

Supplementary Information

One-dimensional hydrogen bonding network of bis-hydroxylated diamantane formed inside double-wall carbon nanotubes

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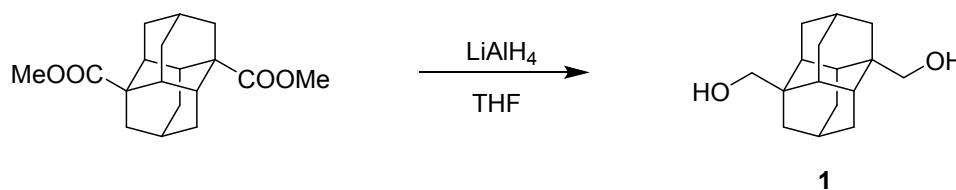
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1. Experimental details

General for the synthesis of the derivatives

Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification. Analytical thin-layer chromatography (TLC) was performed using Merck silica gel 60 F254 precoated plates (0.25 mm) and was visualized by staining with $\text{Na}_3[\text{PO}_4 \cdot 12\text{MoO}_3] \cdot n\text{H}_2\text{O}$. High-resolution mass spectra (HRMS) were obtained utilizing a JEOL JMS-T700TD direct analysis in real time mass spectrometry (DART-MS). Melting points were measured on a MPA100 Optimelt automated melting point system. Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL ECS-400 (^1H 400 MHz, ^{13}C 100 MHz) spectrometer; chemical shifts for ^1H NMR are expressed in parts per million (ppm) relative to tetramethylsilane ($\delta = 0.00$ ppm) or CHCl_3 ($\delta = 7.26$ ppm). Chemical shifts for ^{13}C NMR are expressed in ppm relative to CDCl_3 ($\delta = 77.0$ ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, m = multiplet, br = broad signal), coupling constant (Hz), and integration.

Synthesis of 1,6-bis(hydroxymethyl)diamantane (**1**)



1,6-Dicarboxydiamantane dimethyl ester, the starting material for obtaining 1,6-bis(hydroxymethyl)diamantane (**1**), was prepared from diamantane following procedures reported in the literature.^{S1–S4} A solution of 1,6-dicarboxydiamantane dimethyl ester (0.9 g, 2.96 mmol) in THF (20 mL) was added dropwise to a stirred mixture of LiAlH_4 (1.12 g, 29.57 mmol) in 10 mL of THF under a flow of Ar. The reaction mixture was refluxed overnight. To the cooled (0 °C) mixture was then subsequently slowly added H_2O (1.12 mL), 15% aqueous NaOH and H_2O (3.36 mL). The precipitate was filtered off, and the filtrate was extracted with CH_2Cl_2 . Combined organic layers were washed with brine and dried over Na_2SO_4 . After evaporation of the solvent, the crude product was recrystallized from ethyl acetate to give diol **1** as a colorless solid: m.p. 241–242 °C (0.67 g, 92%).

^1H NMR (200 MHz, $\text{CDCl}_3/\text{CD}_3\text{OD}$, 296 K): δ 3.38–3.27 (m, 4H), 1.88–1.71 (m, 4H), 1.70–1.58 (m, 2H), 1.46–1.36 (m, 4H), 1.35–1.25 (m, 4H), 1.24–1.08 (m, 4H).

^{13}C NMR (50 MHz, $\text{CDCl}_3/\text{CD}_3\text{OD}$, 297 K): δ 66.9 (CH_2), 40.3 (CH_2), 38.0 (C), 37.6 (CH), 31.9 (CH_2), 26.7 (CH).

MS: m/z (%) = 248 (5), 217 (5), 199 (21), 171 (2), 157 (5), 143 (10), 131 (9), 117 (9), 105 (10), 91 (19).

HR-MS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{16}\text{H}_{24}\text{O}_2$: 271.1668; Found 271.1669.

Synthesis of 1,6-bis(methoxymethyl)diamantane

To a 20 mL Schlenk flask containing a magnetic stirring bar were added **1** (25.1 mg, 101 μmol) and dry THF (2 mL). To this solution were added sodium hydride (60% dispersion in paraffin, 24 mg, 0.60 mmol) at 0 °C under a stream of argon. Iodomethane (50 μL , 0.80 mmol) was then added dropwise to this flask and the resultant mixture was stirred at room temperature for 10 h. The mixture was quenched with water, extracted with EtOAc and the combined organic phase was dried over Na_2SO_4 . Filtration and removal of solvents under reduced pressure afforded crude mixture. The residue was subjected to silica gel chromatography (hexane/EtOAc = 20/1) to afford 1,6-bis(methoxymethyl)diamantane (27.5 mg, 98%) as a colorless solid: m.p. 106.5–108.0 °C.

^1H NMR (400 MHz, CDCl_3 , 297 K): δ 1.42 (d, $J = 13$ Hz, 4H), 1.57 (s, 4H), 1.66 (s, 4H), 1.86 (m, 2H), 2.00 (d, $J = 13$ Hz, 4H), 3.34 (s, 10H).

^{13}C NMR (100 MHz, CDCl_3 , 297 K): δ 27.1 (CH), 32.6 (CH_2), 38.0 (C), 38.3 (CH) 41.6 (CH_2), 59.5 (CH_3), 78.6 (CH_2).

HR-MS (EI) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{18}\text{H}_{28}\text{O}_2$: 276.2084; Found 276.2089.

Synthesis of diamondoid-peapods

Closed edges of the double-wall CNTs (DWCNTs) were opened by an oxidative treatment where the temperature is elevated to 490 °C for 6 h under dry air atmosphere. The open-end DWCNTs were subjected to vacuum (10^{-5} Torr) heating at 1200 °C for 72 h to remove residual catalysts that are involved in the growth process of DWCNTs. Prior to the filling experiments, the as-prepared DWCNTs were degassed for 1 h under a vacuum of 10^{-7} Torr. The DWCNTs (0.70 mg) were sealed in H-shaped Pyrex tubes under vacuum (10^{-7} Torr) together with **1** (9.71 mg; 39.1 mmol), and then, heated at 230 °C for 48 h to evaporate **1**. The as-produced samples were subsequently washed with methanol to remove the residual molecules outside the tubes.

Transmission electron microscopy (TEM) characterization

TEM observations were conducted on a JEOL JEM-2100F, and JEM-ARM200F with a CEOS probe and image aberration correctors at an acceleration voltage of 80 keV at room temperature under a pressure of 10^{-5} Pa. The obtained samples were sonicated in 3 mL of dichloroethane for 50 min using an ultrasonic bath sonicator (Nanoruptor, NR-350, Cosmo Bio Co. Ltd), and 10 drops of the dispersion solution were deposited onto carbon-coated copper grids. Prior to the observations, TEM samples were heated at 300 °C under a vacuum of 10^{-6} Pa for 30 min to remove the residual solvent and impurities. TEM images were recorded on a Gatan MSC 794 1 kx1 k CCD camera with a typical exposure time of 0.3 s.

Fourier transform infrared (FTIR) measurement

FTIR spectra of the samples were recorded by using a JASCO FT/IR6100 spectrometer equipped with an attenuated total reflection attachment, JASCO ATR PR410-S detector. The FTIR spectra were obtained with a spectral resolution of 4.0 cm^{-1} for 1000 scans under ambient conditions. A sample (~1 mg) was pressed into self-supported disks. The disks were placed in a silica glass cell equipped with Zn-Ce windows.

Density functional theory (DFT) computation

Intermolecular interaction between two molecules of **1** was investigated by using DFT employing the Gaussian 09 program package.⁵⁵ Full geometry optimizations were carried out at the M06-2X/6-31G(d,p) level of theory within the given symmetry constraint.⁵⁶ All structures were characterized as minima with zero imaginary frequencies.

