Supporting information for

Ferrocene/fullerene hybrids showing large second-order nonlinear optical activities: impact of the cage unit size

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Table S1. Total electronic energies (a.u.) of eclipsed and staggered isomers of complexes **1**-**4** and their relative energies (kcal/mol) (where ΔE_{rel} = E(staggered) - E(eclipsed)).

eclipsed	energy	staggered	energy	ΔE_{rel}
1	-2606.64802716	**1**	-2606.64694805	0.68
2	-2835.08901522	**2**	-2835.08784618	0.73
3	-2987.75677473	**3**	-2987.75562097	0.72
4	-3368.69660652	**4**	-3368.69555729	0.66

Table S2. The charge distributions of H, Cp, Fe, and fullerene of complexes **1**-**4** obtained at the ωB97XD/6-31+G*.

Complex	Charge/a.u.				
	H[a]	Cp	Fe	fullerene	H[b]
1	0.258	-0.160	0.415	-0.255	0.282
2	0.260	-0.131	0.427	-0.296	0.281
3	0.258	-0.157	0.414	-0.257	0.283
4	0.257	-0.162	0.411	-0.249	0.284

[a] the average NBO charge of H atom of Cp. [b] the average NBO charge of H atom of fullerene.

Table S3. Tensorial components (10^{-30} esu) of the studied complexes.

Method	Tensorial component	**1**	**2**	**3**	**4**
BHandHLYP	β_{xxx}	-0.000	-0.062	0.000	4.142
	β_{xxy}	0.005	0.143	-0.005	-0.841
	β_{xyy}	-0.000	0.410	0.000	1.376
	β_{yyy}	-0.000	-13.287	-0.011	-2.505
	β_{xxz}	1.359	2.461	5.582	-77.388
	β_{xyz}	-0.000	0.250	0.000	0.025
	β_{yyz}	1.364	-6.630	5.590	-77.388
	β_{xzz}	-0.000	-0.008	0.000	0.991
	β_{yzz}	0.004	-0.790	-0.001	-0.636
	β_{zzz}	3.740	9.277	5.520	-210.561
CAM-B3LYP	β_{xxx}	-0.000	-0.067	-0.000	7.491
	β_{xxy}	0.005	0.299	-0.005	-1.530
	β_{xyy}	-0.000	0.359	-0.000	2.490
	β_{yyy}	-0.000	-11.232	-0.010	-4.561
	β_{xxz}	1.463	2.114	5.557	-140.505
	β_{xyz}	-0.000	0.023	-0.000	0.007
	β_{yyz}	1.468	-6.057	5.564	-140.530
	β_{xzz}	-0.000	0.010	-0.000	4.497
	β_{yzz}	0.005	-1.425	0.000	-2.821
	β_{zzz}	2.906	8.389	4.490	-535.752
LC-BLYP	β_{xxx}	-0.000	-0.145	-0.000	1.065
	β_{xxy}	0.000	1.370	-0.003	-0.224
	β_{xyy}	-0.000	0.214	0.000	0.356
	β_{yyy}	0.002	-4.485	-0.005	-0.628
	β_{xxz}	1.422	1.693	4.848	-20.521
	β_{xyz}	0.000	0.152	0.000	0.006
	β_{yyz}	1.423	-2.964	4.850	-20.572
	β_{xzz}	-0.000	0.039	-0.000	0.918
	β_{yzz}	0.003	-2.637	0.000	-0.534
	β_{zzz}	3.266	8.095	4.684	-93.653
ωB97XD	β_{xxx}	-0.000	-0.084	-0.000	-1.888
	β_{xxy}	0.013	0.533	-0.009	0.371
	β_{xyy}	-0.000	0.312	0.000	-0.645
	β_{yyy}	0.007	-9.165	-0.019	1.170
	β_{xxz}	1.520	2.105	5.367	34.806
	β_{xyz}	0.000	0.214	0.000	0.104
	β_{yyz}	1.523	-5.177	6.367	34.883
	β_{xzz}	-0.000	0.021	0.000	8.241
	β_{yzz}	0.000	-2.051	-0.013	-4.972

	β_{zzz}	3.488	9.280	4.884	-392.357

Table S4. The transition energies, oscillator strengths, differences of dipole moment between the ground and crucial excited state, and $\Delta\mu_{ge}f_{os}/\Delta E_{ge}^3$ values of complexes **1**-**4** calculated at the TD-ωB97XD/6-31+G* (SDD basis set for Fe ion) level.

complex	f_{os}	ΔE	$\Delta\mu_{ge}$	ΔE_{ge}^3	$\Delta\mu_{ge}f_{os}/\Delta E_{ge}^3$
1	0.0270	3.30	2.32	35.94	0.0017
2	0.0431	2.30	2.73	12.17	0.0097
3	0.0587	2.37	8.18	13.31	0.0361
4	0.0269	1.29	5.81	2.15	0.0728

