Electronic Supplementary Information

On assessing the carbon capture performance of graphynes with particle swarm optimization

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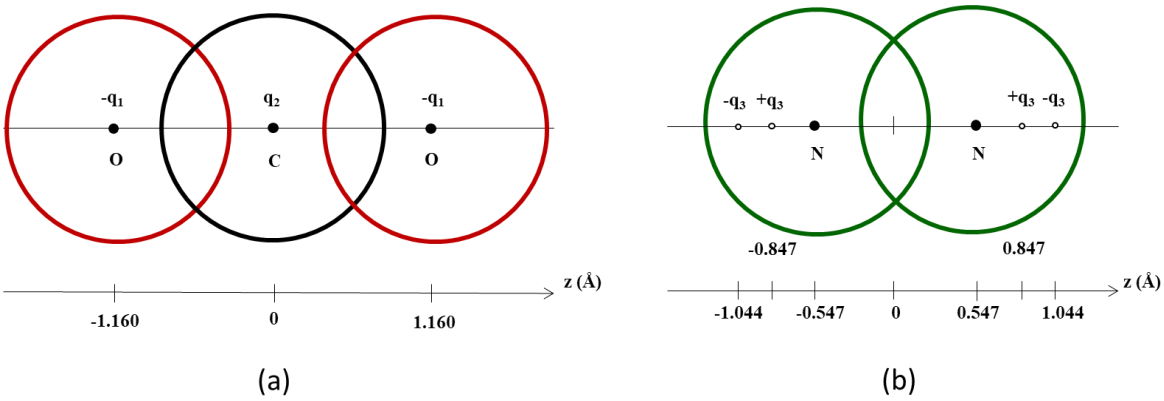


Figure S1. Partial charge distributions in CO_2 and N_2 molecules (q_1=0.350 $|e|$, q_2=0.700 $|e|$, q_3=0.373 $|e|$).

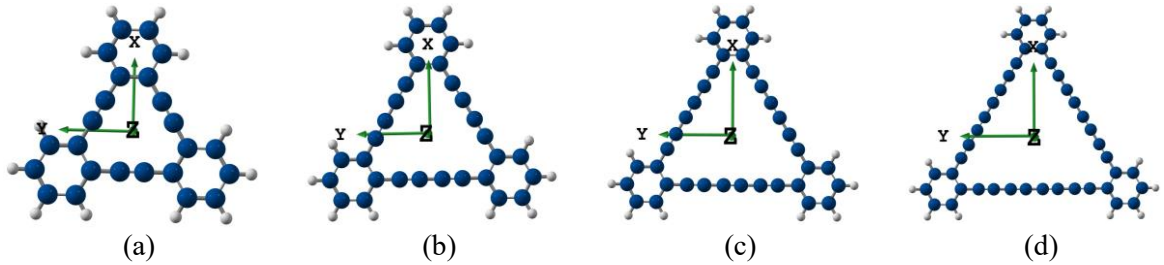
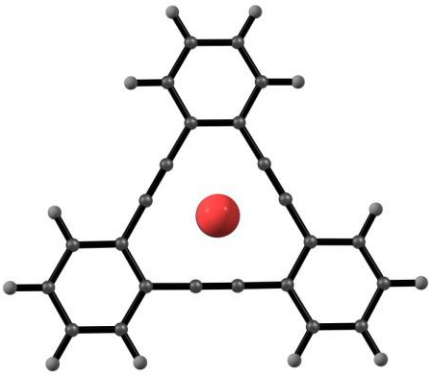
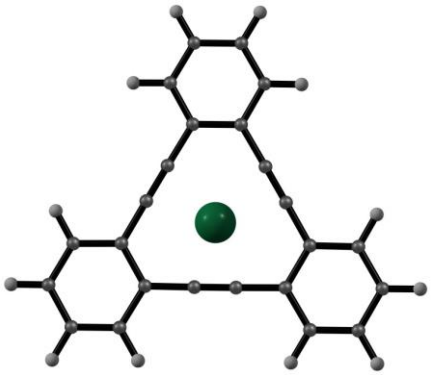


Figure S2. Single-pore model systems of (a) γ-GY-1, (b) γ-GY-2, (c) γ-GY-3, and (4) γ-GY-4 along with a representation of the Cartesian axes used to define the orientations of the molecules.



(a)



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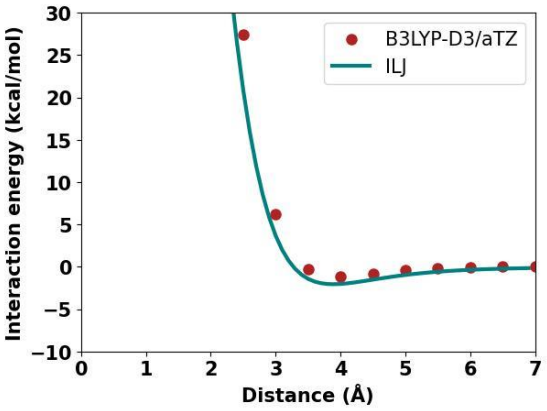
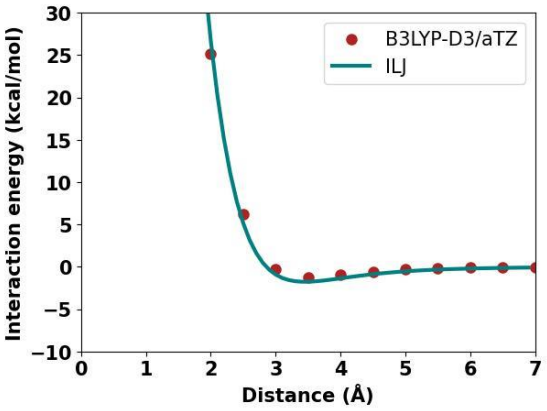

B3LYP-D3/aTZ
ILJ
Interaction energy (kcal/mol)
Distance (Å)

(c)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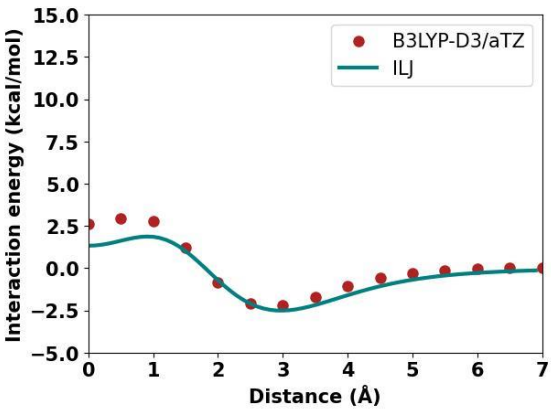
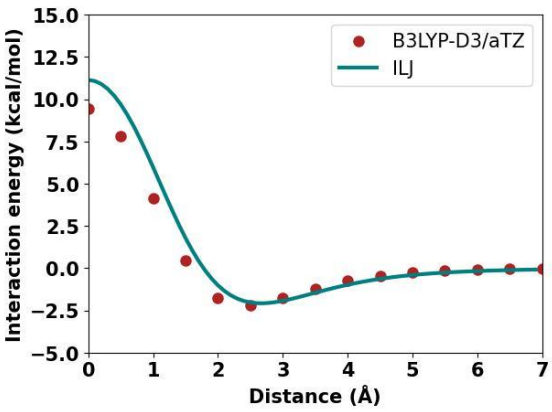
ILJ
Interaction energy (kcal/mol)
Distance (Å)

(d)


B3LYP-D3/aTZ
ILJ
Interaction energy (kcal/mol)
Distance (Å)

(e)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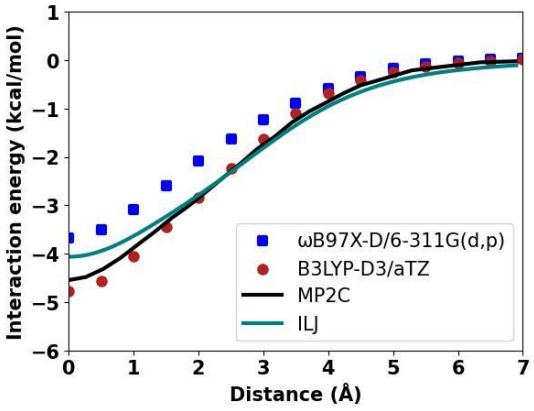
ILJ
Interaction energy (kcal/mol)
Distance (Å)

(f)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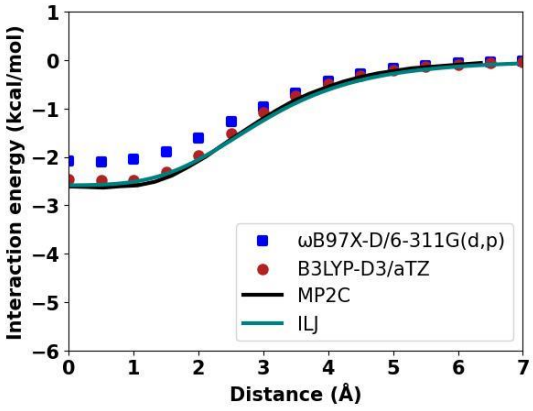
B3LYP-D3/aTZ
MP2C
ILJ
Interaction energy (kcal/mol)
Distance (Å)

