Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information: Charge transfer dynamics at the boron subphthalocyanine chloride/C_{60} interface: non-adiabatic dynamics study with Libra-X

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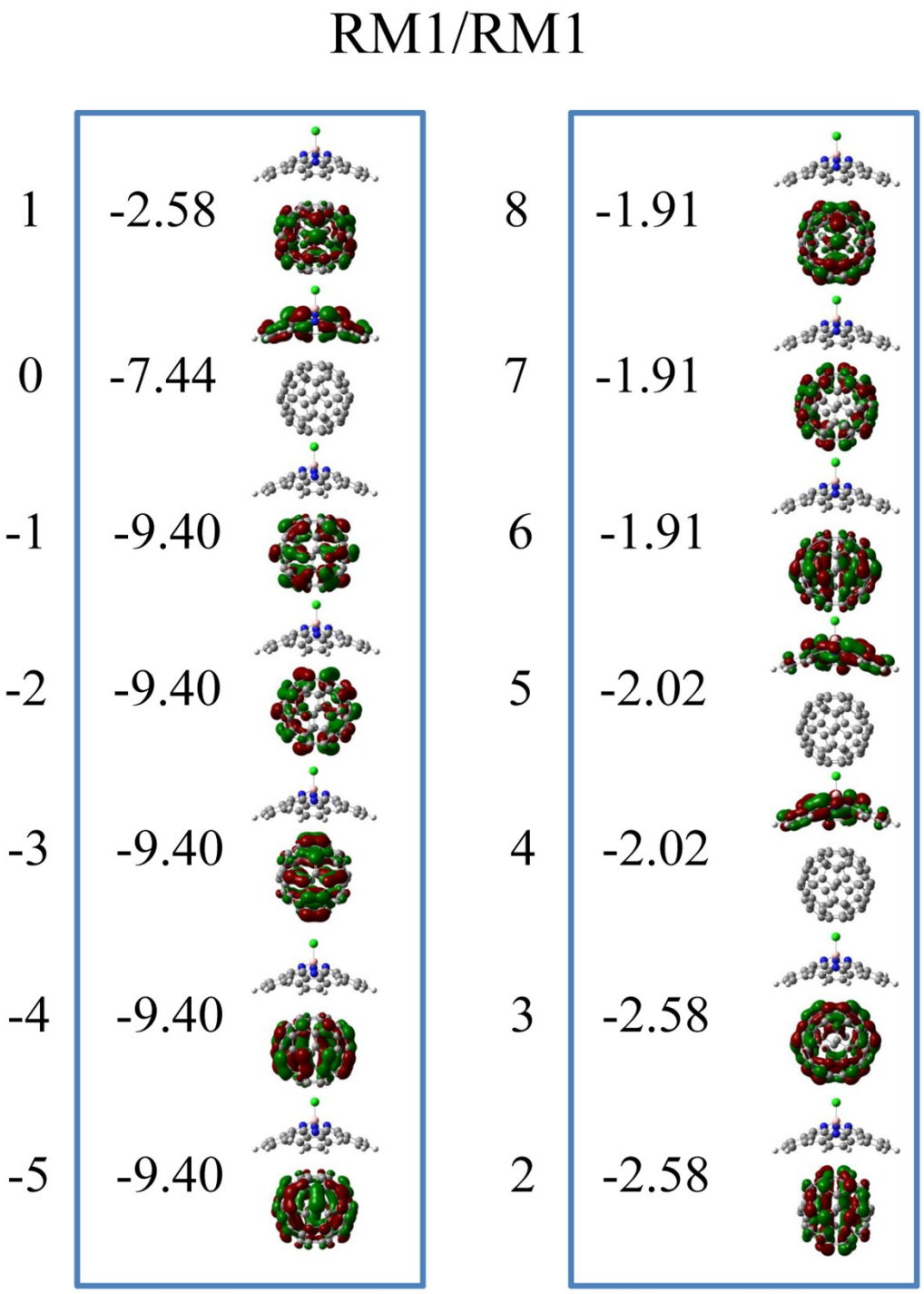

Fig. S1 Molecular orbitals of SubPc/C_{60} computed by RM1/RM1. The numbers outside the blue boxes show indices of each orbital; the index 0 depicts HOMO. The number inside the boxes indicates orbital energy (eV).

