Electronic Supplementary Material (ESI) for Environmental Science: Nano.

Morphological Sensitivity of Silver Nanoparticles to Environment

[Electronic Supplementary Information]

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System	Environment	Contamination	Temperature	Pressure	Calculation Type	Content
Ag147ico	vacuum	-	0 K	0 atm	Geometry optimization	Section 4.1
Ag147cubo	vacuum	-	0 K	0 atm	Geometry optimization	Section 4.1
Ag147ino	vacuum	-	0 K	0 atm	Geometry optimization	Section 4.1
Ag147sito	vacuum	-	0 K	0 atm	Geometry optimization	Section 4.1
Ag201rto	vacuum	-	0 K	0 atm	Geometry optimization	Section 4.1
Ag147ico	vacuum	-	300 K	0 atm	AIMD simulation	Section 4.1
Ag147ino	vacuum	-	300 K	0 atm	AIMD simulation	Section 4.1
Ag147sito	vacuum	-	300 K	0 atm	AIMD simulation	Section 4.1
Ag201rto	vacuum	-	300 K	0 atm	AIMD simulation	Section 4.1
Ag147ico	vacuum	-	600 K	0 atm	AIMD simulation	Section 4.1
Ag147ino	vacuum	-	600 K	0 atm	AIMD simulation	Section 4.1
Ag147sito	vacuum	-	600 K	0 atm	AIMD simulation	Section 4.1
Ag201rto	vacuum	-	600 K	0 atm	AIMD simulation	Section 4.1
Ag147ico	monoadsorption	methanethiol	0 K	0 atm	Geometry optimization	Section 4.2
Ag147sito	monoadsorption	methanethiol	0 K	0 atm	Geometry optimization	Section 4.2
Ag201rto	monoadsorption	methanethiol	0 K	0 atm	Geometry optimization	Section 4.2
Ag147ico	coadsorption	methanethiol	0 K	0 atm	Geometry optimization	Section 4.2
Ag147sito	coadsorption	methanethiol	0 K	0 atm	Geometry optimization	Section 4.2
Ag201rto	coadsorption	methanethiol	0 K	0 atm	Geometry optimization	Section 4.2
Gaseous N_2	gas	dinitrogen	0 K	5 atm	Geometry optimization	Section 4.2
Gaseous N_2	gas	dinitrogen	300 K	5 atm	AIMD simulation	Section 4.2
Gaseous N_2	gas	dinitrogen	0 K	5 atm	Quenching	Section 4.2
Ag147ico	gas + coadsorption	methanethiol	0 K	5 atm	Geometry optimization	Section 4.2
Ag147sito	gas + coadsorption	methanethiol	0 K	5 atm	Geometry optimization	Section 4.2
Ag201rto	gas + coadsorption	methanethiol	0 K	5 atm	Geometry optimization	Section 4.2
Ag147ico	gas + coadsorption	methanethiol	300 K	5 atm	AIMD simulation	Section 4.3
Ag147sito	gas + coadsorption	methanethiol	300 K	5 atm	AIMD simulation	Section 4.3
Ag201rto	gas + coadsorption	methanethiol	300 K	5 atm	AIMD simulation	Section 4.3
Ag147ico	gas + coadsorption	methanethiol	0 K	5 atm	Multiple quenchings	Section 4.3
Ag147sito	gas + coadsorption	methanethiol	0 K	5 atm	Multiple quenchings	Section 4.3
Ag201rto	gas + coadsorption	methanethiol	0 K	5 atm	Multiple quenchings	Section 4.3
Ag147ico	coadsorption	methanethiol	0 K	0 atm	Multiple quenchings	Section 4.3
Ag147sito	coadsorption	methanethiol	0 K	0 atm	Multiple quenchings	Section 4.3
Ag201rto	coadsorption	methanethiol	0 K	0 atm	Multiple quenchings	Section 4.3

Table S1. Summary of all the considered systems and computational conditions for exploring the environment effects on Ag NPs.

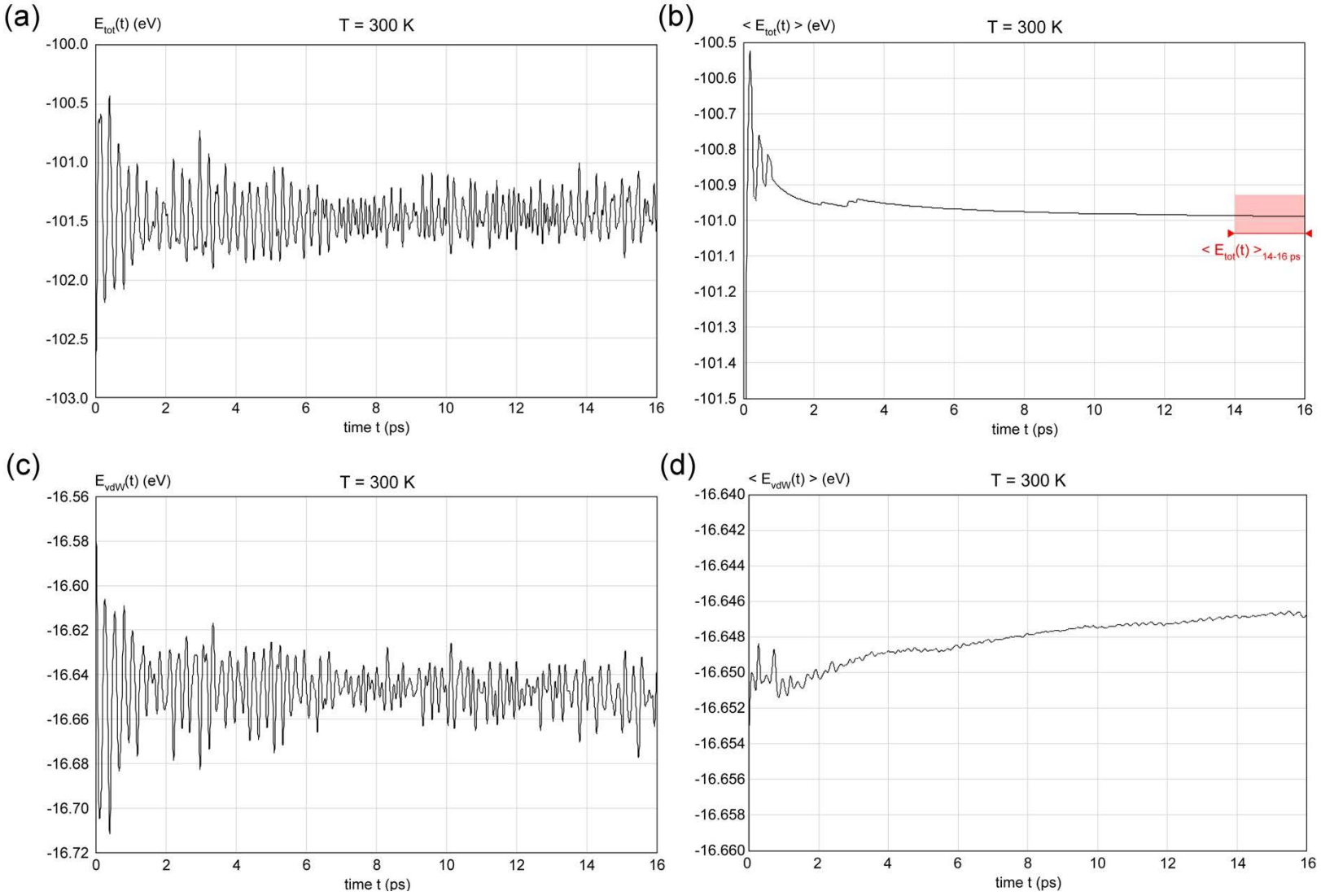

Figure S1. **[Ag Bulk]** AIMD simulation at 300 K of Ag bulk modeled by a 3D box containing 32 atoms: (a) total electronic energy E_{tot} (eV) plotted against time (t) in ps; (b) current average total electronic energy $< E_{tot} >$ (eV) against time (averaged value over the last 2 ps for determining the stability); (c) total van der Waals dispersion energy E_{vdW} (eV) against time; (d) current average total van der Waals dispersion energy $< E_{vdW} >$ (eV) against time.

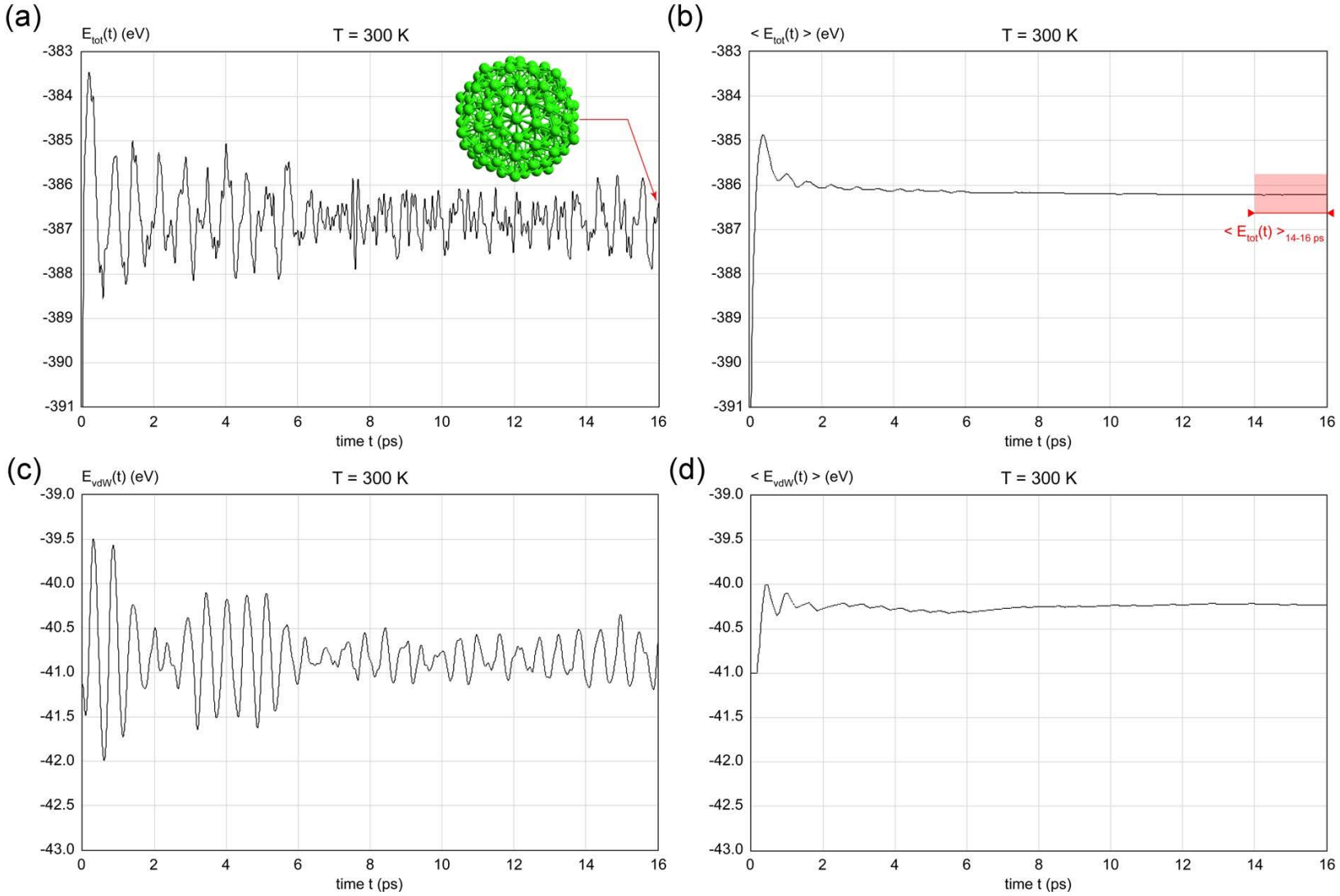

Figure S2. **[Ag147ico]** AIMD simulation at 300 K of Ag147ico nanocluster in vacuum: (a) total electronic energy E_{tot} (eV) plotted against time (t) in ps (a snapshot corresponding to the Ag147ico structure at the end of the MD trajectory is reported); (b) current average total electronic energy $< E_{tot} >$ (eV) against time (averaged value over the last 2 ps for determining the stability); (c) total van der Waals dispersion energy E_{vdW} (eV) against time; (d) current average total van der Waals dispersion energy $< E_{vdW} >$ (eV) against time.

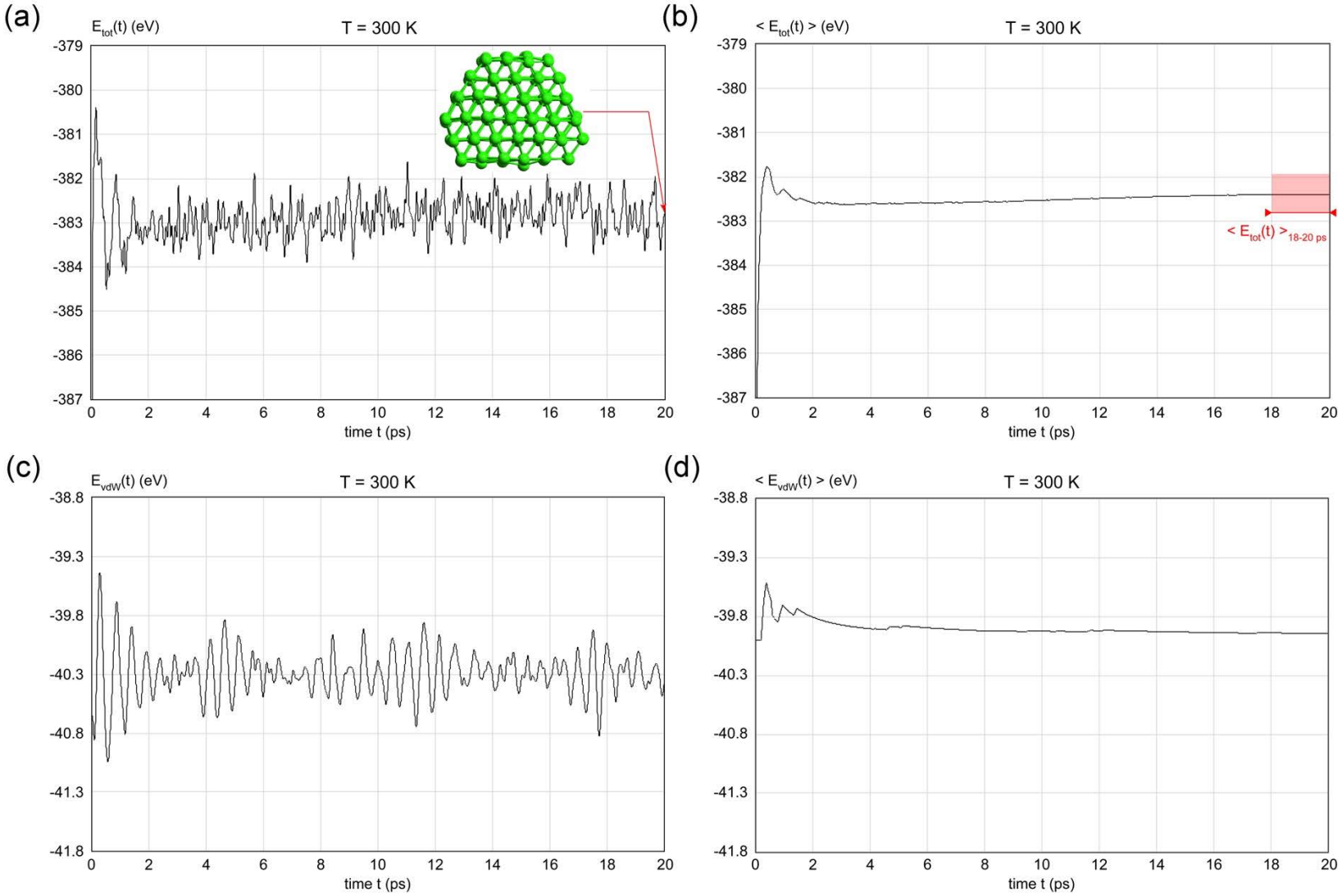

Figure S3. **[Ag147sito]** AIMD simulation at 300 K of Ag147sito nanocluster in vacuum: (a) total electronic energy E_{tot} (eV) plotted against time (t) in ps (a snapshot corresponding to the Ag147sito structure at the end of the MD trajectory is reported); (b) current average total electronic energy $< E_{tot} >$ (eV) against time (averaged value over the last 2 ps for determining the stability); (c) total van der Waals dispersion energy E_{vdW} (eV) against time; (d) current average total van der Waals dispersion energy $< E_{vdW} >$ (eV) against time.

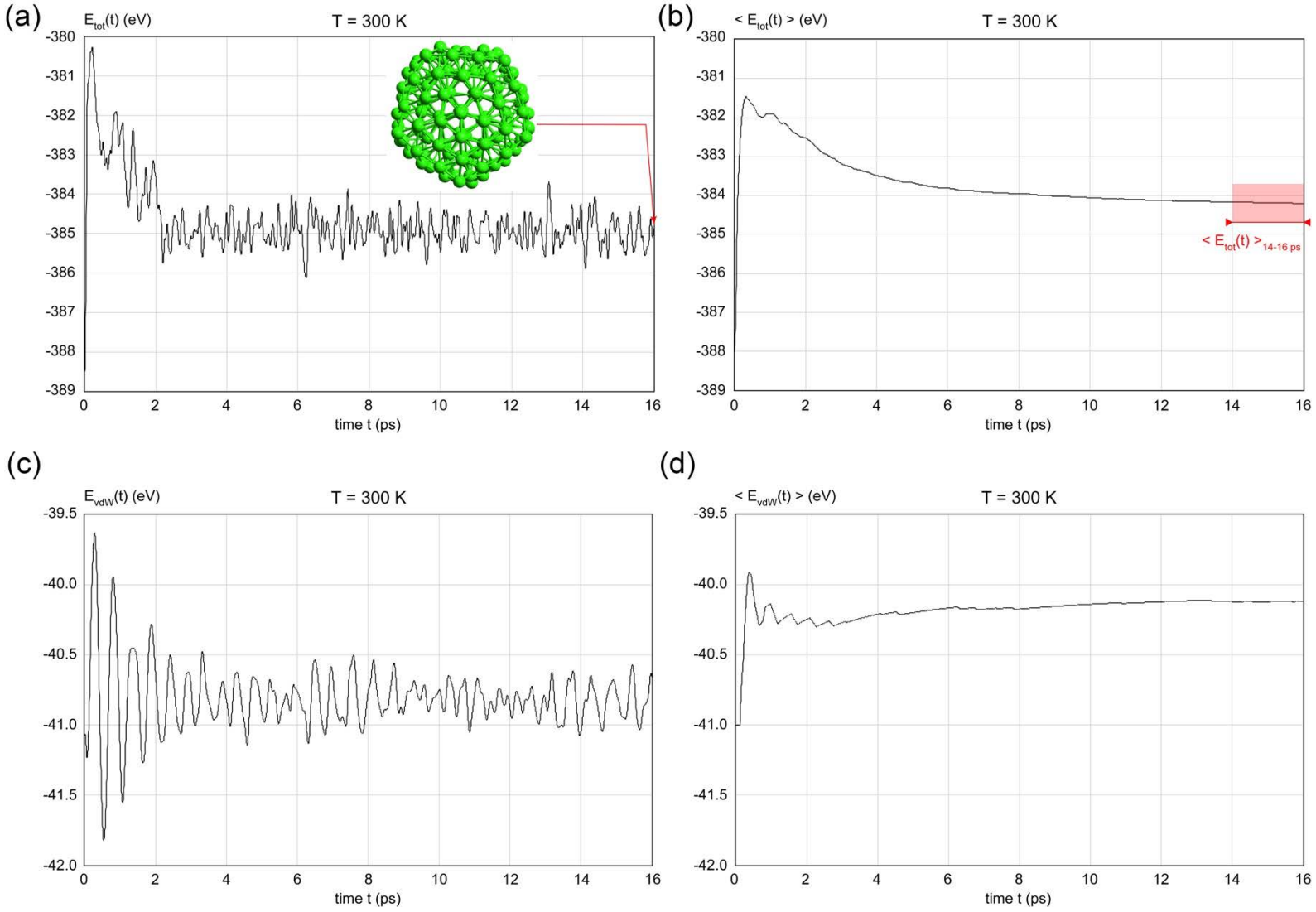

Figure S4. **[Ag147ino]** AIMD simulation at 300 K of Ag147ino nanocluster in vacuum: (a) total electronic energy E_{tot} (eV) plotted against time (t) in ps (a snapshot corresponding to the structure at the end of the MD trajectory is reported); (b) current average total electronic energy $< E_{tot} >$ (eV) against time (averaged value over the last 2 ps for determining the stability); (c) total van der Waals dispersion energy E_{vdW} (eV) against time; (d) current average total van der Waals dispersion energy $< E_{vdW} >$ (eV) against time.

