

Supplementary information to the “Effect of exohedral functionalization on the magnetic properties in the dysprosium-containing endohedral fullerene DySc₂N@C₈₀(CF₂)”

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Optimized cartesian coordinates of conformer 1 of DySc₂N@C₈₀(CF₂)

C	-3.398498520	2.281826001	-0.865964710
C	-3.417180542	2.271002712	0.565733712
C	-3.883022568	0.987874422	0.995470181
C	-4.147158008	0.203935553	-0.176999135
C	-3.847765020	0.996124869	-1.344176535
C	-3.435845012	0.427582101	-2.599021197
C	-2.464076625	1.198702978	-3.339793445
C	-1.962249651	2.446257643	-2.807927700
C	-2.411034474	3.011786830	-1.571944505
C	-1.503554795	3.810238675	-0.819169058
C	-1.520646265	3.794063648	0.613881816
C	-2.439690266	2.979311583	1.316078126
C	-1.987431000	2.388331793	2.547754989
C	-2.473670632	1.128198502	3.021727580
C	-3.386894736	0.383034741	2.185218961
C	-3.257969233	-1.024696686	2.191976086
C	-3.540451387	-1.812501187	1.030884439
C	-3.942065217	-1.195530218	-0.189596414
C	-3.516171987	-1.777220696	-1.434864383
C	-3.315535780	-1.022249244	-2.660055697
C	-2.208279097	-1.664373409	-3.381173100
C	-1.189179323	-0.875805224	-4.057524305
C	-1.359035576	0.559621603	-4.050687570
C	-0.208802242	1.429414198	-3.921435273
C	-0.597629703	2.593767378	-3.195389778
C	0.336614303	3.327974753	-2.404323603
C	-0.142425415	3.972596228	-1.235868046
C	0.676609653	4.093125558	-0.065789079
C	-0.172401810	3.959631754	1.084442955
C	0.285596572	3.315828693	2.259908565
C	-0.660239935	2.572302119	3.050140585
C	-0.303464374	1.439729925	3.885908428
C	-1.464187584	0.524365253	3.873448509
C	-1.262505966	-0.908512829	3.728359710
C	-2.186564708	-1.650719761	2.926315042
C	-1.818688542	-2.837528140	2.204217769
C	-2.645608437	-2.929881517	1.040339354
C	-2.139861315	-3.462512420	-0.177839229
C	-2.597572546	-2.873351926	-1.406324934
C	-1.775447291	-2.793607232	-2.572686522
C	1.634412328	2.860164760	2.286336006
C	2.007506745	1.652462320	2.963931687
C	1.053865662	0.917566211	3.744777430
C	1.222508032	-0.496705921	3.698093089
C	0.089517635	-1.393116435	3.705137889
C	0.468364945	-2.574007794	2.983589509
C	-0.475400125	-3.299092240	2.190919861
C	-0.017088372	-3.941654546	1.011272322
C	-0.838346452	-4.017289562	-0.163626258

C	0.010759226	-3.915692999	-1.316503011
C	-0.416780573	-3.264183388	-2.504524047
C	0.549300213	-2.537943937	-3.253097153
C	0.171438635	-1.334059088	-3.945808132
C	1.310629502	-0.450035028	-3.877006399
C	1.136376159	0.946456760	-3.828575750
C	2.095651915	1.696460111	-3.093106524
C	1.686638234	2.879639108	-2.405380451
C	2.503788588	3.025790822	-1.258171023
C	1.996455163	3.584529684	-0.051178913
C	2.480228236	3.017499281	1.163349560
C	3.474835628	1.982178056	1.172100014
C	3.137577457	1.053076714	2.259801841
C	3.298966015	-0.389010199	2.242029155
C	2.304766912	-1.128905005	2.975387518
C	1.821148301	-2.416319653	2.560169460
C	2.242544309	-2.987142836	1.334162337
C	1.336915693	-3.772567266	0.585594083
C	1.355033295	-3.762425752	-0.847993999
C	2.279963595	-2.964968426	-1.555255712
C	1.891213218	-2.387592608	-2.785983941
C	2.376348936	-1.085688020	-3.158995934
C	3.350189864	-0.353238277	-2.384368660
C	3.202517011	1.089674326	-2.381107136
C	3.503459502	1.996792900	-1.256058198
C	4.194100460	1.707649604	-0.038439460
C	4.554340908	-0.515233614	-0.061901576
C	3.919605831	-1.093336093	1.110211619
C	3.241375429	-2.268752125	0.620950940
C	3.260204746	-2.258593136	-0.801421258
C	3.949850435	-1.075873351	-1.253125838
Sc	-0.364069826	0.404365900	1.926811185
Sc	2.318887767	0.159311068	-0.064332571
N	0.400514602	0.084012277	0.173342465
C	5.326734196	0.743840323	-0.035732560
F	6.121551690	0.885605075	-1.117494192
F	6.090629887	0.855826789	1.072924572
Dy	-1.109233678	-0.229576665	-1.516236683

