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Supporting Information

Non-IPR endohedral fullerene Yb@C_{76}: Density Functional Theory Characterization†

Tao Yang,[a] Xiang Zhao,*[a] Qian Xu,[a] Caihua Zhou,[a] Ling He[a] and Shigeru Nagase[b]

[a] *Institute for Chemical Physics and Department of Chemistry, Faculty of Science, Xi'an Jiaotong University, Xi'an 710049, China.*

E-mail: xzhao@mail.xjtu.edu.cn; Fax: +86 29 8266 8559; Tel: +86 29 8266 5671

[b] *Department of Theoretical and Computational Molecular Science, Institute for Molecular Science, Okazaki 444-8585, Japan*

1. Relative energies of all IPR, PA=1 and main PA=2 isomers of di-anion C_{76}^{2-} and monometallofullerenes Yb@C_{76}.

It is generally proposed that fullerene isomers with three or more fused pentagons cannot be efficiently stabilized by one metal atom and will thus be unstable. Hence, in this work only IPR isomers and non-IPR isomers with adjacent pentagons less than three have been taken into consideration. The number of such isomers is 154 for C_{76}, including two IPR isomers encoded by 19150:D_2 and 19151:T_d. All these isomers at di-anion state were optimized at AM1 level. The further optimizations on these most stable anions were performed at the hybrid density functional theory B3LYP level with the split-valence d-polarized 6-31G* basis set. The molecular structures of endohedral fullerene Yb@C_{76} were optimized at B3LYP/6-31G*-CEP level (6-31G*

basis set for C atoms and CEP-4G basis with the corresponding relativistic effective core potential (ECP) for Yb). All DFT calculations were carried out in the Gaussian 03 program. The calculated results IPR, PA=1 and main PA=2 isomers have been collected in the Table S1. It's interesting that the energy order of Yb@19138:C_{2v} and Yb@17459:C_1 have changed when using the 6-31G* basis set. To further confirm the 6-31G* giving better results, the 4-31G basis set have been employed to calculate the Yb@C_{76} isomers. It is shown that the results are in good agreement with that of 6-31G*. Thus, it's reasonable to use the energy results calculated at 6-31G* level as the final results.

Table S1 Relative energies of all IPR, PA=1 and main PA=2 isomers of di-anion C_{76}^{2-} and monometallofullerenes Yb@C_{76}.

C_{76}			-2		Yb@C_{76}		Yb@C_{76}		Yb@C_{76}	
spiral ID	PA	Sym.	ΔE 6-31G* kcal/mol	Gap eV	ΔE 3-21G kcal/mol	*Gap* eV	ΔE 4-31G eV	*Gap* eV	ΔE 6-31G* kcal/mol	Gap eV
19150	0	D_2	11.1	0.89	14.8	1.01	14.6	1.01	15.9	1.00
19138	1	C_{2v}	0.0	1.40	1.8	1.40	0.0	1.37	0.0	1.40
19151	0	T_d	2.2	0.76	8.4	0.97	5.1	0.95	5.8	0.97
19142	1	C_s	10.4	1.37	18.0	1.15	17.4	1.13	17.5	1.15
17459	1	C_1	3.2	1.55	0.0	1.71	0.3	1.69	1.0	1.69
17418	1	C_1	14.7	1.26	10.2	1.26	12.0	1.25	13.1	1.24
17750	1	C_1	18.3	1.05	12.1	1.26	13.9	1.25	14.7	1.25
17894	1	C_1	11.2	1.19	6.5	1.44	7.5	1.43	8.3	1.41
18632	1	C_1	17.0	1.35	14.2	1.52	16.3	1.49	16.8	1.49
17646	1	C_2	11.5	1.81	5.7	1.93	7.8	1.91	8.8	1.88
17410	1	C_s	16.9	1.72	11.9	1.75	14.2	1.74	15.2	1.70
18439	1	C_1	28.0	1.24					23.7	1.57
18542	1	C_1	20.4	0.97	14.7	1.16	16.9	1.15	17.4	1.16
18720	1	C_1	37.7	1.07					32.5	1.21
18944	2	C_2	13.0	1.67	21.1	1.16	21.8	1.34	20.9	1.38
18943	2	C_1	17.6	1.72					24.9	1.41

For the two most stable isomers, Yb@19138:C_{2v} and Yb@17459:C_1, we have also

calculated the singlet-triplet splitting energy ΔE(S-T). The results show that these energies are 12.6 kcal/mol and 19.9 kcal/mol for Yb@19138:C_{2v} and Yb@17459:C_1 respectively, implying that the ground state for two isomers is the single state. Furthermore, it implies that triplet state would be reached more easily for Yb@19138:C_{2v} than Yb@17459:C_1.

