Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Unprecedented photochemical rearrangement of an open-cage C_{60} derivative

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1. General

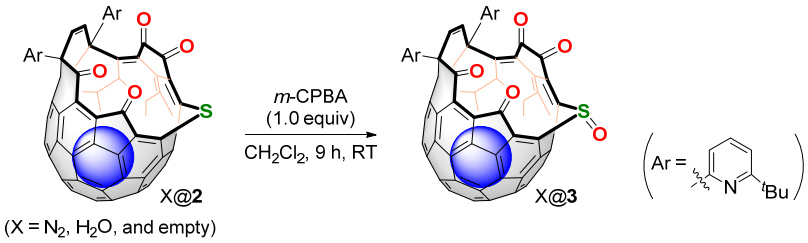
The ^{1}H and ^{13}C NMR measurements were carried out with a Jeol JNM ECA500 and a Bruker Advance III 800US instruments. The NMR chemical shifts are reported in ppm with reference to residual protons and carbons of $CDCl_3$ (δ 7.26 ppm in ^{1}H NMR and δ 77.0 ppm in ^{13}C NMR), CD_2Cl_2 (δ 5.32 ppm in ^{1}H NMR and δ 53.8 ppm in ^{13}C NMR). APCI mass spectra were measured on a Bruker micrOTOF-QII. The high-performance liquid chromatography (HPLC) was performed with the use of a Cosmosil Buckyprep column (250 mm length, 4.6 mm inner diameter) for analytical purpose, and the same columns (two directly connected columns; 250 mm length, 20 mm inner diameter) for preparative purpose.

2. Computational Method

All calculations were conducted with Gaussian 09 packages. The structure was optimized at the M06-2X/6-31G* levels without any symmetry assumptions. The optimized structures including the stationary states and the transition states were confirmed by the frequency calculations at the same level. The required Gibbs energy for the insertion of N_2 into lactone **4'** is calculated by subtracting total energies of **4'** (–2029667.27 kcal/mol) and N_2 (–68712.34 kcal/mol) from that of the transition state (–2098303.85 kcal/mol).

3. Synthesis of Open-Cage Fullerene Derivatives 3 and 4

A mixture of sulfoxides N_2@3, H_2O@3, and empty 3

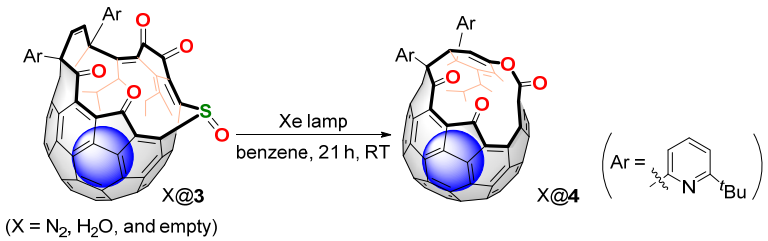


Open-cage fullerene derivative **2** (200 mg, 174 μmol, determined as a mixture of N_2@**2** (20%), H_2O@**2** (40%), and empty **2** (40%)) and *m*-chloroperbenzoic acid with a 77% purity (39.5 mg, 176 μmol) in 20 ml of CH_2Cl_2 were stirred at room temperature for 9 hours under nitrogen atmosphere. To the solution was added sat. $NaHCO_3$ aq. (20 mL), and the organic layer was separated. The aqueous layer was extracted with toluene three times (15 mL × 3). The combined organic layer was washed with brine (30 mL), dried over Na_2SO_4, and filtered. The resulting solution was evaporated under reduced pressure to give open-cage fullerene derivative **3** (168 mg, 144 μmol, determined as a mixture of N_2@**3** (22%), H_2O@**3** (55%), and empty **3** (23%)) in 83% yield as a brown solid.

A mixture of N_2@**3**, H_2O@**3**, and empty **3**: Most signals corresponding to N_2@**3**, H_2O@**3**, and empty **3** were observed separately in the following NMR spectra; ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.65 (t, J = 7.9 Hz, 1H), 7.63 (t, J = 7.9 Hz, 1H), 7.27 (d, J = 7.9 Hz, 1H), 7.25 (d, J = 7.9 Hz, 2H), 7.22 (d, J = 7.9 Hz, 1H), 7.183, 7.179 and 7.167 (three sets of doublet, J = 10.3 Hz, 1H), 6.70 and 6.69 (d, J = 10.3 Hz, 0.8H and 0.2H), 1.189, 1.185 and 1.181 (three sets of singlet, 9H), 1.162, 1.160, and 1.156 (three sets of singlet, 9H), −10.31 (bs, 1.1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.82, 190.78, 190.66, 185.30, 185.20, 183.72, 181.02, 180.96, 168.72, 168.69, 168.35, 163.13, 163.10, 162.94, 161.82, 161.68, 156.41, 156.27, 156.22, 155.87, 155.84, 155.66, 150.88, 150.86, 150.81, 150.75, 150.68, 150.62, 150.57, 150.48, 150.31, 150.28, 150.22, 150.12, 150.06, 149.98, 149.87, 149.82, 149.79, 149.72, 149.69, 149.66, 149.61, 149.57, 149.47, 149.40, 149.36, 149.29, 149.22, 149.15, 149.10, 149.07, 148.94, 148.89, 148.78, 148.68, 148.53, 147.78, 147.68, 147.56, 147.38, 147.36, 147.34, 147.29, 147.16, 147.02, 146.97, 146.92, 146.90, 145.35, 145.30, 145.23, 145.13, 145.08, 144.77, 144.72, 144.69, 144.67, 144.04, 144.00, 143.97, 143.93, 143.89, 143.84, 143.78, 143.73, 143.34, 143.24, 143.20, 143.14, 143.10, 142.86, 142.83, 141.93, 141.83, 141.23, 141.18, 141.07, 140.95, 140.63, 140.58, 140.55, 140.44, 139.92, 139.78, 139.33, 139.28, 139.19, 139.08, 139.05, 138.71, 138.59, 138.54, 138.44, 138.37, 138.32, 138.04, 137.85, 137.77, 137.72, 137.66, 137.60, 137.51, 137.38, 137.29, 137.23, 137.16, 137.09, 137.03, 137.01, 136.96, 136.89, 136.86, 136.81, 136.67, 136.63, 136.57, 136.55, 136.47, 136.40, 136.25, 136.18, 135.16, 134.80, 134.66, 134.36, 134.30, 133.43, 133.27, 133.17, 133.10, 132.88, 132.79, 132.75, 132.72, 132.63, 132.47, 131.96, 131.15, 131.00, 130.82, 130.23, 128.95, 128.35, 128.20, 128.18, 128.13, 128.06, 128.00, 127.00, 126.86, 126.73, 126.68, 126.45, 126.41, 126.18, 126.01, 125.96, 125.21, 120.04, 119.50, 117.62, 117.59, 117.40, 117.37, 59.67, 59.58, 54.73, 54.69, 37.64, 37.59, 29.81; HRMS