(g)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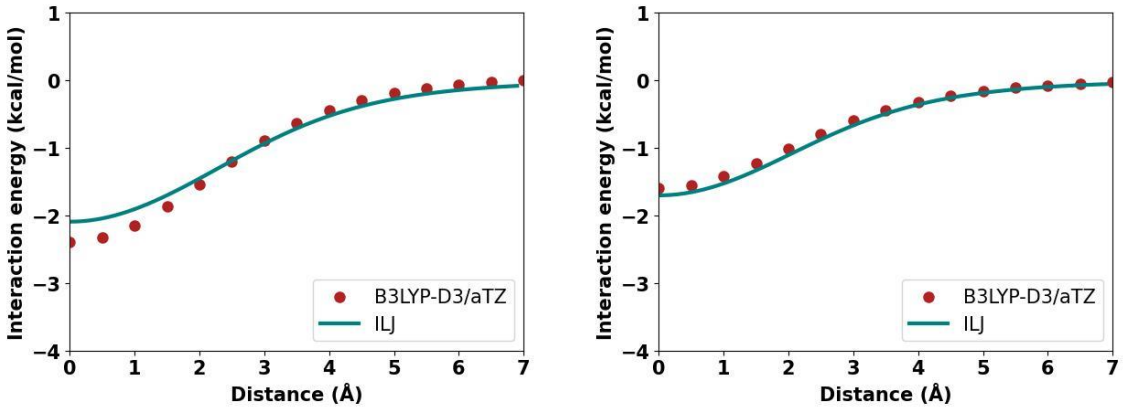
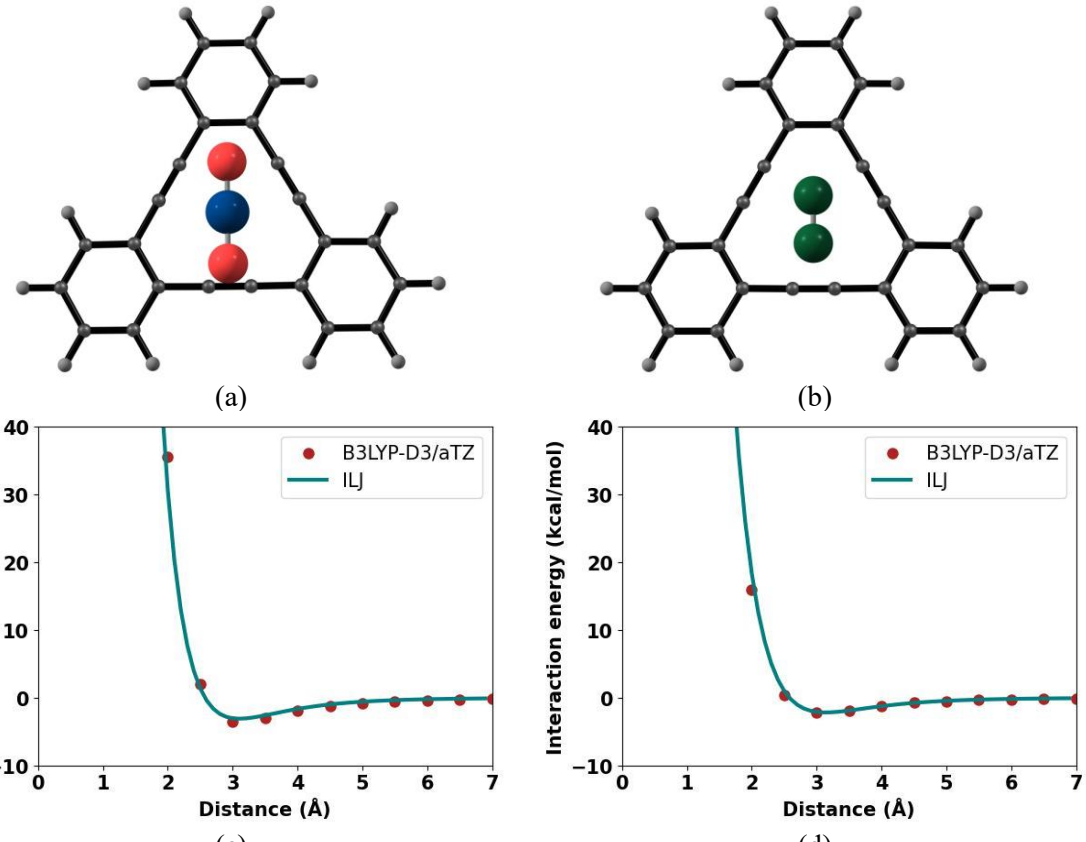
MP2C
ILJ
Interaction energy (kcal/mol)
Distance (Å)

(h)



(i) (j)

Figure S3. Interaction energy profiles evaluated using DFT and ILJ potential for the interaction of CO_2 and N_2 aligned along the Z direction (illustrated in a and b) with γ-GY-1 (c and d), γ-GY-2 (e and f), γ-GY-3 (g and h), and γ-GY-4 (i and j), respectively. Note that the figures in g and h include the MP2C data from reference[1] and the ωB97X-D/6-311G(d,p) data.



(a) (b)

(c) (d)

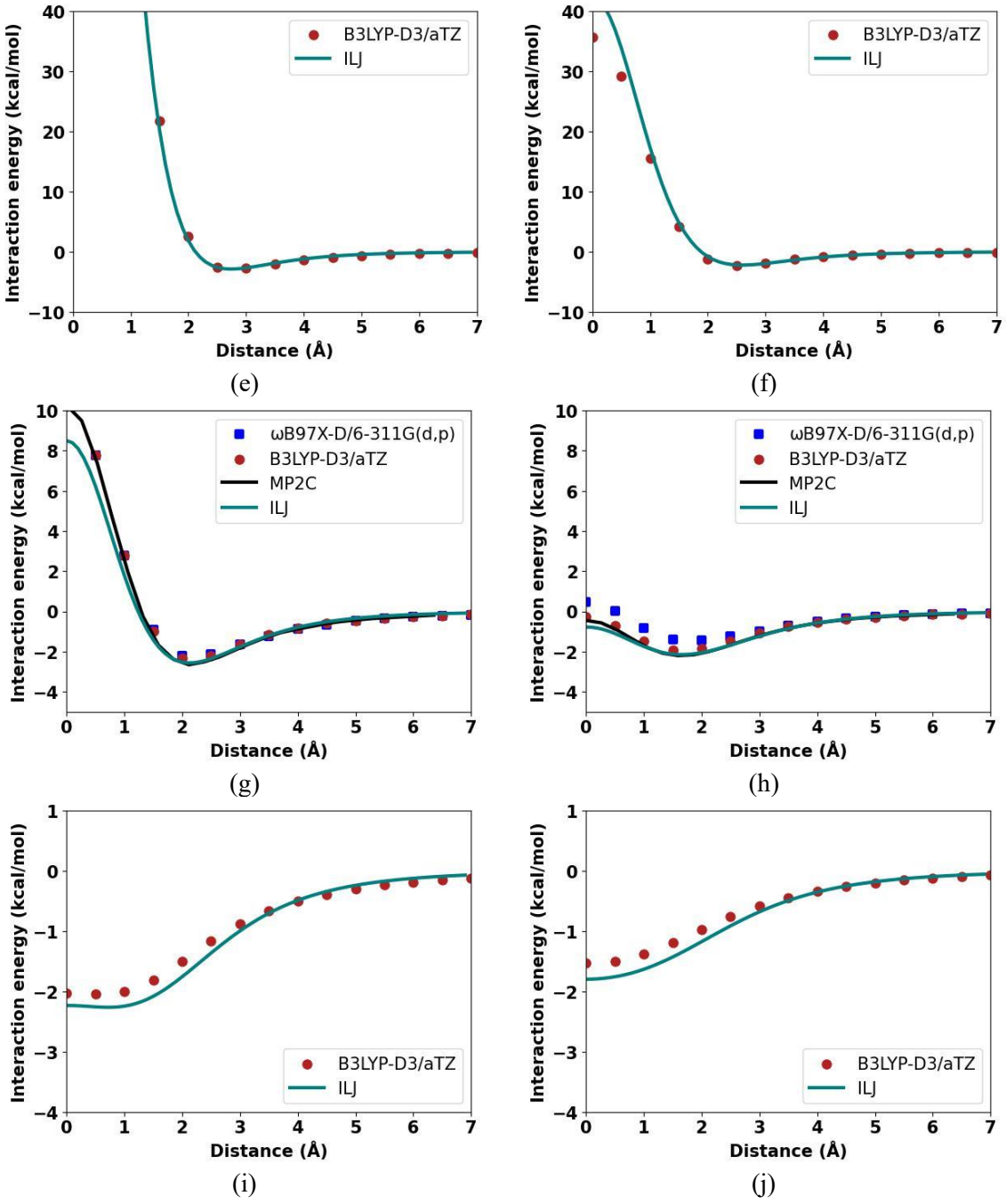
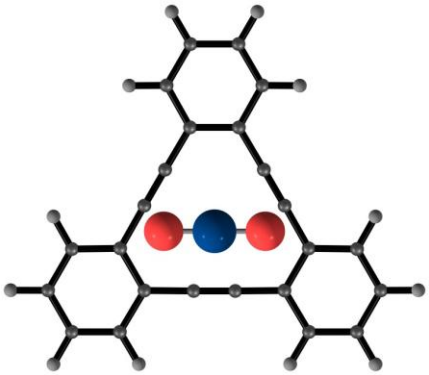
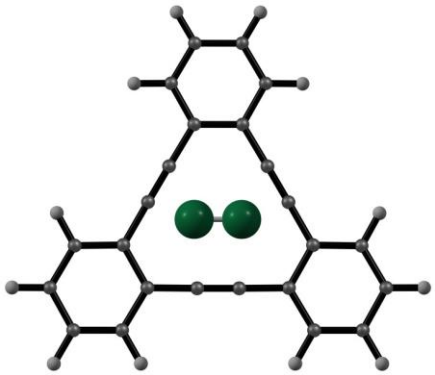


Figure S4. Interaction energy profiles evaluated using DFT and ILJ potential for the interaction of CO_2 and N_2 aligned along the X direction (illustrated in a and b) with γ-GY-1 (c and d), γ-GY-2 (e and f), γ-GY-3 (g and h), and γ-GY-4 (i and j), respectively. Note that the figures in g and h include the MP2C data from reference[1] and the ωB97X-D/6-311G(d,p) data.



