Electronic Supplementary Information

for

Electronic and Electrochemical Properties as well as Flowerlike Supramolecular Assemblies of Fulleropyrrolidines Bearing Ester Substituent with Different Alkyl Chain Length

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Table S1 Comparison of HOMO energy, LUMO energy, and HOMO-LUMO energy gap (E_{gap}) of C_{60} and PCBM calculated with B3LYP and PBE basis sets, as well as the values from experimental measurements.

Compd.	Parameters	Exp. values	B3LYP/ 6-311G(d,p)[c]	PBEPBE/ 6-311G(d,p)[c]	PBEPBE/ 6-311G(d,p)[d]
C_{60}	HOMO / eV	–6.1[a]	–6.401	–5.867	–5.863
	LUMO / eV	–4.3[a]	–3.678	–4.181	–4.210
	E_{gap} / eV	1.8[a]	2.723	1.686	1.653
PCBM	HOMO / eV	–5.55[b]	–6.049	–5.522	–5.517
	LUMO / eV	–3.83[b]	–3.522	–4.006	–4.032
	E_{gap} / eV	1.72[b]	2.527	1.516	1.485

[a] Cited from ref. S1. [b] Cited from ref. S2. [c] Based on the geometry optimized at B3LYP/6-31G(d) level. [d] Based on the geometry optimized at PBEPBE/6-311G(d,p) level.

Table S2 LUMO, HOMO, and molecular properties of the C_{60}, PCBM and **FP1**–**FP4** fullerenes calculated by DFT at PBEPBE/6-311G(d,p) level.

Molecular properties[a]	C_{60}	PCBM	**FP1**	**FP2**	**FP3**	**FP4**
LUMO [eV]	–4.181	–4.006	–4.017	–4.012	–4.010	–4.007
HOMO [eV]	–5.867	–5.522	–5.515	–5.510	–5.508	–5.507
Ionization potential (I)	5.867	5.522	5.515	5.510	5.508	5.507
Electron affinity (A)	4.181	4.006	4.017	4.012	4.010	4.007
Electronegativity (χ)	5.024	4.764	4.766	4.761	4.759	4.757
Global hardness (η)	0.8432	0.7578	0.7491	0.7489	0.7491	0.7502
Global softness (S)	1.186	1.319	1.335	1.335	1.335	1.333
Chemical potential (μ)	–5.024	–4.764	–4.766	–4.761	–4.759	–4.757
Global electophilicity (ω)	14.96	14.98	15.16	15.13	15.11	15.08

[a] The definitions of these properties are described in the ref. S3-S5.

Table S3 MO energies of the **FP1**–**FP4** fullerenes calculated by DFT at PBEPBE/6-311G(d,p) level, where the HOMO and LUMO were indicated in bold font.

FP1		**FP2**		**FP3**		**FP4**	
Energy (eV)	MO	Energy (eV)	MO	Energy (eV)	MO	Energy (eV)	MO
-2.363	MO239	-2.338	MO243	-2.332	MO247	-2.326	MO251
-2.583	MO238	-2.578	MO242	-2.576	MO246	-2.575	MO250
-2.816	MO237	-2.811	MO241	-2.808	MO245	-2.807	MO239
-2.856	MO236	-2.851	MO240	-2.848	MO244	-2.846	MO238
-2.918	MO235	-2.914	MO239	-2.912	MO243	-2.911	MO247
-3.705	MO234	-3.701	MO238	-3.699	MO242	-3.698	MO246
-3.936	MO233	-3.931	MO237	-3.929	MO241	-3.927	MO245
-4.017	**MO232**	**-4.012**	**MO236**	**-4.009**	**MO240**	**-4.007**	**MO244**
-5.515	**MO231**	**-5.510**	**MO235**	**-5.508**	**MO239**	**-5.507**	**MO243**
-5.641	MO230	-5.635	MO234	-5.633	MO238	-5.631	MO242
-5.648	MO229	-5.642	MO233	-5.640	MO237	-5.639	MO241
-5.688	MO228	-5.683	MO232	-5.680	MO236	-5.679	MO240
-5.723	MO227	-5.710	MO231	-5.710	MO235	-5.709	MO239
-6.036	MO226	-6.032	MO230	-6.029	MO234	-6.028	MO238
-6.345	MO225	-6.287	MO229	-6.280	MO233	-6.270	MO237
-6.534	MO224	-6.525	MO228	-6.521	MO232	-6.519	MO236

