Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting material to Surface Chemical Mechanisms of Trimethyl Aluminum in Atomic Layer Deposition of AlN

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Effect of spin polarization

The energy difference between non-spin polarized and spin polarized calculations and magnetization of structures **A_0**, **B_0**, **C_1**, **C_2**, **BC_1**, and **BC_2** are given in Table SI. For the minima structures the magnetization when considering spin polarization was negligible and the difference in energy between spin polarized calculation and non-spin polarized were less than 1.5 kJ mol^{-1}. This agrees with the expected closed shell configuration of these structures as the system can form full octets. For the transition state **BC_1** the magnetization was found to be 1.88 indicating a triplet state with the energy being around 26 kJ mol^{-1} less for the spin polarized triplet compared to the non-polarized singlet state. The transition state **BC_2** has a magnetization of 0.94 with one unpaired electron and an energy difference of -5 kJ mol^{-1}.

	Electronic energy non-spin polarized (eV)	Electron energy spin polarized (eV)	Energy difference (kJ mol^{-1})	Magnetization (spin polarized)
A_0	-1564.550	-1564.550	0.0	0.00
B_0	-1565.507	-1565.507	0.0	0.00
C_1	-1566.506	-1566.518	-1.1	0.05
C_2	-1570.761	-1570.761	0.0	0.00
BC_1	-1564.993	-1565.269	-26.6	1.88
BC_2	-1565.191	-1565.242	-5.0	0.94

Adsorption and Decomposition structures

The adsorption and decomposition structures of a first TMA molecule on amino terminated AlN are shown in Figs. S1 – S8. Surface oxidation and last methyl protonation are shown in Fig. S9 – S12. Adsorption and decomposition of a second TMA molecule are shown in Figs. S13 – S21.

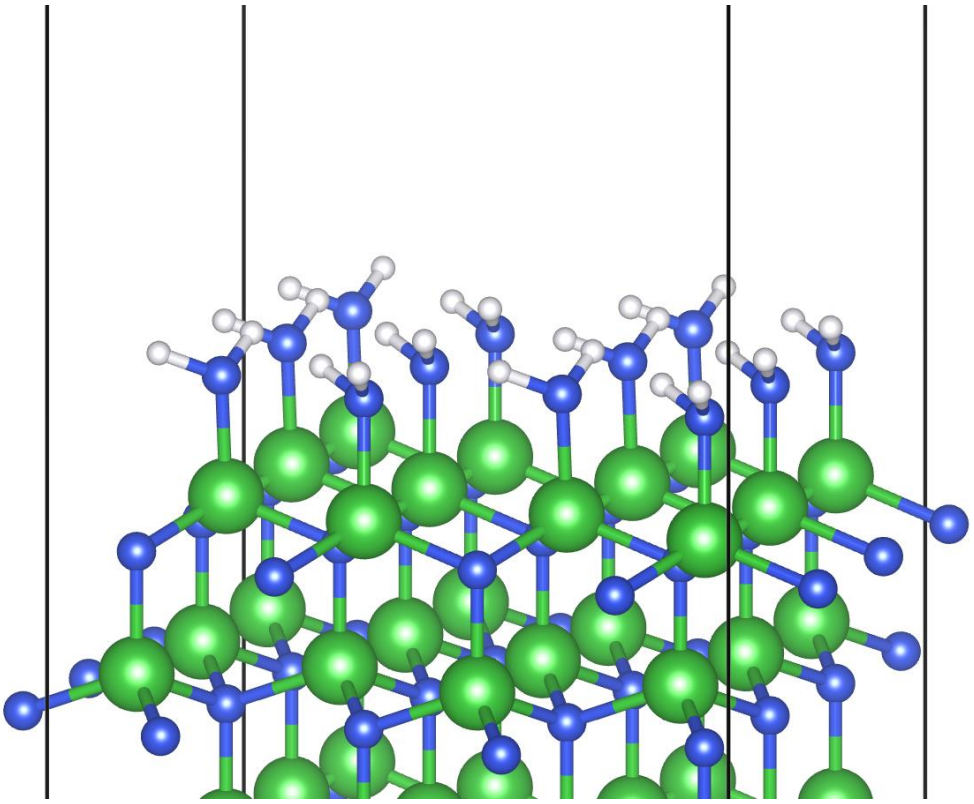

Figure S1. Amino terminated (0001)-AlN surface $\mathbf{A_0}$.

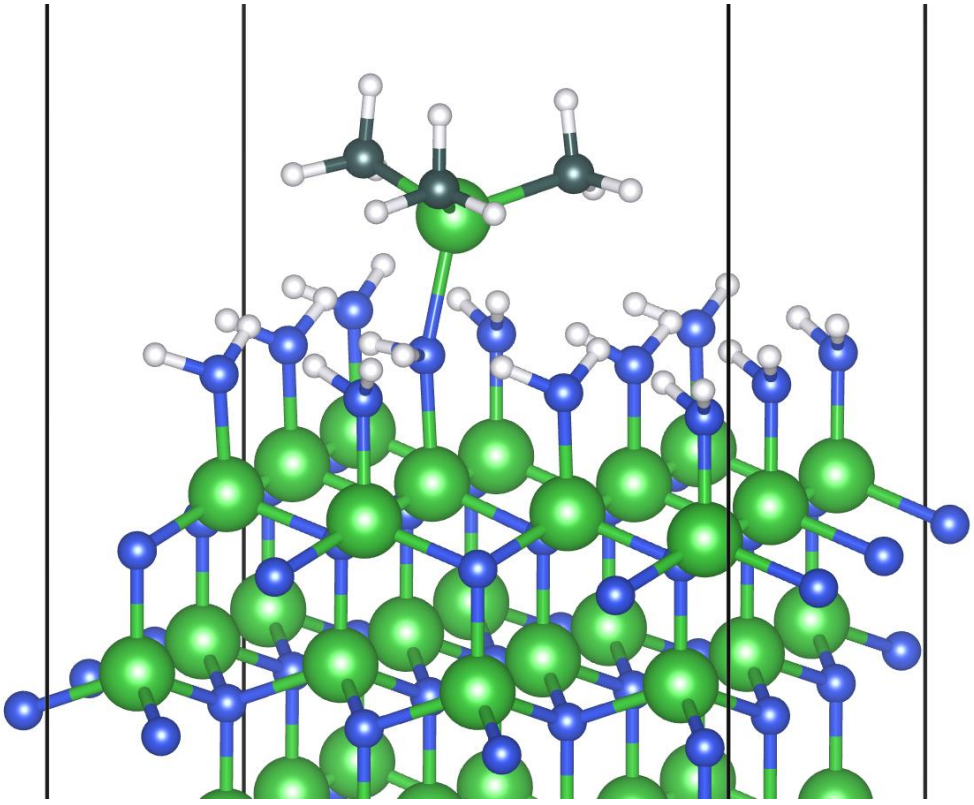

Figure S2. Adduct between surface amino group and TMA molecule ($\mathbf{B_0}$).