(+APCI), calcd for $C_{82}H_{27}N_2O_5S$ ($M+H^{+\bullet}$) 1151.1635, found 1151.1586.

A mixture of lactones N_2@4, H_2O@4, and empty 4



A stirred solution of open-cage fullerene derivative **3** (50.3 mg, 43.2 μmol, determined as a mixture of N_2@**3** (20%), H_2O@**3** (38%), and empty **3** (42%)) in 15 mL of benzene was irradiated with a Xe lamp (500 W) from a distance of 15 cm at room temperature for 11 hours under nitrogen atmosphere. To the solution was added 35 mL of benzene and further irradiation was conducted for 10 h. After removal of the solvent under reduced pressure, the residual brown solid was purified by silica gel column chromatography (toluene/acetone = 20:1) and the following HPLC to give open-cage fullerene derivative **4** (6.1 mg, 5.5 μmol, determined as a mixture of N_2@**4** (20%), H_2O@**4** (38%), and empty **4** (42%)) in 13% yield as a brown solid. The empty material was obtained after recycling HPLC for the characterization.

empty **4**: ^{1}H NMR (800 MHz, CD_2Cl_2) δ 7.76 (t, J = 7.8 Hz, 1H), 7.70 (dd, J = 7.8, 0.7 Hz, 1H), 7.62 (t, J = 7.9 Hz, 1H), 7.40 (dd, J = 7.8, 0.7 Hz, 1H), 7.34 (d, J = 6.1 Hz, 1H), 7.33 (dd, J = 7.8, 0.7 Hz, 1H), 7.22 (dd, J = 7.9, 0.7 Hz, 1H), 5.78 (d, J = 6.1 Hz, 1H), 1.26 (s, 9H), 1.05 (s, 9H); ^{13}C NMR (201 MHz, CD_2Cl_2) δ 194.14, 187.63, 169.97, 169.32, 162.92, 161.53, 159.82, 156.70, 149.87, 149.79, 149.61, 149.60, 149.54, 149.53, 149.28, 149.09, 148.58, 147.81, 147.59, 147.54, 147.40, 147.16, 147.14, 145.84, 145.51, 145.43, 145.20, 145.06, 144.70, 144.66, 144.61, 144.50, 144.41, 144.21, 144.20, 143.45, 143.06, 142.97, 142.81, 141.96, 141.86, 140.54, 140.11, 139.35, 139.19, 139.00, 138.06, 137.84, 137.73, 137.71, 137.20, 136.98, 136.77, 136.40, 136.02, 135.72, 135.29, 134.50, 132.72, 130.67, 130.08, 127.10, 126.79, 125.02, 118.89, 118.71, 118.32, 118.24, 111.45 (two sp^2 carbon signals were overlapped), 75.52, 58.91, 38.12, 37.82, 30.18, 29.93 (one sp^3 carbon signal was overlapped with the signals of CD_2Cl_2); HRMS (–APCI), calcd for $C_{82}H_{26}N_2O_4$ ($M^{-\bullet}$) 1102.1898, found 1102.1881.