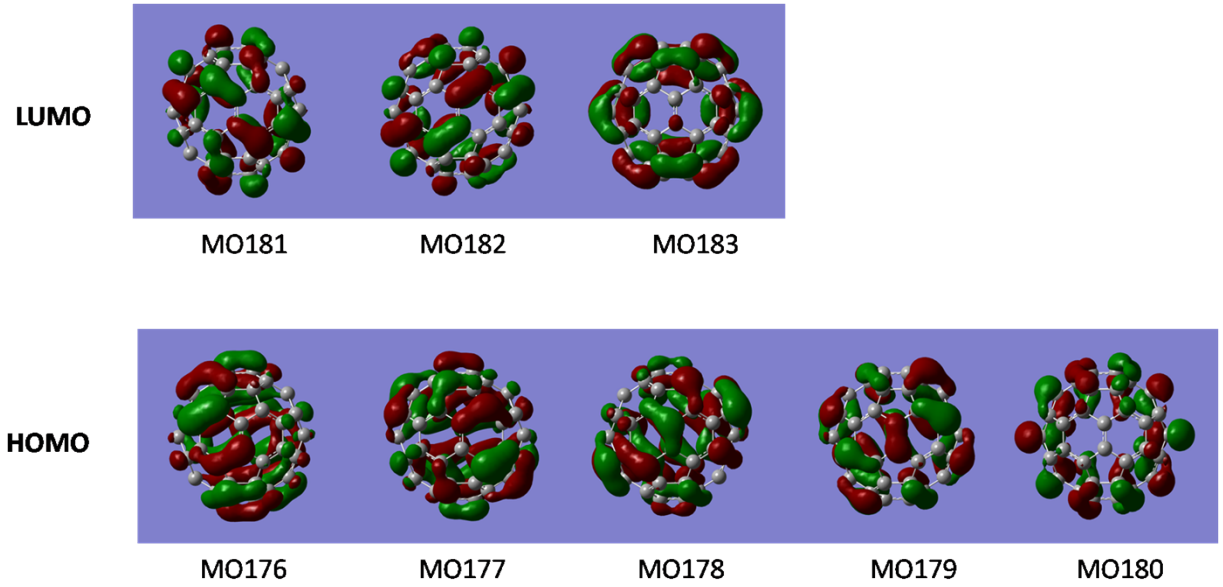

Fig. S1 Contours of 3-fold degenerated LUMOs and 5-fold degenerated HOMOs of C_{60} calculated by DFT at PBEPBE/6-311G(d,p) level.