X-ray crystal structure determination

Diffraction data for **1** were collected at low temperatures (100 K) using φ - and ω -scans on a BRUKER D8 Venture system equipped with dual μS microfocus sources, a PHOTON100 detector and an OXFORD CRYOSYSTEMS 700 low temperature system. Mo- K_{α} radiation with wavelength 0.71073 Å and a collimating Quazar multilayer mirror were used. Semi-empirical absorption correction from equivalents was applied using SADABS-2016/2⁵⁷ and the structure was solved by direct methods using SHELXT2014/5.⁵⁸ The unit cell was determined using 9820 reflections and the structure was solved in the triclinic space group $P\bar{1}$. Refinement was performed against F^2 on all data by full-matrix least squares using SHELXL2016/6.⁵⁸ All non-hydrogen atoms were refined anisotropically and C-H hydrogen atoms were positioned at geometrically calculated positions and refined using a riding model. O-H hydrogen atoms were located in the Fourier difference map and set to ideal distances. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2x or 1.5x (O-H hydrogens) the U_{eq} value of the atoms they are linked to. The crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as CCDC No. 1579272 and can be obtained free of charge.⁵⁹

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2. Details of X-ray crystal structure determination

Table 1. Crystal data and structure refinement for **1**.

CCDC No.	1579272	
Empirical formula	$C_{16}H_{24}O_2$	
Formula weight	248.35	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	$a = 6.5853(3)$ Å	$a = 92.3437(15)^\circ$.
	$b = 8.4322(3)$ Å	$b = 91.5258(15)^\circ$.
	$c = 11.3892(4)$ Å	$\gamma = 93.7139(15)^\circ$.
Volume	$630.30(4)$ Å ³	
Z	2	
Density (calculated)	1.309 Mg/m ³	
Absorption coefficient	0.084 mm ⁻¹	
F(000)	272	
Crystal size	0.307 x 0.253 x 0.148 mm ³	
Theta range for data collection	2.423 to 32.030°.	
Index ranges	$-9 \leq h \leq 9$, $-12 \leq k \leq 12$, $-16 \leq l \leq 16$	
Reflections collected	42244	
Independent reflections	4381 [R(int) = 0.0399]	
Completeness to theta = 25.242°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4381 / 2 / 169	
Goodness-of-fit on F ²	1.059	
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0391, wR2 = 0.1045	
R indices (all data)	R1 = 0.0468, wR2 = 0.1090	
Largest diff. peak and hole	0.422 and -0.341 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **1**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	10710(1)	4565(1)	6660(1)	16(1)
C(1)	11684(1)	5433(1)	7649(1)	13(1)
C(2)	10942(1)	4816(1)	8825(1)	9(1)
C(3)	11469(1)	3068(1)	8874(1)	13(1)
C(4)	10807(1)	2354(1)	10028(1)	13(1)
C(5)	8500(1)	2452(1)	10119(1)	13(1)
C(6)	7982(1)	4204(1)	10129(1)	10(1)
C(7)	11913(1)	3312(1)	11054(1)	12(1)
C(8)	11377(1)	5057(1)	11040(1)	9(1)
O(11)	8009(1)	6339(1)	5550(1)	16(1)
C(11)	6061(1)	6889(1)	5828(1)	11(1)
C(12)	5470(1)	8304(1)	5118(1)	8(1)
C(13)	5076(1)	7704(1)	3832(1)	10(1)
C(14)	4441(1)	9046(1)	3068(1)	10(1)
C(15)	2470(1)	9665(1)	3545(1)	11(1)
C(16)	2849(1)	10316(1)	4815(1)	9(1)
C(17)	6158(1)	10367(1)	3122(1)	11(1)
C(18)	6494(1)	11028(1)	4396(1)	9(1)

Table 3. Bond lengths [Å] and angles [°] for **1**.

O(1)-C(1)	1.4315(10)	O(1)-C(1)-H(1A)	109.1
O(1)-H(1)	0.815(12)	C(2)-C(1)-H(1A)	109.1
C(1)-C(2)	1.5364(11)	O(1)-C(1)-H(1AB)	109.1
C(1)-H(1A)	0.9900	C(2)-C(1)-H(1AB)	109.1
C(1)-H(1AB)	0.9900	H(1A)-C(1)-H(1AB)	107.9
C(2)-C(3)	1.5390(11)	C(1)-C(2)-C(3)	107.41(6)
C(2)-C(8)#1	1.5494(11)	C(1)-C(2)-C(8)#1	112.26(6)
C(2)-C(6)#1	1.5503(11)	C(3)-C(2)-C(8)#1	110.06(7)
C(3)-C(4)	1.5300(12)	C(1)-C(2)-C(6)#1	110.61(7)
C(3)-H(3A)	0.9900	C(3)-C(2)-C(6)#1	109.58(6)
C(3)-H(3AB)	0.9900	C(8)#1-C(2)-C(6)#1	106.91(6)
C(4)-C(7)	1.5330(12)	C(4)-C(3)-C(2)	111.18(6)
C(4)-C(5)	1.5335(12)	C(4)-C(3)-H(3A)	109.4
C(4)-H(4)	1.0000	C(2)-C(3)-H(3A)	109.4
C(5)-C(6)	1.5366(12)	C(4)-C(3)-H(3AB)	109.4
C(5)-H(5A)	0.9900	C(2)-C(3)-H(3AB)	109.4
C(5)-H(5AB)	0.9900	H(3A)-C(3)-H(3AB)	108.0
C(6)-C(8)#1	1.5511(11)	C(3)-C(4)-C(7)	108.82(7)
C(6)-H(6)	1.0000	C(3)-C(4)-C(5)	108.50(7)
C(7)-C(8)	1.5355(11)	C(7)-C(4)-C(5)	110.00(7)
C(7)-H(7A)	0.9900	C(3)-C(4)-H(4)	109.8
C(7)-H(7AB)	0.9900	C(7)-C(4)-H(4)	109.8
C(8)-H(8)	1.0000	C(5)-C(4)-H(4)	109.8
O(11)-C(11)	1.4305(10)	C(4)-C(5)-C(6)	109.46(7)
O(11)-H(11)	0.803(12)	C(4)-C(5)-H(5A)	109.8
C(11)-C(12)	1.5328(11)	C(6)-C(5)-H(5A)	109.8
C(11)-H(11A)	0.9900	C(4)-C(5)-H(5AB)	109.8
C(11)-H(11B)	0.9900	C(6)-C(5)-H(5AB)	109.8
C(12)-C(13)	1.5405(11)	H(5A)-C(5)-H(5AB)	108.2
C(12)-C(18)#2	1.5502(11)	C(5)-C(6)-C(2)#1	111.73(6)
C(12)-C(16)#2	1.5511(11)	C(5)-C(6)-C(8)#1	109.67(6)
C(13)-C(14)	1.5283(11)	C(2)#1-C(6)-C(8)#1	109.36(6)
C(13)-H(13A)	0.9900	C(5)-C(6)-H(6)	108.7
C(13)-H(13B)	0.9900	C(2)#1-C(6)-H(6)	108.7
C(14)-C(17)	1.5331(12)	C(8)#1-C(6)-H(6)	108.7
C(14)-C(15)	1.5344(11)	C(4)-C(7)-C(8)	110.00(6)
C(14)-H(14)	1.0000	C(4)-C(7)-H(7A)	109.7
C(15)-C(16)	1.5346(11)	C(8)-C(7)-H(7A)	109.7
C(15)-H(15A)	0.9900	C(4)-C(7)-H(7AB)	109.7
C(15)-H(15B)	0.9900	C(8)-C(7)-H(7AB)	109.7
C(16)-C(18)#2	1.5512(11)	H(7A)-C(7)-H(7AB)	108.2
C(16)-H(16)	1.0000	C(7)-C(8)-C(2)#1	110.53(7)
C(17)-C(18)	1.5376(11)	C(7)-C(8)-C(6)#1	110.41(6)
C(17)-H(17A)	0.9900	C(2)#1-C(8)-C(6)#1	108.88(6)
C(17)-H(17B)	0.9900	C(7)-C(8)-H(8)	109.0
C(18)-H(18)	1.0000	C(2)#1-C(8)-H(8)	109.0
		C(6)#1-C(8)-H(8)	109.0
C(1)-O(1)-H(1)	107.0(10)	C(11)-O(11)-H(11)	109.3(11)
O(1)-C(1)-C(2)	112.29(7)	O(11)-C(11)-C(12)	113.77(7)

