Supporting Information for

Size-dependence of carbon nanotube confinement in catalysis

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Supplementary Figure S1. Optimized geometries of encapsulated and supported catalysts (Fe-*in*, Fe-*out*, Ru-*in*, and Ru-*out*) and the catalysts adsorbed with dissociative CO molecules (Fe-*in*-4CO, Fe-*out*-4CO, Ru-*in*-3CO, and Ru-*out*-3CO).

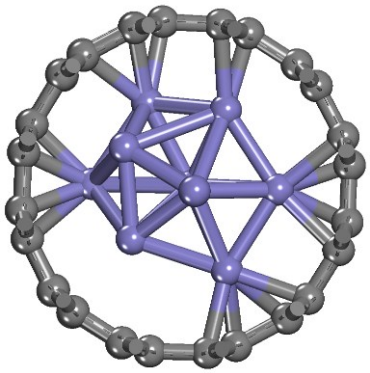
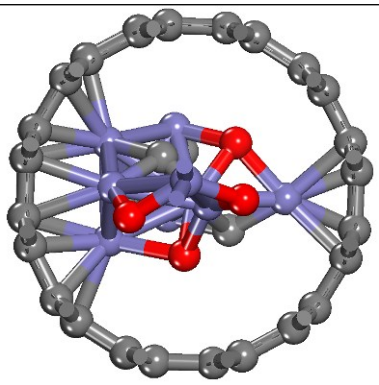
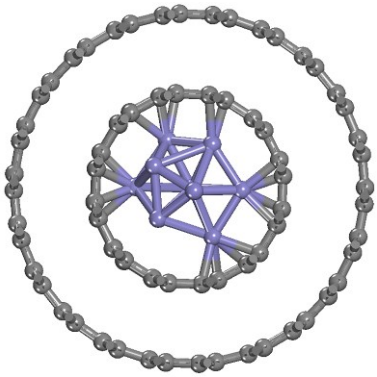
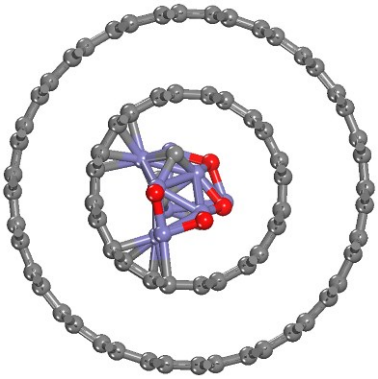
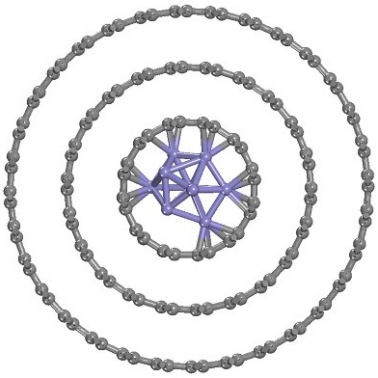
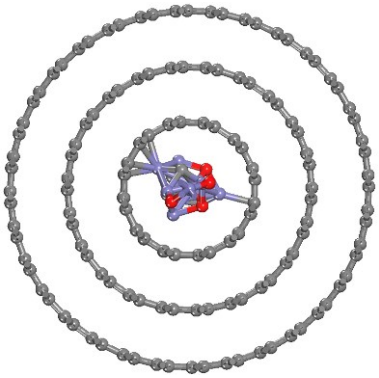
Supplementary Figure S2. Chemical origins of the weakening of binding energies between reactants and confined catalysts compared with the supported cases.

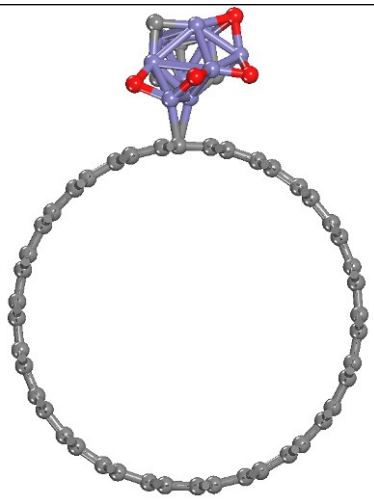
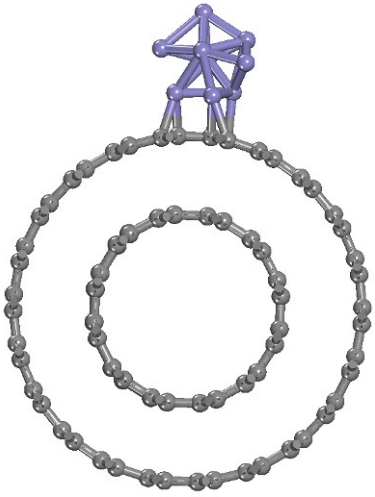
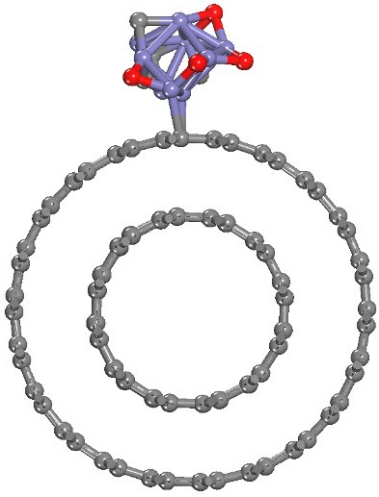
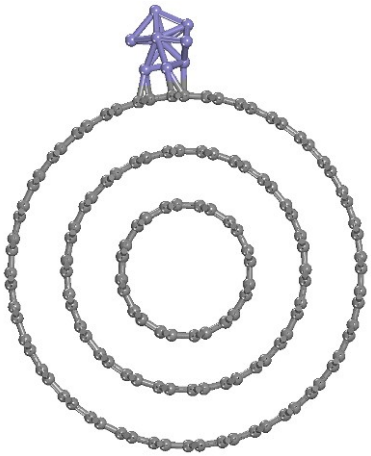
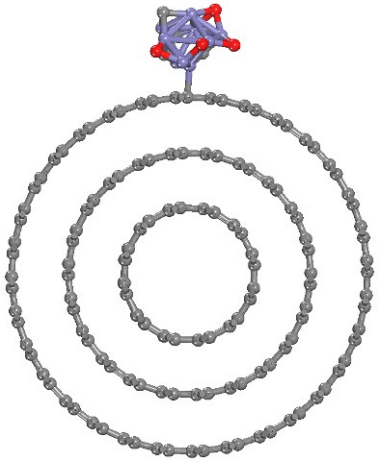
Supplementary Figure S3. Optimized geometries of encapsulated and supported Pt clusters (Pt-*in*-CNT(8,8), Pt-*out*-CNT(8,8), Pt-*in*-CNT(12,0), and Pt-*out*-CNT(12,0)) and the clusters adsorbed with different amount of oxygen (3O, 6O, and 9O atoms).