(a)



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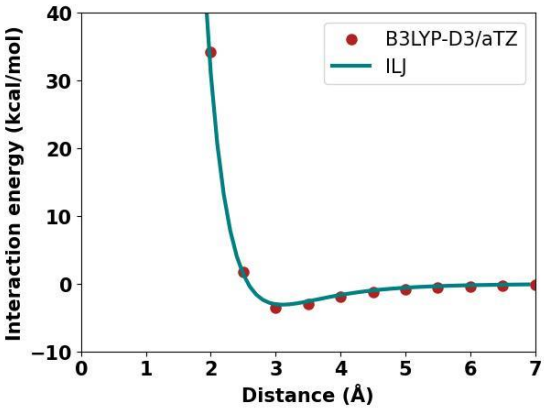
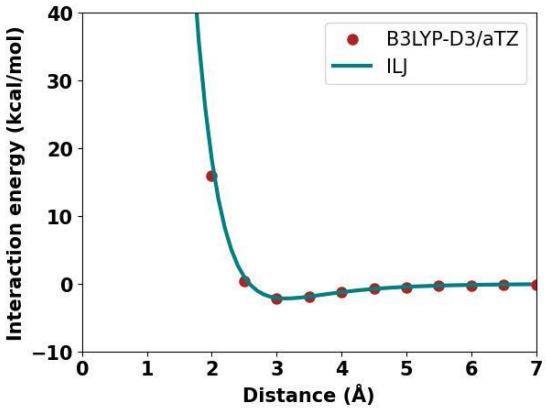

B3LYP-D3/aTZ
ILJ
Interaction energy (kcal/mol)
Distance (Å)

(c)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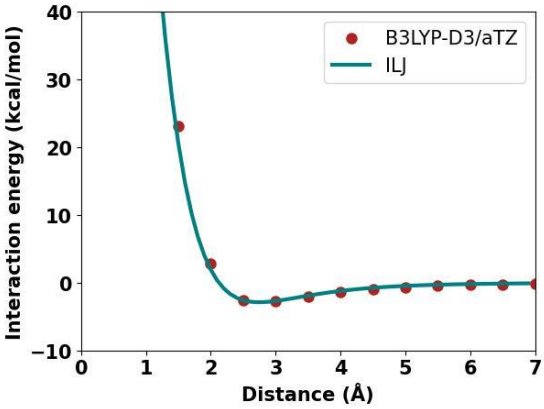
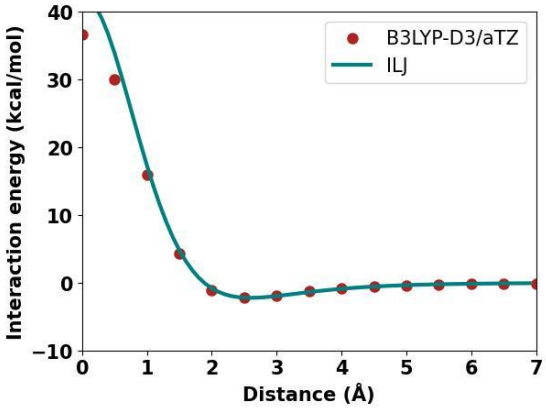
ILJ
Interaction energy (kcal/mol)
Distance (Å)

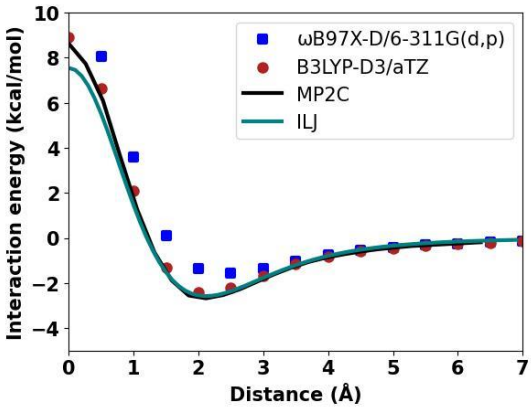
(d)


B3LYP-D3/aTZ
ILJ
Interaction energy (kcal/mol)
Distance (Å)

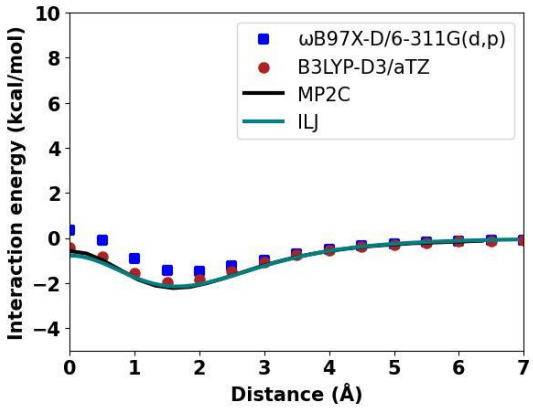
(e)


B3LYP-D3/aTZ
ILJ
Interaction energy (kcal/mol)
Distance (Å)

(f)


ωB97X-D/6-311G(d,p)
B3LYP-D3/aTZ
MP2C
ILJ
Interaction energy (kcal/mol)
Distance (Å)

(g)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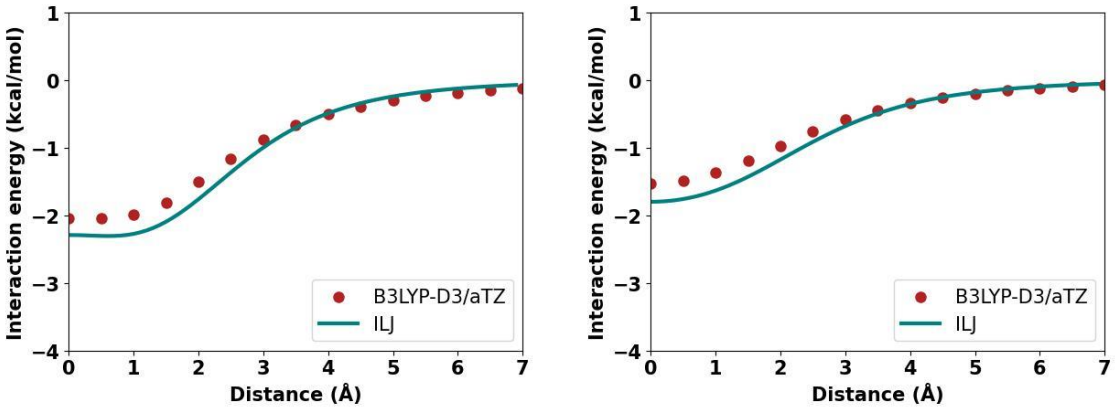
B3LYP-D3/aTZ
MP2C
ILJ
Interaction energy (kcal/mol)
Distance (Å)

(h)



(i) (j)

Figure S5. Interaction energy profiles evaluated using DFT and ILJ potential for the interaction of CO_2 and N_2 aligned along the Y direction (illustrated in a and b) with γ-GY-1 (c and d), γ-GY-2 (e and f), γ-GY-3 (g and h), and γ-GY-4 (i and j), respectively. Note that the figures in g and h include the MP2C data from reference[1] and the ωB97X-D/6-311G(d,p) data.

