Electronic Supplementary Information

Leveraging Metaheuristics to Uncover Water Confinement in Multilayer Graphynes

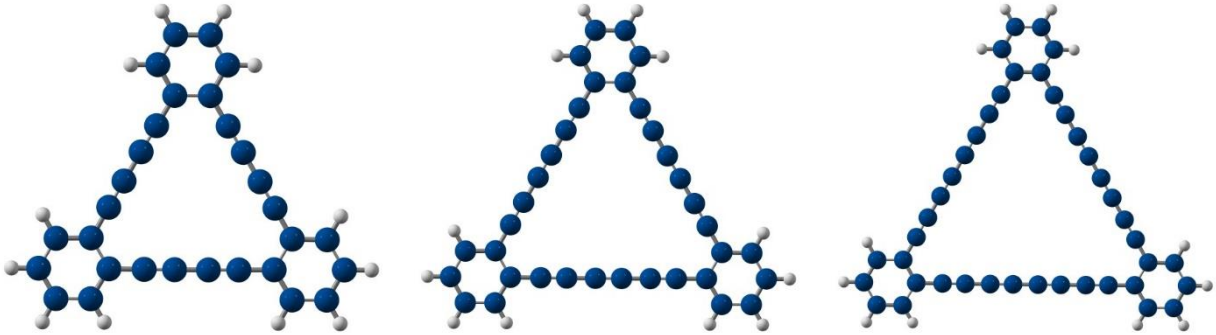
Megha Rajeevan[a] *and Rotti Srinivasamurthy Swathi*[a*]

[a]School of Chemistry, Indian Institute of Science Education and Research Thiruvananthapuram (IISER TVM), Thiruvananthapuram 695 551, India

[*]E-mail: swathi@iisertvm.ac.in

O-H bond distance (Å)	0.9572
O-M distance (Å)	0.1500
HOH angle (°)	104.52
ϵ_{LJ}(O-O) (kcal/mol)	0.155
σ_{LJ}(O-O) (Å)	3.154
$q_M\,(e)$	-1.04
$q_H\,(e)$	0.52

Table S1. Structural and potential parameters of the TIP4P water model[1].



(a) (b) (c)

Figure S1. The single-pore models of (a) γ-GY-2, (b) γ-GY-3, and (c) γ-GY-4.

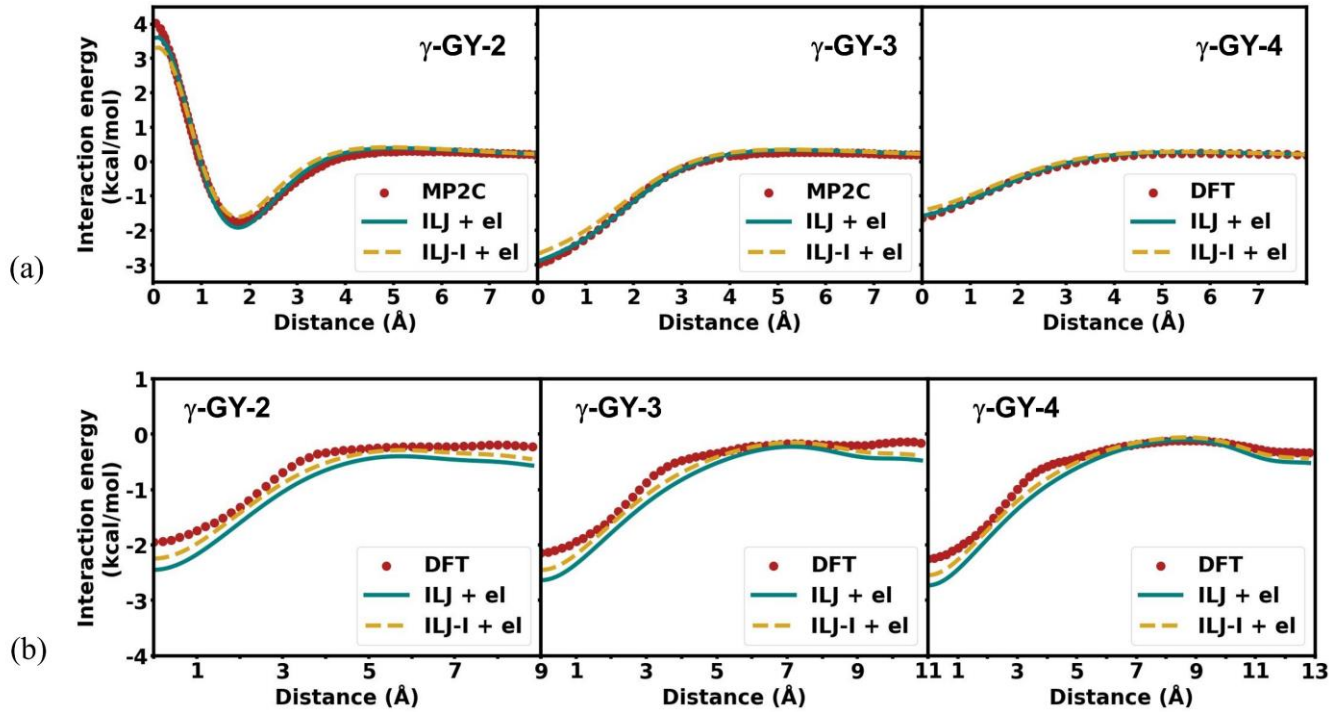


Figure S2. Interaction energy profiles evaluated using the reference electronic structure method and fitted intermolecular analytic potentials with electrostatic and non-electrostatic components (ILJ and ILJ-I potentials) for the (a) vertical and (b) lateral motion of a single water molecule through and above the triangular pores of various GYs, respectively.

ILJ-I potential				
Interaction	GY	ε (kcal/mol)	r_m (Å)	β
C-H_2O	γ-GY-2	0.209	3.510	8.500
	γ-GY-N (N=3,4)	0.187	3.610	9.000
H-H_2O	γ-GY-N (N=2,3,4)	0.150	3.500	8.500

Table S2. Numerical values of the parameters of the ILJ potential (denoted as ILJ-I) obtained after the inclusion of interaction energy profiles corresponding to the lateral motion of a water molecule above GY models in the reference data for parametrization.

H-ILP								
Interaction	GY	α	β (Å)	γ (Å)	ε (kcal/mol)	C (kcal/mol)	r^{eff} (Å)	C_6 (kcal Å^6/mol)
C-C	γ-GY-N (N=2,3,4)	11.999	2.887	0.958	0.150	3.000	3.518	583.456

Table S3. Numerical values of parameters of the H-ILP obtained after the inclusion of electrostatics in the parametrization of the potential.

