Supporting Information

Elucidation of Nano-sized Molecular Structure of Methylaluminoxane using Synchrotron X-ray Total Scattering

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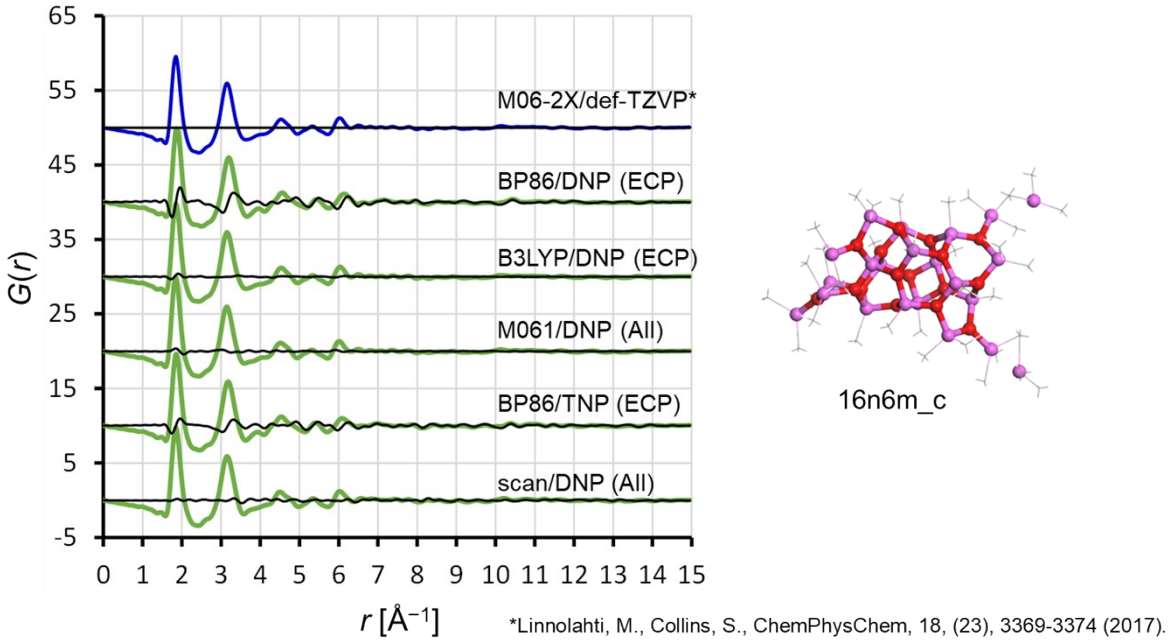

Figure S1. PDF curves calculated from various 16n6m_c models, optimized using different functionals and basis sets. (ECP) means that the effective core potential approximation has been applied, and (All) means that the all the electrons were considered. The thin black lines represent the differences from the top PDF curve, which is derived from the 16n6m_c model in the library, optimized using the M06-2X functional and def-TZVP basis set.

