Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Pressure-Induced Annulative Orifice Closure of a Cage-Opened C_{60} Derivative

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1. General

The ^{1}H and ^{13}C NMR measurements were carried out at room temperature with JEOL JNM ECA500 and Bruker Avance III 800US Plus instruments. The NMR chemical shifts were reported in ppm with reference to residual protons and carbons of $CDCl_3$ (δ 7.26 ppm in ^{1}H NMR, δ 77.00 ppm in ^{13}C NMR), *o*-dichlorobenzene-d_4 (ODCB-d_4, δ 7.20 ppm in ^{1}H NMR, δ 132.35 ppm in ^{13}C NMR) and acetone-d_6 (δ 2.05 ppm in ^{1}H NMR, δ 29.92 ppm in ^{13}C NMR). APCI (atmospheric pressure chemical ionization) mass spectra were measured on a Bruker micrOTOF-Q II. Cyclic voltammetry was conducted on a BAS Electrochemical Analyzer ALS620C using a three-electrode cell with a glassy carbon working electrode, a platinum wire counter electrode, and a $Ag/AgNO_3$ reference electrode. The measurements were carried out under N_2 atmosphere using ODCB solutions of 0.50 mM samples and 0.10 M tetrabutylammonium tetrafluoroborate (*n*-$Bu_4N{\cdot}BF_4$) as a supporting electrolyte. The redox potentials were calibrated with ferrocene used as an internal standard which was added after each measurement. The high-performance liquid chromatography (HPLC) was performed with the use of a Cosmosil Buckyprep column (250 mm in length, 4.6 mm in inner diameter) for analytical purpose and the same columns (250 mm in length, 20 mm in inner diameter) for preparative purpose. Thin layer chromatography (TLC) was performed on glass plates coated with 0.25 mm thick silica gel 60F-254 (Merck). Column chromatography was performed using PSQ 60B (Fuji Silysia).

Toluene was purchased from Kanto Chemical Co., Inc. Trifluoroacetic anhydride, chloroform, and carbon disulfide were purchased from FUJIFILM Wako Pure Chemical Corporation. Ethyl acetate was purchased from Nacalai Tesque, Inc. *o*-Dichlorobenzene (ODCB) and 1-chloronaphthalene were purchased from Sigma-Aldroch Co. LLC.

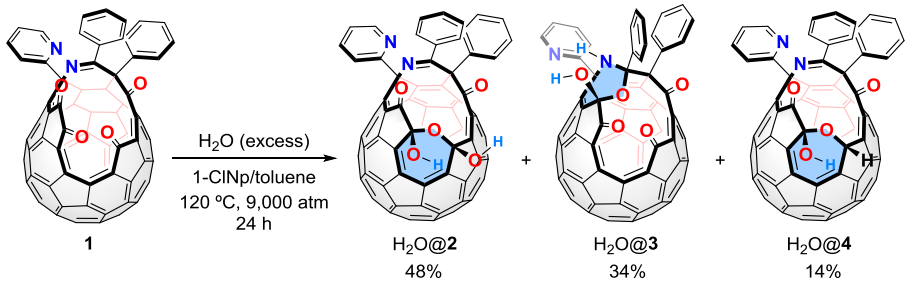
Unless otherwise noted, all reactions were carried out under Ar atmosphere. Materials purchased from commercial suppliers were used without further purification.

2. Computational Methods

All calculations were conducted using the Gaussian 09 program. All structures at the stationary states were optimized at the B3LYP-D3/6-31G(d) level of theory without any symmetry assumptions and confirmed by the frequency analyses at the same level of theory.

3. Synthesis

3.1. Synthesis of H_2O@2 and H_2O@3



A typical procedure was shown. Powdery **1** (20.0 mg, 18.7 μmol) was dissolved in a mixed solvent system of 1-chloronaphthalene and toluene (9:1, 4.0 mL). The reaction mixture was heated at 120 °C under 9,000 atm for 24 h. The crude mixture was purified by silica gel column chromatography (CS_2/EtOAc (40:1) to (20:1)) to give H_2O@**1** (H_2O: 99%, 9.87 mg, 8.95 μmol, 48%) and a mixture of H_2O@**2** and H_2O@**3** (ca. 10 mg). The mixture was then purified by HPLC equipped with the Buckyprep column (7.5 mL/min, toluene, 50 °C) to give H_2O@**2** (H_2O: 81%, 7.02 mg, 6.38 μmol, 34%) and H_2O@**3** (H_2O: 93%, 2.94 mg, 2.71 μmol, 14%) as a brown powder.

H_2O@**2** (H_2O: 82%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (d, 1H, J = 4.58 Hz), 8.29 (d, 2H, J = 6.87 Hz), 7.90 (d, 1H, J = 8.02 Hz), 7.81 (t, 1H, J = 8.02 Hz), 7.74 (br, 1H), 7.42–733 (m, 1H), 7.28–7.21 (m, 3H), 5.61 (br s, 1H), 5.20 (s, 1H), –9.93 (s, 1.64H); ^{13}C NMR (126 MHz, CS_2/acetone-d_6 (2:1)) δ 194.15, 191.13, 165.49, 159.81, 150.89, 150.74, 150.66, 150.43, 150.37, 150.34, 150.10, 149.91, 149.65, 149.37, 149.31, 149.04, 148.99, 148.88, 148.51, 148.41, 147.96, 147.84, 147.27, 147.21, 146.67, 146.38, 146.22, 146.02, 145.97, 145.38, 144.77, 144.51, 144.02, 143.71, 143.21, 143.05, 142.42, 141.90, 141.54, 141.39, 141.35, 141.33, 141.06, 140.07, 139.65, 139.16, 138.63, 138.49, 138.10, 137.89, 137.78, 137.67, 137.64, 137.07, 136.91, 135.53, 135.13, 135.06, 134.66, 134.18, 132.13, 131.72, 131.40, 130.57, 130.19, 130.08, 128.24, 127.16, 126.60, 125.58, 124.67, 123.41, 110.38, 96.91, 72.78, 60.08 (The sum of carbon signals must be 76 in theory. Observed 76.); HRMS (APCI) m/z: $[M]^{\bullet-}$ Calcd for $C_{80}H_{18}N_2O_6$ (H_2O@**2**) 1102.1170; Found 1102.1145.

H_2O@**3** (H_2O: 87%): ^{1}H NMR (800 MHz, ODCB-d_4) δ 8.88 (d, 1H, J = 7.34 Hz), 8.49 (d, 1H, J = 4.40 Hz), 7.71 (br, 2H), 7.64 (d, 1H, J = 8.07 Hz), 7.55–7.49 (m, 2H), 7.24–

7.22 (m, 2H), 7.14 (br, 2H), 7.02–6.99 (m, 1H), 6.75 (t, 1H, J = 6.60 Hz), 6.62 (d, 1H, J = 6.60 Hz), –9.47 (s, 1.74H); ^{13}C NMR (201 MHz, ODCB-d_4) δ 193.38, 191.18, 186.96, 165.00, 155.60, 149.93, 149.89, 149.55, 149.31, 149.22, 148.81, 148.75, 148.08, 147.97, 147.63, 147.21, 147.17, 146.88, 146.75, 146.57, 146.50, 145.79, 144.68, 144.55, 144.21, 144.17, 143.96, 143.90, 143.87, 143.70, 143.61, 143.08, 142.38, 141.86, 141.78, 141.00, 140.48, 140.36, 139.49, 139.45, 139.40, 139.10, 138.81, 137.87, 137.66, 137.05, 136.88, 136.71, 136.60, 136.57, 136.36, 135.53, 135.42, 135.39, 135.07, 134.87, 134.20, 133.90, 133.69, 131.15, 130.57, 129.20, 128.23, 128.20, 127.95, 127.79, 127.65, 126.58, 126.41, 126.27, 122.73, 121.84, 96.45, 93.65, 67.04, 63.27 (The sum of carbon signals must be 76 in theory. Observed 76.); HRMS (APCI) m/z: $[M]^{\bullet-}$ Calcd for $C_{80}H_{18}N_2O_6$ (H_2O@**3**) 1102.1170; Found 1102.1169.

H_2O@**4** (H_2O: 85%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 (d, 1H, J = 4.58 Hz), 8.26 (d, 2H, J = 8.02 Hz), 7.88 (d, 1H, J = 8.02 Hz), 7.81–7.73 (m, 2H), 7.67 (s, 1H), 7.43–7.29 (m, 5H), 7.26–7.17 (m, 3H), –9.81 (s, 1.70H); ^{13}C NMR (126 MHz, $CDCl_3$) δ194.87, 191.28, 164.52, 161.30, 150.40, 150.06, 149.93, 149.77, 149.56, 148.95, 148.89, 148.83, 148.74, 148.64, 148.02, 147.93, 147.87, 147.76, 147.34, 147.23, 147.02, 146.59, 146.37, 146.27, 146.06, 145.87, 145.71, 145.10, 144.79, 144.73, 144.38, 143.78, 143.75, 142.39, 142.34, 141.77, 140.94, 140.87, 140.82, 139.80, 139.34, 139.09, 138.47, 137.42, 137.29, 137.15, 136.55, 136.10, 135.31, 134.46, 134.25, 133.21, 133.05, 132.68, 130.45, 129.84, 129.56, 127.61, 126.77, 125.62, 124.09, 122.71, 94.42, 80.49, 76.27, 59.69 (The sum of carbon signals must be 76 in theory. Observed 67. The nine sp^2 carbon signals are overlapped in the aromatic region.); HRMS (APCI) m/z: $[M]^{\bullet-}$ Calcd for $C_{80}H_{18}N_2O_5$ (H_2O@**4**) 1102.1221; Found 1086.1216.

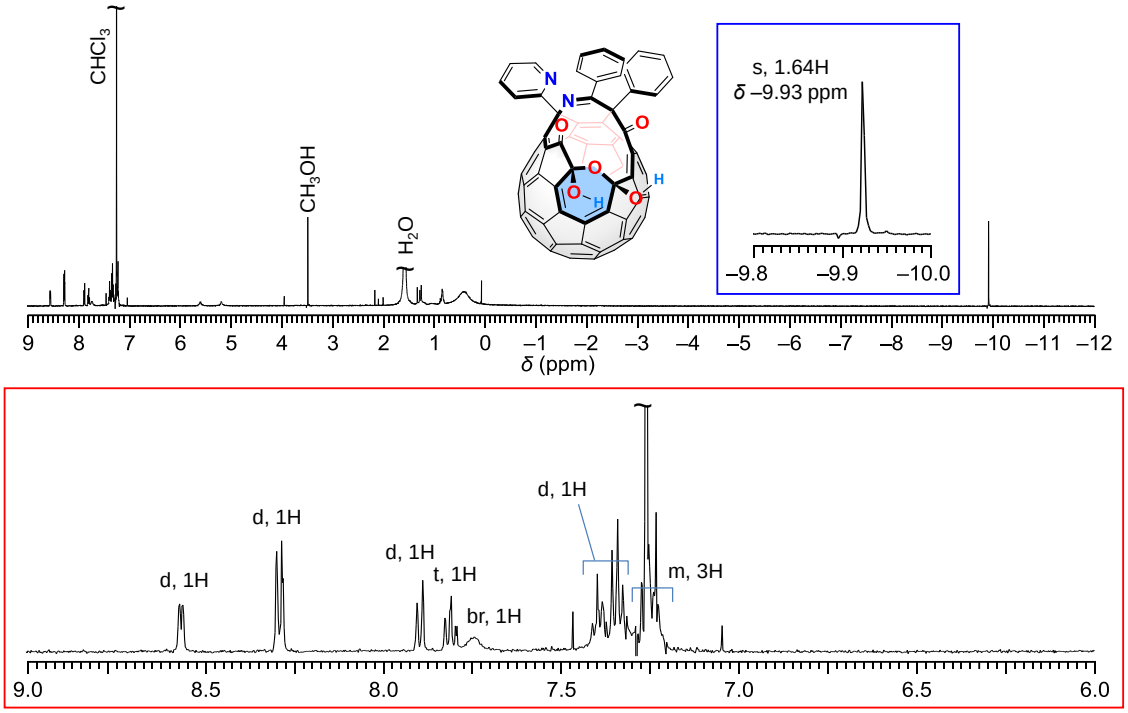


Figure S1. ^{1}H NMR spectra (500 MHz, $CDCl_3$) of H_2O@**2**.

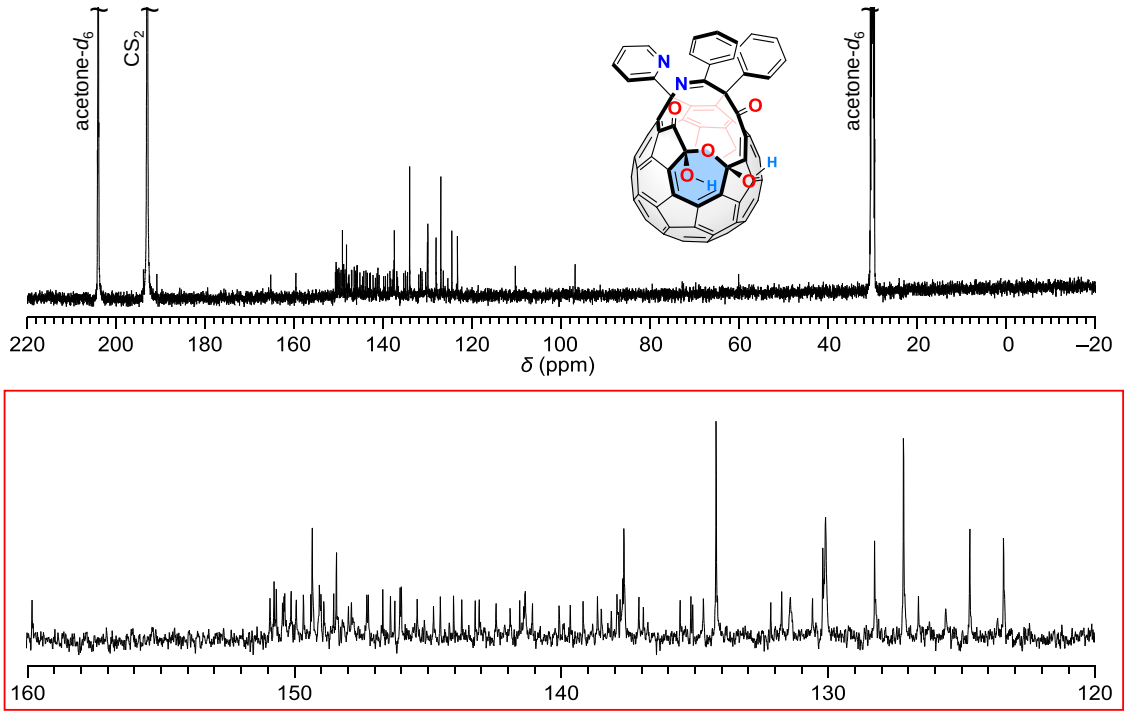


Figure S2. ^{13}C NMR spectra (126 MHz, CS_2/acetone-d_6 (2:1)) of H_2O@**2**.