2. Optimized Cartesian coordinates of the two Yb@C_{76} structures.

The optimization of mono-metallofullerenes Yb@C_{76} was performed at B3LYP/6-31G*-CEP level. The Cartesian coordinates of Yb@19138:C_{2v} and Yb@17459:C_1 structures are presented respectively.

xyz-file of Yb@19138:C_{2v}:

C	0.900116	-0.709918	-3.697035
C	-0.498991	-1.141829	-3.693748
C	1.910346	-1.464288	-3.032849
C	1.522127	-2.691798	-2.319480
C	0.146753	-3.094878	-2.356013
C	-0.847139	-2.312337	-3.052015
C	-1.897985	-3.253419	-1.225354
C	-2.102525	-2.385729	-2.345525
C	-0.500353	-3.665068	-1.225469
C	-0.496831	1.142030	-3.693337
C	-1.365362	0.000917	-3.664695
C	0.901455	0.707470	-3.696774
C	-3.009254	-1.270711	-2.301837
C	-2.593770	0.001947	-2.918392
C	-3.908997	-1.245298	-1.179127
C	-3.646805	-2.064765	-0.000388
C	-2.595352	-3.037839	-0.000510
C	-4.437160	0.003037	0.716941
C	-4.437095	0.003292	-0.717065
C	-3.909113	-1.245714	1.178615
C	-3.006869	1.275177	-2.301401

C	-3.906641	1.251048	-1.178686
C	0.152599	3.093380	-2.354903
C	-0.842768	2.312961	-3.051182
C	1.527203	2.687672	-2.318510
C	1.913100	1.459688	-3.032317
C	-2.098010	2.388471	-2.344664
C	-1.891847	3.255390	-1.224196
C	-0.493433	3.664380	-1.224156
C	-3.642911	2.069594	0.000348
C	-2.589611	3.040676	0.000575
C	3.030931	0.712497	-2.568729
C	3.029583	-0.719364	-2.568988
C	3.812016	1.153820	-1.418563
C	3.404289	2.284187	-0.723023
C	2.267531	3.059346	-1.171023
C	3.809830	-1.162561	-1.418973
C	4.282512	-0.004942	-0.704885
C	-3.906753	1.250621	1.179062
C	-3.007096	1.274350	2.301874
C	-2.594064	0.000907	2.918464
C	-3.009484	-1.271526	2.301408
C	-1.898108	-3.253853	1.224328
C	-2.102760	-2.386558	2.344783
C	-0.843077	2.311872	3.052247
C	-2.098248	2.387634	2.345630
C	-0.497206	1.140714	3.694024
C	-1.365732	-0.000387	3.664889
C	-1.891971	3.254952	1.225491
C	-0.847448	-2.313423	3.051433
C	0.146514	-3.095717	2.355252
C	-0.500476	-3.665503	1.224439
C	0.205353	-3.861087	-0.000514
C	-0.499366	-1.143145	3.693622
C	0.899743	-0.711236	3.697203
C	1.910039	-1.465369	3.032847
C	1.521891	-2.692623	2.318998
C	0.901082	0.706151	3.697448
C	-0.493558	3.663944	1.225742
C	0.152361	3.092542	2.356351
C	1.912793	1.458606	3.033362
C	1.526970	2.686847	2.319955
C	3.399889	-2.292658	0.723694
C	2.261636	-3.065689	1.171585
C	3.399963	-2.292399	-0.723840