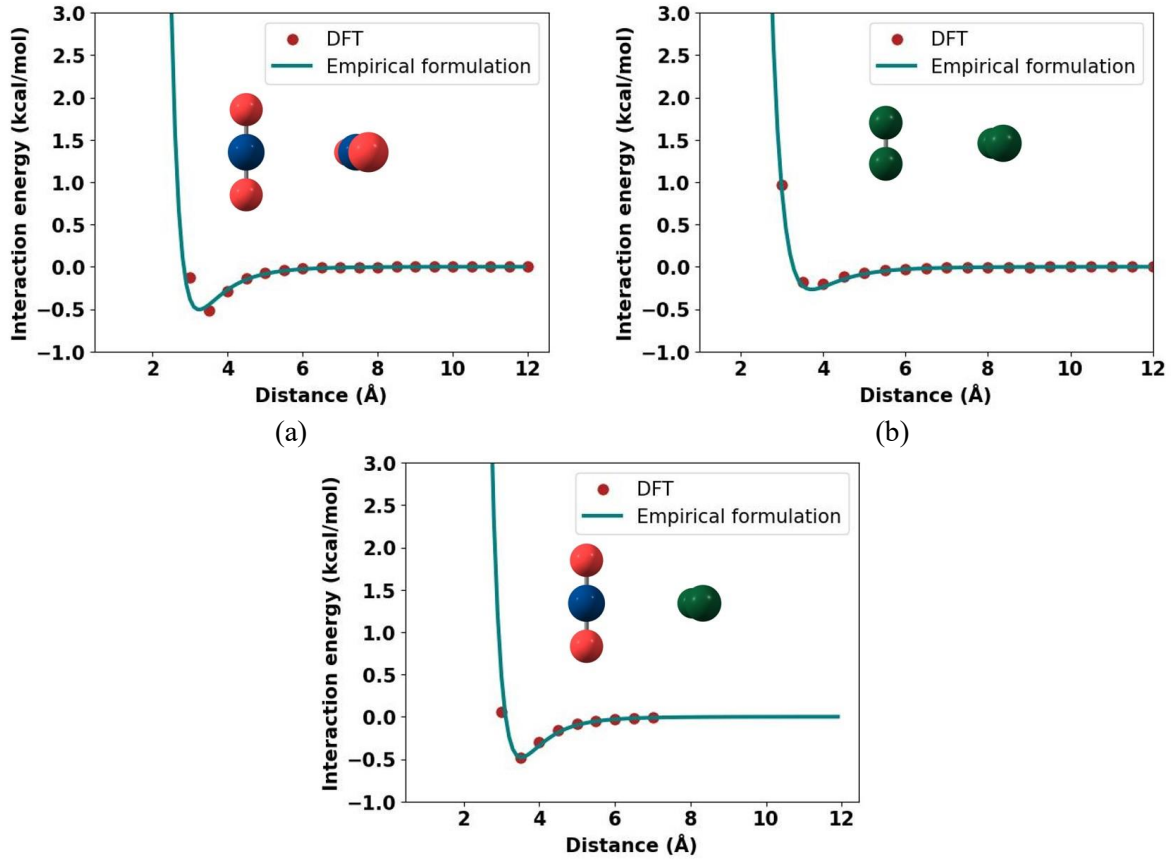


Figure S6. Interaction energy profiles evaluated using DFT and the empirical potentials for the interaction between (a) CO_2 and CO_2, (b) N_2 and N_2, and (c) CO_2 and N_2. The orientations of the molecules considered for computing the profiles are given in the insets.

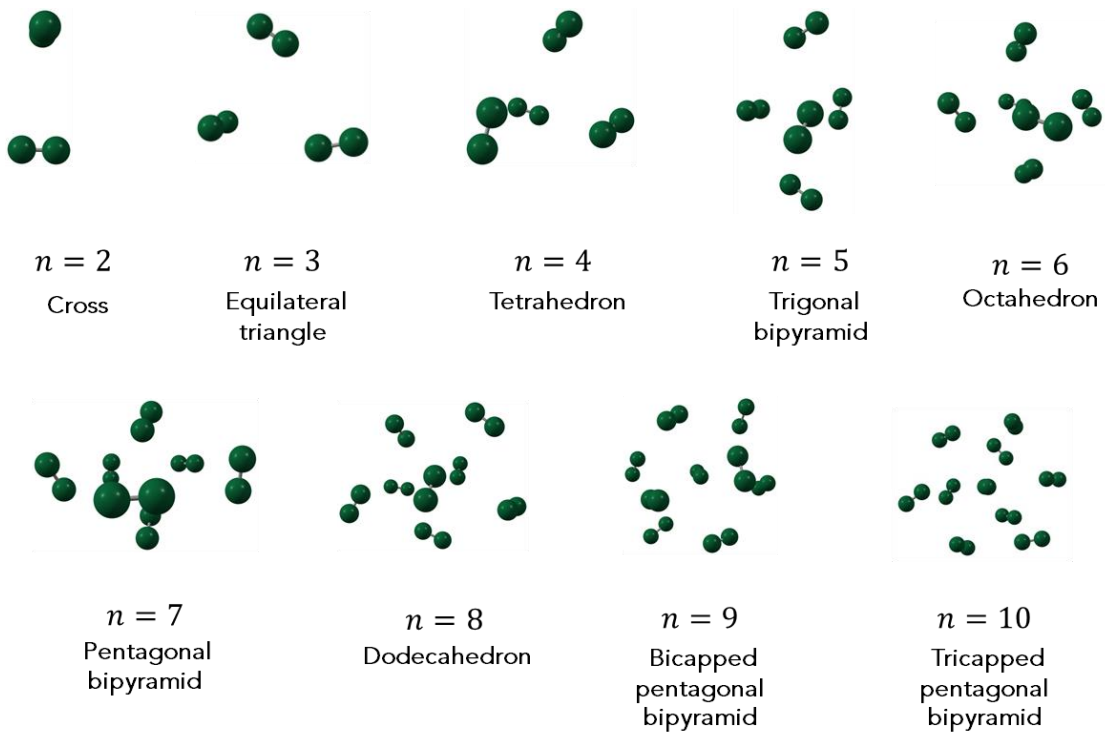


Figure S7. Putative global minimum geometries of bare N_2 clusters evaluated using PSO.[2]

	Interaction energy components (kcal/mol)				Total SAPT0 (kcal/mol)
	Electrostatics	Exchange	Induction	Dispersion	
CO_2-CO_2	-1.742	1.618	-0.185	-1.410	-1.719
CO_2-N_2	-0.567	0.552	-0.078	-0.801	-0.893
N_2-N_2	-0.060	0.292	-0.008	-0.485	-0.261

Table S1. Intermolecular interaction energies and constituent components for CO_2-CO_2, CO_2-N_2, and N_2-N_2 dimers evaluated using SAPT.

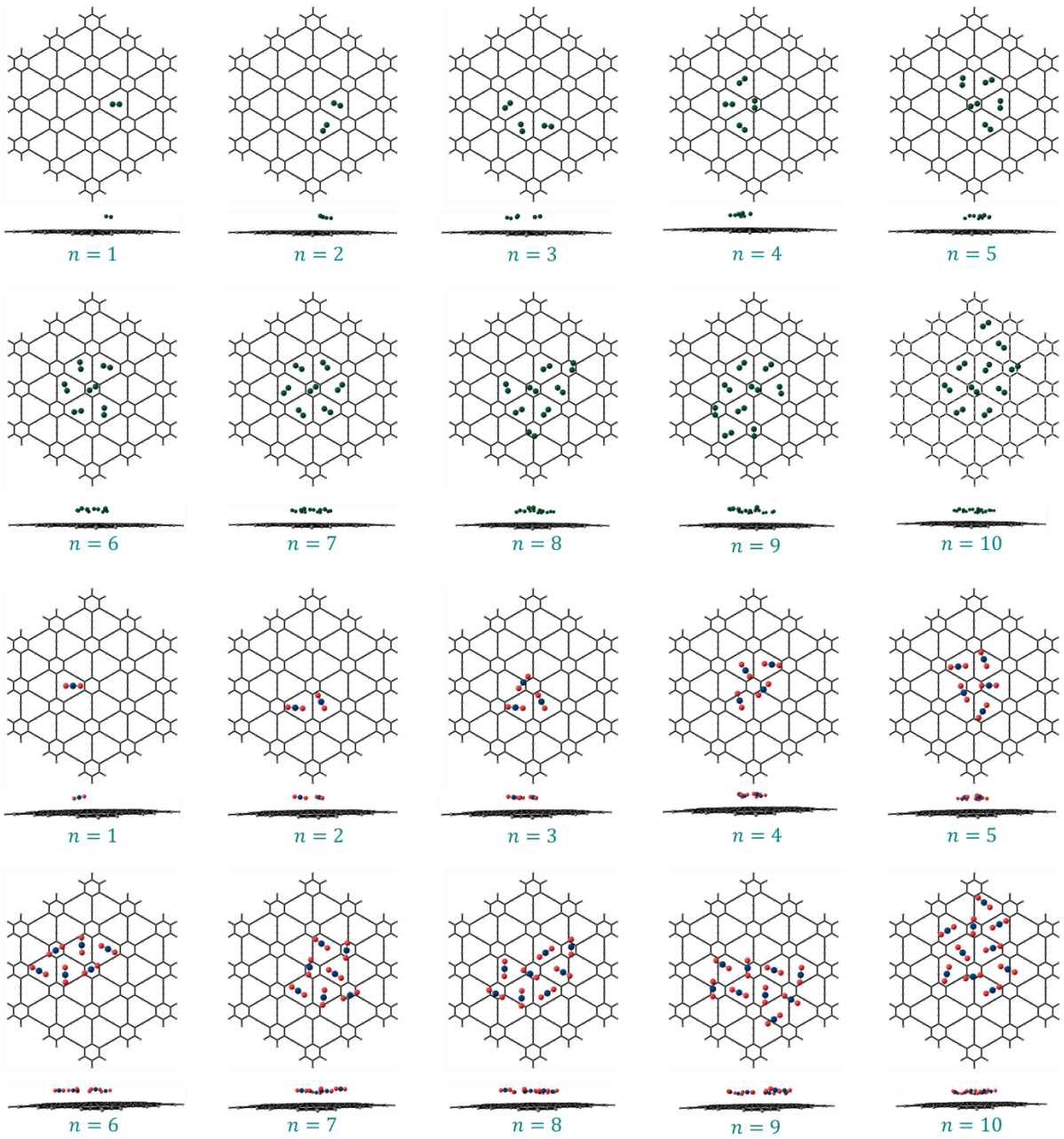


Figure S8. Putative global minimum geometries (top and side views) of N_2 and CO_2 clusters of size n =1-10 adsorbed on γ-GY-1 evaluated using PSO.