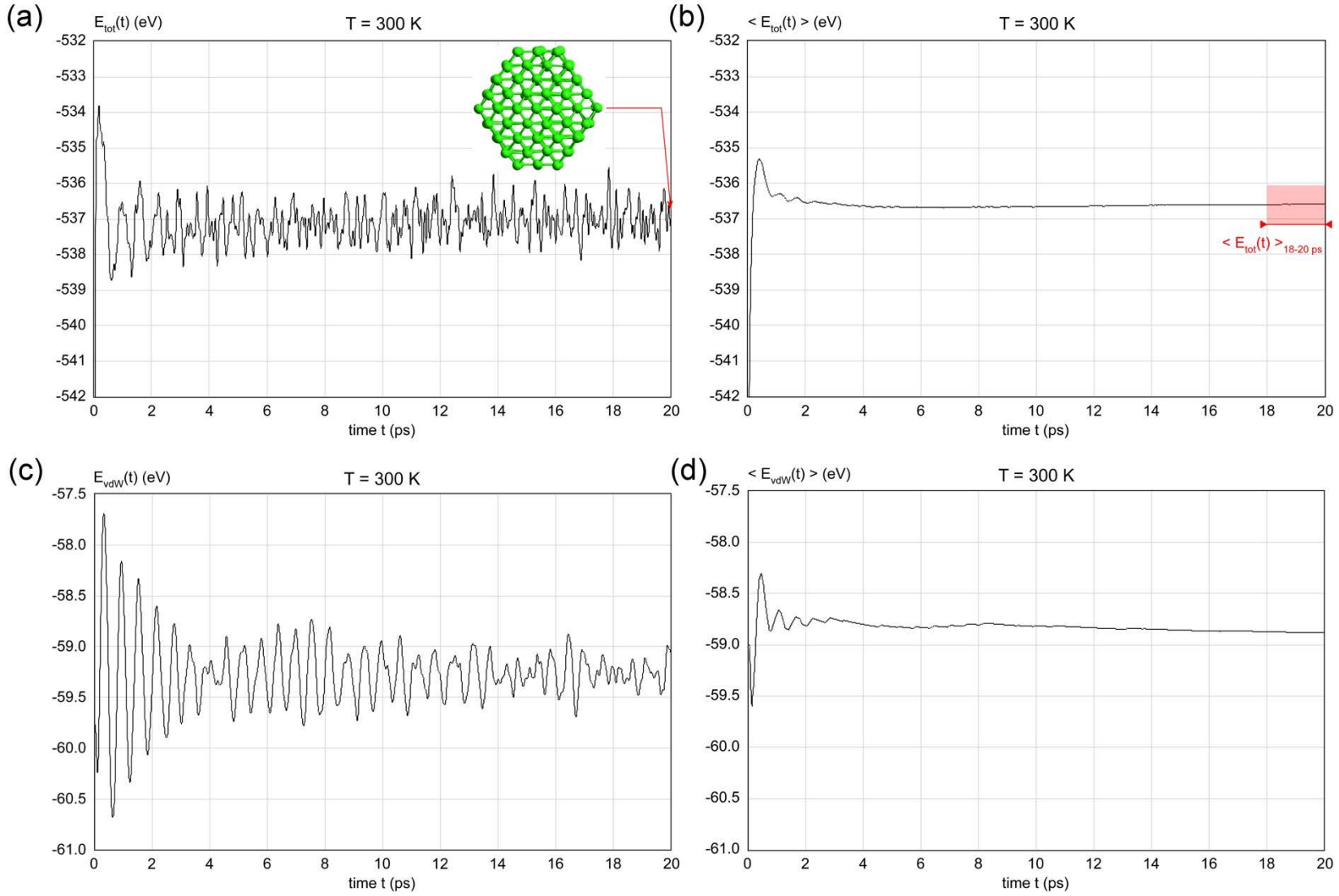

Figure S5. **[Ag201rto]** AIMD simulation at 300 K of Ag201rto nanocluster in vacuum: (a) total electronic energy E_{tot} (eV) plotted against time (t) in ps (a snapshot corresponding to the Ag201rto structure at the end of the MD trajectory is reported); (b) current average total electronic energy $< E_{tot} >$ (eV) against time (averaged value over the last 2 ps for determining the stability); (c) total van der Waals dispersion energy E_{vdW} (eV) against time; (d) current average total van der Waals dispersion energy $< E_{vdW} >$ (eV) against time.

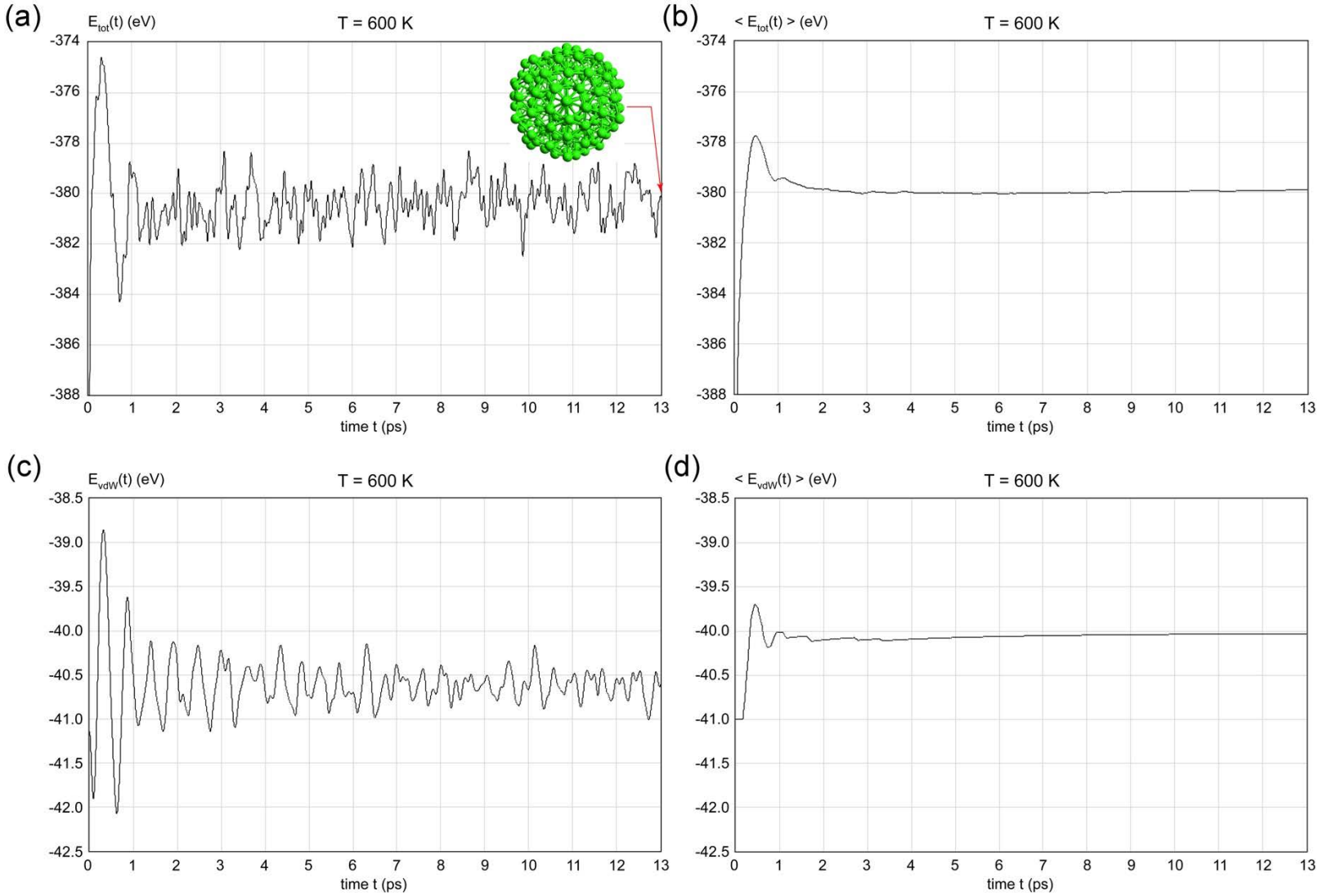

Figure S6. **[Ag147ico]** AIMD simulation at 600 K of Ag147ico nanocluster in vacuum: (a) total electronic energy E_{tot} (eV) plotted against time (t) in ps (a snapshot corresponding to the Ag147ico structure at the end of the MD trajectory is reported); (b) current average total electronic energy $< E_{tot} >$ (eV) against time; (c) total van der Waals dispersion energy E_{vdW} (eV) against time; (d) current average total van der Waals dispersion energy $< E_{vdW} >$ (eV) against time.

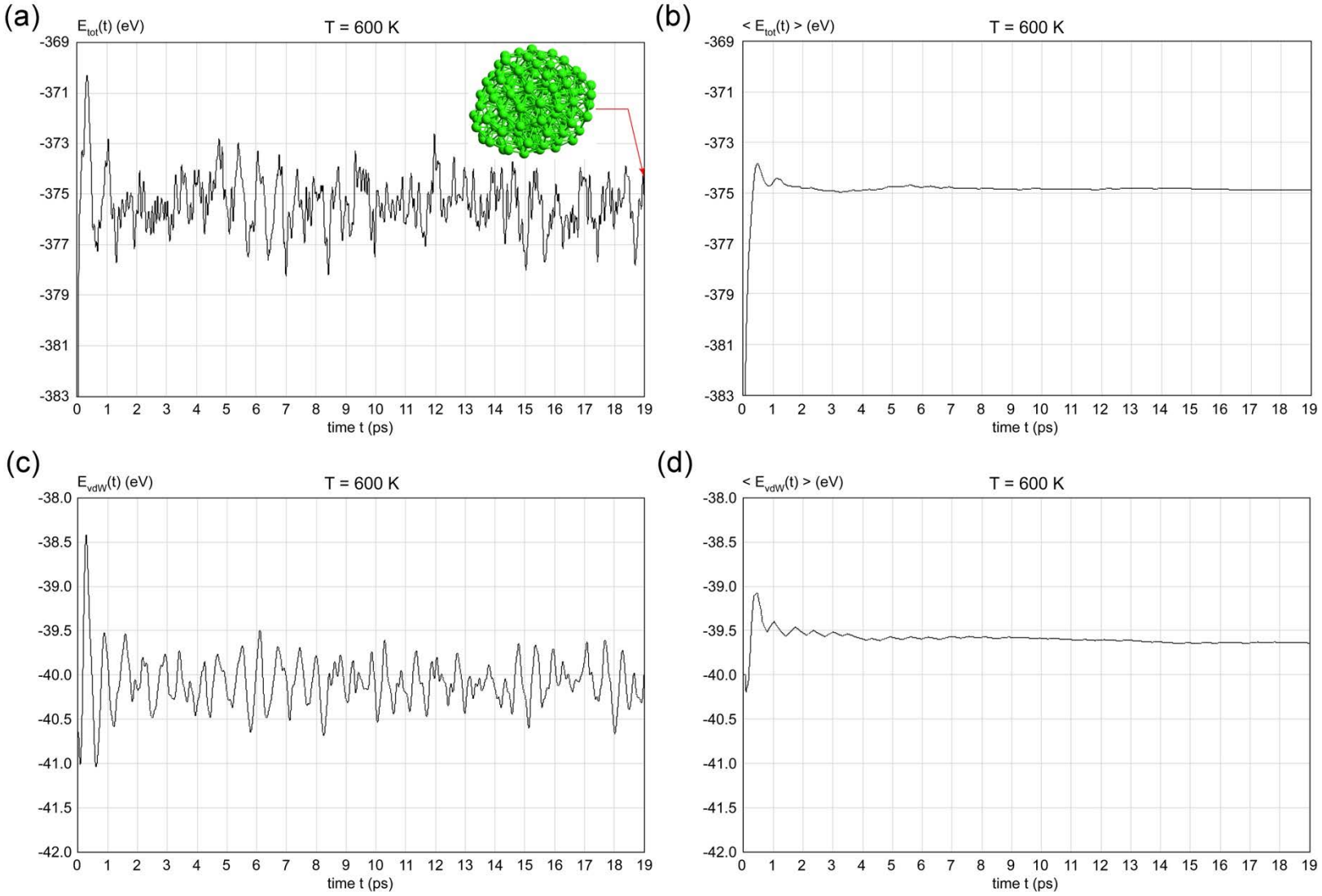

Figure S7. **[Ag147sito]** AIMD simulation at 600 K of Ag147sito nanocluster in vacuum: (a) total electronic energy E_{tot} (eV) plotted against time (t) in ps (a snapshot corresponding to the structure at the end of the MD trajectory is reported); (b) current average total electronic energy $< E_{tot} >$ (eV) against time; (c) total van der Waals dispersion energy E_{vdW} (eV) against time; (d) current average total van der Waals dispersion energy $< E_{vdW} >$ (eV) against time.

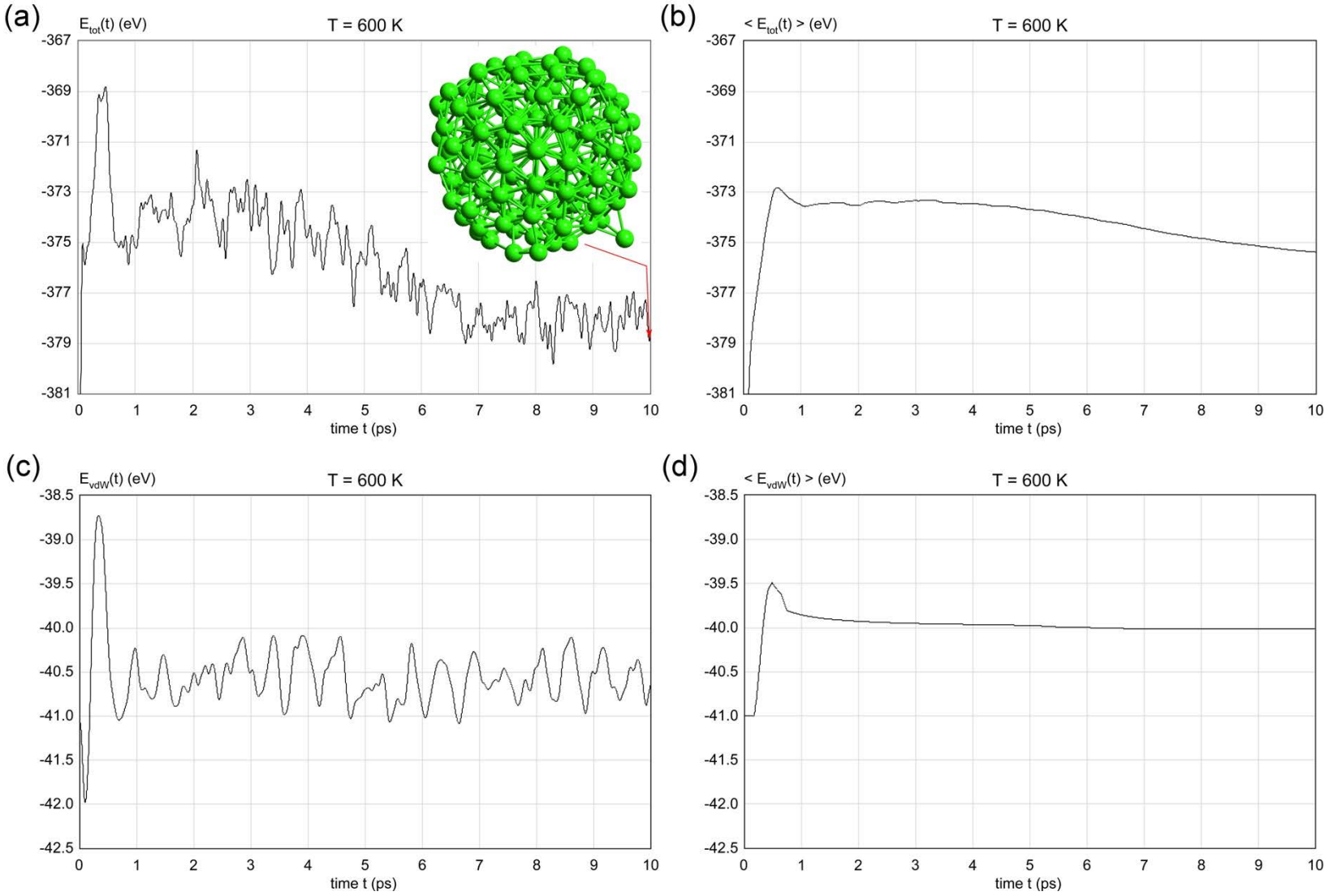

Figure S8. **[Ag147ino]** AIMD simulation at 600 K of Ag147ino nanocluster in vacuum: (a) total electronic energy E_{tot} (eV) plotted against time (t) in ps (a snapshot corresponding to the structure at the end of the MD trajectory is reported); (b) current average total electronic energy $< E_{tot} >$ (eV) against time; (c) total van der Waals dispersion energy E_{vdW} (eV) against time; (d) current average total van der Waals dispersion energy $< E_{vdW} >$ (eV) against time.

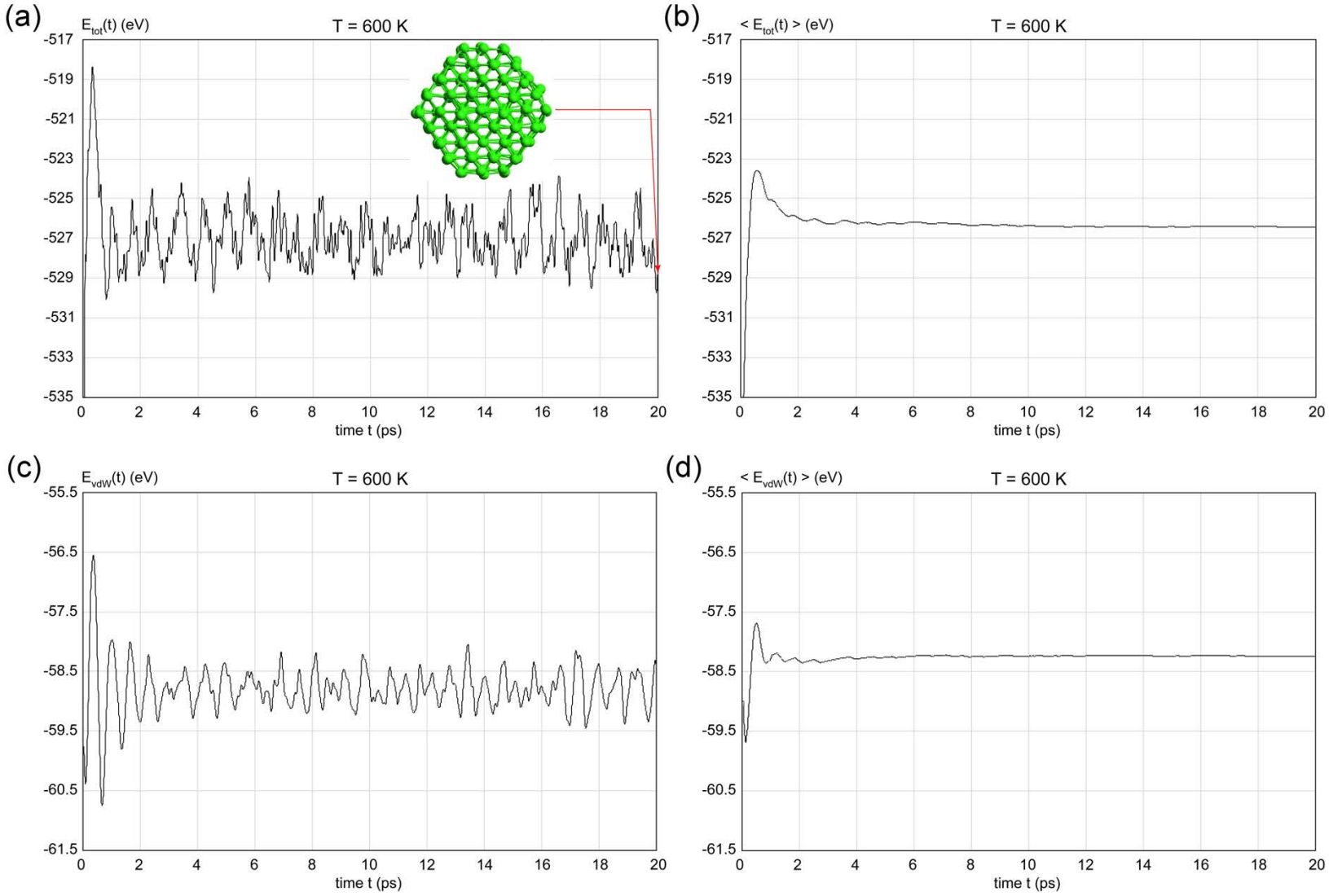

Figure S9. **[Ag201rto]** AIMD simulation at 600 K of Ag201rto nanocluster in vacuum: (a) total electronic energy E_{tot} (eV) plotted against time (t) in ps (a snapshot corresponding to the Ag201rto structure at the end of the MD trajectory is reported); (b) current average total electronic energy $< E_{tot} >$ (eV) against time; (c) total van der Waals dispersion energy E_{vdW} (eV) against time; (d) current average total van der Waals dispersion energy $< E_{vdW} >$ (eV) against time.

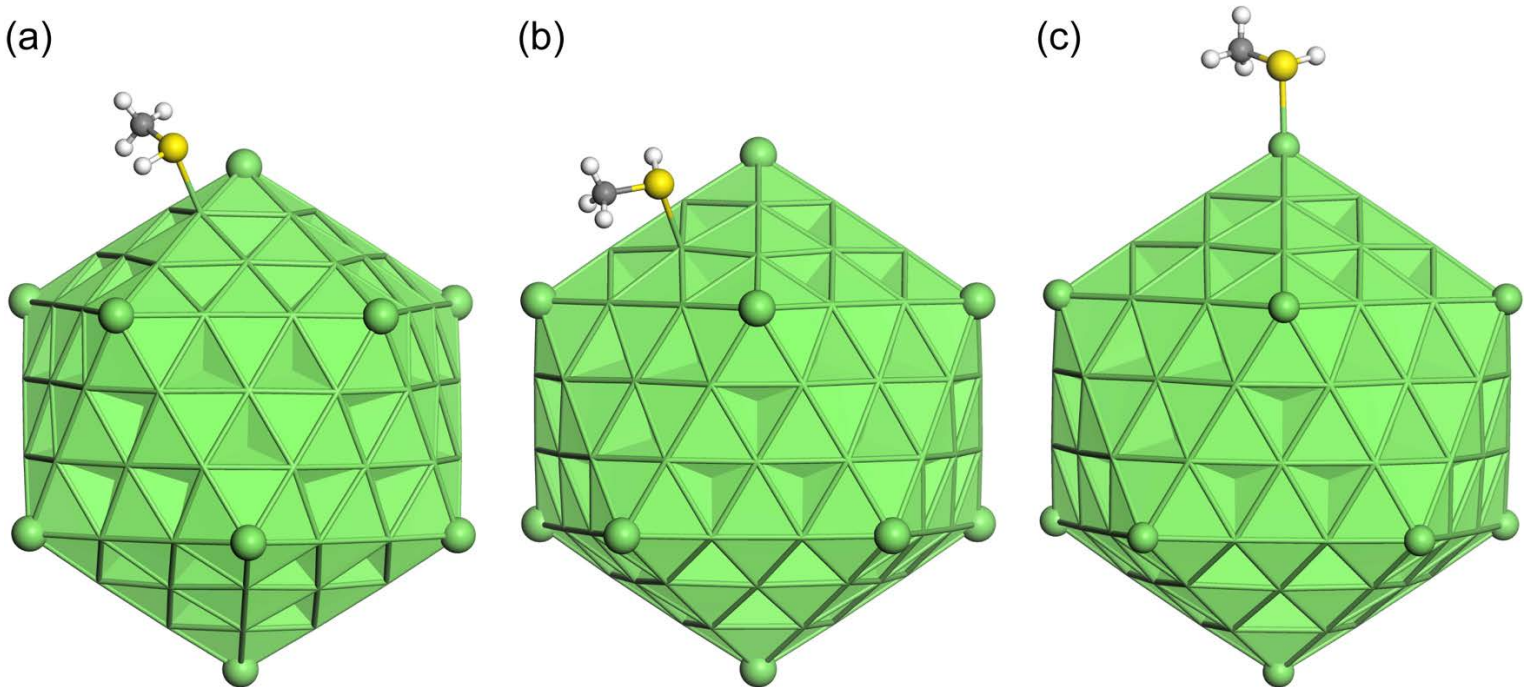

Figure S10. **[Ag147ico]** Monoadsorption of one methanethiol molecule on the Ag147ico nanocluster in vacuum at various adsorption sites: optimized structures on (a) edge, (b) (111) facet, (c) vertex (see Table 1 of article for adsorption energies). The color labels are green for Ag, yellow for S, gray for C and white for H atoms.

