Supporting Information for

Structural and electrochemical studies of Sm@D_{3h}-C_{74} reveal a weak metal-cage interaction and a small band gap species

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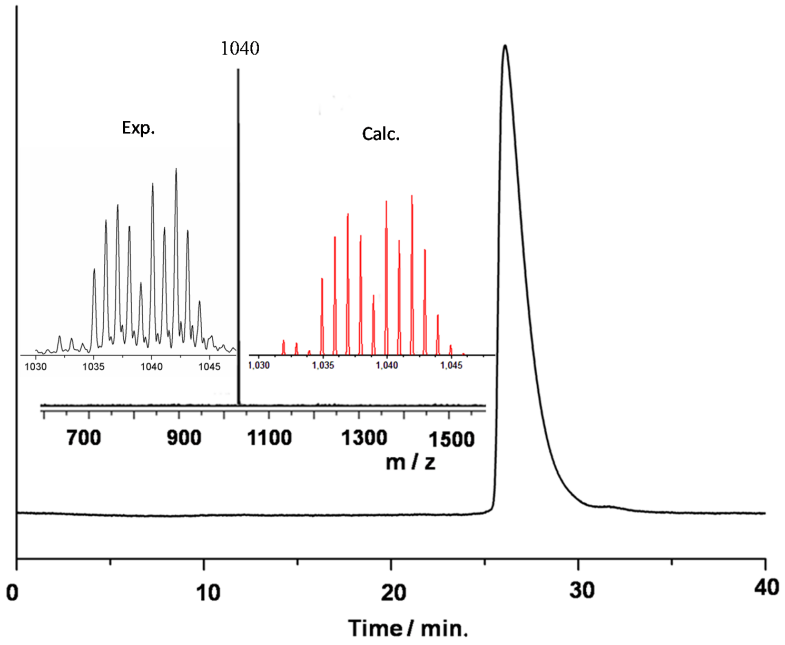

Fig. S1 HPLC profile of the isolated Sm@C_{74} on Buckyprep column (Cosmosil, Ø25×250 mm) using toluene as eluent (flow rate: 12 mL/min; detection wavelength: 330 nm). The inset shows MALDI-TOF mass spectra of the purified sample of Sm@C_{74}.

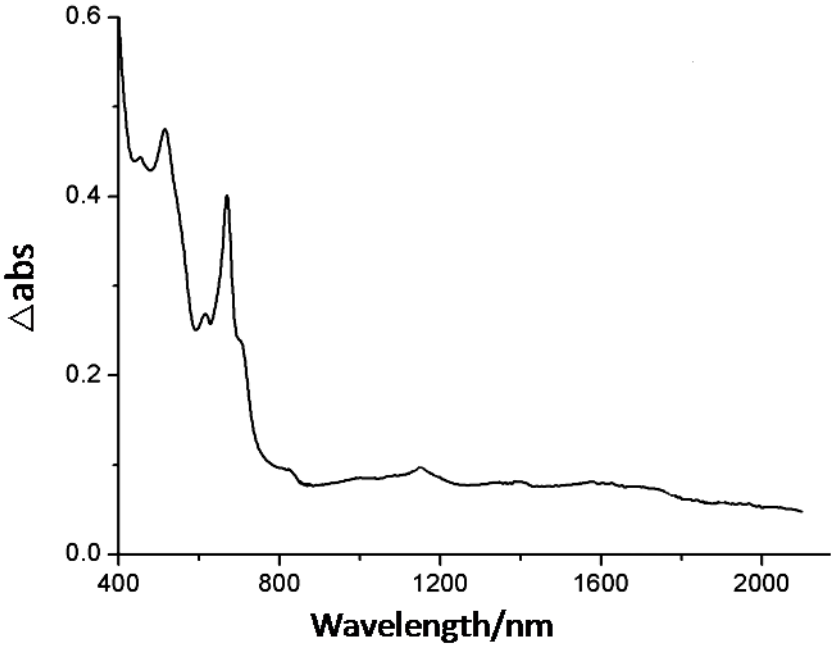

Fig. S2 UV-VIS-NIR spectrum of Sm@C_{74} in toluene.

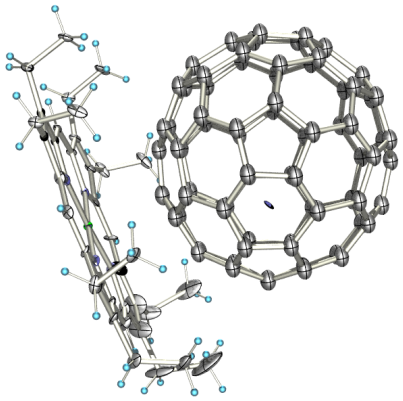

Fig. S3 Ortep drawing of Sm@D_{3h}-C_{74}•Ni^{II}(OEP) with 25 % thermal ellipsoids, showing the intermolecular interaction. The Sm site with second highest occupancy of 0.221 and the minor cage position with fractional occupancy of 0.327 are depicted. The solvent molecules are omitted for clarity.