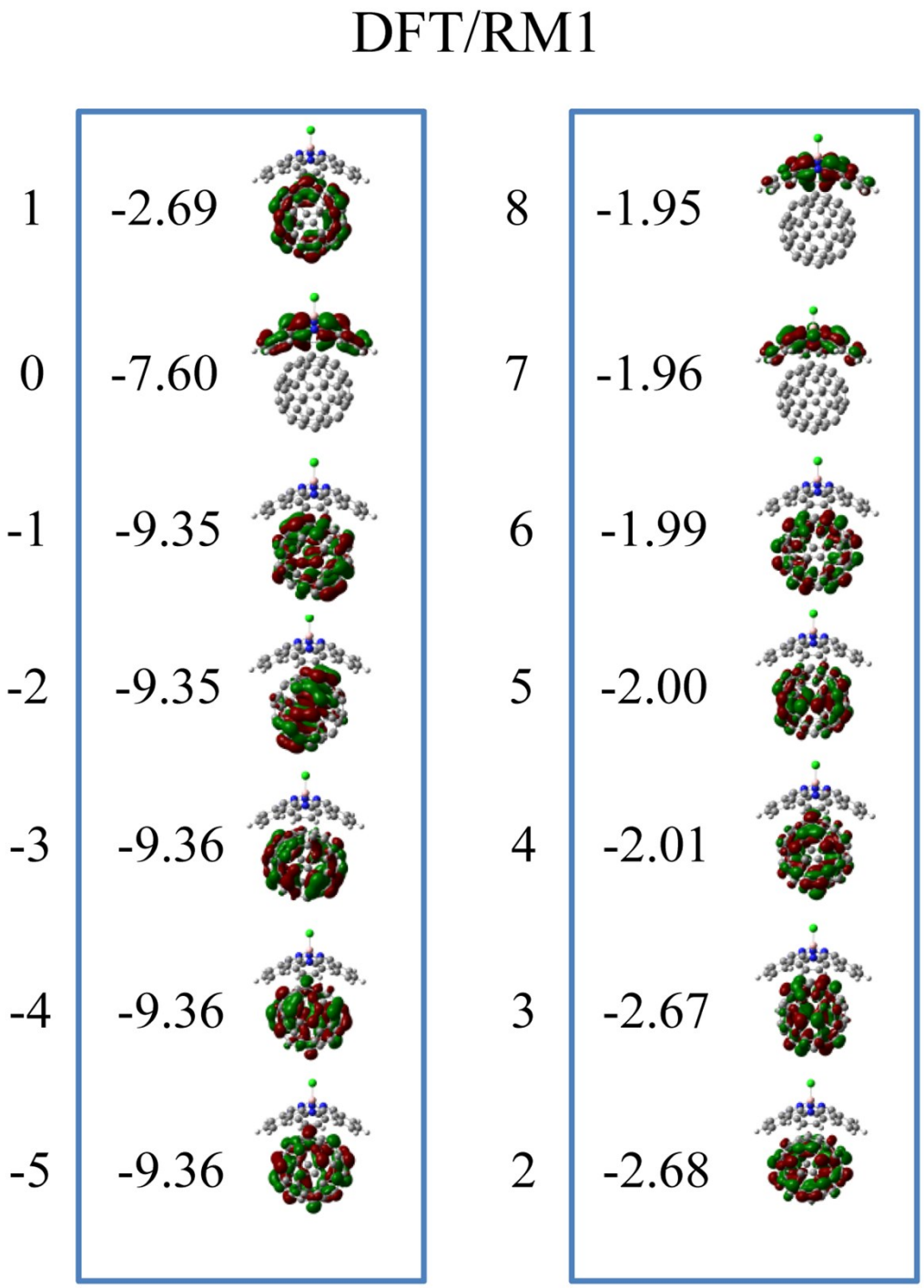

Fig. S2 Molecular orbitals of SubPc/C_{60} computed by DFT/RM1. The numbers outside the blue boxes show indices of each orbital; the index 0 depicts HOMO. The number inside the boxes indicates orbital energy (eV).