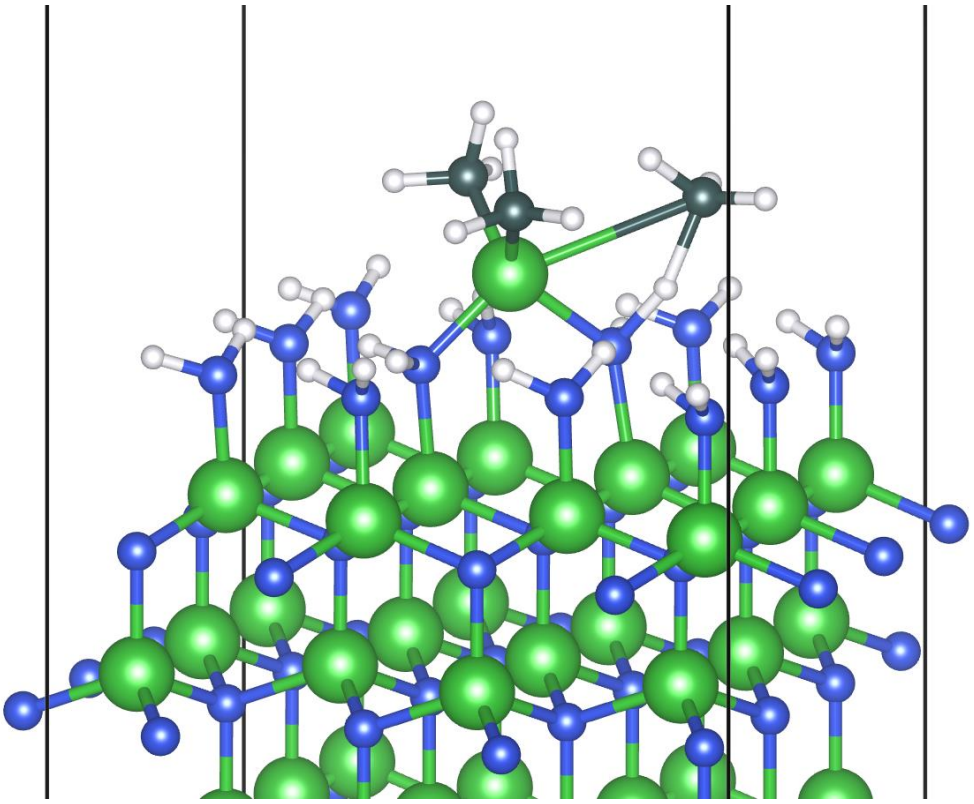

Figure S3. Methyl protonation transition state (**BC_1**) from TMA adduct.

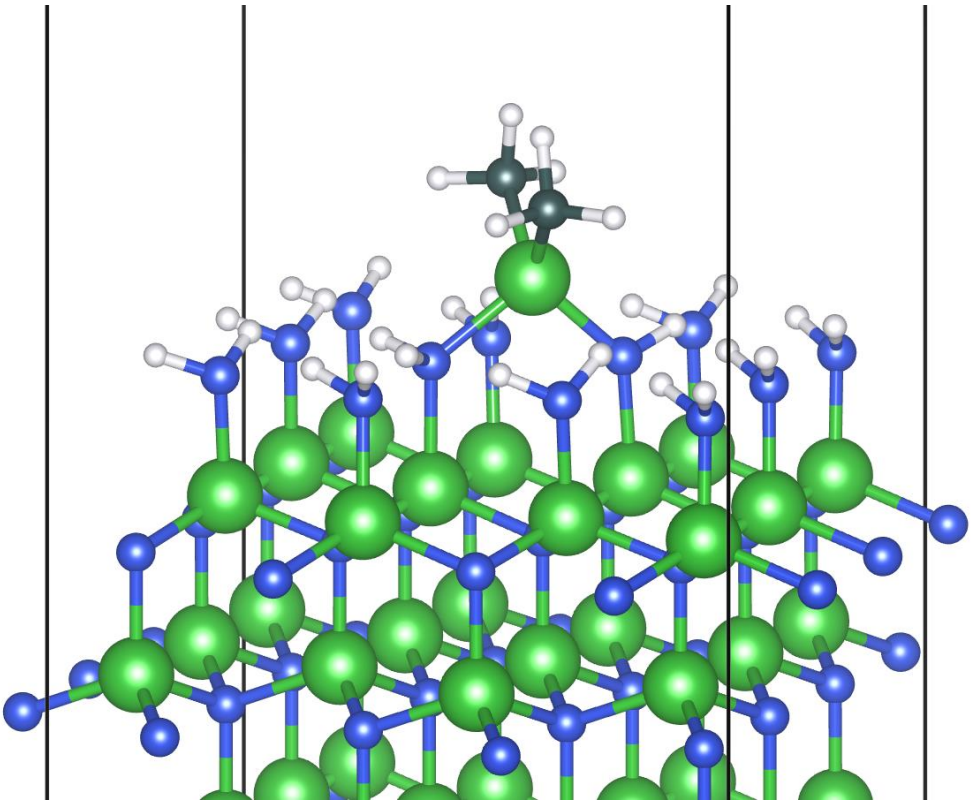

Figure S4. DMA fragment (**C_1**) bridging adduct amino group and deprotonated amino group.

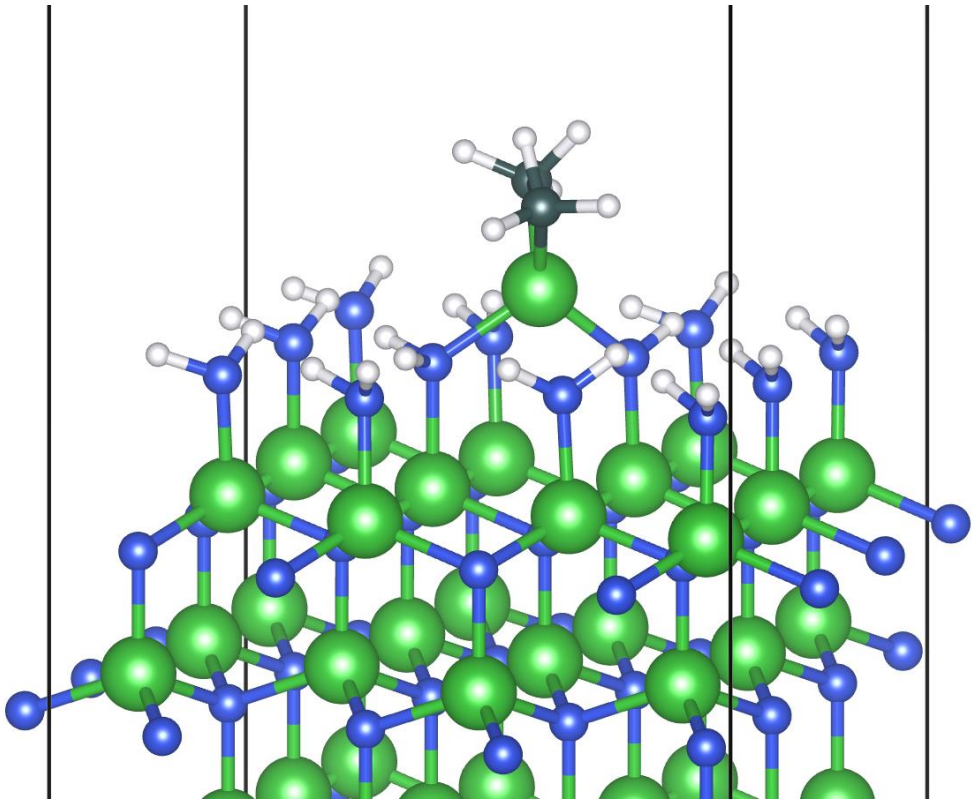

Figure S5. Reductive elimination transition state (**CD$_1$**) from DMA fragment (**C$_1$**). Methyl groups are pushed together.