O(11)-C(11)-H(11A)	108.8	C(14)-C(15)-H(15A)	109.8
C(12)-C(11)-H(11A)	108.8	C(16)-C(15)-H(15A)	109.8
O(11)-C(11)-H(11B)	108.8	C(14)-C(15)-H(15B)	109.8
C(12)-C(11)-H(11B)	108.8	C(16)-C(15)-H(15B)	109.8
H(11A)-C(11)-H(11B)	107.7	H(15A)-C(15)-H(15B)	108.2
C(11)-C(12)-C(13)	107.83(6)	C(15)-C(16)-C(12)#2	111.05(6)
C(11)-C(12)-C(18)#2	110.01(6)	C(15)-C(16)-C(18)#2	109.96(6)
C(13)-C(12)-C(18)#2	109.44(6)	C(12)#2-C(16)-C(18)#2	109.16(6)
C(11)-C(12)-C(16)#2	112.19(6)	C(15)-C(16)-H(16)	108.9
C(13)-C(12)-C(16)#2	109.98(6)	C(12)#2-C(16)-H(16)	108.9
C(18)#2-C(12)-C(16)#2	107.37(6)	C(18)#2-C(16)-H(16)	108.9
C(14)-C(13)-C(12)	111.00(6)	C(14)-C(17)-C(18)	109.66(6)
C(14)-C(13)-H(13A)	109.4	C(14)-C(17)-H(17A)	109.7
C(12)-C(13)-H(13A)	109.4	C(18)-C(17)-H(17A)	109.7
C(14)-C(13)-H(13B)	109.4	C(14)-C(17)-H(17B)	109.7
C(12)-C(13)-H(13B)	109.4	C(18)-C(17)-H(17B)	109.7
H(13A)-C(13)-H(13B)	108.0	H(17A)-C(17)-H(17B)	108.2
C(13)-C(14)-C(17)	108.53(6)	C(17)-C(18)-C(12)#2	111.40(6)
C(13)-C(14)-C(15)	108.37(7)	C(17)-C(18)-C(16)#2	109.43(6)
C(17)-C(14)-C(15)	110.86(6)	C(12)#2-C(18)-C(16)#2	108.98(6)
C(13)-C(14)-H(14)	109.7	C(17)-C(18)-H(18)	109.0
C(17)-C(14)-H(14)	109.7	C(12)#2-C(18)-H(18)	109.0
C(15)-C(14)-H(14)	109.7	C(16)#2-C(18)-H(18)	109.0
C(14)-C(15)-C(16)	109.58(6)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+1,-z+2 #2 -x+1,-y+2,-z+1

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **1**. The anisotropic displacement factor exponent takes the form: $-2p^2 [h^2 a^{*2}U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	22(1)	19(1)	7(1)	1(1)	-2(1)	8(1)
C(1)	15(1)	16(1)	7(1)	3(1)	2(1)	2(1)
C(2)	10(1)	11(1)	6(1)	2(1)	1(1)	2(1)
C(3)	18(1)	13(1)	9(1)	1(1)	2(1)	6(1)
C(4)	19(1)	10(1)	10(1)	2(1)	0(1)	4(1)
C(5)	17(1)	11(1)	10(1)	2(1)	-1(1)	-3(1)
C(6)	9(1)	13(1)	8(1)	2(1)	0(1)	-1(1)
C(7)	13(1)	14(1)	9(1)	4(1)	-1(1)	4(1)
C(8)	10(1)	12(1)	7(1)	2(1)	-1(1)	1(1)
O(11)	18(1)	18(1)	14(1)	3(1)	2(1)	11(1)
C(11)	14(1)	10(1)	9(1)	2(1)	1(1)	4(1)
C(12)	9(1)	8(1)	7(1)	1(1)	0(1)	1(1)
C(13)	14(1)	9(1)	8(1)	0(1)	-1(1)	2(1)
C(14)	14(1)	11(1)	6(1)	1(1)	-1(1)	2(1)
C(15)	11(1)	12(1)	10(1)	1(1)	-3(1)	1(1)
C(16)	8(1)	10(1)	8(1)	1(1)	0(1)	1(1)
C(17)	13(1)	12(1)	7(1)	2(1)	2(1)	3(1)
C(18)	9(1)	9(1)	8(1)	2(1)	1(1)	1(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **1**.

	x	y	z	U(eq)
H(1)	9780(20)	5078(16)	6438(12)	23
H(1A)	11412	6571	7607	15
H(1AB)	13174	5350	7614	15
H(3A)	10780	2445	8205	16
H(3AB)	12956	3002	8799	16
H(4)	11157	1218	10039	15
H(5A)	8033	1965	10849	15
H(5AB)	7793	1860	9442	15
H(6)	6476	4253	10200	12
H(7A)	13402	3251	10987	14
H(7AB)	11507	2856	11806	14
H(8)	12119	5667	11710	11
H(11)	8030(20)	6113(17)	4859(11)	24
H(11A)	6066	7201	6675	13
H(11B)	5014	6001	5682	13
H(13A)	6327	7271	3523	12
H(13B)	3988	6834	3796	12
H(14)	4200	8633	2237	12
H(15A)	1388	8791	3521	13
H(15B)	2008	10517	3049	13
H(16)	1559	10723	5114	10
H(17A)	5796	11231	2609	13
H(17B)	7428	9938	2837	13
H(18)	7600	11900	4419	10

Table 6. Hydrogen bonds for **1** [\AA and $^\circ$].

D-H...A	d(D-H)	d(H...A)	d(D...A)	\angle (DHA)
O(1)-H(1)...O(11)	0.815(12)	1.922(13)	2.7165(9)	164.6(14)
O(11)-H(11)...O(1)#3	0.803(12)	2.017(13)	2.7693(9)	155.9(14)

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+1,-z+2 #2 -x+1,-y+2,-z+1 #3 -x+2,-y+1,-z+1

3. Computed data

1,6-Bis(hydroxymethyl)diamantane monomer (1)

(Symmetry: C_i)

xyz-Coordinates

C	-0.01185	1.55024	0.88168	C	-2.28416	3.48498	2.84588
C	0.19422	2.98810	2.95638	H	-2.11978	4.50575	3.21850
C	-1.43603	1.10310	2.92751	H	-3.27587	3.16796	3.19777
C	-1.21153	2.54872	3.44774	C	-2.24530	3.47507	1.32132
C	-1.41760	1.11087	1.37303	H	-3.01719	4.14871	0.93107
C	0.21265	2.99587	1.40190	C	-0.86013	3.95862	0.87170
H	0.37924	4.01554	3.30492	H	-0.67538	4.95981	1.28421
H	-2.43122	0.76584	3.25493	H	-0.81089	4.02866	-0.21528
H	-1.60262	0.08342	1.02450	C	-2.51643	2.04301	0.84149
H	1.20783	3.33312	1.07448	H	-3.48718	1.70880	1.23210
C	1.06078	0.61398	1.48353	H	-2.56049	2.00378	-0.24731
H	2.05249	0.93101	1.13164	C	0.19580	1.39463	-0.63210
H	0.89640	-0.40679	1.11091	H	1.24235	1.66596	-0.84551
C	1.29305	2.05595	3.48792	H	0.08052	0.32419	-0.86719
H	2.26380	2.39016	3.09731	C	-1.41918	2.70433	4.96151
H	1.33711	2.09518	4.57672	H	-2.46573	2.43301	5.17492
C	1.02192	0.62389	3.00809	H	-1.30390	3.77477	5.19660
H	1.79381	-0.04974	3.39834	O	-0.67695	2.16353	-1.44282
C	-0.36325	0.14035	3.45772	H	-0.45554	1.98505	-2.36255
H	-0.54800	-0.86085	3.04521	O	-0.54643	1.93544	5.77223
H	-0.41249	0.07030	4.54469	H	-0.76784	2.11392	6.69196