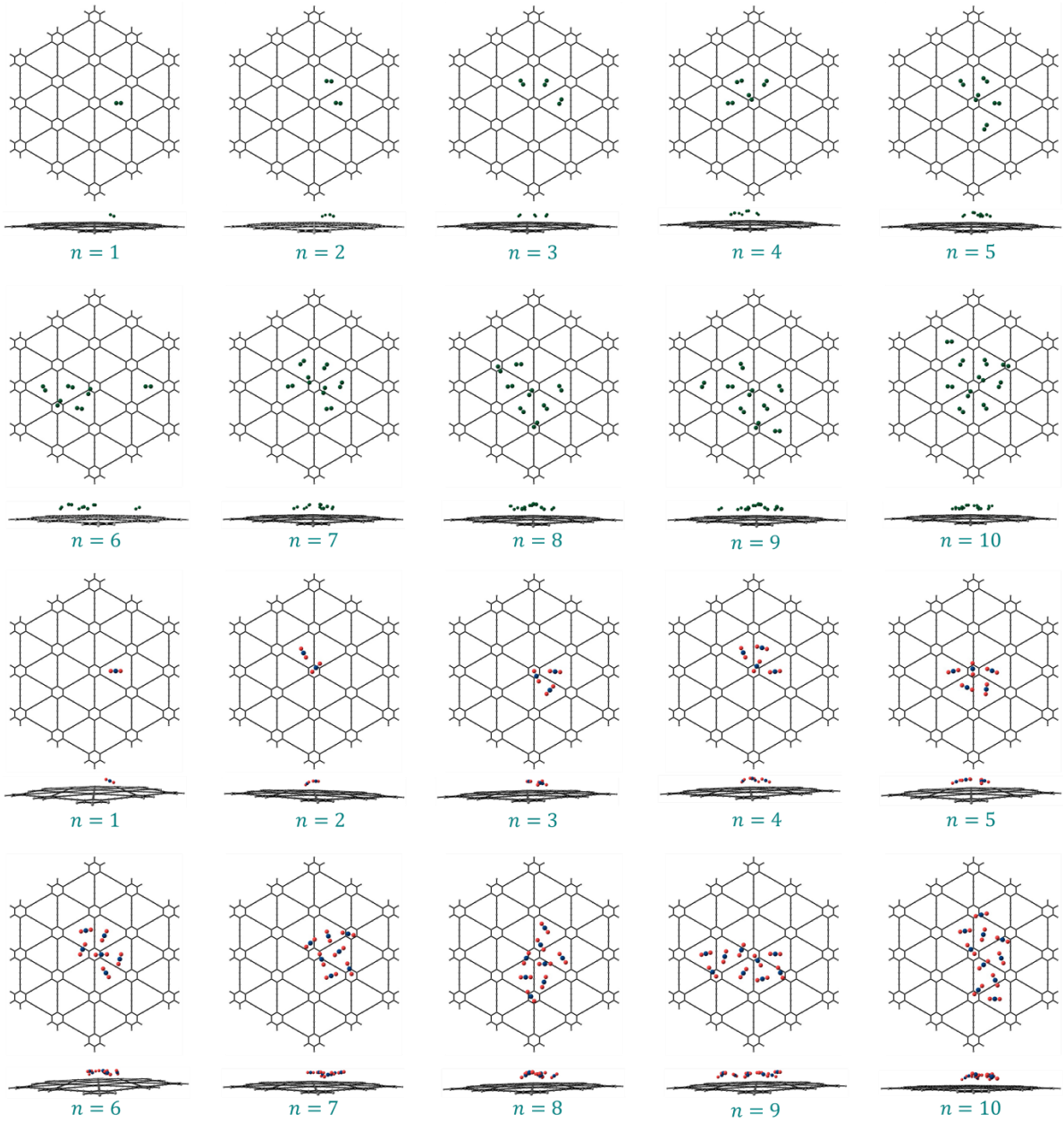


Figure S9. Putative global minimum geometries (top and side views) of N_2 and CO_2 clusters of size n =1-10 adsorbed on γ-GY-2 evaluated using PSO.

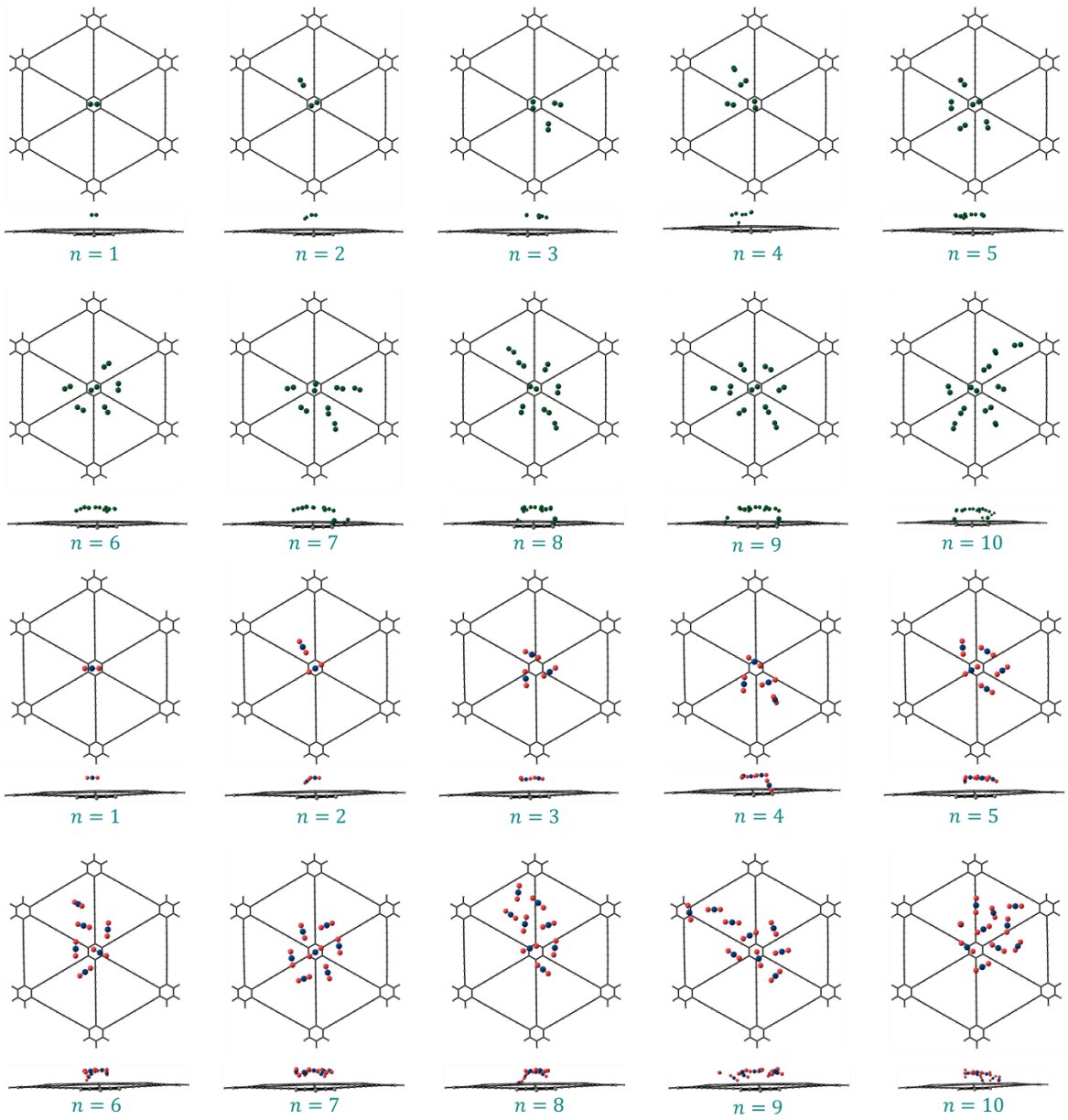


Figure S10. Putative global minimum geometries (top and side views) of N_2 and CO_2 clusters of size n =1-10 adsorbed on γ-GY-4 evaluated using PSO.