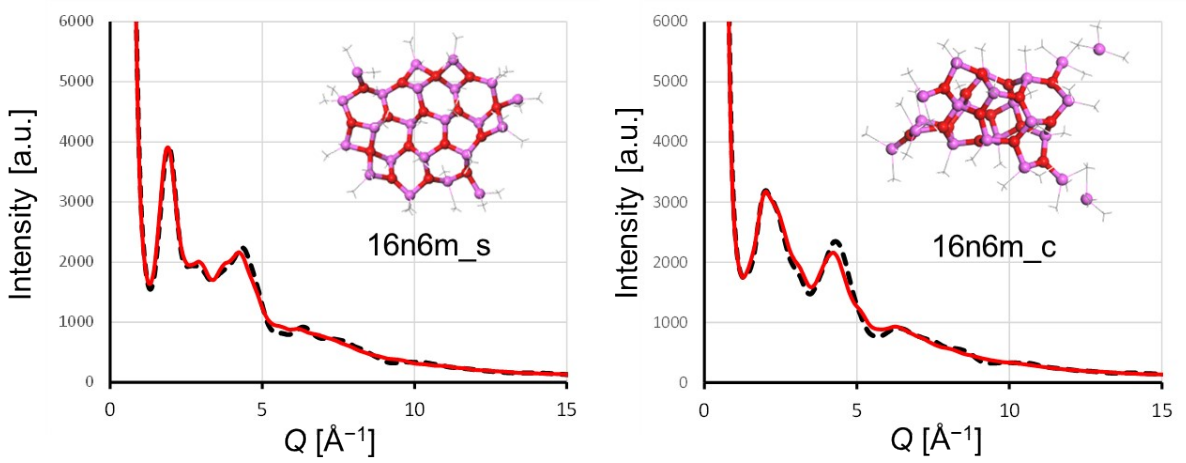

Figure S2. Simulated X-ray scattering patterns with varying Debye-Waller factors applied. The U_{iso} values for all atoms were set at 0 (black lines) and 0.02 Å^2 (red lines).