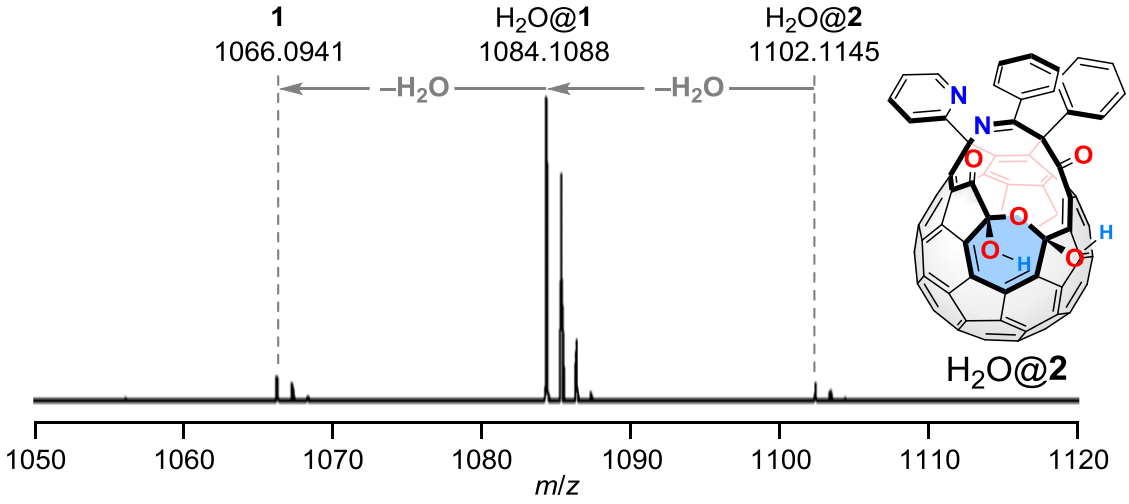


Figure S3. APCI mass spectrum (negative ion mode) of H_2O@**2** (H_2O: 90%).

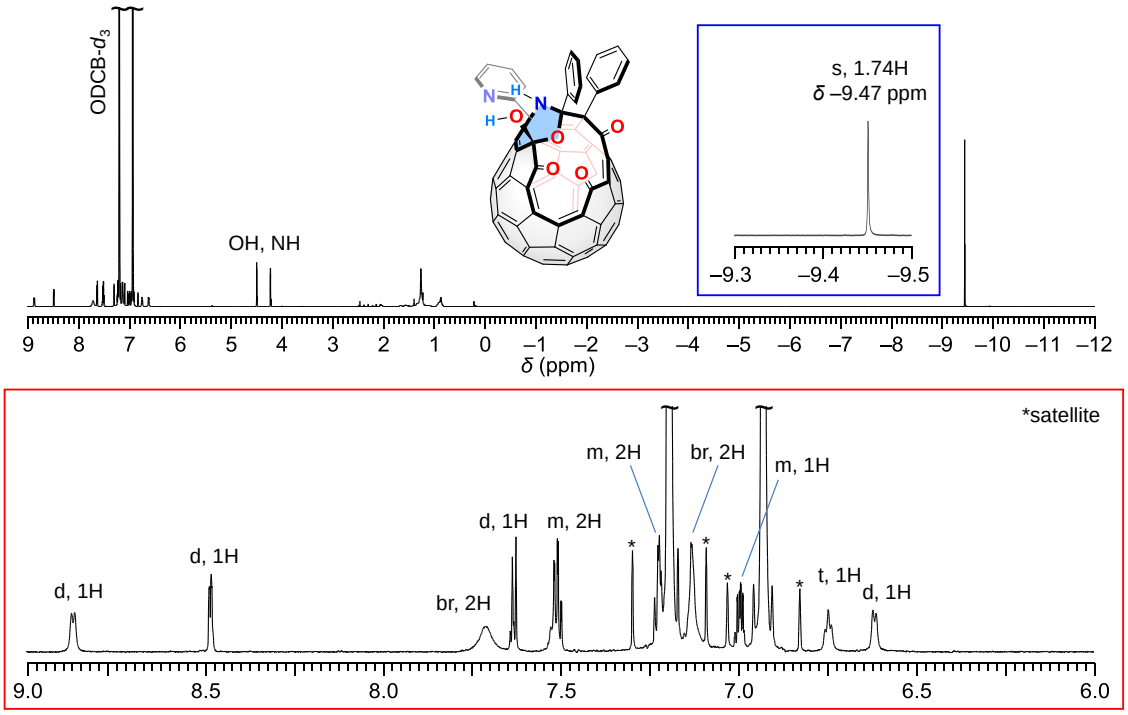


Figure S4. ^{1}H NMR spectra (800 MHz, ODCB-d_4) of H_2O@**3**.

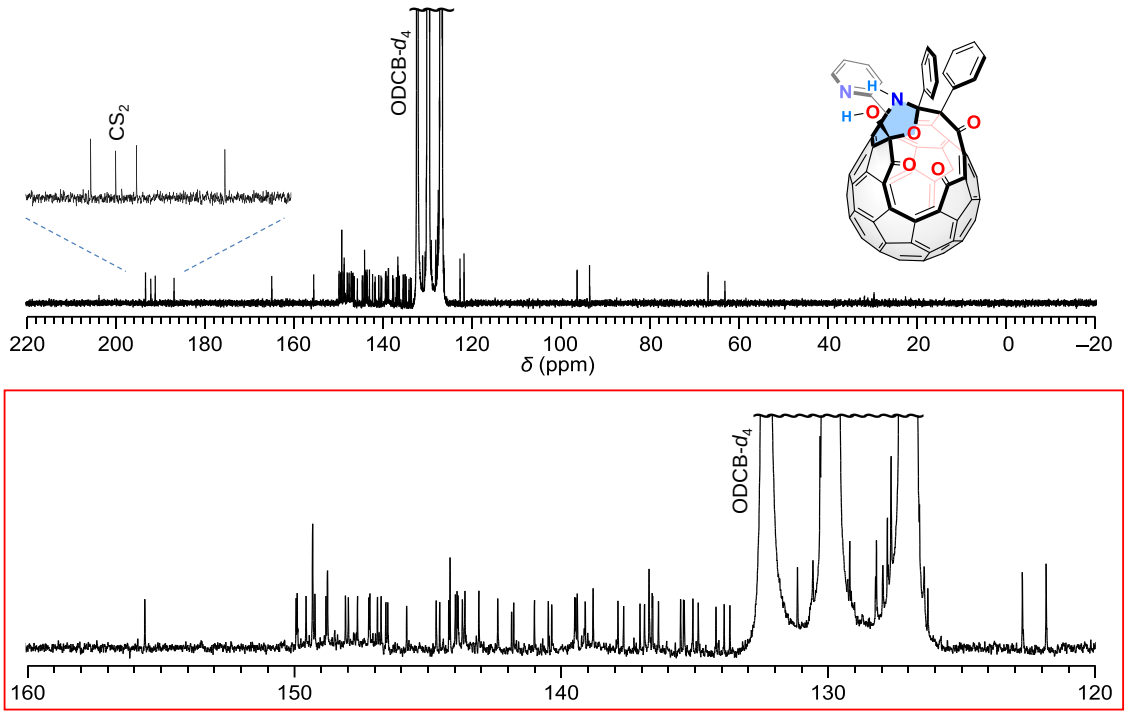


Figure S5. ^{13}C NMR spectra (201 MHz, ODCB-d_4) of H_2O@**3**.

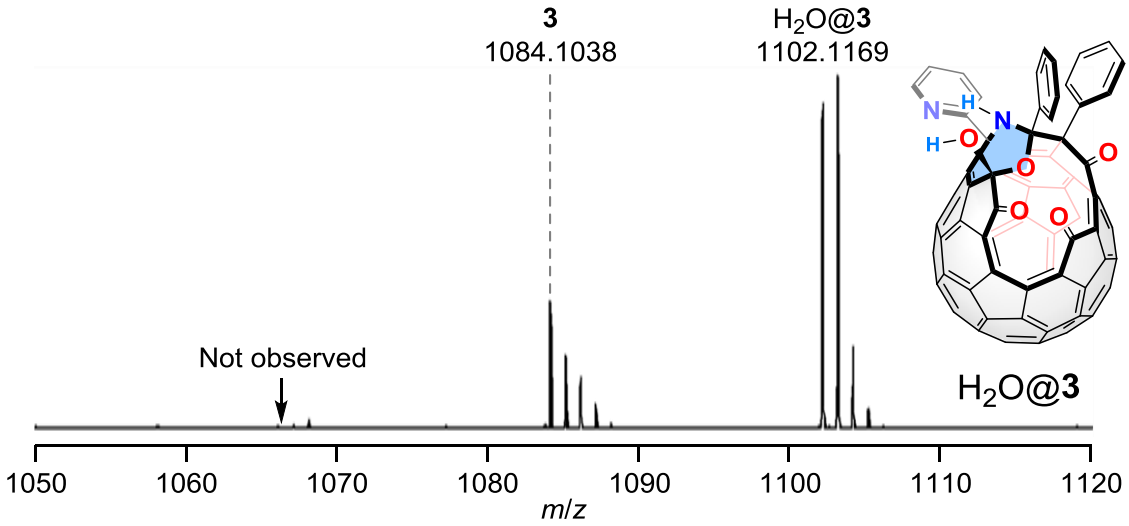


Figure S6. APCI mass spectrum (negative ion mode) of H_2O@**3** (H_2O: 70%).

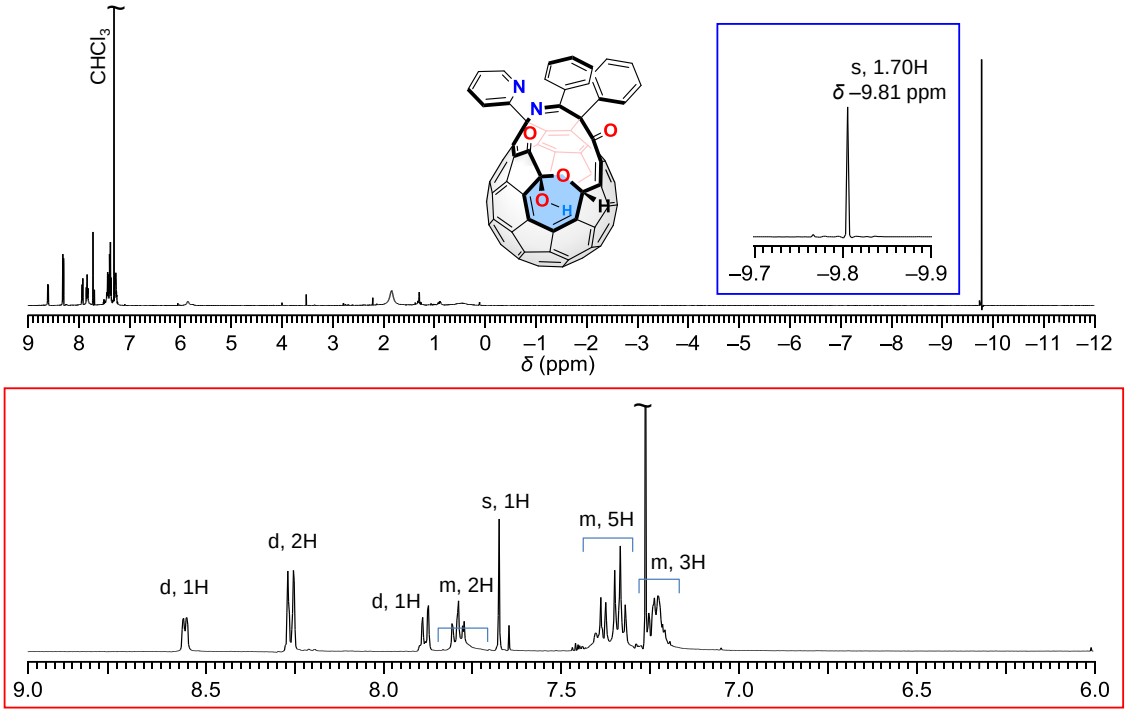


Figure S7. ^{1}H NMR spectra (500 MHz, $CDCl_3$) of H_2O@**4**.

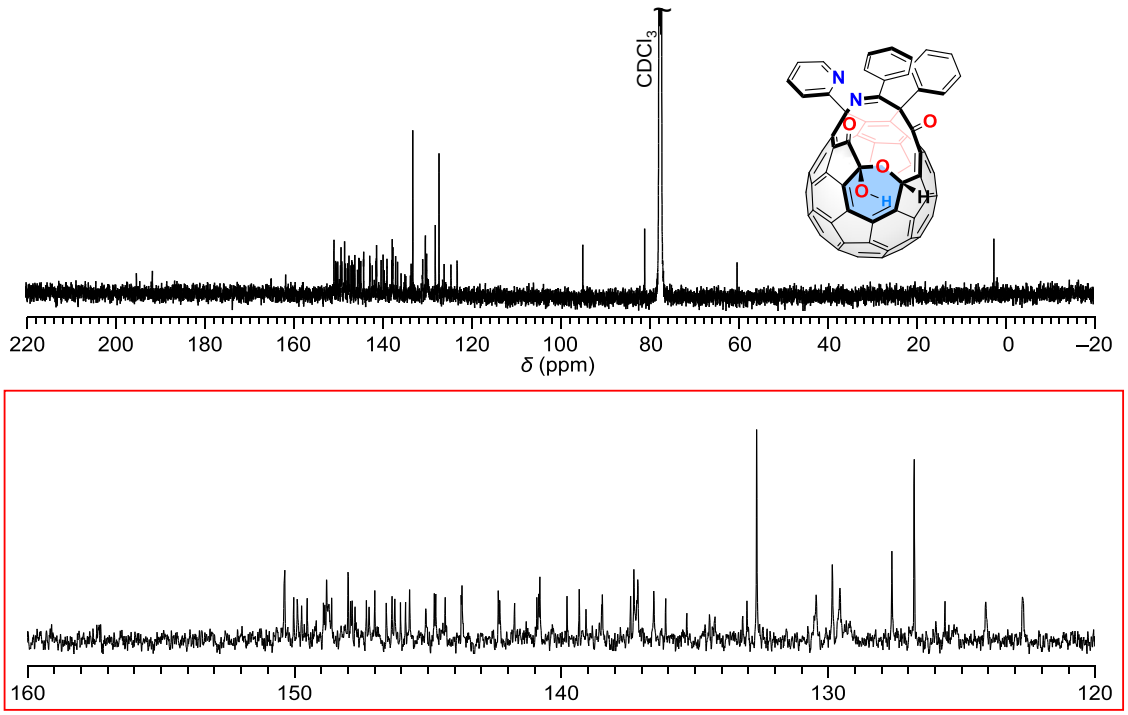


Figure S8. ^{13}C NMR spectra (126 MHz, $CDCl_3$) of H_2O@**4**.