$E = -774.3195621$

Zero-point vibration energy = 242.0 kcal mol⁻¹

1,6-Bis(hydroxymethyl)diamantane dimer (1₂)(Symmetry: C_i)

xyz-Coordinates

C	-2.87053	-0.67435	-0.73426	C	5.21931	-0.20220	-0.89274
C	-5.23360	-1.10410	0.07362	C	2.92889	-0.67620	0.09227
C	-4.27886	1.19459	0.21942	C	3.65068	1.67788	-0.26157
C	-5.20991	0.18134	0.94204	C	2.84967	0.75397	0.69295
C	-2.83821	0.61046	0.14084	C	5.13671	1.22847	-0.29912
C	-3.79612	-1.68777	-0.00976	C	4.41688	-1.13209	0.06036
H	-5.87661	-1.84774	0.56857	H	2.37493	-1.36405	0.75249
H	-4.23684	2.11694	0.81780	H	3.61628	2.70116	0.14117
H	-2.18256	1.35237	-0.33687	H	5.68810	1.91239	-0.96235
H	-3.83973	-2.60952	-0.60998	H	4.45348	-2.15650	-0.34139
C	-3.45757	-0.34142	-2.12563	C	4.57342	-0.20235	-2.29609
H	-3.46241	-1.25276	-2.74102	H	4.64313	-1.21063	-2.72807
H	-2.80205	0.38413	-2.62557	H	5.14263	0.47047	-2.95231
C	-5.76187	-0.82109	-1.34024	C	2.35727	-0.74118	-1.33532
H	-5.73475	-1.75105	-1.92445	H	2.47963	-1.76357	-1.72286
H	-6.79607	-0.47836	-1.30199	H	1.29578	-0.49773	-1.35682
C	-4.86797	0.22651	-2.01642	C	3.11542	0.23690	-2.23918
H	-5.25113	0.44890	-3.01908	H	2.68522	0.21598	-3.24728
C	-4.79571	1.51797	-1.19041	C	3.04328	1.66058	-1.67093
H	-4.09948	2.21657	-1.67316	H	3.60962	2.34055	-2.32100
H	-5.77335	1.99796	-1.13987	H	2.00630	2.00438	-1.64178
C	-4.63446	-0.16024	2.33467	C	3.50662	0.76466	2.08967
H	-5.29595	-0.88649	2.82742	H	2.94124	0.09901	2.75642
H	-4.62887	0.74597	2.95607	H	3.43256	1.77775	2.50994
C	-3.22224	-0.72473	2.23214	C	4.96432	0.32094	2.02977
H	-2.84352	-0.94994	3.23593	H	5.39814	0.34162	3.03635
C	-3.26841	-2.01049	1.39535	C	5.00140	-1.11244	1.48092
H	-3.94019	-2.73441	1.87554	H	4.39271	-1.76097	2.12567
H	-2.27617	-2.46410	1.33798	H	6.02029	-1.50044	1.48079
C	-2.33295	0.33114	1.56634	C	5.72997	1.28752	1.11621
H	-2.38044	1.26509	2.14189	H	5.62488	2.30974	1.50401
H	-1.29327	0.00631	1.56966	H	6.79230	1.04241	1.09913
C	-1.49169	-1.25494	-1.08211	C	6.65195	-0.68433	-1.16713
H	-1.65441	-2.21071	-1.60039	H	6.57556	-1.67319	-1.64799
H	-1.00505	-0.56795	-1.79248	H	7.08936	0.00600	-1.90631
C	-6.60330	0.74093	1.26706	C	1.41688	1.26702	0.96346
H	-6.45701	1.60732	1.93210	H	1.50192	2.32500	1.24546
H	-7.13584	-0.03045	1.84655	H	1.03629	0.73235	1.84832
O	-0.61576	-1.45766	0.03017	O	7.49030	-0.76523	-0.02734
H	0.13138	-1.98782	-0.27420	H	8.35712	-1.06303	-0.32174
O	-7.37949	1.12005	0.14301	O	0.45853	1.19429	-0.07214
H	-8.22014	1.45796	0.46839	H	0.04412	0.32066	0.00140

 $E = -1548.6557139$ Zero-point vibration energy = 485.6 kcal mol⁻¹Dissociation energy $D_0 = 8.8$ kcal mol⁻¹

1,6-Bis(hydroxymethyl)diamantane trimer (1₃)*(Symmetry: C_i)*

xyz-Coordinates

C	6.82927	1.52976	-0.09189	H	-1.52129	2.53350	-0.19959
C	9.31690	1.06274	0.03199	C	1.60710	1.45733	0.74948
C	8.06574	0.53582	-2.05917	H	1.56290	1.94146	1.73620
C	9.22340	0.05248	-1.14177	H	2.61319	1.59198	0.35393
C	6.72846	0.51184	-1.26286	C	0.60080	2.13141	-0.18943
C	7.98190	1.04396	0.82681	H	0.87849	3.18196	-0.33422
H	10.12215	0.73799	0.70842	C	0.56130	1.41299	-1.54558
H	7.97071	-0.16765	-2.89981	H	-0.18178	1.89906	-2.19162
H	5.91316	0.81787	-1.93377	H	1.53409	1.47842	-2.03892
H	8.07831	1.74938	1.66634	C	0.79959	-2.24219	-0.21456
C	7.16844	2.93192	-0.64893	H	1.54085	-2.72887	0.43398
H	7.22303	3.64650	0.18510	H	0.81032	-2.78027	-1.17326
H	6.35293	3.26218	-1.30619	C	-0.58177	-2.32799	0.42213
C	9.60291	2.48582	-0.46899	H	-0.85909	-3.37858	0.56699
H	9.63348	3.16800	0.39155	C	-0.54604	-1.60858	1.77782
H	10.57151	2.52993	-0.96745	H	0.19291	-2.09558	2.42781
C	8.48266	2.92394	-1.42128	H	-1.52153	-1.67185	2.26680
H	8.69056	3.93164	-1.79926	C	-1.58821	-1.65503	-0.51742
C	8.33449	1.94913	-2.59747	H	-1.54184	-2.13869	-1.50445
H	7.48469	2.26044	-3.21935	H	-2.59387	-1.79363	-0.12202
H	9.22899	1.95875	-3.22074	C	-2.58047	0.71606	1.38438
C	8.89731	-1.34848	-0.57777	H	-2.39239	1.10551	2.39396
H	9.71806	-1.67053	0.07835	H	-3.14914	1.49140	0.84680
H	8.84347	-2.06857	-1.40598	C	2.59885	-0.91147	-1.15008
C	7.58194	-1.34779	0.19233	H	2.41342	-1.32791	-2.14938
H	7.37895	-2.35573	0.57258	H	3.17859	-1.66615	-0.59499
C	7.70167	-0.36590	1.36586	O	-3.38725	-0.43324	1.53251
H	8.53038	-0.67444	2.01697	H	-3.90012	-0.50884	0.71277
H	6.78757	-0.37342	1.96410	O	3.38928	0.24518	-1.32773
C	6.46627	-0.92033	-0.76753	H	3.92592	0.33486	-0.52479
H	6.45278	-1.59235	-1.63590	C	-9.21423	0.10928	0.97054
H	5.49593	-1.00752	-0.28050	C	-6.77257	-0.53124	1.24795
C	5.51510	1.77782	0.66367	C	-7.90311	-0.89766	-0.94470
H	5.74309	2.42191	1.52483	C	-6.85675	-1.49701	0.03269
H	4.84160	2.33802	-0.00410	C	-9.29058	-0.84898	-0.24716
C	10.55154	-0.16897	-1.88149	C	-8.16257	-0.48795	1.94699
H	10.37267	-0.94541	-2.64274	H	-6.03107	-0.91793	1.96188
H	11.26423	-0.58462	-1.15091	H	-7.98617	-1.56432	-1.81667
O	4.83667	0.60148	1.11363	H	-10.01999	-0.44373	-0.96488
H	4.14422	0.87596	1.72766	H	-8.08092	0.17661	2.82002
O	11.10411	0.98601	-2.48982	C	-8.75278	1.50277	0.48829
H	11.92484	0.72578	-2.92044	H	-8.70975	2.18712	1.34686
C	-1.20749	0.58248	0.68517	H	-9.49983	1.90562	-0.20985
C	1.25026	-0.03142	0.90751	C	-6.37763	0.89523	0.83051
C	0.17136	-0.05691	-1.33540	H	-6.38037	1.53346	1.72410
C	1.22569	-0.77855	-0.45232	H	-5.37132	0.92900	0.41601
C	-1.23242	-0.16540	-0.67457	C	-7.38814	1.43527	-0.18717
C	-0.15346	-0.13957	1.56792	H	-7.08885	2.43906	-0.51062
H	1.98251	-0.52811	1.56569	C	-7.48889	0.50705	-1.40527
H	0.13064	-0.56896	-2.30878	H	-8.24570	0.89631	-2.09924
H	-1.96375	0.33309	-1.33260	H	-6.53564	0.47144	-1.93776
H	-0.11259	0.37245	2.54128	C	-7.33136	-2.89034	0.50692
C	-0.78011	2.04592	0.44826	H	-6.59063	-3.30135	1.20589
H	-0.79074	2.58291	1.40764	H	-7.37401	-3.56892	-0.35726