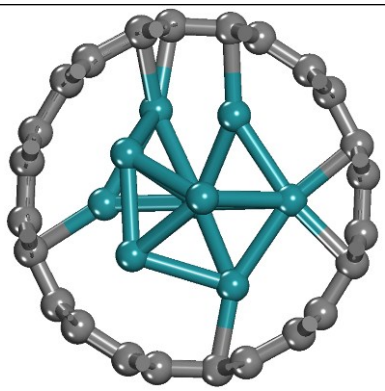
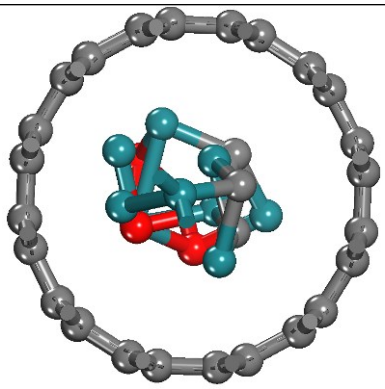
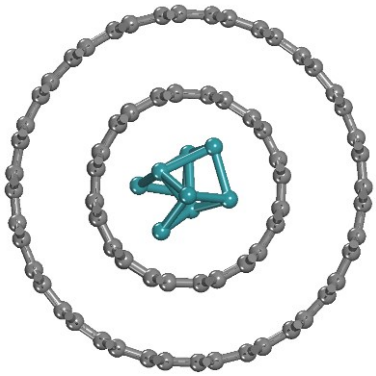
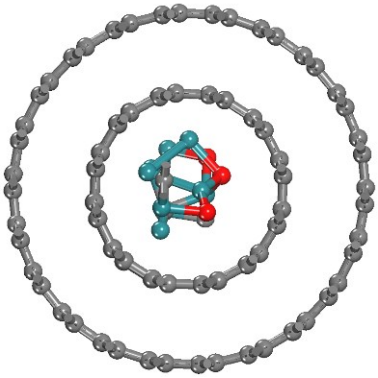
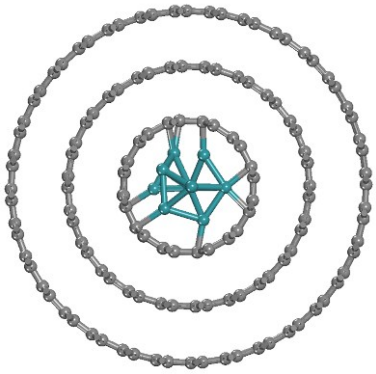
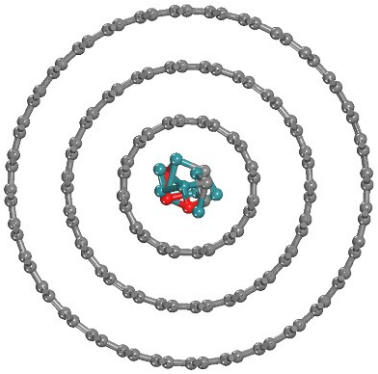
Supplementary Figure S4. Optimized geometries of encapsulated and supported Pt clusters (CNT(10,0), CNT(6,6), CNT(13,0), CNT(10,10), and the clusters adsorbed with a monolayer of oxygen. Pt_{13}-CNT(18,0) with adsorbed 3O atoms was used to examine the particle size dependence for comparison.

Supplementary Figure S5. Optimized geometries of encapsulated and supported Re clusters (CNT(10,0), CNT(6,6), CNT(13,0), CNT(10,10), CNT(8,8), CNT(12,0) and the clusters adsorbed with a monolayer of nitrogen. Re_{13}-CNT(18,0) with adsorbed 3N atoms was used to examine the particle size dependence for comparison.

Supplementary Figure S1. Optimized geometries of encapsulated and supported catalysts (Fe-*in*, Fe-*out*, Ru-*in*, and Ru-*out*) and the catalysts adsorbed with dissociative CO molecules (Fe-*in*-4CO, Fe-*out*-4CO, Ru-*in*-3CO, and Ru-*out*-3CO).

Fe_9-*in*-**SWCNT**		Fe_9-4CO-*in*-**SWCNT**	
Fe_9-*in*-**DWCNT**		Fe_9-4CO-*in*-**DWCNT**	
Fe_9-*in*-**TWCNT**		Fe_9-4CO-*in*-**TWCNT**	

Fe_9-*out*-**SWCNT**		Fe_9-4CO-*out*-**SWCNT**	
Fe_9-*out*-**DWCNT**		Fe_9-4CO-*out*-**DWCNT**	
Fe_9-*out*-**TWCNT**		Fe_9-4CO-*out*-**TWCNT**	

