Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electron Diffraction of 1,4-Dichlorobenzene Embedded in Superfluid Helium Droplets

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Supplementary Materials

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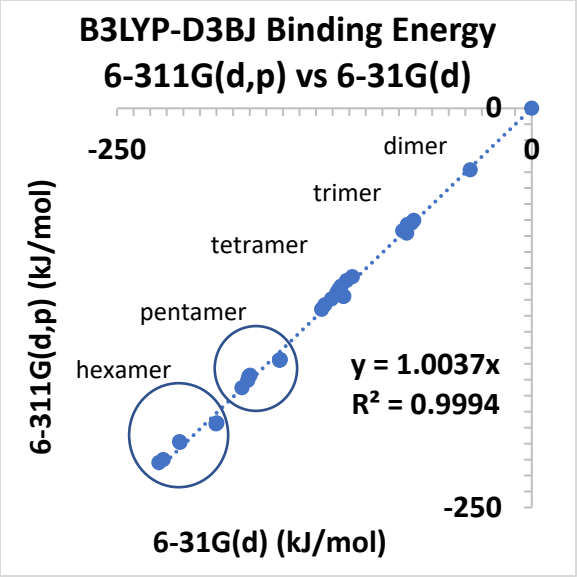
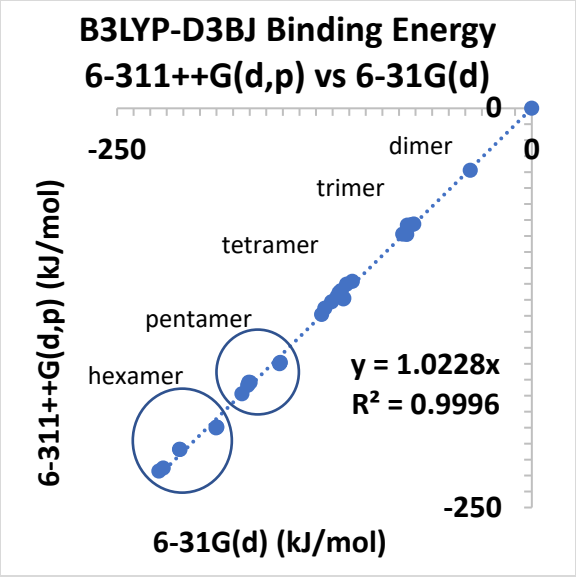


(a)



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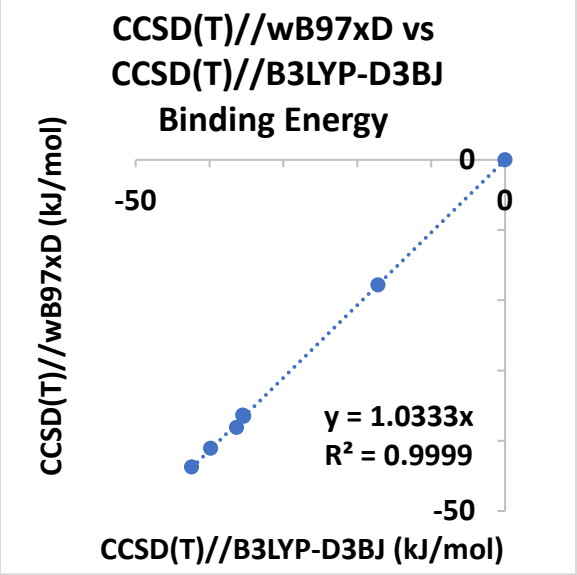


(c)

Fig. S1: Comparisons of binding energies of 1,4-dichlorobenzene (2ClB) clusters obtained using different calculation methods. (a) Basis set effect for B3LYP-D3BJ: 6-311G(d,p) vs 6-31G(d). (b) Basis set effect for B3LYP-D3BJ: 6-311++G(d,p) vs 6-31G(d). (c) CCSD(T)//ωB97xD/6-31G(d) vs CCSD(T)//B3LYP-D3BJ/6-31G(d) binding energies of 2ClB clusters (up to trimers).