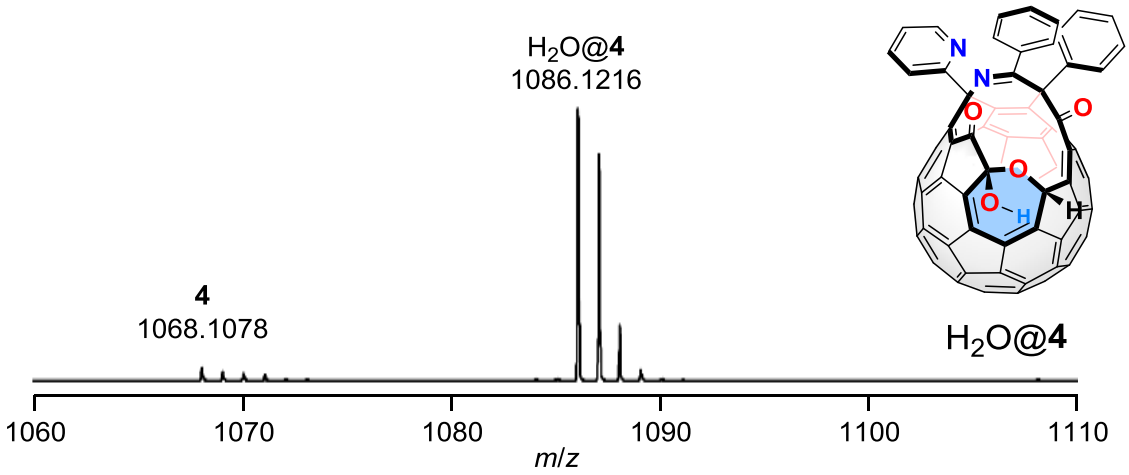
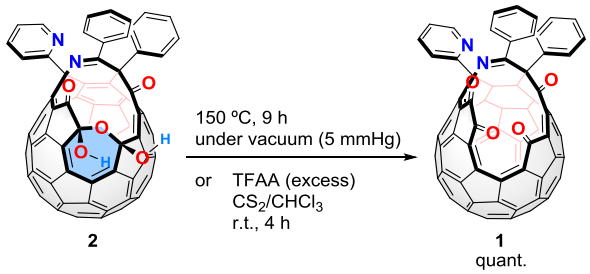


Figure S9. APCI mass spectrum (negative ion mode) of H_2O@**4** (H_2O: 95%).

3.2. Conversion of 2 into 1



Powdery **2** (10.5 mg, 9.68 μmol) was placed into a vial which was heated at 150 °C (aluminum block) under vacuum (5 mmHg) for 9 h, quantitatively affording **1** (10.3 mg, 9.65 μmol) as a brown powder. The reaction progress was monitored by HPLC and ^{1}H NMR.

As an alternative method, to a vial containing **1** (10.3 mg, 9.49 μmol), a mixed solvent of TFAA (trifluoroacetic anhydride, 0.30 mL), CS_2 (1.00 mL), and $CHCl_3$ (1.00 mL) were added. The resultant suspension was stirred at room temperature for 4 h. During the reaction, the suspension became clear dark brown solution (nearly one hour later). After the removal of solvent by evaporation, **1** (10.1 mg, 9.47 μmol) was quantitatively obtained as a brown powder. The reaction progress was monitored by HPLC and ^{1}H NMR.

1: ^{1}H NMR (500 MHz, ODCB-d_4) δ 8.46 (d, 1H, J = 4.01 Hz), 8.09 (d, 2H, J = 7.14 Hz), 7.85 (d, 1H, J = 8.02 Hz), 7.66–7.52 (m, 2H), 7.32 (br, 1H), 7.18–6.99 (m, 7H); ^{13}C NMR (126 MHz, ODCB-d_4) δ 191.56, 187.59, 183.32, 179.94, 165.05, 163.84, 150.69, 149.93, 149.80, 149.58, 149.53, 149.08, 148.63, 148.57, 148.35, 148.13, 147.89, 147.73, 147.33, 147.27, 146.77, 146.66, 146.58, 146.30, 144.48, 144.37, 144.34, 144.30, 144.20, 144.17, 143.90, 143.78, 143.61, 143.27, 142.13, 141.85, 141.78, 141.54, 141.28, 140.55, 139.99, 139.24, 139.11, 138.83, 138.74, 138.06, 137.05, 136.93, 136.89, 136.20, 135.37, 134.97, 134.93, 134.01, 133.69, 133.49, 132.82, 132.63, 132.10, 131.62, 130.42, 129.58, 129.50, 129.12, 128.70, 127.71, 127.56, 126.72, 124.19, 122.67, 73.08, 60.78 (The sum of carbon signals must be 76 in theory. Observed 72. The four sp^2 carbon signals are overlapped in the aromatic region.); HRMS (APCI) m/z: $[M]^{\bullet-}$ Calcd for $C_{80}H_{14}N_2O_4$ (**1**) 1066.0959; Found 1066.0955.

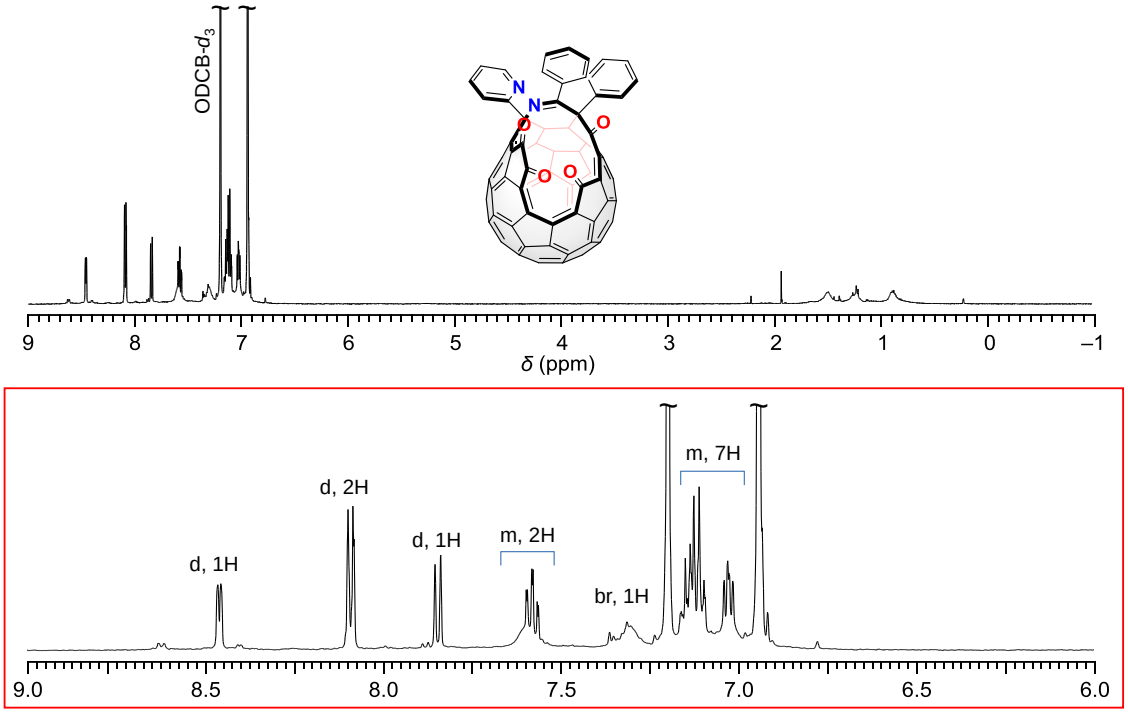


Figure S10. ^{1}H NMR spectra (500 MHz, ODCB-d_4) of **1**.

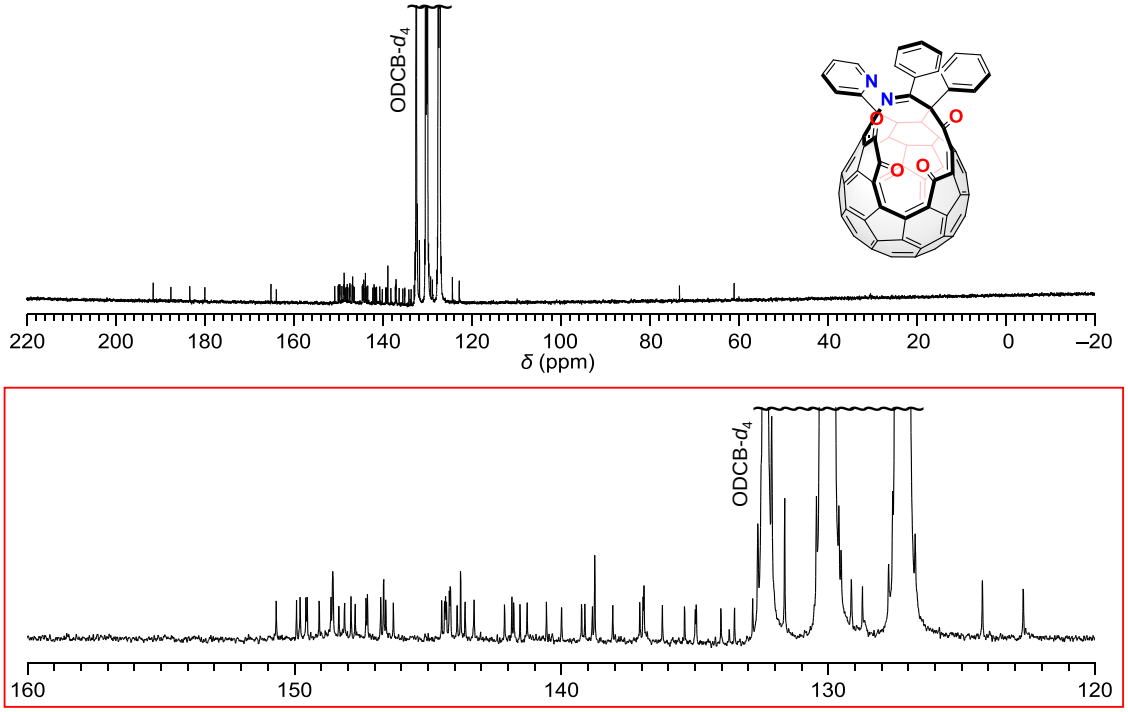


Figure S11. ^{13}C NMR spectra (126 MHz, ODCB-d_4) of **1**.

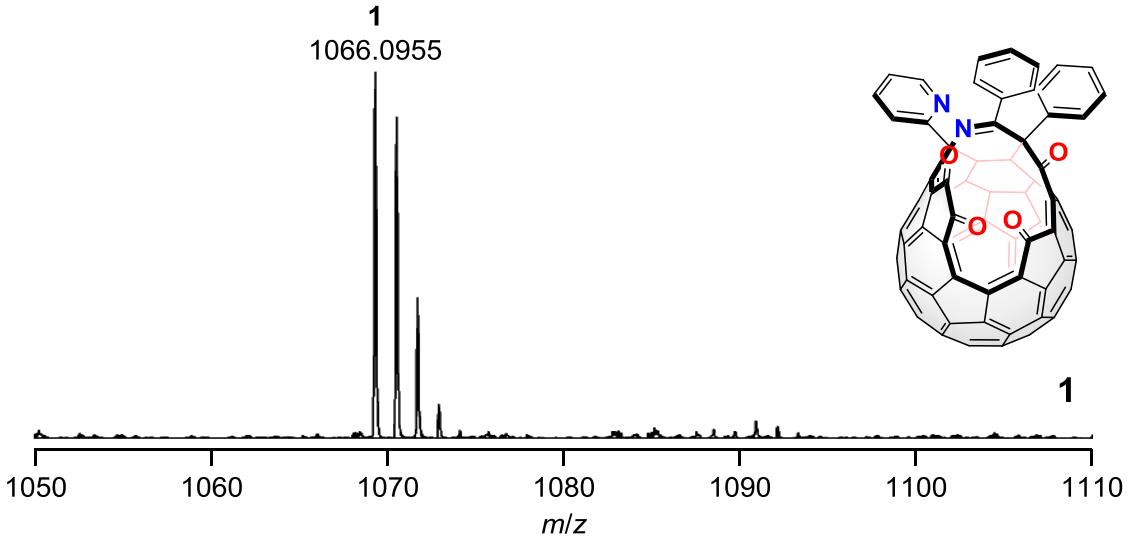


Figure S12. APCI mass spectrum (negative ion mode) of **1**.

4. Single Crystal X-Ray-Structures

4.1. Crystal Structure of 2•$(CHCl_3)_2$•EtOH

Single crystals of **2** were obtained from a $CHCl_3$/ethanol solution by slow evaporation. Intensity data were collected at 100 K on a Bruker Single Crystal CCD X-ray Diffractometer (SMART APEX II) with Mo Kα radiation (λ = 0.71073 Å) and graphite monochromator. A total of 12897 reflections were measured at the maximum 2θ angle of 49.98°, of which 9398 were independent reflections (R_{int} = 0.0198). The structure was solved by direct methods (SHELXT-2014/5[1]) and refined by the full-matrix least-squares on F^2 (SHELXL-2018/3[1]). A chloroform molecule was disordered, which was solved using appropriate models. Thus, (C84–Cl4–Cl5–Cl6) and (C85–Cl7–Cl8–Cl9) were placed and their occupancies were refined to be 0.870(3) and 0.130(3), respectively. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: $C_{84}H_{24}Cl_6N_2O_6$; FW = 1369.75, crystal size 0.21 × 0.05 × 0.02 mm^3, triclinic, *P*-1, a = 9.957(3) Å, b = 15.514(5) Å, c = 19.041(6) Å, α = 77.394(4)°, β = 85.946(3)°, γ = 71.397(3)°, V = 2720.4(14) $Å^3$, Z = 2, D_c = 1.672 g cm^{-3}. The refinement converged to R_1 = 0.0491, wR_2 = 0.1194 ($I > 2\sigma(I)$), GOF = 1.053. The data was deposited at the Cambridge Crystallographic Data Centre (CCDC 2040746).