Ru_9-*in*-**SWCNT**		Ru_9-3CO-*in*-**SWCNT**	
Ru_9-*in*-**DWCNT**		Ru_9-3CO-*in*-**DWCNT**	
Ru_9-*in*-**TWCNT**		Ru_9-3CO-*in*-**TWCNT**	
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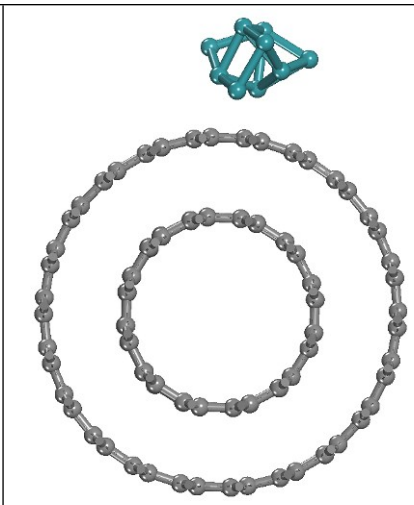
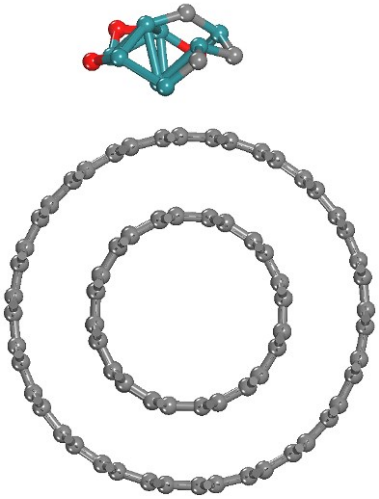
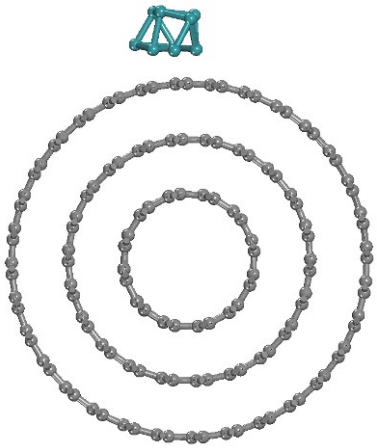
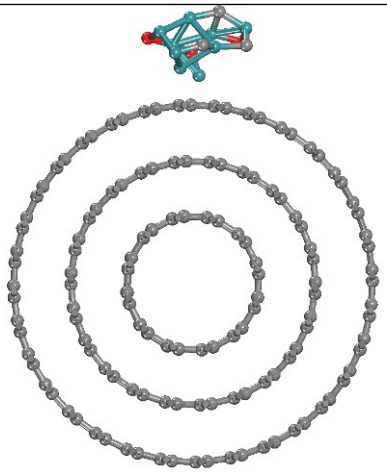
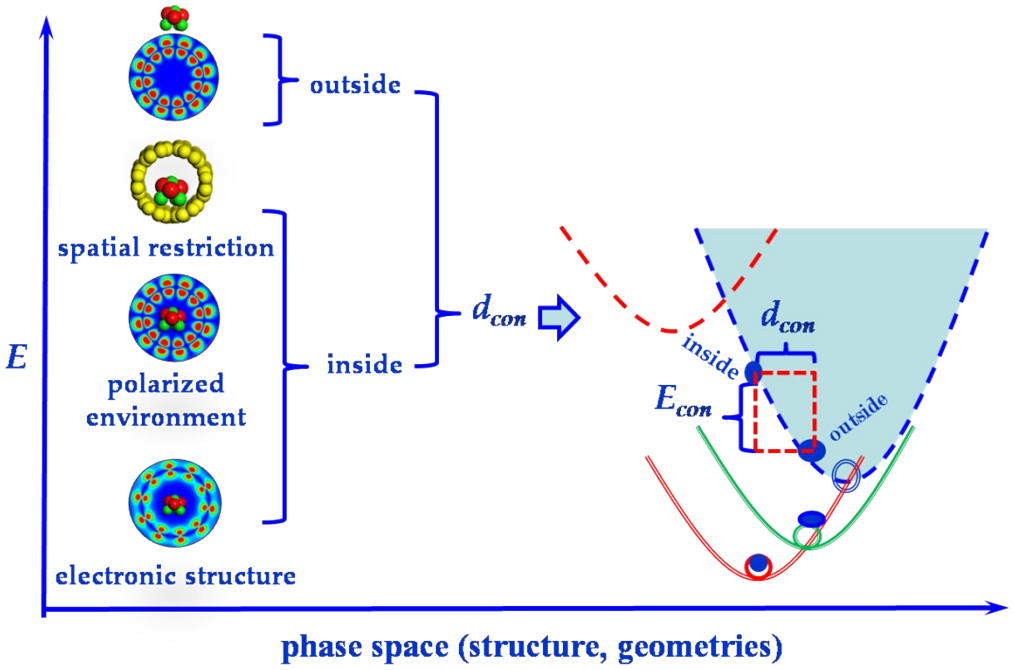
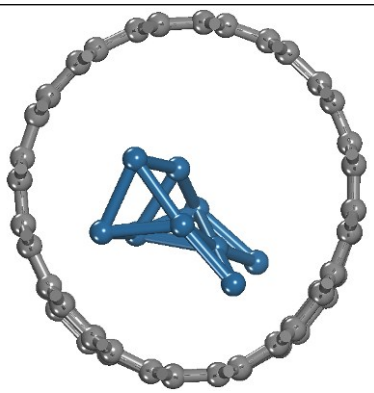
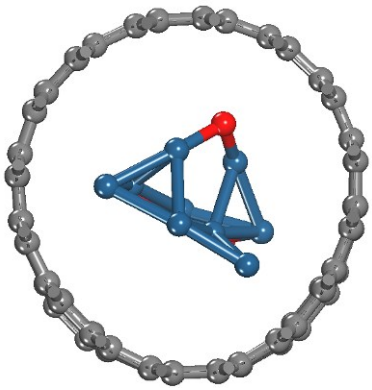
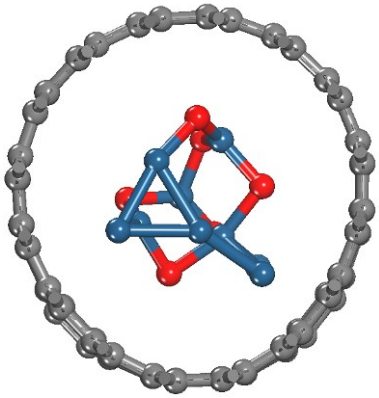
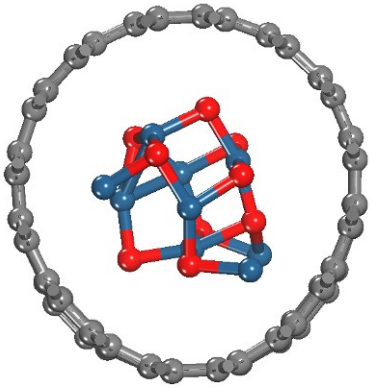
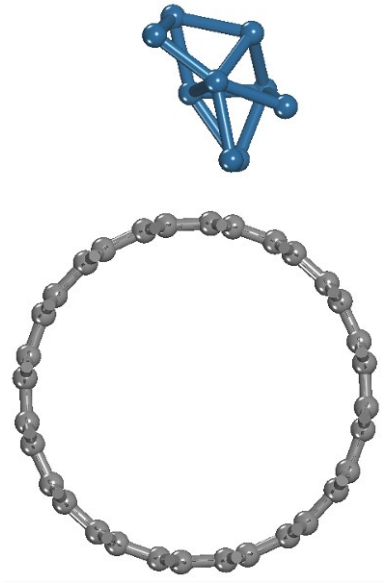
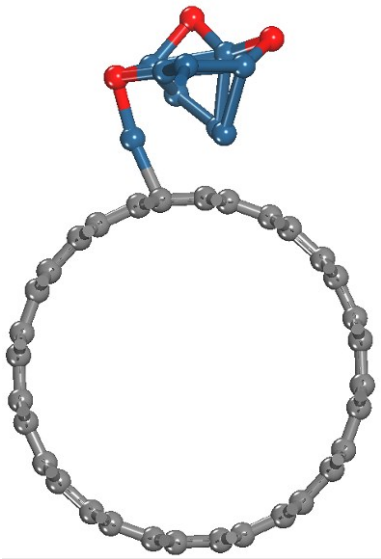
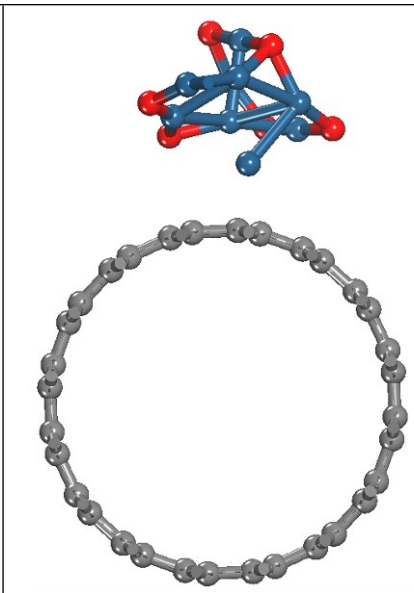
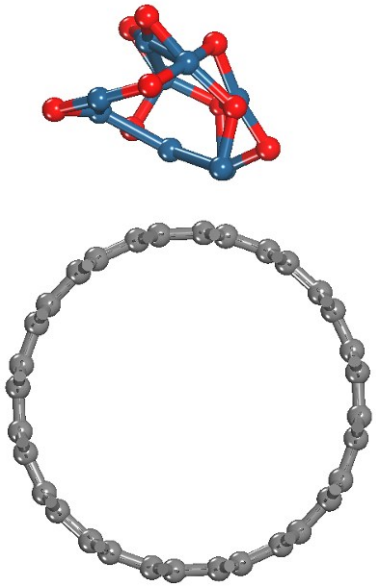
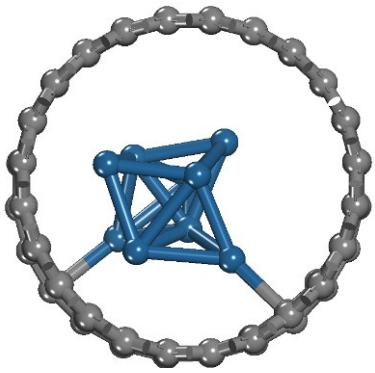
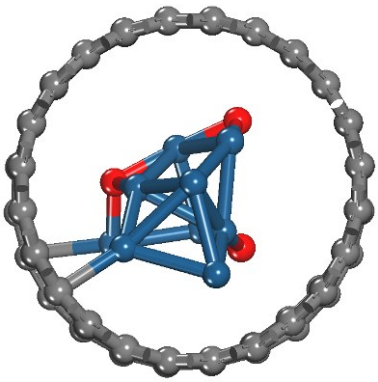
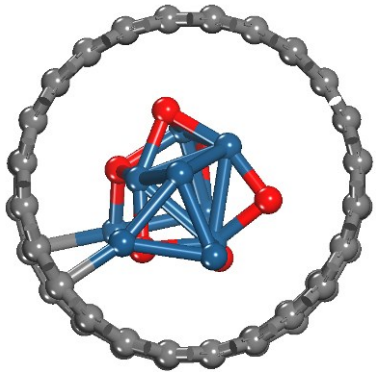
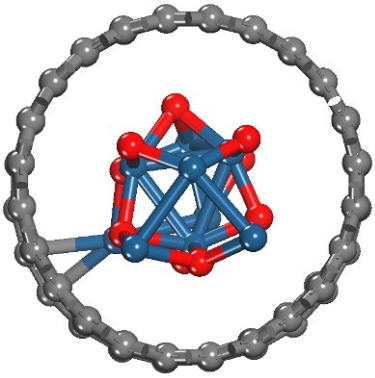
Ru_9-*out*-**DWCNT**		Ru_9-3CO-*out*-**DWCNT**	
Ru_9-*out*-**TWCNT**		Ru_9-3CO-*out*-**TWCNT**	