C	-8.69497	-2.81570	1.18450	H	-10.39913	1.13237	2.42611
H	-8.99887	-3.81882	1.50540	H	-11.20229	0.88864	0.86209
C	-8.56669	-1.89666	2.40698	C	-5.51044	-1.81007	-0.63729
H	-7.78808	-2.28995	3.07406	H	-5.71772	-2.40761	-1.53641
H	-9.50293	-1.86440	2.96473	H	-4.92636	-2.43840	0.05383
C	-9.70947	-2.26502	0.17378	O	-11.24760	-0.73574	2.14436
H	-9.72313	-2.91204	-0.71390	H	-12.07631	-0.43296	2.52949
H	-10.71295	-2.25787	0.59976	O	-4.72469	-0.66919	-0.99263
C	-10.57464	0.39798	1.62348	H	-4.00963	-0.96887	-1.56780

$E = -2322.9920565$

Zero-point vibration energy = n.a.

Diamantane*(Symmetry: D_{3d})*

xyz-Coordinates

C	0.00000	1.44657	-0.26864	H	0.00000	0.00000	-3.41685
C	1.25277	-0.72329	-0.26864	C	-1.25175	-0.72270	-1.80290
C	-1.25277	-0.72329	-0.26864	H	-2.15524	-0.22395	-2.17643
C	0.00000	-1.44657	0.26864	H	-1.27157	-1.75451	-2.17643
C	-1.25277	0.72329	0.26864	C	0.00000	-1.44539	1.80290
C	1.25277	0.72329	0.26864	H	0.88367	-1.97846	2.17643
H	2.14927	-1.24088	0.10095	H	-0.88367	-1.97846	2.17643
H	-2.14927	-1.24088	0.10095	C	0.00000	0.00000	2.32063
H	-2.14927	1.24088	-0.10095	H	0.00000	0.00000	3.41685
H	2.14927	1.24088	-0.10095	C	1.25175	0.72270	1.80290
C	0.00000	1.44539	-1.80290	H	2.15524	0.22395	2.17643
H	0.88367	1.97846	-2.17643	H	1.27157	1.75451	2.17643
H	-0.88367	1.97846	-2.17643	C	-1.25175	0.72270	1.80290
C	1.25175	-0.72270	-1.80290	H	-2.15524	0.22395	2.17643
H	2.15524	-0.22395	-2.17643	H	-1.27157	1.75451	2.17643
H	1.27157	-1.75451	-2.17643	H	0.00000	-2.48176	-0.10095
C	0.00000	0.00000	-2.32063	H	0.00000	2.48176	0.10095

 $E = -545.36244$ Zero-point vibration energy = 200.2 kcal mol⁻¹

Diamantane linear dimer (restricted to the D_{3d} stationary structure)

(Symmetry: D_{3d})

xyz-Coordinates

H	0.00000	-2.48175	-4.98150	C	-1.25289	-0.72336	4.61173
C	0.00000	-1.44671	-4.61173	C	-0.00000	1.44671	4.61173
C	1.25289	0.72336	-4.61173	C	1.25289	-0.72336	4.61173
C	-1.25289	0.72336	-4.61173	C	1.25298	0.72341	5.14909
C	-0.00000	1.44682	-5.14909	C	0.00000	-1.44682	5.14909
C	-1.25298	-0.72341	-5.14909	C	-1.25298	0.72341	5.14909
C	1.25298	-0.72341	-5.14909	H	-0.00000	2.48175	4.98150
H	2.14926	1.24088	-4.98150	H	2.14926	-1.24088	4.98150
H	-2.14926	1.24088	-4.98150	H	2.14928	1.24089	4.77911
H	-0.00000	2.48177	-4.77911	H	0.00000	-2.48177	4.77911
H	-2.14928	-1.24089	-4.77911	H	-2.14928	1.24089	4.77911
H	2.14928	-1.24089	-4.77911	C	-0.00000	1.44553	3.07786
C	1.25187	0.72277	-3.07786	H	-0.88358	1.97847	2.70392
H	2.15520	0.22403	-2.70392	H	0.88358	1.97847	2.70392
H	1.27162	1.75444	-2.70392	C	-1.25187	-0.72277	3.07786
C	0.00000	-1.44553	-3.07786	H	-2.15520	-0.22403	2.70392
H	0.88358	-1.97847	-2.70392	H	-1.27162	-1.75444	2.70392
H	-0.88358	-1.97847	-2.70392	C	1.25187	-0.72277	3.07786
C	-1.25187	0.72277	-3.07786	H	1.27162	-1.75444	2.70392
H	-2.15520	0.22403	-2.70392	H	2.15520	-0.22403	2.70392
H	-1.27162	1.75444	-2.70392	C	0.00000	0.00000	2.56010
C	0.00000	0.00000	-2.56010	C	0.00000	-1.44557	6.68293
C	-1.25190	-0.72279	-6.68293	H	0.88360	-1.97848	7.05685
H	-2.15521	-0.22402	-7.05685	H	-0.88360	-1.97848	7.05685
H	-1.27161	-1.75446	-7.05685	C	-1.25190	0.72279	6.68293
C	1.25190	-0.72279	-6.68293	H	-1.27161	1.75446	7.05685
H	2.15521	-0.22402	-7.05685	H	-2.15521	0.22402	7.05685
H	1.27161	-1.75446	-7.05685	C	1.25190	0.72279	6.68293
C	-0.00000	1.44557	-6.68293	H	1.27161	1.75446	7.05685
H	0.88360	1.97848	-7.05685	H	2.15521	0.22402	7.05685
H	-0.88360	1.97848	-7.05685	C	0.00000	0.00000	7.20059
C	0.00000	0.00000	-7.20059	H	0.00000	0.00000	8.29674
H	0.00000	0.00000	-8.29674	H	0.00000	0.00000	-1.46377
H	-2.14926	-1.24088	4.98150	H	0.00000	0.00000	1.46377