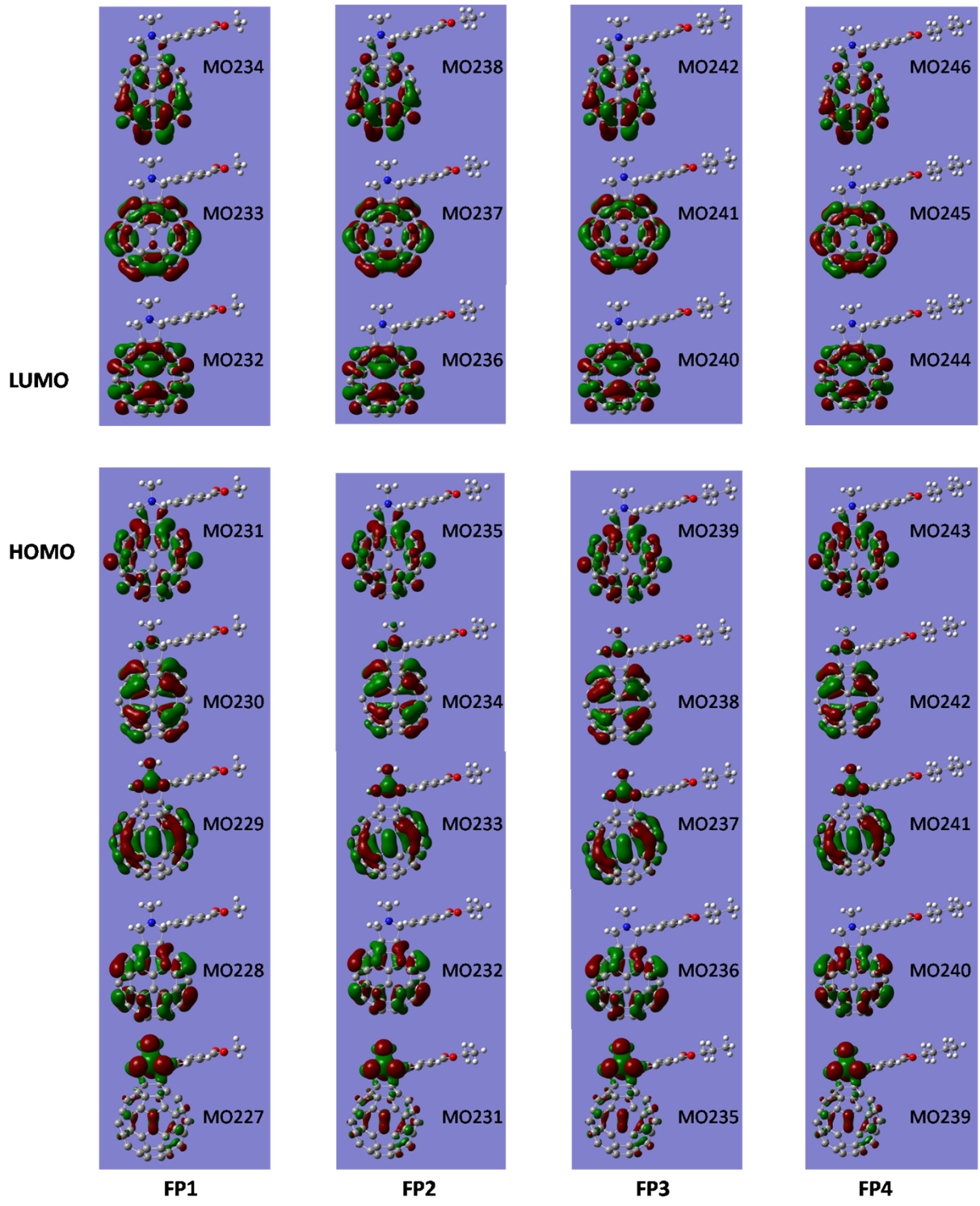

Fig. S2 Contours of the related eight non-degenerated MOs of the **FP1**–**FP4** fullerenes calculated by DFT at PBEPBE/6-311G(d,p) level.

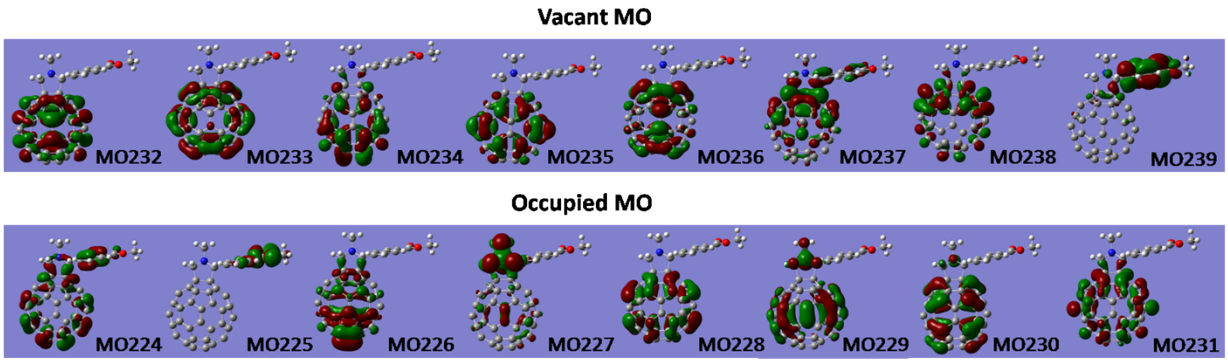

Fig. S3 Contours of the MOs of the **FP1** calculated by DFT at PBEPBE/6-311G(d,p) level.