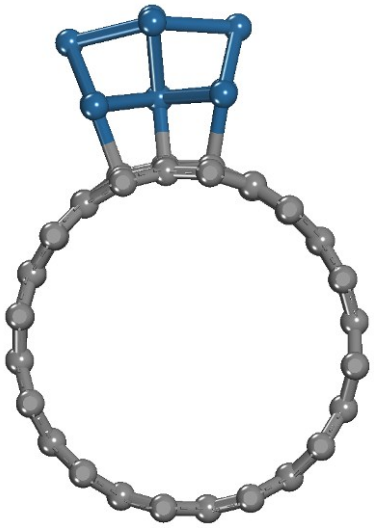
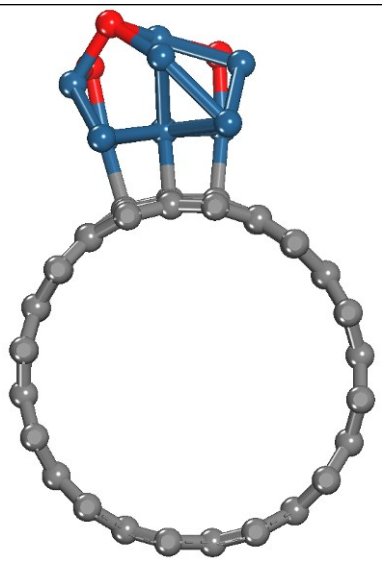
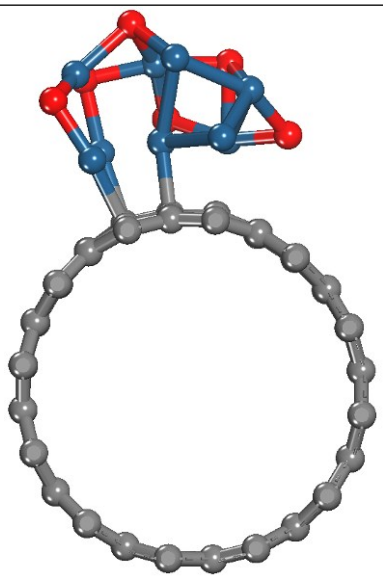
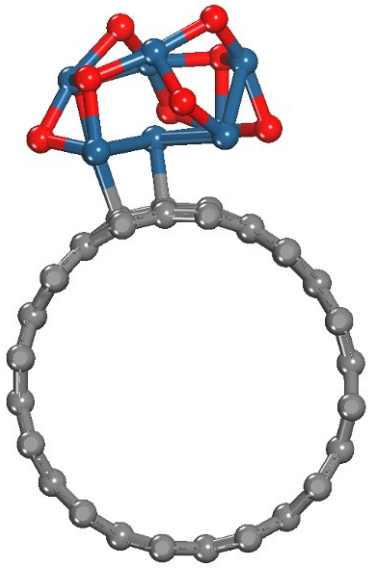
Supplementary Figure S2. Chemical origins of the weakening of binding energies between reactants and confined catalysts compared with the supported cases.



