Electronic Supplementary Information

Unexpected Formation of 1,2- and 1,4-Bismethoxyl $Sc_3N@I_h$-C_{80} Derivatives via Regioselective Anion Addition: Unambiguous Structural Identification and Mechanism Study

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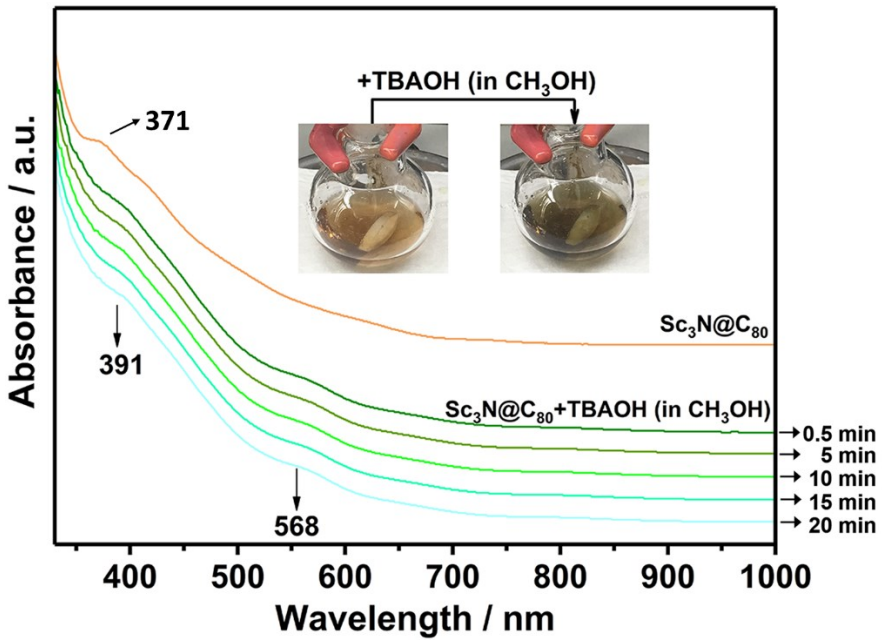

Fig. S1 In-situ UV−vis−NIR spectra of the reaction mixture of $Sc_3N@I_h$-C_{80} with TBAOH (in CH_3OH) in *o*-DCB probed at different times.

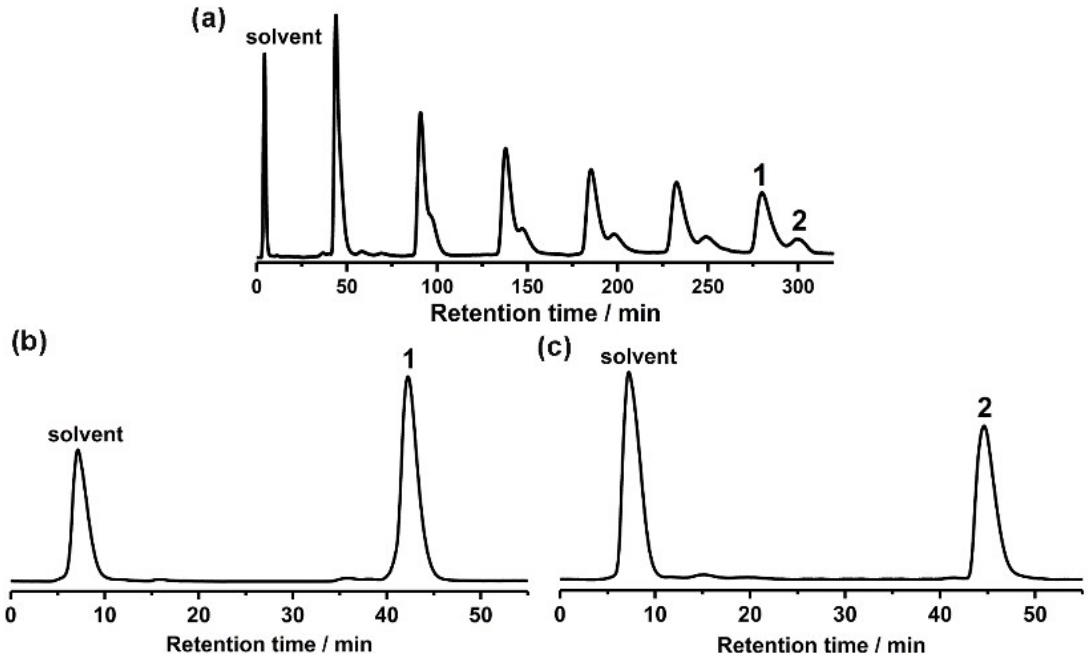

Fig. S2 (a) Recycling HPLC profile of the products isolated from Buckyprep column. HPLC profiles of pure **1** (b) and **2** (c). Conditions: 5PBB column (φ 10 × 250 mm); eluent: toluene, 5 ml/min.