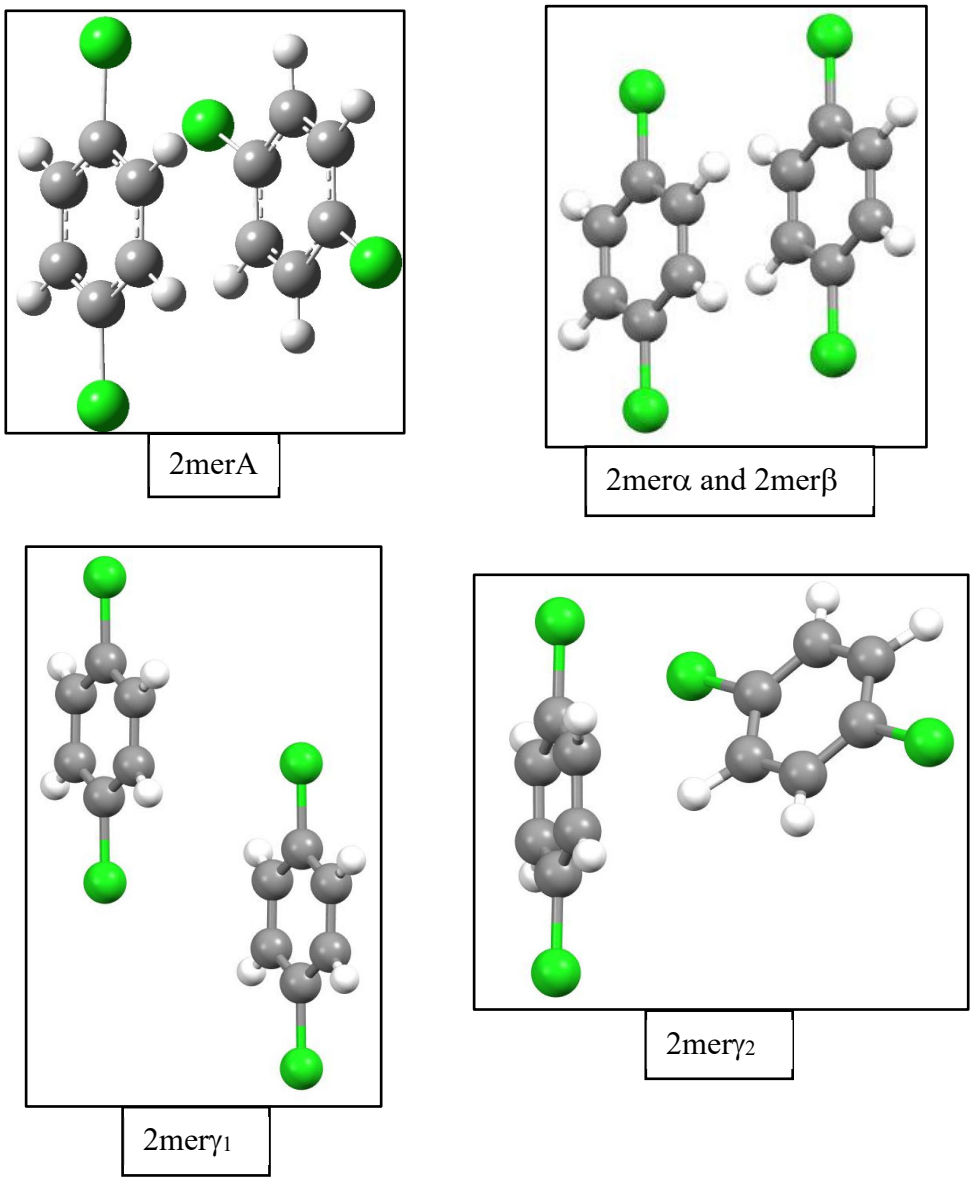


Fig. S2: Theoretical gas phase dimer structure (2merA), and cuts from crystals of α, β, and γ structures of 1,4-dichlorobenzene. The structures 2merα and 2merβ are identical, with a very slight difference in interlayer spacing, and hence only one figure is used for both. These structures are used for fittings of the experimental data.