C	2.261755	-3.065271	-1.172122
C	1.599835	-3.586794	-0.000396
C	3.809687	-1.163068	1.419274
C	3.029324	-0.720280	2.569368
C	3.030671	0.711582	2.569619
C	3.811871	1.153313	1.419689
C	4.282440	-0.005194	0.705646
C	3.404216	2.283929	0.724512
C	2.267414	3.058930	1.172675
C	1.606594	3.581694	0.000885
C	0.212639	3.858638	0.000863
Yb	-1.939003	0.000750	-0.000007

xyz-file of Yb@17459:C_1:

C	-0.015737	-0.065775	0.111266
C	1.370549	-0.057514	0.110734
C	2.106782	1.185499	0.105432
C	3.296430	0.975818	-0.671971
C	3.935933	2.042422	-1.351049
C	4.586002	1.736098	-2.585742
C	4.727536	2.724182	-3.620501
C	4.657245	2.043103	-4.888260
C	4.167352	2.691920	-6.069862
C	3.405873	1.863897	-6.970865
C	2.205386	2.385144	-7.611940
C	1.196767	1.348093	-7.608868
C	-0.159785	1.594392	-7.240102
C	-0.925810	0.494613	-6.640590
C	-2.028000	0.789549	-5.719565
C	-2.402439	-0.162443	-4.724789
C	-2.795983	0.238432	-3.402602
C	-2.349667	-0.784803	-2.466283
C	-1.894680	-0.421970	-1.206497
C	-0.734597	-1.069417	-0.636189
C	-0.726309	1.201251	0.000590
C	-1.877640	0.983274	-0.819225
C	-2.365793	1.993550	-1.693413
C	-2.837185	1.603545	-3.030758
C	-2.709290	2.539892	-4.095785
C	-2.305239	2.144910	-5.405652
C	-1.557294	3.231329	-6.006914
C	-0.517849	2.991806	-6.938251
C	0.468459	4.033027	-7.066580

C	1.838043	3.728779	-7.460535
C	2.726099	4.607666	-6.750237
C	3.823108	4.095523	-5.967086
C	3.734136	4.726529	-4.652250
C	4.167241	4.034700	-3.466745
C	3.490848	4.335043	-2.247047
C	3.388536	3.348174	-1.184123
C	2.155935	3.534641	-0.488927
C	1.439482	2.439952	0.084077
C	-0.028670	2.443925	0.000497
C	-0.673418	3.512288	-0.686593
C	-1.805790	3.289148	-1.518566
C	-1.723994	4.236079	-2.625128
C	-2.183815	3.866032	-3.873350
C	-1.471490	4.297392	-5.044648
C	-0.325830	5.144442	-4.955724
C	0.547002	5.114660	-6.087298
C	1.931649	5.466139	-5.928785
C	2.518477	5.532723	-4.627144
C	1.677726	5.576327	-3.459263
C	2.272674	5.096005	-2.249964
C	1.467920	4.613708	-1.155455
C	0.090574	4.608571	-1.272836
C	-0.539306	5.042697	-2.487416
C	0.221587	5.462332	-3.620934
C	2.096721	-1.015964	-0.702761
C	3.249857	-0.359925	-1.241707
C	3.665861	-0.590027	-2.579040
C	4.414277	0.455098	-3.200761
C	4.418620	0.645018	-4.619283
C	3.611234	-0.155711	-5.473696
C	3.165997	0.465488	-6.679099
C	1.861531	0.145640	-7.189703
C	1.135461	-0.890701	-6.651914
C	-0.282100	-0.764863	-6.484557
C	-0.657441	-1.703839	-5.449235
C	-1.720235	-1.434006	-4.609049
C	-1.669001	-1.817511	-3.211834
C	-0.513578	-2.408003	-2.690734
C	-0.031942	-2.027110	-1.386126
C	1.412819	-1.962732	-1.452887
C	1.830017	-2.226325	-2.818804
C	2.896982	-1.508444	-3.427578
C	2.835488	-1.260339	-4.877351

C	1.678540	-1.691242	-5.573812
C	0.559336	-2.286826	-4.902493
C	0.642248	-2.589064	-3.554418
Yb	1.740102	3.012053	-4.917527

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