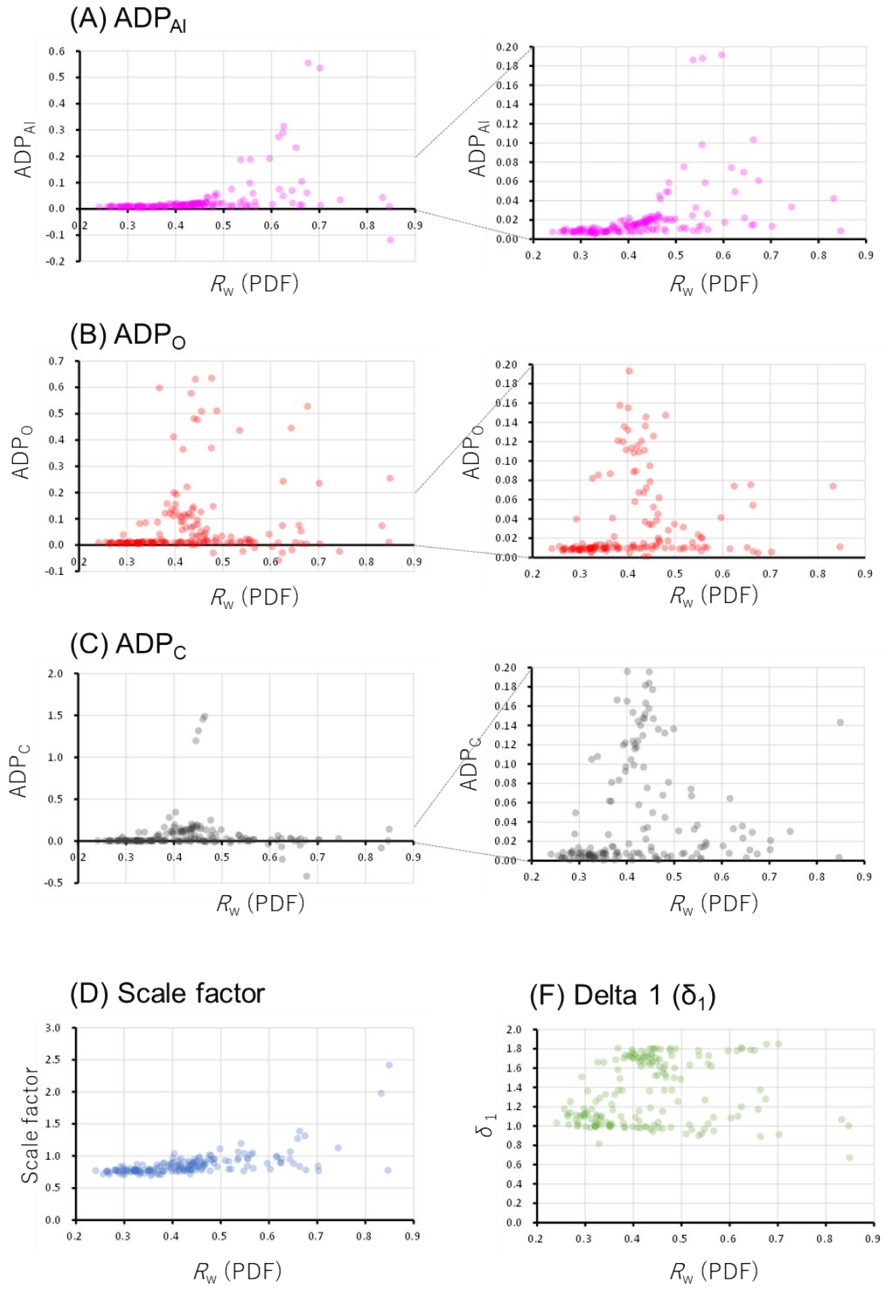

Figure S3. Fitting parameters of all the PDF fitting curves for MAO-dried sample.

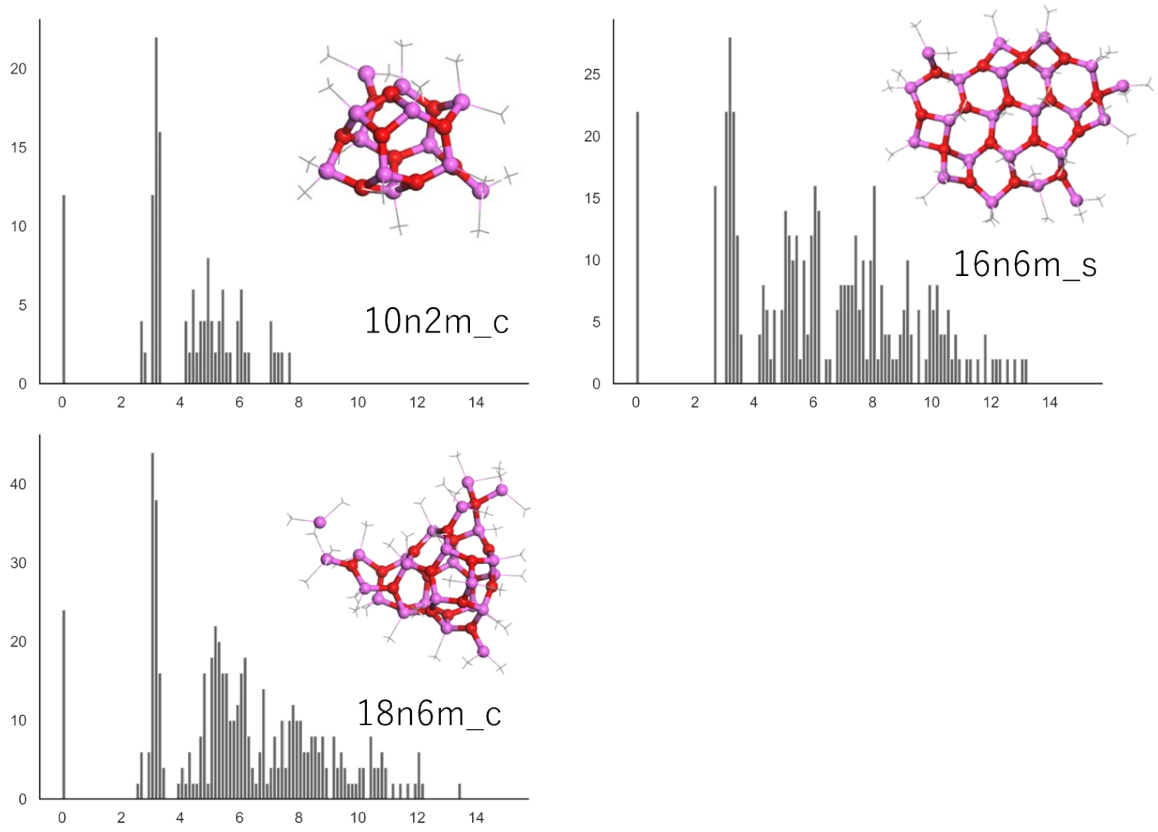

Figure S4. Histogram for Al-Al distance in selected molecular models.