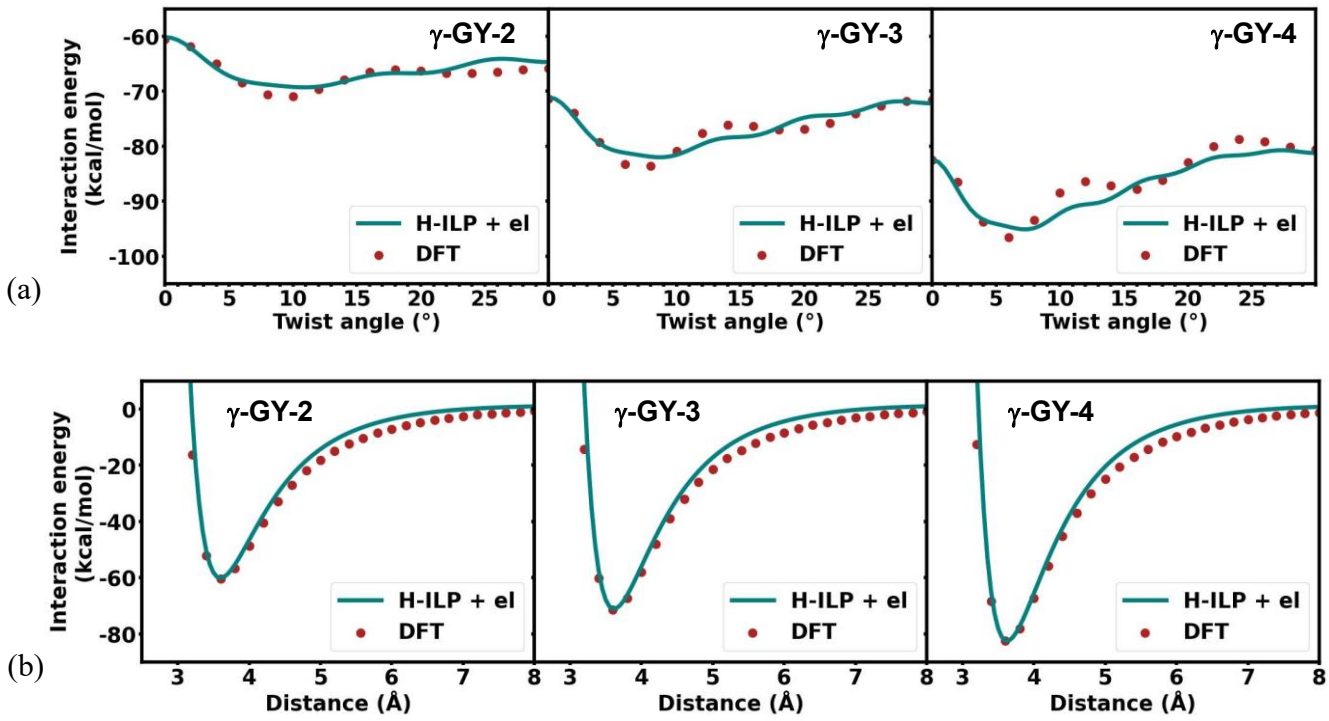


Figure S3. A comparison of the (a) twisting and (b) stacking interaction energy profiles obtained using DFT and H-ILP with electrostatics for various γ-GY bilayers.

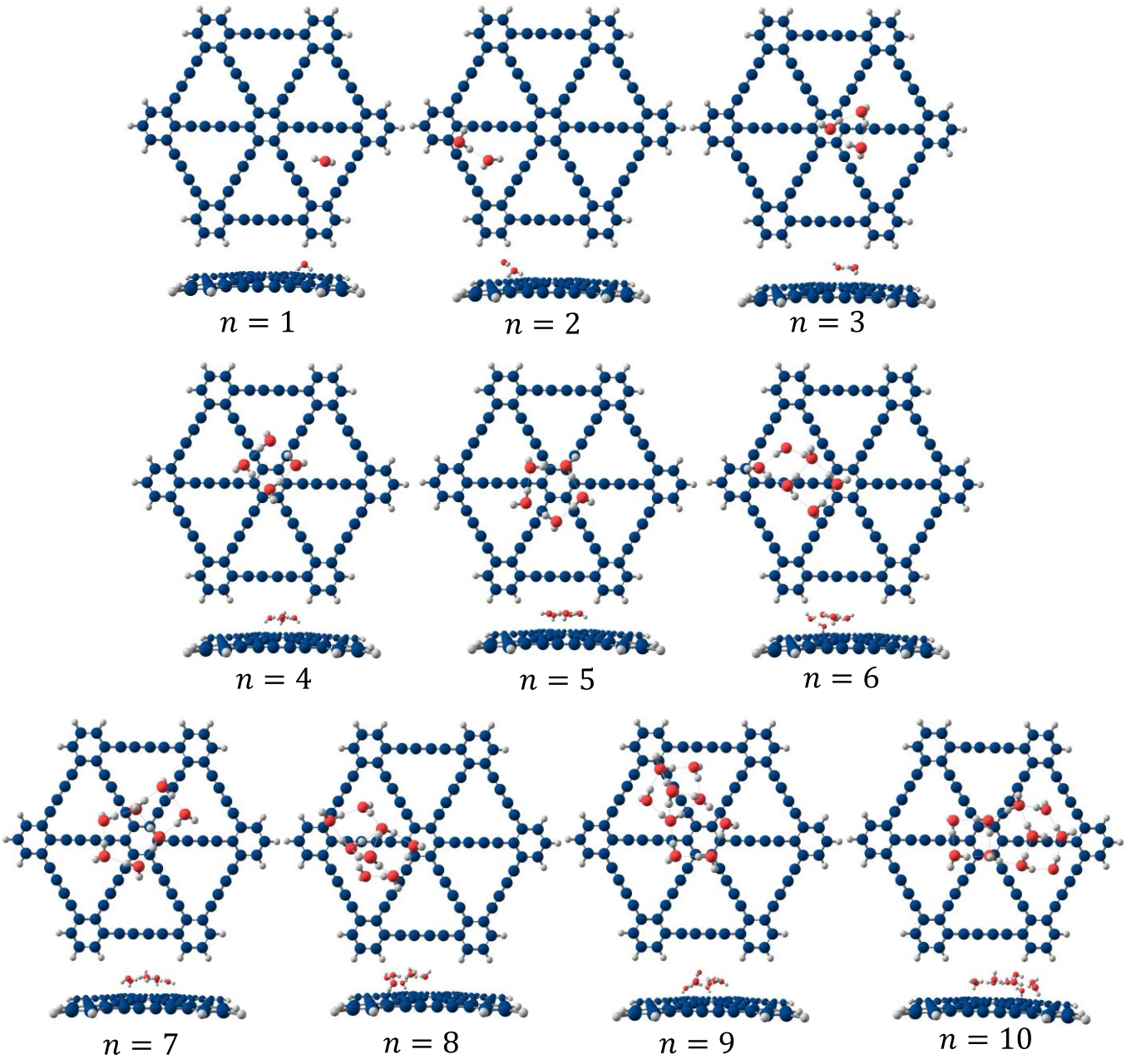


Figure S4. Putative global minimum geometries (top and side views) obtained using PSO for the adsorption of 1-10 water molecules on monolayer γ-GY-2.