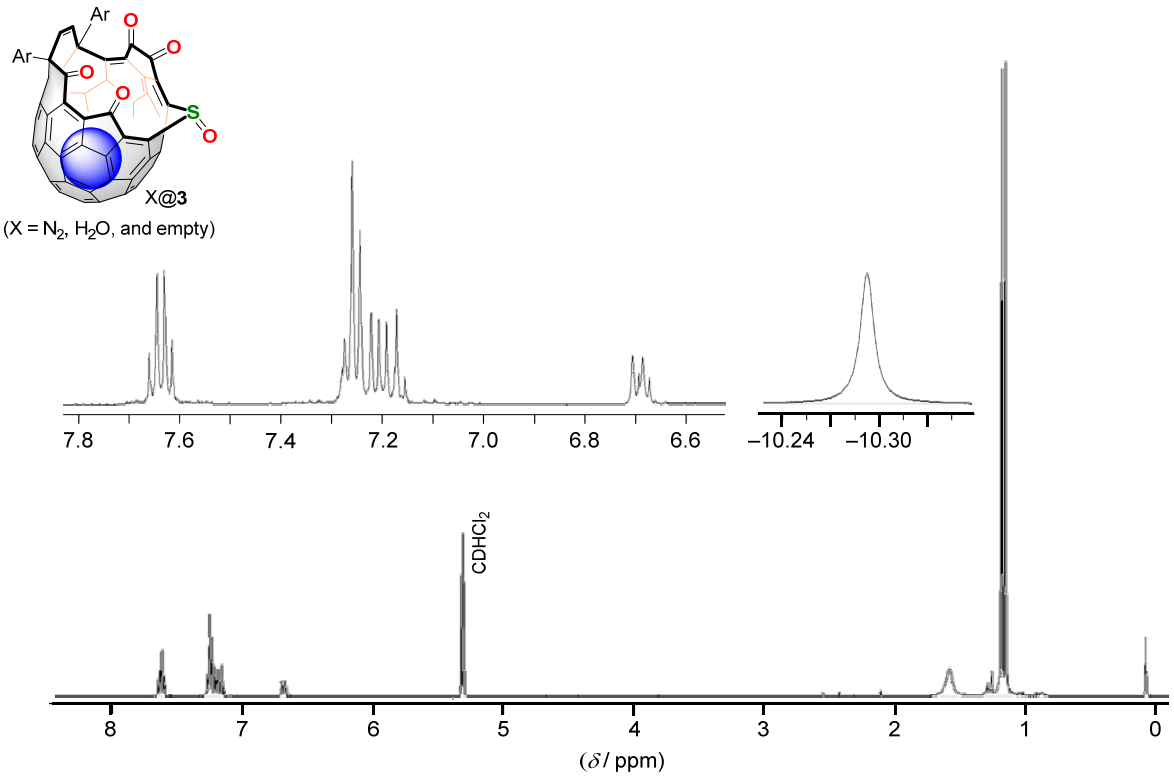


Fig. S1. ^{1}H NMR (500 MHz, CD_2Cl_2) spectrum of a mixture of N_2@**3**, H_2O@**3**, and empty **3**.

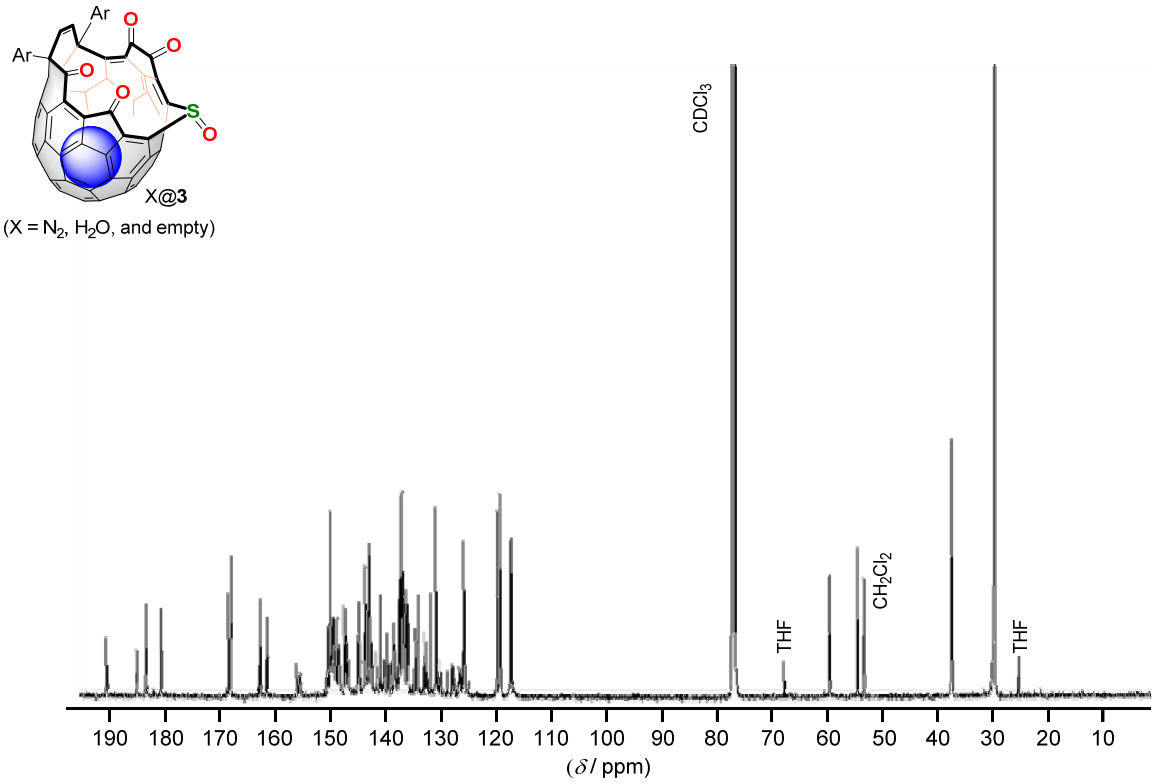


Fig. S2. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of a mixture of N_2@**3**, H_2O@**3**, and empty **3**.