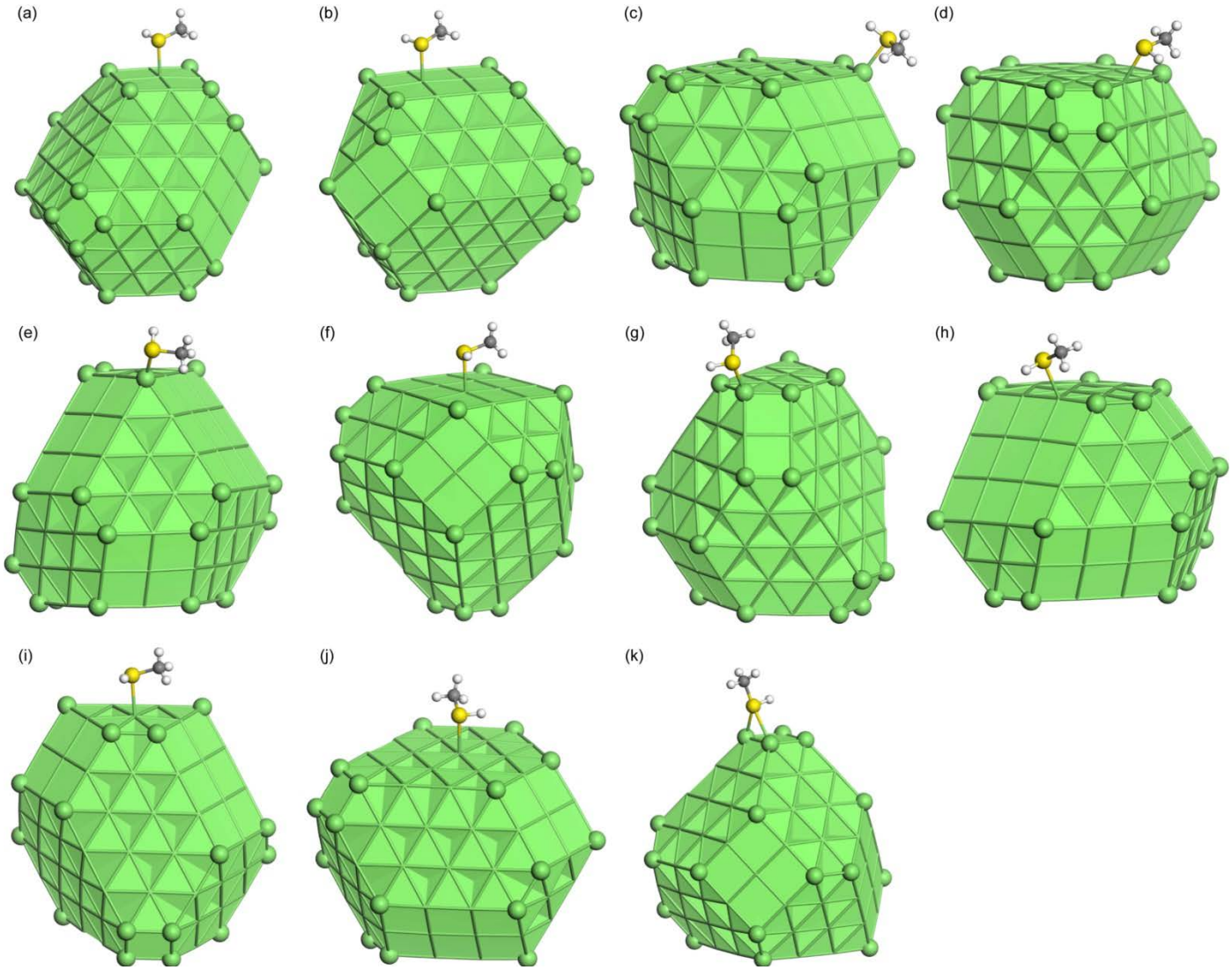

Figure S11. **[Ag147sito]** Monoadsorption of one methanethiol molecule on the Ag147sito nanocluster in vacuum at various adsorption sites: optimized structures on (a) (100) facet of 9 atoms, (b) (100) facet of 12 atoms, (c) vertex (neighbor of 1 vertex), (d) edge (111|111), (e) vertex, (f) (100) facet of 16 atoms, (g) vertex (neighbor of 2 vertices), (h) edge (111|100), (i) (111) facet of 9 atoms, (j) (111) facet of 21 atoms, (k) bridge position (see Table 1 of article for adsorption energies). The color labels are green for Ag, yellow for S, gray for C and white for H atoms.

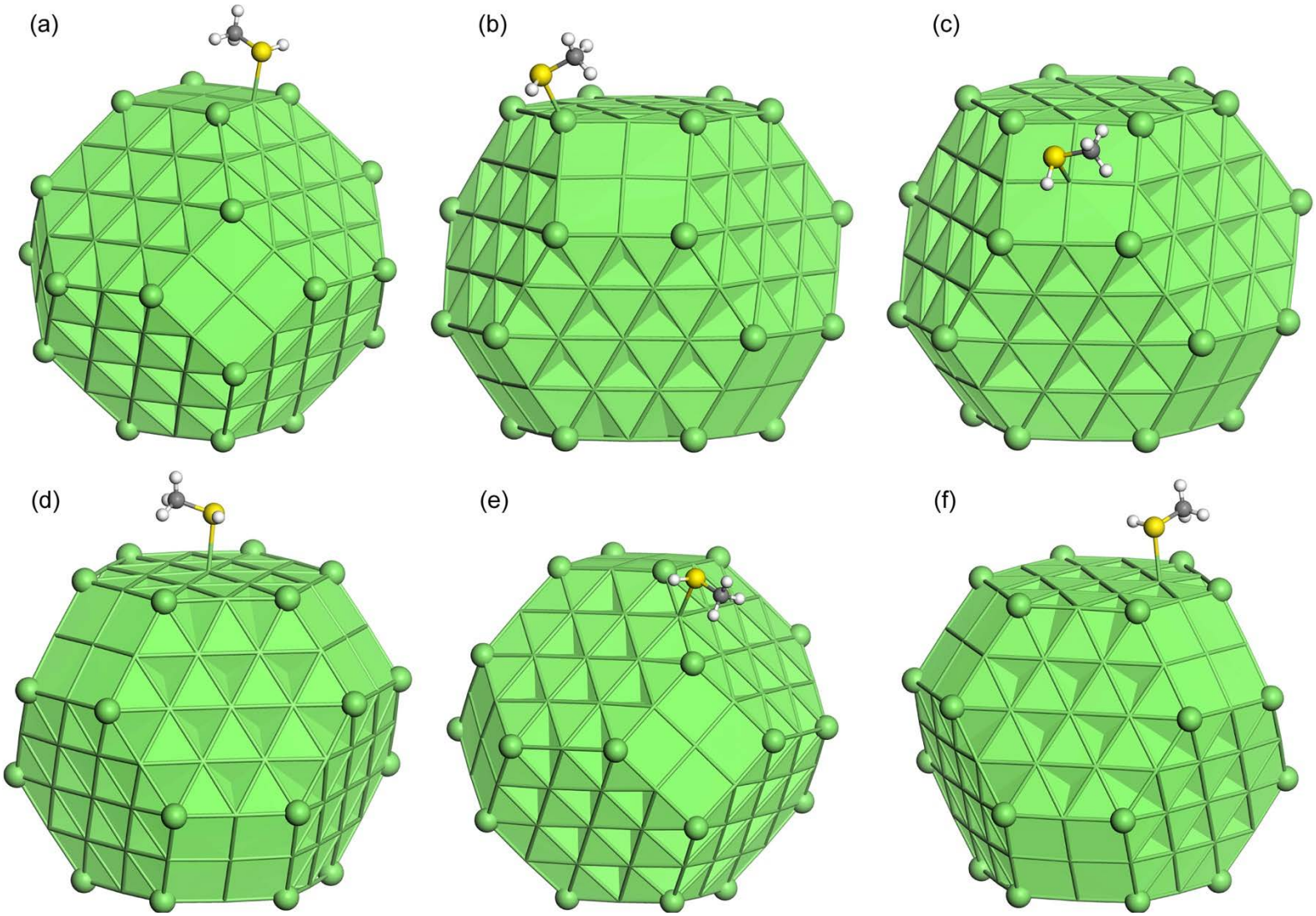

Figure S12. **[Ag201rto]** Monoadsorption of one methanethiol molecule on the Ag201rto nanocluster in vacuum at various adsorption sites: optimized structures on (a) edge (111|100), (b) vertex, (c) (100) facet, (d) (111) facet (center), (e) edge (111|111), (f) (111) facet (middle layer) (see Table 1 of article for adsorption energies). The color labels are green for Ag, yellow for S, gray for C and white for H atoms.

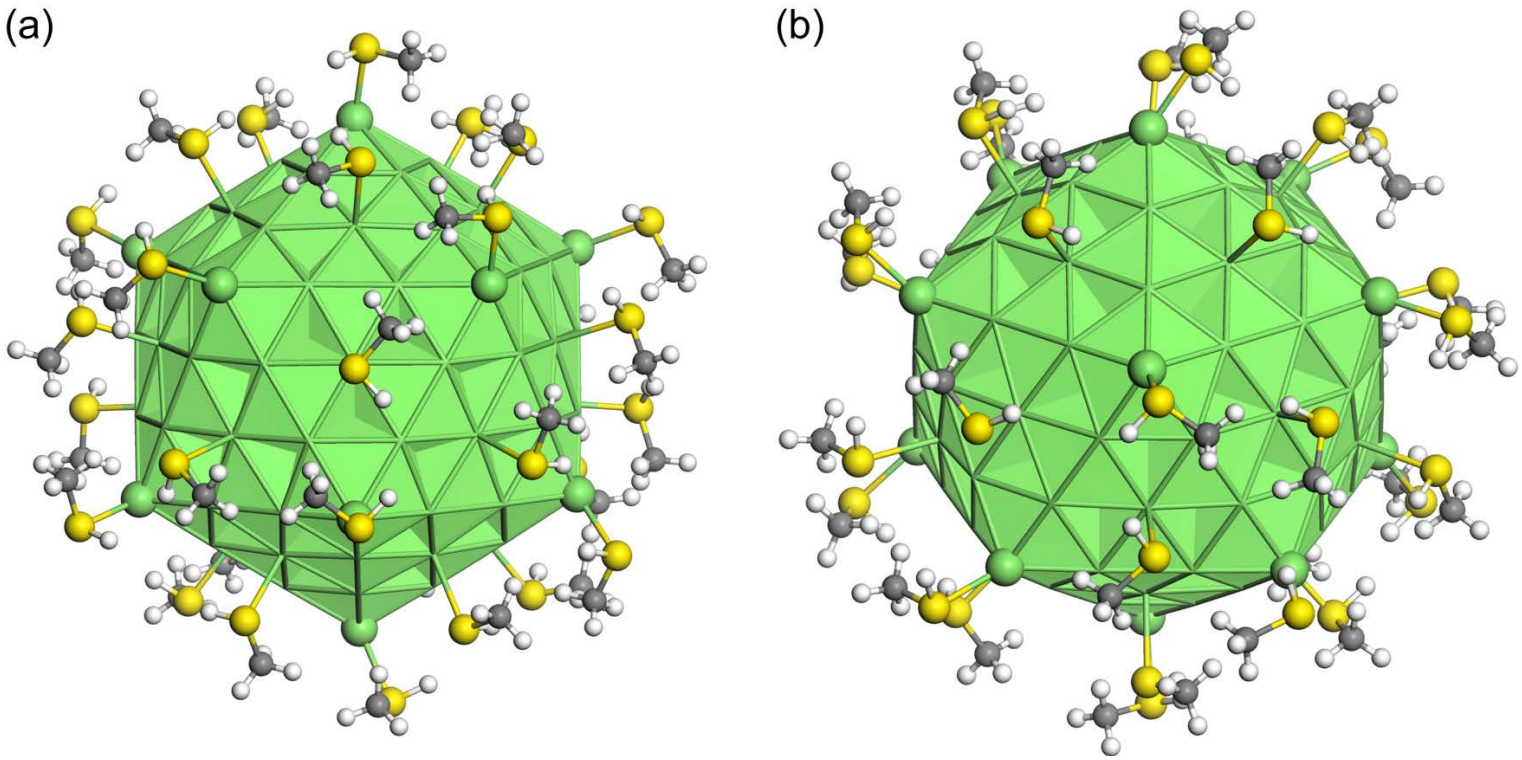

Figure S13. **[Ag147ico]** A shell of 32 methanethiol molecules (coadsorption 1) on the Ag147ico nanocluster in vacuum: (a) lateral and (b) top views of the optimized structure (see Table 2 of article for more details about molecule surface density, coverage and energetics). The color labels are green for Ag, yellow for S, gray for C and white for H atoms.

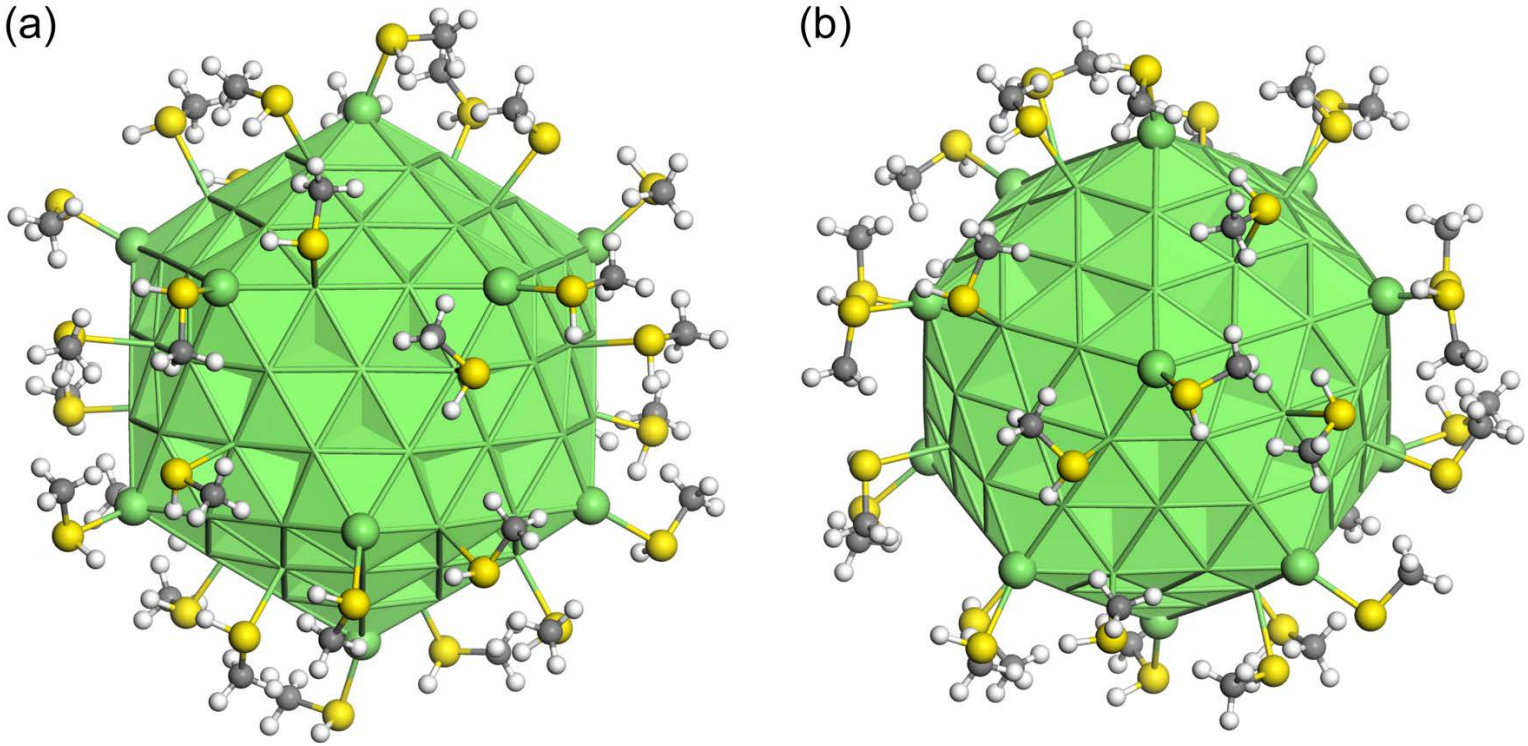

Figure S14. **[Ag147ico]** A shell of 32 methanethiol molecules (coadsorption 2) on the Ag147ico nanocluster in vacuum: (a) lateral and (b) top views of the optimized structure (see Table 2 of article for more details about molecule surface density, coverage and energetics). The color labels are green for Ag, yellow for S, gray for C and white for H atoms.

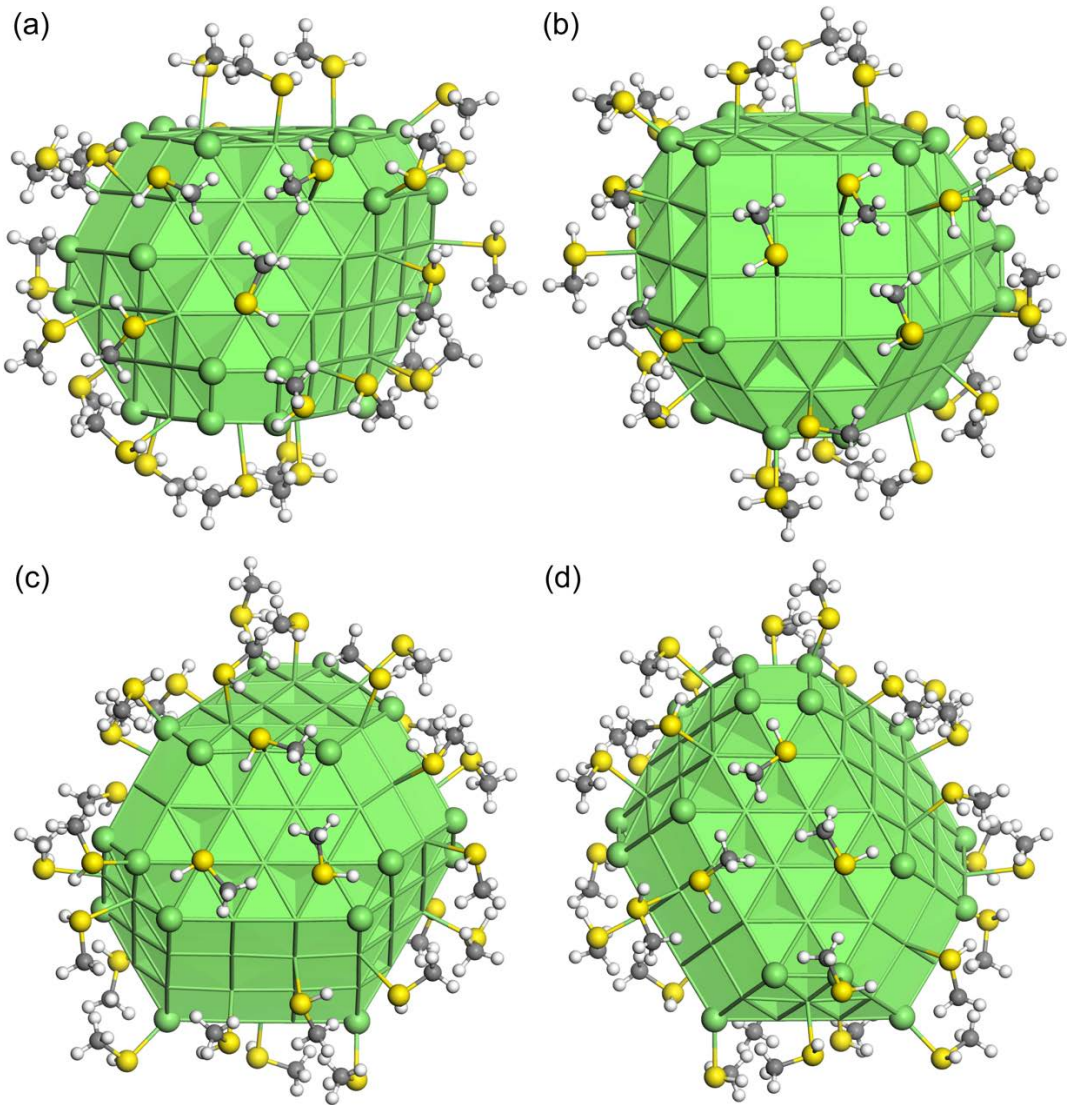

Figure S15. **[Ag147sito]** A shell of 32 methanethiol molecules on the Ag147sito nanocluster in vacuum: (a-d) several views of the optimized structure (see Table 2 of article for more details about molecule surface density, coverage and energetics). The color labels are green for Ag, yellow for S, gray for C and white for H atoms.