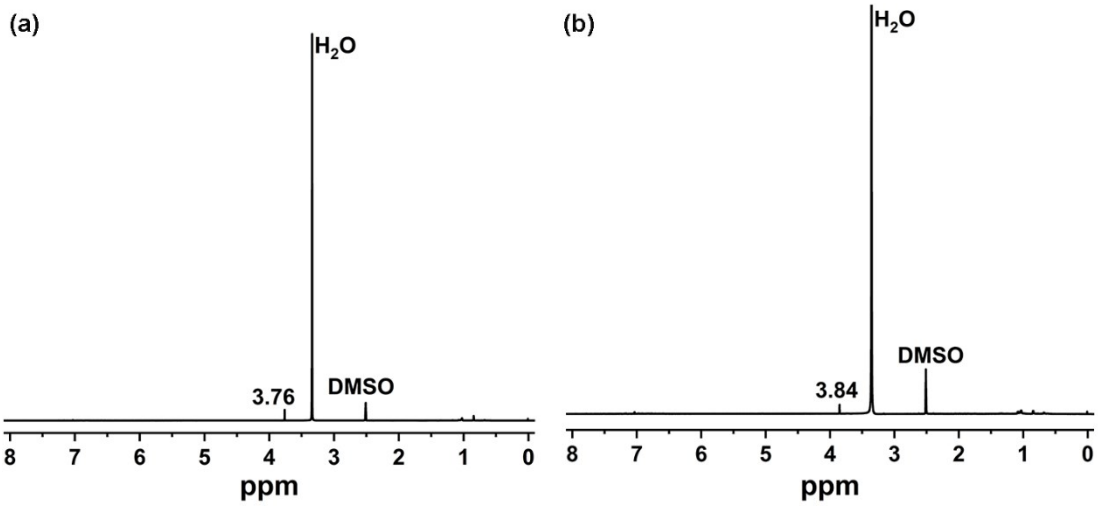

Fig. S3 Full ^{1}H NMR spectra of (a) **1** and (b) **2** in CS_2 with DMSO-d_6 as the external lock solvent.

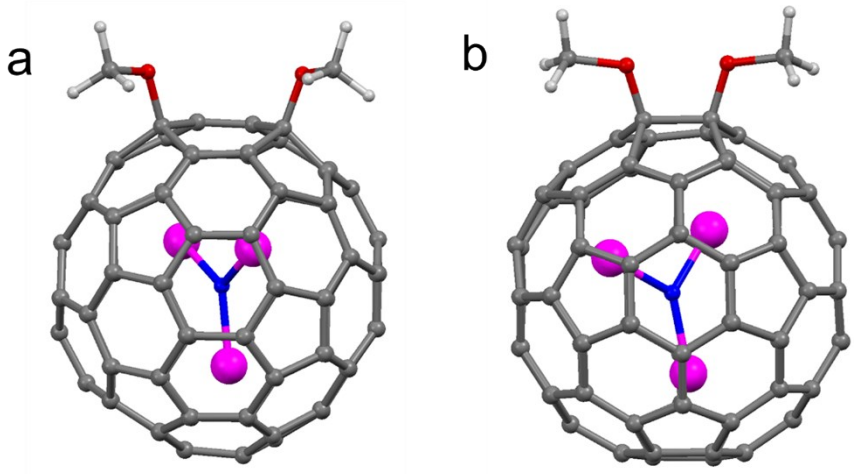

Fig. S4 DFT optimized structures of **1** (a) and **2** (b) without the DPC molecules.