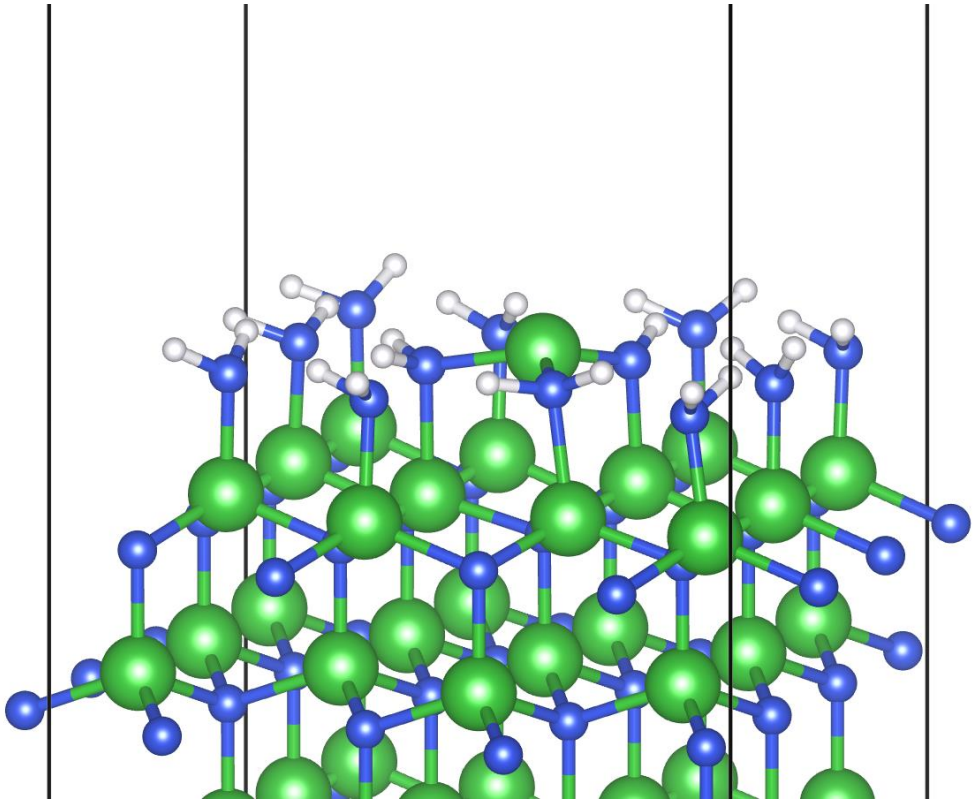

Figure S6. Aluminum adatom bridging two adduct amino group and one deprotonating amino group (**D$_1$**).

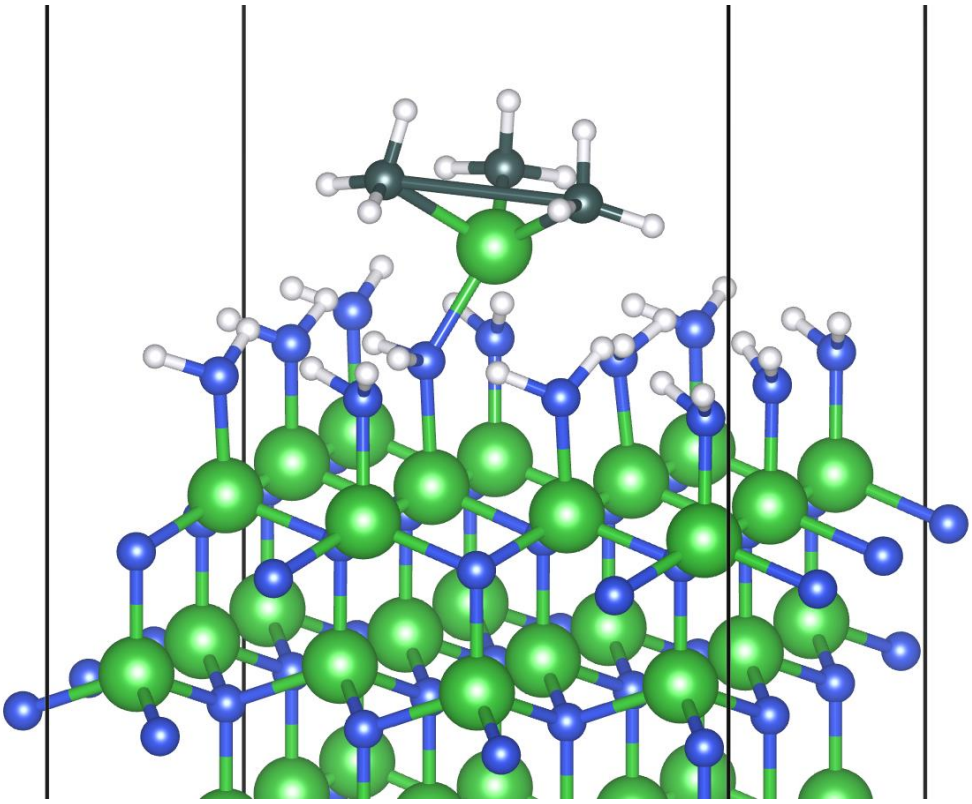

Figure S7. Reductive elimination transition state (**CD_2**) from TMA adduct (**B_0**).