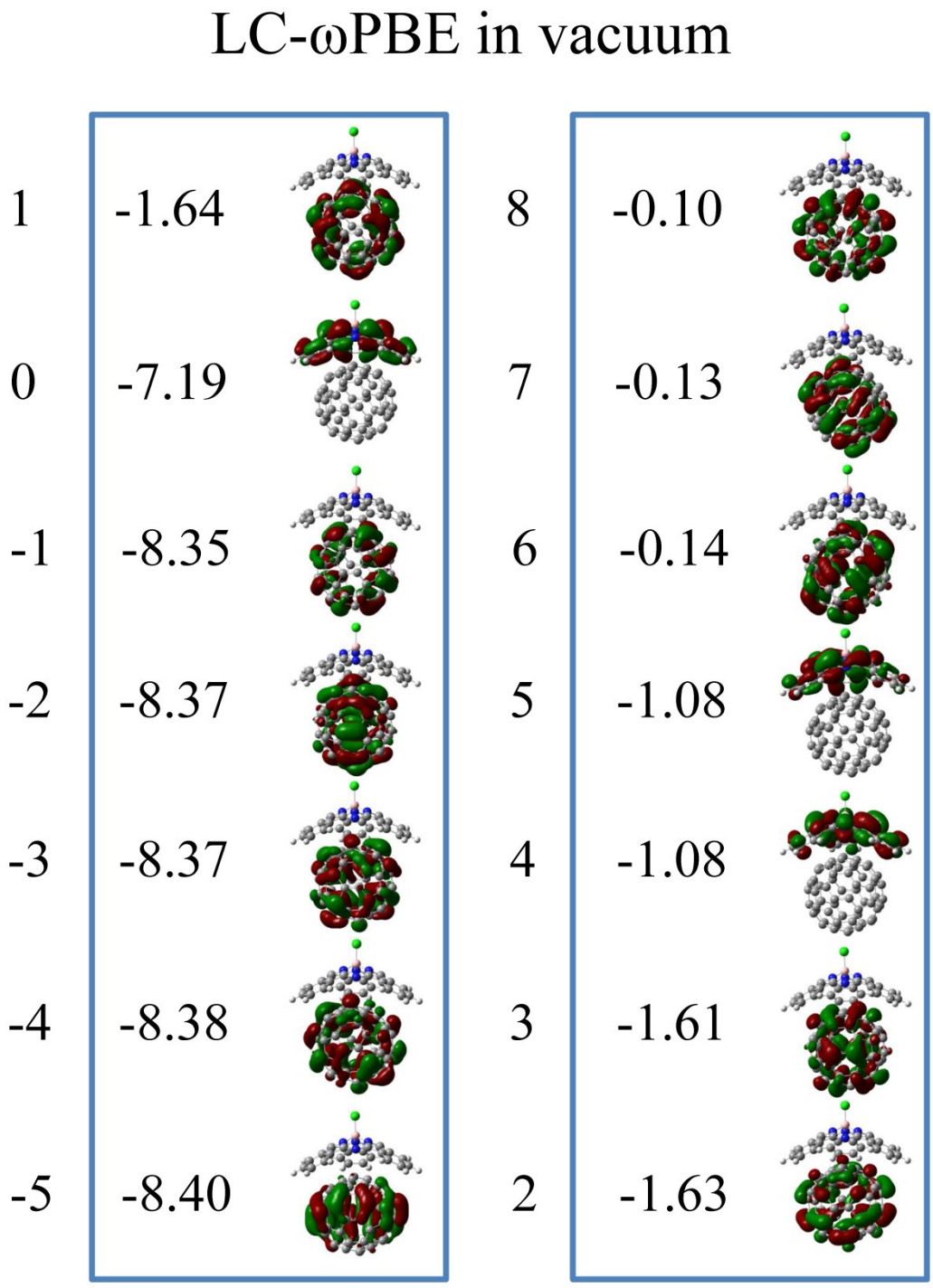

Fig. S3 Molecular orbitals of SubPc/C_{60} computed by LC-ωPBE at the structure optimized by DFT with ωB97XD functional. The numbers outside the blue boxes show indices of each orbital; the index 0 depicts HOMO. The number inside the boxes indicates orbital energy (eV).