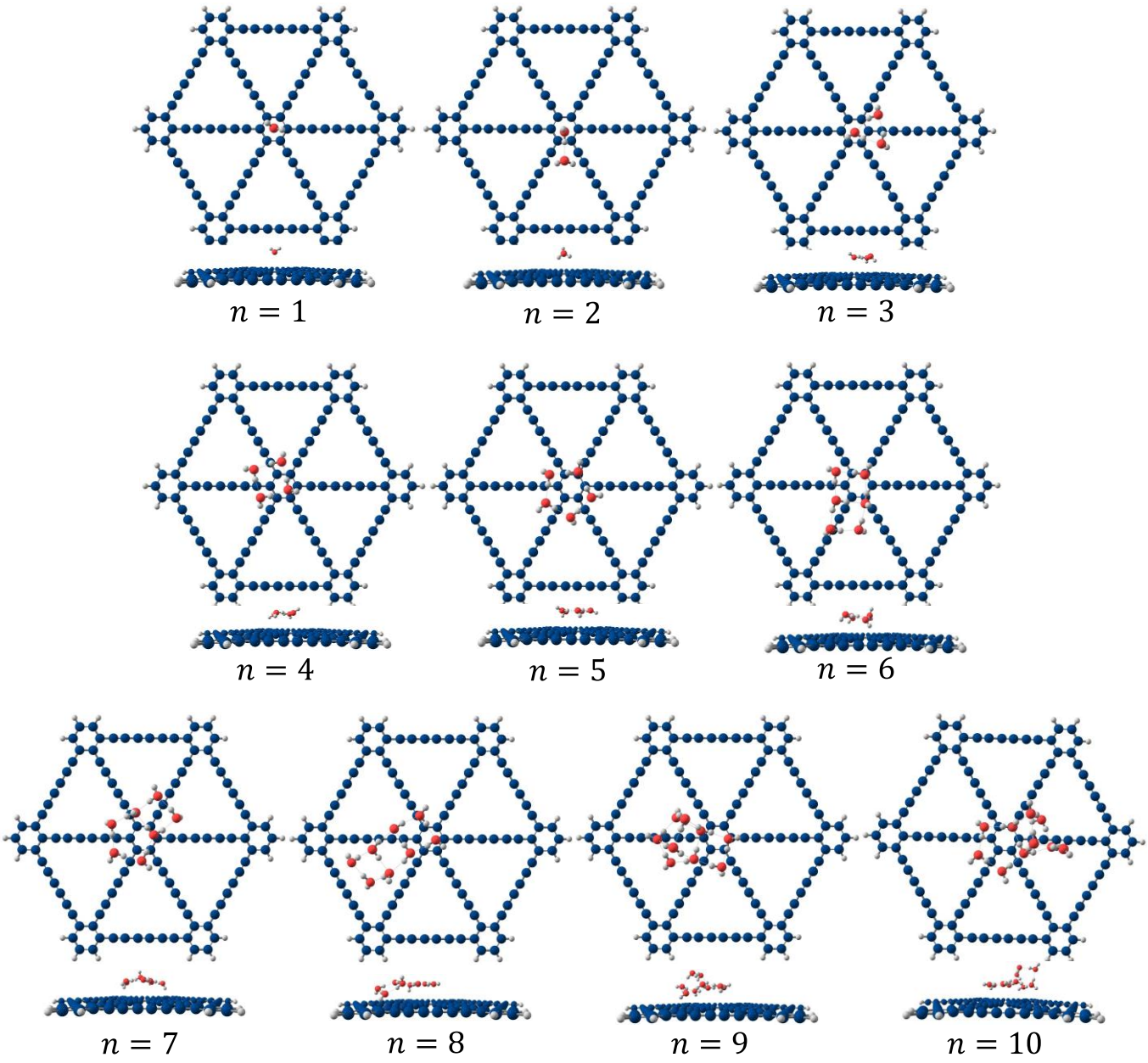


Figure S5. Putative global minimum geometries (top and side views) obtained using PSO for the adsorption of 1-10 water molecules on monolayer γ-GY-3.

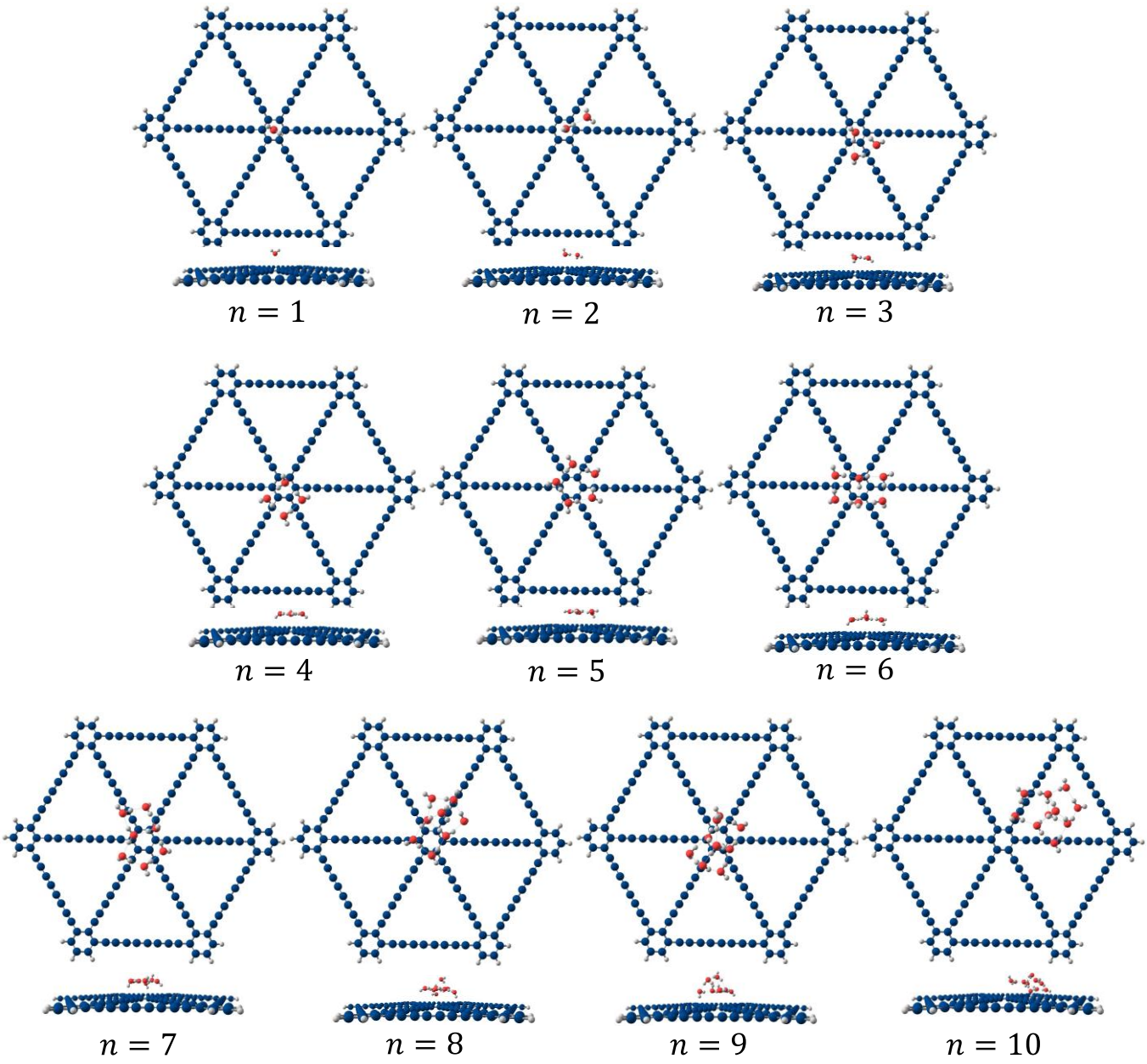


Figure S6. Putative global minimum geometries (top and side views) obtained using PSO for the adsorption of 1-10 water molecules on monolayer γ-GY-4.

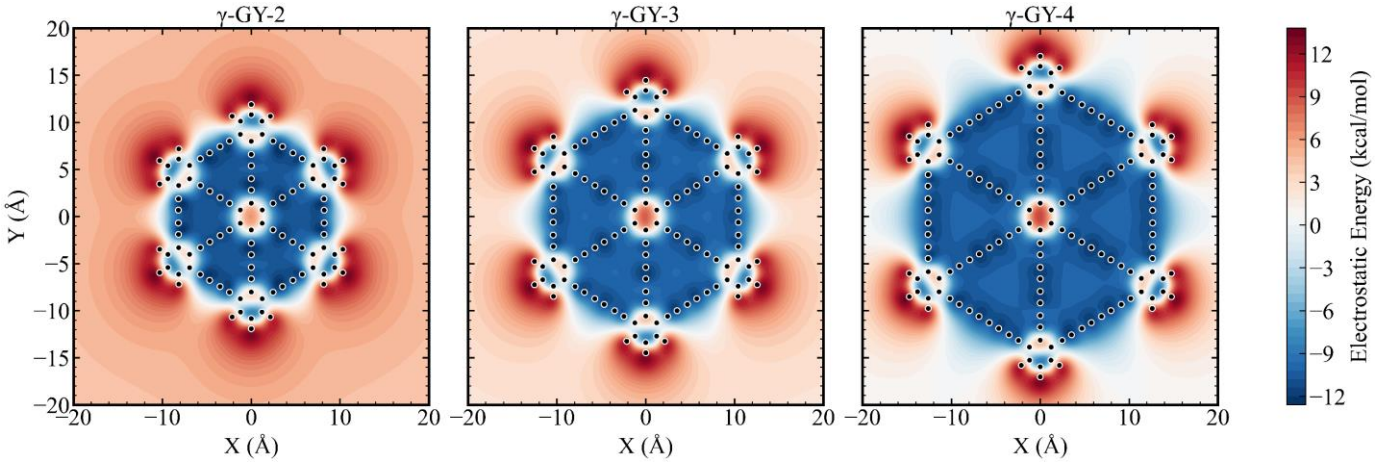


Figure S7. The electrostatic potential energy surfaces of γ-GY-2, γ-GY-3, and γ-GY-4 obtained using a lateral scan of a positive text charge over the GY models at a distance of 1.5 Å from the GY plane.