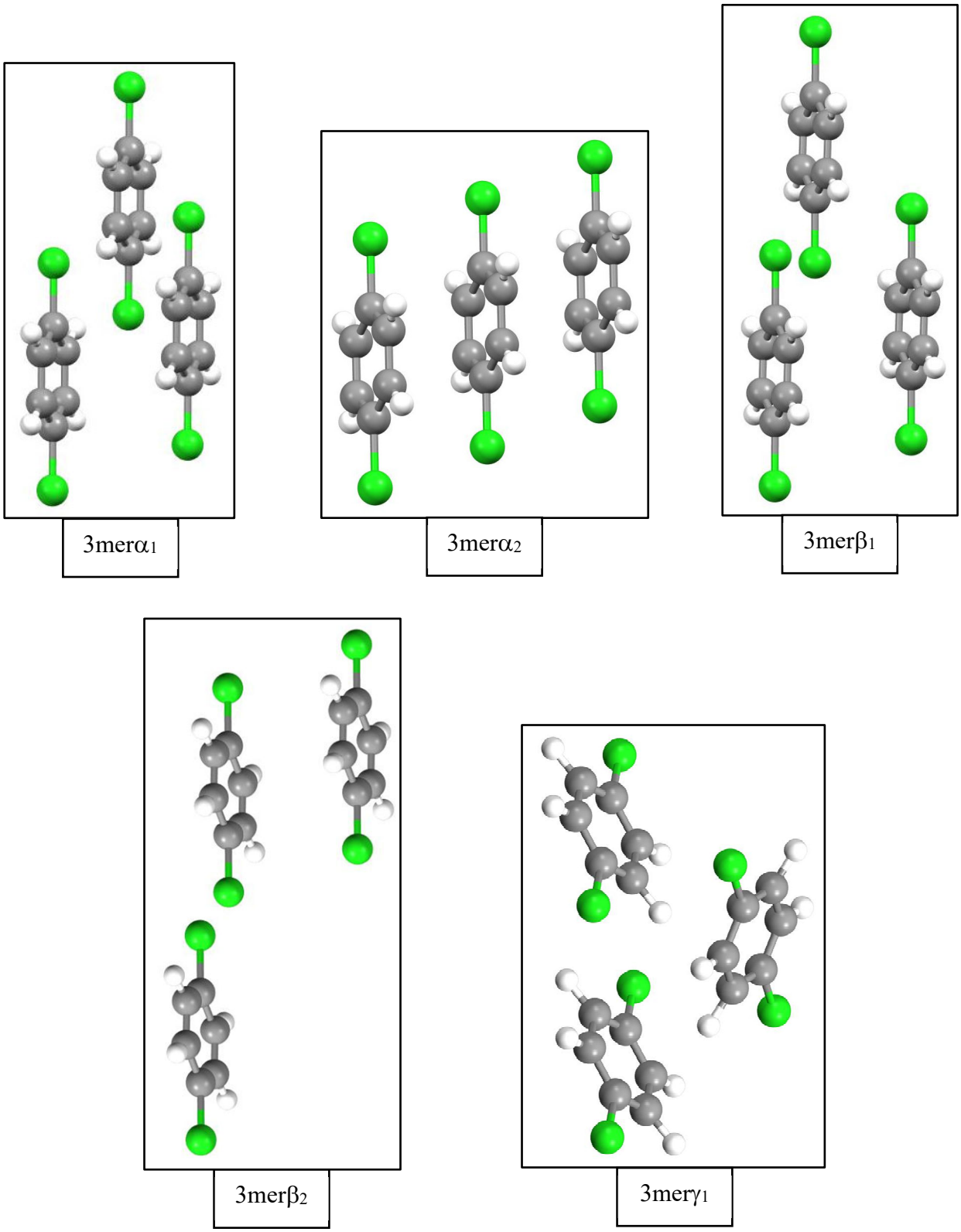


Fig. S3: Trimer structures cut from crystals of α, β, and γ structures of 1,4-dichlorobenzene.