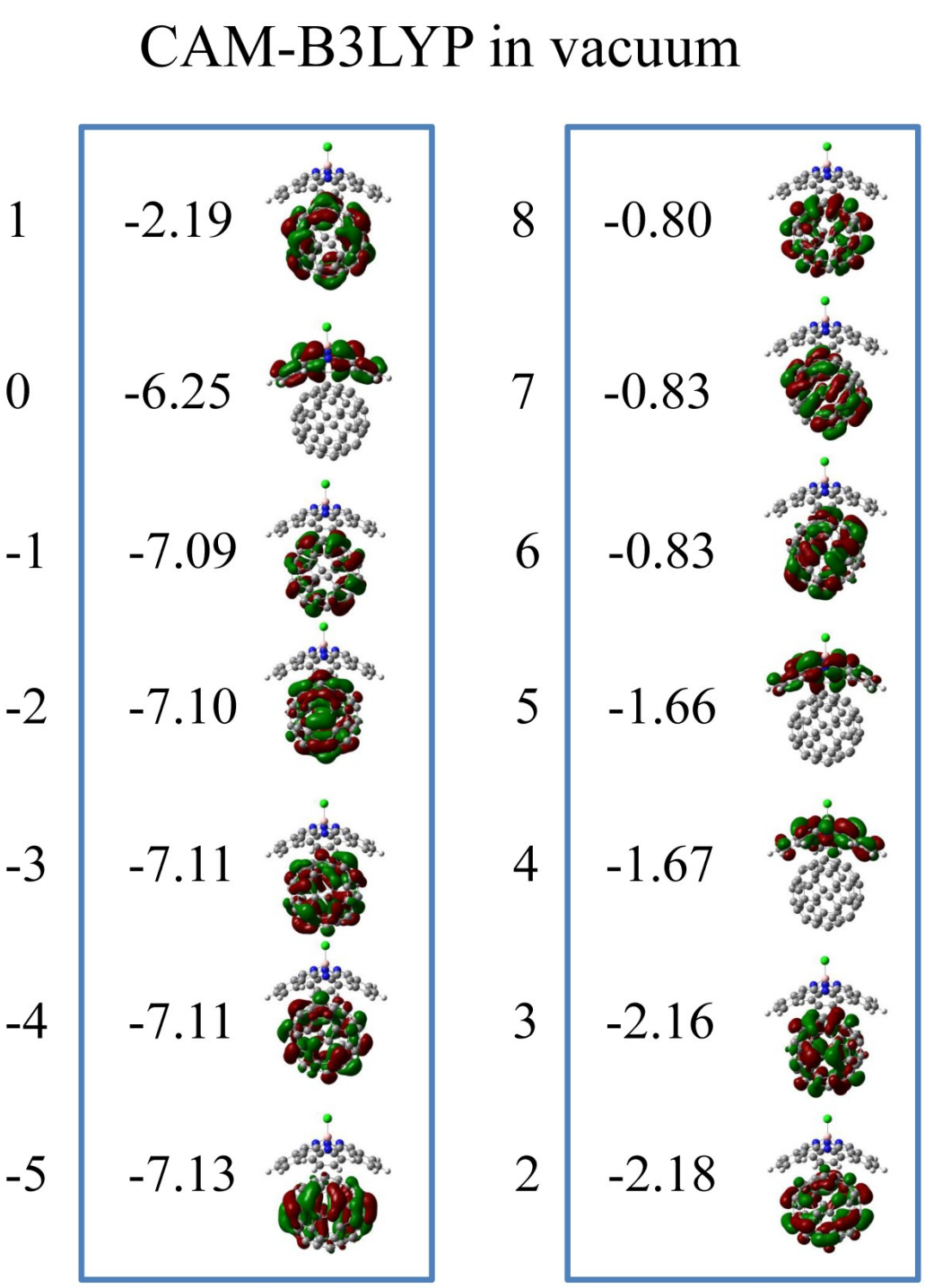

Fig. S4 Molecular orbitals of SubPc/C_{60} computed by CAM-B3LYP at the structure optimized by DFT with ωB97XD functional. The numbers outside the blue boxes show indices of each orbital; the index 0 depicts HOMO. The number inside the boxes indicates orbital energy (eV).