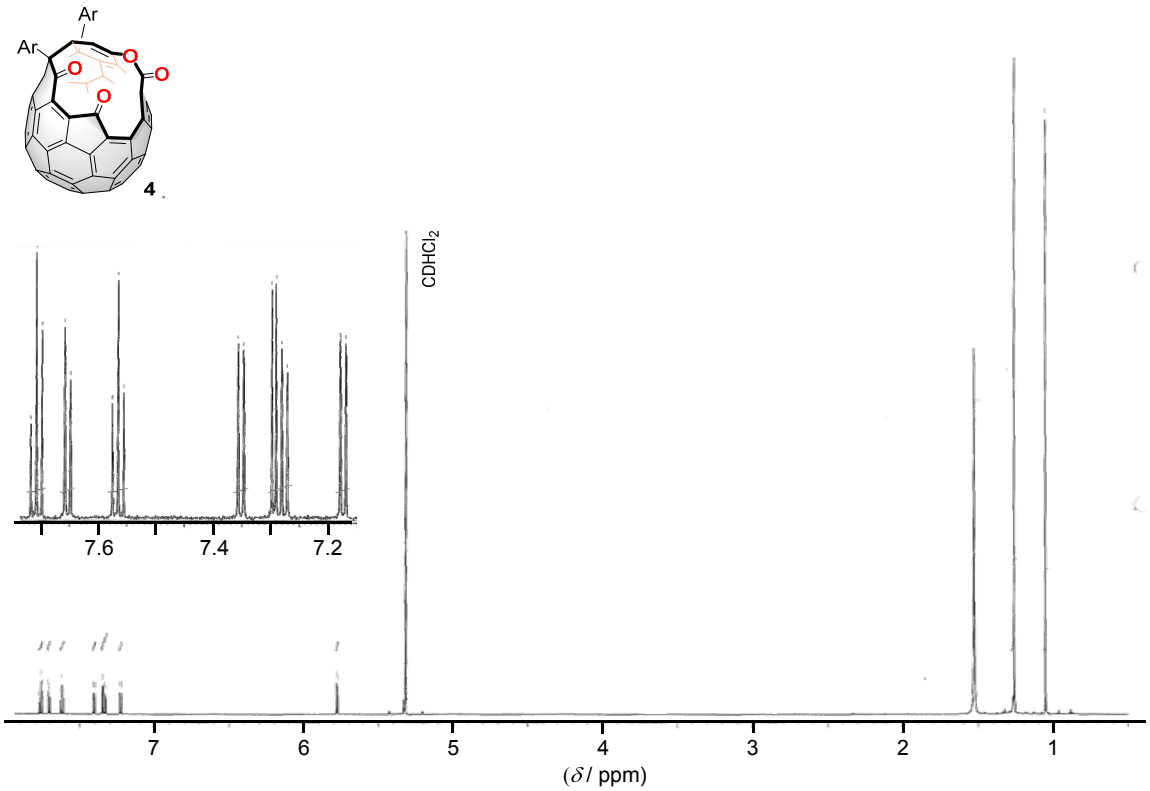


Fig. S3. ^{1}H NMR (800 MHz, CD_2Cl_2) spectrum of empty **4**.

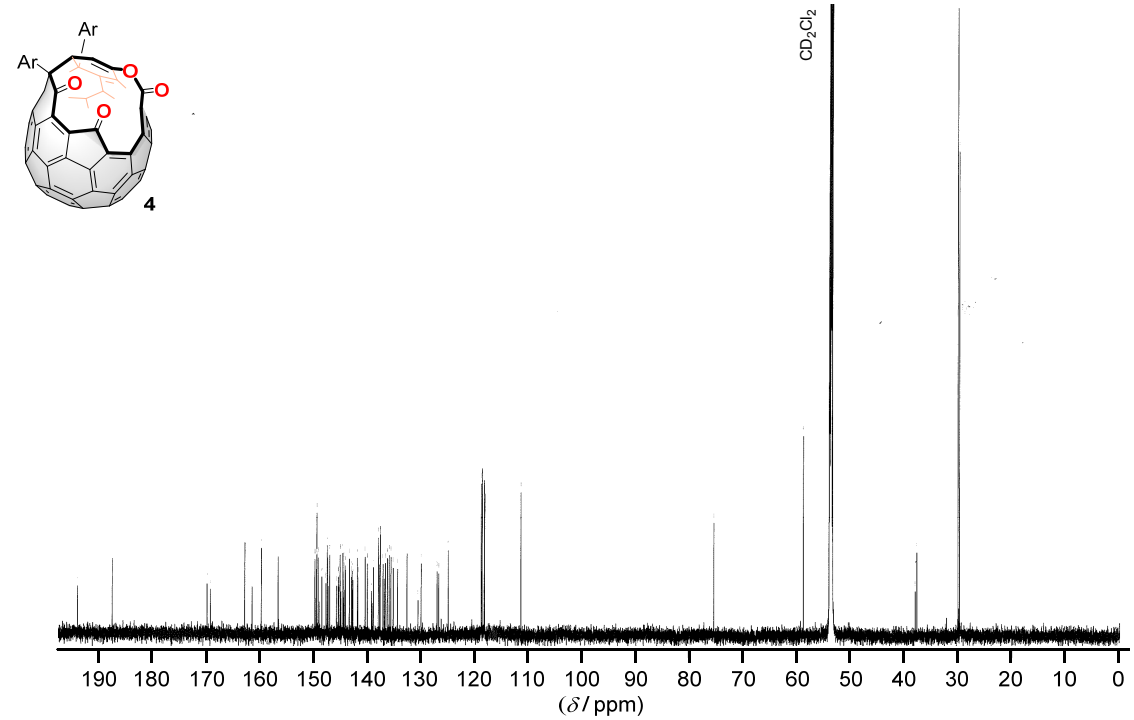


Fig. S4. ^{13}C NMR (201 MHz, CD_2Cl_2) spectrum of empty **4**.