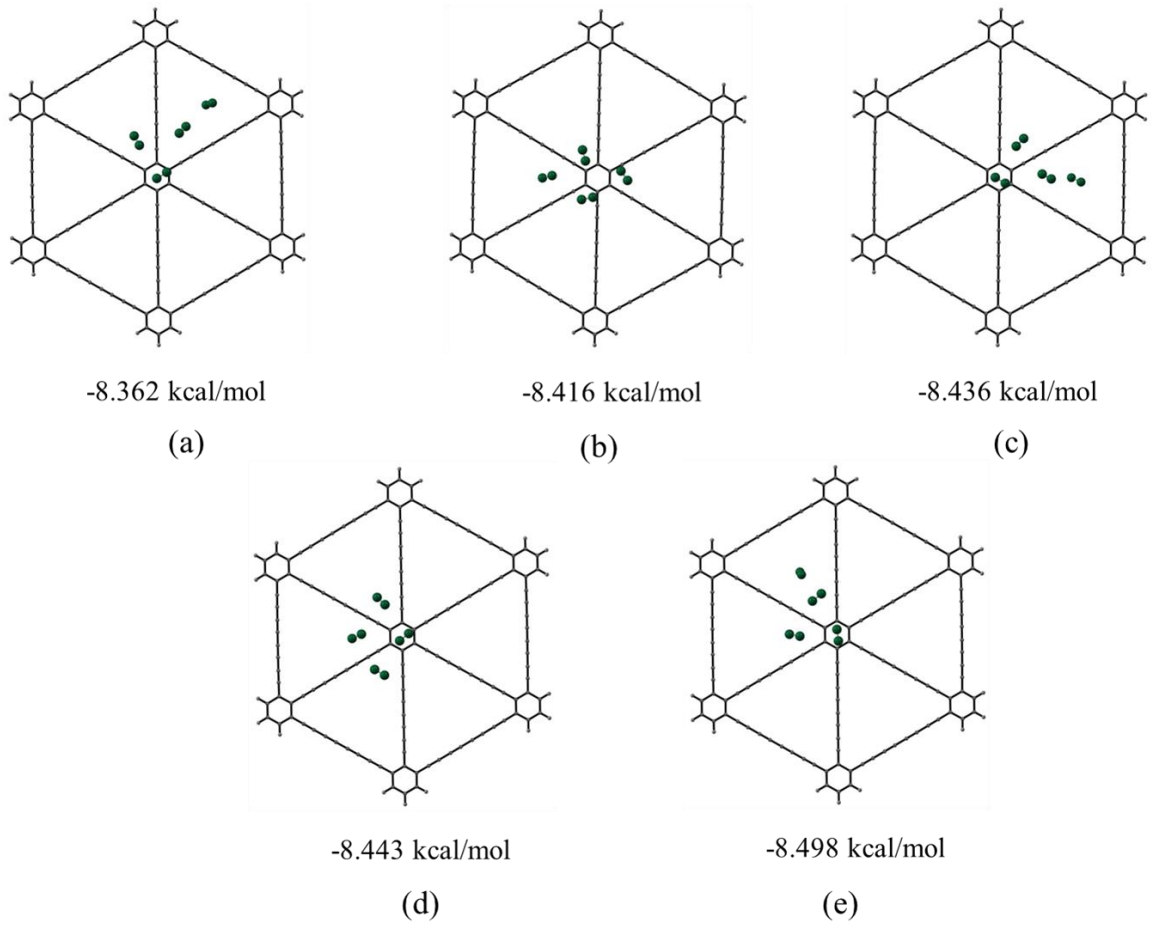


Figure S11. (a-d) Local minimum geometries and (e) putative global minimum geometry along with the respective interaction energies of the $(N_2)_4$ cluster adsorbed on γ-GY-4 evaluated using PSO.

Adsorption of CO_2 clusters on graphene (represented by circumcircumcoronene)

We have studied the adsorption of 2 to 10 CO_2 molecules on circumcircumcoronene using PSO. The total interaction energy of the system is given by

$$E_{CO_2}^{adsorbed} = E_{CO_2-CO_2} + E_{CO_2-Gr}$$

where E_{CO_2-Gr} is the energy of interaction between CO_2 molecules and circumcircumcoronene. It is modelled using the LJ potential and is expressed as

$$E_{CO_2-Gr} = \sum_{i=1}^{p}\sum_{j=1}^{n}\sum_{k=1}^{3} 4\varepsilon_{k_j i}\left[\left(\frac{\sigma_{k_j i}}{r_{k_j i}}\right)^{12} - \left(\frac{\sigma_{k_j i}}{r_{k_j i}}\right)^{6}\right].$$

where p is the number of C atoms in the circumcircumcoronene and n is the number of CO_2 molecules. The LJ parameters for the CO_2-circumcircumcoronene are obtained by applying Lorentz-Berthelot mixing rules[3]. The parameters of C-C interactions in circumcircumcoronene are taken from literature[4], whereas for C-C and O-O interactions in CO_2, the parameters used are given in Table 1 of the manuscript. The methodology and parameters for PSO calculations are same as those mentioned in the manuscript.

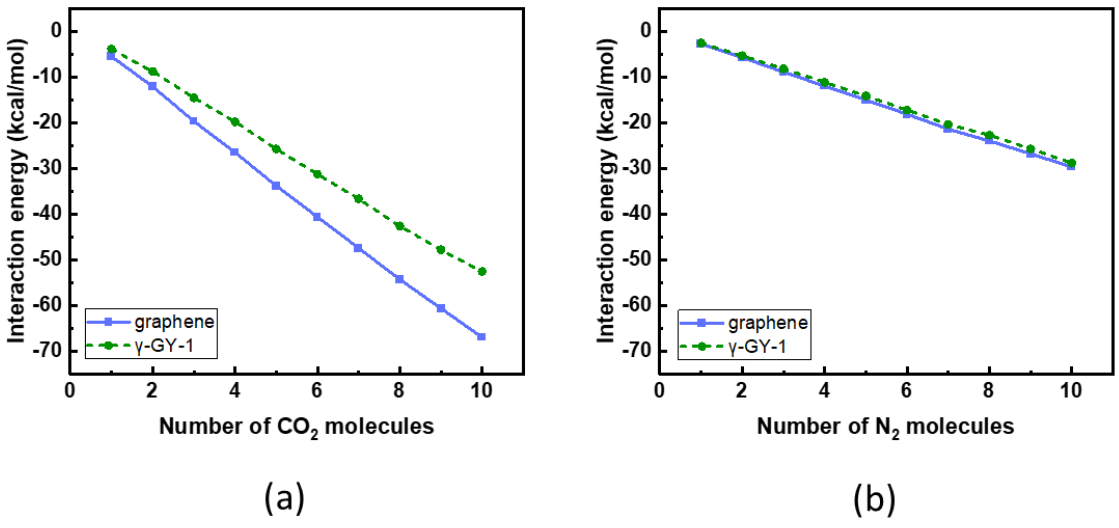


Figure S12. A comparison of interaction energies of (a) CO_2 clusters and (b) N_2 clusters of size n=1-10 adsorbed on γ-GY-1 and graphene (represented by circumcircumcoronene) evaluated using PSO.

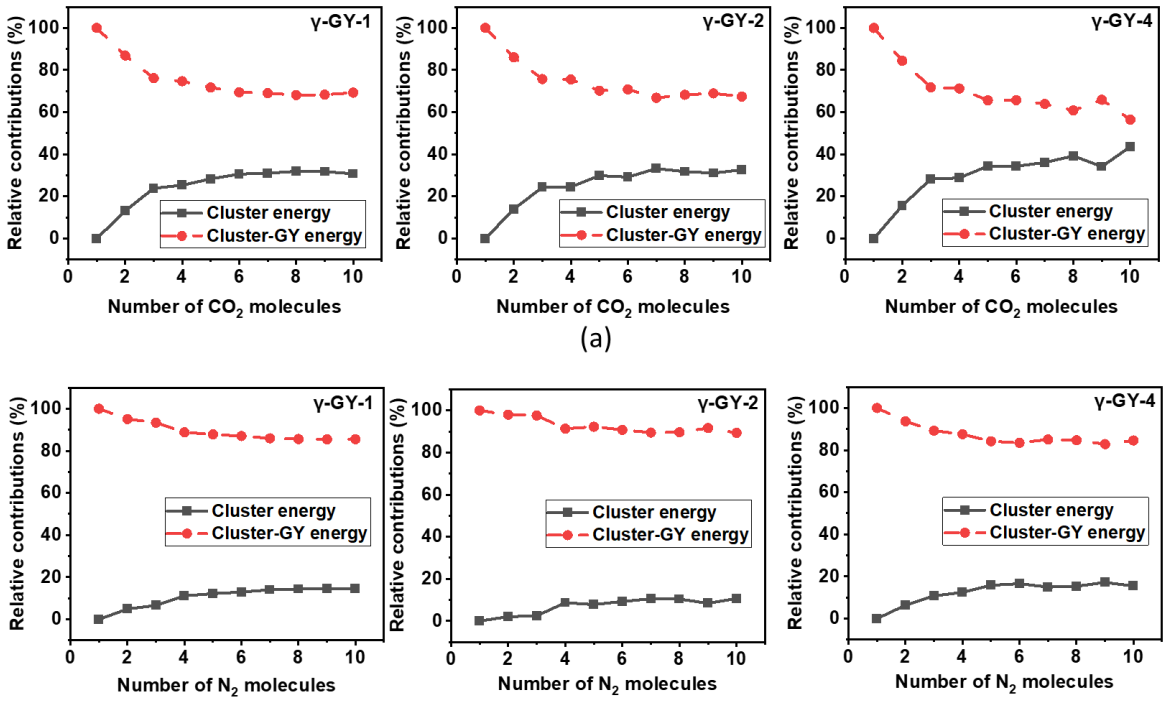
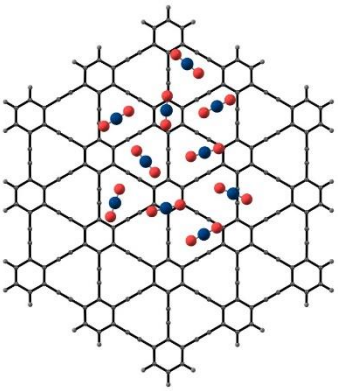


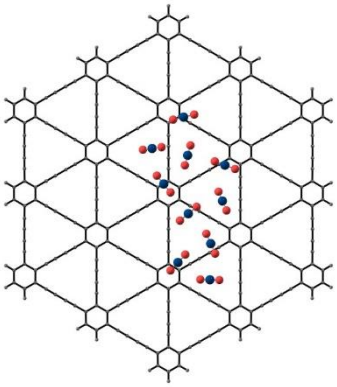
Figure S13. Variation of the percentage relative contributions of various terms to the total interaction energies for the adsorption of (a) CO_2 and (b) N_2 clusters on γ-GY-1, γ-GY-2, and γ-GY-4 as a function of cluster size.