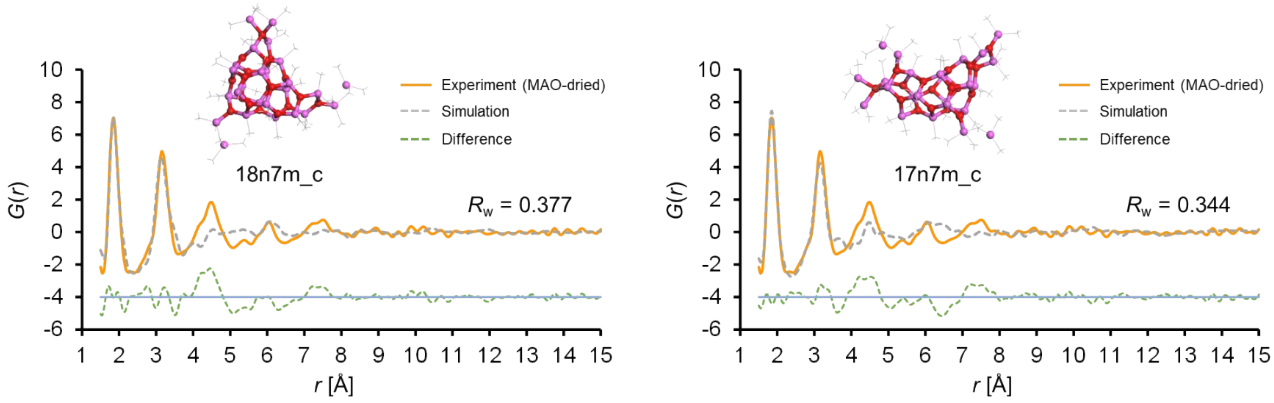

Figure S5. Typical fitting results for the PDF curve of the MAO-dried sample using large cage models.

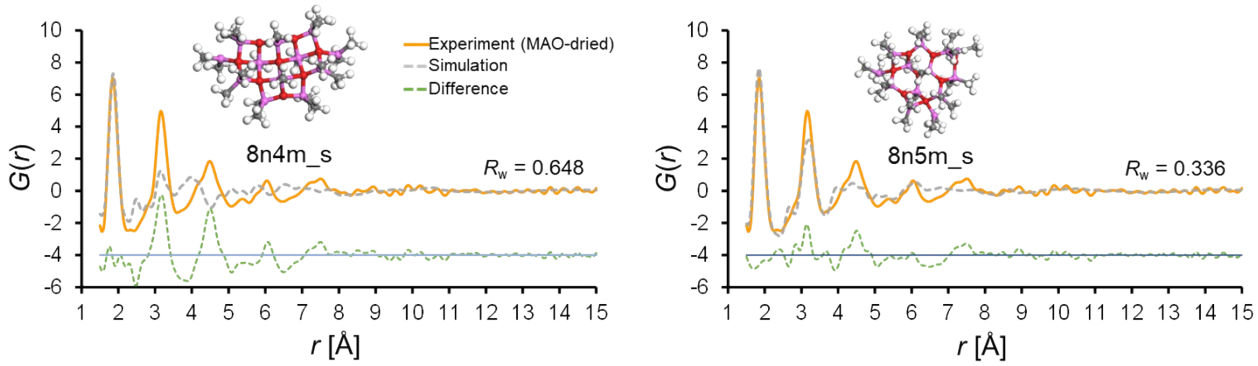

Figure S6. Comparison of PDF fitting results for MAO-dried sample using 8n4m_s and 8n5m_s, expressing the impact of Al-O ring structures. The two structures have a similar molecular weight (the difference is only a single TMAL molecule), but the raito of 4-membered rings and 6-membered rings were totally different. 8n4m is composed of ten 4-membered rings, and 8n5m is composed of two 4-membered rings and four 6-memebred rings.