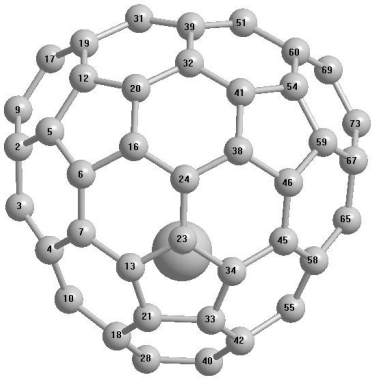

Fig. S4 DFT-optimized Sm@D_{3h}-C_{74}, each atom was labeled by a serial number.

Table S1. A list of Mulliken charges on the cage carbons of Sm@D_{3h}-C_{74}. The Mulliken charges on the pyracylene motif which is close to the Sm atom are highlighted by color.

Serial No.	Mulliken charge	Serial No.	Mulliken charge	Serial No.	Mulliken charge	Serial No.	Mulliken charge
2	-0.00029	**21**	**-0.09391**	**40**	**-0.1162**	59	-0.01332
3	0.007126	22	-0.01332	41	0.013551	60	-0.00498
4	-0.05551	23	-0.03595	**42**	**-0.08413**	61	-0.06905
5	-0.01332	24	-0.03383	43	0.013551	62	0.013551
6	0.020192	**25**	**-0.08413**	44	-0.02045	63	-0.02045
7	-0.07081	26	-0.07081	45	-0.07081	64	-0.07081
8	0.007126	27	-0.00498	46	0.020192	65	0.007126
9	-0.01541	**28**	**-0.1162**	**47**	**-0.09391**	66	-0.00498
10	-0.06905	29	-0.00681	48	-0.03595	67	-0.00029
11	-0.00029	30	0.020192	**49**	**-0.08413**	68	-0.05551
12	-0.00681	31	0.006584	50	-0.02614	69	-0.00712
13	-0.00267	32	-0.03725	51	0.006584	70	-0.00681
14	-0.05551	**33**	**-0.09391**	52	-0.03383	71	0.020192
15	-0.06905	34	-0.00267	53	-0.03725	72	0.007126
16	-0.02045	**35**	**-0.09391**	54	-0.00681	73	-0.01541
17	-0.00712	36	-0.00267	55	-0.06905	74	-0.01332
18	**-0.08413**	37	0.006584	56	0.006584	75	-0.00029
19	-0.00498	38	-0.02045	57	-0.00267		
20	0.013551	39	-0.02614	58	-0.05551		

Table S2 *xyz*-file of DFT-optimized pristine Sm@D_{3h}-C_{74}

Sm	0.000000	0.000000	1.450582
C	-3.885880	1.167234	-0.799485
C	-3.794977	0.721883	0.583395
C	-3.068274	1.452031	1.551689
C	-3.166414	2.285088	-1.186873
C	-2.405103	3.046912	-0.227040
C	-2.343216	2.662593	1.127216
C	-3.794977	-0.721883	0.583395
C	-3.923728	0.000000	-1.654543
C	-2.575616	0.712439	2.673238

C	-3.885880	-1.167234	-0.799485
C	-2.435734	2.284458	-2.447605
C	-1.176606	3.027347	1.874226
C	-3.068274	-1.452031	1.551689
C	-2.575616	-0.712439	2.673238
C	-1.215566	3.529993	-0.913796
C	-3.222186	0.000000	-2.864583
C	-1.430310	1.160771	3.477655
C	-2.451877	1.163504	-3.248463
C	-1.214076	3.048098	-2.262277
C	-0.735174	2.285867	3.020327
C	-3.166414	-2.285088	-1.186873
C	0.000000	3.495061	1.190216
C	0.000000	3.726919	-0.211592
C	-1.430310	-1.160771	3.477655
C	-2.343216	-2.662593	1.127216
C	-2.451877	-1.163504	-3.248463
C	-0.723129	0.000000	3.983047
C	-2.435734	-2.284458	-2.447605
C	-2.405103	-3.046912	-0.227040
C	-1.203393	0.714089	-3.873876
C	0.000000	2.668329	-2.895217
C	0.735174	2.285867	3.020327
C	1.176606	3.027347	1.874226
C	-0.735174	-2.285867	3.020327
C	-1.176606	-3.027347	1.874226
C	-1.203393	-0.714089	-3.873876
C	1.215566	3.529993	-0.913796
C	0.000000	1.452445	-3.738662
C	0.723129	0.000000	3.983047
C	1.214076	3.048098	-2.262277
C	1.430310	1.160771	3.477655
C	-1.214076	-3.048098	-2.262277
C	-1.215566	-3.529993	-0.913796
C	2.343216	2.662593	1.127216
C	2.405103	3.046912	-0.227040
C	0.735174	-2.285867	3.020327