Putative global minima geometries and interaction energies from 25 independent runs



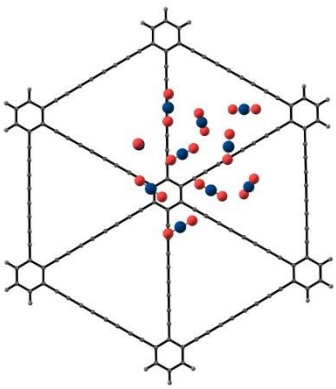
$(CO_2)_{10}$-γ-GY-1

-52.604 kcal/mol



$(CO_2)_{10}$-γ-GY-2

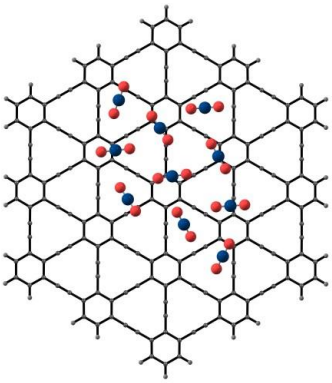
-47.224 kcal/mol



$(CO_2)_{10}$-γ-GY-4

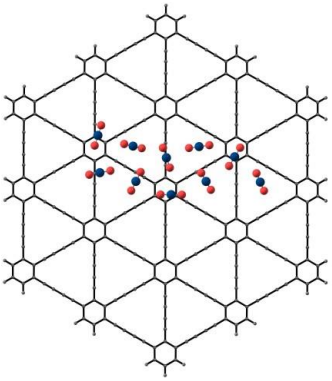
-42.357 kcal/mol

Putative global minima geometries and interaction energies from 100 independent runs



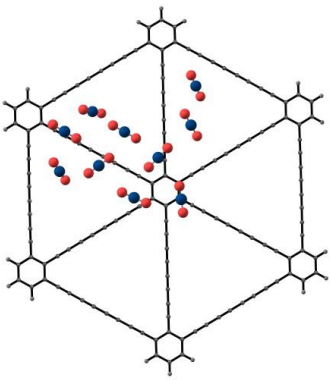
$(CO_2)_{10}$-γ-GY-1

-54.342 kcal/mol



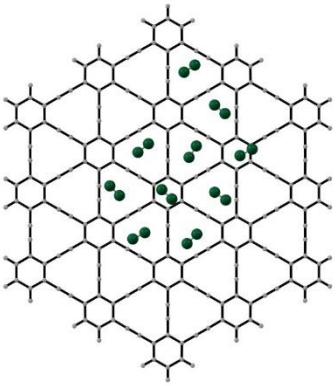
$(CO_2)_{10}$-γ-GY-2

-48.037 kcal/mol



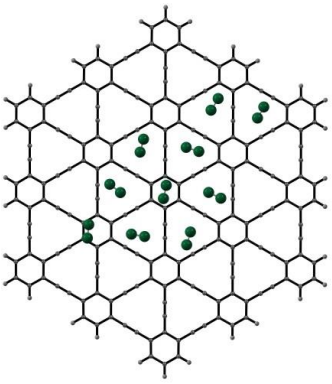
$(CO_2)_{10}$-γ-GY-4

-41.202 kcal/mol



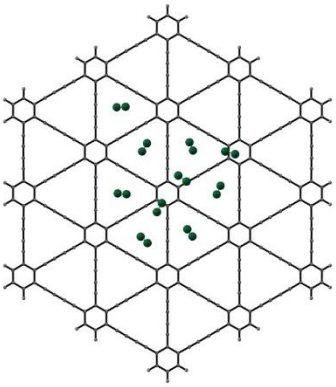
$(N_2)_{10}$-γ-GY-1

-28.855 kcal/mol



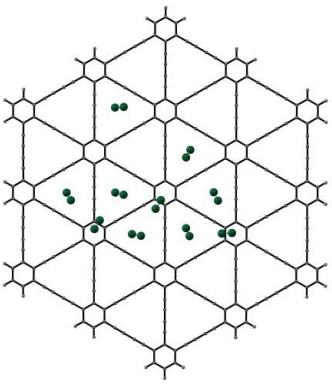
$(N_2)_{10}$-γ-GY-1

-28.692 kcal/mol



$(N_2)_{10}$-γ-GY-2

-25.810 kcal/mol



$(N_2)_{10}$-γ-GY-2

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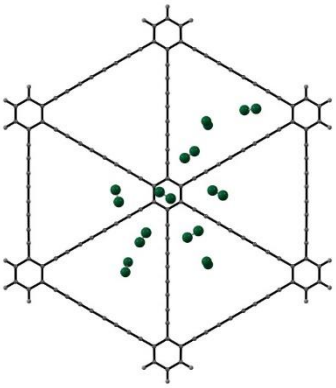
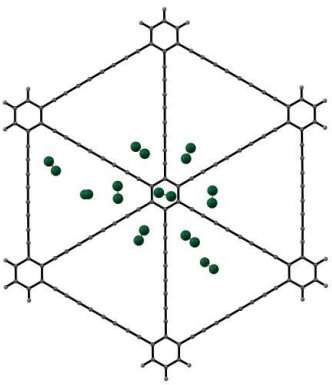


$(N_2)_{10}$-γ-GY-4

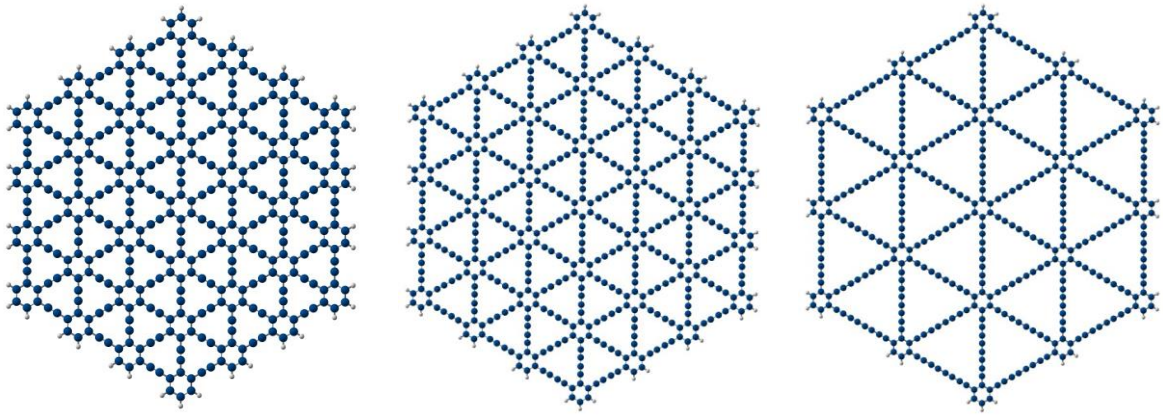
-21.446 kcal/mol



$(N_2)_{10}$-γ-GY-4

-21.790 kcal/mol

Figure S14. Putative global minimum geometries and the interaction energies of CO_2 and N_2 clusters of size 10 adsorbed on γ-GY-1, γ-GY-2, and γ-GY-4 obtained using PSO after performing 25 and 100 independent runs.



(a) (b) (c)

Figure S15. Larger annulenic model systems of (a) γ-GY-1 ($C_{402}H_{42}$), (b) γ-GY-2 ($C_{582}H_{42}$), and (c) γ-GY-4 ($C_{450}H_{30}$). The geometries were generated by translating the corresponding unit cells whose lattice parameters were obtained from the optimized model systems employed throughout the current study.