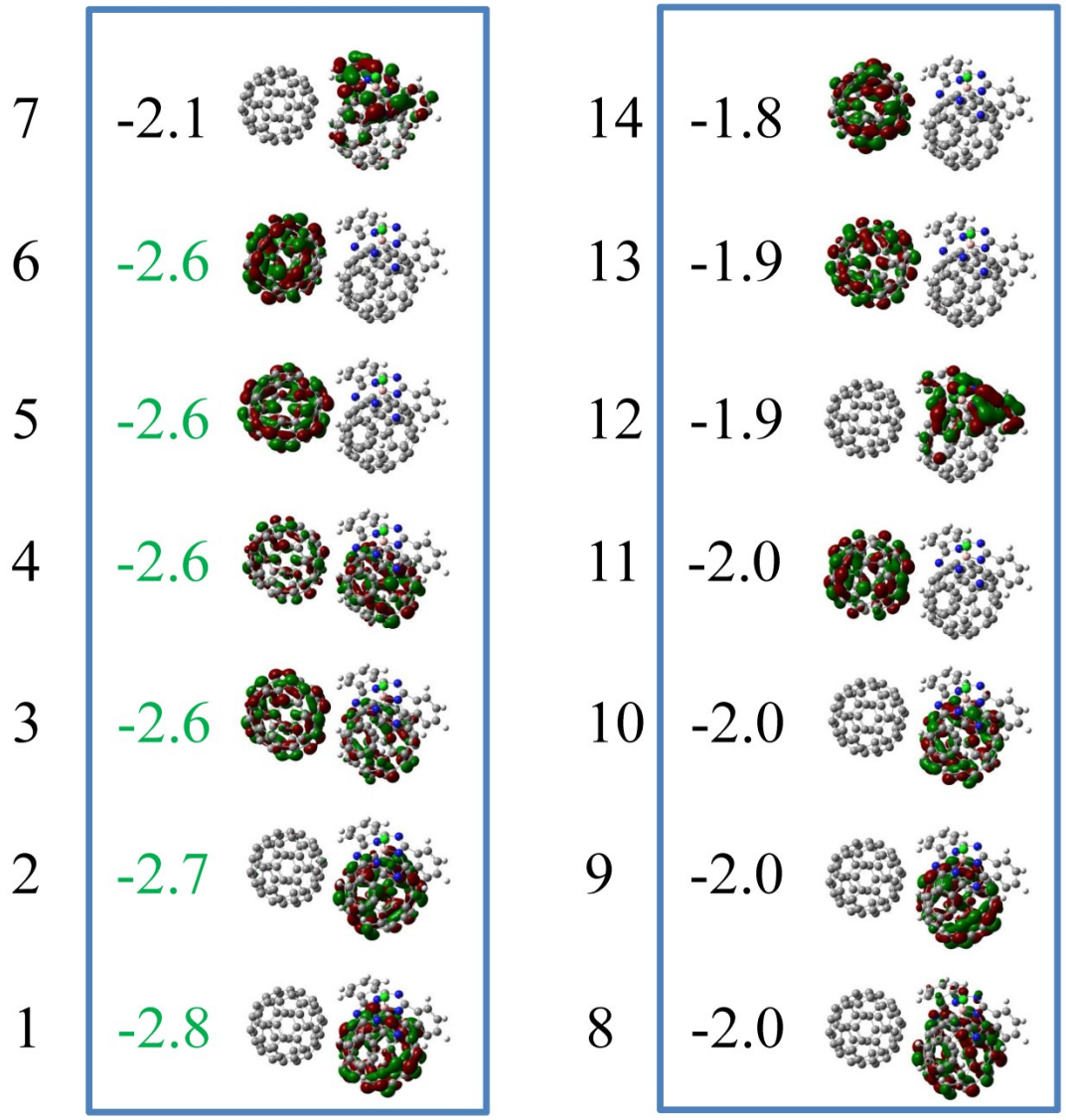

Fig. S5 Molecular orbitals and the energies of SubPc/$(C_{60})_2$. The numbers outside the blue boxes show indices of each orbital; the index 1 depicts LUMO. The number inside the boxes indicates orbital energy (eV); the green-colored number (indices 1, 2, 3, 4, 5, and 6) shows C_{60}-derived LUMO.