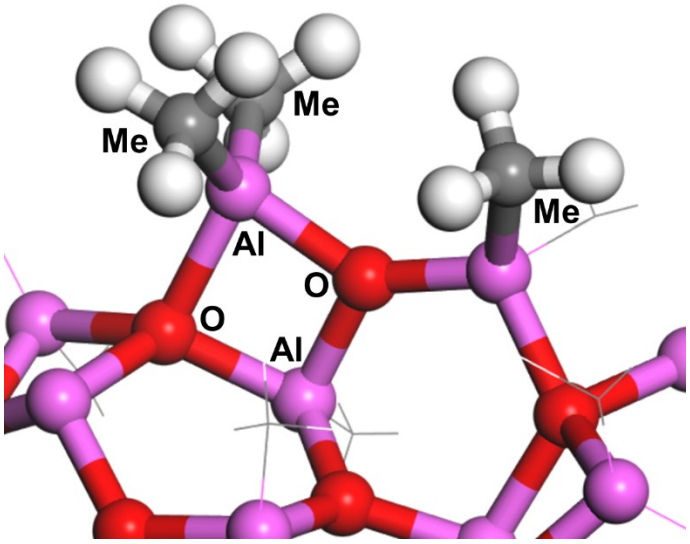

Figure S7. A typical four-membered aluminoxane ring (-Al-O-Al(Me)$_2$-O-) formed by the chemisorption of a TMAL molecule to an edge of a sheet model. On the chemisorption, one of the methyl groups of TMAL migrates to a 3-coordinated Al site.