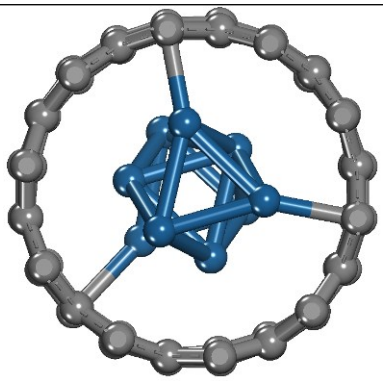
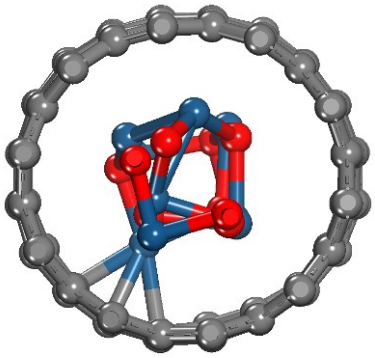
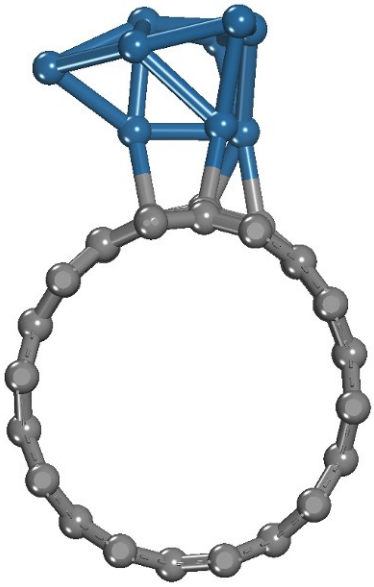
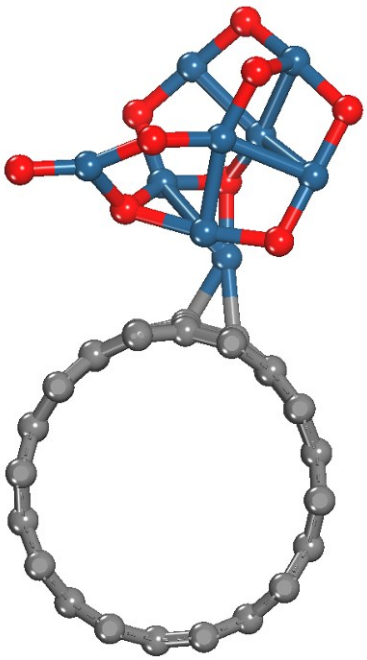
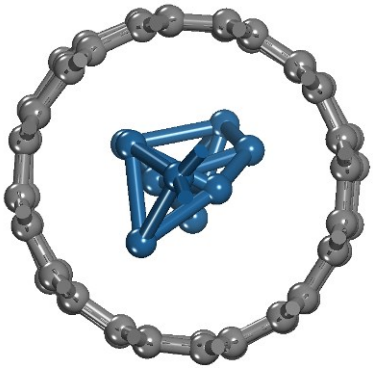
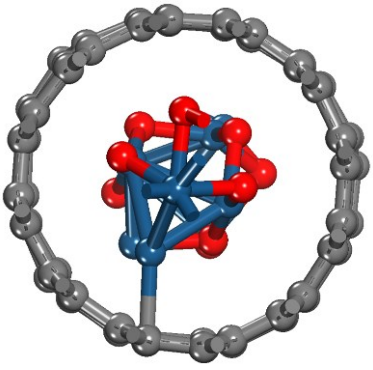
Supplementary Figure S3. Optimized geometries of encapsulated and supported Pt clusters (Pt-*in*-CNT(8,8), Pt-*out*-CNT(8,8), Pt-*in*-CNT(12,0), and Pt-*out*-CNT(12,0)) and the clusters adsorbed with different amount of oxygen (3O, 6O, and 9O atoms).

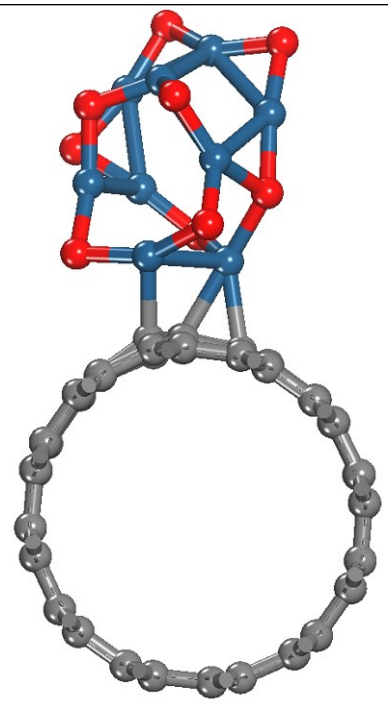
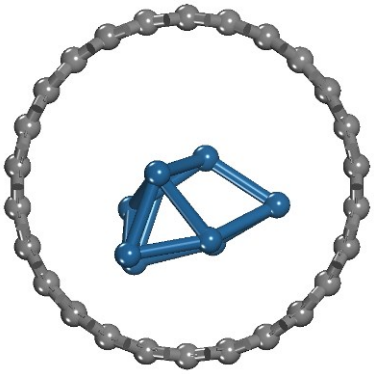
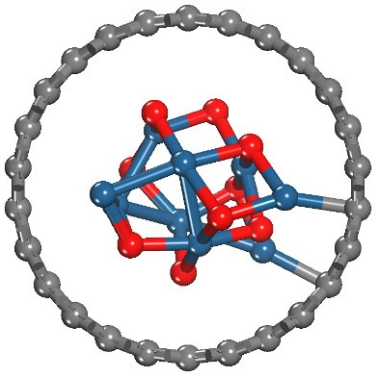
Pt_9-*in*-**CNT(8,8)**		Pt_9-3O-*in*-**CNT(8,8)**	
Pt_9-6O-*in*-**CNT(8,8)**		Pt_9-9O-*in*-**CNT(8,8)**	
Pt_9-*out*-**CNT(8,8)**		Pt_9-3O-*out*-**CNT(8,8)**	

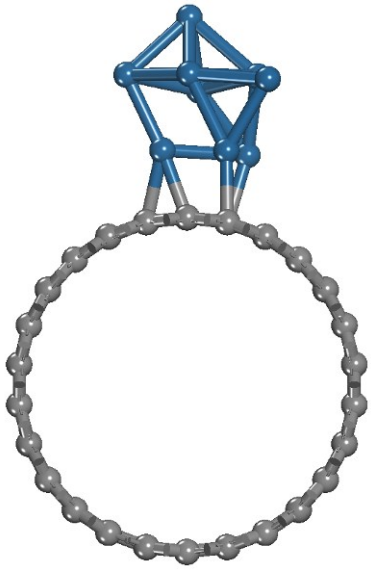
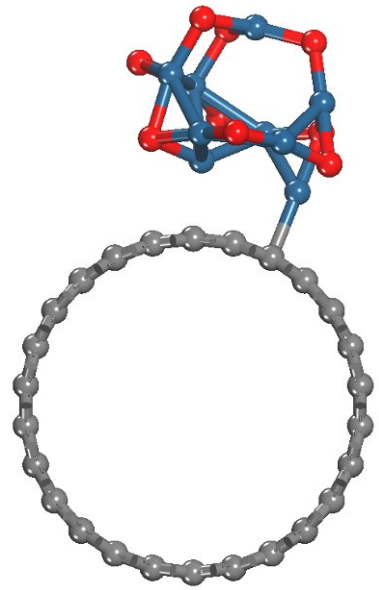
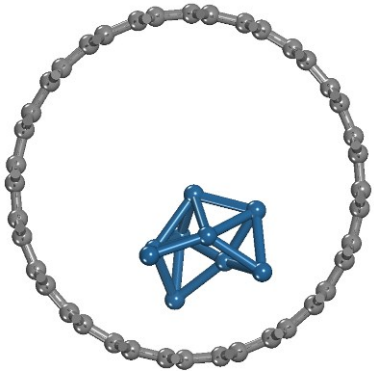
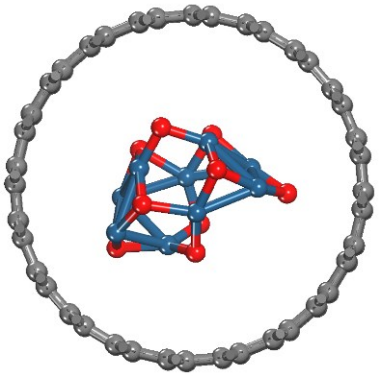
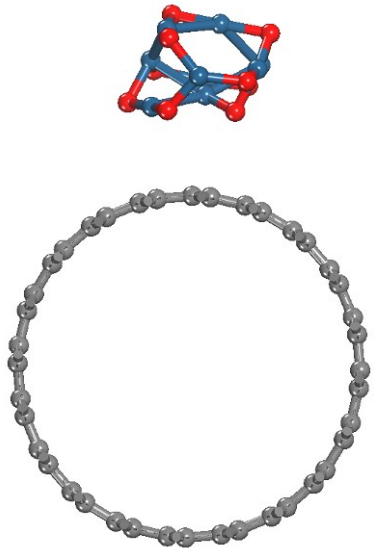
Pt_9-6O-*out*-**CNT(8,8)**		Pt_9-9O-*out*-**CNT(8,8)**	
Pt_9-*in*-**CNT(12,0)**		Pt_9-3O-*in*-**CNT(12,0)**	
Pt_9-6O-*in*-**CNT(12,0)**		Pt_9-9O-*in*-**CNT(12,0)**	