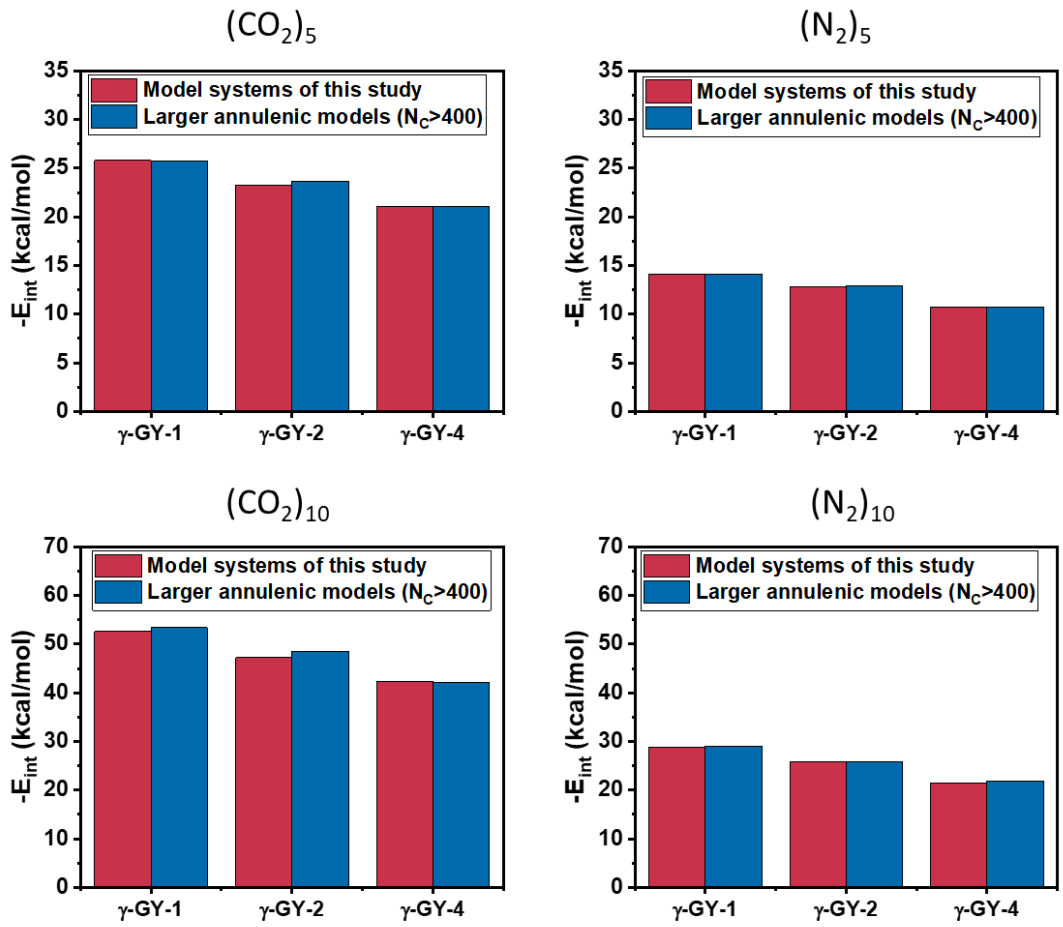


Figure S16. Comparison of the variation of interaction energies obtained using PSO for the adsorption of CO_2 and N_2 clusters of size 5 and 10 on various annulenic molecular models of γ-GY-1, γ-GY-2, and γ-GY-4. Note: N_C refers to the number of carbon atoms in the molecular model.

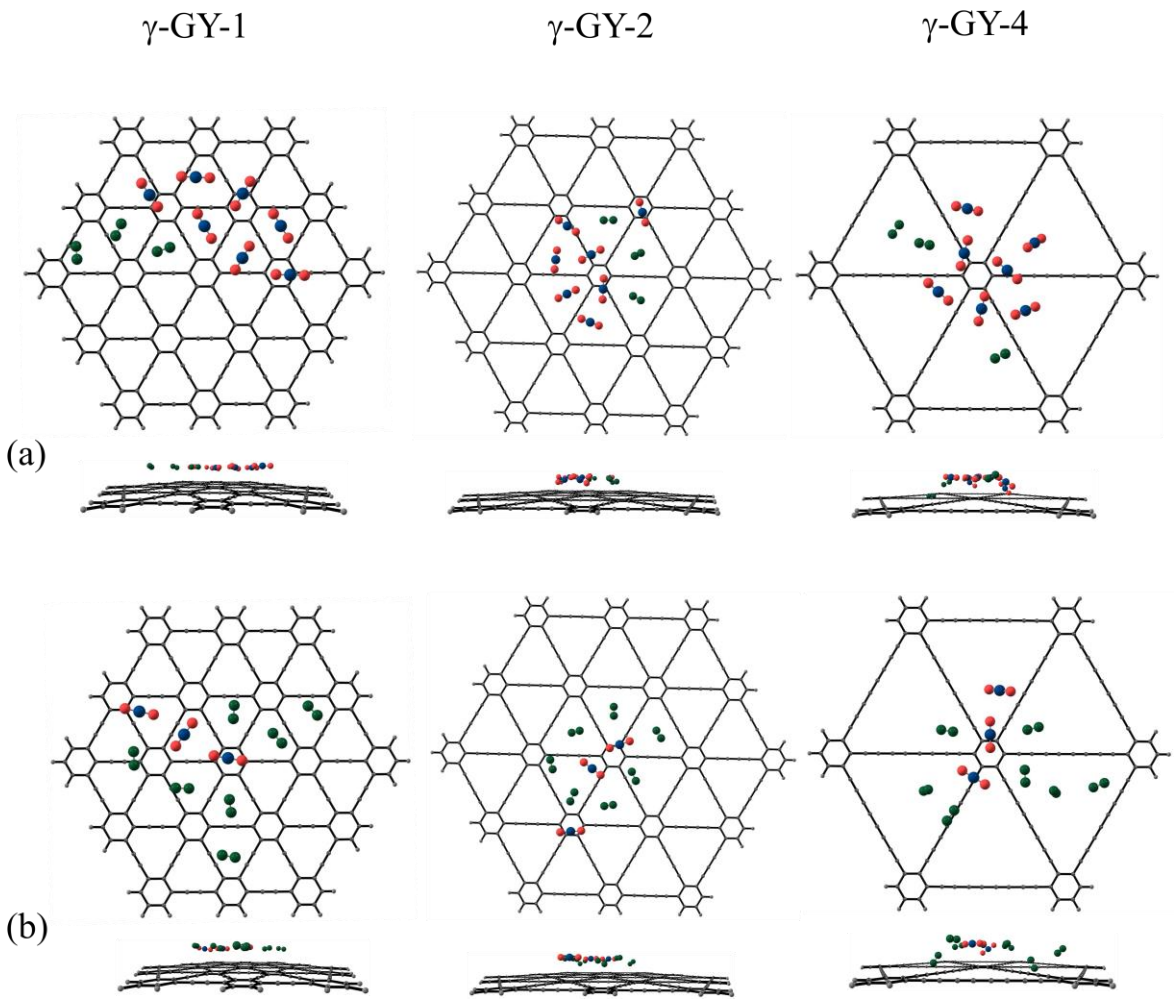


Figure S17. Putative global minimum geometries (top and side views) of binary clusters of N_2 and CO_2 in the ratio (a) 3:7 and (b) 7:3 adsorbed on γ-GY-1, γ-GY-2 and γ-GY-4 evaluated using PSO.

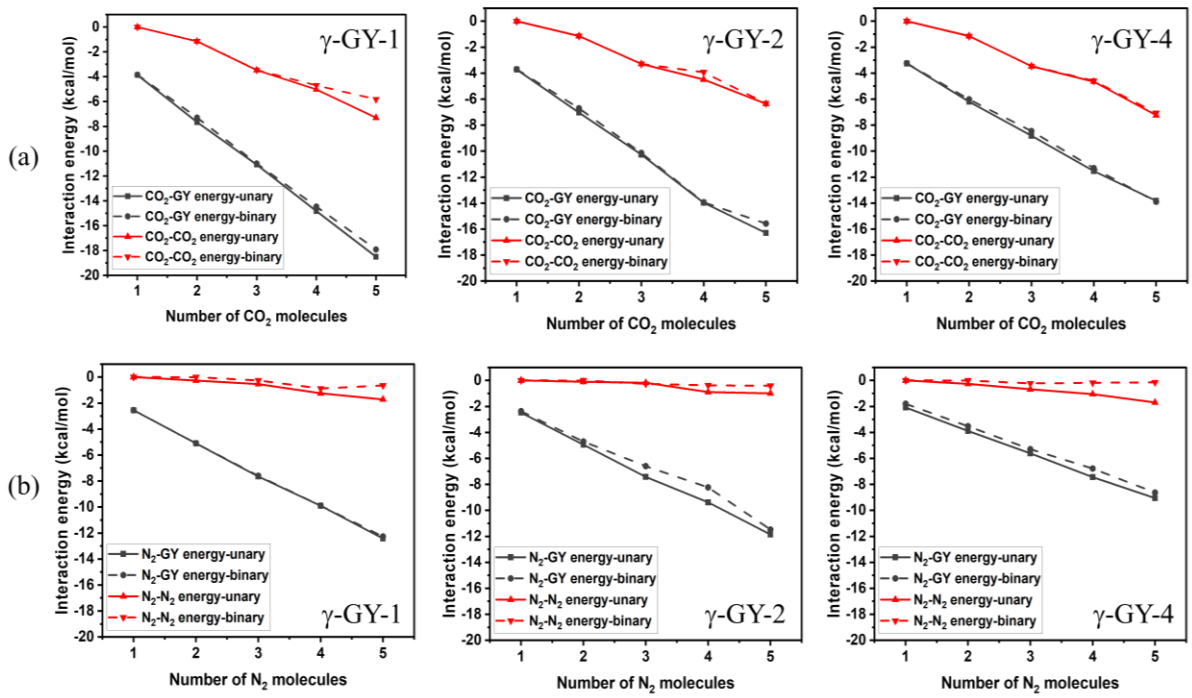


Figure S18. Variation of cluster energies and cluster-GY energies of adsorbed unary and binary (with equal number of N_2 and CO_2 molecules) clusters of (a) CO_2 and (b) N_2 as a function of cluster size.

References

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