C	0.000000	-3.495061	1.190216
C	1.430310	-1.160771	3.477655
C	0.000000	-1.452445	-3.738662
C	1.203393	0.714089	-3.873876
C	0.000000	-3.726919	-0.211592
C	0.000000	-2.668329	-2.895217
C	2.435734	2.284458	-2.447605
C	2.575616	0.712439	2.673238
C	1.203393	-0.714089	-3.873876
C	1.176606	-3.027347	1.874226
C	3.068274	1.452031	1.551689
C	3.166414	2.285088	-1.186873
C	2.451877	1.163504	-3.248463
C	2.575616	-0.712439	2.673238
C	1.214076	-3.048098	-2.262277
C	1.215566	-3.529993	-0.913796
C	2.343216	-2.662593	1.127216
C	3.794977	0.721883	0.583395
C	2.451877	-1.163504	-3.248463
C	3.885880	1.167234	-0.799485
C	3.068274	-1.452031	1.551689
C	3.222186	0.000000	-2.864583
C	2.435734	-2.284458	-2.447605
C	2.405103	-3.046912	-0.227040
C	3.794977	-0.721883	0.583395
C	3.923728	0.000000	-1.654543
C	3.166414	-2.285088	-1.186873
C	3.885880	-1.167234	-0.799485

Table S3 *xyz*-file of DFT-optimized Sm@D_{3h}-C_{74}/[Ni^{II}(OEP)] with lowest formation energy

H	-1.757807	-5.147197	4.336635
H	-1.618293	-1.000069	6.639233
C	-1.970907	-4.584090	3.423070
H	-1.329549	-4.958786	2.619123
H	-3.681273	-5.769612	2.786245
H	-1.720491	-3.529258	3.589607

H	-4.106778	-4.424595	3.843439
C	-1.881748	-0.601702	5.654849
C	-3.458354	-4.721253	3.010976
H	-4.022599	-0.986934	5.835232
H	-1.710214	-1.378953	4.902716
C	3.622783	0.189241	3.836159
C	2.835132	-1.026492	3.687554
H	-3.529334	0.609775	6.400268
H	-1.221865	0.241540	5.424398
C	3.268360	-2.094464	2.866868
C	-3.361697	-0.138966	5.618927
C	4.778208	0.330673	3.085537
C	5.242652	-0.734945	2.230100
C	4.522398	-1.940052	2.107040
C	1.440953	-0.662352	3.766093
C	2.716331	1.307027	3.985515
H	-3.763119	-2.230477	3.951304
H	-3.644931	-6.353606	0.648133
C	2.251002	-2.954680	2.347608
C	1.367313	0.781015	3.959891
H	-1.324044	-5.430323	0.198537
C	5.076248	1.597887	2.432969
C	4.645979	-2.670806	0.881706
C	0.462794	-1.360854	3.021072
C	0.873756	-2.595445	2.422525
C	-3.742920	-3.872145	1.805637
C	5.846182	-0.111565	1.061774
C	3.003771	2.524581	3.358406
H	-1.787076	-6.663054	-0.999810
C	2.439539	-3.761284	1.132498
C	-3.864169	-1.693751	3.014695
C	4.199057	2.654192	2.554071
C	-3.477776	-5.580510	-0.109301
C	-2.015815	-5.663332	-0.618459
C	5.725236	1.312448	1.165385
C	-3.690183	0.455000	4.279642
H	-3.718129	2.739276	5.825904