2. Optimized xyz coordinates 1 and 2.

1,4-$Sc_3N@C_{80}(OCH_3)_2$

Sc	-0.033719	-0.187312	1.964982
Sc	-1.460288	-0.045301	-1.218201
Sc	1.954909	0.375612	-0.862505
N	0.153829	0.059650	-0.021709
C	-3.157906	2.396450	-0.135094
C	-3.613790	1.288855	-0.917982
C	-3.138929	1.176877	-2.276167
C	4.174230	0.023312	-1.320799
C	-2.982320	2.282841	1.289389
C	-2.361390	0.714837	3.046320
C	-3.227734	1.048684	1.952493
C	-3.767363	-0.039122	1.207301
C	-3.691219	-1.218144	-0.809742
C	-3.173802	-1.351537	-2.145638
C	-2.953476	-0.138234	-2.918707
C	-2.235576	-2.420494	-2.307111
C	-3.360015	-2.135379	0.260368
C	-1.590188	-3.574906	1.148685
C	-2.426579	-3.196786	0.057007
C	-1.895859	-3.344753	-1.260790
C	-2.022653	-0.642952	3.385930
C	-2.501969	-1.724209	2.555882
C	-3.411322	-1.405655	1.499288
C	-1.627095	-2.831389	2.373724
C	0.599919	2.791717	-3.009234
C	0.138984	1.678939	-3.764905
C	-1.746803	-0.022063	-3.719586
C	-1.363248	1.459238	-3.921016
C	-0.248720	3.549810	-2.133046
C	-2.174444	3.321540	-0.637364
C	-1.600560	3.129407	-1.929822
C	-2.108740	2.059888	-2.725896
C	0.869281	3.794381	1.409957
C	-0.000220	4.069742	0.312551
C	0.542211	3.989768	-1.011904
C	-1.389381	3.781759	0.473202
C	2.031717	-0.005869	3.611559
C	0.189509	-1.730719	3.753187
C	1.572589	-1.383124	3.568262
C	-0.285793	-2.803697	2.929604
C	3.179343	0.110820	2.748919
C	3.962098	1.178889	0.709093
C	3.419634	1.319902	2.033827
C	2.566820	2.431494	2.264071
C	3.501930	-2.434750	0.066571
C	3.925335	-1.318298	0.835273
C	3.429502	-1.184173	2.167222
C	4.239923	-0.103435	0.121386
C	0.573007	-3.537082	2.028792
C	1.940658	-3.171017	1.853044
C	2.437539	-2.101305	2.661235
C	2.521013	-3.360525	0.563245
C	-0.225250	-3.998703	0.926543
C	-0.541217	-3.785512	-1.490327
C	0.326538	-4.080903	-0.386000
C	1.716084	-3.796715	-0.548826
C	3.670607	2.104734	-0.348019
C	2.730552	3.178411	-0.116349
C	2.227965	3.350267	1.202682
C	1.890039	3.541799	-1.209546
C	0.374387	3.159399	2.600762
C	-0.992235	2.780572	2.715194
C	-1.881974	3.137421	1.663828
C	-1.273840	1.562701	3.437473
C	1.417473	2.310310	3.129390
C	-0.735528	-0.647904	4.065934
C	1.124753	1.084806	3.811370
C	-0.261271	0.748149	4.072129
C	3.822574	1.417856	-1.621562
C	2.334099	0.616920	-3.429767
C	2.845194	1.709258	-2.659812
C	1.925574	2.783326	-2.439132
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C	2.696271	-0.767240	-3.145589
C	3.578664	-1.079582	-2.057016
C	-3.933454	0.079607	-0.217904
C	-0.052449	-3.170922	-2.689044
C	1.639311	-1.622629	-3.547791
C	1.328447	-2.781959	-2.807858
C	2.201482	-3.147684	-1.736263
C	-1.081647	-2.301764	-3.180128

C	1.021764	0.634078	-3.994468
C	-0.817091	-1.068039	-3.816725
C	0.597396	-0.796203	-4.328062
O	0.679188	-0.957329	-5.767758
C	0.415679	-2.308860	-6.217258
H	0.595215	-2.301453	-7.297154
H	1.096887	-3.025436	-5.734077
H	-0.627420	-2.597353	-6.017986
O	-1.718353	2.015363	-5.212682
C	-3.122774	1.910319	-5.542275
H	-3.433741	0.856920	-5.616093
H	-3.747549	2.429025	-4.799427
H	-3.235913	2.395874	-6.516822