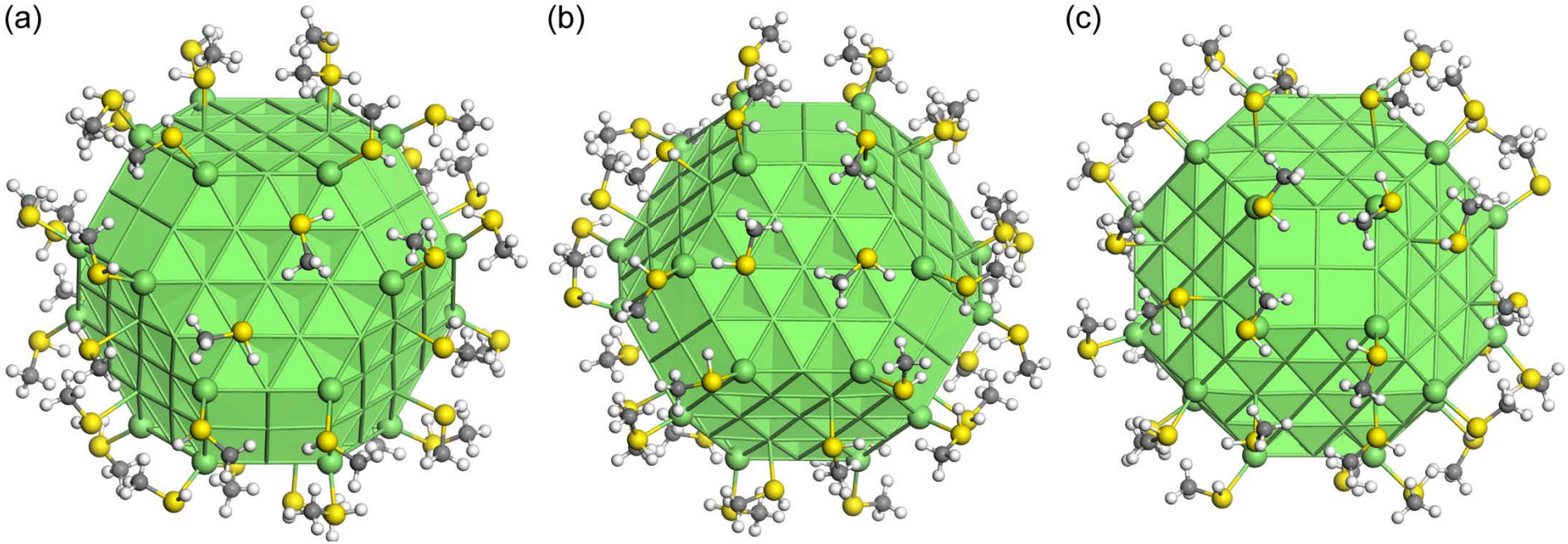

Figure S16. **[Ag201rto]** A shell of 40 methanethiol molecules (coadsorption 1) on the Ag201rto nanocluster in vacuum: (a-c) several views of the optimized structure (see Table 2 of article for more details about molecule surface density, coverage and energetics). The color labels are green for Ag, yellow for S, gray for C and white for H atoms.

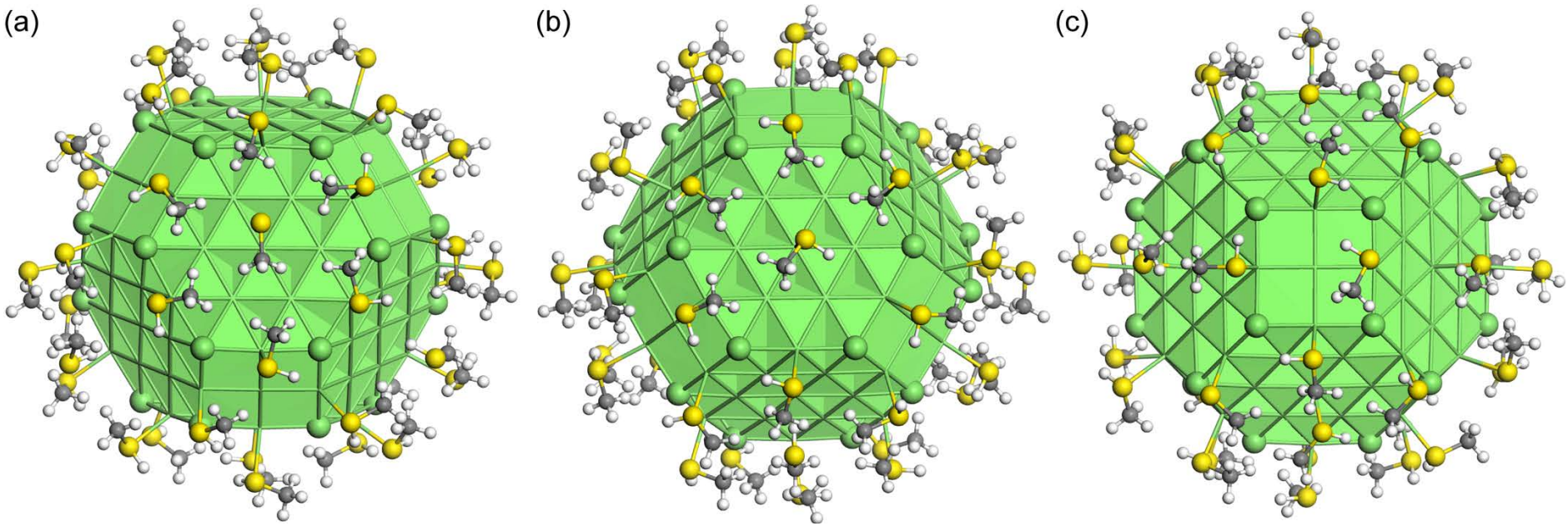

Figure S17. **[Ag201rto]** A shell of 44 methanethiol molecules (coadsorption 2) on the Ag201rto nanocluster in vacuum: (a-c) several top views of the optimized structure (see Table 2 of article for more details about molecule surface density, coverage and energetics). The color labels are green for Ag, yellow for S, gray for C and white for H atoms.

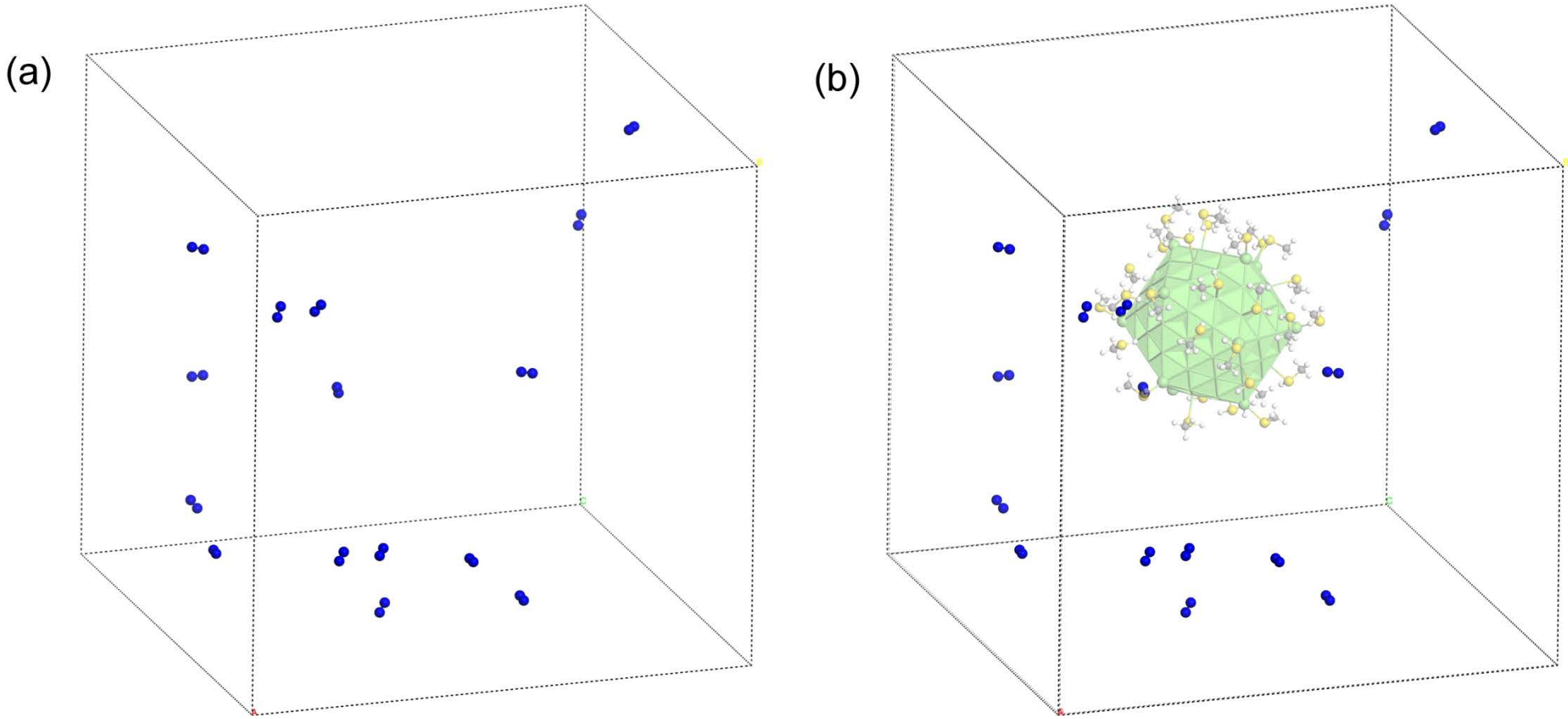

Figure S18. **[N_2 gas]** Atmospheric pressure modeled by equilibrating a pure N_2 gas at 300 K in a 3D box of 125 nm^3, corresponding to a pressure of 5 atm (i.e. 15 N_2 molecules): (a) optimized structure obtained after extraction from the AIMD simulation (see Figure S19) and quenching at zero temperature and, (b) same structure with a Ag147ico nanocluster positioned at the center of the 3D box to show an initial configuration for immersing the cluster. The color labels are blue for N, green for Ag, yellow for S, gray for C and white for H atoms.

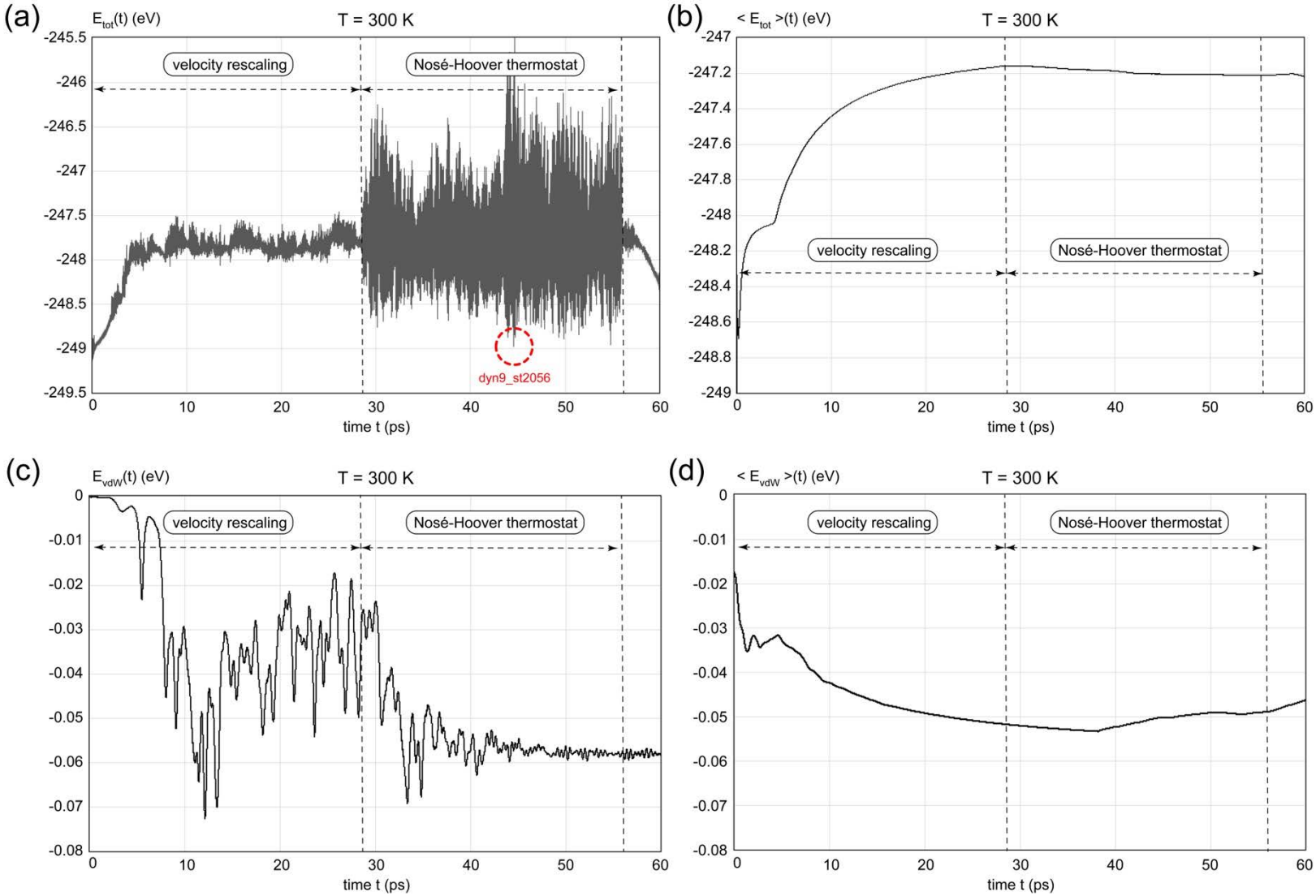

Figure S19. **[N_2 gas]** AIMD simulation (velocity rescaling and Nosé-Hoover thermostats) of a pure N_2 gas at 300 K in a 3D box of 125 nm^3 (P = 5 atm) (see Figure S18): (a) total electronic energy E_{tot} (eV) plotted against time (t) in ps (the red dotted circle marking the "dyn9_step2056" structure extracted from the trajectory to immerse Ag nanoparticles in gaseous pressure); (b) current average total electronic energy < E_{tot} > (eV) against time; (c) total van der Waals dispersion energy E_{vdW} (eV) against time; (d) current average total van der Waals dispersion energy < E_{vdW} > (eV) against time.

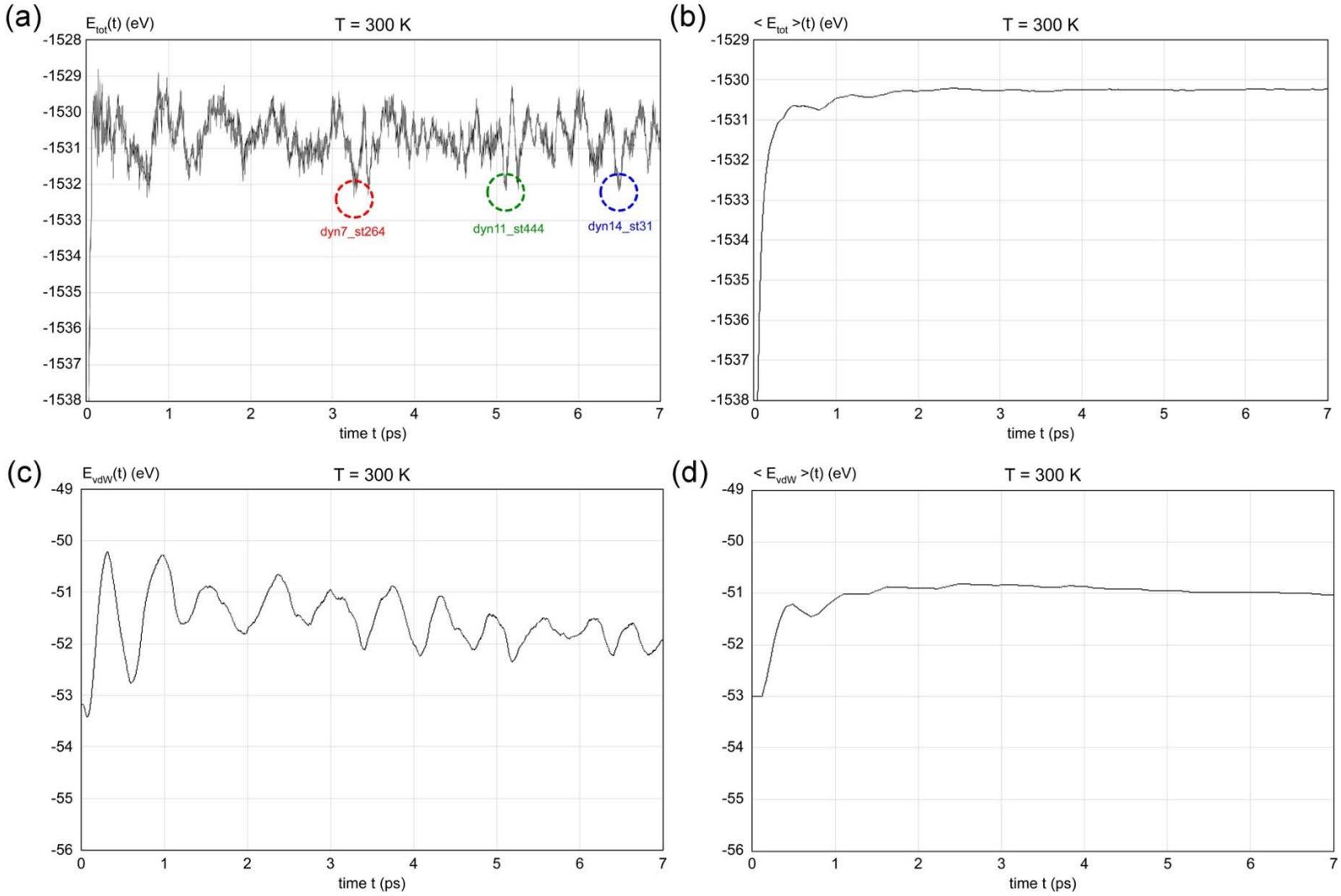

Figure S20. **[Ag147ico]** AIMD simulation at 300 K of Ag147ico nanocluster covered by a shell of 32 methanethiol contaminants (coadsorption 1) and immersed in 5 atm of N_2: (a) total electronic energy E_{tot} (eV) plotted against time (t) in ps (the red, green and blue dotted circles marking respectively the "dyn7_step264", "dyn11_step444" and "dyn14_step31" structures extracted from the trajectory after thermalization step); (b) current average total electronic energy $< E_{tot} >$ (eV) against time; (c) total van der Waals dispersion energy E_{vdW} (eV) against time; (d) current average total van der Waals dispersion energy $< E_{vdW} >$ (eV) against time.

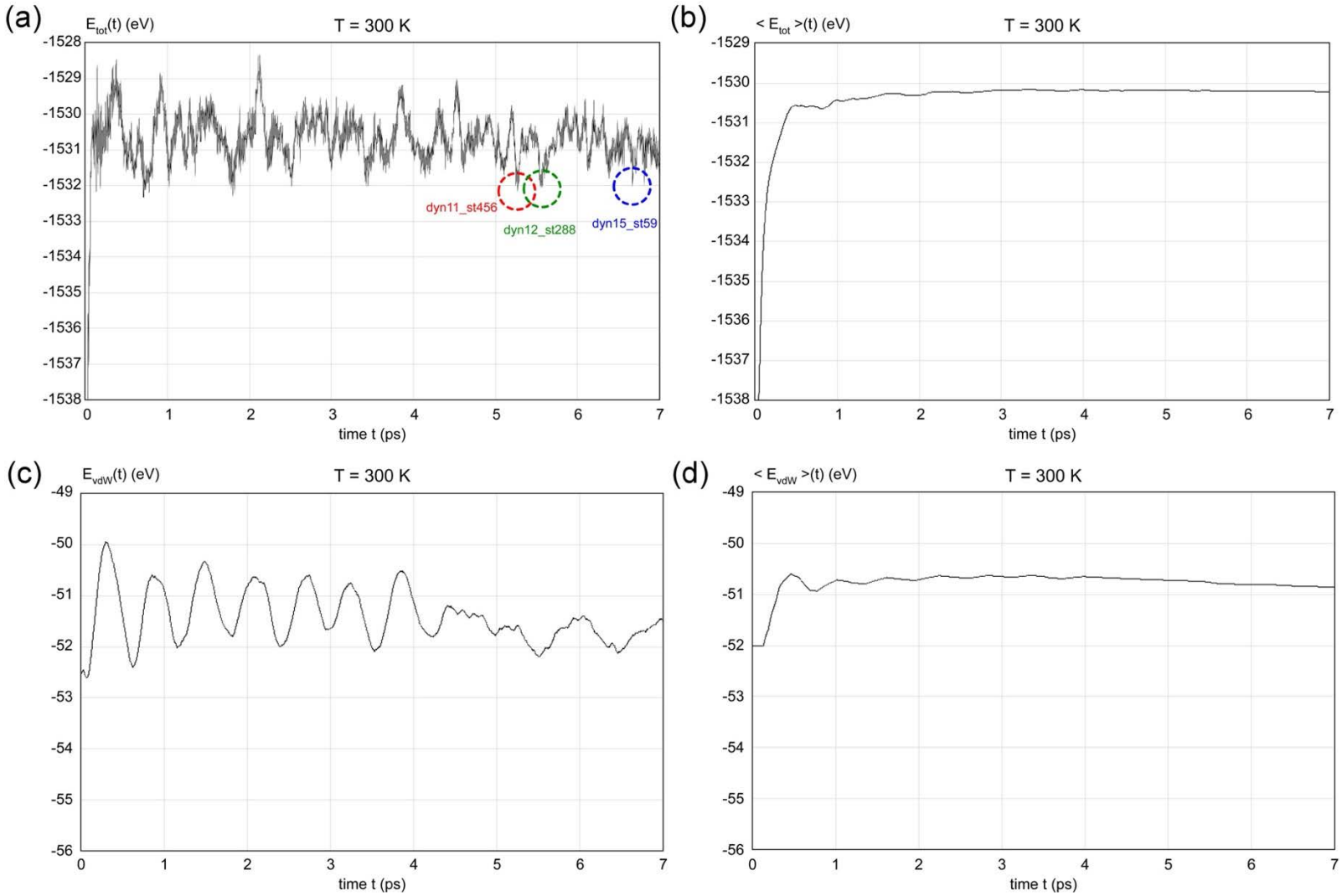

Figure S21. **[Ag147ico]** AIMD simulation at 300 K of Ag147ico nanocluster covered by a shell of 32 methanethiol contaminants (coadsorption 2) and immersed in 5 atm of N_2: (a) total electronic energy E_{tot} (eV) plotted against time (t) in ps (the red, green and blue dotted circles marking respectively the "dyn11_step456", "dyn12_step288" and "dyn15_step59" structures extracted from the trajectory after thermalization step); (b) current average total electronic energy $< E_{tot} >$ (eV) against time; (c) total van der Waals dispersion energy E_{vdW} (eV) against time; (d) current average total van der Waals dispersion energy $< E_{vdW} >$ (eV) against time.