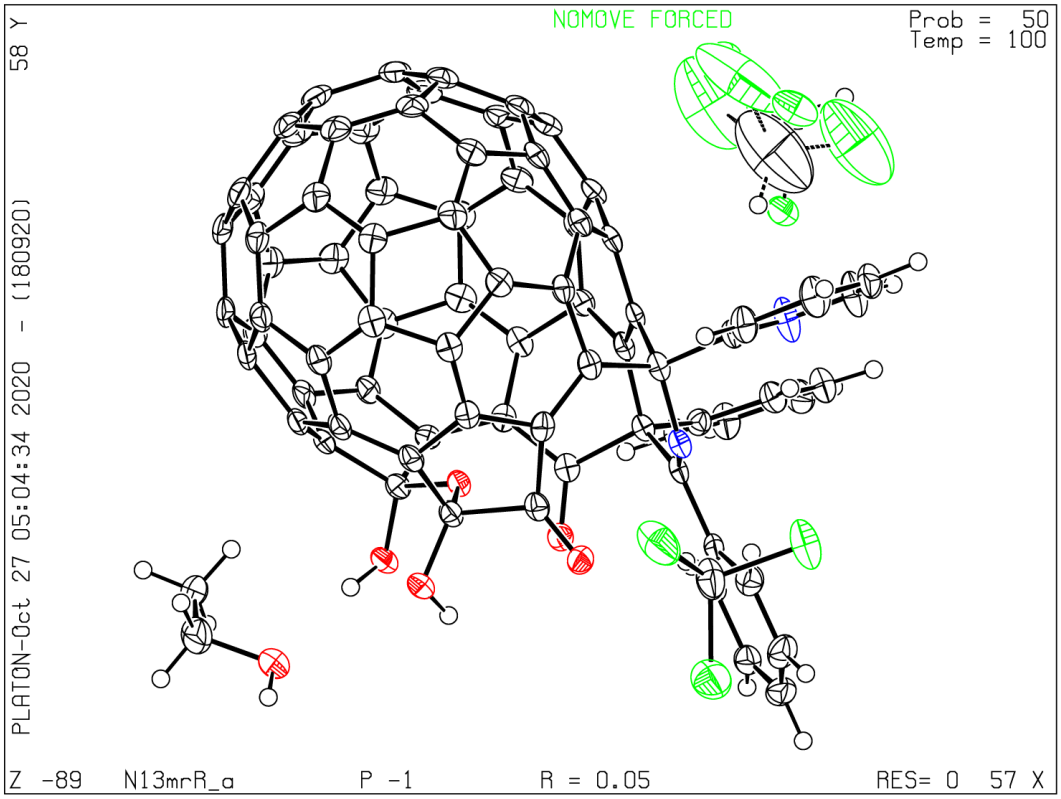


Figure S13. Single crystal X-ray structure of **2**•$(CHCl_3)_2$•EtOH.

4.2. Crystal Structure of $[(H_2O)_{0.808(7)}@3]\bullet(ODCB)_2$

Single crystals of **2** were obtained from an ODCB solution at 160 °C. Intensity data were collected at 100 K on a Bruker Single Crystal CCD X-ray Diffractometer (SMART APEX II) with Mo Kα radiation (λ = 0.71073 Å) and graphite monochromator. A total of 22927 reflections were measured at the maximum 2θ angle of 50.08°, of which 8680 were independent reflections (R_{int} = 0.0275). The structure was solved by direct methods (SHELXT-2014/5[1]) and refined by the full-matrix least-squares on F^2 (SHELXL-2018/3[1]). A chloroform molecule was disordered, which was solved using appropriate models. Thus, (C4–C5–C6–C7–C8–C9–Cl1–Cl2) and (C10–C11–C12–C13–C14–C15–Cl3–Cl4) were placed and their occupancies were refined to be 0.791(2) and 0.209(2), respectively. The occupancy of the encapsulated water molecule was refined to be 0.808(7). All non-hydrogen atoms were refined anisotropically. All hydrogen atoms except for that of the encapsulated water molecule were placed using AFIX instructions. The crystal data are as follows: $C_{86}H_{21.62}Cl_2N_2O_{5.81}$; FW = 1246.49, crystal size 0.18 × 0.14 × 0.03 mm^3, monoclinic, $P2_1/n$, a = 10.198(7) Å, b = 28.838(19) Å, c = 17.362(11) Å, β = 104.033(8)°, V = 4953(6) Å^3, Z = 4, D_c = 1.671 g cm^{-3}. The refinement converged to R_1 = 0.0406, wR_2 = 0.1010 ($I > 2\sigma(I)$), GOF = 1.025. The data was deposited at the Cambridge Crystallographic Data Centre (CCDC 2040747).

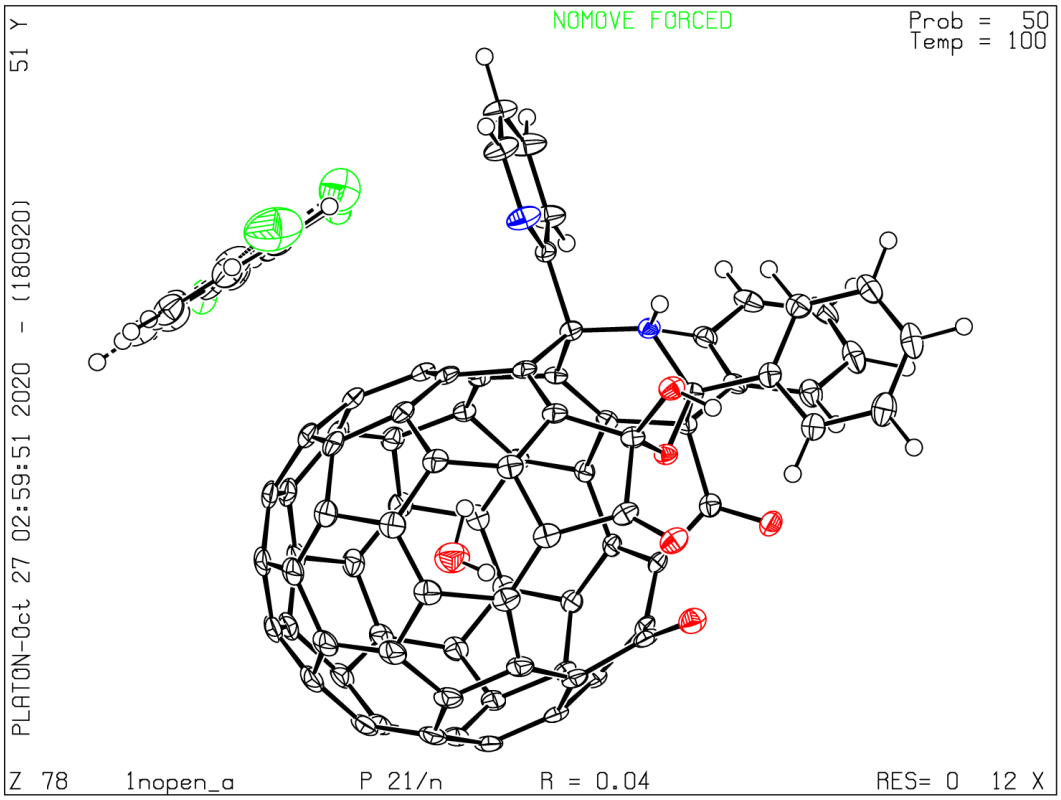


Figure S14. Single crystal X-ray structure of $[(H_2O)_{0.808(7)}@\mathbf{3}]\bullet(ODCB)_2$.

5. DFT Calculations

The energy profile on the transannular cyclization of **1** was computed at the B3LYP-D3/6-31G(d) level of theory (298 K, 1 atm). The reaction volumes ΔV and the volumes of activation $\Delta V^{\ddagger}$, which are defined as volume changes in the reaction systems, were calculated using the equation: $\Delta H = \Delta U + P\Delta V$, where H is enthalpy, U internal energy, and P pressure. The reactions with negative ΔV values are considered to be effective at high pressures.

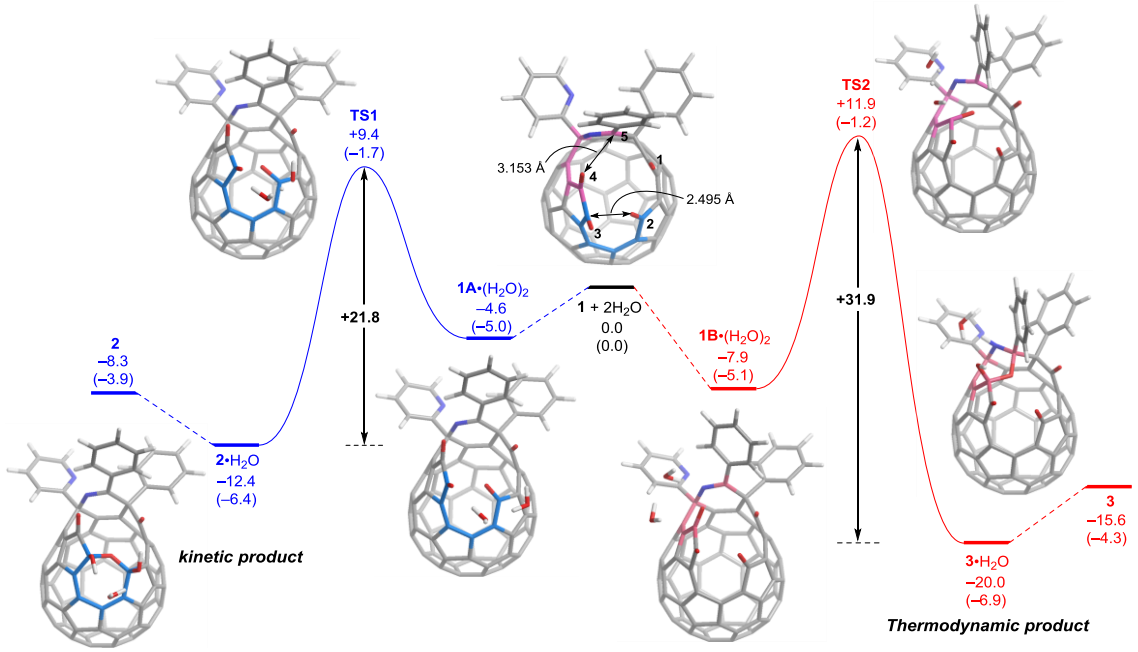


Figure S15. Energy profile on the transannular cyclization of **1**, calculated at the B3LYP-D3/6-31G(d) level of theory.

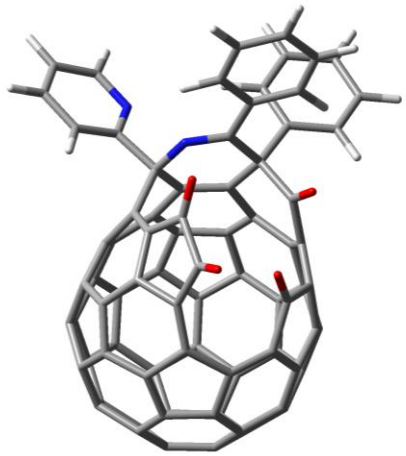
Table S1. Optimized structure of H_2O (B3LYP-D3/6-31G(d))

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.000000	0.000000	0.119774
2	1	0	-0.000000	0.761454	-0.479095
3	1	0	-0.000000	-0.761454	-0.479095

The total electronic energy was calculated to be –76.4089616 Hartree.

Table S2. Optimized structure of **1** (B3LYP-D3/6-31G(d))

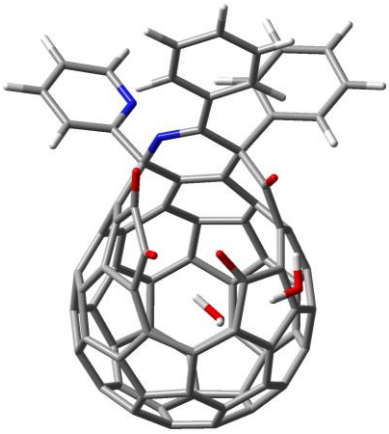


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.690557	1.119115	-2.925423
2	6	0	-2.276658	1.196985	-3.252778
3	6	0	-1.567681	0.032425	-3.499608
4	6	0	-2.221232	-1.261912	-3.415266
5	6	0	-3.567665	-1.343156	-3.061541
6	6	0	-4.317912	-0.124627	-2.810829
7	6	0	-1.668617	2.256938	-2.469247
8	6	0	-0.226945	-0.093333	-2.995553
9	6	0	-1.260387	-2.182883	-2.849669
10	6	0	-4.001972	-2.348565	-2.105820
11	6	0	-5.220038	-0.377233	-1.700207
12	6	0	-3.978619	2.172634	-1.975186
13	6	0	-3.069557	-3.235331	-1.559656
14	6	0	-1.671460	-3.154222	-1.945151
15	6	0	-3.113136	-3.548378	-0.145026
16	6	0	-0.850871	-3.411069	-0.781102
17	6	0	-0.370355	2.125812	-1.924856
18	6	0	-0.020099	-1.475552	-2.617934
19	6	0	-1.745502	-3.655231	0.322669
20	6	0	0.827507	-1.780655	-1.555895
21	6	0	0.382445	0.921931	-2.249928
22	6	0	-5.013365	-1.746099	-1.255351
23	6	0	-5.482238	0.629893	-0.769494
24	6	0	-0.072129	2.753653	-0.625260
25	6	0	-4.868743	1.939092	-0.918734
26	6	0	-2.746641	2.896762	-1.734509
27	6	0	-5.518513	0.316042	0.648526
28	6	0	-4.566234	2.448233	0.402473
29	6	0	-2.487702	3.430237	-0.484630
30	6	0	0.381083	-2.762117	-0.570492
31	6	0	-5.049009	-2.046357	0.111710
32	6	0	1.501739	0.553385	-1.421386
33	6	0	-4.932046	1.426534	1.372347
34	6	0	-3.420958	3.209440	0.611486
35	6	0	-1.144670	3.378030	0.038296
36	6	0	-1.260020	3.230794	1.459008
37	6	0	1.090208	2.327032	0.160067
38	6	0	1.748914	-0.755384	-1.115046
39	6	0	2.193259	-1.953169	1.015556
40	6	0	-2.628967	3.017746	1.805826
41	6	0	-2.913810	1.969361	2.686725
42	6	0	-1.874103	1.175940	3.326560
43	6	0	-4.093353	1.175880	2.461877
44	6	0	-4.074253	-2.957336	0.674463
45	6	0	1.833660	1.790425	2.716842
46	6	0	-5.287266	-0.987573	1.082038
47	6	0	-4.426495	-1.228230	2.227524
48	6	0	1.008250	2.301147	1.552133
49	6	0	0.830516	-2.531043	0.787604
50	6	0	-0.096866	-2.637902	1.823986
51	6	0	-0.275989	2.573773	2.156034
52	6	0	-0.563028	1.657905	3.236480
53	6	0	-3.797405	-0.169270	2.888888
54	6	0	-2.410765	-0.234912	3.367366
55	6	0	0.785346	1.425732	3.846297
56	6	0	-3.696179	-2.440848	1.982983
57	6	0	-1.392025	-3.162921	1.574429
58	6	0	-0.237407	-1.656550	2.981691
59	6	0	-2.378525	-2.501008	2.410020
60	6	0	-1.731795	-1.439408	3.144421
61	6	0	2.211860	1.658935	-0.660057
62	6	0	2.859015	-1.192438	-0.176347
63	6	0	3.668809	0.019516	0.358490
64	7	0	3.312337	1.233099	0.165895
65	6	0	3.753201	-2.123540	-1.028514
66	6	0	2.866323	2.651810	-1.647827
67	8	0	2.756401	-2.121638	2.076607
68	8	0	3.023175	1.767984	2.901224
69	6	0	3.011507	4.006437	-1.339309
70	6	0	3.682147	4.826002	-2.244381
71	6	0	4.185943	4.263858	-3.417564
72	6	0	4.000594	2.896976	-3.625224
73	7	0	3.357333	2.100782	-2.763115
74	6	0	3.828194	-3.504932	-0.826726
75	6	0	4.615098	-4.297279	-1.665135
76	6	0	5.329085	-3.717502	-2.713717
77	6	0	5.247341	-2.338833	-2.924183
78	6	0	4.460039	-1.545770	-2.091934
79	8	0	0.643631	-1.046288	3.542055
80	8	0	1.063621	1.266287	5.007259
81	6	0	6.726078	-1.508968	2.096537
82	6	0	5.509121	-1.418339	1.423016
83	6	0	4.947789	-0.169373	1.113278
84	6	0	5.648730	0.986365	1.510907
85	6	0	6.859497	0.894498	2.186562
86	6	0	7.408811	-0.356026	2.480777
87	1	0	2.612496	4.401557	-0.411286
88	1	0	3.810497	5.884628	-2.036088
89	1	0	4.713111	4.865064	-4.151897
90	1	0	4.384655	2.415192	-4.522465
91	1	0	3.293835	-3.971276	-0.004466
92	1	0	4.669389	-5.368724	-1.492657
93	1	0	5.942995	-4.334819	-3.363690
94	1	0	5.795763	-1.877795	-3.741152
95	1	0	4.376643	-0.476865	-2.274471
96	1	0	7.135685	-2.489481	2.323444
97	1	0	5.003732	-2.332078	1.154687