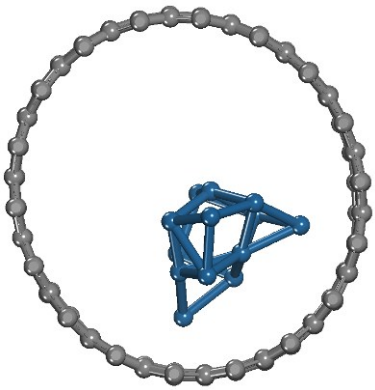
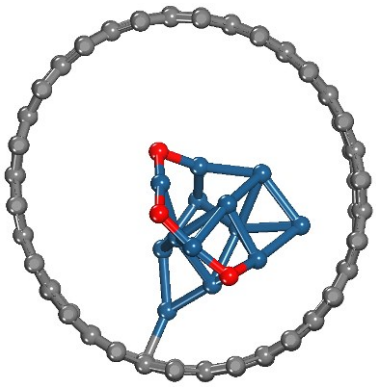
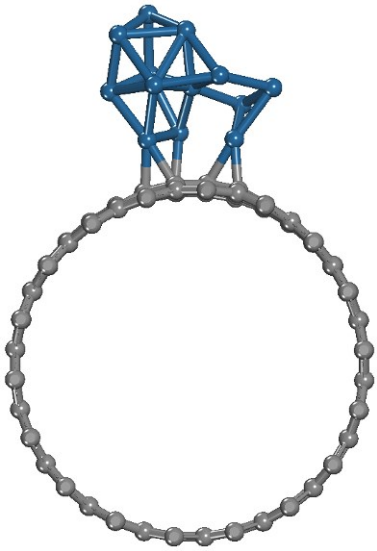
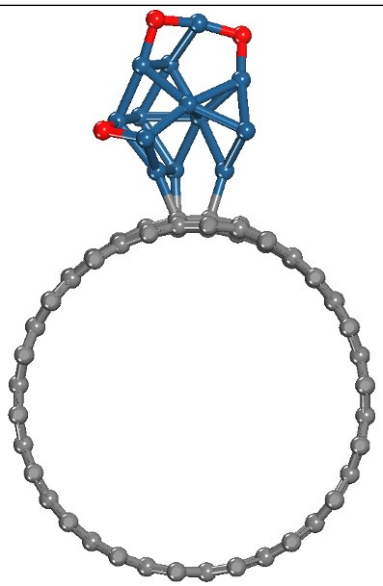
Pt_9-*out*-**CNT(12,0)**		Pt_9-3O-*out*-**CNT(12,0)**	
Pt_9-6O-*out*-**CNT(12,0)**		Pt_9-9O-*out*-**CNT(12,0)**	

Supplementary Figure S4. Optimized geometries of the encapsulated and supported Pt clusters (CNT(10,0), CNT(6,6), CNT(13,0), CNT(10,10), and the clusters adsorbed with a monolayer of oxygen. Pt_{13}-CNT(18,0) with adsorbed 3O atoms was used to examine the particle size dependence for comparison.

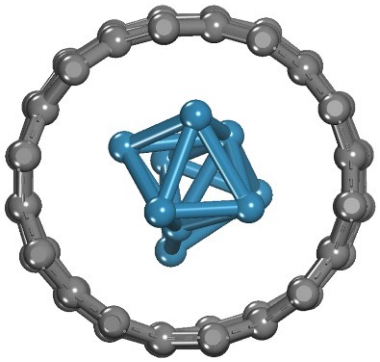
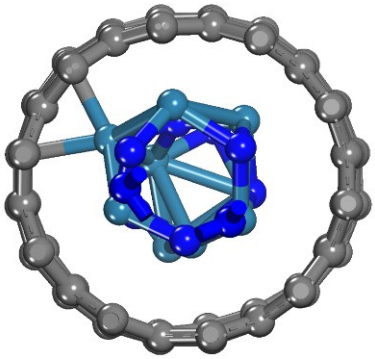
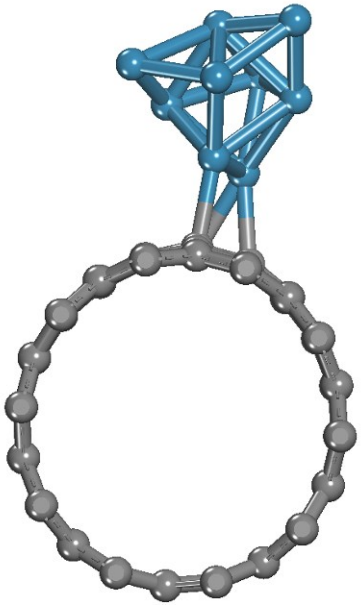
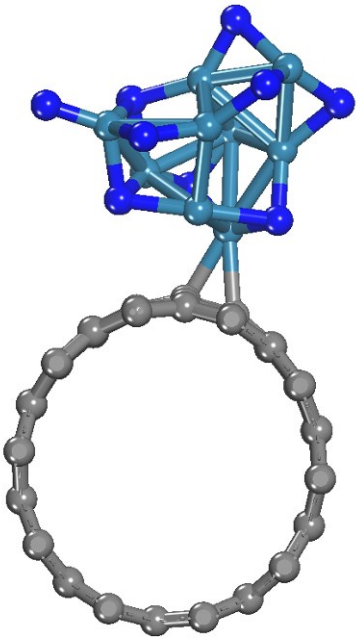
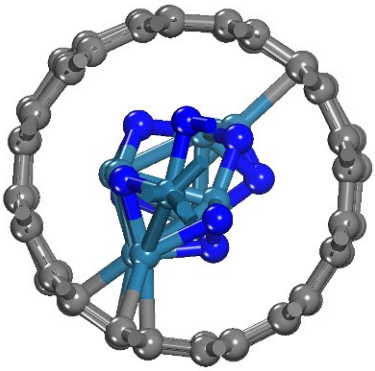
Pt_9-*in*-**CNT(10,0)**		Pt_9-9O-*in*-**CNT(10,0)**	
Pt_9-*out*-**CNT(10,0)**		Pt_9-9O-*out*-**CNT(10,0)**	
Pt_9-*in*-**CNT(6,6)**		Pt_9-9O-*in*-**CNT(6,6)**	