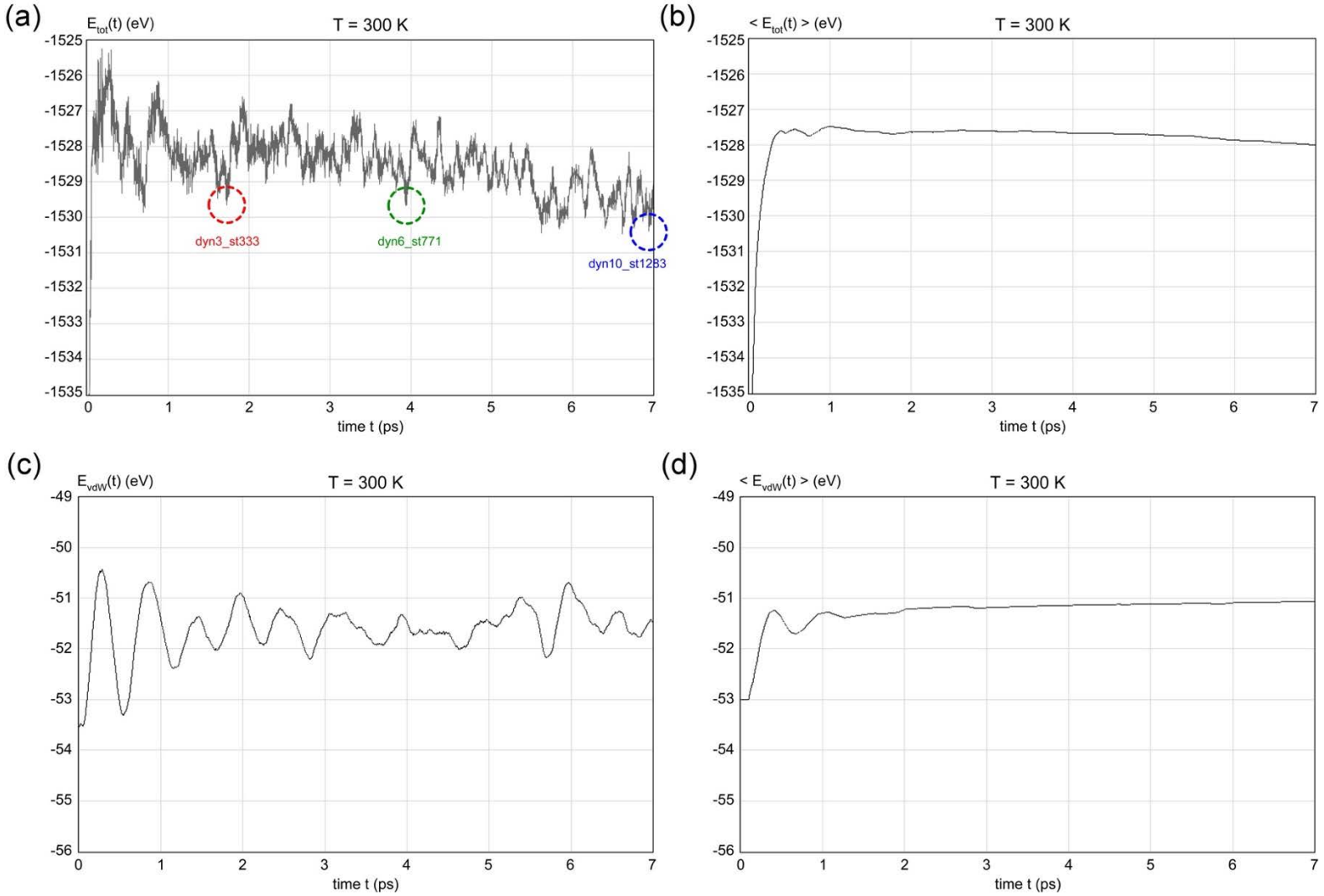

Figure S22. **[Ag147sito]** AIMD simulation at 300 K of Ag147sito nanocluster covered by a shell of 32 methanethiol contaminants and immersed in 5 atm of N_2: (a) total electronic energy E_{tot} (eV) plotted against time (t) in ps (the red, green and blue dotted circles marking respectively the "dyn3_step333", "dyn6_step771" and "dyn10_step1283" structures extracted from the trajectory after thermalization step); (b) current average total electronic energy $< E_{tot} >$ (eV) against time; (c) total van der Waals dispersion energy E_{vdW} (eV) against time; (d) current average total van der Waals dispersion energy $< E_{vdW} >$ (eV) against time.

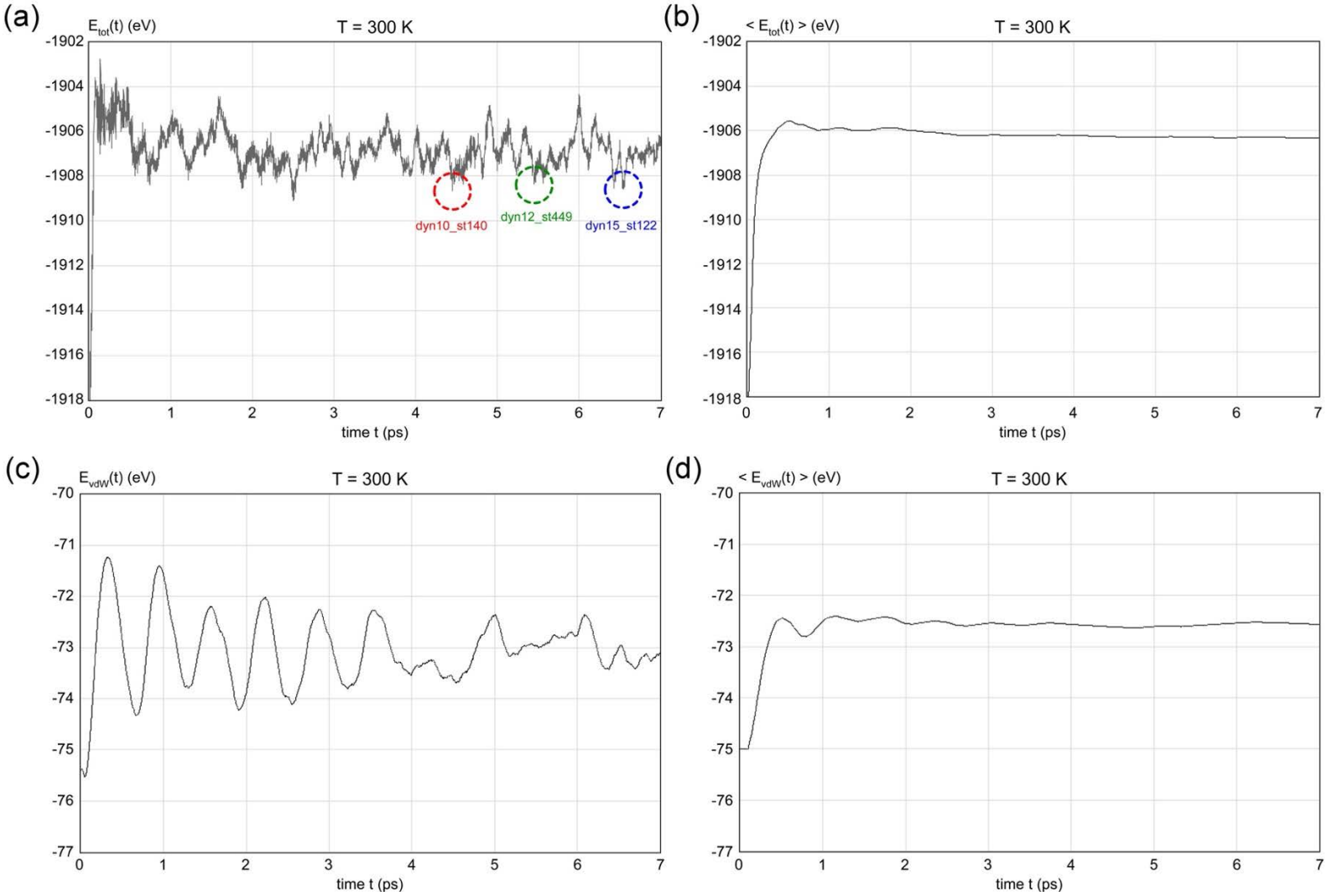

Figure S23. **[Ag201rto]** AIMD simulation at 300 K of Ag201rto nanocluster covered by a shell of 40 methanethiol contaminants (coadsorption 1) and immersed in 5 atm of N_2: (a) total electronic energy E_{tot} (eV) plotted against time (t) in ps (the red, green and blue dotted circles marking respectively the "dyn10_step140", "dyn12_step449" and "dyn15_step122" structures extracted from the trajectory after thermalization step); (b) current average total electronic energy $< E_{tot} >$ (eV) against time; (c) total van der Waals dispersion energy E_{vdW} (eV) against time; (d) current average total van der Waals dispersion energy $< E_{vdW} >$ (eV) against time.

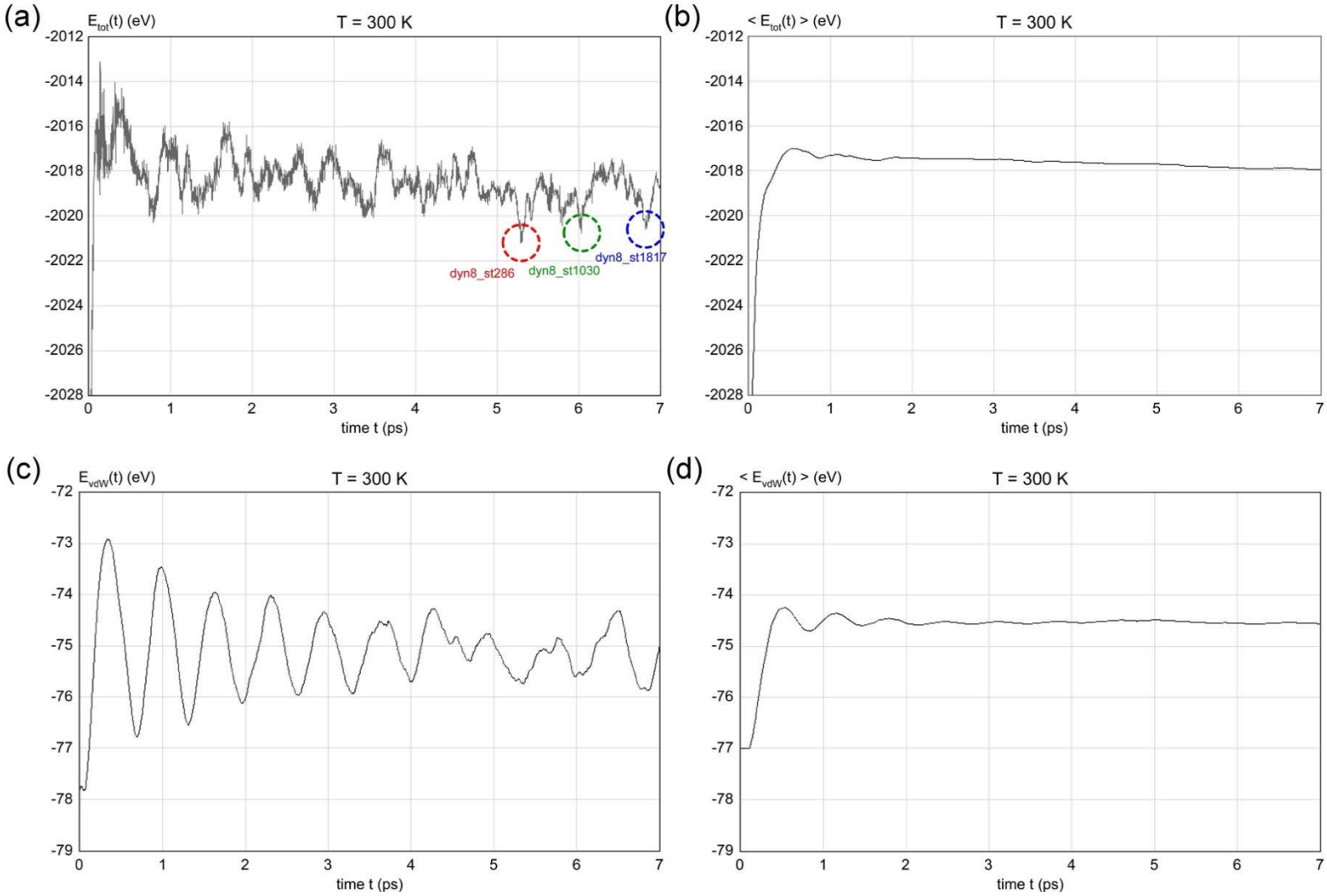

Figure S24. **[Ag201rto]** AIMD simulation at 300 K of Ag201rto nanocluster covered by a shell of 44 methanethiol contaminants (coadsorption 2) and immersed in 5 atm of N_2: (a) total electronic energy E_{tot} (eV) plotted against time (t) in ps (the red, green and blue dotted circles marking respectively the "dyn8_step286", "dyn8_step1030" and "dyn8_step1817" structures extracted from the trajectory after thermalization step); (b) current average total electronic energy $< E_{tot} >$ (eV) against time; (c) total van der Waals dispersion energy E_{vdW} (eV) against time; (d) current average total van der Waals dispersion energy $< E_{vdW} >$ (eV) against time.

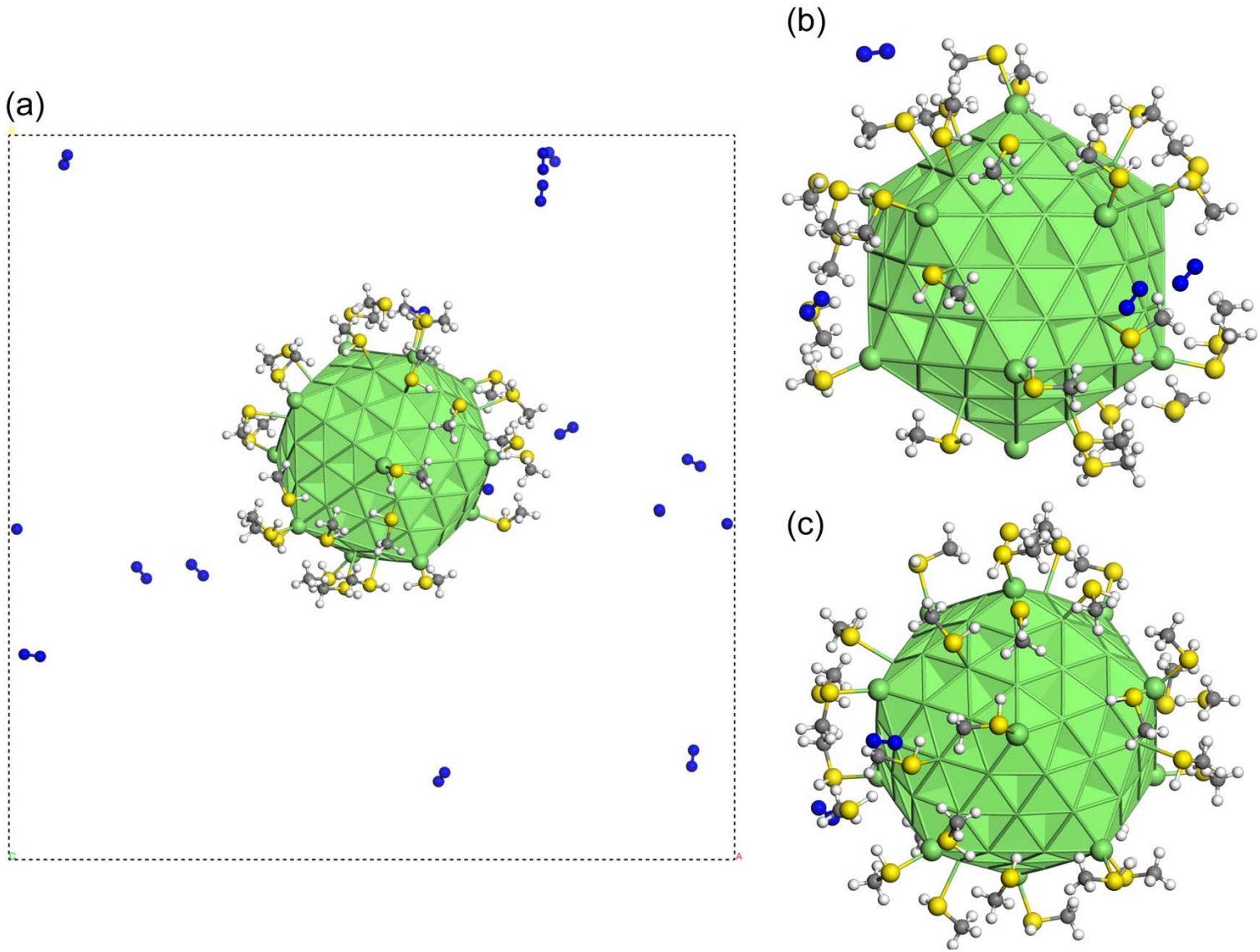

Figure S25. **[Ag147ico]** Optimized coadsorption structure "1_dyn7_step264" corresponding to a shell of 32 methanethiol molecules on the Ag147ico nanocluster in presence of N_2 gas: (a) illustration of the complete system, (b) lateral and (c) top views focused on the nanoparticle (see Table 3 of article for more details about energetics). The color labels are blue for N, green for Ag, yellow for S, gray for C and white for H atoms.

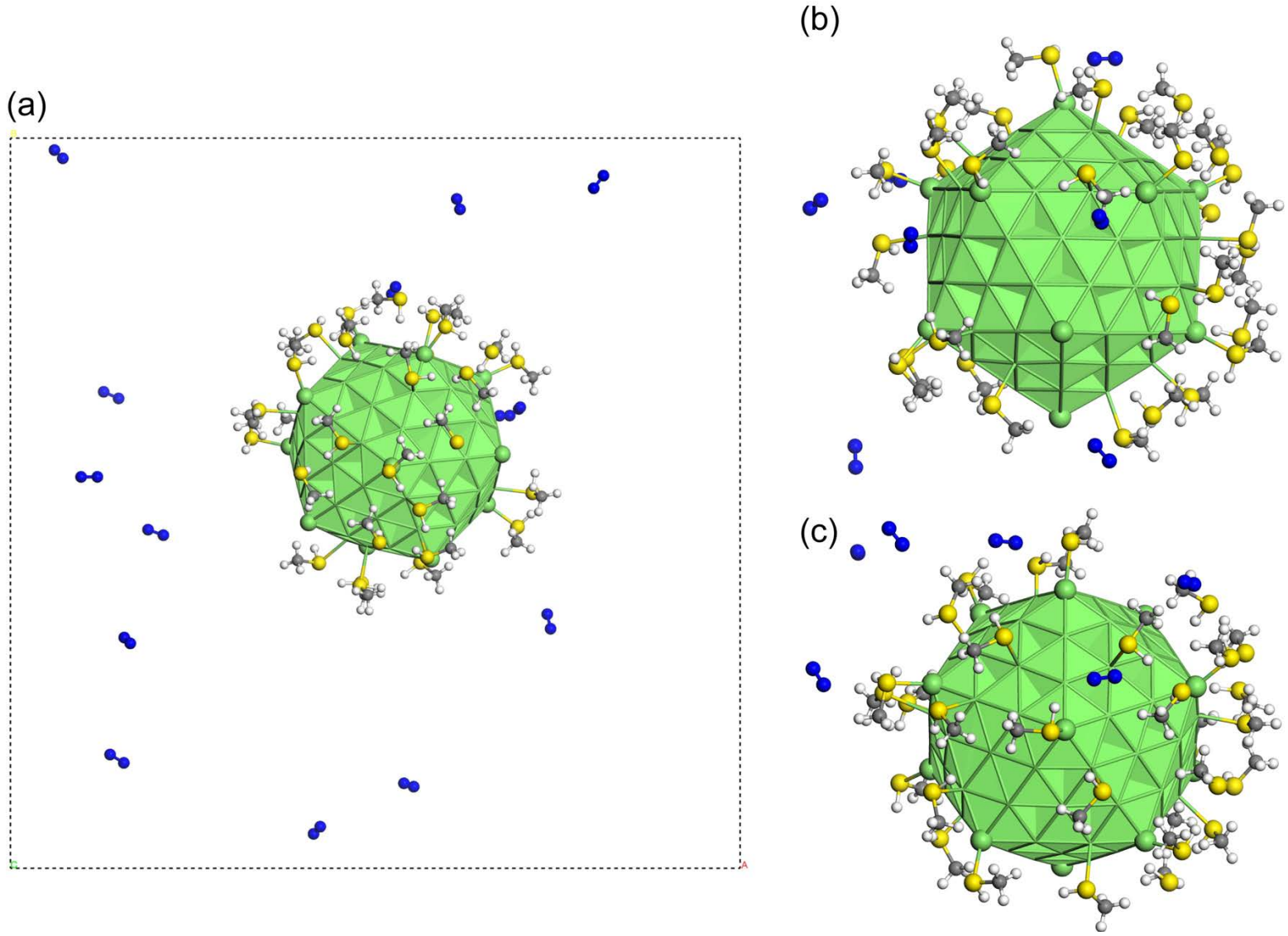

Figure S26. **[Ag147ico]** Optimized coadsorption structure "1_dyn11_step444" corresponding to a shell of 32 methanethiol molecules on the Ag147ico nanocluster in presence of N_2 gas: (a) illustration of the complete system, (b) lateral and (c) top views focused on the nanoparticle (see Table 3 of article for more details about energetics). The color labels are blue for N, green for Ag, yellow for S, gray for C and white for H atoms.