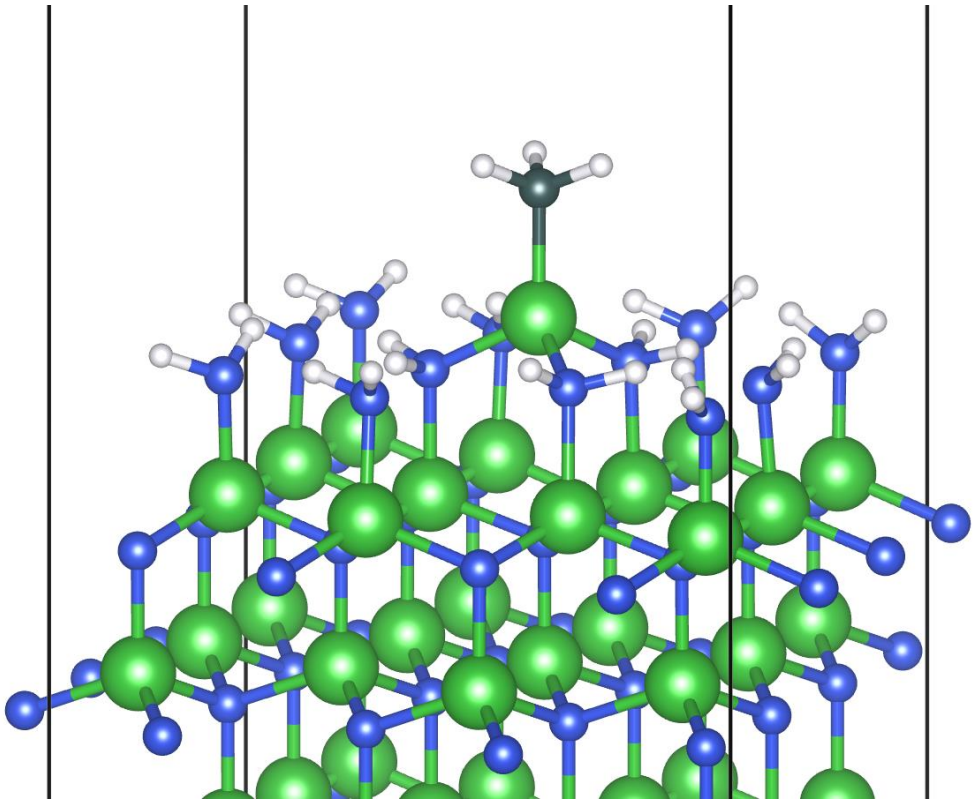

Figure S8. MMA fragment bridging three adduct amino groups (**C_2**).

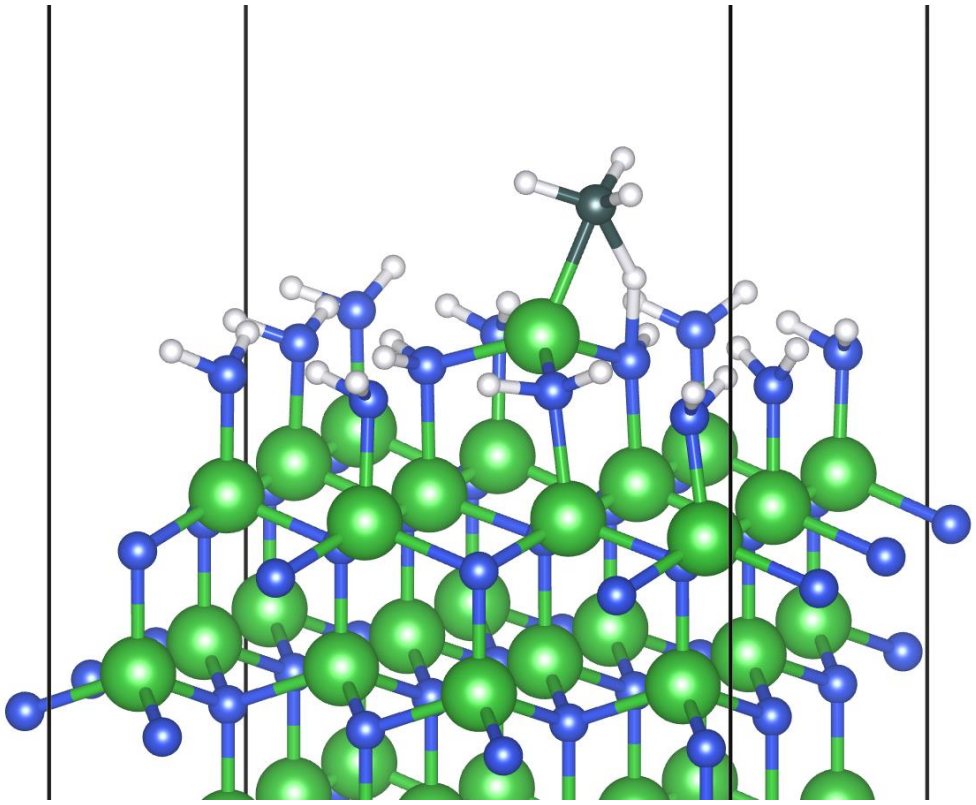

Figure S9. Methyl protonation transition state (**CD_2**) from MMA fragment.

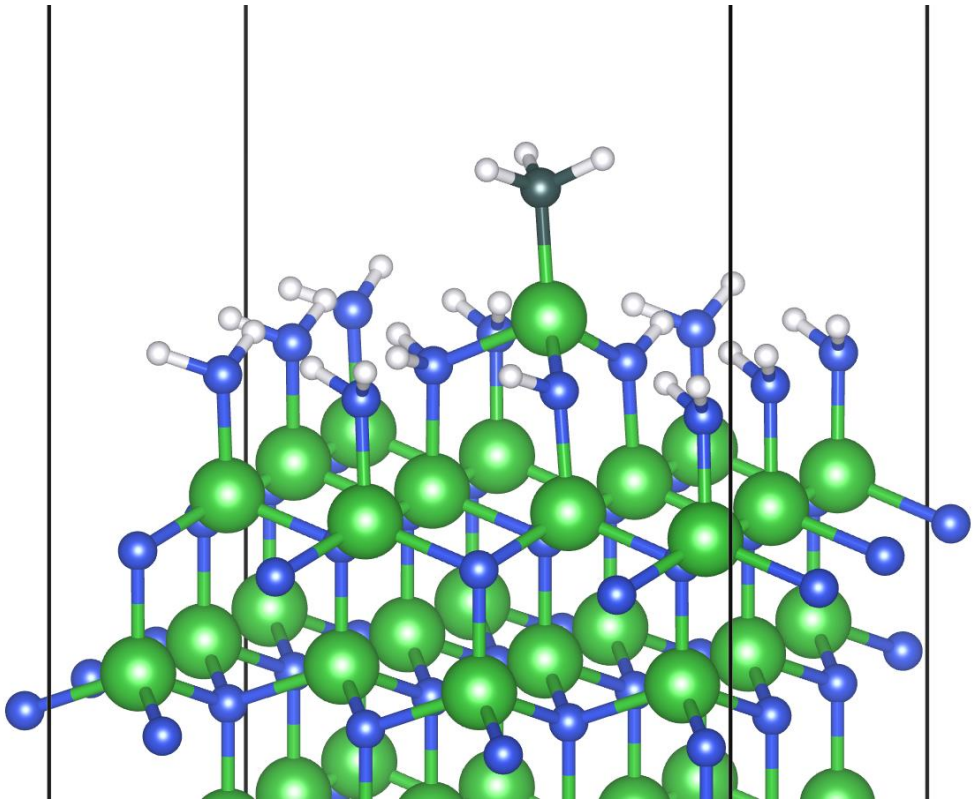

Figure S10. MMA fragment bridging one adduct amino groups (**D_3**) and two deprotonated amino groups after oxidation of the surface.