98	1	0	5.213299	1.951922	1.291058	----------
99	1	0	7.374812	1.802475	2.488260	The total electronic energy was calculated to be –3467.2768334 Hartree.
100	1	0	8.356706	-0.429767	3.007724	

Table S3. Optimized structure of **1A•**$(H_2O)_2$ (B3LYP-D3/6-31G(d))

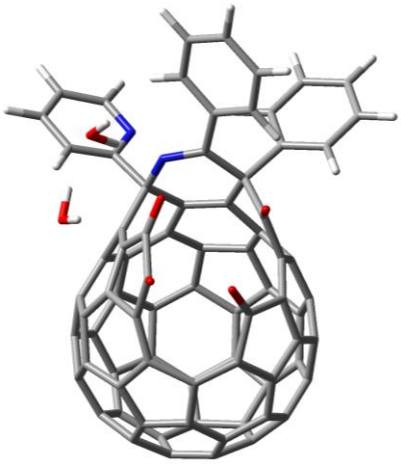


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.699507	-3.323535	0.214638
2	6	0	-2.285081	-3.652640	0.271689
3	6	0	-1.571051	-3.400916	1.431637
4	6	0	-2.219621	-2.796907	2.582268
5	6	0	-3.566046	-2.438858	2.516062
6	6	0	-4.321248	-2.707637	1.304269
7	6	0	-1.683015	-3.370479	-1.018547
8	6	0	-0.231535	-2.886605	1.334569
9	6	0	-1.254853	-1.909323	3.192812
10	6	0	-3.994891	-1.153741	3.042546
11	6	0	-5.221251	-1.588037	1.082060
12	6	0	-3.993812	-2.889718	-1.134716
13	6	0	-3.058653	-0.295942	3.626644
14	6	0	-1.662319	-0.686810	3.712819
15	6	0	-3.094408	1.122822	3.330102
16	6	0	-0.835269	0.477920	3.481483
17	6	0	-0.387920	-2.814266	-1.127592
18	6	0	-0.015703	-1.987894	2.448305
19	6	0	-1.725331	1.588532	3.242243
20	6	0	0.841024	-0.899832	2.302050
21	6	0	0.369658	-2.612936	0.100542
22	6	0	-5.005396	-0.620814	2.146350
23	6	0	-5.488578	-1.152595	-0.217040
24	6	0	-0.096363	-1.894554	-2.241084
25	6	0	-4.883925	-1.829399	-1.351963
26	6	0	-2.765728	-2.967887	-1.899436
27	6	0	-5.521964	0.269541	-0.514394
28	6	0	-4.586114	-0.836135	-2.362363
29	6	0	-2.513902	-2.052690	-2.905619
30	6	0	0.401665	0.397240	2.812891
31	6	0	-5.032227	0.748850	1.856678
32	6	0	1.486393	-1.702433	0.094714
33	6	0	-4.944630	0.470192	-1.828308
34	6	0	-3.448819	-0.963909	-3.153068
35	6	0	-1.171952	-1.556082	-3.084454
36	6	0	-1.290122	-0.205382	-3.549524
37	6	0	1.063938	-1.000973	-2.185386
38	6	0	1.750803	-0.904261	1.173730
39	6	0	2.220184	1.522164	1.446651
40	6	0	-2.658363	0.201398	-3.481503
41	6	0	-2.935315	1.437421	-2.886764
42	6	0	-1.887104	2.339871	-2.432764
43	6	0	-4.103433	1.563186	-2.055520
44	6	0	-4.050459	1.631476	2.451224
45	6	0	1.805852	1.534888	-2.798687
46	6	0	-5.274695	1.198517	0.494017
47	6	0	-4.407769	2.335365	0.237139
48	6	0	0.984297	0.265294	-2.763204
49	6	0	0.852298	1.536963	2.045637
50	6	0	-0.077584	2.507843	1.692213
51	6	0	-0.300801	0.700311	-3.259168
52	6	0	-0.584939	2.062513	-2.864746
53	6	0	-3.788659	2.500229	-1.004508
54	6	0	-2.396658	2.944494	-1.149262
55	6	0	0.750831	2.711655	-2.867828
56	6	0	-3.666388	2.606092	1.437358
57	6	0	-1.368449	2.520043	2.270460
58	6	0	-0.209557	3.052045	0.283909
59	6	0	-2.344022	3.004812	1.310347
60	6	0	-1.696641	3.211300	0.033728
61	6	0	2.186873	-1.452617	-1.230346
62	6	0	2.869743	0.125587	1.188283
63	6	0	3.647972	0.148081	-0.155549
64	7	0	3.272342	-0.506480	-1.188714
65	6	0	3.789587	-0.304387	2.355533
66	6	0	2.864290	-2.750739	-1.730643
67	8	0	2.802137	2.568147	1.238145
68	8	0	2.990585	1.721396	-2.902023
69	6	0	3.019396	-3.016814	-3.093296
70	6	0	3.708640	-4.166591	-3.471961
71	6	0	4.221058	-5.002952	-2.479915
72	6	0	4.025192	-4.640082	-1.147353
73	7	0	3.363841	-3.538572	-0.772703
74	6	0	4.491195	-1.509542	2.216697
75	6	0	5.302528	-1.971902	3.250857
76	6	0	5.412815	-1.245736	4.439137
77	6	0	4.702484	-0.054397	4.586392
78	6	0	3.891830	0.414422	3.550543
79	8	0	0.667177	2.999002	-0.558856
80	8	0	1.045911	3.863100	-3.119652
81	8	0	0.218269	5.378972	1.029997
82	6	0	4.920522	0.923794	-0.308430
83	6	0	5.518133	1.678568	0.713754
84	6	0	6.728790	2.336930	0.503470
85	6	0	7.369160	2.261836	-0.732402
86	6	0	6.784807	1.518864	-1.761210
87	6	0	5.581255	0.856419	-1.551352
88	1	0	2.613388	-2.335038	-3.832844
89	1	0	3.844692	-4.404043	-4.523481
90	1	0	4.762809	-5.910207	-2.728904
91	1	0	4.415626	-5.258027	-0.340909
92	1	0	4.383058	-2.091577	1.304593
93	1	0	5.847029	-2.904279	3.128307
94	1	0	6.045549	-1.607599	5.244862
95	1	0	4.777979	0.517479	5.507231
96	1	0	3.360480	1.352886	3.675637
97	1	0	0.054322	5.111757	-2.187495

98	1	0	1.146451	5.095330	0.997532	104	8	0	-0.451538	5.751567	-1.642439
99	1	0	5.046927	1.769831	1.678917	105	1	0	0.014546	5.622385	0.095479
100	1	0	7.167454	2.912909	1.313782	106	1	0	-0.261723	6.613405	-2.041210
101	1	0	8.312200	2.777842	-0.894072	---					
102	1	0	7.267874	1.456420	-2.732719	The total electronic energy was calculated to be –3620.1410692 Hartree.					
103	1	0	5.120910	0.287248	-2.347432						

Table S4. Optimized structure of **1B•**$(H_2O)_2$ (B3LYP-D3/6-31G(d))

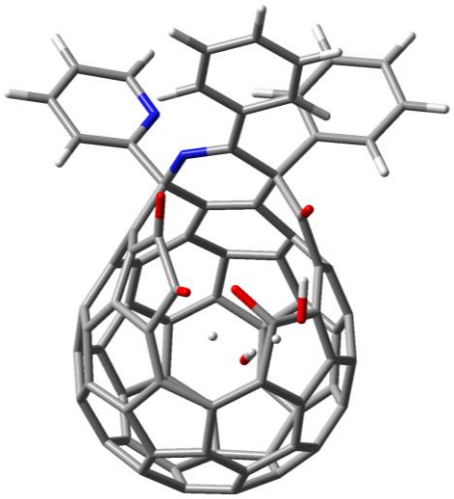


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.803265	0.269658	-3.164919
2	6	0	-2.392717	0.167875	-3.500309
3	6	0	-1.751236	-1.055805	-3.394407
4	6	0	-2.470329	-2.226921	-2.924639
5	6	0	-3.812697	-2.124687	-2.562599
6	6	0	-4.494500	-0.847780	-2.687714
7	6	0	-1.716640	1.376218	-3.062854
8	6	0	-0.408380	-1.102085	-2.881874
9	6	0	-1.549379	-2.987348	-2.108901
10	6	0	-4.283207	-2.773786	-1.350301
11	6	0	-5.392954	-0.709148	-1.554459
12	6	0	-4.019208	1.571134	-2.568421
13	6	0	-3.388831	-3.504121	-0.561720
14	6	0	-1.993324	-3.614152	-0.951311
15	6	0	-3.429452	-3.374872	0.880863
16	6	0	-1.169869	-3.541596	0.237557
17	6	0	-0.418240	1.338089	-2.505204
18	6	0	-0.268400	-2.316626	-2.104984
19	6	0	-2.061629	-3.398045	1.360055
20	6	0	0.582744	-2.334157	-1.001886
21	6	0	0.267413	0.053007	-2.475455
22	6	0	-5.251926	-1.892693	-0.721736
23	6	0	-5.588425	0.541907	-0.965564
24	6	0	-0.071111	2.291427	-1.435820
25	6	0	-4.905935	1.711477	-1.493104
26	6	0	-2.745547	2.262026	-2.548108
27	6	0	-5.627645	0.665857	0.481591
28	6	0	-4.558951	2.571149	-0.380226
29	6	0	-2.438133	3.119308	-1.506650
30	6	0	0.094022	-2.919632	0.244222
31	6	0	-5.287822	-1.770684	0.672200
32	6	0	1.388729	-0.117346	-1.588263
33	6	0	-4.974413	1.907767	0.846714
34	6	0	-3.367417	3.289669	-0.398920
35	6	0	-1.094596	3.140548	-0.984323
36	6	0	-1.196470	3.420567	0.417738
37	6	0	1.068358	2.026145	-0.548872
38	6	0	1.576298	-1.287802	-0.907650
39	6	0	1.937309	-1.698589	1.504715
40	6	0	-2.572950	3.414824	0.803176
41	6	0	-2.917918	2.704251	1.957729
42	6	0	-1.924764	2.086353	2.820873
43	6	0	-4.143191	1.947941	1.968917
44	6	0	-4.353098	-2.521501	1.483951
45	6	0	1.770762	2.063435	2.070378
46	6	0	-5.462413	-0.461250	1.283895
47	6	0	-4.607595	-0.396538	2.456903
48	6	0	0.995177	2.371418	0.798200
49	6	0	0.564885	-2.294130	1.467253
50	6	0	-0.352587	-2.052243	2.494045
51	6	0	-0.248886	2.928321	1.281303
52	6	0	-0.587428	2.426851	2.591811
53	6	0	-3.921574	0.777670	2.782450
54	6	0	-2.539199	0.784448	3.276447
55	6	0	0.751918	2.294319	3.241575
56	6	0	-3.939795	-1.662840	2.584592
57	6	0	-1.671454	-2.574481	2.410051
58	6	0	-0.445101	-0.795659	3.361405
59	6	0	-2.622837	-1.659664	3.017165
60	6	0	-1.925022	-0.464697	3.420989
61	6	0	2.145663	1.130665	-1.183023
62	6	0	2.662166	-1.470917	0.135671
63	6	0	3.591923	-0.232382	0.196012
64	7	0	3.280888	0.899438	-0.315278
65	6	0	3.482042	-2.715882	-0.267899
66	6	0	2.788538	1.811097	-2.413612
67	8	0	2.473026	-1.457604	2.567051
68	8	0	2.358248	4.643530	2.088997
69	6	0	3.085872	3.176831	-2.407023
70	6	0	3.744695	3.713486	-3.510226
71	6	0	4.081753	2.871316	-4.570847
72	6	0	3.754109	1.519349	-4.470525
73	7	0	3.124235	0.990278	-3.413855
74	6	0	4.092365	-2.703068	-1.530307
75	6	0	4.849406	-3.791436	-1.956590
76	6	0	4.998293	-4.909942	-1.132156
77	6	0	4.387579	-4.928269	0.121088
78	6	0	3.633035	-3.835011	0.553685
79	8	0	0.454535	-0.124015	3.809233
80	8	0	1.062959	2.549244	4.378652
81	6	0	6.639539	-1.164157	2.319926
82	6	0	5.333526	-1.164796	1.832748
83	6	0	4.962967	-0.309872	0.783971
84	6	0	5.949634	0.524888	0.222532
85	6	0	7.253506	0.521317	0.709564
86	6	0	7.604562	-0.323725	1.764670
87	1	0	2.827008	3.793844	-1.553642
88	1	0	3.993769	4.770435	-3.537529
89	1	0	4.592795	3.248534	-5.451361
90	1	0	4.008508	0.825607	-5.269698
91	1	0	3.970122	-1.835724	-2.175318