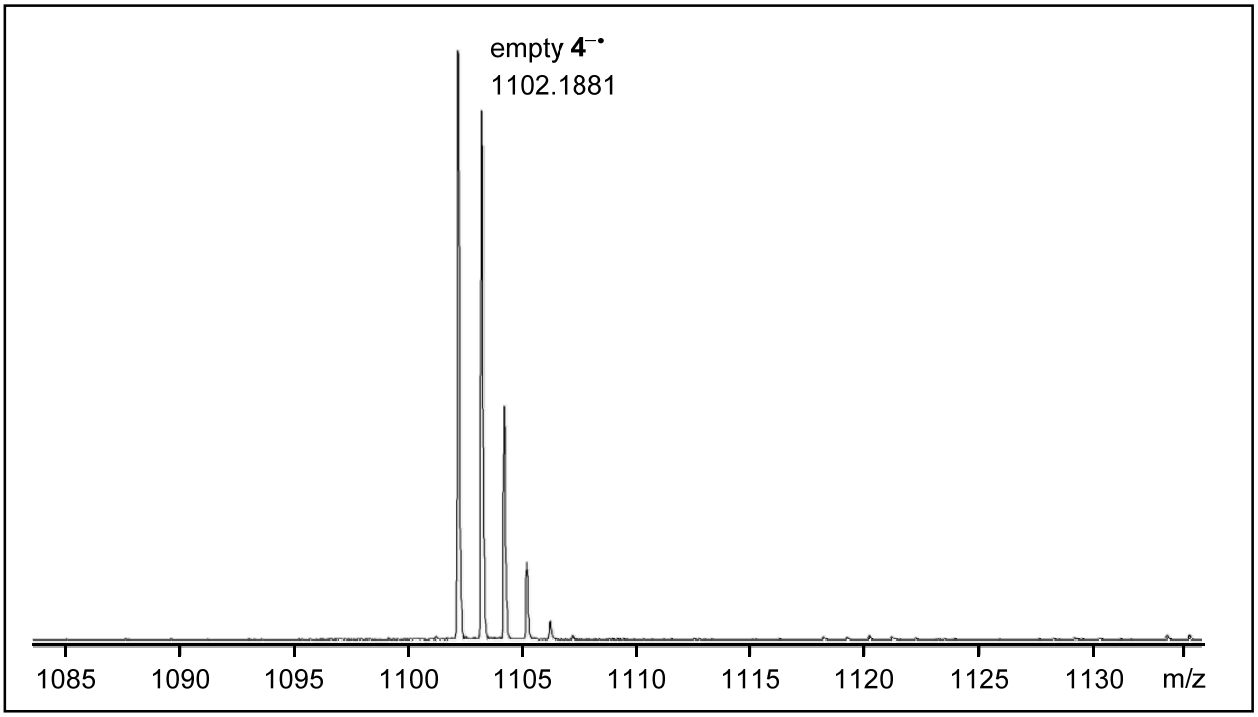


Fig. S5. APCI-MS spectrum (negative ionization mode) of empty **4** in pure form.

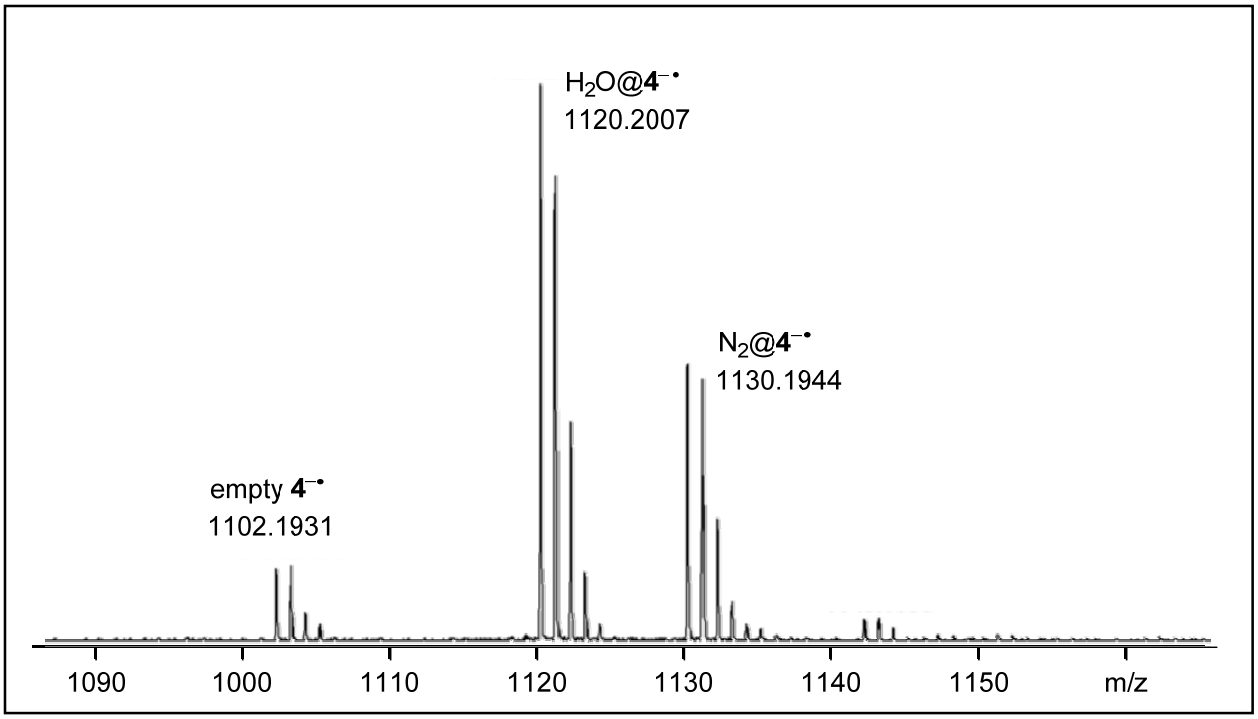


Fig. S6. APCI-MS spectrum (negative ionization mode) of a mixture of N_2@**4**, H_2O@**4**, and empty **4**.