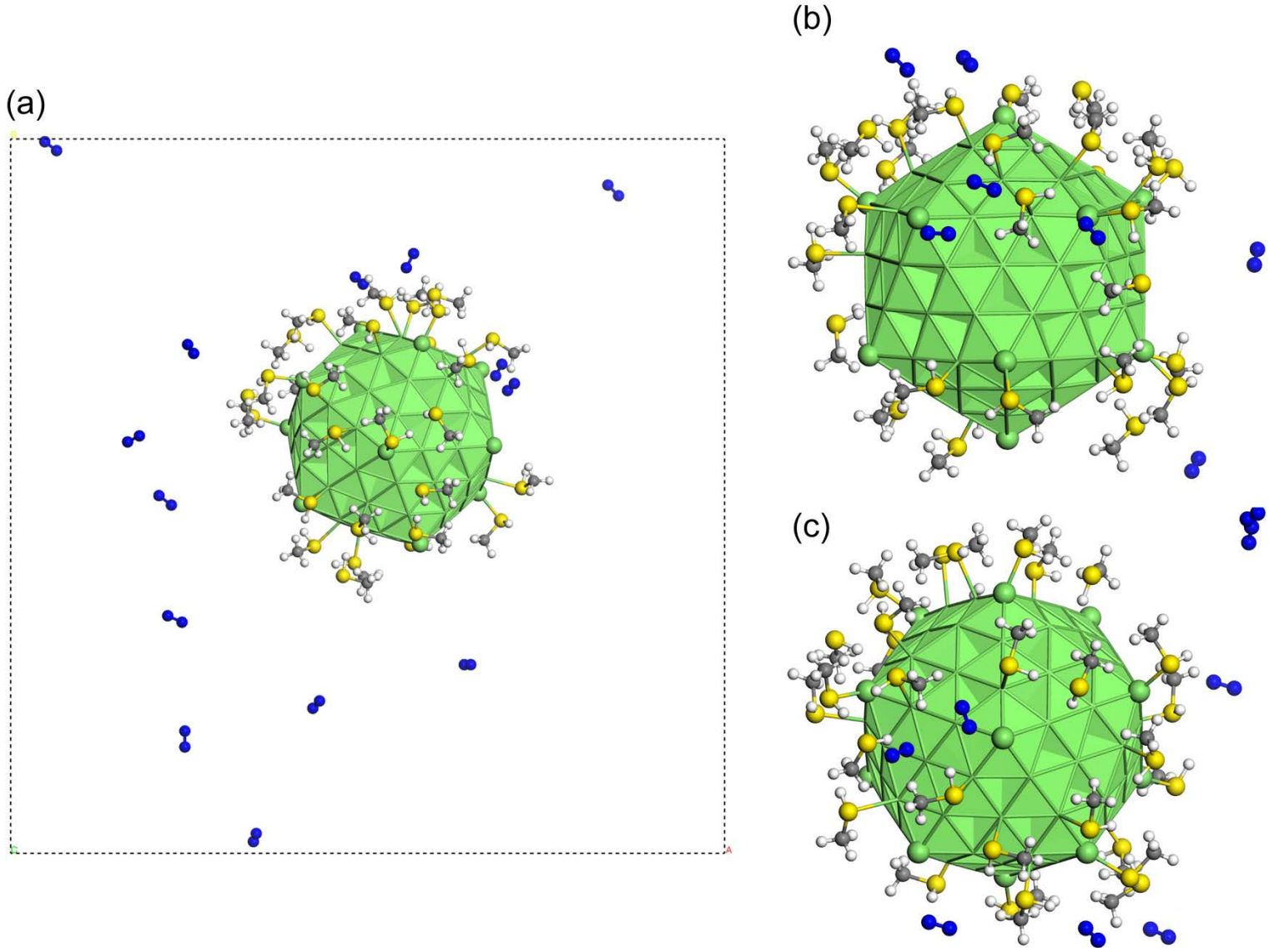

Figure S27. **[Ag147ico]** Optimized coadsorption structure "1_dyn14_step31" corresponding to a shell of 32 methanethiol molecules on the Ag147ico nanocluster in presence of N_2 gas: (a) illustration of the complete system, (b) lateral and (c) top views focused on the nanoparticle (see Table 3 of article for more details about energetics). The color labels are blue for N, green for Ag, yellow for S, gray for C and white for H atoms.

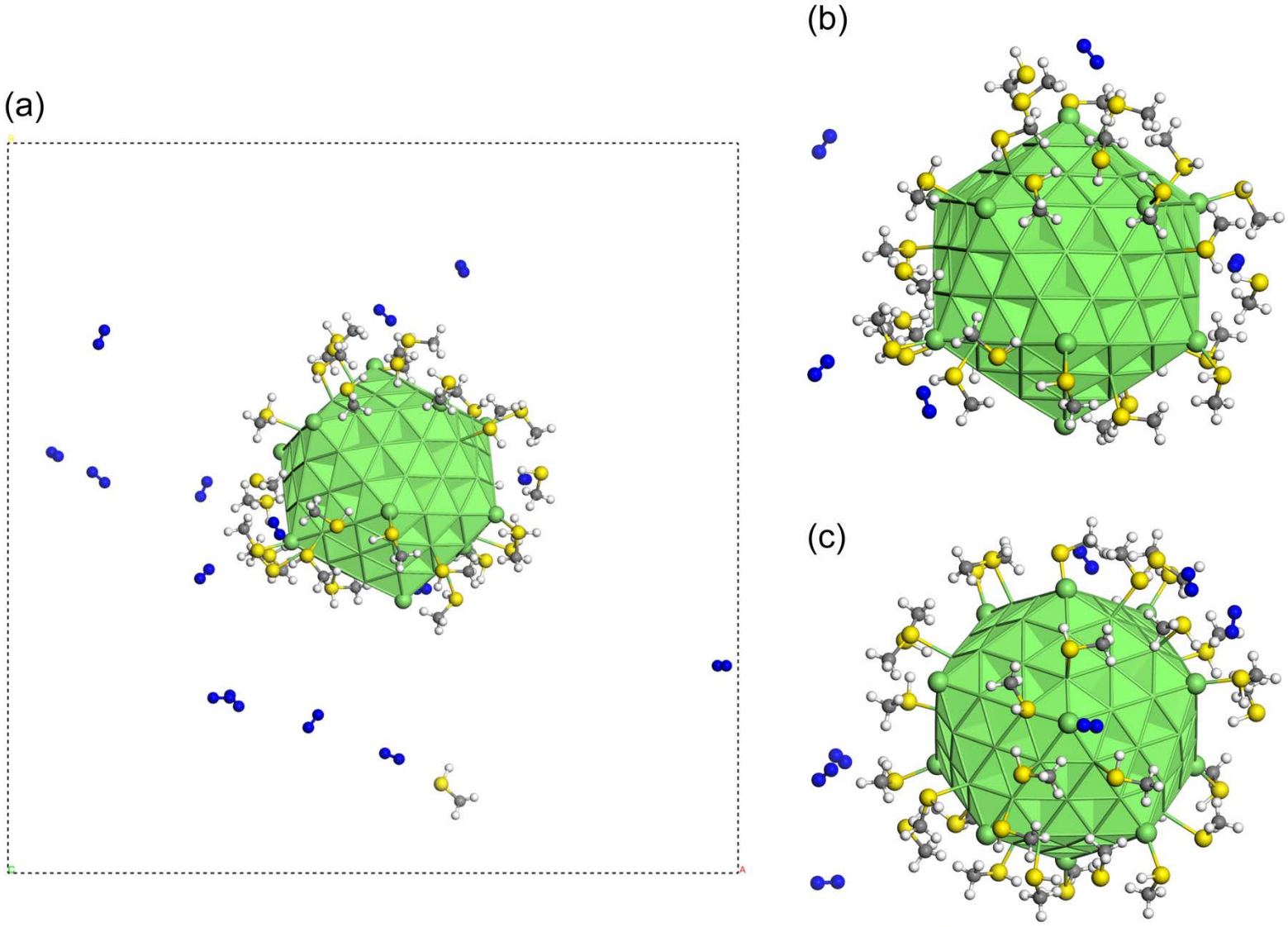

Figure S28. **[Ag147ico]** Optimized coadsorption structure "2_dyn11_step456" corresponding to a shell of 32 methanethiol molecules on the Ag147ico nanocluster in presence of N_2 gas: (a) illustration of the complete system, (b) lateral and (c) top views focused on the nanoparticle (see Table 3 of article for more details about energetics). The color labels are blue for N, green for Ag, yellow for S, gray for C and white for H atoms.

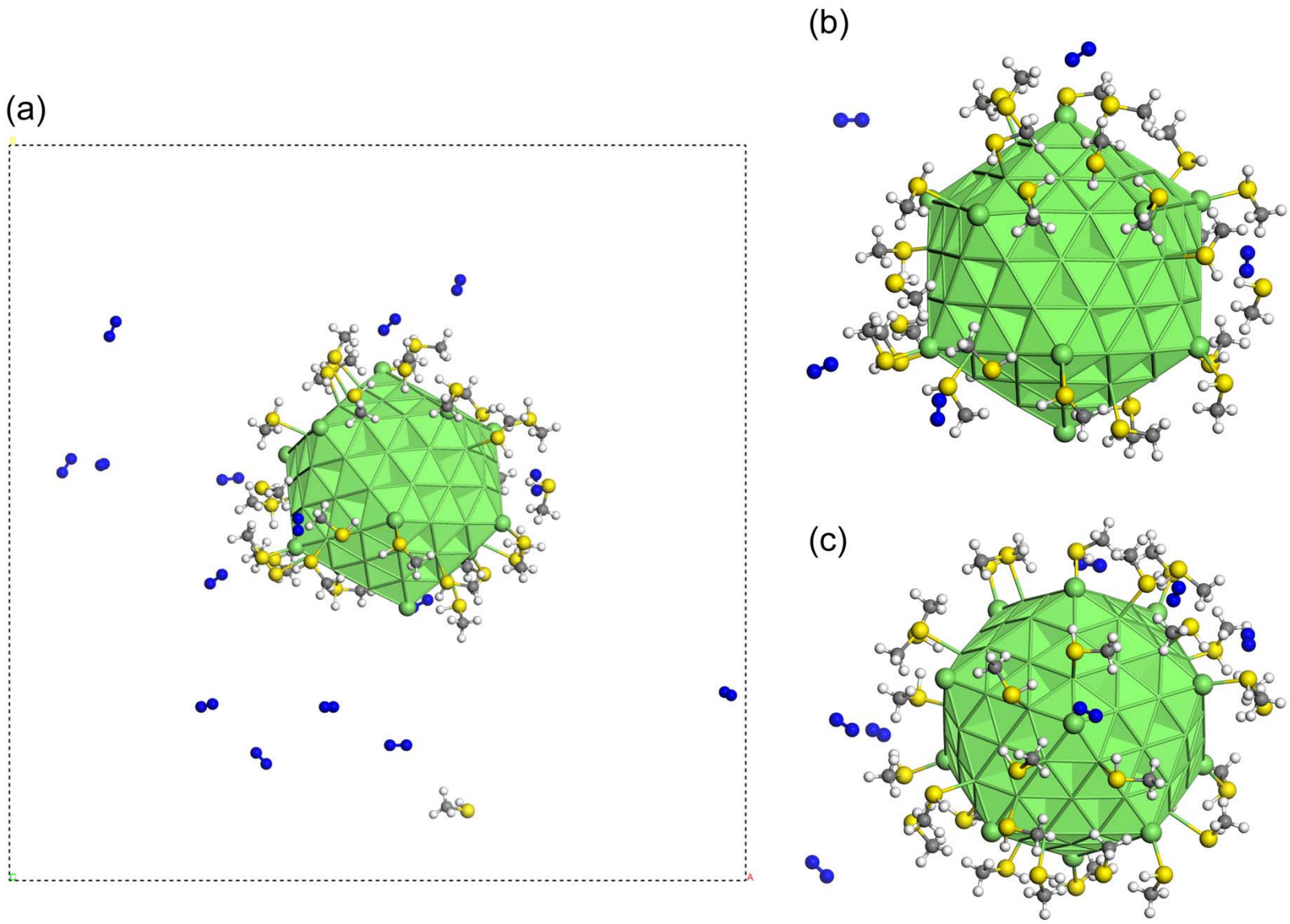

Figure S29. **[Ag147ico]** Optimized coadsorption structure "2_dyn12_step288" corresponding to a shell of 32 methanethiol molecules on the Ag147ico nanocluster in presence of N_2 gas: (a) illustration of the complete system, (b) lateral and (c) top views focused on the nanoparticle (see Table 3 of article for more details about energetics). The color labels are blue for N, green for Ag, yellow for S, gray for C and white for H atoms.

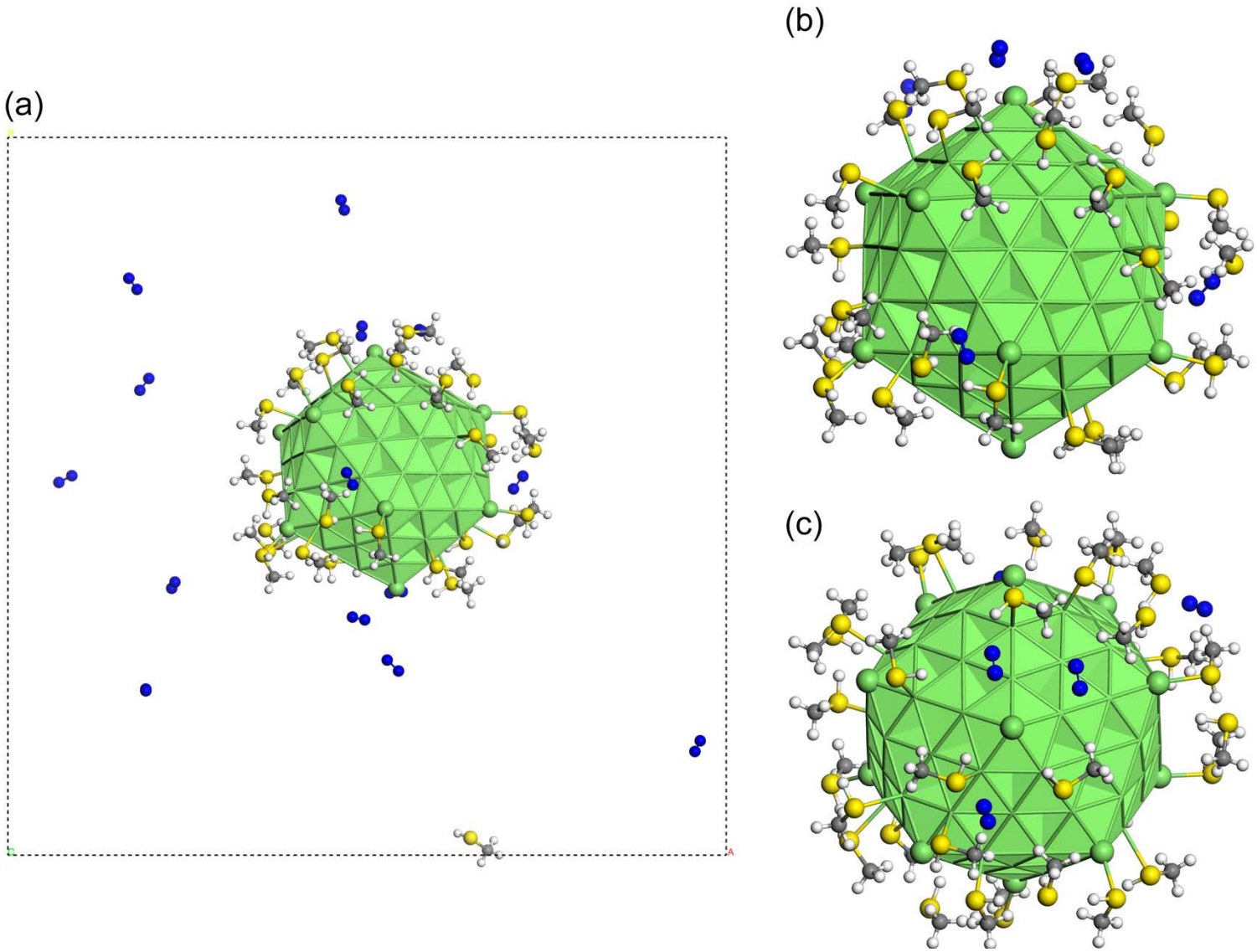

Figure S30. **[Ag147ico]** Optimized coadsorption structure "2_dyn15_step59" corresponding to a shell of 32 methanethiol molecules on the Ag147ico nanocluster in presence of N_2 gas: (a) illustration of the complete system, (b) lateral and (c) top views focused on the nanoparticle (see Table 3 of article for more details about energetics). The color labels are blue for N, green for Ag, yellow for S, gray for C and white for H atoms.

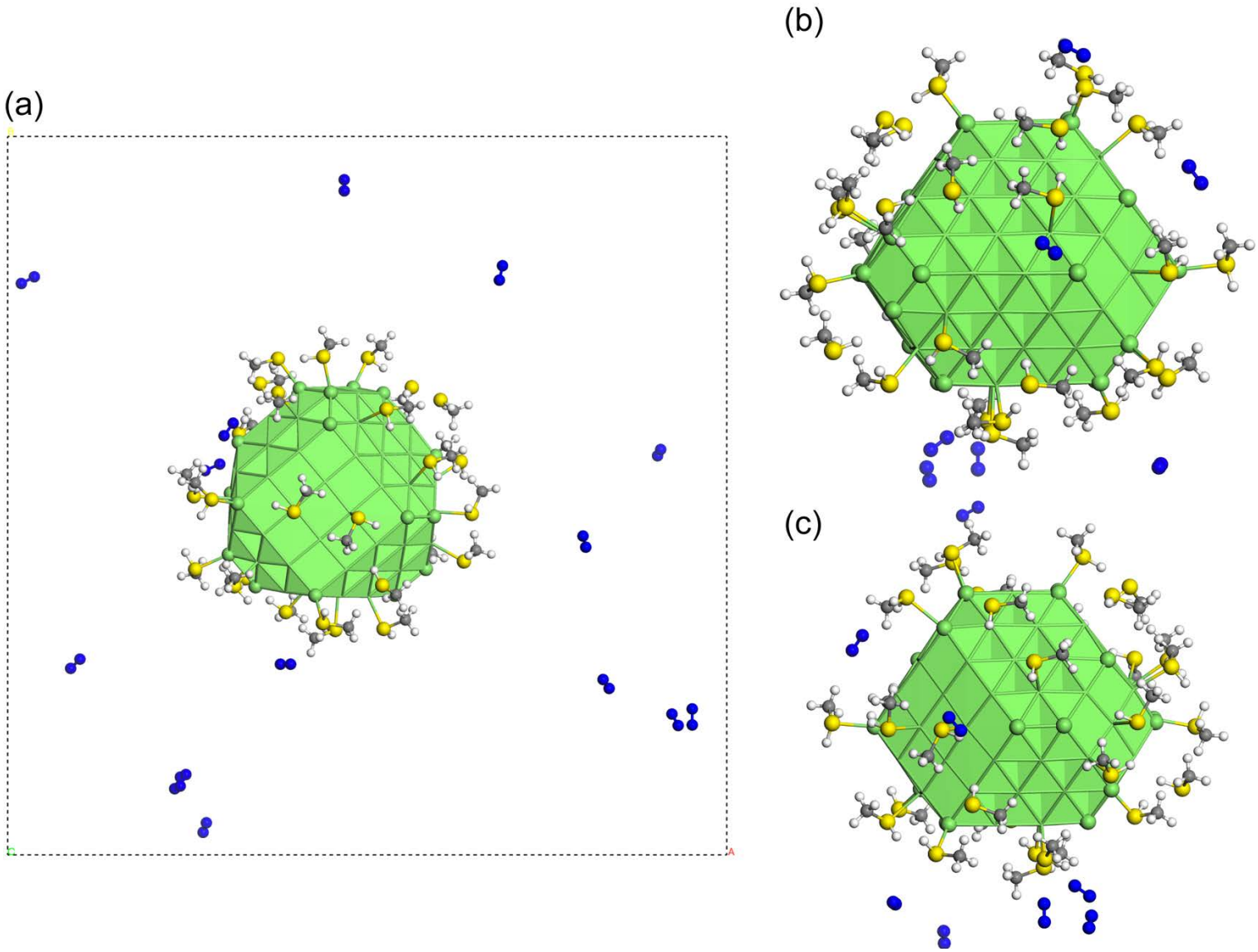

Figure S31. **[Ag147sito]** Optimized coadsorption structure "dyn3_step333" corresponding to a shell of 32 methanethiol molecules on the Ag147sito nanocluster in presence of N_2 gas: (a) illustration of the complete system, (b-c) several views focused on the nanoparticle (see Table 3 of article for more details about energetics). The color labels are blue for N, green for Ag, yellow for S, gray for C and white for H atoms.