$E = -1090.72518$

Zero-point vibration energy = 400.6 kcal mol⁻¹

Dissociation energy D_0 = 0.0 kcal mol⁻¹

4. Supplementary figures

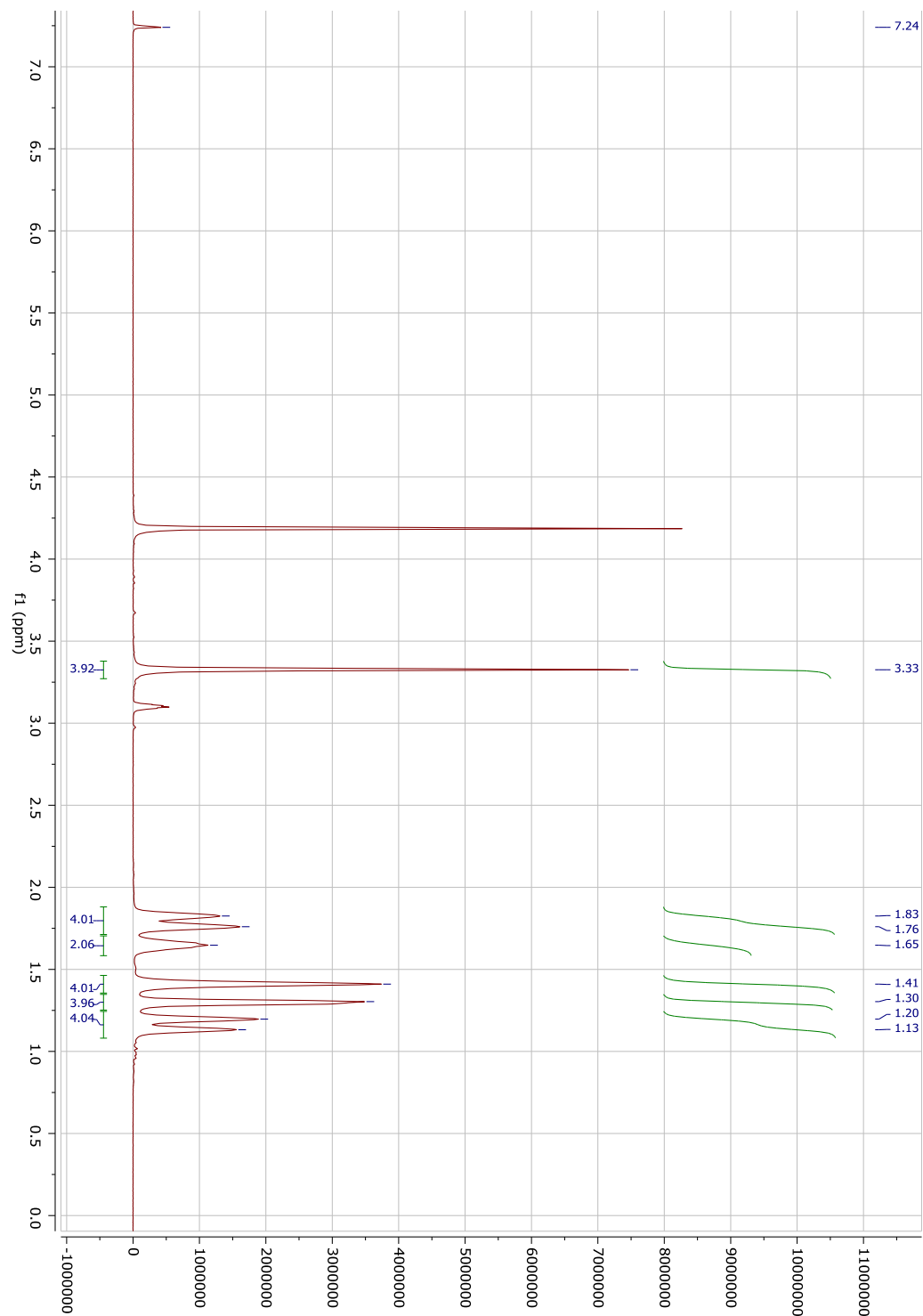


Figure S1. ^1H NMR spectrum of 1,6-bis(hydroxymethyl)diamantane ($\text{CDCl}_3/\text{CD}_3\text{OD}$).

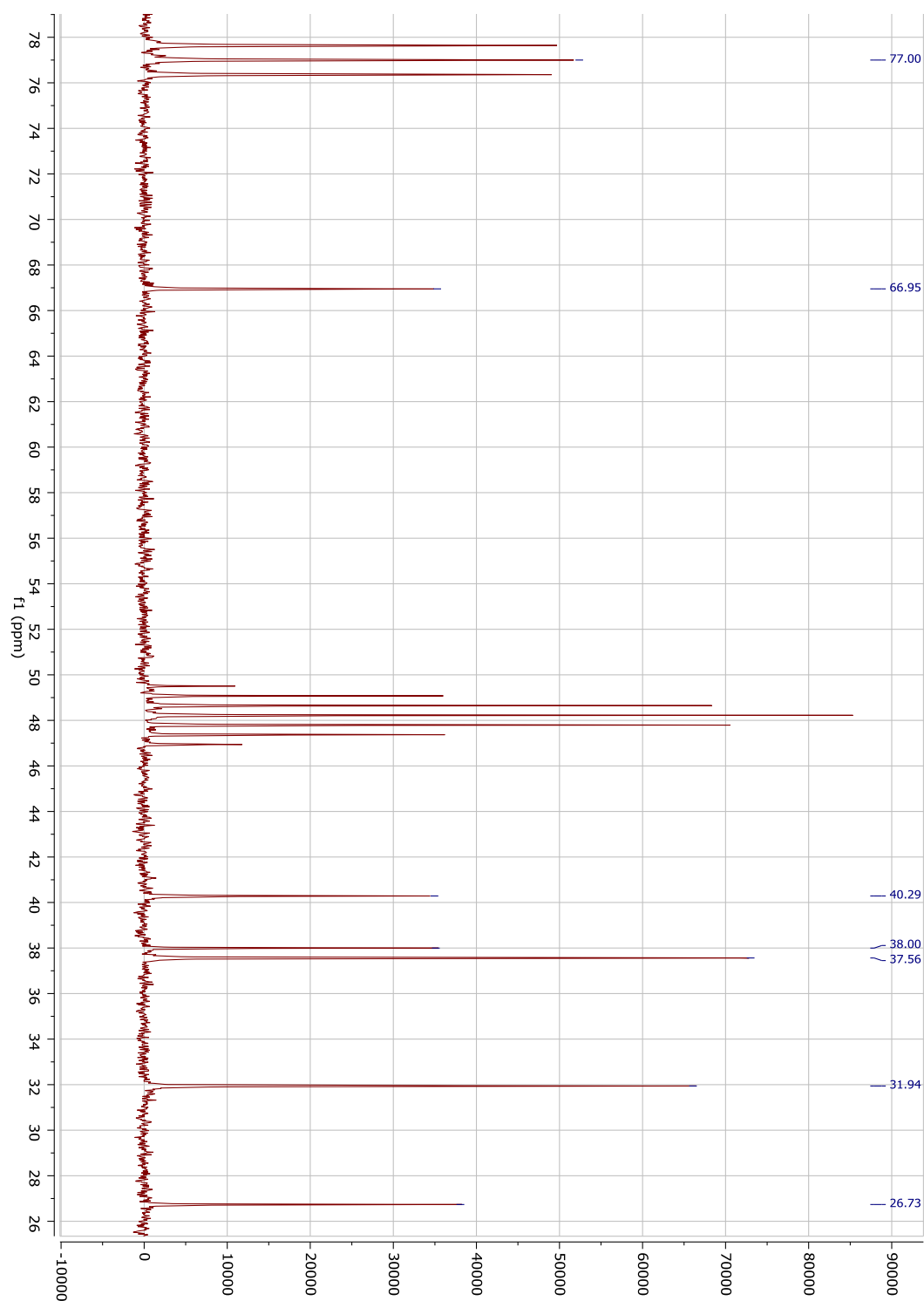


Figure S2. ^{13}C NMR spectrum of 1,6-bis(hydroxymethyl)diamantane ($\text{CDCl}_3/\text{CD}_3\text{OD}$).