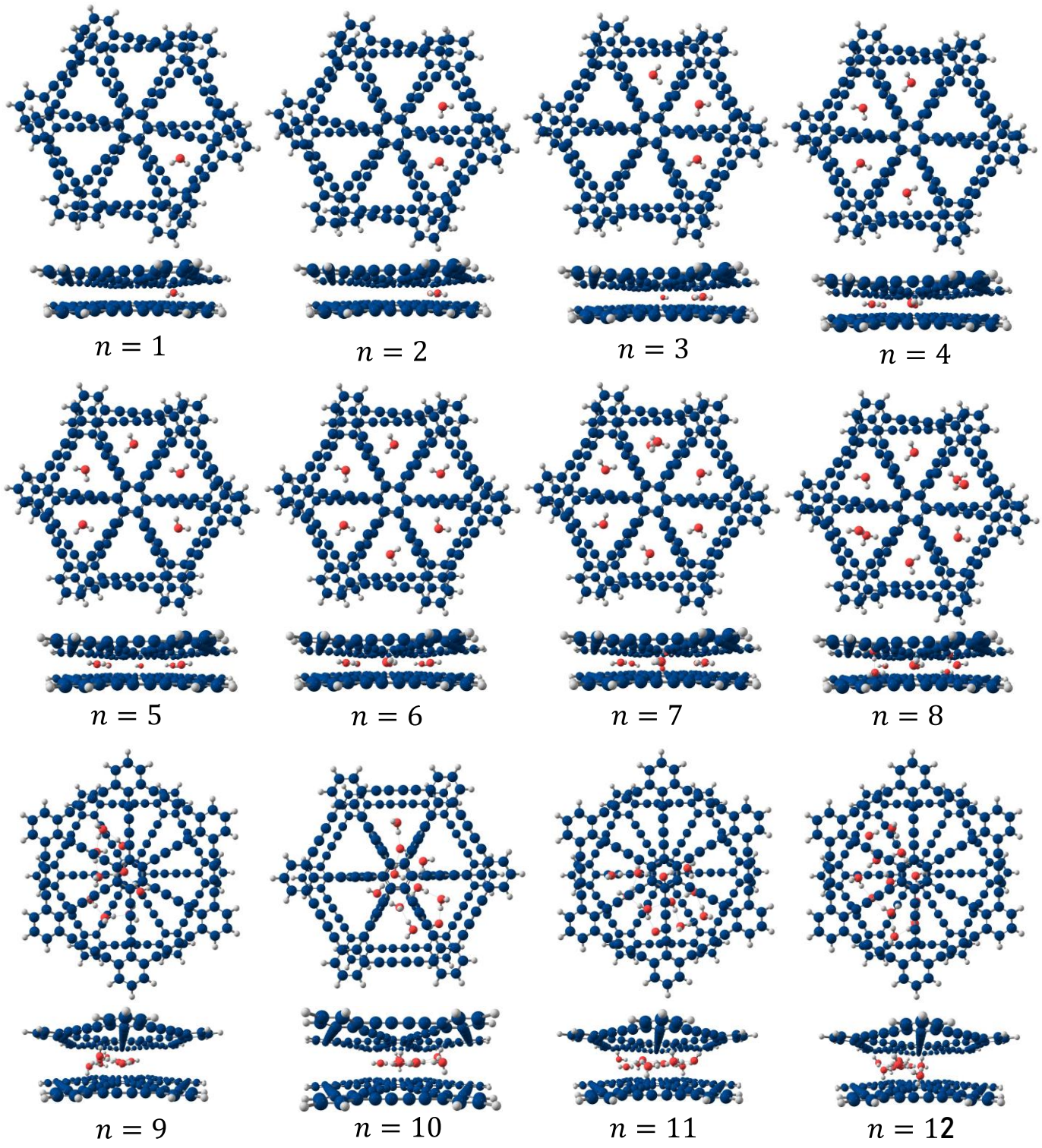


Figure S8. Putative global minimum geometries (top and side views) obtained using PSO for the intercalation of 1-12 water molecules within bilayer γ-GY-2.

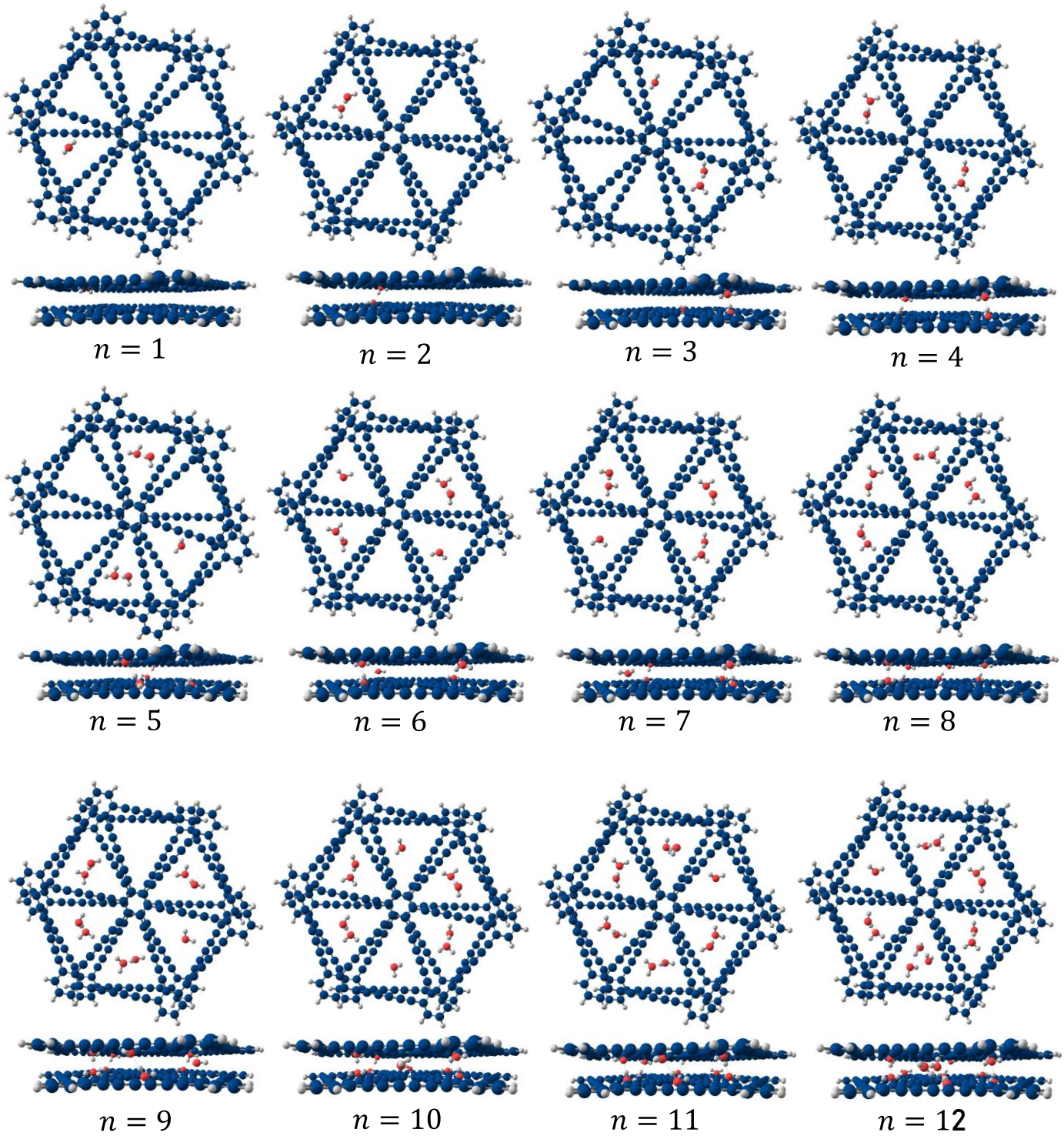


Figure S9. Putative global minimum geometries (top and side views) obtained using PSO for the intercalation of 1-12 water molecules within bilayer γ-GY-3.