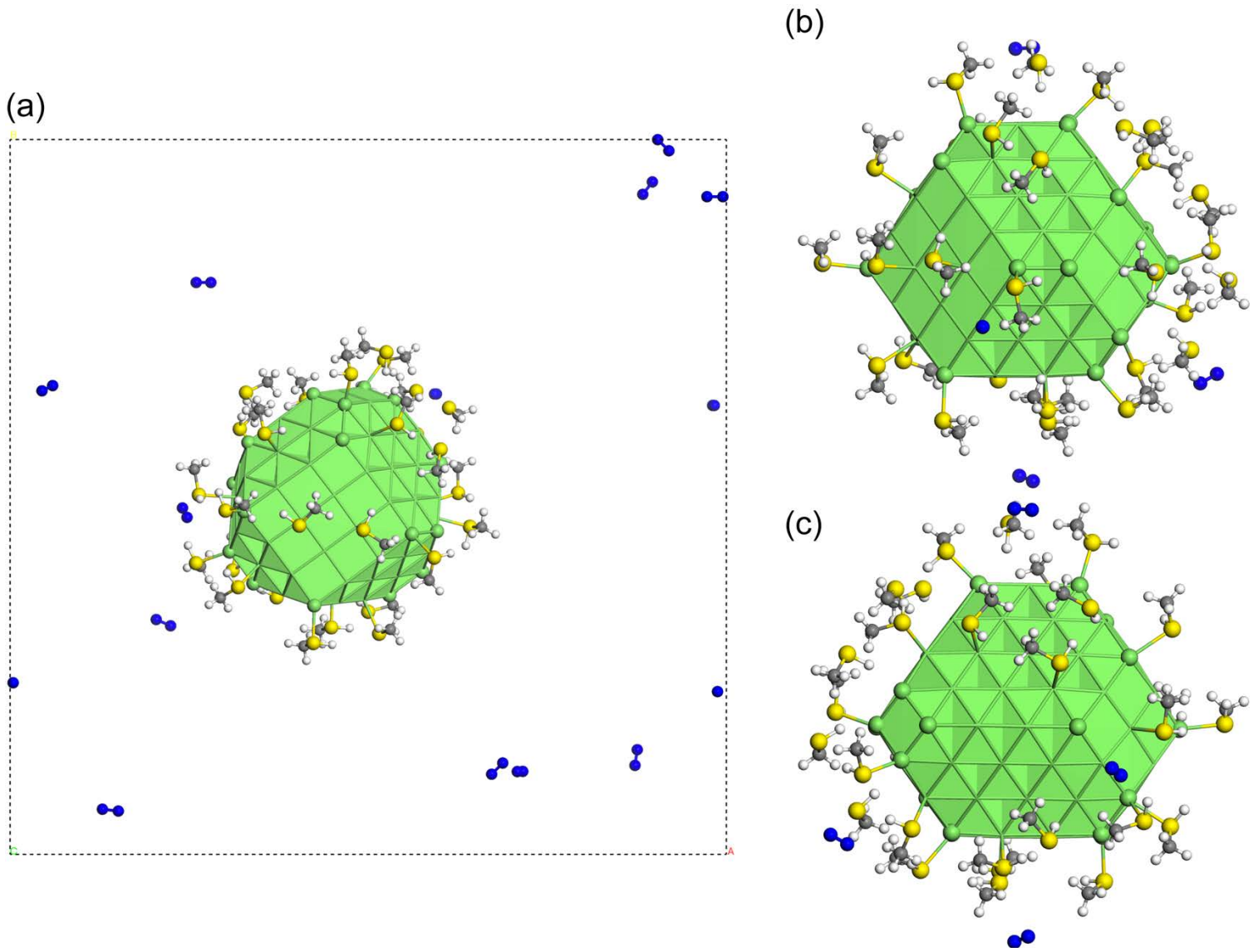

Figure S32. **[Ag147sito]** Optimized coadsorption structure "dyn6_step771" corresponding to a shell of 32 methanethiol molecules on the Ag147sito nanocluster in presence of N_2 gas: (a) illustration of the complete system, (b-c) several views focused on the nanoparticle (see Table 3 of article for more details about energetics). The color labels are blue for N, green for Ag, yellow for S, gray for C and white for H atoms.

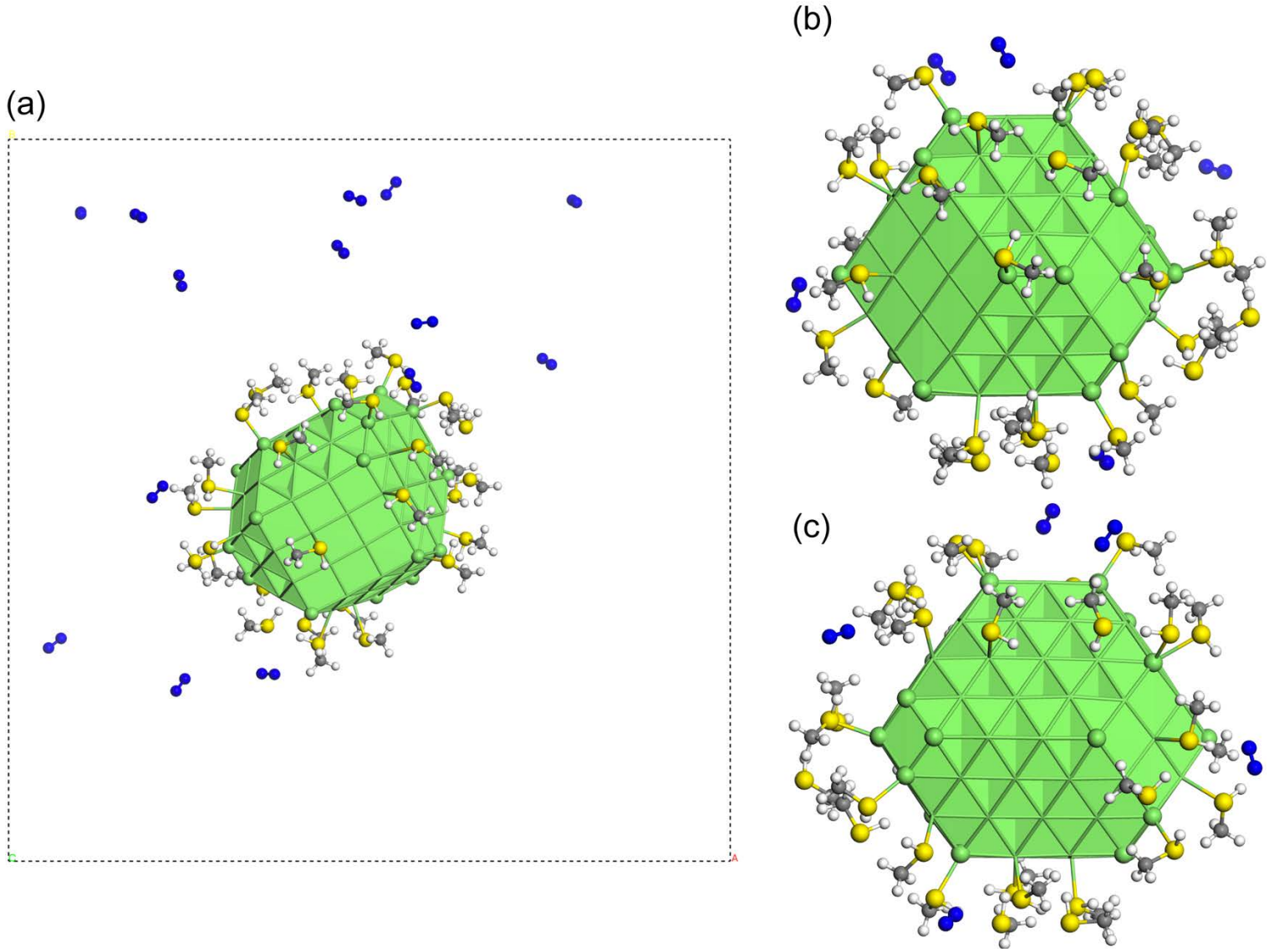

Figure S33. **[Ag147sito]** Optimized coadsorption structure "dyn10_step1283" corresponding to a shell of 32 methanethiol molecules on the Ag147sito nanocluster in presence of N_2 gas: (a) illustration of the complete system, (b-c) several views focused on the nanoparticle (see Table 3 of article for more details about energetics). The color labels are blue for N, green for Ag, yellow for S, gray for C and white for H atoms.

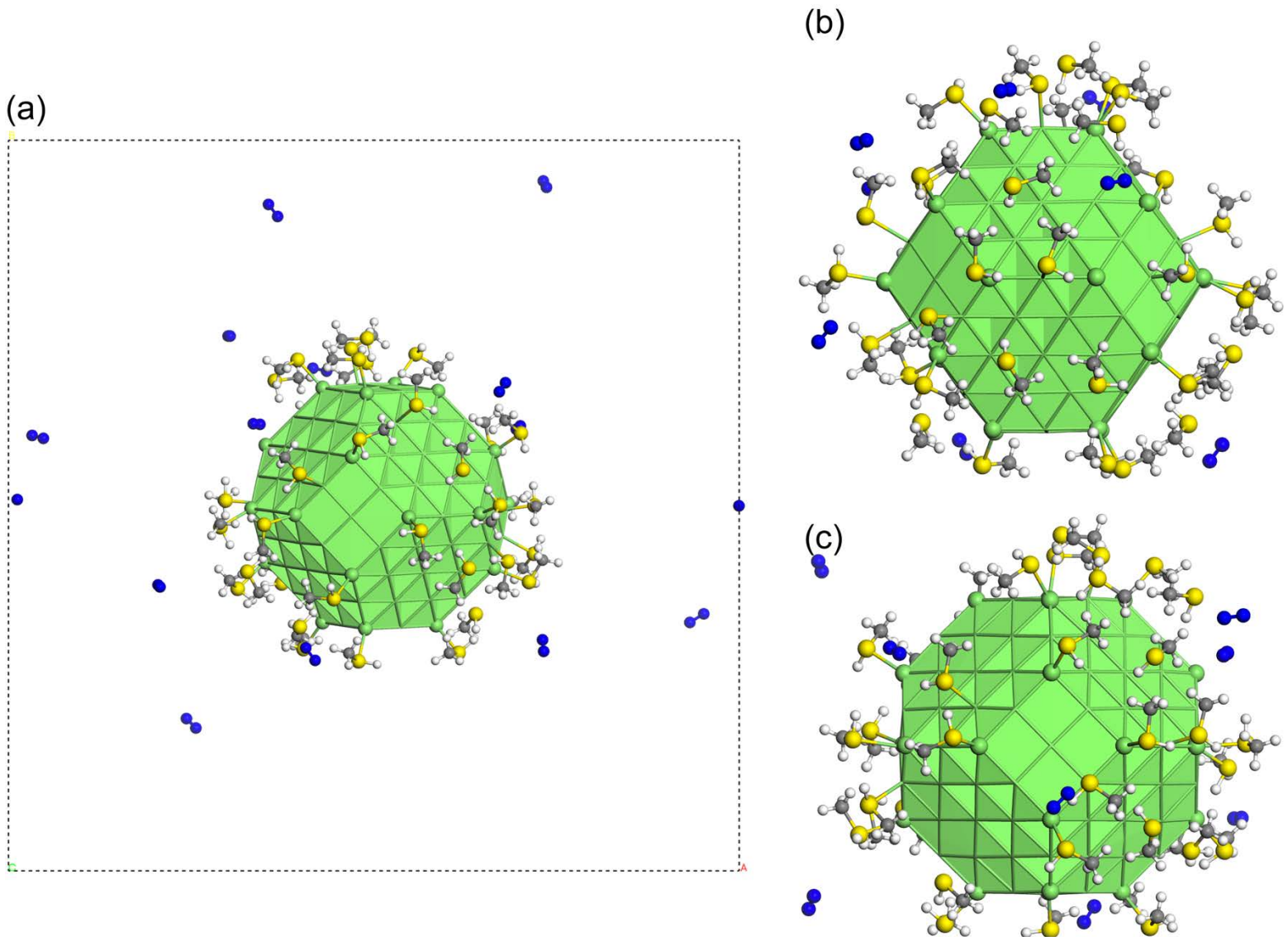

Figure S34. **[Ag201rto]** Optimized coadsorption structure "1_dyn10_step140" corresponding to a shell of 40 methanethiol molecules on the Ag201rto nanocluster in presence of N_2 gas: (a) illustration of the complete system, (b-c) several views focused on the nanoparticle (see Table 3 of article for more details about energetics). The color labels are blue for N, green for Ag, yellow for S, gray for C and white for H atoms.

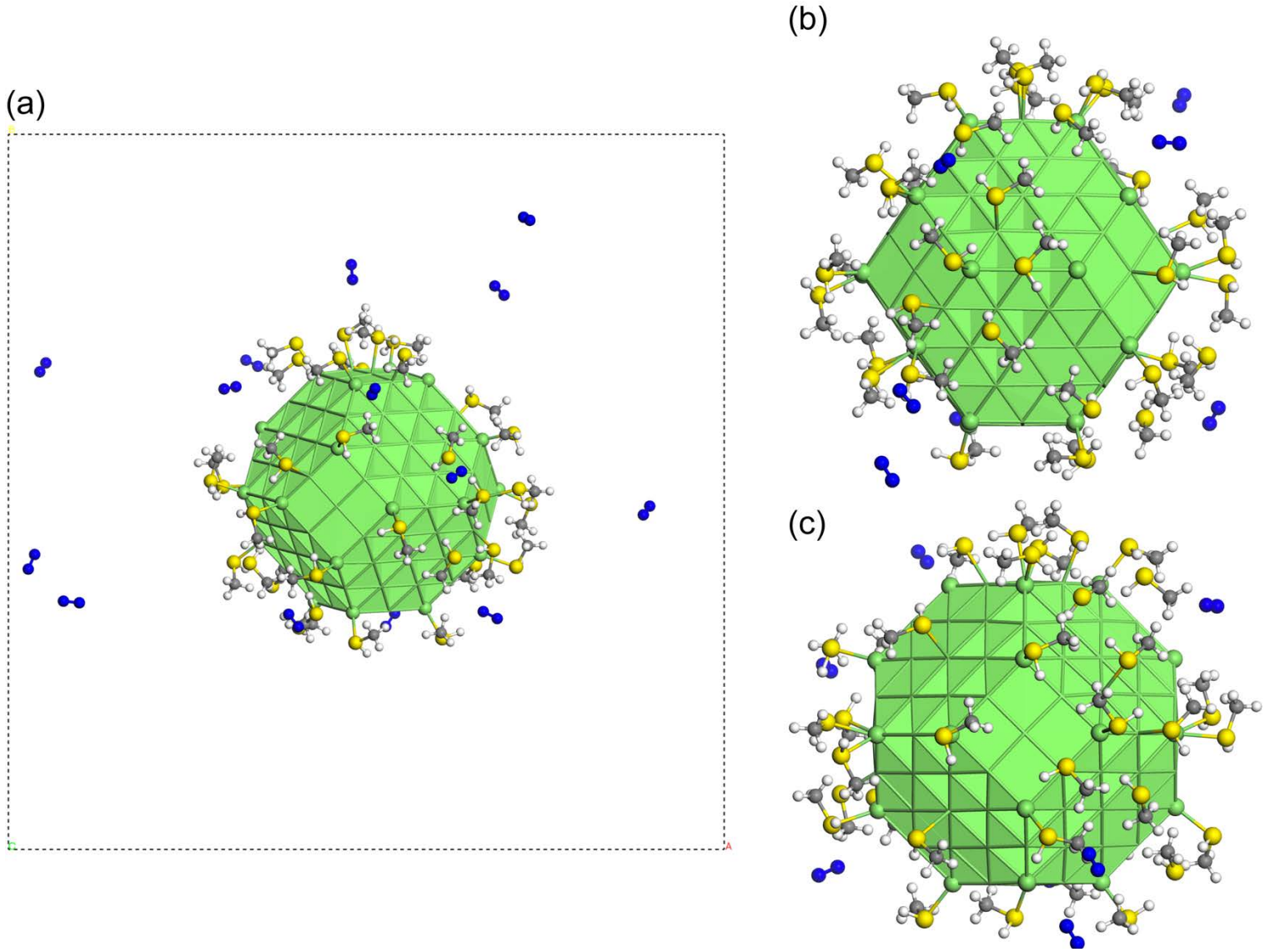

Figure S35. **[Ag201rto]** Optimized coadsorption structure "1_dyn12_step449" corresponding to a shell of 40 methanethiol molecules on the Ag201rto nanocluster in presence of N_2 gas: (a) illustration of the complete system, (b-c) several views focused on the nanoparticle (see Table 3 of article for more details about energetics). The color labels are blue for N, green for Ag, yellow for S, gray for C and white for H atoms.

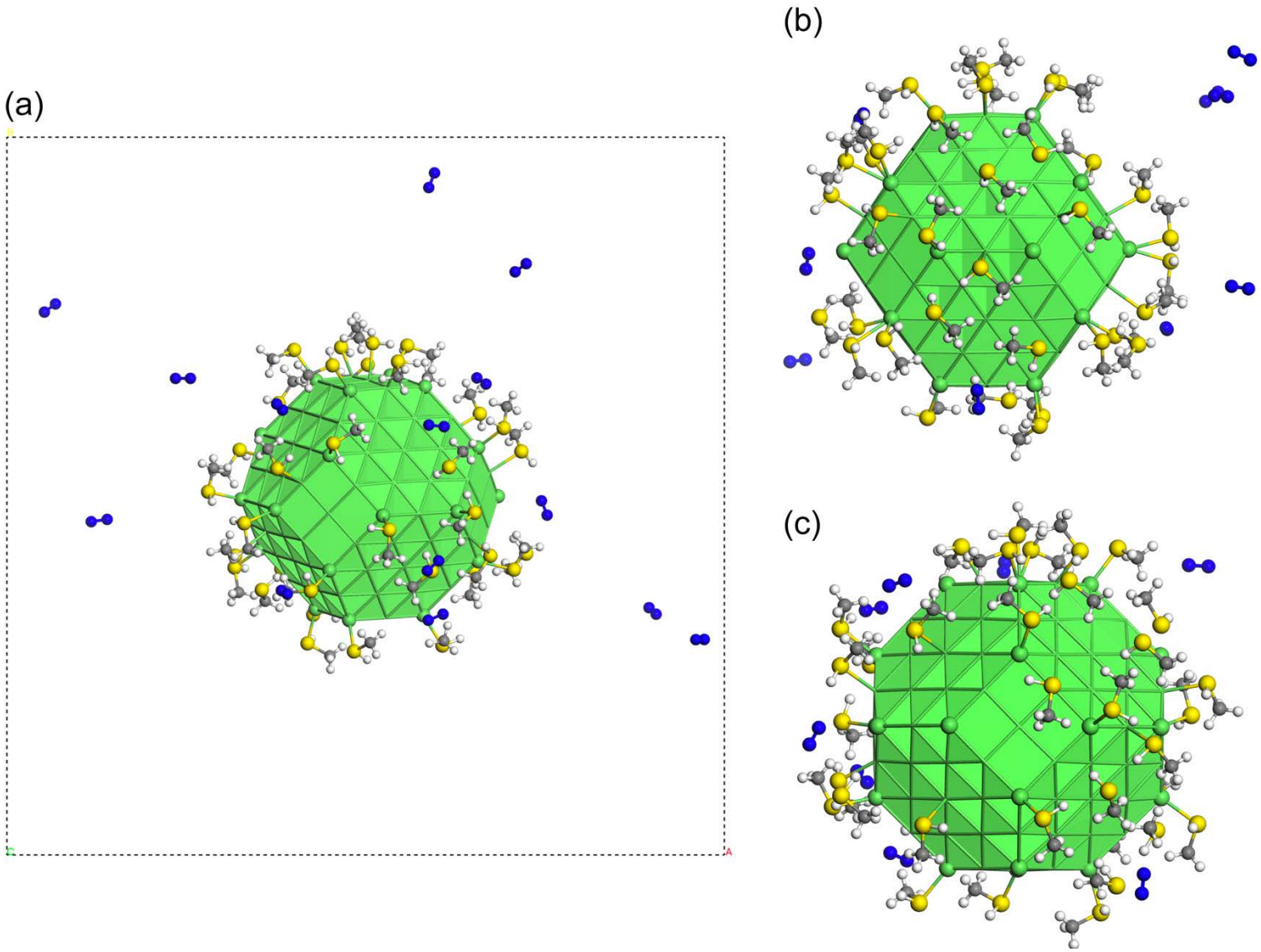

Figure S36. **[Ag201rto]** Optimized coadsorption structure "1_dyn15_step122" corresponding to a shell of 40 methanethiol molecules on the Ag201rto nanocluster in presence of N_2 gas: (a) illustration of the complete system, (b-c) several views focused on the nanoparticle (see Table 3 of article for more details about energetics). The color labels are blue for N, green for Ag, yellow for S, gray for C and white for H atoms.

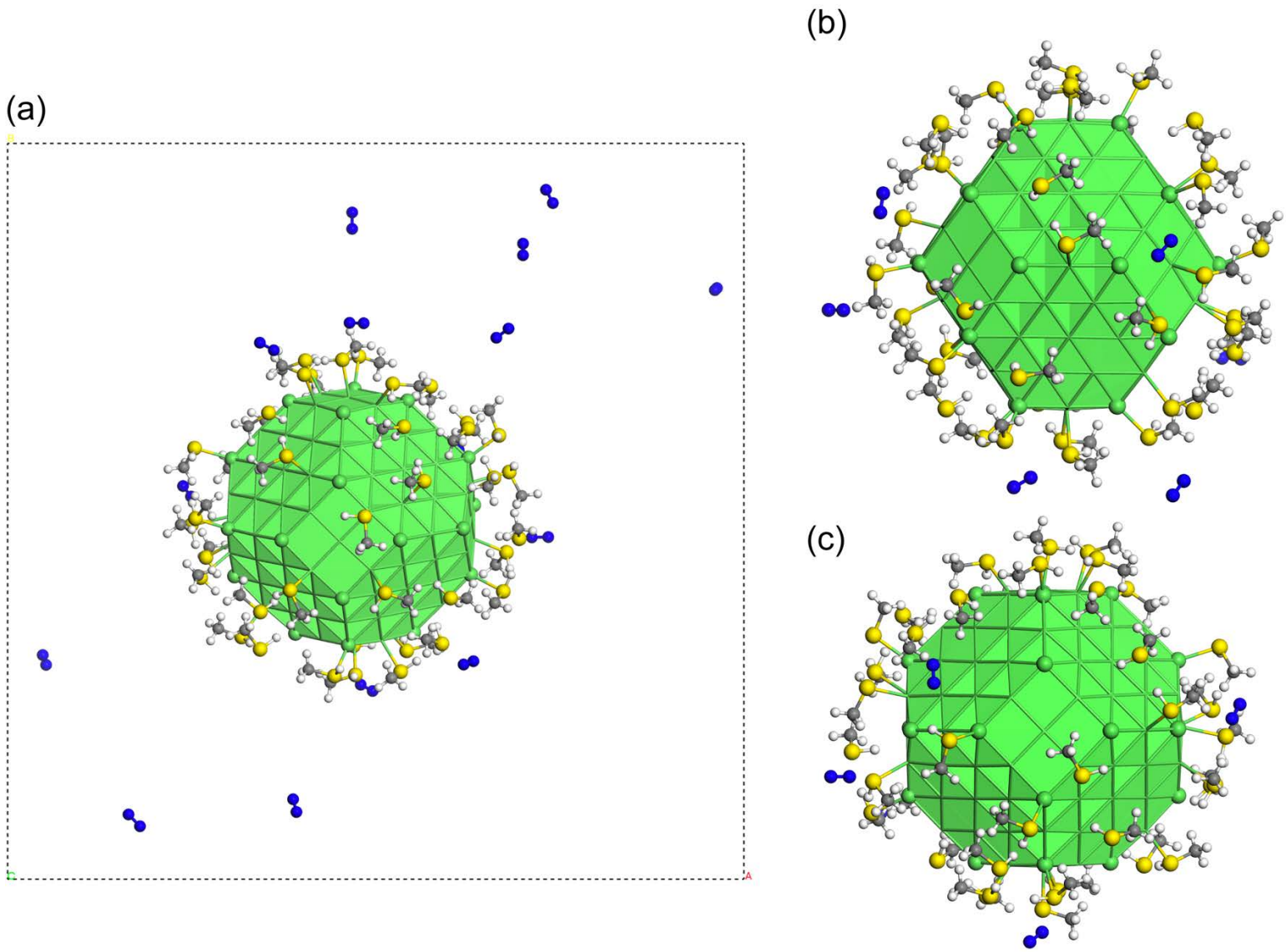

Figure S37. **[Ag201rto]** Optimized coadsorption structure "2_dyn8_step286" corresponding to a shell of 44 methanethiol molecules on the Ag201rto nanocluster in presence of N_2 gas: (a) illustration of the complete system, (b-c) several views focused on the nanoparticle (see Table 3 of article for more details about energetics). The color labels are blue for N, green for Ag, yellow for S, gray for C and white for H atoms.