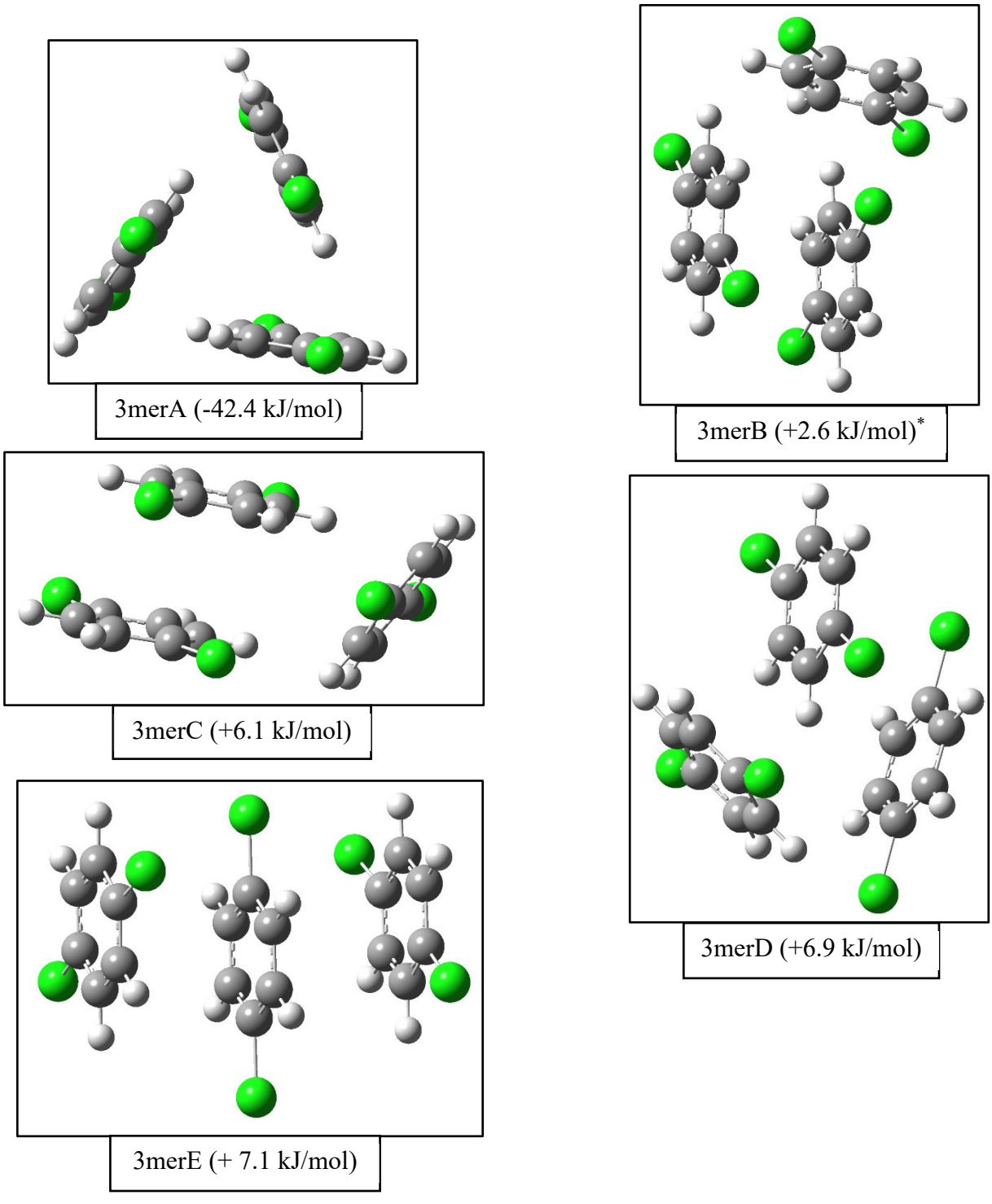
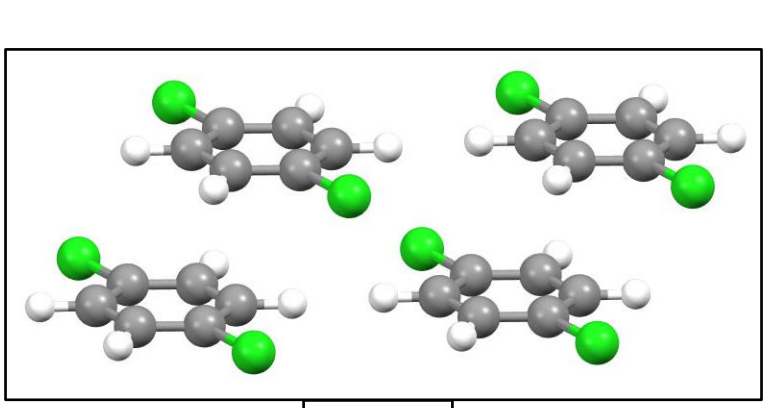
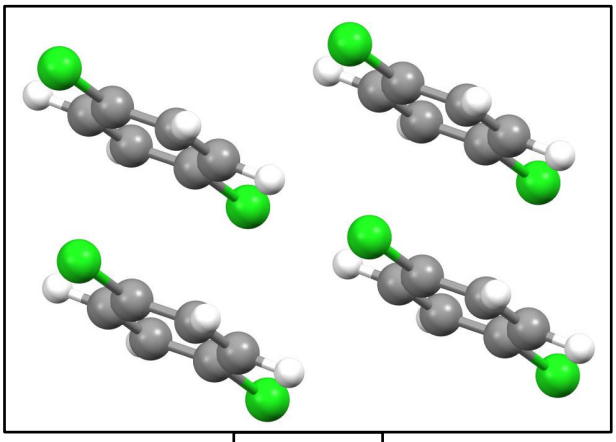