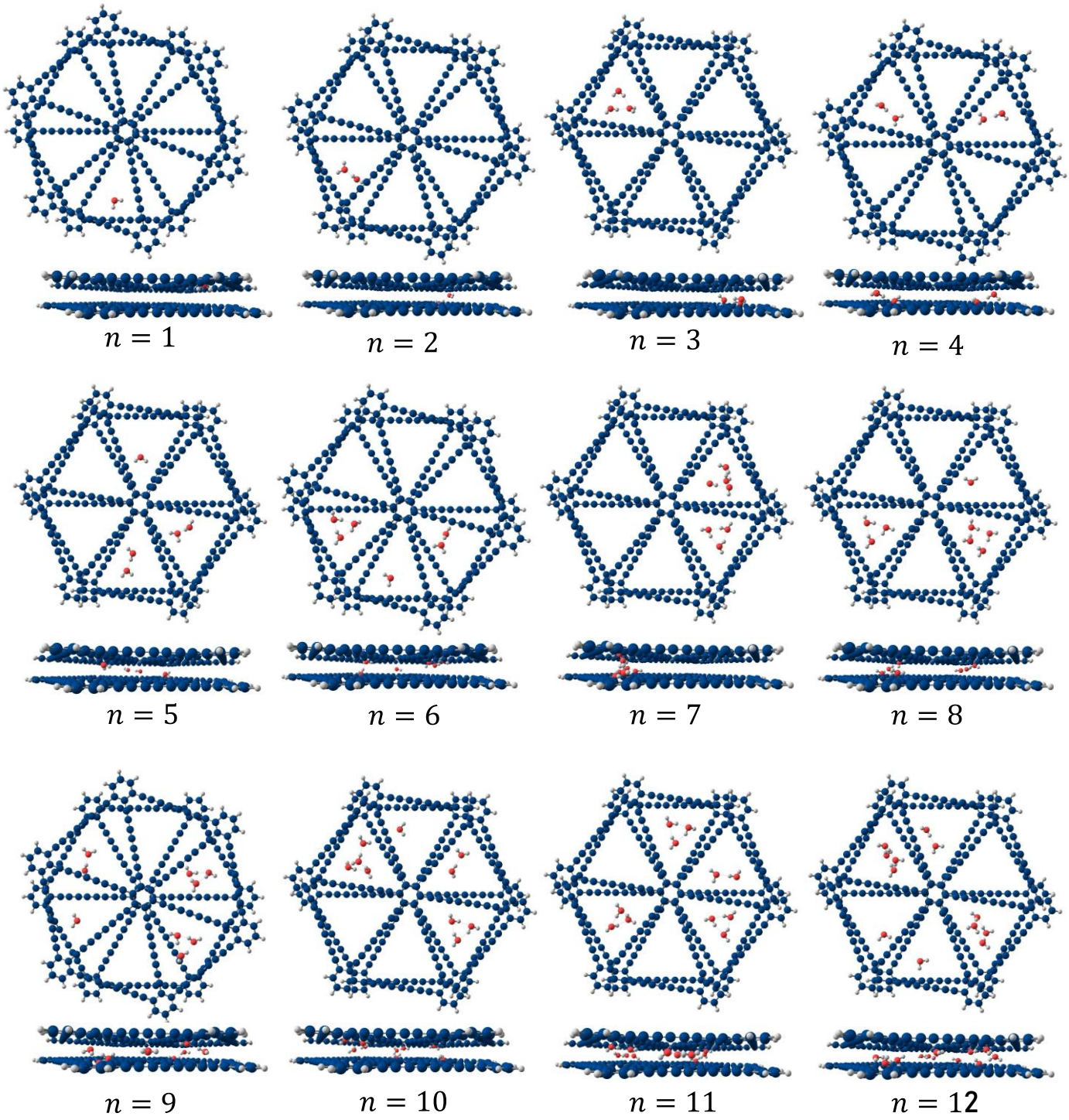


Figure S10. Putative global minimum geometries (top and side views) obtained using PSO for the intercalation of 1-12 water molecules within bilayer γ-GY-4.

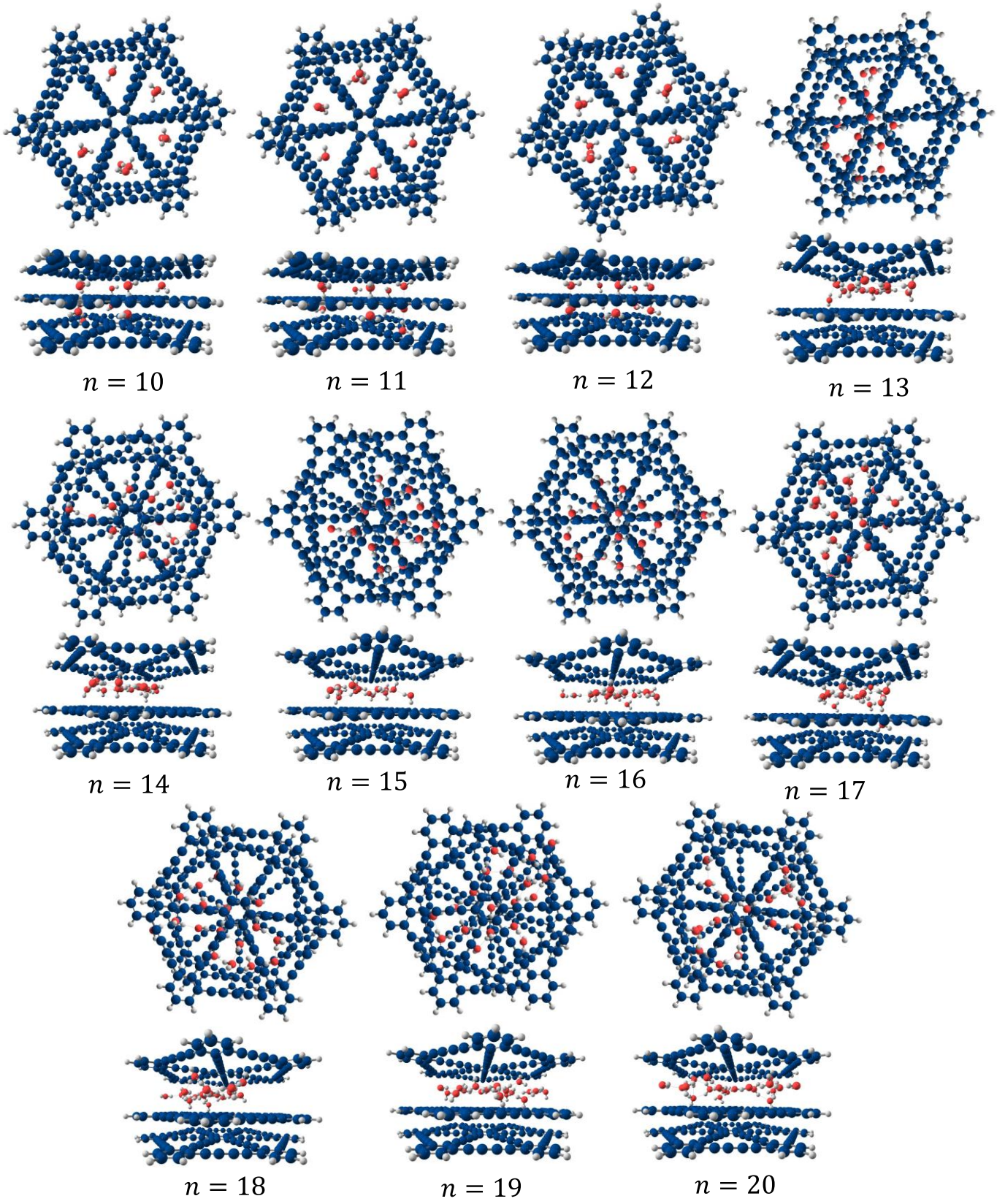


Figure S11. Putative global minimum geometries (top and side views) obtained using PSO for the intercalation of 10-20 water molecules within trilayer γ-GY-2.

