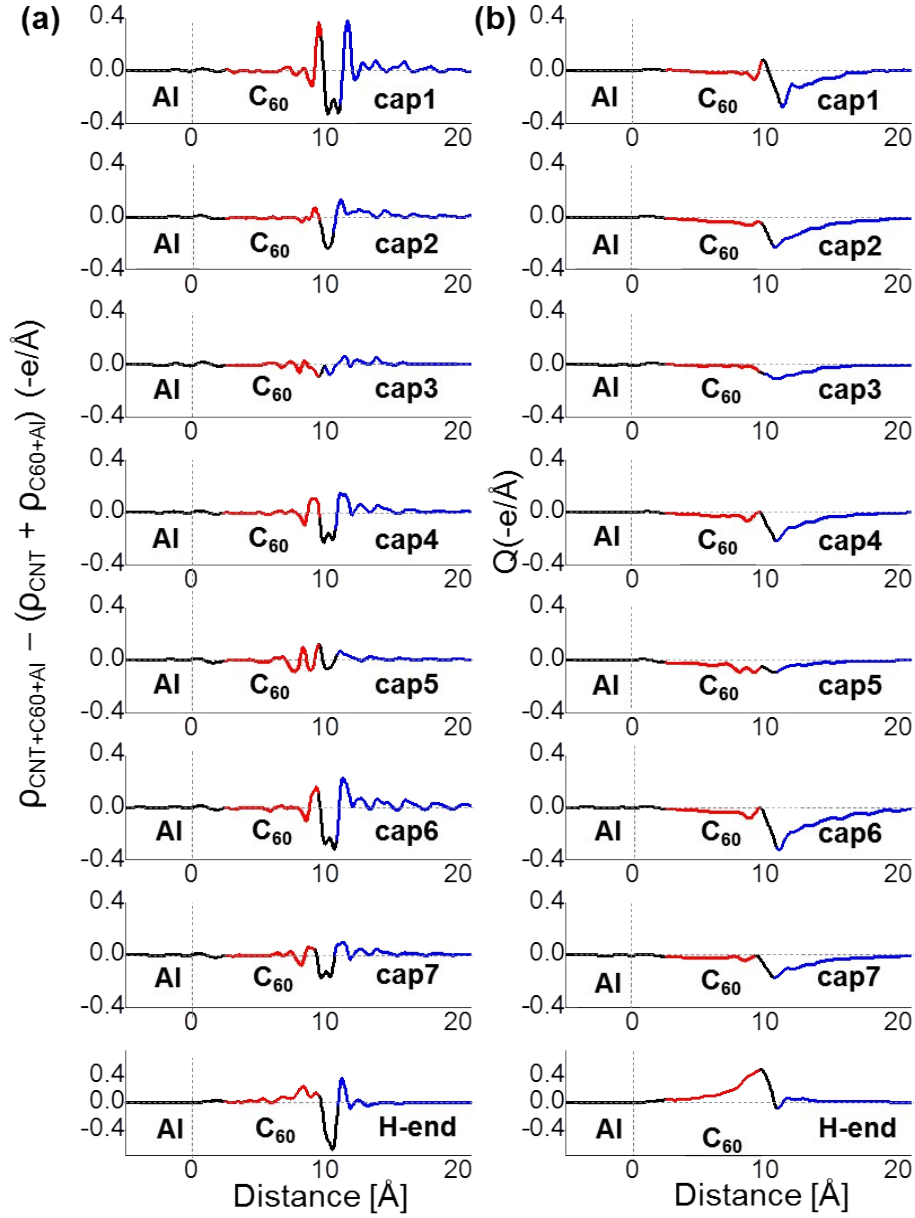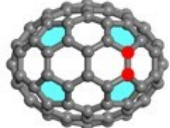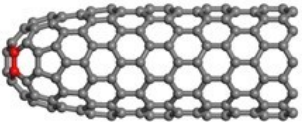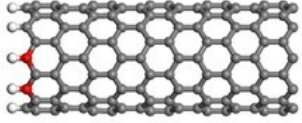
Figure S4: (a) Plane-averaged charge density differences at the C_{60}|CNT contacts $\Delta\rho = \rho_{Al+C60+CNT} - (\rho_{Al+C60} + \rho_{CNT})$ and (b) their integration $Q(z)$ for the C_{60}-CNT complexes *sandwiched between Al electrodes*. For the **cap** models, due to the additional interactions at the Al|C_{60} interfaces, the charge transfer at the C_{60}|CNT interfaces (i) has been reduced on the C_{60} side, while (ii) became larger and longer-ranged along the CNT side. The latter indicates a strong Al-CNT coupling in the **cap** models in spite of the additional C_{60} interfacial layer. In general, however, the qualitative nature of charge transfer at the C_{60}|CNT interfaces is preserved even with the introduction of the metal electrodes.

Table S1. The energetic stability of the C_{60} binding for the seven (10,0) CNT cap models. The energetically most favorable bonding configuration is highlighted in boldface.

Model	Cap bonding geometry	C-C bond length (Å)	Binding energy (eV)
cap1	**66**	**1.587**	**-0.276**
	56	1.596	0.210
cap2	**66**	**1.593**	**-0.200**
	66′	1.595	0.514
	56	1.591	0.435
cap3	**66**	**1.590**	**-0.466**
	66′	1.599	0.194
	66″	1.541	2.843
	56	1.603	0.011
cap4	**66**	**1.592**	**-0.158**
	66′	1.600	-0.033
	66″	1.602	0.761
	56	1.595	0.218
cap5	**66**	**1.592**	**-0.224**
	66′	1.596	0.082
	66″	1.590	0.994
	56	1.606	0.279
cap6	**56**	**1.615**	**-0.476**
	66′	1.616	0.028
cap7	**66**	**1.588**	**-0.425**
	56	1.593	0.332

Table S2. Details of the CNB junction models based on (10,0) CNT **cap3** and **H-end** models employed for the MGF calulations. The red circles indicate the sites for the C_{60} cycloaddition bonding disccused in Fig. 1. Pentagon topological defects are highlighted by cyan color. The total number of Al electrode atoms is 144, making the total number of atoms in the two junction models to be 640 and 564, respectively.

Model	Top view	Side view	Length (Å) (Number of atoms)	
			CNT	C_{60}+CNT+C_{60}
cap3			39.857 (376)	55.070 (496)
H-end			43.264 (420)	57.612 (536)