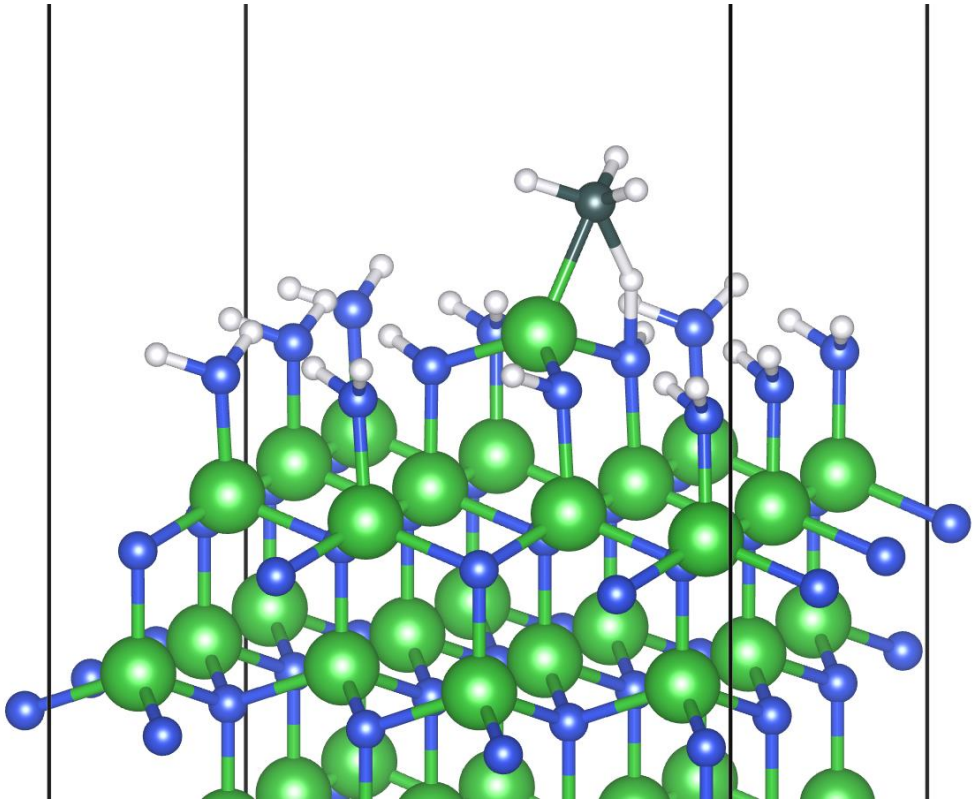

Figure S11. Methyl protonation transition state (**DE_3**) from MMA fragment at oxidized surface.

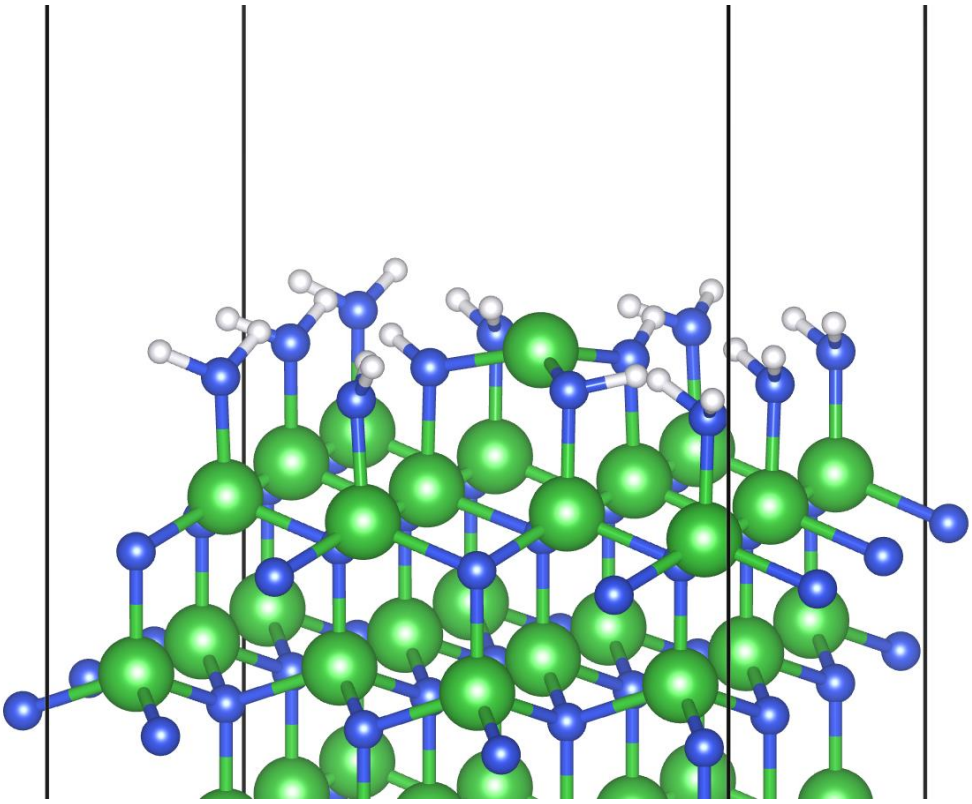

Figure S12. Aluminum adatom bridging three deprotonated amino groups (**E**$_3$).

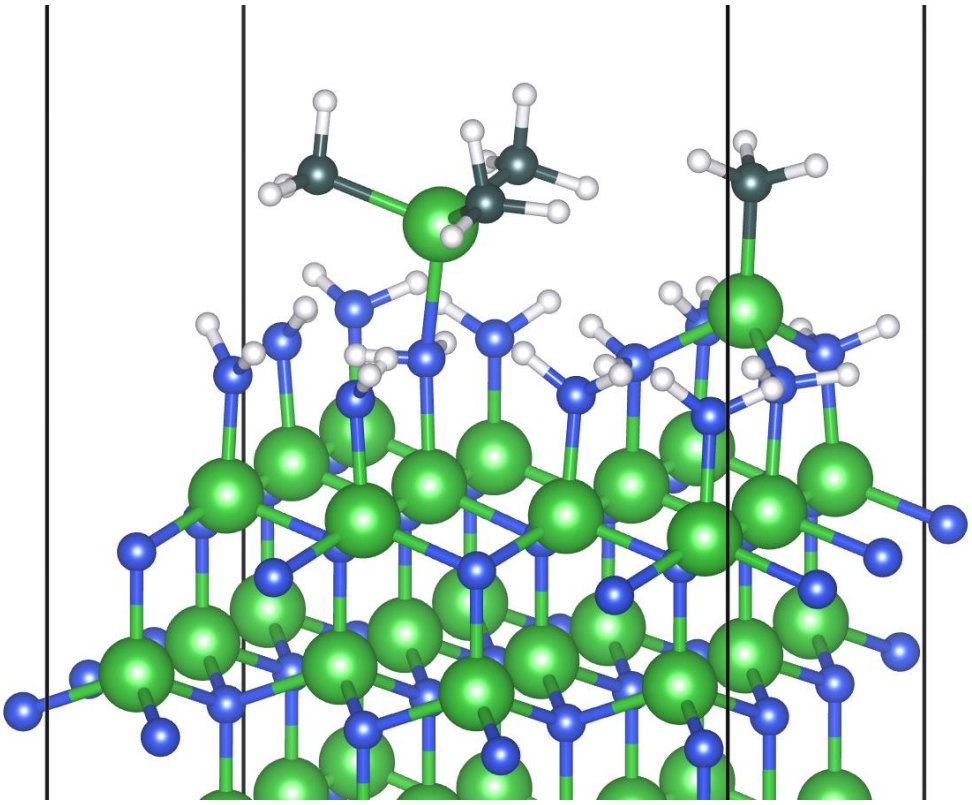

Figure S13. Adduct between surface amino group and TMA molecule (**D**$_5$) with a neighboring MMA fragment.