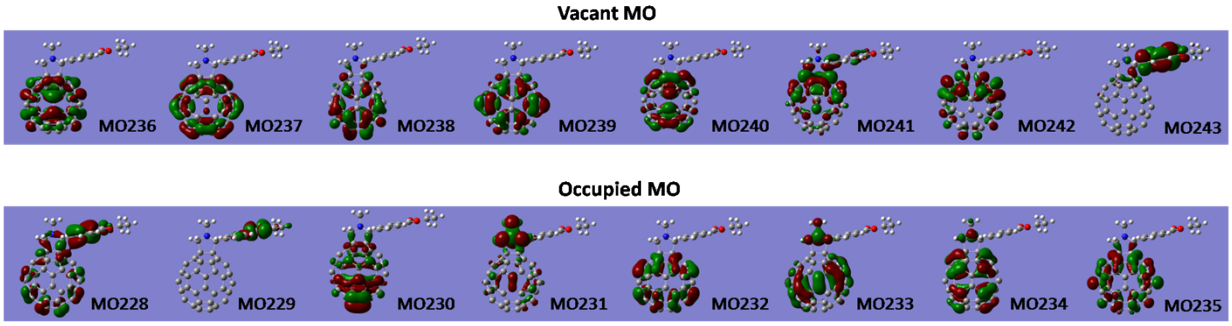

Fig. S4 Contours of the MOs of the **FP2** calculated by DFT at PBEPBE/6-311G(d,p) level.

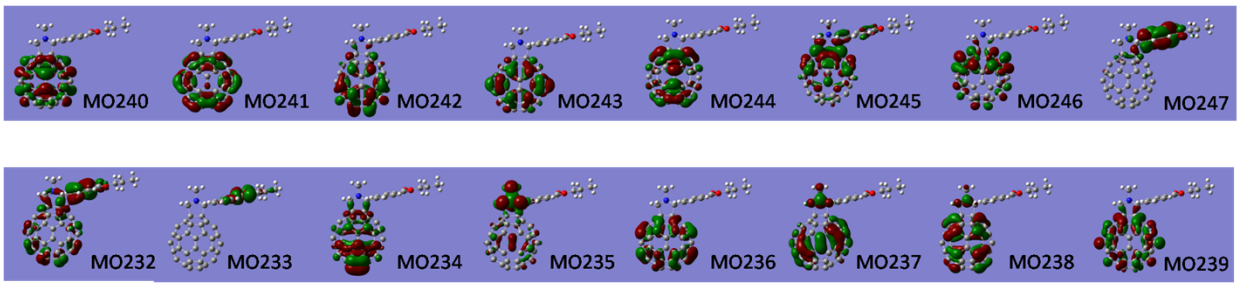

Fig. S5 Contours of the MOs of the **FP3** calculated by DFT at PBEPBE/6-311G(d,p) level.

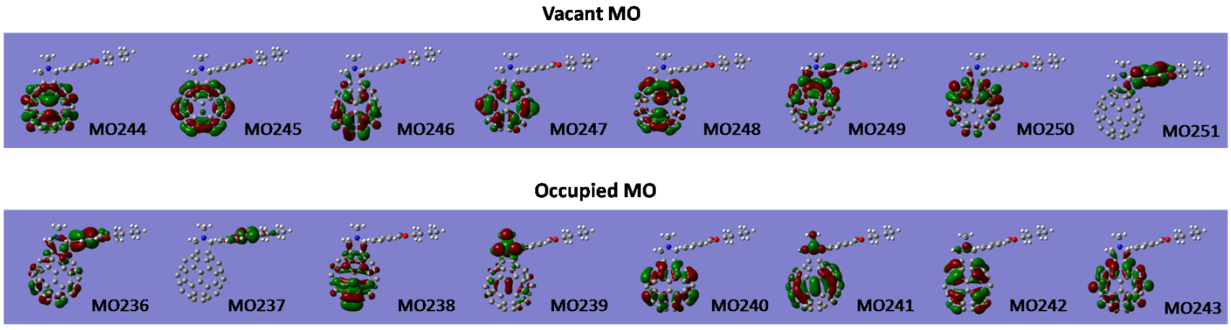

Fig. S6 Contours of the MOs of the **FP4** calculated by DFT at PBEPBE/6-311G(d,p) level.

References

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[S2] G. D. Han, W. R. Collins, T. L. Andrew, V. Bulović and T. M. Swager. *Adv. Funct. Mater.* 2013, **23**, 3061–3069.

[S3] R. G. Parr, L. v. Szentpály, S. Liu. *J. Am. Chem. Soc.* 1999**, 121**, 1922–1924.

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[S5] R. G. Parr, Z. Zhou. *Acc. Chem. Res.* 1993**, 26**, 256–258.