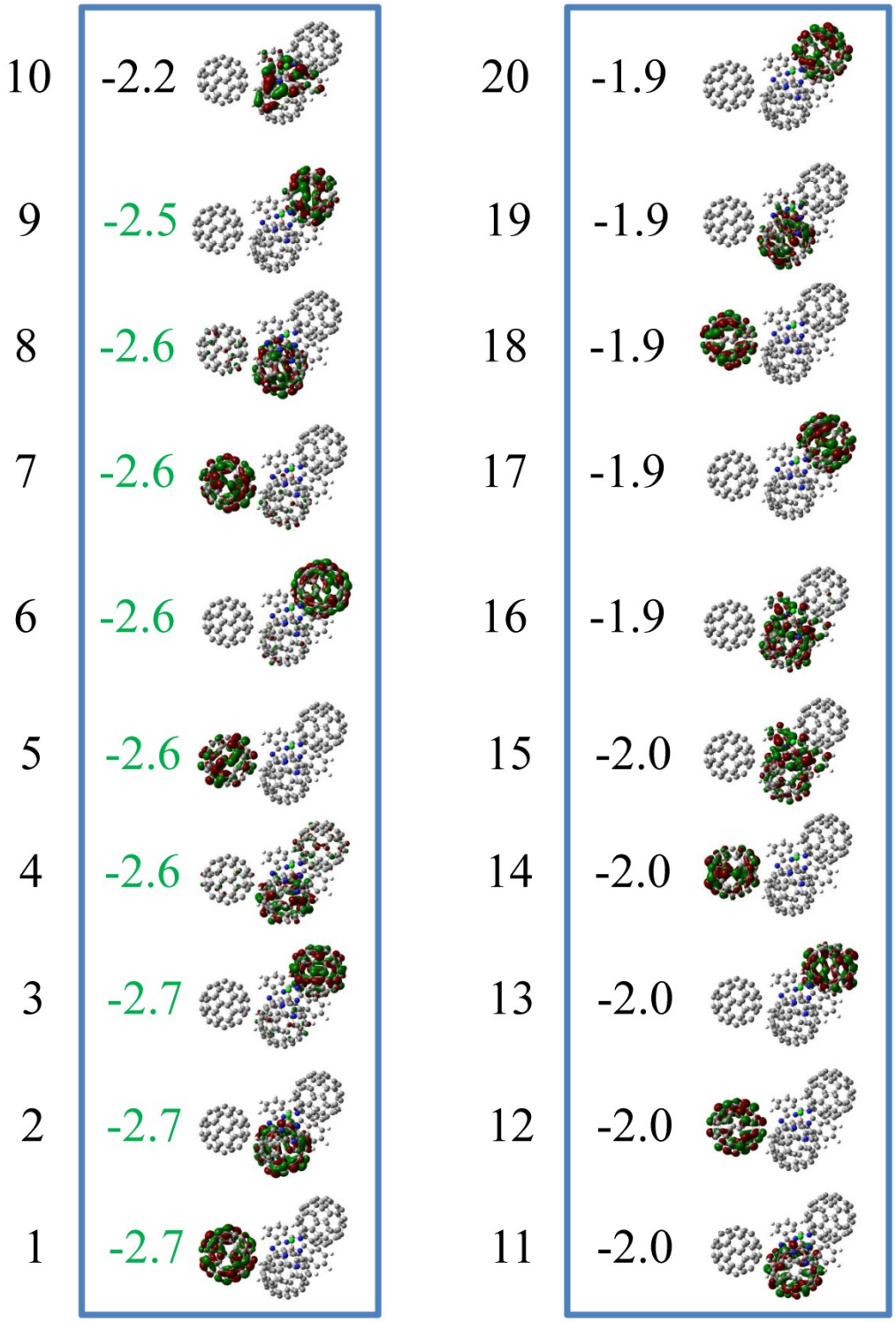

Fig. S6 Molecular orbitals and the energies of SubPc/$(C_{60})_3$. The numbers outside the blue boxes show indices of each orbital; the index 1 depicts LUMO. The number inside the boxes indicates orbital energy (eV); the green-colored number (indices 1, 2, 3, 4, 5, 6, 7, 8, and 9) shows C_{60}-derived LUMO.