Optimized cartesian coordinates of conformer 2 of DySc₂N@C₈₀(CF₂)

C	-3.397197223	2.227759058	-0.716962360
C	-3.398316590	2.228066893	0.709165100
C	-3.839850369	0.933116528	1.165180081
C	-4.111725129	0.140484051	-0.003966112
C	-3.837988422	0.932543666	-1.173166282
C	-3.412370479	0.356082298	-2.420358598
C	-2.506420301	1.133272119	-3.254715023
C	-1.975549037	2.359431340	-2.690151219
C	-2.412282657	2.944444205	-1.446974516
C	-1.489854795	3.739394753	-0.720822101
C	-1.490963007	3.739654155	0.715425182
C	-2.414528041	2.945029987	1.440444753
C	-1.979658772	2.360594933	2.684558594
C	-2.511352538	1.134689557	3.248794423
C	-3.415595999	0.357130517	2.413022587
C	-3.234075903	-1.067369421	2.401070352
C	-3.492537557	-1.858093593	1.220584093
C	-3.915890209	-1.263292885	-0.003479126
C	-3.490677128	-1.858600187	-1.226691307
C	-3.230729978	-1.068530615	-2.407376816
C	-2.140870019	-1.708681152	-3.123345730
C	-1.179131202	-0.950999491	-3.873256925
C	-1.394137620	0.481566985	-3.970940570
C	-0.229056871	1.328254656	-3.811746572
C	-0.605854615	2.488354456	-3.071660078
C	0.341417079	3.241212731	-2.313790080
C	-0.130725037	3.900580971	-1.157369020
C	0.705023925	4.029067790	-0.001035151
C	-0.132519762	3.901063681	1.154052549
C	0.337836219	3.242265389	2.311523929
C	-0.610613301	2.489735141	3.068297665
C	-0.235054415	1.330059840	3.809742954
C	-1.400450707	0.483394107	3.967624550
C	-1.185259220	-0.949281035	3.870708068
C	-2.145575995	-1.707221167	3.119243105
C	-1.761443929	-2.878464750	2.374579893
C	-2.596323830	-2.970807275	1.218430100
C	-2.110398185	-3.531523114	-0.001546875
C	-2.594374337	-2.971238903	-1.222527596
C	-1.757730877	-2.879447920	-2.377431233
C	1.689331310	2.793466382	2.335064149
C	2.094754672	1.605090212	3.015489029
C	1.123113734	0.847971919	3.727800703
C	1.307863987	-0.543703506	3.768704349
C	0.166411966	-1.423700494	3.807789705
C	0.541229319	-2.617290409	3.106817051
C	-0.413511337	-3.346275861	2.342412970
C	0.032666190	-3.996890662	1.162035750
C	-0.803850073	-4.079690346	-0.000416899