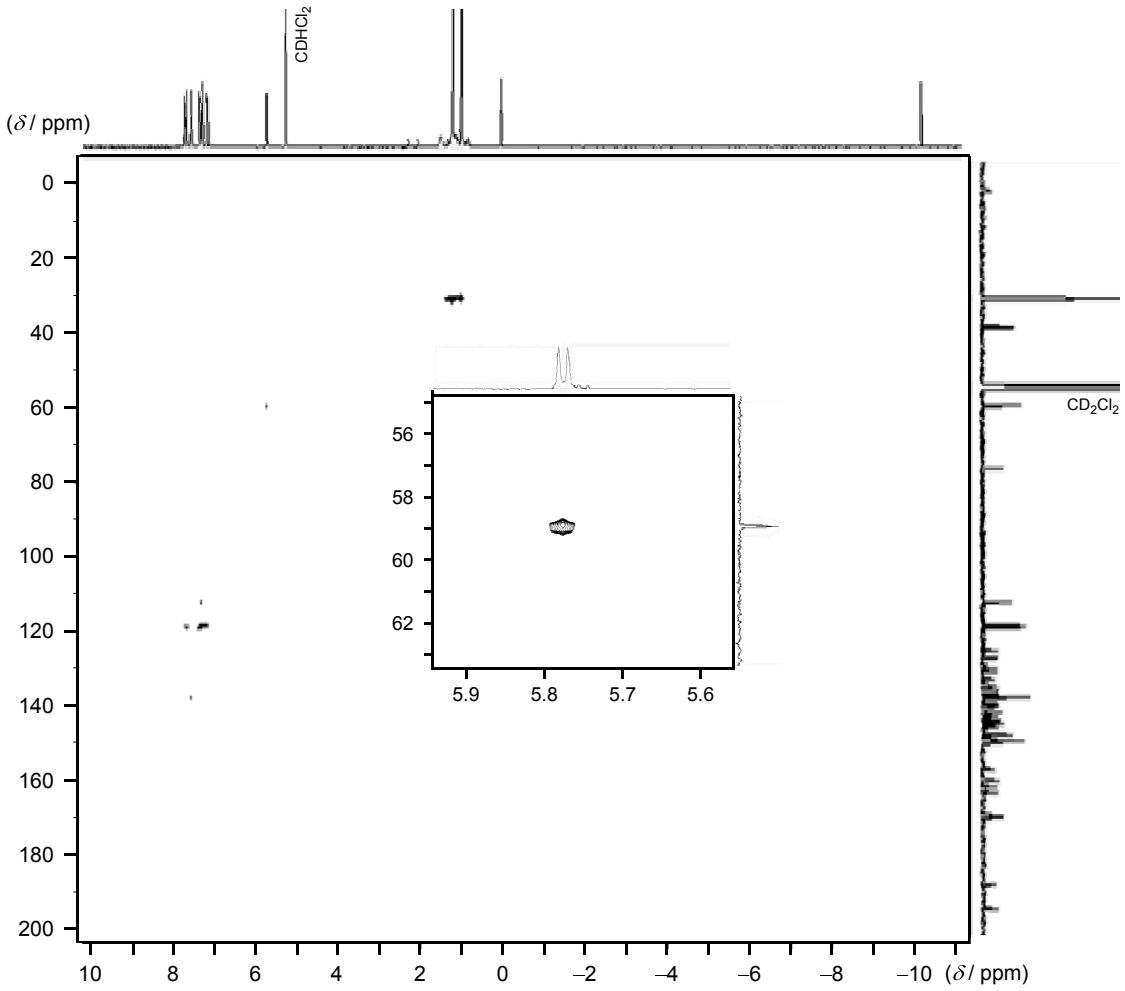


Fig. S7. ^{1}H-^{13}C HSQC NMR spectrum of a mixture of N_2@**4**, H_2O@**4**, and empty **4**.