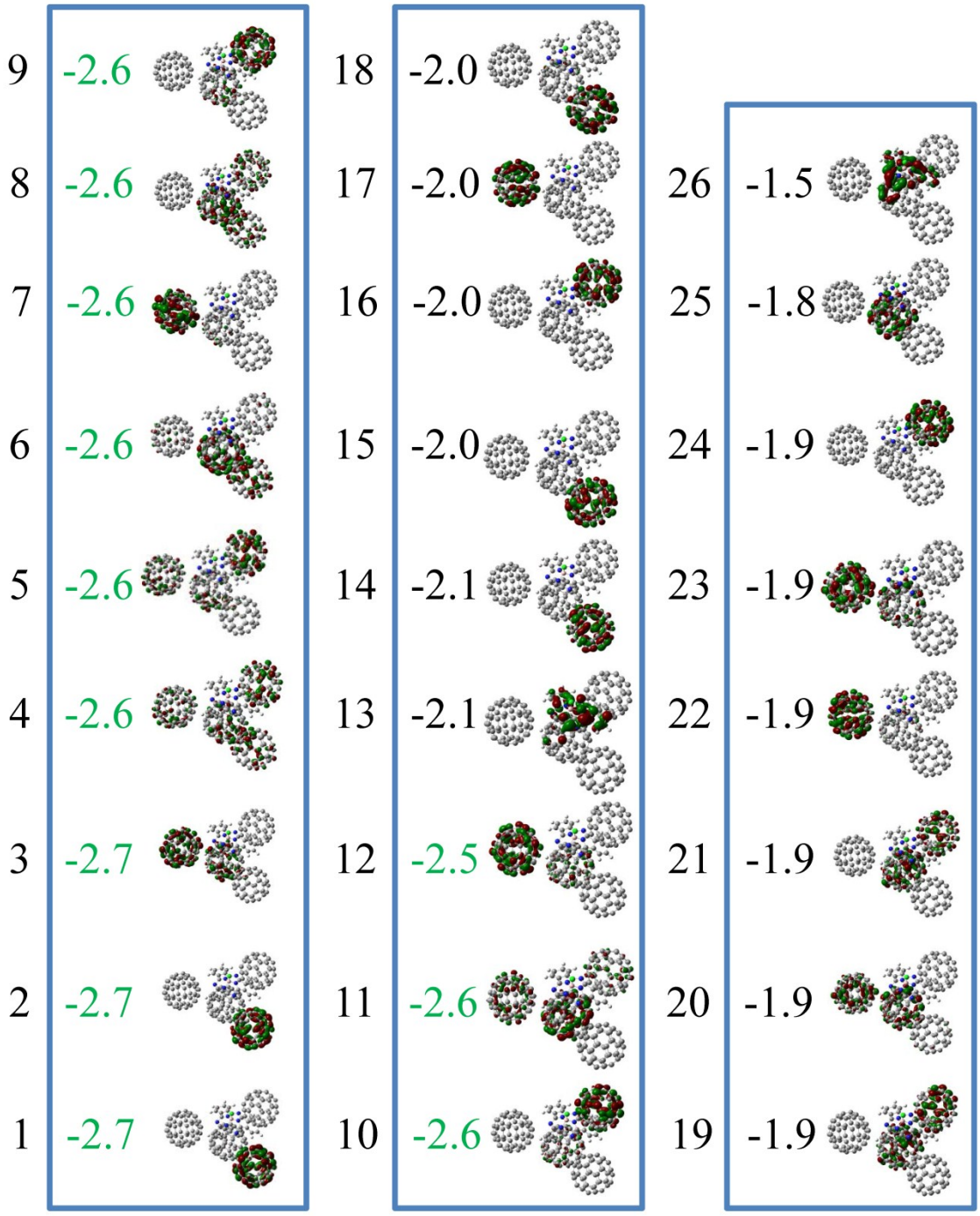

Fig. S7 Molecular orbitals and the energies of SubPc/$(C_{60})_4$. The numbers outside the blue boxes show indices of each orbital; the index 1 depicts LUMO. The number inside the boxes indicates orbital energy (eV); the green-colored number (indices 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, and 12) shows C_{60}-derived LUMO.