92	1	0	5.323029	-3.766099	-2.934152	101	8	0	2.900358	1.692057	2.274937
93	1	0	5.587616	-5.759738	-1.465191	102	1	0	4.025721	2.553545	0.283234
94	1	0	4.498502	-5.792051	0.770805	103	1	0	2.648481	4.439556	2.991647
95	1	0	3.180743	-3.859612	1.540085	104	8	0	4.424476	3.413740	0.556652
96	1	0	6.899263	-1.823531	3.143450	105	1	0	3.096292	4.316489	1.523928
97	1	0	4.597212	-1.802725	2.295938	106	1	0	5.000140	3.139644	1.287988
98	1	0	5.684623	1.173828	-0.604364	---					
99	1	0	7.997173	1.171638	0.256795	The total electronic energy was calculated to be –3620.1472889 Hartree.					
100	1	0	8.622349	-0.330925	2.145758						

Table S5. Optimized structure of **TS1** (B3LYP-D3/6-31G(d))

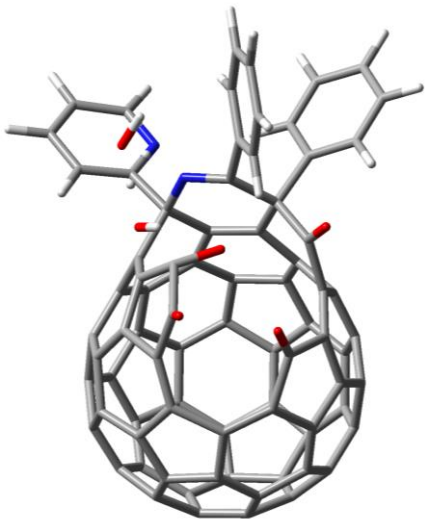


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.716697	-3.284507	0.162740
2	6	0	-2.303721	-3.622187	0.206906
3	6	0	-1.583010	-3.401586	1.369189
4	6	0	-2.221670	-2.817178	2.535398
5	6	0	-3.566264	-2.449477	2.482028
6	6	0	-4.329616	-2.689230	1.268876
7	6	0	-1.706018	-3.315325	-1.079867
8	6	0	-0.240330	-2.895091	1.277055
9	6	0	-1.248091	-1.949267	3.159917
10	6	0	-3.983574	-1.172396	3.035158
11	6	0	-5.225181	-1.561352	1.074486
12	6	0	-4.014559	-2.820347	-1.175461
13	6	0	-3.037995	-0.331463	3.628963
14	6	0	-1.644308	-0.733237	3.703112
15	6	0	-3.064390	1.092036	3.354780
16	6	0	-0.809530	0.430540	3.489508
17	6	0	-0.407724	-2.767434	-1.183536
18	6	0	-0.012003	-2.021498	2.408210
19	6	0	-1.692737	1.547234	3.264469
20	6	0	0.854722	-0.938136	2.282045
21	6	0	0.358000	-2.601181	0.046314
22	6	0	-4.996415	-0.616222	2.155567
23	6	0	-5.496758	-1.098135	-0.214470
24	6	0	-0.117094	-1.822947	-2.276649
25	6	0	-4.901104	-1.752941	-1.366999
26	6	0	-2.789214	-2.885781	-1.947404
27	6	0	-5.529344	0.329440	-0.482878
28	6	0	-4.607035	-0.740107	-2.360406
29	6	0	-2.536835	-1.947624	-2.931834
30	6	0	0.425005	0.352772	2.816379
31	6	0	-5.017585	0.758821	1.892172
32	6	0	1.483367	-1.701735	0.057465
33	6	0	-4.963183	0.554549	-1.798927
34	6	0	-3.469780	-0.852339	-3.155837
35	6	0	-1.193404	-1.450291	-3.105194
36	6	0	-1.307159	-0.086645	-3.537403
37	6	0	1.046622	-0.939316	-2.195339
38	6	0	1.757356	-0.925085	1.149449
39	6	0	2.217396	1.497556	1.423493
40	6	0	-2.679492	0.316805	-3.470913
41	6	0	-2.966929	1.544305	-2.861788
42	6	0	-1.918737	2.425981	-2.381033
43	6	0	-4.126802	1.653405	-2.015218
44	6	0	-4.020684	1.622663	2.490095
45	6	0	1.762472	1.626374	-2.564877
46	6	0	-5.272665	1.236907	0.542595
47	6	0	-4.404652	2.377806	0.301686
48	6	0	0.959943	0.350922	-2.707721
49	6	0	0.875300	1.500454	2.063329
50	6	0	-0.058352	2.462521	1.709975
51	6	0	-0.312075	0.809484	-3.210737
52	6	0	-0.611198	2.139915	-2.746939
53	6	0	-3.799015	2.564000	-0.941817
54	6	0	-2.407313	3.001306	-1.085799
55	6	0	0.692183	2.767336	-2.381130
56	6	0	-3.642234	2.616799	1.492249
57	6	0	-1.337825	2.491507	2.298345
58	6	0	-0.137229	3.087594	0.299297
59	6	0	-2.312814	3.007988	1.357273
60	6	0	-1.677512	3.246633	0.080298
61	6	0	2.174341	-1.431320	-1.266313
62	6	0	2.876202	0.108114	1.169020
63	6	0	3.654645	0.136626	-0.173236
64	7	0	3.277059	-0.505042	-1.212257
65	6	0	3.796406	-0.322937	2.334405
66	6	0	2.828202	-2.727135	-1.801341
67	8	0	2.774421	2.552219	1.163071
68	8	0	2.936082	1.847507	-2.710309
69	6	0	2.925325	-2.992600	-3.169304
70	6	0	3.598202	-4.141950	-3.578105
71	6	0	4.152604	-4.979094	-2.609905
72	6	0	4.013026	-4.617357	-1.269760
73	7	0	3.368557	-3.516544	-0.866167
74	6	0	4.506986	-1.521946	2.188443
75	6	0	5.320578	-1.985045	3.220424
76	6	0	5.424819	-1.265758	4.413570
77	6	0	4.705828	-0.080600	4.567966
78	6	0	3.892704	0.388574	3.534186
79	8	0	0.558825	2.383018	-0.559996
80	8	0	1.023882	3.960765	-2.592833
81	8	0	0.456787	4.538629	0.463437
82	6	0	4.926598	0.915160	-0.320091
83	6	0	5.518695	1.668049	0.706165
84	6	0	6.726235	2.334032	0.500999
85	6	0	7.368288	2.268862	-0.734698
86	6	0	6.787257	1.530324	-1.768608
87	6	0	5.586332	0.861270	-1.563542

88	1	0	2.486611	-2.311482	-3.890308	99	1	0	5.045282	1.751222	1.671420
89	1	0	3.688947	-4.378398	-4.634790	100	1	0	7.162041	2.906841	1.315307
90	1	0	4.683337	-5.886136	-2.882501	101	1	0	8.309646	2.789324	-0.892322
91	1	0	4.437221	-5.236516	-0.481359	102	1	0	7.270719	1.476952	-2.740530
92	1	0	4.403318	-2.098198	1.272003	103	1	0	5.126333	0.296959	-2.363637
93	1	0	5.871399	-2.913014	3.092701	104	8	0	-0.245545	5.744233	-1.508399
94	1	0	6.059121	-1.628624	5.217649	105	1	0	0.147820	5.212792	-0.461713
95	1	0	4.775785	0.485292	5.493014	106	1	0	0.238590	6.570956	-1.670109
96	1	0	3.351174	1.320588	3.665277						
97	1	0	0.179544	5.014168	-2.159407	The total electronic energy was calculated to be –3620.1212434 Hartree.					
98	1	0	1.421479	4.354205	0.485013	An imaginary frequency was found at –703.30 cm^{-1}.					

Table S6. Optimized structure of **TS2** (B3LYP-D3/6-31G(d))



Standard orientation:

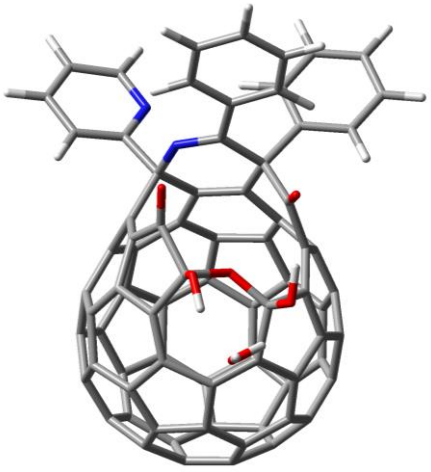
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.853640	2.876979	1.273938
2	6	0	2.447136	3.139856	1.529191
3	6	0	1.797085	2.451547	2.540975
4	6	0	2.503700	1.461852	3.333865
5	6	0	3.844197	1.182274	3.070017
6	6	0	4.533274	1.905568	2.015090
7	6	0	1.772151	3.368783	0.263731
8	6	0	0.451335	1.992345	2.324272
9	6	0	1.570868	0.388740	3.597380
10	6	0	4.301752	-0.196814	3.049008
11	6	0	5.420496	0.972734	1.341434
12	6	0	4.067508	2.989127	-0.153081
13	6	0	3.397772	-1.231741	3.307034
14	6	0	2.004925	-0.930283	3.588845
15	6	0	3.425557	-2.434018	2.498791
16	6	0	1.173786	-1.932062	2.958469
17	6	0	0.462178	2.894934	0.024981
18	6	0	0.298046	0.719327	2.994838
19	6	0	2.054482	-2.858719	2.296368
20	6	0	-0.552339	-0.249435	2.460018
21	6	0	-0.225674	2.224469	1.124440
22	6	0	5.266935	-0.329123	1.971526
23	6	0	5.609681	1.063832	-0.039421
24	6	0	0.099815	2.455967	-1.333621
25	6	0	4.937784	2.103545	-0.801537
26	6	0	2.798439	3.335276	-0.764361
27	6	0	5.626329	-0.141568	-0.850334
28	6	0	4.572509	1.552704	-2.090348
29	6	0	2.478290	2.849292	-2.019894
30	6	0	-0.084084	-1.630902	2.404294
31	6	0	5.284280	-1.488807	1.187437
32	6	0	-1.352129	1.372958	0.833946
33	6	0	4.964507	0.151334	-2.106478
34	6	0	3.385581	1.939881	-2.704206
35	6	0	1.122438	2.441219	-2.296794
36	6	0	1.197246	1.337310	-3.211372
37	6	0	-1.060453	1.580282	-1.527104
38	6	0	-1.525749	0.178073	1.479981
39	6	0	-2.016067	-2.224559	0.910967
40	6	0	2.566255	0.962885	-3.387366
41	6	0	2.886827	-0.398163	-3.319581
42	6	0	1.878239	-1.432852	-3.177544
43	6	0	4.109774	-0.796270	-2.674499
44	6	0	4.341883	-2.555115	1.455057
45	6	0	-1.743476	-0.802999	-2.558803
46	6	0	5.449490	-1.388595	-0.255297
47	6	0	4.576531	-2.372373	-0.874526
48	6	0	-1.004906	0.550766	-2.458002
49	6	0	-0.579221	-2.421510	1.292468
50	6	0	0.321234	-3.216503	0.589490
51	6	0	0.225001	0.360350	-3.189238
52	6	0	0.550884	-1.042246	-3.341828
53	6	0	3.873518	-2.072746	-2.045088
54	6	0	2.484146	-2.487165	-2.275689
55	6	0	-0.787505	-1.686029	-3.420883
56	6	0	3.911517	-3.093211	0.172723
57	6	0	1.651035	-3.374194	1.071504
58	6	0	0.391774	-3.474289	-0.917474
59	6	0	2.589902	-3.463623	-0.031539
60	6	0	1.874993	-3.236581	-1.264185
61	6	0	-2.131019	1.704557	-0.420183
62	6	0	-2.630022	-0.797788	1.122374
63	6	0	-3.421767	-0.327915	-0.118057
64	7	0	-3.287380	0.849519	-0.642325
65	6	0	-3.653001	-0.785585	2.298408
66	6	0	-2.726931	3.124325	-0.346540
67	8	0	-2.691141	-3.183344	0.602730
68	8	0	-2.941267	-0.547876	-3.615548
69	6	0	-2.913934	3.895445	-1.496204
70	6	0	-3.542792	5.133129	-1.372960
71	6	0	-3.960578	5.553314	-0.110670
72	6	0	-3.737762	4.703652	0.973825
73	7	0	-3.138727	3.512496	0.866673
74	6	0	-4.066588	0.465726	2.785320
75	6	0	-5.013811	0.550857	3.803974
76	6	0	-5.559517	-0.609109	4.357297
77	6	0	-5.154913	-1.852436	3.873677

78	6	0	-4.213361	-1.944275	2.845843	94	1	0	-5.576110	-2.763556	4.290065
79	8	0	-0.486170	-3.808113	-1.670178	95	1	0	-3.937467	-2.919590	2.466907
80	8	0	-1.144211	-2.613977	-4.111287	96	1	0	-6.133991	-3.671993	-2.025439
81	6	0	-6.072784	-2.729996	-1.487161	97	1	0	-3.913109	-2.748112	-1.411237
82	6	0	-4.818477	-2.224181	-1.141355	98	1	0	-5.825377	0.622233	0.425702
83	6	0	-4.725550	-1.005895	-0.455813	99	1	0	-8.051566	-0.285923	-0.187347
84	6	0	-5.901227	-0.315466	-0.115749	100	1	0	-8.211209	-2.441927	-1.427903
85	6	0	-7.151429	-0.829263	-0.461856	101	8	0	-2.091812	-1.443042	-1.505105
86	6	0	-7.239695	-2.039394	-1.153648	102	1	0	-4.109627	1.077436	-1.814090
87	1	0	-2.579184	3.528684	-2.460587	103	1	0	-3.223776	-1.455137	-3.840407
88	1	0	-3.702220	5.757078	-2.247950	104	8	0	-4.609457	0.986415	-2.790102
89	1	0	-4.449454	6.511849	0.033703	105	1	0	-3.848199	0.166403	-3.243141
90	1	0	-4.053850	4.989153	1.975493	106	1	0	-5.452996	0.546596	-2.583682
91	1	0	-3.658919	1.379010	2.360281						

The total electronic energy was calculated to be –3620.1164999 Hartree.

An imaginary frequency was found at –885.56 cm^{-1}.