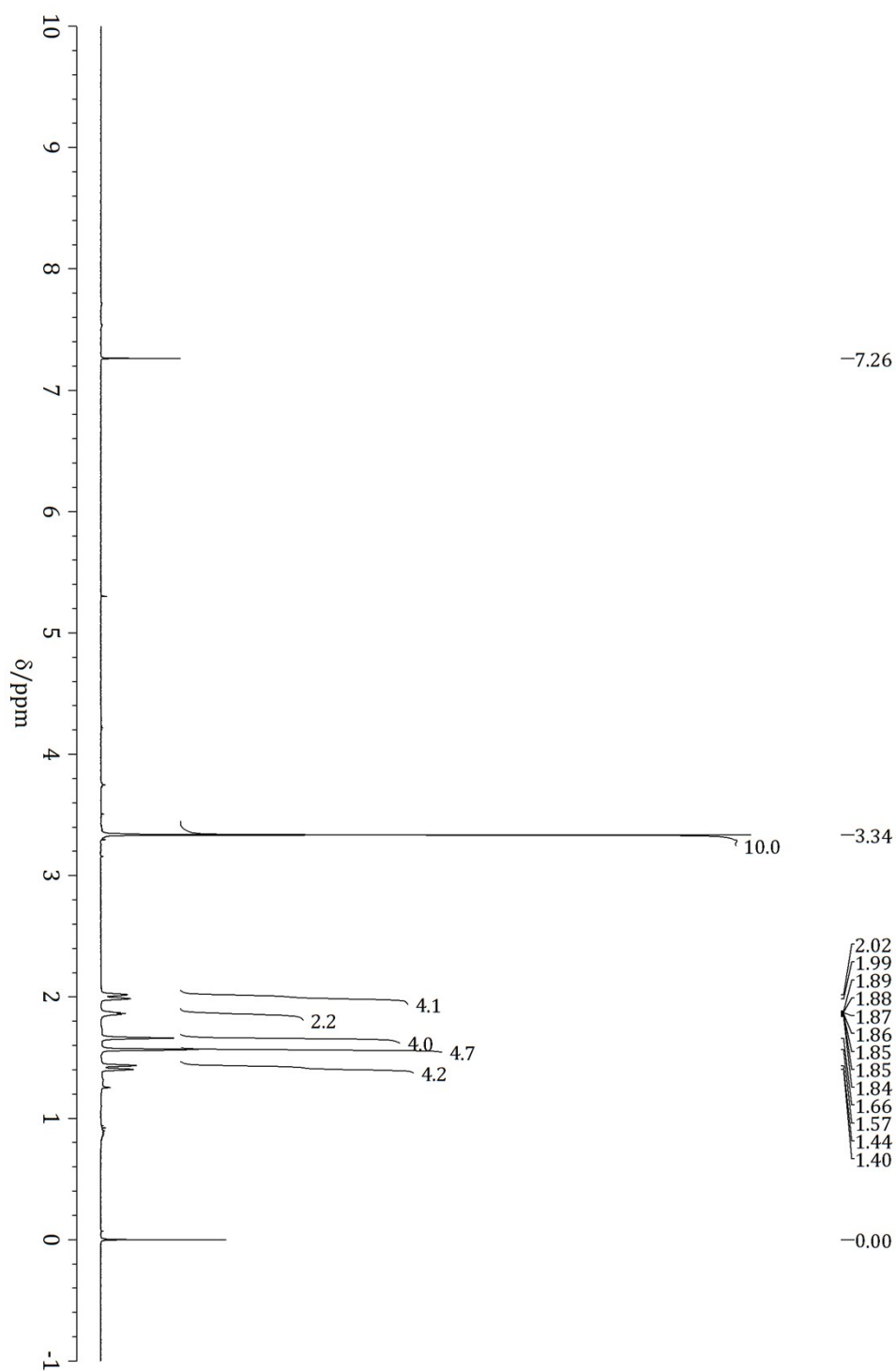


Figure S3. ^1H NMR spectrum of 1,6-bis(methoxymethyl)diamantane (CDCl_3).