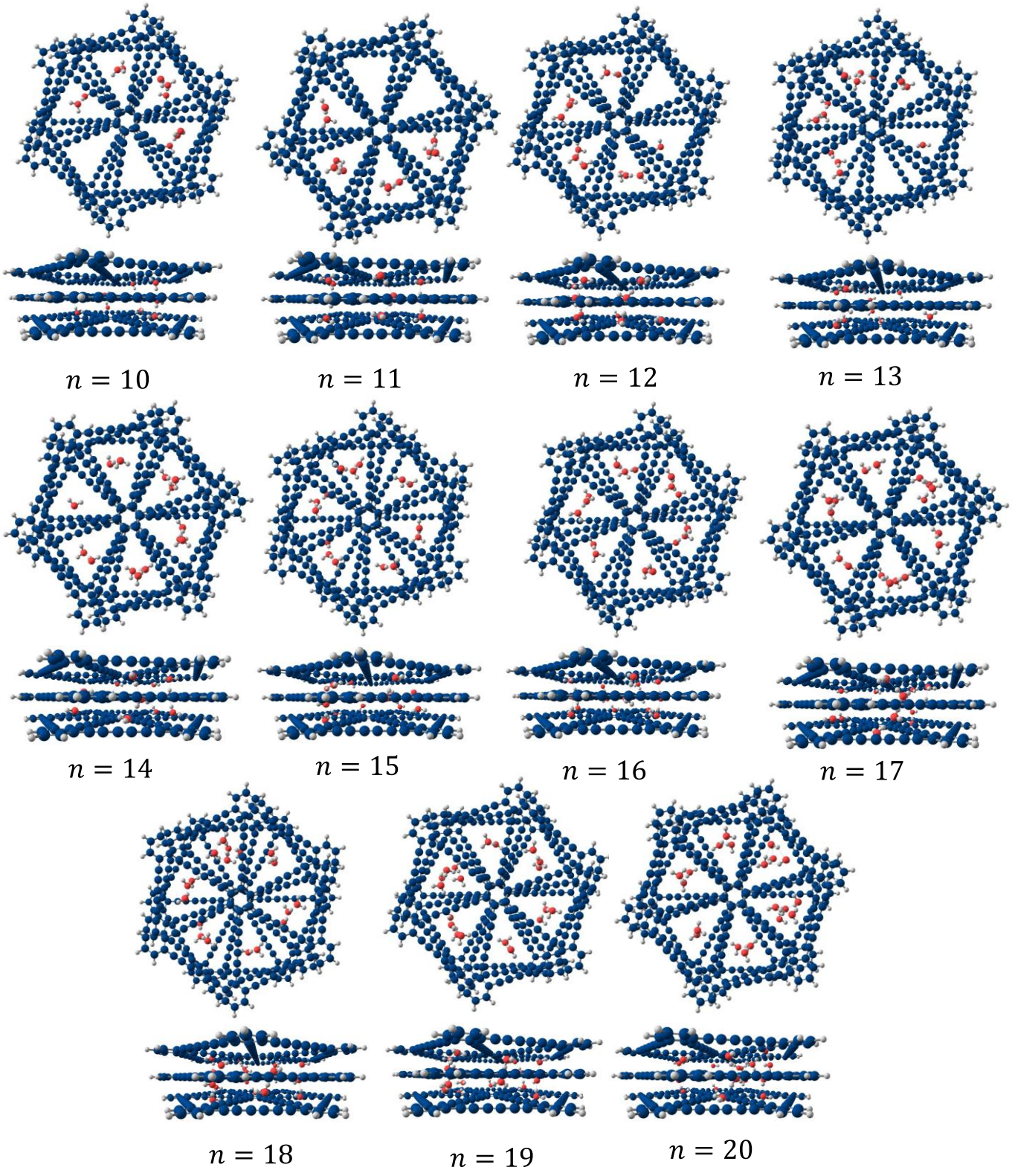


Figure S12. Putative global minimum geometries (top and side views) obtained using PSO for the intercalation of 10-20 water molecules within trilayer γ-GY-3.

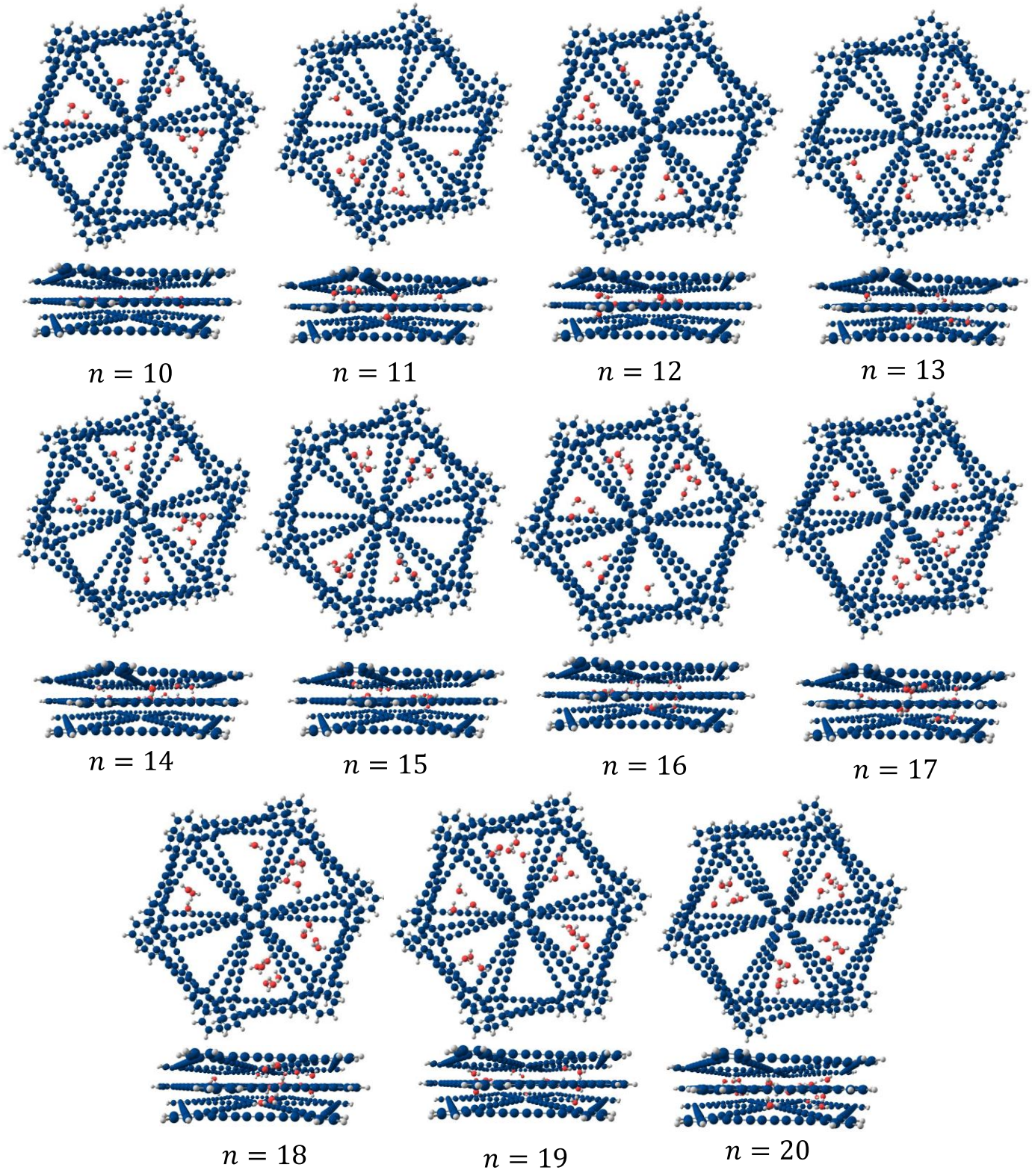


Figure S13. Putative global minimum geometries (top and side views) obtained using PSO for the intercalation of 10-20 water molecules within trilayer γ-GY-4.