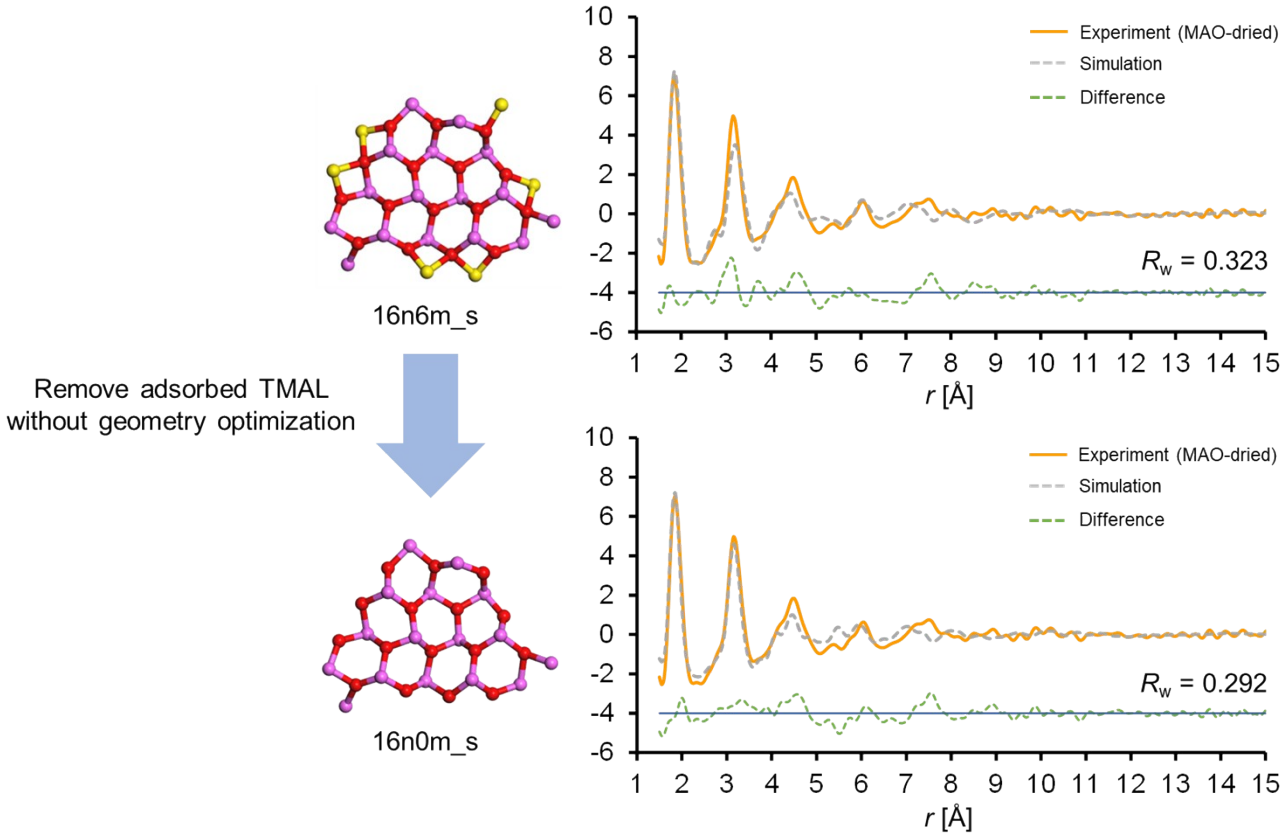

Figure S8. Comparison of PDF fitting results for MAO-dried sample using 16n6m_s and 16n0m_s.

Table S1. Atomic configuration of 25n7m_s in xyz format.

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O	13.0608	19.2477	13.6695
Al	11.3349	18.7431	13.4964
O	15.9393	19.0761	13.8711
Al	14.4609	18.2157	13.3248
Al	9.5769	17.0394	15.4107
O	11.2326	17.3073	14.6022
Al	12.6234	16.3983	15.297
O	14.1993	16.8456	14.5323
O	9.795	15.2325	15.7662
Al	8.9361	14.4585	17.1483
O	12.3792	14.6913	14.5683
Al	10.6008	14.2638	14.4873
O	15.1209	14.2863	13.6599
Al	13.4412	13.6665	13.5549
O	8.2989	12.894	16.4742
Al	9.0897	11.7372	15.3903
O	10.7178	12.5664	15.1365
Al	12.1638	11.7645	15.8052
O	13.5903	12.0006	14.5134
Al	15.5013	15.6315	14.8326
Al	17.0751	18.2001	14.9592
O	18.5037	19.1049	14.1825
O	20.9802	18.6921	14.6673
Al	19.9431	18.2211	13.2924
Al	22.2735	17.6139	15.2709
O	16.9503	16.5405	14.2662
Al	18.0426	15.9123	12.9666
O	19.677	16.4463	13.4394
Al	21.1506	15.3303	13.1649
O	22.3833	16.287	14.0361
Al	16.4025	13.4466	12.6708
O	17.9262	14.1555	13.3458
O	20.7372	13.8075	14.0238
Al	19.0785	13.5399	14.6388

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Al	17.9694	11.0175	13.2258
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O	12.0918	10.0467	15.2082
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Al	13.2468	10.1511	13.8615
Al	16.0527	8.460599	14.031
O	17.5743	9.3015	13.5324
O	19.9152	9.1092	15.1023
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C	16.7508	18.3204	16.8597
C	20.3943	18.8967	11.5392
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C	17.6382	16.4613	11.1522

C	21.441	15.105	11.2548
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C	16.1316	13.4178	10.749
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H	19.9506	14.4789	16.7883
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H	11.787	10.1838	11.7729
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H	14.3379	6.6759	13.3422
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Al	12.7146	20.7651	14.6127
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C	13.2399	20.5941	16.4844
C	7.0833	15.3954	17.3268
Al	6.5361	13.362	16.6707
C	5.5956	13.6863	14.9931
C	5.7468	12.3783	18.1623
Al	9.2862	9.470401	17.904
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Al	21.7131	9.315299	14.412
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C	21.7116	8.9007	12.4926
C	22.8144	13.4109	16.3014
Al	24.1452	16.6581	13.6314
C	25.4304	15.5685	14.6163
C	24.4188	17.2083	11.7798
C	22.1325	17.1756	17.1552
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