1,2-$Sc_3N@C_{80}(OCH_3)_2$

Sc	-0.034044	-0.225849	1.940453
Sc	-1.318269	-0.250176	-1.403885
Sc	1.417517	1.356357	-0.968644
N	0.045140	0.206388	-0.016279
C	-3.148777	2.425830	-0.119115
C	-3.592976	1.310265	-0.896255
C	-3.097872	1.163062	-2.244732
C	4.065720	-0.042090	-1.254027
C	-2.960492	2.295370	1.303091
C	-2.357172	0.709291	3.041395
C	-3.221688	1.058363	1.955215
C	-3.779600	-0.022359	1.204039
C	-3.703537	-1.192733	-0.823490
C	-3.208785	-1.346913	-2.169128
C	-2.956776	-0.125981	-2.928388
C	-2.266511	-2.419851	-2.331056
C	-3.371129	-2.111938	0.241870
C	-1.623624	-3.585614	1.131572
C	-2.450095	-3.187475	0.038995
C	-1.919350	-3.331963	-1.278889
C	-2.032921	-0.654889	3.375345
C	-2.517848	-1.724242	2.538282
C	-3.427199	-1.392339	1.486200
C	-1.655105	-2.842373	2.358347
C	0.696689	2.726316	-2.957232
C	0.197262	1.624906	-3.710102
C	-1.726240	-0.025803	-3.728503
C	-1.174700	1.308048	-3.563242
C	-0.166611	3.431631	-2.037355
C	-2.138850	3.331565	-0.609598
C	-1.542545	3.111186	-1.875959
C	-2.033310	2.029951	-2.670234
C	0.921633	3.775101	1.458620
C	0.057586	4.041181	0.359197
C	0.629399	3.918679	-0.957554
C	-1.337251	3.771312	0.500898
C	2.030086	-0.063387	3.618011
C	0.170584	-1.767209	3.745383
C	1.557028	-1.435297	3.572732
C	-0.316250	-2.830682	2.916495
C	3.182038	0.043781	2.761635
C	4.036047	1.127292	0.751586
C	3.450256	1.254611	2.048018
C	2.595285	2.373086	2.284821
C	3.492295	-2.486488	0.071671
C	3.926541	-1.376562	0.845955
C	3.415337	-1.249514	2.176678
C	4.261629	-0.163674	0.161901
C	0.538255	-3.571412	2.016403
C	1.914123	-3.220870	1.849876
C	2.419326	-2.159400	2.666379
C	2.496563	-3.400213	0.564193
C	-0.262808	-4.023370	0.915313
C	-0.560533	-3.790251	-1.502936
C	0.295891	-4.102335	-0.396166
C	1.683592	-3.821742	-0.552881
C	3.727530	2.062359	-0.310129
C	2.820124	3.162129	-0.089001
C	2.271178	3.303483	1.232773
C	2.015605	3.573483	-1.216687
C	0.413258	3.130710	2.638536
C	-0.960860	2.760411	2.736211
C	-1.846975	3.130208	1.687451
C	-1.260968	1.541705	3.442578
C	1.445571	2.262937	3.151089
C	-0.744955	-0.677211	4.050901
C	1.132465	1.032709	3.817188
C	-0.255961	0.709701	4.064064
C	3.765448	1.337972	-1.567878
C	2.373103	0.591476	-3.425380
C	2.916876	1.681821	-2.689505
C	2.072929	2.869485	-2.511386
C	3.292874	-2.353321	-1.353703
C	2.664482	-0.784542	-3.113880
C	3.524930	-1.123841	-2.010187
C	-3.946221	0.105432	-0.213787
C	-0.056061	-3.178262	-2.686693
C	1.645392	-1.640851	-3.563673

C	1.322727	-2.800766	-2.807951
C	2.183081	-3.180668	-1.737482
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C	1.168359	0.664745	-4.359647
C	-0.794742	-1.090994	-3.847422
C	0.626428	-0.876284	-4.410016
O	0.579813	-1.257606	-5.799743
O	1.495095	1.023620	-5.714786
C	2.072655	2.337400	-5.877449
H	1.369865	3.129758	-5.579186
H	3.007987	2.437533	-5.306516
H	2.289021	2.427488	-6.946868
C	0.482320	-2.677411	-6.049856
H	0.490478	-2.776786	-7.140094
H	1.340234	-3.215486	-5.621260
H	-0.453808	-3.099435	-5.653176