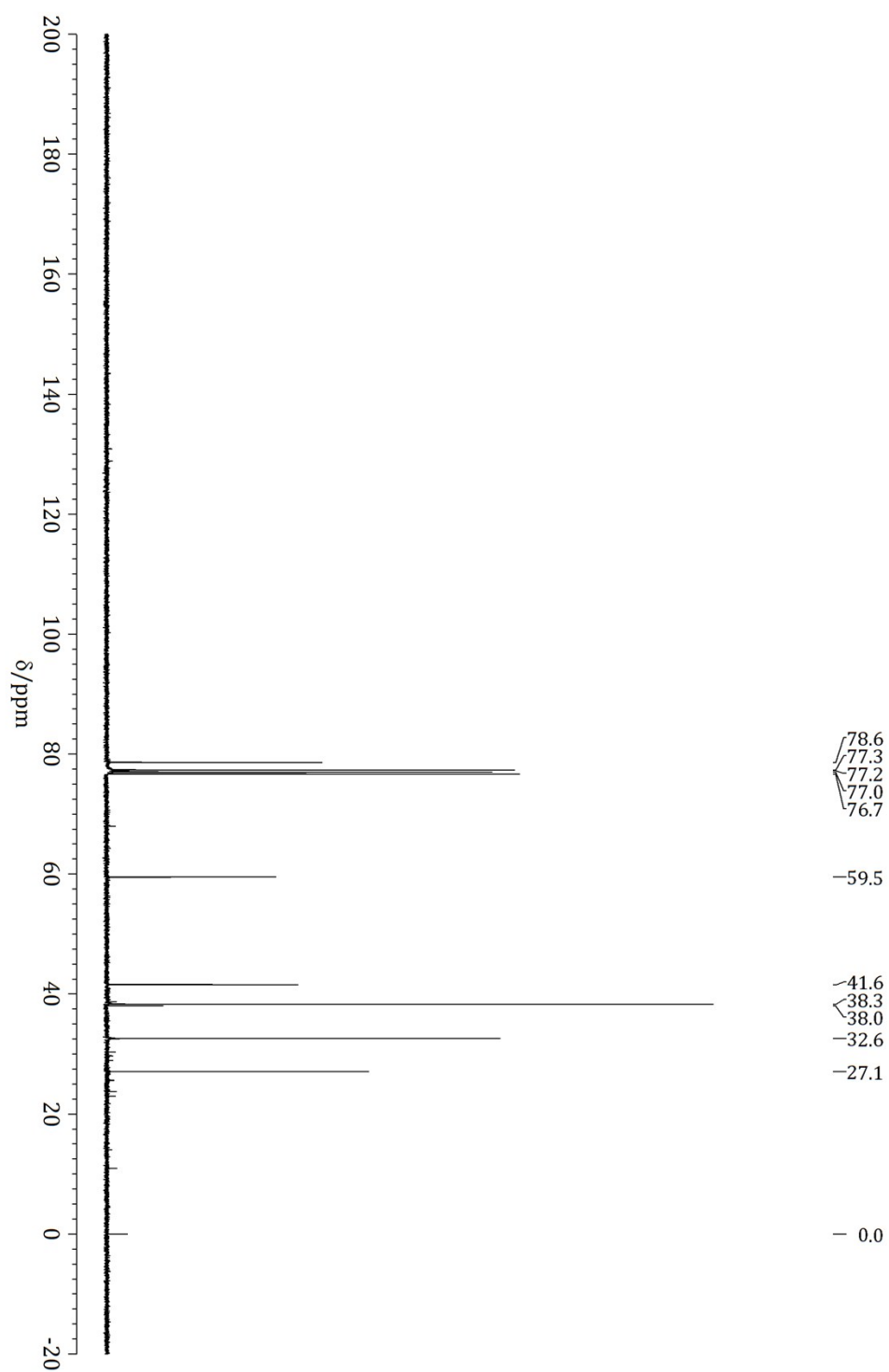


Figure S4. ^{13}C NMR spectrum of 1,6-bis(methoxymethyl)diamantane (CDCl_3).

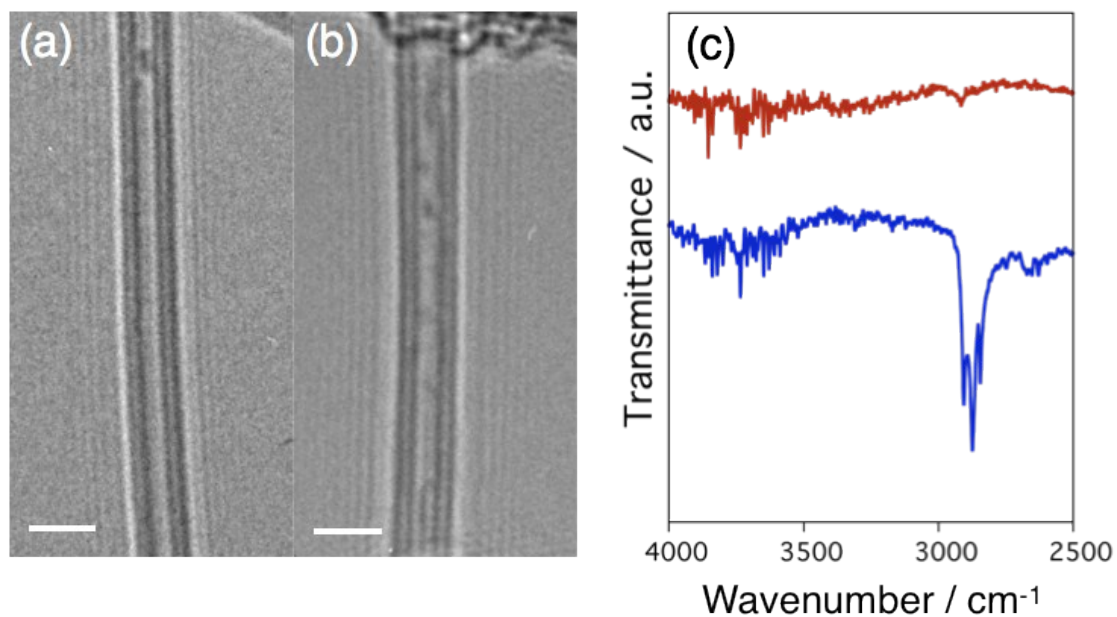


Figure S5. (a, b) TEM images of diamantane@DWCNTs. The scale bar is 2 nm. (c) FTIR spectra of diamantane@DWCNTs (red) and **1**@DWCNTs (blue).

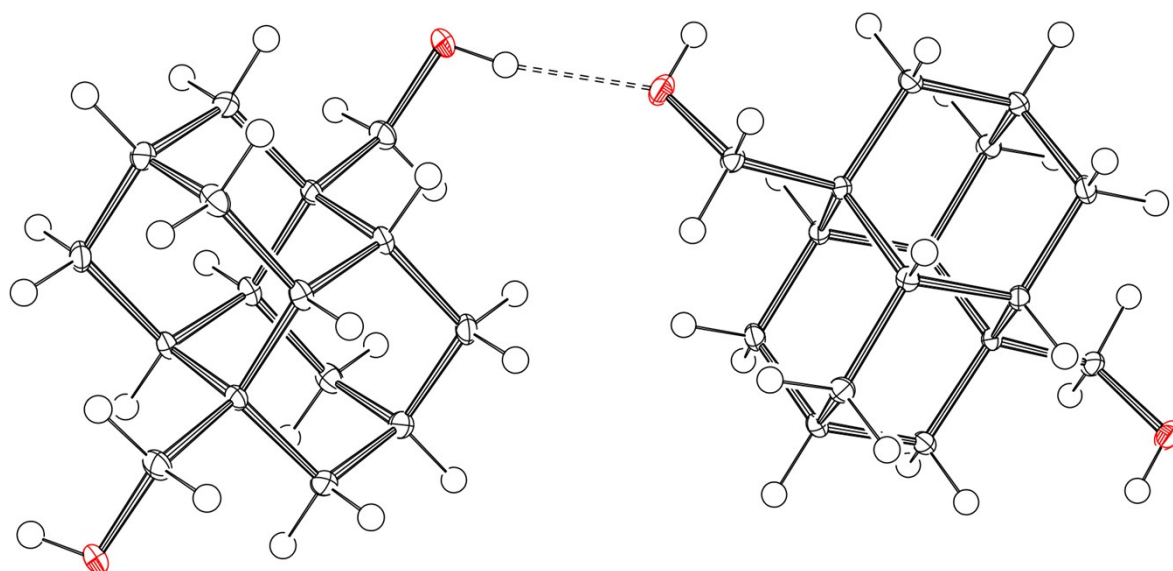


Figure S6. ORTEP plot of the molecular structure of **1**.

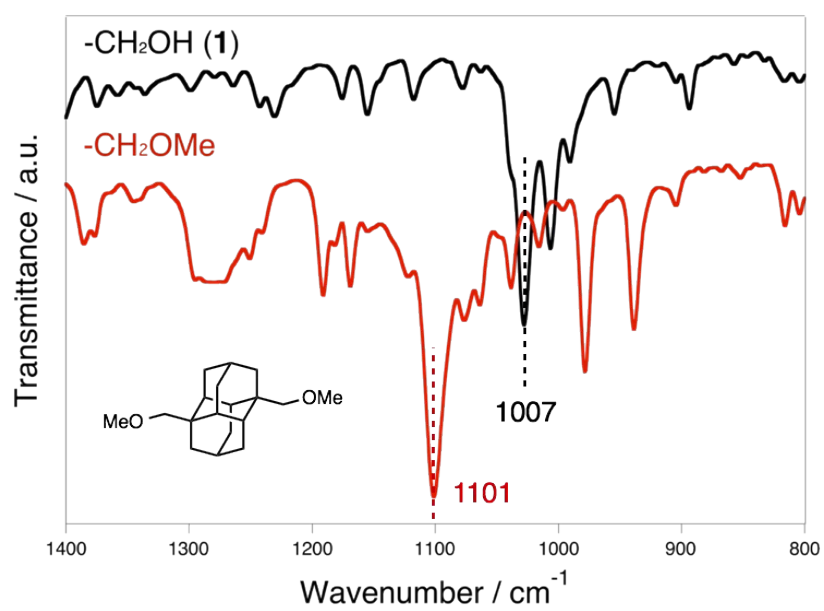


Figure S7. FTIR spectra of precursor **1** (black) and 1,6-bis(methoxymethyl)diamantane (red, inset).