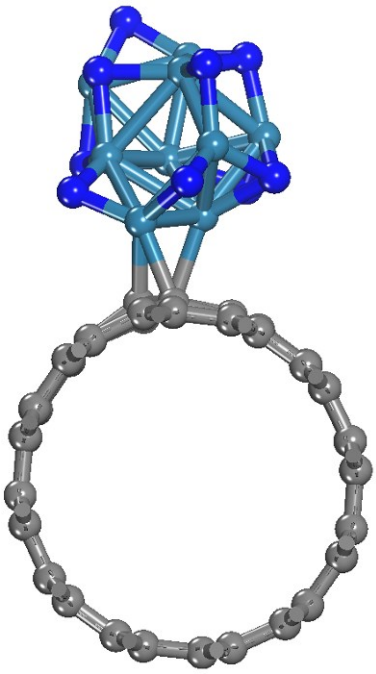
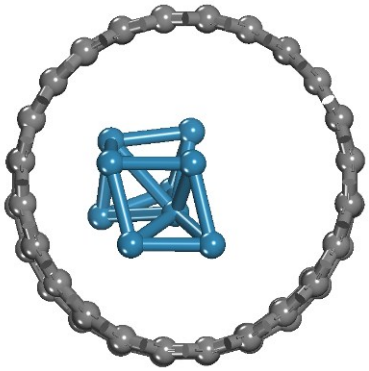
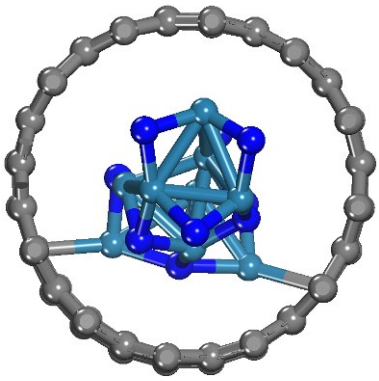
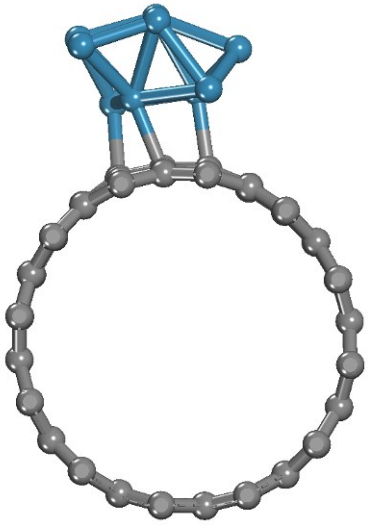
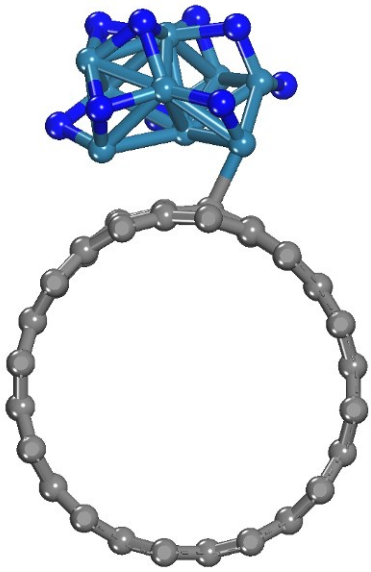
Pt_9-*out*-**CNT(6,6)**		Pt_9-9O-*out*-**CNT(6,6)**	
Pt_9-*in*-**CNT(13,0)**		Pt_9-9O-*in*-**CNT(13,0)**	

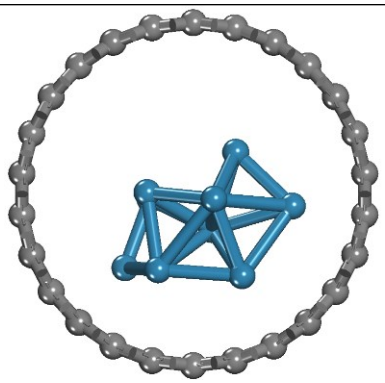
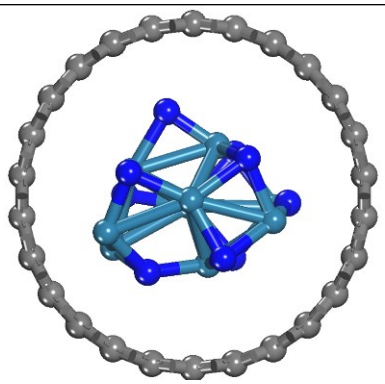
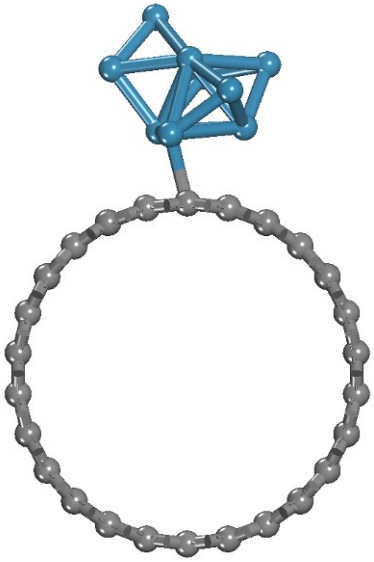
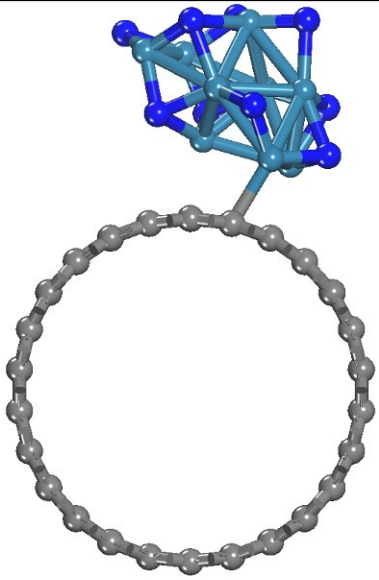
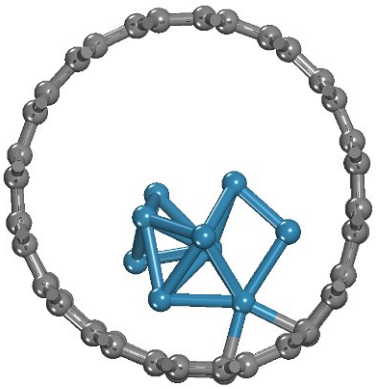
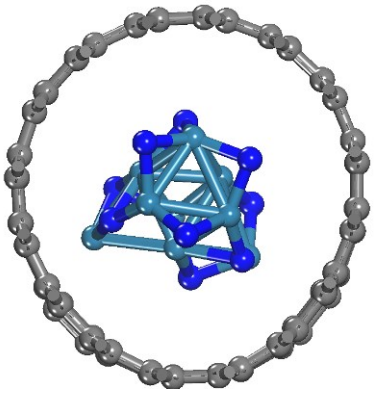
Pt_9-*out*-**CNT(13,0)**		Pt_9-9O-*out*-**CNT(13,0)**	
Pt_9-*in*-**CNT(10,10)**		Pt_9-9O-*in*-**CNT(10,10)**	
Pt_9-*out*-**CNT(10,10)**		Pt_9-9O-*out*-**CNT(10,10)**	