Table S7. Optimized structure of **2**•H_2O (B3LYP-D3/6-31G(d))

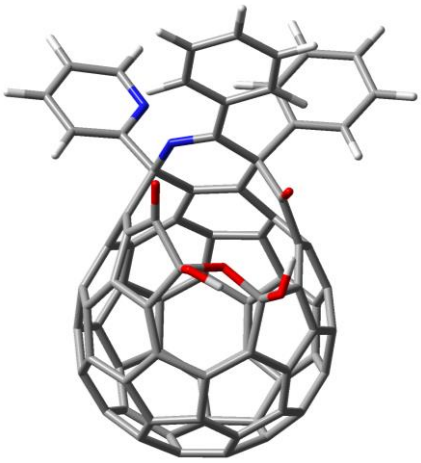


Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.648647	3.338889	0.196808
2	6	0	2.231526	3.658216	0.240678
3	6	0	1.510973	3.416857	1.399220
4	6	0	2.154541	2.827281	2.560314
5	6	0	3.504197	2.480233	2.507993
6	6	0	4.267740	2.743362	1.299509
7	6	0	1.640917	3.356288	-1.050812
8	6	0	0.174924	2.894325	1.298200
9	6	0	1.192395	1.935571	3.169181
10	6	0	3.939587	1.204422	3.050475
11	6	0	5.181961	1.632191	1.098441
12	6	0	3.954863	2.888676	-1.144293
13	6	0	3.004745	0.341262	3.630095
14	6	0	1.604373	0.718912	3.698154
15	6	0	3.057581	-1.079048	3.343256
16	6	0	0.791721	-0.456233	3.460195
17	6	0	0.347984	2.799034	-1.163916
18	6	0	-0.041094	1.998212	2.414765
19	6	0	1.693829	-1.556198	3.234792
20	6	0	-0.885801	0.899835	2.266685
21	6	0	-0.419215	2.611894	0.063204
22	6	0	4.966541	0.674500	2.171095
23	6	0	5.463635	1.183650	-0.193863
24	6	0	0.071553	1.859515	-2.264870
25	6	0	4.857626	1.836653	-1.341943
26	6	0	2.729985	2.942384	-1.918409
27	6	0	5.524061	-0.240650	-0.472962
28	6	0	4.580165	0.825980	-2.342670
29	6	0	2.491278	2.004801	-2.907867
30	6	0	-0.433883	-0.393627	2.773019
31	6	0	5.015862	-0.697540	1.898167
32	6	0	-1.534839	1.699911	0.063940
33	6	0	4.962789	-0.465685	-1.792030
34	6	0	3.439703	0.924215	-3.135616
35	6	0	1.154546	1.490607	-3.086794
36	6	0	1.286821	0.124601	-3.516339
37	6	0	-1.083022	0.965744	-2.183442
38	6	0	-1.792346	0.896041	1.139675
39	6	0	-2.207465	-1.542856	1.366408
40	6	0	2.666714	-0.256060	-3.455213
41	6	0	2.983895	-1.483525	-2.861000
42	6	0	1.951961	-2.374811	-2.364474
43	6	0	4.150022	-1.579547	-2.019066
44	6	0	4.032452	-1.584853	2.484748
45	6	0	-1.725841	-1.618782	-2.443960
46	6	0	5.286241	-1.160989	0.546203
47	6	0	4.445290	-2.319580	0.295492
48	6	0	-0.965372	-0.330503	-2.664744
49	6	0	-0.858575	-1.539636	1.994824
50	6	0	0.087626	-2.494721	1.650610
51	6	0	0.306786	-0.783970	-3.165076
52	6	0	0.632900	-2.091406	-2.664619
53	6	0	3.845779	-2.506269	-0.950734
54	6	0	2.466297	-2.969037	-1.093750
55	6	0	-0.616747	-2.669587	-2.041474
56	6	0	3.681272	-2.581331	1.481180
57	6	0	1.361748	-2.500987	2.262718
58	6	0	0.194478	-3.222880	0.282030
59	6	0	2.360743	-3.000992	1.340241
60	6	0	1.740535	-3.245949	0.061691
61	6	0	-2.222299	1.440741	-1.261711
62	6	0	-2.891859	-0.156985	1.144401
63	6	0	-3.677425	-0.168934	-0.194010
64	7	0	-3.314086	0.500282	-1.221584
65	6	0	-3.813261	0.232664	2.323374
66	6	0	-2.884535	2.735920	-1.784319
67	8	0	-2.749008	-2.598829	1.085143
68	8	0	-2.875702	-1.904627	-2.639612
69	6	0	-2.971174	3.022040	-3.148662
70	6	0	-3.651167	4.171574	-3.545417
71	6	0	-4.222855	4.987498	-2.569236

72	6	0	-4.092591	4.605661	-1.233672	91	1	0	-4.530080	5.208104	-0.439637
73	7	0	-3.441054	3.504921	-0.841597	92	1	0	-4.455412	2.020296	1.303030
74	6	0	-4.544353	1.422604	2.207284	93	1	0	-5.927087	2.770113	3.149064
75	6	0	-5.360144	1.848965	3.253245	94	1	0	-6.082204	1.435836	5.245521
76	6	0	-5.446114	1.101570	4.430552	95	1	0	-4.762999	-0.662191	5.467404
77	6	0	-4.706936	-0.074601	4.555058	96	1	0	-3.334812	-1.433178	3.614251
78	6	0	-3.891559	-0.507085	3.507140	97	1	0	-0.231449	-4.547792	-2.366242
79	8	0	-0.537251	-2.424301	-0.607899	98	1	0	-1.263690	-4.462424	0.413649
80	8	0	-1.000449	-3.924248	-2.406693	99	1	0	-5.037620	-1.837584	1.623908
81	8	0	-0.293391	-4.551588	0.331753	100	1	0	-7.127411	-3.034261	1.244728
82	6	0	-4.933002	-0.969637	-0.354735	101	1	0	-8.271775	-2.909313	-0.963915
83	6	0	-5.510667	-1.750316	0.658839	102	1	0	-7.257713	-1.547813	-2.790050
84	6	0	-6.702699	-2.439433	0.440515	103	1	0	-5.141159	-0.326451	-2.390236
85	6	0	-7.342848	-2.370206	-0.795904	104	8	0	0.899065	-5.770007	-1.842464
86	6	0	-6.775755	-1.604247	-1.817593	105	1	0	0.563946	-5.620559	-0.932515
87	6	0	-5.590271	-0.912545	-1.599452	106	1	0	0.534929	-6.628281	-2.109495
88	1	0	-2.518768	2.357186	-3.876440	---					
89	1	0	-3.733863	4.424508	-4.598911	The total electronic energy was calculated to be –3620.1626738 Hartree.					
90	1	0	-4.759546	5.893844	-2.832278						

Table S8. Optimized structure of **2** (B3LYP-D3/6-31G(d))



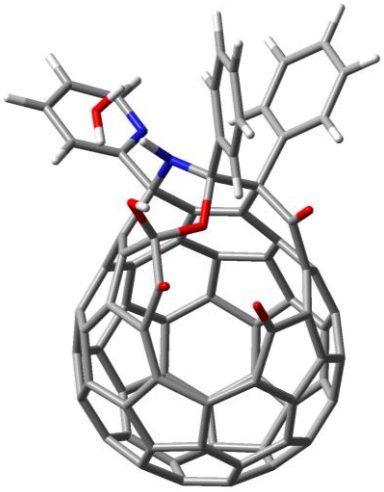
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.716035	2.676170	1.711625
2	6	0	2.304136	2.947699	1.923590
3	6	0	1.583205	2.170452	2.815128
4	6	0	2.220884	1.073476	3.522252
5	6	0	3.564471	0.782140	3.288717
6	6	0	4.328534	1.602964	2.364231
7	6	0	1.705292	3.337948	0.660408
8	6	0	0.238674	1.784222	2.481289
9	6	0	1.246637	0.008945	3.618346
10	6	0	3.981831	-0.599141	3.119943
11	6	0	5.224587	0.728750	1.626729
12	6	0	4.010714	2.950147	0.321356
13	6	0	3.035800	-1.624999	3.204847
14	6	0	1.642108	-1.314935	3.468541
15	6	0	3.064312	-2.714415	2.248105
16	6	0	0.809781	-2.206589	2.687507
17	6	0	0.403202	2.927768	0.297663
18	6	0	0.012595	0.453817	3.005832
19	6	0	1.692977	-3.059158	1.933432
20	6	0	-0.850161	-0.414748	2.340779
21	6	0	-0.363587	2.161789	1.275483
22	6	0	4.997121	-0.633428	2.082010
23	6	0	5.495498	0.980566	0.279964
24	6	0	0.108884	2.668232	-1.122415
25	6	0	4.896251	2.126482	-0.383962
26	6	0	2.785021	3.398407	-0.309505
27	6	0	5.530255	-0.115974	-0.672237
28	6	0	4.599725	1.753278	-1.752239
29	6	0	2.528410	3.084512	-1.632405
30	6	0	-0.418229	-1.795635	2.138483
31	6	0	5.022222	-1.687306	1.161156
32	6	0	-1.491327	1.382071	0.831842
33	6	0	4.961629	0.353631	-1.922057
34	6	0	3.458435	2.248924	-2.378446
35	6	0	1.182891	2.747278	-2.031114
36	6	0	1.292363	1.776863	-3.087794
37	6	0	-1.061713	1.871299	-1.487167
38	6	0	-1.757879	0.152049	1.366851
39	6	0	-2.211592	-2.072726	0.362519
40	6	0	2.665492	1.396135	-3.236023
41	6	0	2.963427	0.031117	-3.334853
42	6	0	1.917239	-0.972699	-3.333401
43	6	0	4.129326	-0.488107	-2.664652
44	6	0	4.025476	-2.735575	1.238782
45	6	0	-1.746986	-0.225211	-2.998651
46	6	0	5.280405	-1.418541	-0.244685
47	6	0	4.418671	-2.286743	-1.029692
48	6	0	-0.968643	0.992861	-2.557119
49	6	0	-0.864984	-2.399464	0.901252
50	6	0	0.064698	-3.065960	0.114962
51	6	0	0.297227	0.827491	-3.225302
52	6	0	0.602949	-0.560742	-3.432435
53	6	0	3.812084	-1.819689	-2.196418
54	6	0	2.422501	-2.129290	-2.533591
55	6	0	-0.648303	-1.356866	-3.128914
56	6	0	3.653195	-3.093704	-0.124039
57	6	0	1.341746	-3.389634	0.623305
58	6	0	0.150134	-2.991864	-1.430058
59	6	0	2.325589	-3.372411	-0.439899
60	6	0	1.693579	-2.934222	-1.660918
61	6	0	-2.189558	1.828118	-0.438357
62	6	0	-2.874298	-0.750410	0.858407
63	6	0	-3.659499	-0.088625	-0.306170
64	7	0	-3.290220	1.001000	-0.864979
65	6	0	-3.790169	-0.982806	2.082169

66	6	0	-2.839604	3.214759	-0.227067
67	8	0	-2.763211	-2.844035	-0.406205
68	8	0	-2.893670	-0.366101	-3.324556
69	6	0	-2.893706	4.172438	-1.241680
70	6	0	-3.560409	5.370467	-0.991255
71	6	0	-4.151536	5.564941	0.256675
72	6	0	-4.053663	4.539514	1.198033
73	7	0	-3.415249	3.386872	0.968783
74	6	0	-4.503869	0.117714	2.575417
75	6	0	-5.313986	-0.019942	3.700759
76	6	0	-5.412211	-1.251147	4.353615
77	6	0	-4.690202	-2.343986	3.874279
78	6	0	-3.880182	-2.210743	2.744690
79	8	0	-0.550519	-1.811437	-1.767420
80	8	0	-1.024803	-2.313937	-4.046004
81	8	0	-0.402349	-4.114189	-2.088359
82	6	0	-4.920331	-0.695076	-0.839832
83	6	0	-5.511070	-1.865705	-0.337947
84	6	0	-6.705846	-2.349266	-0.868830
85	6	0	-7.336166	-1.679466	-1.916405
86	6	0	-6.756983	-0.517270	-2.431826
87	6	0	-5.568936	-0.030698	-1.899520
88	1	0	-2.426432	3.979709	-2.201174
89	1	0	-3.617518	6.137556	-1.758641
90	1	0	-4.678574	6.483234	0.496690
91	1	0	-4.506987	4.645334	2.181979
92	1	0	-4.406943	1.083870	2.085481
93	1	0	-5.867334	0.839184	4.070188
94	1	0	-6.044174	-1.356531	5.231087
95	1	0	-4.755654	-3.305871	4.375513
96	1	0	-3.337124	-3.075823	2.375986
97	1	0	-0.693865	-3.179140	-3.737721
98	1	0	-1.330111	-4.150251	-1.774989
99	1	0	-5.047530	-2.418195	0.463840
100	1	0	-7.140459	-3.257047	-0.459037
101	1	0	-8.266826	-2.059731	-2.329868
102	1	0	-7.230971	0.011120	-3.254721
103	1	0	-5.110365	0.861975	-2.303418

The total electronic energy was calculated to be –3543.7276623 Hartree.

Table S9. Optimized structure of **3**•H_2O (B3LYP-D3/6-31G(d))



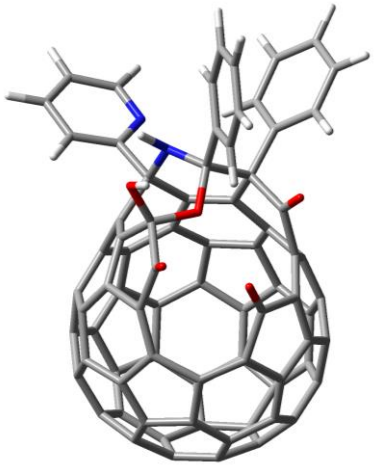
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.919879	2.904680	1.063298
2	6	0	2.524521	3.186070	1.355306
3	6	0	1.901957	2.528915	2.403938
4	6	0	2.630486	1.570319	3.212951
5	6	0	3.963303	1.278832	2.921104
6	6	0	4.618930	1.957005	1.816233
7	6	0	1.810083	3.383937	0.107913
8	6	0	0.551646	2.058717	2.239428
9	6	0	1.705160	0.510677	3.547979
10	6	0	4.419541	-0.100517	2.942685
11	6	0	5.476231	0.992813	1.147899
12	6	0	4.085171	2.963886	-0.373620
13	6	0	3.527180	-1.121186	3.281346
14	6	0	2.144486	-0.805591	3.596838
15	6	0	3.526139	-2.360505	2.529791
16	6	0	1.293607	-1.837980	3.054020
17	6	0	0.488698	2.918752	-0.072595
18	6	0	0.416003	0.813829	2.960200
19	6	0	2.150824	-2.801442	2.408336
20	6	0	-0.449695	-0.177149	2.489219
21	6	0	-0.163449	2.254058	1.057030
22	6	0	5.342334	-0.281470	1.835965
23	6	0	5.613776	1.028092	-0.241405
24	6	0	0.074779	2.477495	-1.411905
25	6	0	4.923168	2.044309	-1.018022
26	6	0	2.801094	3.306444	-0.954527
27	6	0	5.585863	-0.209159	-1.002594
28	6	0	4.502657	1.446474	-2.268209
29	6	0	2.435722	2.786302	-2.185207
30	6	0	0.017156	-1.561634	2.529138
31	6	0	5.326028	-1.472843	1.100582
32	6	0	-1.294974	1.386533	0.822339
33	6	0	4.871913	0.039517	-2.239715
34	6	0	3.302259	1.827827	-2.855888
35	6	0	1.064313	2.402185	-2.408656
36	6	0	1.088886	1.252598	-3.271839
37	6	0	-1.107576	1.637691	-1.542934
38	6	0	-1.443595	0.197002	1.498961
39	6	0	-1.951948	-2.249503	1.146354
40	6	0	2.440255	0.833966	-3.459311
41	6	0	2.730199	-0.529667	-3.329937
42	6	0	1.707450	-1.535361	-3.079134
43	6	0	3.977255	-0.917646	-2.725609
44	6	0	4.397086	-2.526034	1.452769
45	6	0	-1.930044	-0.680904	-2.428381
46	6	0	5.427193	-1.429421	-0.351223
47	6	0	4.519885	-2.427961	-0.891089
48	6	0	-1.107944	0.592321	-2.444307
49	6	0	-0.517449	-2.428557	1.505403
50	6	0	0.351593	-3.257605	0.805737
51	6	0	0.096692	0.300412	-3.170666
52	6	0	0.378833	-1.119699	-3.201242
53	6	0	3.758124	-2.162031	-2.033159
54	6	0	2.354305	-2.566476	-2.174107
55	6	0	-0.985107	-1.716243	-3.154076
56	6	0	3.909261	-3.112570	0.211838
57	6	0	1.701296	-3.383367	1.229275
58	6	0	0.343115	-3.497278	-0.696813
59	6	0	2.583993	-3.498144	0.083639
60	6	0	1.804347	-3.298472	-1.117091
61	6	0	-2.135987	1.725095	-0.394081