4. DFT Calculations

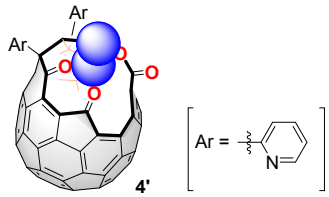


Table S1. Transition state for N_2 insertion into **4'** (M06-2X/6-31G*)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-2.149282	-0.920393	4.079190
2	8	0	-0.616254	-2.238587	5.028477
3	7	0	-4.009410	3.066938	1.501467
4	7	0	-4.372844	-0.850221	-2.611890
5	6	0	-2.103606	-0.186647	-1.361158
6	6	0	-3.836749	2.347663	0.393905
7	6	0	-0.838022	-1.344653	4.269247
8	6	0	-2.042585	1.079048	-0.857966
9	6	0	-0.895810	-2.709278	-0.982683
10	6	0	-6.423668	-2.451327	-1.620131
11	6	0	-4.959123	4.004947	1.492328
12	6	0	-1.172955	-0.636629	-2.349737
13	6	0	-2.774902	1.248080	0.452142
14	6	0	-3.000881	-1.110049	-0.596415
15	6	0	-0.662132	2.563667	1.062297
16	6	0	-4.271060	-1.422553	-1.414187
17	6	0	4.981953	-0.786759	0.078286
18	6	0	4.785159	-1.061883	-1.335523
19	6	0	5.047826	0.520432	0.524057
20	6	0	4.634403	1.359314	-1.749477
21	6	0	4.129415	2.662250	0.276878
22	6	0	0.805587	3.458563	-0.720235
23	6	0	-1.083520	2.027666	-1.324556
24	6	0	0.123980	-3.402944	-0.325031
25	6	0	4.871776	1.620589	-0.406463
26	6	0	3.655189	-0.080674	2.448695
27	6	0	-0.418708	2.884448	-0.351356
28	6	0	2.873327	3.073650	-1.795183
29	6	0	-4.603526	2.524986	-0.761485
30	6	0	-3.479207	-0.152174	0.663519
31	6	0	1.530050	-0.865219	3.212469
32	6	0	-3.371658	-0.684693	2.063062
33	6	0	-0.479412	0.360251	-3.033061
34	6	0	0.388434	2.785162	1.960545
35	6	0	1.437261	3.153491	-1.991349
36	6	0	2.022599	1.590307	3.096666
37	6	0	2.203245	-1.986982	2.345248
38	6	0	-0.550262	-1.950417	-2.175890
39	6	0	3.517696	-1.428031	1.974095
40	6	0	3.618408	2.109491	-2.463730
41	6	0	1.444069	-3.383998	-0.853287
42	6	0	1.730948	-2.975781	1.464774
43	6	0	0.824336	2.289273	-2.874036
44	6	0	0.622461	1.829429	3.002158
45	6	0	-0.446747	1.713021	-2.525026
46	6	0	-5.276125	-2.232223	-0.872533
47	6	0	2.426864	-3.214230	0.213083
48	6	0	4.601316	-0.010527	-2.229326
49	6	0	0.691585	-2.160413	-2.791634
50	6	0	-2.460000	-0.214418	2.922097
51	6	0	-6.534451	-1.862143	-2.877416
52	6	0	1.599064	1.301524	-3.596380
53	6	0	0.786789	0.110258	-3.679986
54	6	0	0.437683	-3.798224	1.153136
55	6	0	-1.681902	1.614764	1.458499
56	6	0	4.401350	0.873856	1.766750
57	6	0	-5.770974	4.267048	0.393991
58	6	0	-5.586475	3.505874	-0.756703
59	6	0	-1.534463	0.861511	2.605086
60	6	0	-5.482435	-1.073296	-3.323622
61	6	0	3.882257	2.222357	1.632056
62	6	0	3.141992	3.369603	-0.405659
63	6	0	3.971079	-2.249789	-1.446160
64	6	0	3.007888	-2.345286	-2.438274
65	6	0	4.238028	-1.777650	0.835676
66	6	0	0.224987	-0.517814	3.612244
67	6	0	-0.257708	0.812832	3.271937
68	6	0	1.877387	3.651462	0.238972
69	6	0	1.364397	-1.137615	-3.566862
70	6	0	2.794131	-1.247272	-3.351587
71	6	0	3.657724	-2.689658	-0.098300
72	6	0	1.715395	-2.910204	-2.120577
73	6	0	2.438570	0.264113	3.119023
74	6	0	2.967462	1.203259	-3.391044
75	6	0	3.579502	-0.103695	-3.255519
76	6	0	2.703017	2.557529	2.269090
77	6	0	1.674622	3.287039	1.551407
78	6	0	-2.293019	-2.501940	-0.400604
79	8	0	-2.859819	-3.413384	0.152228
80	8	0	-0.000586	-4.696481	1.801849
81	1	0	-7.219956	-3.076527	-1.228038
82	1	0	-5.072287	4.573208	2.412755
83	1	0	-4.425833	1.902208	-1.635372
84	1	0	-4.541079	0.006725	0.454400
85	1	0	-3.939249	-1.572718	2.328224
86	1	0	-5.141696	-2.688893	0.101405
87	1	0	-7.412785	-2.008867	-3.496538
88	1	0	-6.524323	5.045767	0.443056
89	1	0	-6.196761	3.676841	-1.638448
90	1	0	-5.523773	-0.592452	-4.298249
91	7	0	-1.367179	-2.469619	2.117142
92	7	0	-0.797634	-1.713465	1.556601