Table S1 Frontier orbital energies (eV) of SubPc/C_{60} dimer, computed with various functionals and environments. Orbitals are abbreviated as follows: H – HOMO, L – LUMO, L+1 – LUMO+1, L+2 - LUMO+2. The H, L, L+1, and L+2 orbital labels are defined for all methods.

Orbital index/label	(ωB97XD, vacuum)	(LC-ωPBE, vacuum)	(CAM-B3LYP, vacuum)	(ωB97XD, PCM)	(LC-ωPBE, PCM)	(CAM-B3LYP, PCM)
8, L+2	-0.33	-0.10	-0.80	-0.30	-0.08	-0.76
7, L+2	-0.36	-0.13	-0.83	-0.32	-0.10	-0.79
6, L+2	-0.36	-0.14	-0.83	-0.33	-0.11	-0.80
5, L+1	-1.17	-1.08	-1.66	-1.21	-1.13	-1.70
4, L+1	-1.17	-1.08	-1.67	-1.22	-1.13	-1.71
3, L	-1.72	-1.61	-2.16	-1.69	-1.59	-2.13
2, L	-1.74	-1.63	-2.18	-1.70	-1.60	-2.14
1, L	-1.75	-1.64	-2.19	-1.72	-1.61	-2.15
0, H	-6.80	-7.19	-6.25	-6.83	-7.22	-6.27
-1, H-1	-7.74	-8.35	-7.09	-7.71	-8.33	-7.06
-2, H-1	-7.75	-8.37	-7.10	-7.72	-8.34	-7.07
-3, H-1	-7.76	-8.37	-7.11	-7.73	-8.34	-7.07
-4, H-1	-7.77	-8.38	-7.11	-7.74	-8.35	-7.08
-5, H-1	-7.78	-8.40	-7.13	-7.75	-8.37	-7.09

Table S2 The energy offsets (eV) between groups of orbitals in the SubPc/C_{60} dimer, computed with various functionals and environments at DFT-level. Orbitals are abbreviated as follows: H – HOMO, H-1 – HOMO-1, L+1 – LUMO+1, and L+2 – LUMO+2. The H, L, L+1, and L+2 orbital labels are defined for all methods.

	ωB97XD in vacuum	LC-ωPBE in vacuum	CAM-B3LYP in vacuum	ωB97XD in PCM	LC-ωPBE in PCM	CAM-B3LYP in PCM
H – H-1	0.94	1.17	0.84	0.88	1.11	0.79
H – L	5.06	5.55	4.06	5.11	5.60	4.11
L+1 – L	0.55	0.53	0.50	0.47	0.45	0.42
L+2 – L+1	0.80	0.94	0.83	0.88	1.02	0.91

Table S3 Coefficients corresponding to intra-SubPc and charge transfer excitations. The orbital number 0 corresponds to HOMO.

	In vacuum			In PCM		
Functional	ωB97XD	LC-ωPBE	CAM-B3LYP	ωB97XD	LC-ωPBE	CAM-B3LYP
Intra-SubPc excitation	8→4: -0.12 0→3: 0.13 0→4: -0.14 0→5: 0.65	-8→4: -0.10 0→4: -0.20 0→5: 0.65	-8→5: 0.13 0→4: 0.63 0→5: 0.17	0→3: 0.10 0→5: 0.67	0→4: -0.13 0→5: 0.67	-5→1: 0.11 -4→3: -0.13 -2→2: 0.10 0→4: 0.61 0→5: 0.14
CT excitation	-3→1: -0.12 0→1: -0.30 0→2: -0.58 0→3: 0.12	0→2: -0.13 0→3: 0.64 0→8: 0.20	0→1: 0.61 0→2: -0.27 0→6: -0.11 0→7: -0.12	-3→3: -0.16 0→2: 0.15 0→3: 0.60 0→8: 0.19	0→2: 0.16 0→3: 0.64 0→8: 0.19	-3→2: -0.11 0→1: 0.60 0→2: -0.23 0→6: 0.11