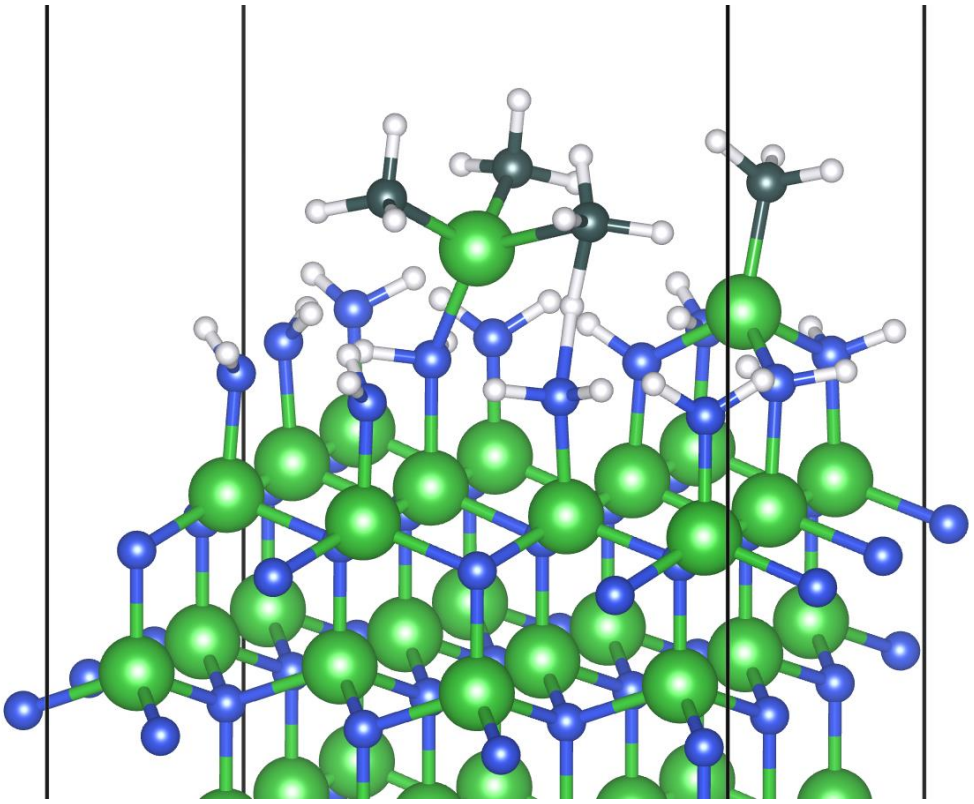

Figure S14. Methyl protonation transition state (**DE$_5$**) from a TMA adduct with neighboring MMA fragment.

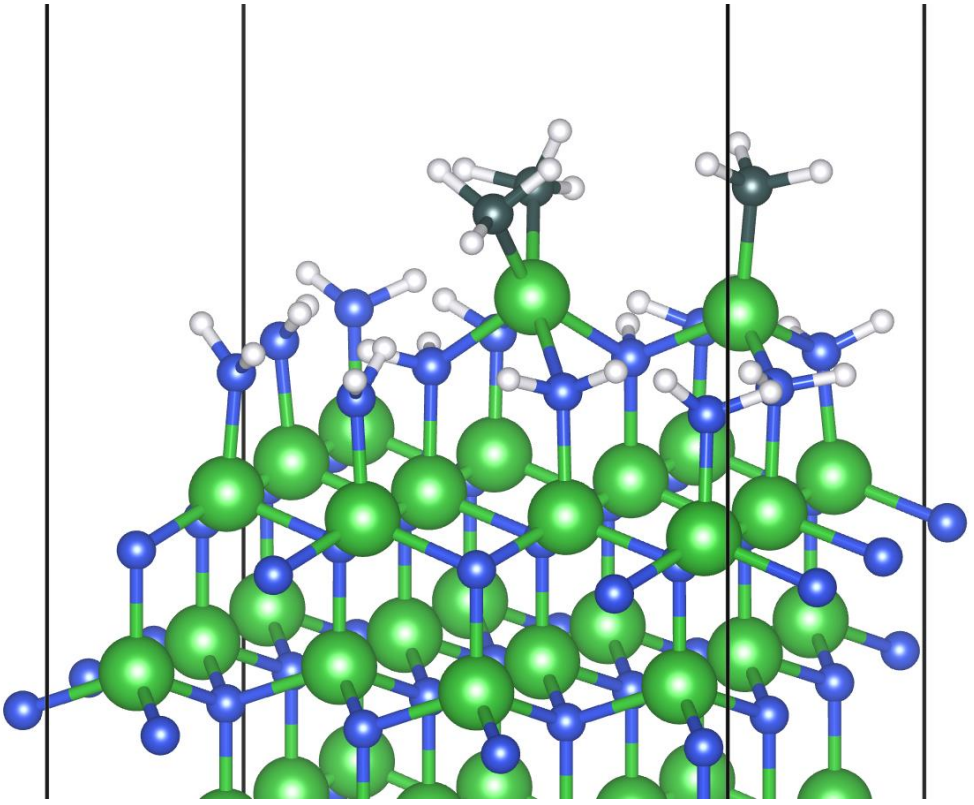

Figure S15. DMA fragment bridging two adduct amino groups and a deprotonated amino group (**E$_5$**), shared with an MMA fragment.

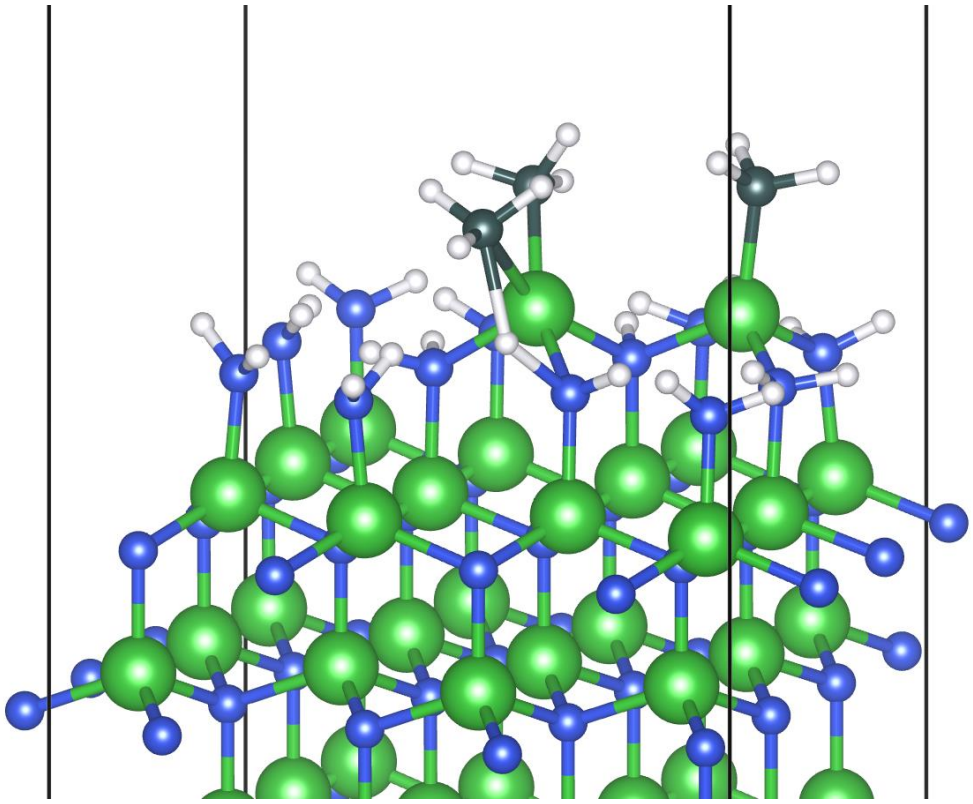

Figure S16. Methyl protonation transition state (**EF$_5$**) from DMA fragment with neighboring MMA fragment.