An imaginary frequency was found at –104.66 cm^{-1}

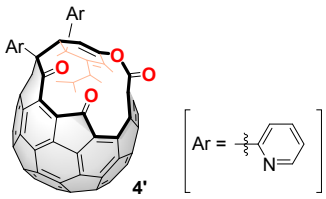


Table S2. Optimized structure of **4'** (M06-2X/6-31G*)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	2.006053	-2.500203	3.245698
2	8	0	0.439557	-2.765364	4.806090
3	7	0	4.267719	-2.948828	-1.076413
4	7	0	4.411780	2.882949	-0.545652
5	6	0	2.249052	1.253905	-0.655314
6	6	0	3.802765	-1.810504	-1.601749
7	6	0	0.702217	-2.549124	3.660771
8	6	0	2.122502	0.108613	-1.385185
9	6	0	1.038739	2.189139	1.650320
10	6	0	6.544813	2.647748	1.232121
11	6	0	5.185186	-3.623935	-1.765466
12	6	0	1.318865	2.329144	-0.802803
13	6	0	2.787055	-1.079538	-0.727698
14	6	0	3.138448	1.099845	0.539042
15	6	0	0.627320	-2.262894	-1.420996
16	6	0	4.385571	1.986514	0.437455
17	6	0	-4.949738	0.482093	0.823302
18	6	0	-4.692249	1.802562	0.274425
19	6	0	-5.054126	-0.610279	-0.022329
20	6	0	-4.596923	0.811006	-1.976153
21	6	0	-4.153737	-1.609466	-1.943208
22	6	0	-0.825678	-1.288869	-3.176668
23	6	0	1.116279	-0.025385	-2.391639
24	6	0	0.029008	1.935495	2.565424
25	6	0	-4.868209	-0.445409	-1.452494
26	6	0	-3.756785	-1.961777	1.558288
27	6	0	0.406931	-1.293412	-2.508499
28	6	0	-2.872430	-0.143155	-3.445099
29	6	0	4.240227	-1.304326	-2.824328
30	6	0	3.526589	-0.448776	0.518621
31	6	0	-1.648880	-2.182925	2.627199
32	6	0	3.274604	-1.123688	1.831416
33	6	0	0.576978	2.344378	-1.979969
34	6	0	-0.440040	-3.107344	-1.088375
35	6	0	-1.436661	-0.055477	-3.638753
36	6	0	-2.095544	-3.411433	0.516176
37	6	0	-2.276046	-0.881090	3.062850
38	6	0	0.713220	2.872582	0.415099
39	6	0	-3.598313	-0.825988	2.431352
40	6	0	-3.587687	0.965027	-3.007079
41	6	0	-1.264106	2.482565	2.378688
42	6	0	-1.645345	0.340325	3.288202
43	6	0	-0.794508	1.148178	-3.437037
44	6	0	-0.685955	-3.423504	0.286190
45	6	0	0.496853	1.158424	-2.803613
46	6	0	5.427270	1.835000	1.358576
47	6	0	-2.279648	1.563257	2.861317
48	6	0	-4.519090	1.964733	-1.097234
49	6	0	-0.533074	3.502862	0.306350
50	6	0	2.287603	-2.000605	1.987276
51	6	0	6.584282	3.582766	0.200868
52	6	0	-1.538787	2.313076	-3.003519
53	6	0	-0.690971	3.030802	-2.080398
54	6	0	-0.153655	0.633526	3.336562
55	6	0	1.633095	-2.032341	-0.405890
56	6	0	-4.462324	-1.872636	0.365746
57	6	0	5.681286	-3.209712	-3.000672
58	6	0	5.196287	-2.023754	-3.535633
59	6	0	1.433355	-2.455530	0.893517
60	6	0	5.492230	3.660717	-0.654747
61	6	0	-3.932389	-2.505045	-0.830340
62	6	0	-3.164734	-1.455113	-2.911677
63	6	0	-3.829123	2.507041	1.195938
64	6	0	-2.843707	3.355019	0.714942
65	6	0	-4.218776	0.365368	2.072687
66	6	0	-0.316037	-2.574557	2.565459
67	6	0	0.179018	-3.026967	1.283946
68	6	0	-1.911799	-2.167792	-2.787309
69	6	0	-1.233985	3.623059	-0.956254
70	6	0	-2.659209	3.525968	-0.709000
71	6	0	-3.541167	1.608371	2.303108
72	6	0	-1.531793	3.341561	1.327352
73	6	0	-2.548667	-2.735002	1.639037
74	6	0	-2.904032	2.222972	-2.777019
75	6	0	-3.480587	2.843229	-1.599433
76	6	0	-2.761051	-3.238768	-0.752894
77	6	0	-1.721429	-3.048855	-1.746633
78	6	0	2.388302	1.550602	1.814343
79	8	0	2.892410	1.458740	2.907880
80	8	0	0.713418	-0.091650	3.747928
81	1	0	7.370614	2.555861	1.930890
82	1	0	5.542213	-4.544018	-1.307901
83	1	0	3.845294	-0.369512	-3.207759
84	1	0	4.599852	-0.492339	0.306552
85	1	0	3.831538	-0.803905	2.705076
86	1	0	5.345193	1.108954	2.160623
87	1	0	7.436672	4.239167	0.063778
88	1	0	6.426428	-3.802291	-3.519976
89	1	0	5.555810	-1.658341	-4.492762
90	1	0	5.476628	4.380426	-1.469987

5. X-Ray Crystal Structure Analysis

A mixture of N_2@4, H_2O@4, and empty 4 (CCDC 1523319)

Single crystals of a mixture of N_2@**4**, H_2O@**4**, and empty **4** were grown from the CH_2Cl_2 solution by slow evaporation of the solvent. Intensity data were collected at 100 K on a Brucker SMART APEX II with Mo Kα radiation (λ = 0.71073 Å) and graphite monochromator. A total of 24418 reflections were measured at the maximum 2θ angle of 51.0°, of which 9283 were independent reflections (R_{int} = 0.0380). The structure was solved by direct methods (SHELXS-97)[1] and refined by the full-matrix least-squares on F^2 (SHELXL-97).[1] The open-cage moiety was disordered. Thus, two sets of disordered moieties, (C1–C8, C11–C25, C29–C64, and O1A–O4A) and (C65–C123 and O1B–O4B), were placed and their occupancies were refined to be 0.80 and 0.20, respectively. The electron density inside of the fullerene cage indicated the presence of a water molecule (O5, H5A, and H5B) in addition to a nitrogen molecule (N3–N4). Thus, these occupancies were refined to be 0.50 for the water molecule (O5, H5A, and H5B) and 0.18 for the nitrogen molecule (N3–N4). These encapsulated molecules were restrained using SIMU and DELU instructions during the refinements. The N3 and N4 as well as the hydrogen atoms (H5A–H5B) of the encapsulated water molecule were restrained using DFIX instruction. All other hydrogen atoms were placed using AFIX instructions. All non-hydrogen atoms were refined anisotropically except for the minor components. The crystal data are as follows: $C_{83}H_{29}N_{2.36}O_{4.50}Cl_2$; FW = 1202.02, crystal size 0.05 × 0.06 × 0.07 mm^3, Monoclinic, *P*21/a, a = 19.9364(18) Å, b = 11.5274(10) Å, c = 22.498(2) Å, β = 104.9076(13)°, V = 4996.3(8) $Å^3$, Z = 4, D_c = 1.598 g cm^{-3}. The refinement converged to R_1 = 0.0725, wR_2 = 0.1712 ($I > 2\sigma(I)$), GOF = 1.148.

6. Reference

1) Sheldrick, G. M. *SHELX-97, Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.