C	3.620668	-3.558081	0.409893
H	-1.368596	2.699639	4.962837
C	0.363588	1.488190	3.318540
C	-3.752294	-4.230811	0.489412
C	5.234096	-2.047203	-0.273446
C	-3.926549	-2.429216	1.850911
C	5.816081	-0.752803	-0.201837
H	-4.171114	-5.780723	-0.934838
C	0.198536	-3.174382	1.251742
C	-3.871537	-0.317819	3.058623
C	-0.621587	-0.590281	2.384438
H	-1.884104	4.385393	5.214685
C	1.952256	3.246324	2.673833
C	1.165864	-3.910196	0.457447
H	-1.851676	-4.936446	-1.420284
C	-2.058844	3.479247	4.626740
C	-3.518342	2.984147	4.777391
C	0.664191	2.758096	2.665172
C	-3.742970	1.769746	3.924304
C	-0.653756	0.813196	2.548598
C	3.883336	3.459846	1.369777
C	5.478484	2.104635	0.012287
C	3.571249	-3.454512	-1.053960
C	4.565318	-2.504986	-1.463436
H	-4.216760	3.779949	4.493031
C	-0.798476	-2.405088	0.646156
C	-3.951790	-3.008321	-0.276703
C	-1.177592	-1.132898	1.188716
N	-4.051272	-1.914048	0.569567
H	-1.837152	3.690052	3.574169
C	2.503055	3.822028	1.442750
C	5.763451	0.060655	-1.361713
C	4.519894	3.226316	0.124312
Sm	1.774305	-1.411058	-0.123250
C	1.115500	-3.808838	-0.985905
N	-4.003114	0.523537	1.963664
C	5.642303	1.483263	-1.255403

C	-3.939945	1.808293	2.481858
C	2.342954	-3.562215	-1.718946
C	-0.166498	2.864462	1.479340
C	-0.978155	1.681372	1.427444
H	-3.863346	-3.894915	-2.195019
C	-3.953647	-2.959151	-1.654391
C	4.363065	-1.609063	-2.562844
C	5.079397	-0.395527	-2.563902
C	-0.849062	-2.299492	-0.824084
C	-1.477323	-0.271310	0.082952
C	0.099841	-2.976297	-1.602814
C	1.713331	3.962565	0.272368
Ni	-4.138051	0.004371	0.050328
C	3.800015	3.628628	-1.030121
C	-1.360368	1.137427	0.178334
C	0.322490	3.458791	0.284175
C	-3.985202	2.972483	1.748004
C	4.909382	1.940975	-2.423448
H	-3.914668	3.912923	2.282751
H	-1.817848	-3.557085	-3.481177
C	2.076937	-2.593803	-2.790514
C	2.420704	3.990483	-0.957412
C	-1.258505	-0.969832	-1.153718
C	3.060844	-1.661681	-3.250999
C	4.562883	0.776619	-3.226719
C	4.030448	2.998456	-2.334653
C	-4.009983	-1.793279	-2.387073
C	0.699535	-2.232868	-2.718270
H	-1.789433	-4.206251	-5.139883
H	-4.170489	-3.779923	-4.409220
C	-2.037429	-3.331592	-4.531013
N	-4.136618	-0.513537	-1.867547
C	-0.254011	3.037475	-0.947590
C	-4.070556	3.017664	0.373409
C	-1.057281	1.853172	-1.004544
H	-1.975405	4.997820	1.333888
N	-4.174738	1.921011	-0.468479

C	-0.784826	-0.262421	-2.300875
C	2.578497	-0.491989	-3.882053
C	1.783327	3.590498	-2.217347
C	-3.527131	-2.936820	-4.686876
H	-1.400847	-2.494588	-4.835032
C	3.358324	0.736226	-3.909798
C	0.254302	-0.927697	-3.107608
C	2.782467	2.977243	-3.066307
C	-3.831369	-1.742669	-3.829865
C	0.496184	3.101070	-2.190550
C	-0.811358	1.149866	-2.255984
H	-4.387396	5.754789	1.070539
C	1.182081	-0.126557	-3.811951
C	-2.254573	5.767336	0.606146
H	-2.068445	6.753768	1.041579
C	2.448128	1.859085	-3.838616
C	-4.063492	0.334094	-2.962409
H	-3.737527	-2.701082	-5.735289
C	0.145771	1.934965	-2.995696
C	-3.973468	4.248959	-0.397833
C	1.101636	1.327899	-3.795819
C	-4.137390	2.442959	-1.752664
C	-3.740182	5.607185	0.197770
H	-1.614255	5.637685	-0.271829
C	-3.855835	-0.425645	-4.185106
C	-4.103446	1.710268	-2.917274
C	-4.011336	3.892372	-1.712833
H	-4.005255	6.377005	-0.534773
H	-1.412888	-0.117534	-5.364187
H	-4.051320	2.250021	-3.856107
C	-3.567116	0.185377	-5.525842
H	-3.716285	-0.564701	-6.309658
H	-1.655993	4.986375	-2.583937
H	-1.952966	1.474164	-4.809922
C	-2.106384	0.704376	-5.572895
H	-2.064263	3.595408	-3.594422
H	-4.261822	1.008988	-5.729403

C	-3.793910	4.751570	-2.923889
C	-2.317664	4.640991	-3.383900
H	-4.027152	5.794273	-2.683833
H	-4.465528	4.447052	-3.735013
H	-1.868811	1.126578	-6.553917
H	-2.134618	5.238536	-4.282047