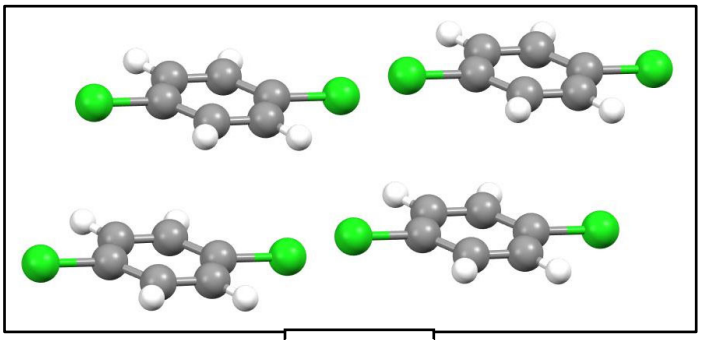
Fig. S4: Calculated gas phase trimer structures indicating the CCSD(T)//B3LYP-D3BJ/6-31G(d) energy of the global minimum (relative to the constituent monomers), and energies of other structures relative to the global minimum. *Indicates the structure from fitting of the diffraction pattern.



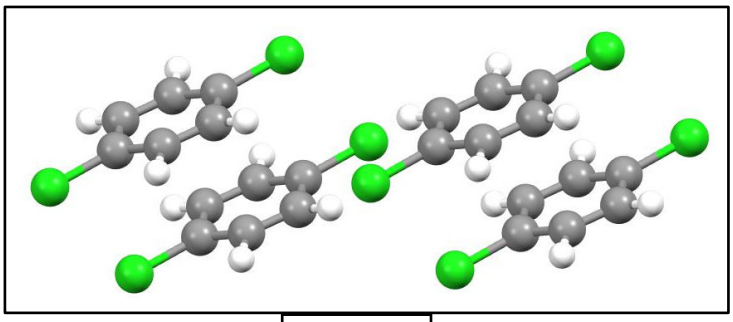
4merα_1



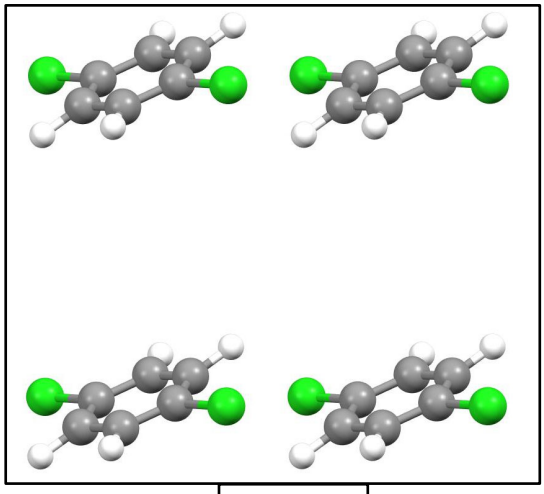
4merα_2