C	0.034478915	-3.997361723	-1.161599247
C	-0.409846893	-3.347284363	-2.342986903
C	0.546103994	-2.618696672	-3.106226962
C	0.172402410	-1.425436401	-3.808332570
C	1.313767736	-0.545426527	-3.767941692
C	1.128964878	0.846259643	-3.727820974
C	2.099449547	1.603733126	-3.014346828
C	1.692947457	2.792403556	-2.335056125
C	2.533288384	2.953761347	-1.206642687
C	2.028602277	3.515941697	0.000101148
C	2.531453191	2.954334494	1.207893939
C	3.551818277	1.939840399	1.220256999
C	3.236555648	1.015364981	2.333102551
C	3.385656184	-0.435795622	2.322620696
C	2.385173966	-1.171809728	3.059031765
C	1.890797840	-2.466888862	2.662515178
C	2.303581131	-3.048662977	1.441986590
C	1.384009416	-3.843839562	0.718089795
C	1.385124744	-3.844163826	-0.715632393
C	2.305822053	-3.049284766	-1.438448390
C	1.894981353	-2.468096608	-2.659894435
C	2.389981076	-1.173215992	-3.056316330
C	3.389163159	-0.436842813	-2.318559254
C	3.240107597	1.014288881	-2.329906852
C	3.553587026	1.939172377	-1.216928408
C	4.253998804	1.661213369	0.002230339
C	4.591847195	-0.582180680	0.002987357
C	3.985450990	-1.155499049	1.185208435
C	3.306534749	-2.341756970	0.714594212
C	3.307593090	-2.342022700	-0.709787789
C	3.987173970	-1.155949853	-1.179839408
Sc	-1.181688326	0.132429125	1.745392588
Sc	-1.181413019	0.131153789	-1.747330122
N	-0.334688752	0.119164415	-0.000901261
C	5.362685661	0.674788741	0.003319906
F	6.143881820	0.794573043	-1.093226219
F	6.142147788	0.795048163	1.101045882
Dy	1.969564575	0.129207689	0.001174991

Table S1. Relative energy (in cm^{-1}) of the lowest Kramers doublets in $\text{DySc}_2\text{N@C}_{80}\text{CF}_2$ (conformer 1) depending on the selection of states for the SOC-CI computation.

Kramers doublet	Sextet states only	Sextet + quartet states	Sextet + octet states	Sextet + quartet + octet states
1	0	0	0	0
2	413	411	418	411
3	709	707	715	707
4	932	929	938	929
5	1090	1088	1097	1088
6	1210	1207	1218	1207
7	1293	1285	1301	1285
8	1386	1377	1396	1378

Table S2. XMCQDPT2 vs CASSCF relative energy (cm^{-1}) of the lowest Kramers doublets in the two conformers of $\text{DySc}_2\text{N@C}_{80}\text{CF}_2$, M_S value, and spin magnetization angles with respect to the Dy-N bond.

Kramers doublet	Sc- CF_2 conformer				Dy- CF_2 conformer			
	CASSCF	XMCQDPT2	M_S	Angle, deg.	CASSCF	XMCQDPT2	M_S	Angle, deg.
1	0	0	2.25	7.4	0	0	2.41	0.3
2	411	493	1.53	9.6	255	315	1.62	2.2
3	707	839	1.20	9.2	503	606	1.48	1.2
4	929	1091	0.86	5.7	706	844	1.12	3.5
5	1088	1270	0.98	8.0	845	1003	0.98	8.8
6	1207	1405	0.15	31.7	928	1094	0.97	36.4
7	1285	1500	1.02	18.2	991	1156	1.64	44.7
8	1378	1604	2.29	12.9	1006	1196	1.96	42.8

Table S3. A survey of the relative energy estimates (w.r.t. the ground state) for some types of electronic states in DySc₂N@C₈₀(CF₂) (see the main text for more detail)

Type of the state	Relative energy
4f ⁹ sextet states of Dy ³⁺ and the ground state of the fullerene subunit	0 – 4 eV
4f ⁹ quartet states of Dy ³⁺ and the ground state of the fullerene subunit	from ca. 3.0 eV
4f ⁸ 5d ¹ states of Dy ³⁺	from ca. 4.3 eV
Lowest excitations in the fullerene subunit	from ca. 1.5 eV
Excitations from the fullerene subunit into the 4f-shell (4f ¹⁰)	from ca. 4 eV
Excitations from the 4f-shell into the fullerene subunit (4f ⁸)	above 5 eV