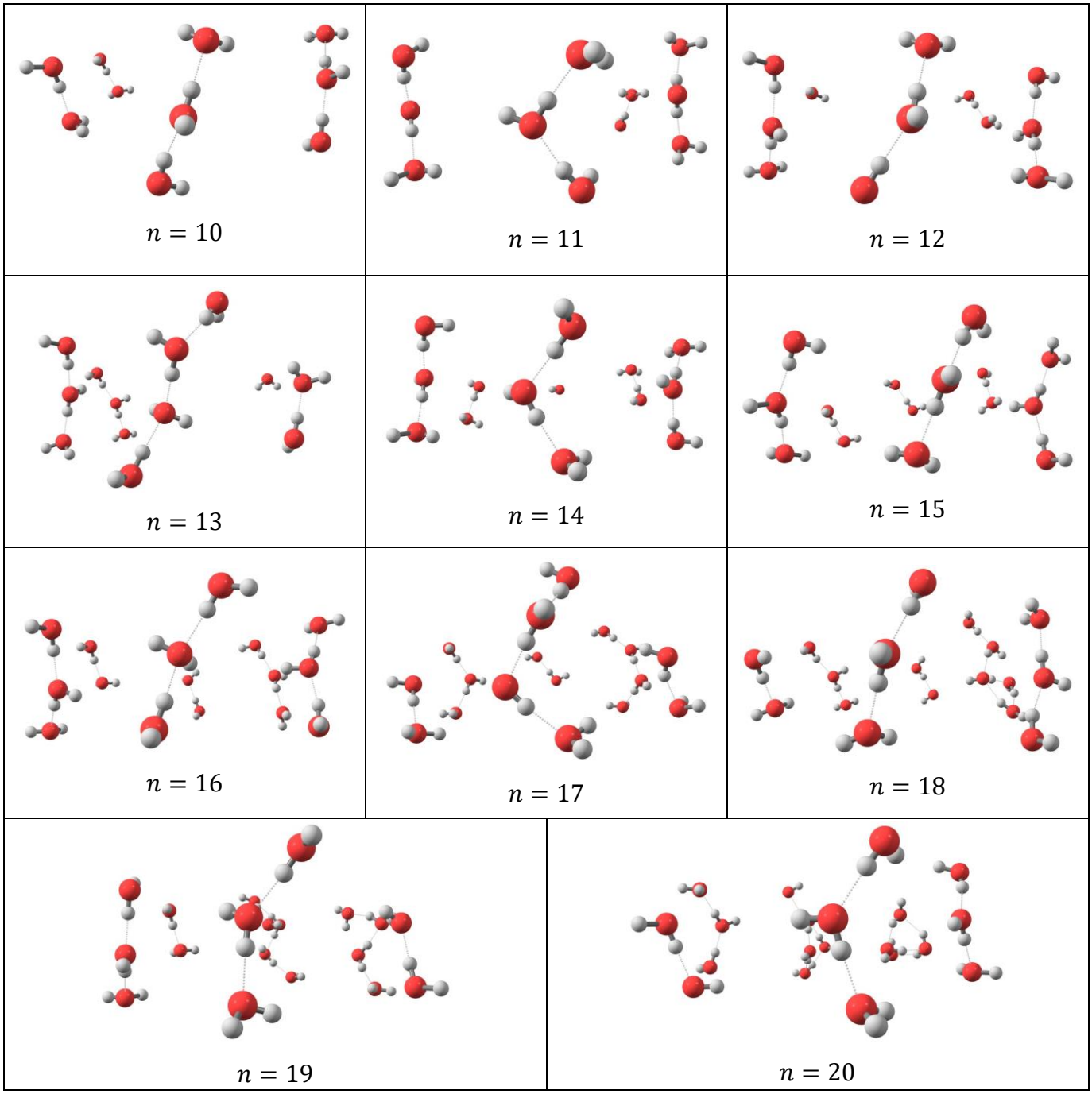
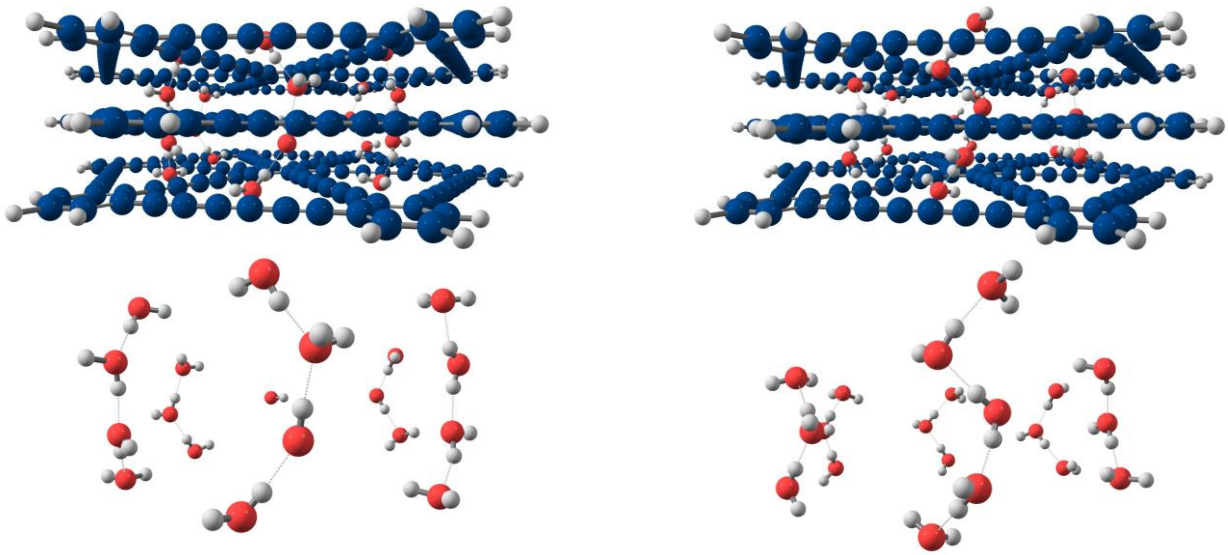


Figure S14. The geometries of 10-20 water molecules confined within trilayer γ-GY-3 (after removing the GY framework) as seen in the putative global minimum geometries obtained using PSO.



(a) (b)

Figure S15. The putative global minimum geometries of water clusters of size (a) 19 and (b) 20 confined in trilayer γ-GY-3 obtained using PSO with unconstrained local optimization. For the sake of clarity, the geometries of clusters after removing the GY framework are also shown.

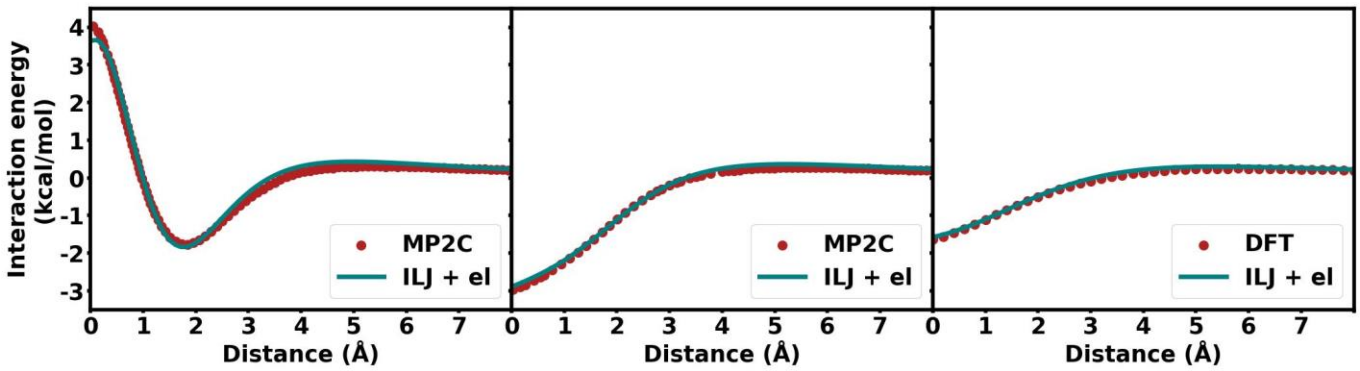


Figure S16. Interaction energy profiles evaluated using the reference electronic structure method and fitted intermolecular analytic potential with electrostatic and non-electrostatic components (ILJ potential) for the interaction of a single water molecule with various GYs. Here, for the analytical potential, water is considered within SPC/E description[2].