62	6	0	-2.548940	-0.813605	1.178135
63	6	0	-3.126703	-0.560683	-0.285214
64	7	0	-3.271090	0.833118	-0.503467
65	6	0	-3.667567	-0.661659	2.235062
66	6	0	-2.742936	3.136245	-0.288628
67	8	0	-2.624153	-3.229491	0.887870
68	8	0	-3.111487	-0.590196	-3.179096
69	6	0	-3.153073	3.813365	-1.440214
70	6	0	-3.776729	5.051169	-1.298021
71	6	0	-3.962462	5.567779	-0.016195
72	6	0	-3.524736	4.808980	1.070096
73	7	0	-2.930243	3.617247	0.945897
74	6	0	-4.017259	0.627613	2.669180
75	6	0	-5.070574	0.815191	3.563897
76	6	0	-5.787510	-0.277702	4.051982
77	6	0	-5.442680	-1.560867	3.629424
78	6	0	-4.396466	-1.753550	2.726042
79	8	0	-0.595410	-3.734491	-1.418052
80	8	0	-1.438456	-2.652187	-3.770803
81	6	0	-5.751619	-3.089656	-1.466870
82	6	0	-4.521697	-2.496300	-1.182082
83	6	0	-4.469155	-1.245544	-0.556229
84	6	0	-5.667527	-0.610467	-0.200428
85	6	0	-6.897390	-1.204917	-0.490834
86	6	0	-6.943469	-2.445294	-1.130077
87	1	0	-3.006040	3.369650	-2.418722
88	1	0	-4.112353	5.599508	-2.173644
89	1	0	-4.438188	6.530746	0.142436
90	1	0	-3.656257	5.170805	2.088250
91	1	0	-3.486021	1.496825	2.298928
92	1	0	-5.326410	1.823719	3.878407
93	1	0	-6.606017	-0.130766	4.751854
94	1	0	-5.994141	-2.423411	3.994145
95	1	0	-4.172509	-2.755685	2.385623
96	1	0	-5.774822	-4.060526	-1.954355
97	1	0	-3.599038	-3.003074	-1.438079
98	1	0	-5.633329	0.343179	0.314350
99	1	0	-7.816760	-0.700344	-0.205631
100	1	0	-7.899909	-2.908848	-1.356823
101	8	0	-2.094269	-1.187041	-1.129175
102	1	0	-3.911302	1.087201	-1.258910
103	1	0	-3.305017	-1.502288	-3.476511
104	8	0	-5.101402	1.342094	-2.757149
105	1	0	-4.504840	0.681456	-3.159498
106	1	0	-5.796792	0.797166	-2.352770

The total electronic energy was calculated to be –3620.1770762 Hartree.

Table S10. Optimized structure of **3** (B3LYP-D3/6-31G(d))



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.846539	2.915768	-0.977684
2	6	0	-2.447179	3.240967	-1.196288
3	6	0	-1.770202	2.663127	-2.257489
4	6	0	-2.446646	1.743911	-3.153079
5	6	0	-3.783226	1.408673	-2.932458
6	6	0	-4.495119	2.003233	-1.814331
7	6	0	-1.785422	3.374957	0.087789
8	6	0	-0.416646	2.209488	-2.069471
9	6	0	-1.486712	0.725542	-3.516976
10	6	0	-4.208058	0.024752	-3.057119
11	6	0	-5.355240	0.982395	-1.240640
12	6	0	-4.067829	2.881880	0.452519
13	6	0	-3.281569	-0.955073	-3.423370
14	6	0	-1.895133	-0.593205	-3.665171
15	6	0	-3.281396	-2.238227	-2.749304
16	6	0	-1.043124	-1.640942	-3.154148
17	6	0	-0.461602	2.925786	0.290870
18	6	0	-0.227006	1.016376	-2.861766
19	6	0	-1.902672	-2.658699	-2.601585
20	6	0	0.642021	0.014825	-2.420498
21	6	0	0.250458	2.344908	-0.850162
22	6	0	-5.167612	-0.243344	-2.000293
23	6	0	-5.546354	0.928243	0.141581
24	6	0	-0.092174	2.410182	1.615386
25	6	0	-4.909596	1.907765	1.005841
26	6	0	-2.814656	3.212149	1.103579
27	6	0	-5.519693	-0.353418	0.826006
28	6	0	-4.524358	1.241298	2.232673
29	6	0	-2.486144	2.623252	2.313253
30	6	0	0.205929	-1.373099	-2.564194
31	6	0	-5.152261	-1.477588	-1.339248
32	6	0	1.391636	1.484651	-0.626211
33	6	0	-4.858726	-0.168278	2.102762
34	6	0	-3.356831	1.608963	2.890694
35	6	0	-1.116575	2.253464	2.566801
36	6	0	-1.149696	1.053434	3.357941
37	6	0	1.098910	1.584284	1.740987
38	6	0	1.590761	0.344072	-1.371743
39	6	0	2.134851	-2.111926	-1.157301
40	6	0	-2.497111	0.597133	3.466905
41	6	0	-2.747585	-0.761941	3.240804
42	6	0	-1.691951	-1.730802	2.971384
43	6	0	-3.961390	-1.135809	2.564097
44	6	0	-4.187844	-2.488074	-1.719019
45	6	0	1.944317	-0.756610	2.513659
46	6	0	-5.308612	-1.526769	0.107346
47	6	0	-4.400552	-2.538678	0.620098
48	6	0	1.082154	0.485610	2.572950
49	6	0	0.719057	-2.292033	-1.576441
50	6	0	-0.156031	-3.179107	-0.961669
51	6	0	-0.135297	0.127630	3.239823
52	6	0	-0.377982	-1.298265	3.176023
53	6	0	-3.688134	-2.329759	1.805465
54	6	0	-2.281824	-2.714895	1.976989
55	6	0	1.010273	-1.858363	3.147346

56	6	0	-3.734659	-3.141532	-0.498188	81	6	0	5.785462	-3.118968	1.523763
57	6	0	-1.485500	-3.303694	-1.443446	82	6	0	4.566440	-2.499495	1.252480
58	6	0	-0.196990	-3.512943	0.522877	83	6	0	4.536760	-1.206784	0.712787
59	6	0	-2.407005	-3.507632	-0.341875	84	6	0	5.744220	-0.552623	0.440142
60	6	0	-1.677191	-3.368274	0.898514	85	6	0	6.962569	-1.177870	0.709426
61	6	0	2.171687	1.758317	0.648004	86	6	0	6.987960	-2.461183	1.255012
62	6	0	2.703177	-0.664996	-1.071464	87	1	0	2.647952	3.423966	2.797414
63	6	0	3.202711	-0.512327	0.429479	88	1	0	3.754666	5.669465	2.736661
64	7	0	3.327955	0.877502	0.748125	89	1	0	4.430215	6.614206	0.504391
65	6	0	3.859089	-0.427045	-2.072273	90	1	0	3.978369	5.255693	-1.544304
66	6	0	2.754724	3.183357	0.654739	91	1	0	3.657662	1.728940	-1.985724
67	8	0	2.816968	-3.095492	-0.944933	92	1	0	5.535548	2.184130	-3.485775
68	8	0	3.109672	-0.615273	3.261227	93	1	0	6.862799	0.309106	-4.457197
69	6	0	2.964058	3.864159	1.856921	94	1	0	6.259631	-2.037160	-3.876341
70	6	0	3.578079	5.115904	1.818612	95	1	0	4.397246	-2.499834	-2.351132
71	6	0	3.954392	5.641711	0.584323	96	1	0	5.792318	-4.121767	1.942312
72	6	0	3.701338	4.882430	-0.560094	97	1	0	3.635722	-3.019823	1.446349
73	7	0	3.118418	3.680234	-0.534167	98	1	0	5.728413	0.439738	0.003800
74	6	0	4.206026	0.892806	-2.403651	99	1	0	7.890977	-0.657821	0.488842
75	6	0	5.282363	1.153277	-3.251354	100	1	0	7.936671	-2.947485	1.466795
76	6	0	6.026345	0.105044	-3.793788	101	8	0	2.139619	-1.181534	1.179336
77	6	0	5.686246	-1.207840	-3.470732	102	1	0	3.828308	1.006169	1.622288
78	6	0	4.616512	-1.474065	-2.614820	103	1	0	3.431221	-1.519034	3.446283
79	8	0	0.718687	-3.779053	1.262544	---					
80	8	0	1.456858	-2.825392	3.715799	The total electronic energy was calculated to be –3543.7415901 Hartree.					

6. Possible Formation Mechanism of 4

Since **3** has an electron-rich amine moiety, the single electron transfer (SET) between two molecules of **3** would occur to provide $\mathbf{3}^{\bullet+}$ and $\mathbf{3}^{\bullet-}$. The former one produces H^+ and $\mathbf{INT1}^{\bullet}$ which is further converted into **1** and $OH^{\bullet}$. Therefore, $\mathbf{3}^{\bullet+}$ works as a source of H^+ and $OH^{\bullet}$. Note that regenerated **1** could be transformed again into **3** or **2** by the reaction with water. The dehydration from radical anion $\mathbf{3}^{\bullet-}$ affords ketyl radical $\mathbf{1}^{\bullet-}$ which is also formed via SET between **3** and **1**. The intramolecular nucleophilic addition in $\mathbf{1}^{\bullet-}$ leads to the formation of $\mathbf{INT2}^{\bullet-}$. The subsequent protonation gives $\mathbf{INT3}^{\bullet}$ which undergoes an H-abstraction from the solvent molecules (H–Sol) such as toluene to give **4** together with HO-Sol via a radical combination with $OH^{\bullet}$. Importantly, a part of $\mathbf{INT2}^{\bullet-}$ and $\mathbf{INT3}^{\bullet}$ could be converted into **2**. Therefore, at higher temperatures, **3** is consumed to generate both **2** and **4**, thus lowering the yield of **3** at 160 °C.

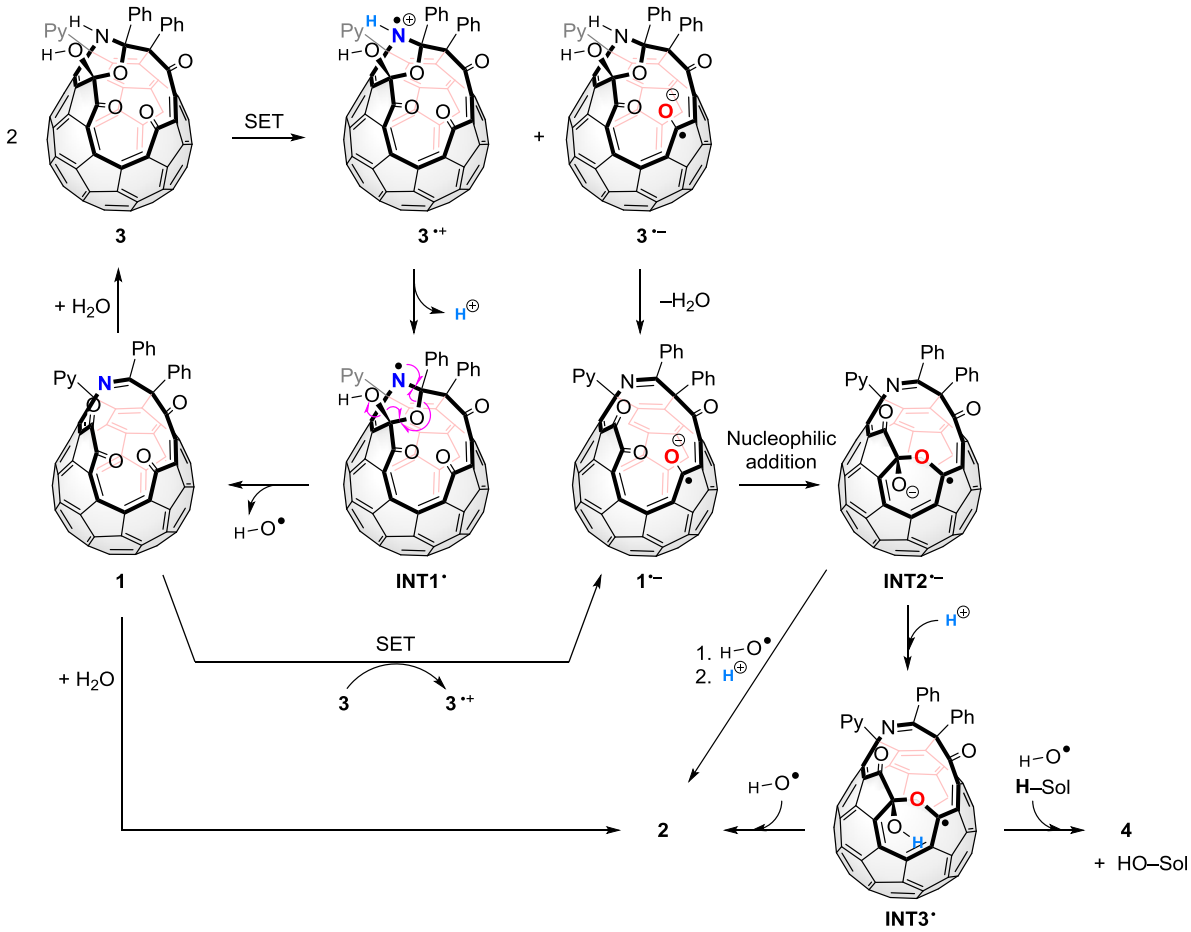


Figure S16. Possible formation mechanism of **4**. H–Sol denotes a solvent molecule such as toluene.

7. References

(1) G. M. Sheldrick, *Acta Crystallogr*. *A* 2015, **71**, 3–8.