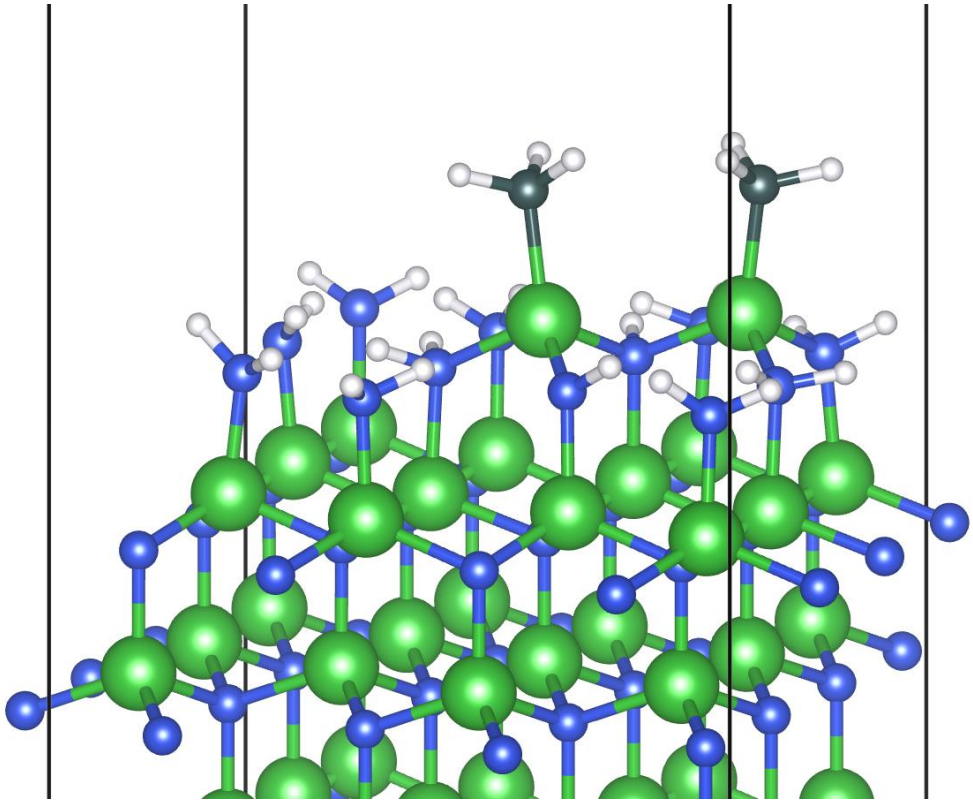

Figure S17. Bridging MMA fragment between two deprotonated amino groups and one adduct amino group (**F$_5$**) with neighboring MMA fragment.

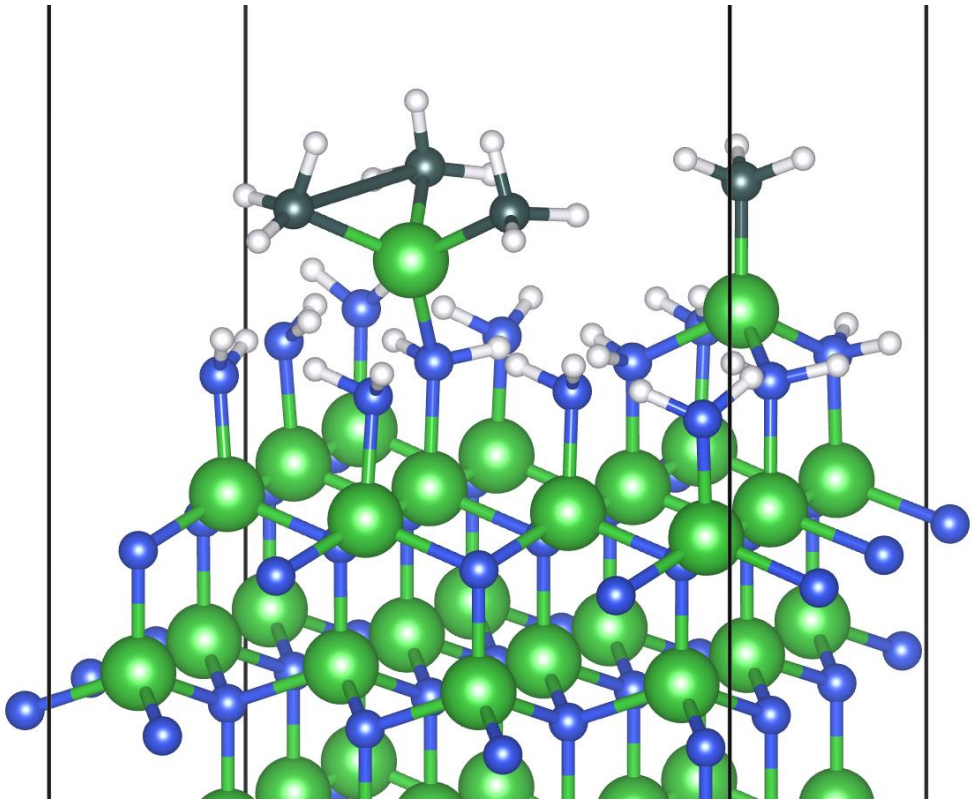

Figure S18. Reductive elimination transition state (**DE_6**) from a TMA adduct with neighboring MMA fragment.