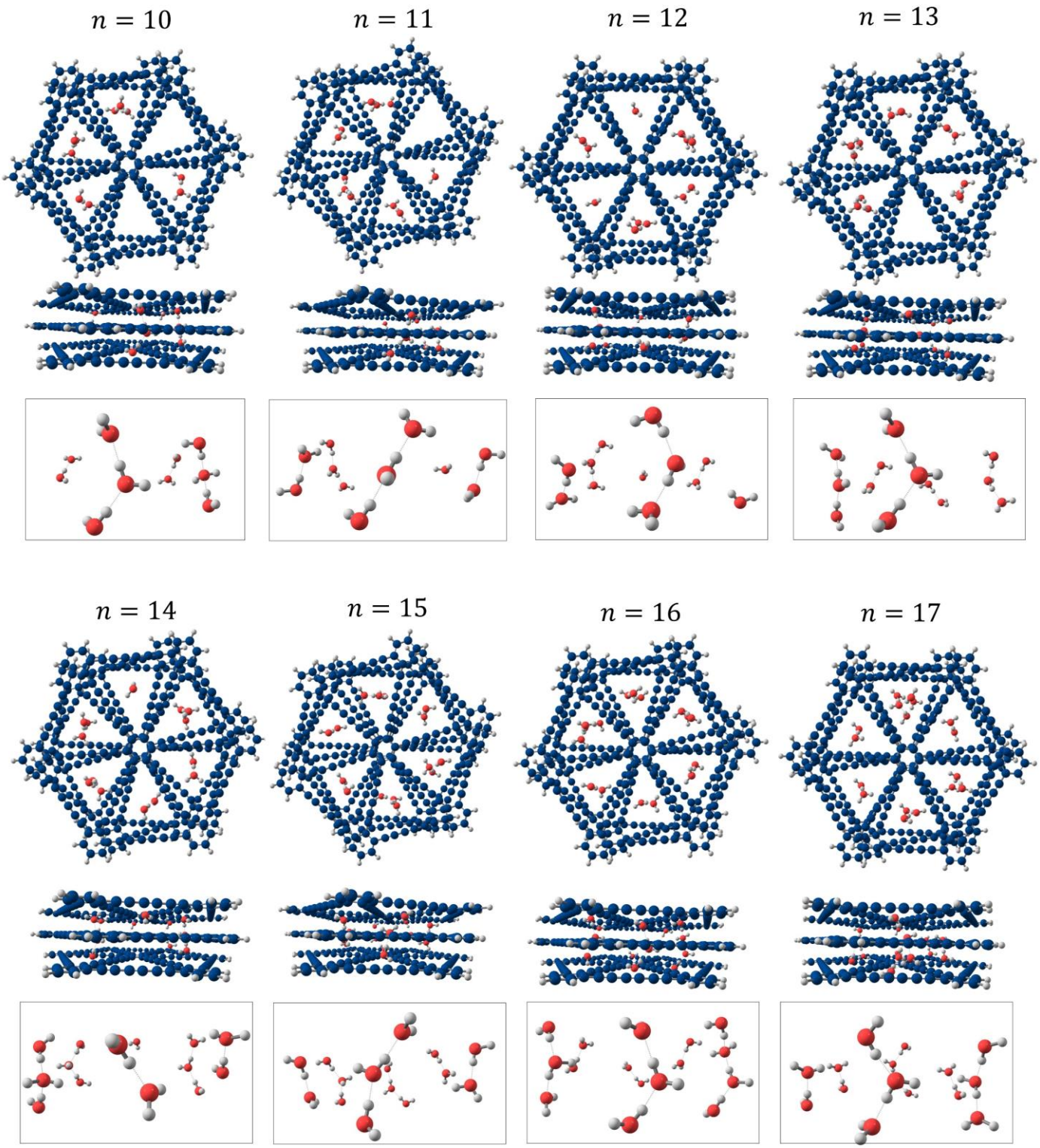


Figure S17. Putative global minimum geometries (top and side views) obtained using PSO for the intercalation of 10-17 water molecules within trilayer γ-GY-3, with the water molecules described using the SPC/E model.[2] For the sake of clarity, the geometries of clusters after removing the GY frameworks are also shown.

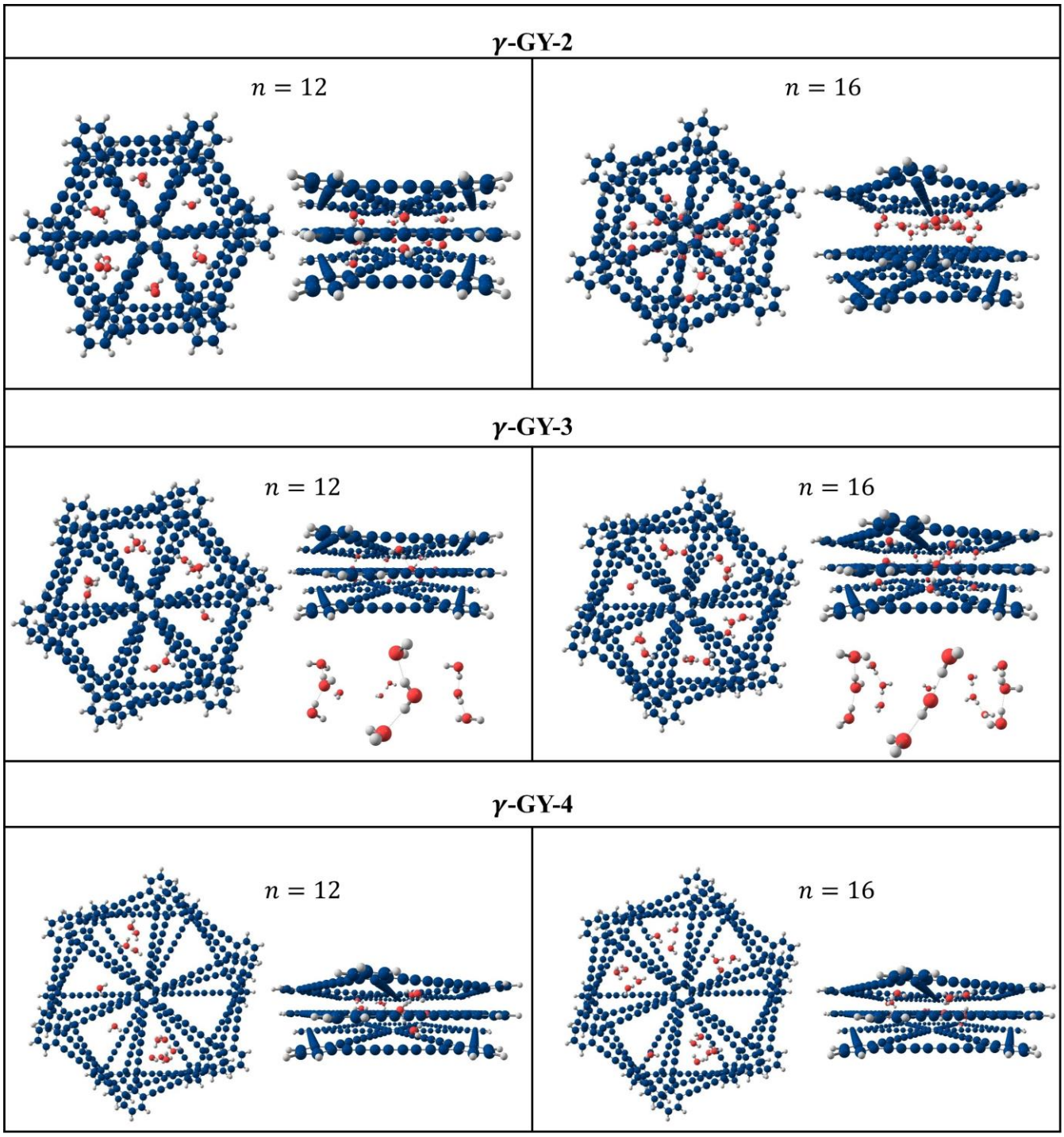


Figure S18. Putative global minimum geometries (top and side views) obtained using PSO for the intercalation of 12 and 16 water molecules within trilayer γ-GY-N (N=2-4), with the GY-water non-electrostatic interactions described using the ILJ-I potential. For the sake of clarity, the geometries of clusters after removing the GY framework are also shown for γ-GY-3.

References

1. W. L. Jorgensen, J. Chandrasekhar, J. D. Madura, R. W. Impey and M. L. Klein, *J. Chem. Phys.*, 1983, **79**, 926-935.
2. H. J. C. Berendsen, J. R. Grigera and T. P. Straatsma, *J. Phys. Chem.*, 1987, **91**, 6269-6271.