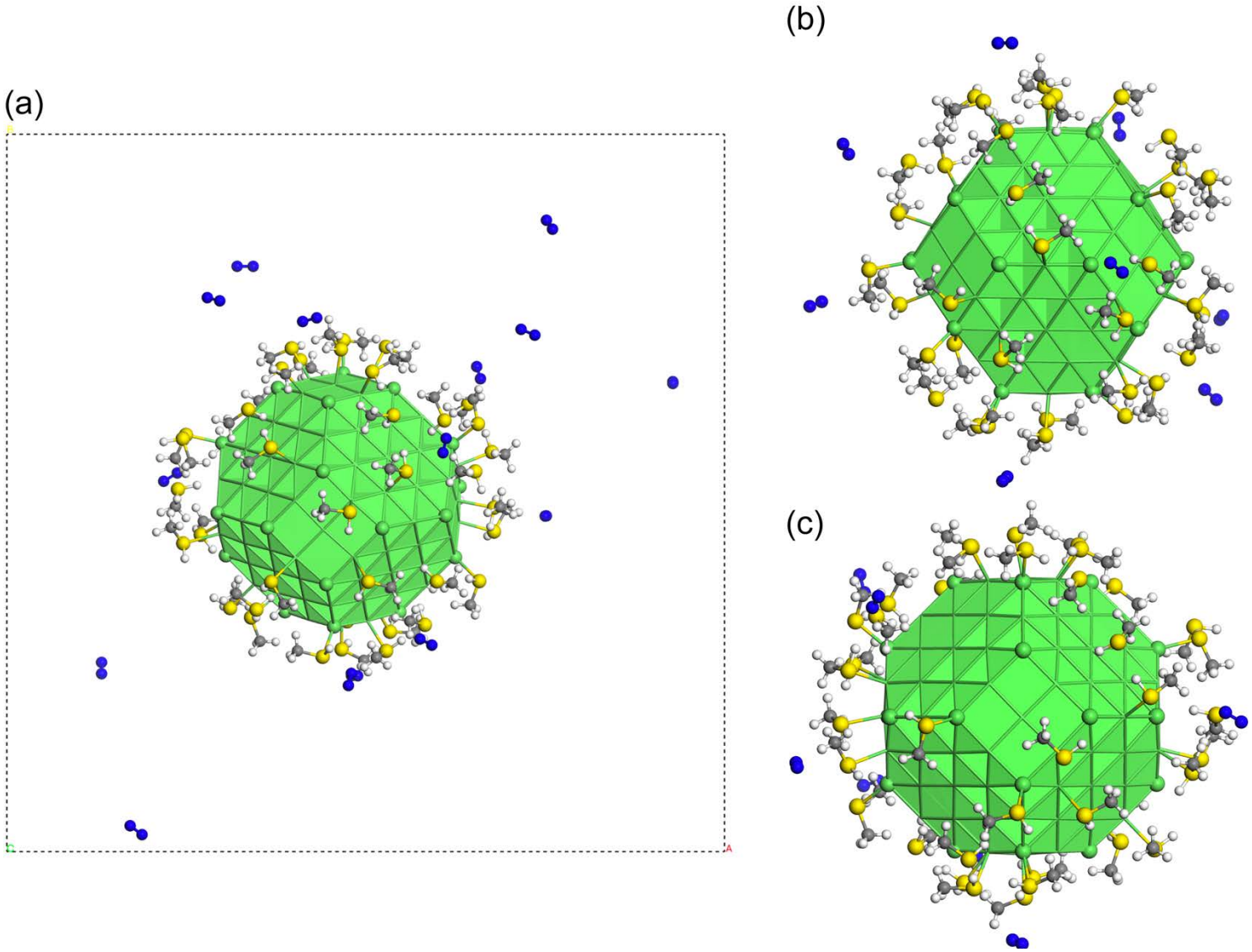

Figure S38. **[Ag201rto]** Optimized coadsorption structure "2_dyn8_step1030" corresponding to a shell of 44 methanethiol molecules on the Ag201rto nanocluster in presence of N_2 gas: (a) illustration of the complete system, (b-c) several views focused on the nanoparticle (see Table 3 of article for more details about energetics). The color labels are blue for N, green for Ag, yellow for S, gray for C and white for H atoms.

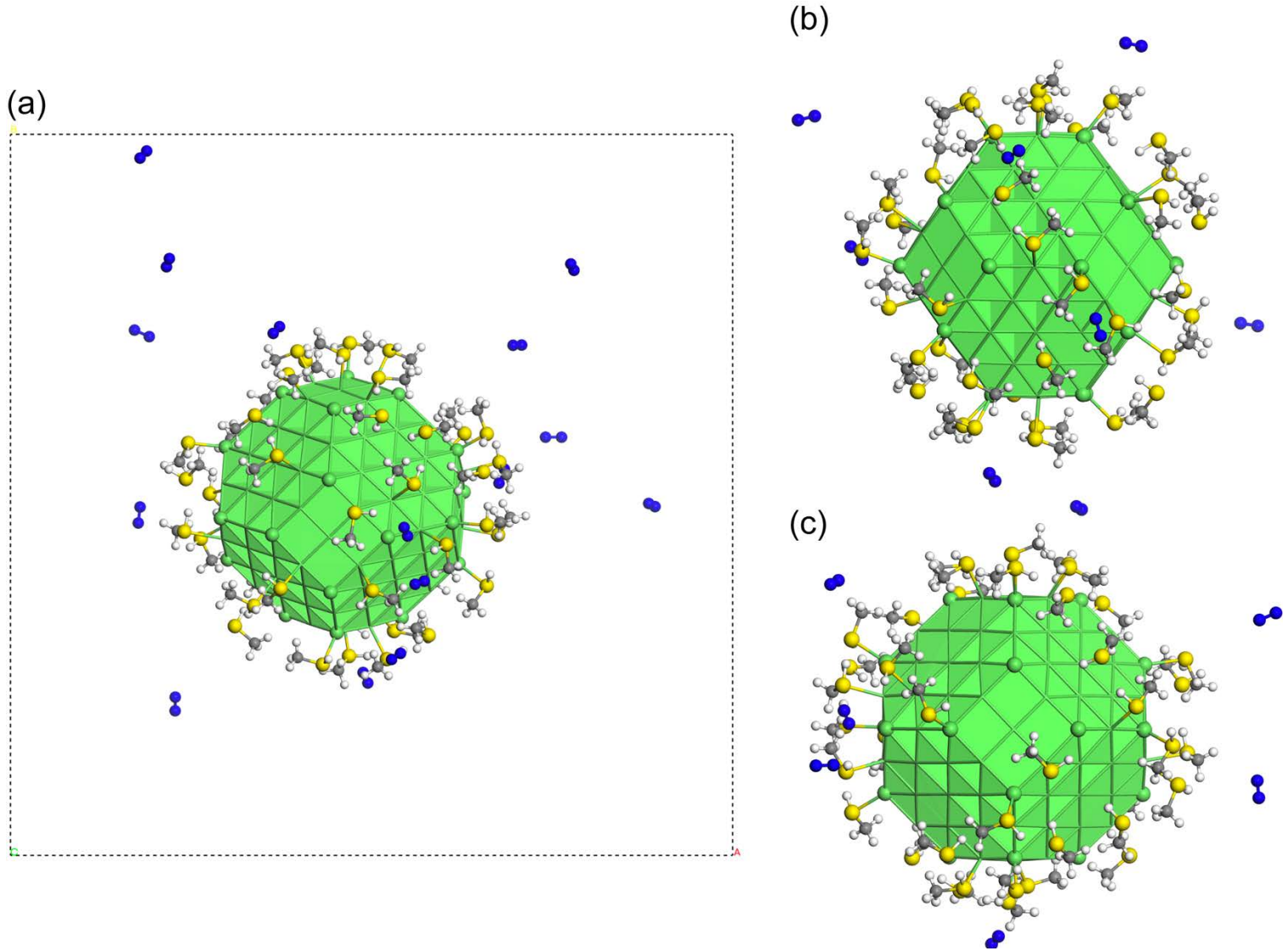

Figure S39. **[Ag201rto]** Optimized coadsorption structure "2_dyn8_step1817" corresponding to a shell of 44 methanethiol molecules on the Ag201rto nanocluster in presence of N_2 gas: (a) illustration of the complete system, (b-c) several views focused on the nanoparticle (see Table 3 of article for more details about energetics). The color labels are blue for N, green for Ag, yellow for S, gray for C and white for H atoms.

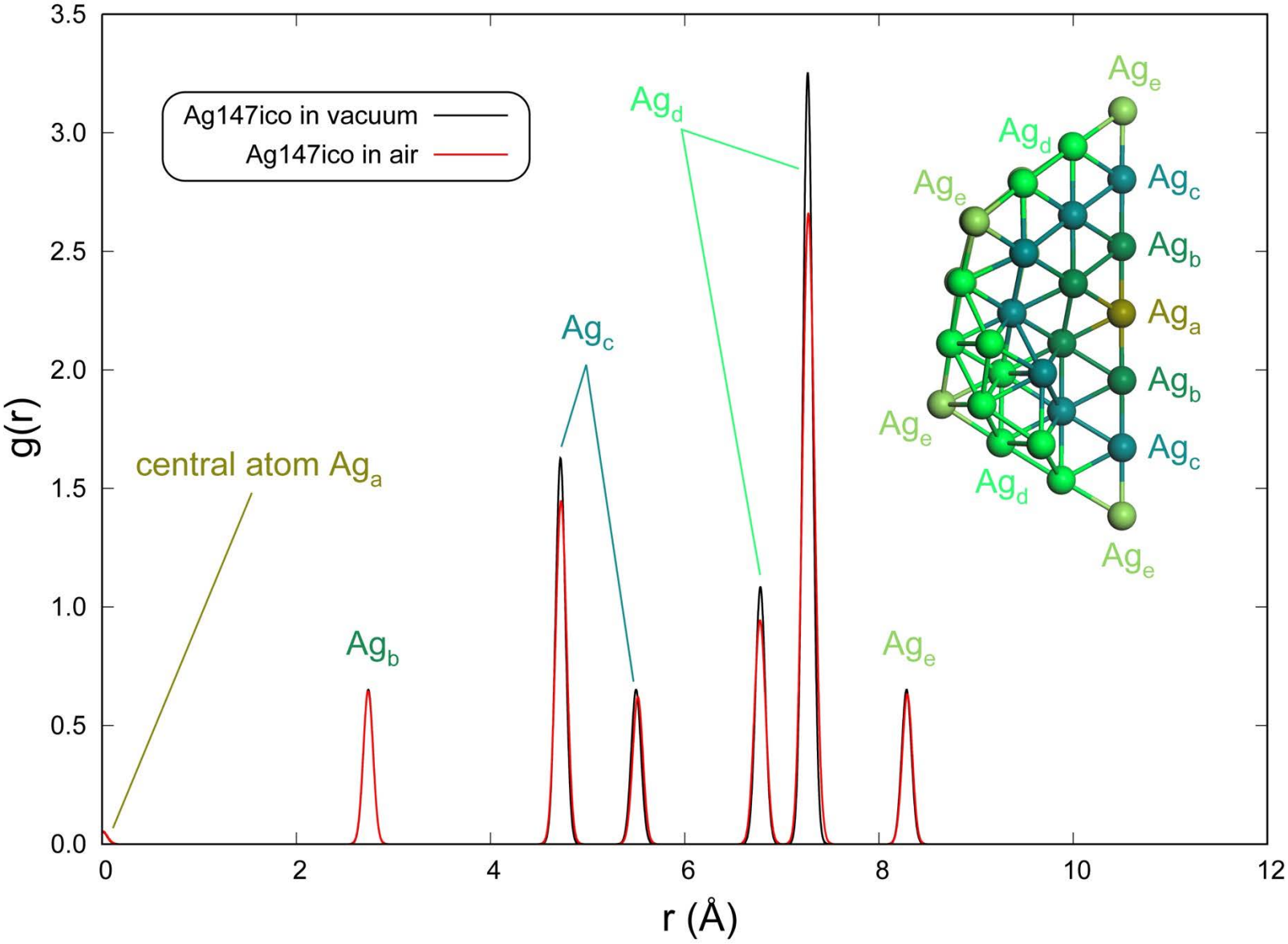

Figure S40. **[Ag147ico]** Radial distribution functions g(r) of Ag147ico nanoparticle optimized either in vacuum (black) or after air exposure (red) at 300 K and corresponding to "1_dyn14_step31" structure. Several families of silver atoms are defined with different green colors, and illustrated accordingly.

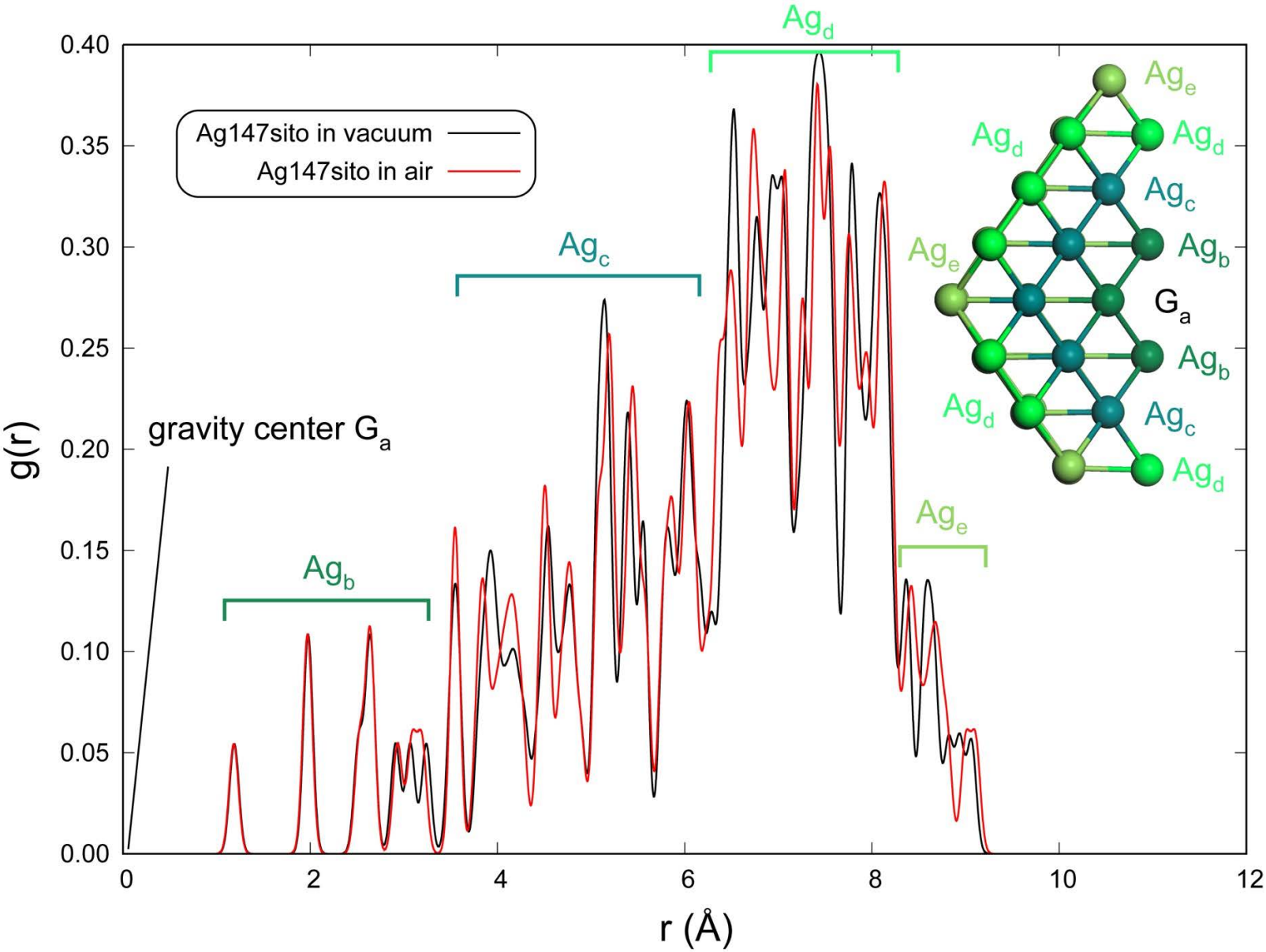

Figure S41. **[Ag147sito]** Radial distribution functions g(r) of Ag147sito nanoparticle optimized either in vacuum (black) or after air exposure (red) at 300 K and corresponding to "dyn3_step333" structure. Several families of silver atoms are defined with different green colors, and illustrated accordingly.

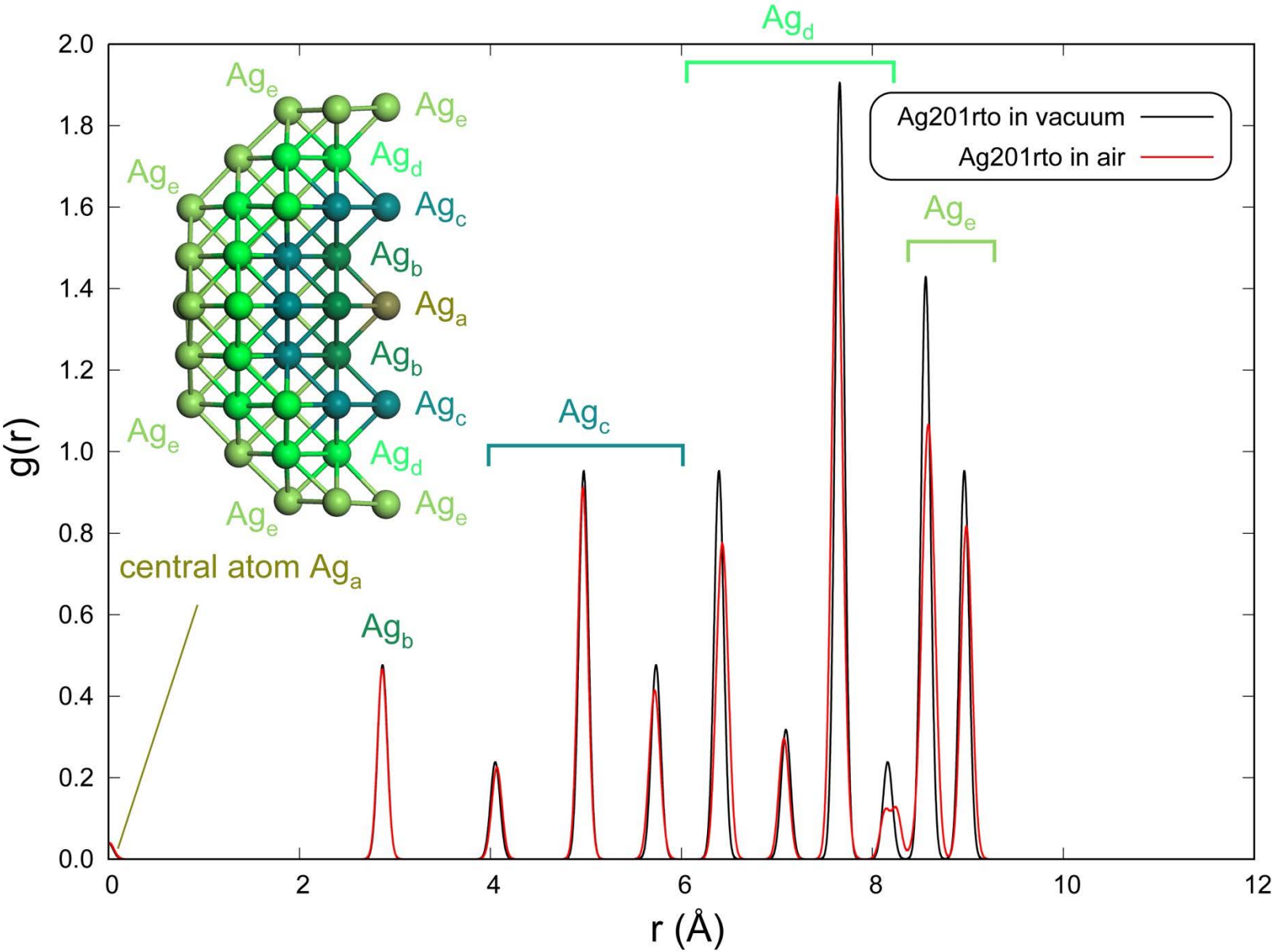

Figure S42. **[Ag201rto]** Radial distribution functions g(r) of Ag201rto nanoparticle optimized either in vacuum (black) or after air exposure (red) at 300 K and corresponding to "2_dyn8_step286" structure. Several families of silver atoms are defined with different green colors, and illustrated accordingly.