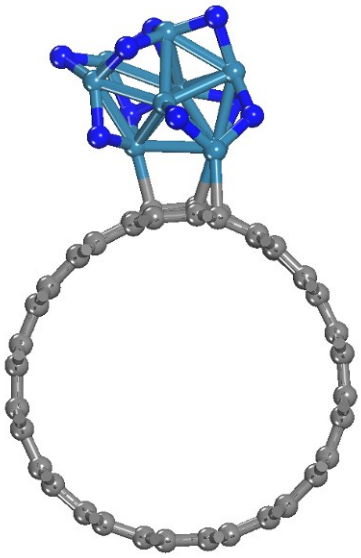
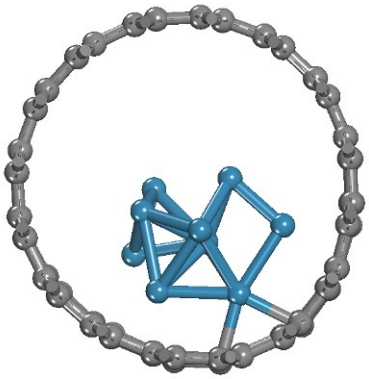
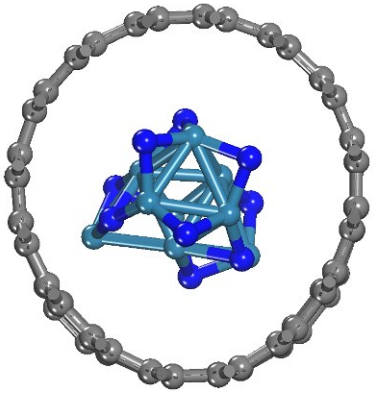
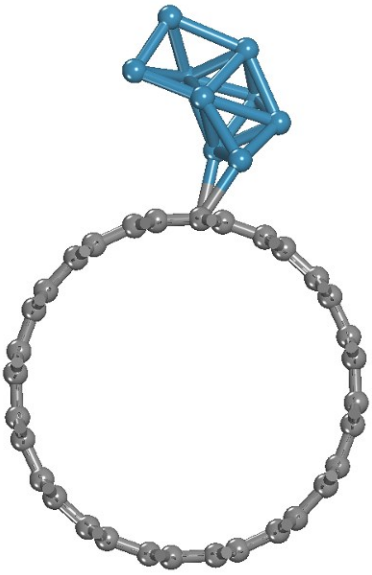
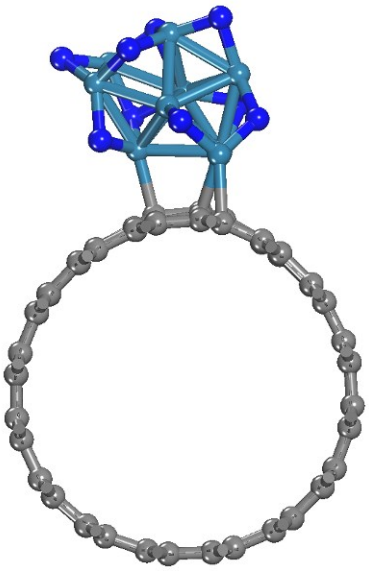
Pt_{13}-*in*-**CNT(18,0)**		Pt_{13}-3O-*in*-**CNT(18,0)**	
Pt_{13}-*out*-**CNT(18,0)**		Pt_{13}-3O-*out*-**CNT(18,0)**	

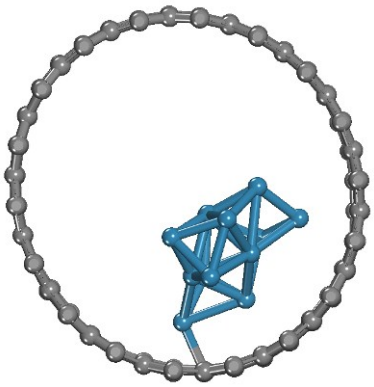
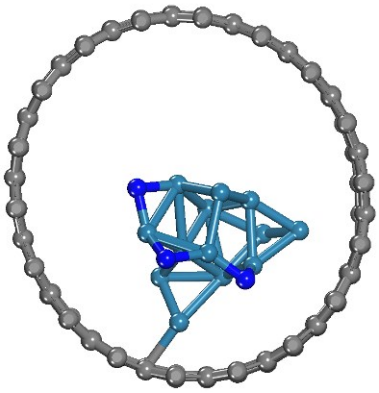
Supplementary Figure S5. Optimized geometries of the encapsulated and supported Re clusters (CNT(10,0), CNT(6,6), CNT(13,0), CNT(10,10), CNT(8,8), CNT(12,0) and the clusters adsorbed with a monolayer of nitrogen. Re_{13}-CNT(18,0) with adsorbed 3N atoms was used to examine the size dependence for comparison.

Re_9-*in*-**CNT(10,0)**		Re_9-9N-*in*-**CNT(10,0)**	
Re_9-*out*-**CNT(10,0)**		Re_9-9N-*out*-**CNT(10,0)**	
Re_9-*in*-**CNT(6,6)**		Re_9-9N-*in*-**CNT(6,6)**	

Re_9-*out*-**CNT(6,6)**		Re_9-9N-*out*-**CNT(6,6)**	
Re_9-*in*-**CNT(12,0)**		Re_9-9N-*in*-**CNT(12,0)**	
Re_9-*out*-**CNT(12,0)**		Re_9-9N-*out*-**CNT(12,0)**	

Re_9-*in*-**CNT(13,0)**		Re_9-9N-*in*-**CNT(13,0)**	
Re_9-*out*-**CNT(13,0)**		Re_9-9N-*out*-**CNT(13,0)**	
Re_9-*in*-**CNT(8,8)**		Re_9-9N-*in*-**CNT(8,8)**	

Re_9-*out*-**CNT(8,8)**		Re_9-9N-*out*-**CNT(8,8)**	
Re_9-*in*-**CNT(10,10)**		Re_9-9N-*in*-**CNT(10,10)**	
Re_9-*out*-**CNT(10,10)**		Re_9-9N-*out*-**CNT(10,10)**	

Re_{13}-*in*-**CNT(18,0)**		Re_{13}-3N-*in*-**CNT(18,0)**	
Re_{13}-*out*-**CNT(18,0)**		Re_{13}-3N-*out*-**CNT(18,0)**