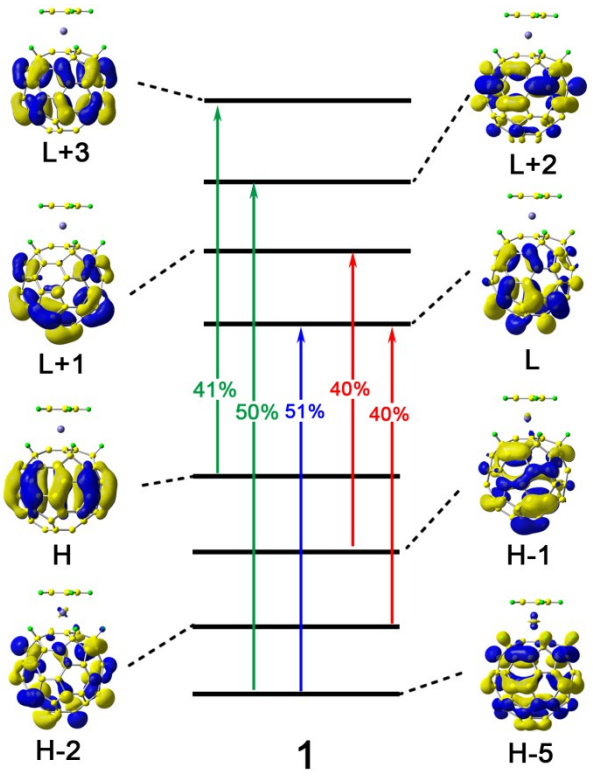

Figure S1. The molecular orbitals involved in the relatively intense electronic transitions in the absorption spectrum of complex **1**

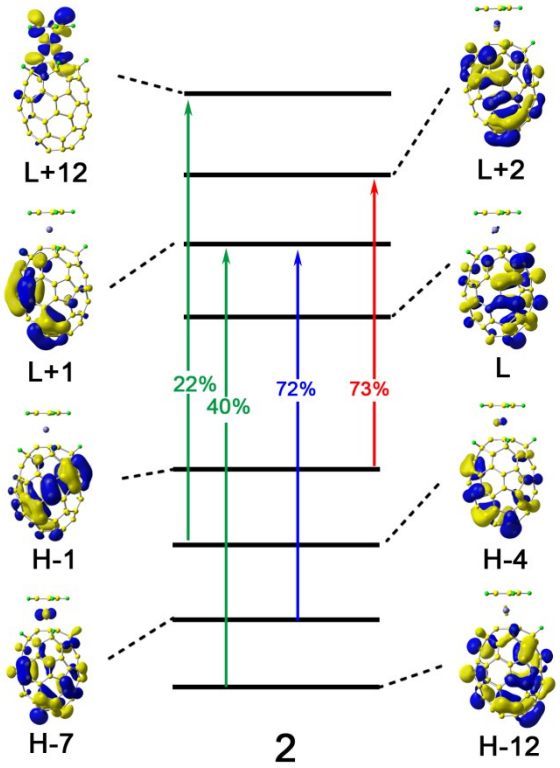

Figure S2. The molecular orbitals involved in the relatively intense electronic transitions in the absorption spectrum of complex **2**

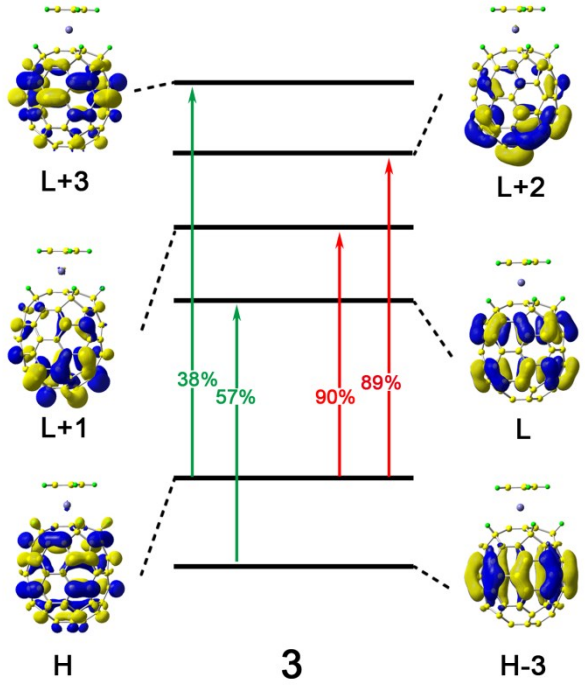

Figure S3. The molecular orbitals involved in the relatively intense electronic transitions in the absorption spectrum of complex **3**.

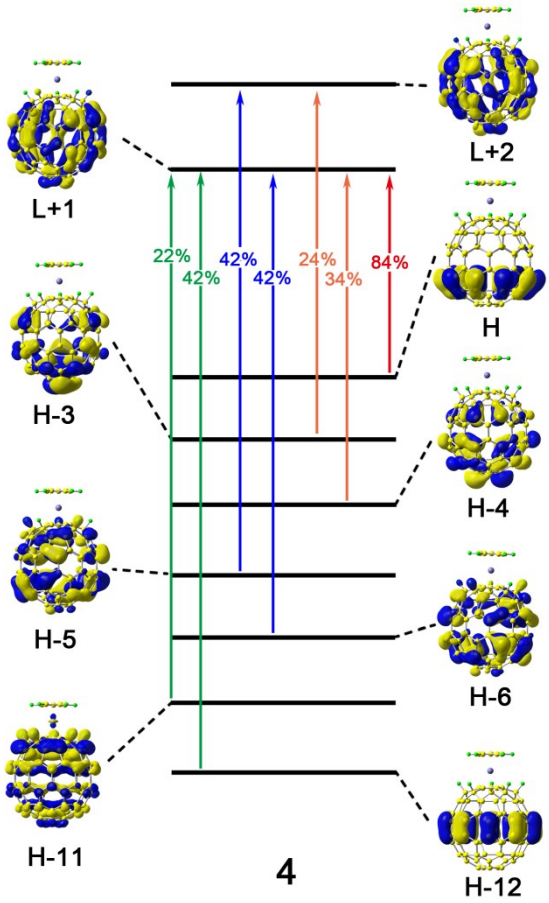

Figure S4. The molecular orbitals involved in the relatively intense electronic transitions in the absorption spectrum of complex **4**.