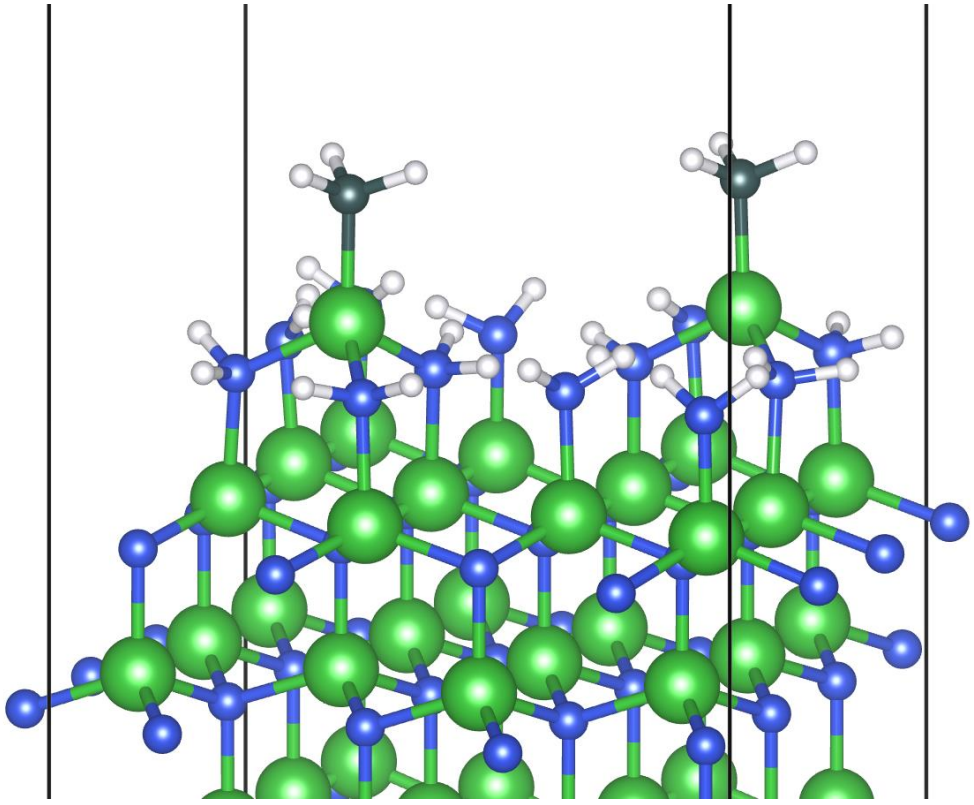

Figure S19. Bridging MMA fragment three adduct amino groups (**E_6**) with neighboring MMA fragment.

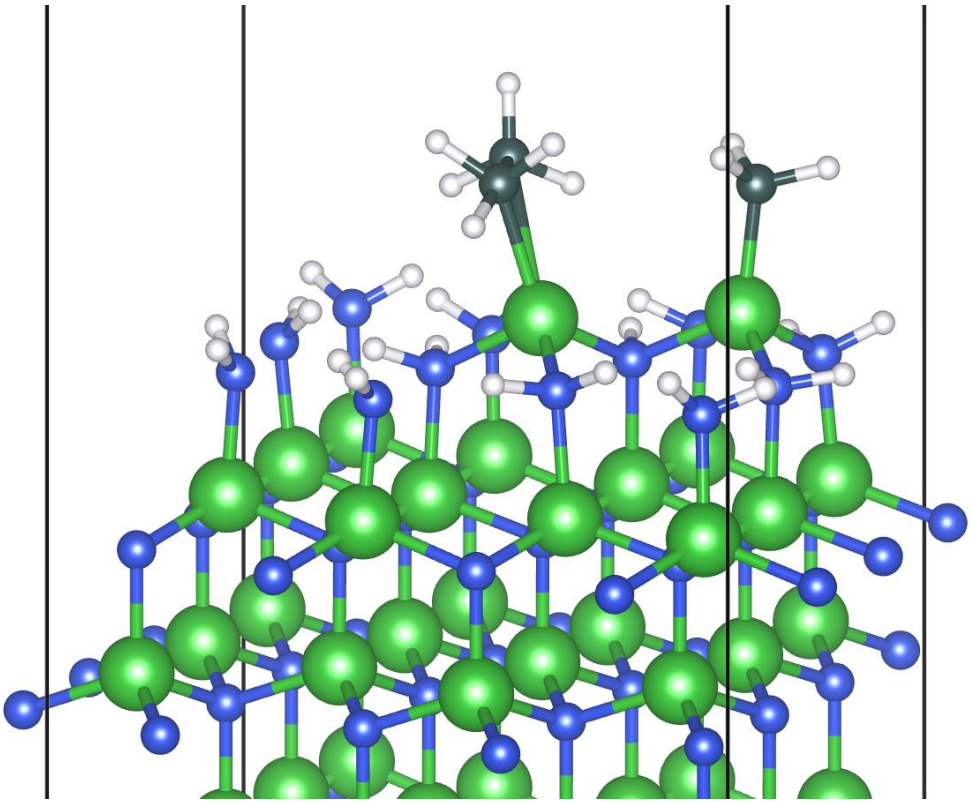

Figure S20. Reductive elimination transition state (**EF$_7$**) from a DMA fragment bridging three amino groups with neighboring MMA fragment.

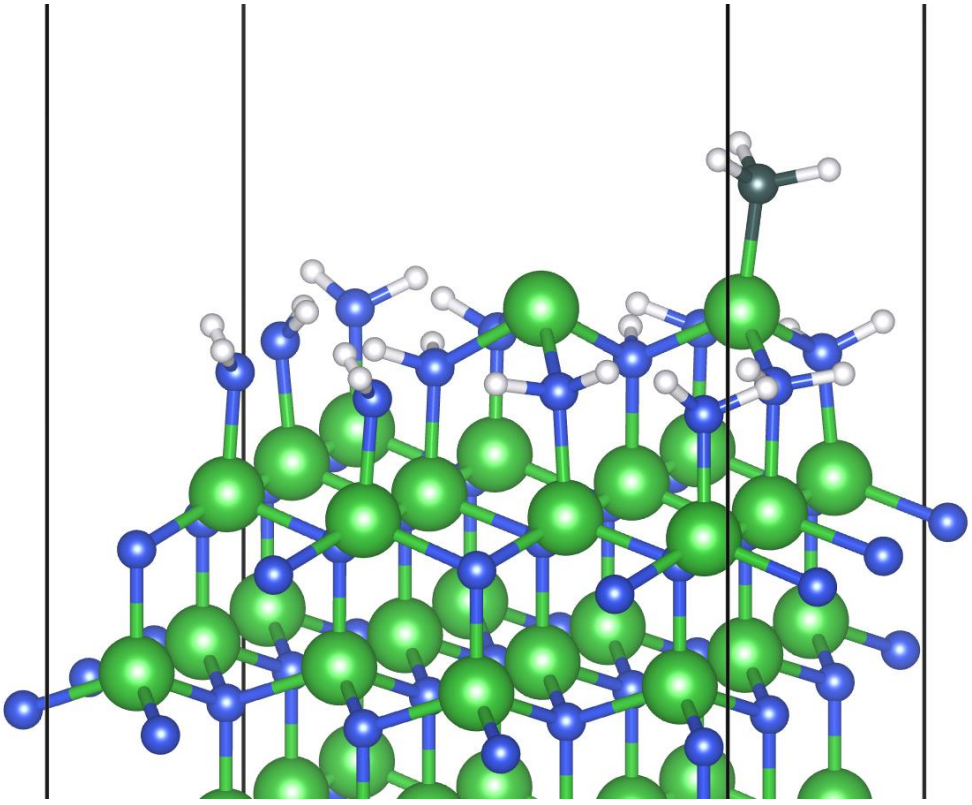

Figure S21. Bridging aluminum adatom between two adduct amino groups and one deprotonated amino group (**F$_7$**) with neighboring MMA fragment.