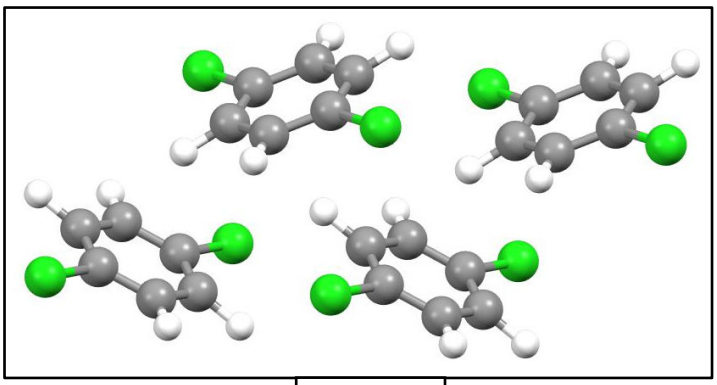
4merβ_1



4merβ_2

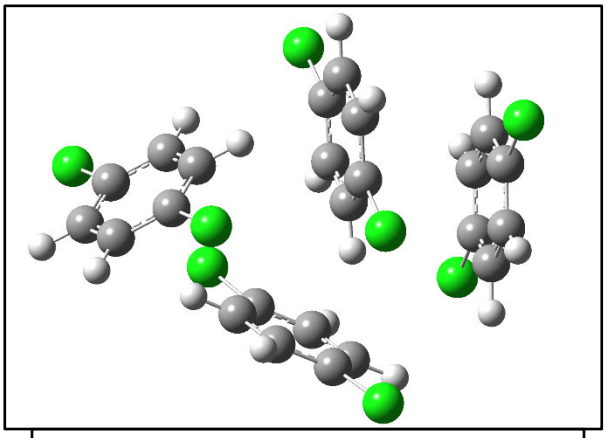


4merγ_1

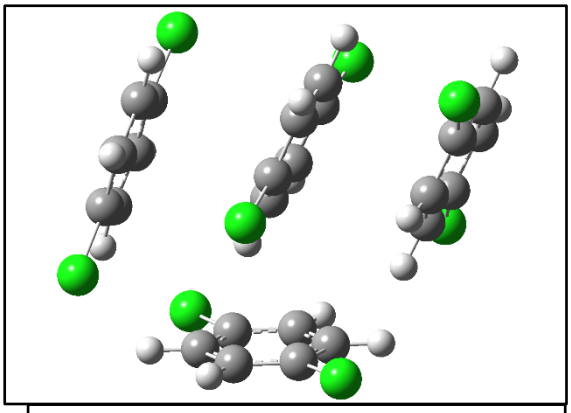


4merγ_2

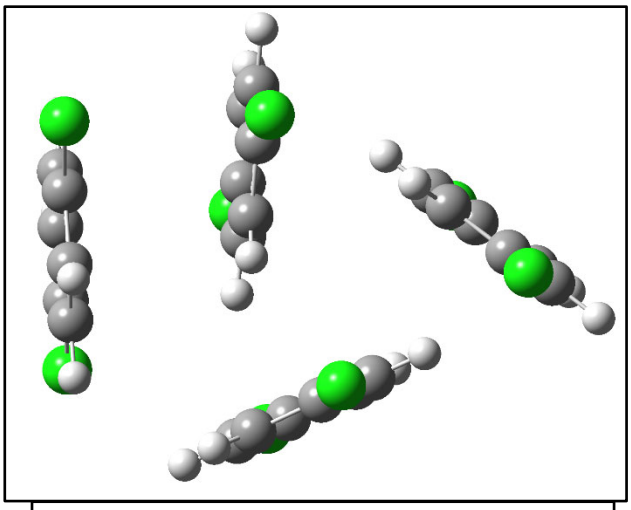
Fig. S5: Tetramer structure cuts from crystals of α, β, and γ structures of 1,4-dichlorobenzene.



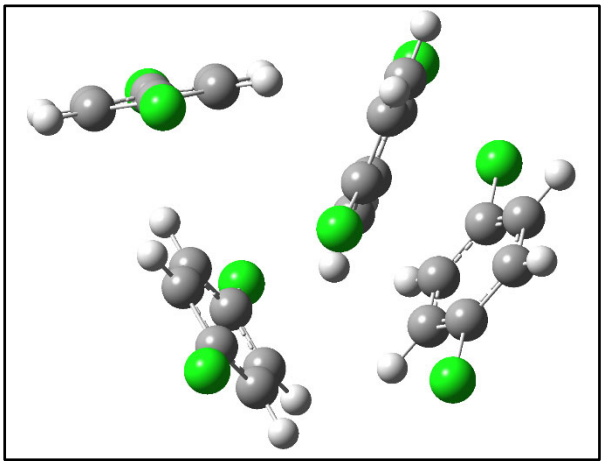
4merA (-65.1 kJ/mol)



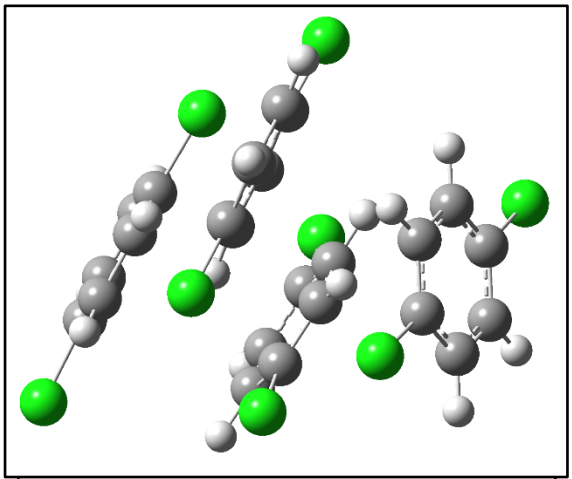
4merB (+2.5kJ/mol)



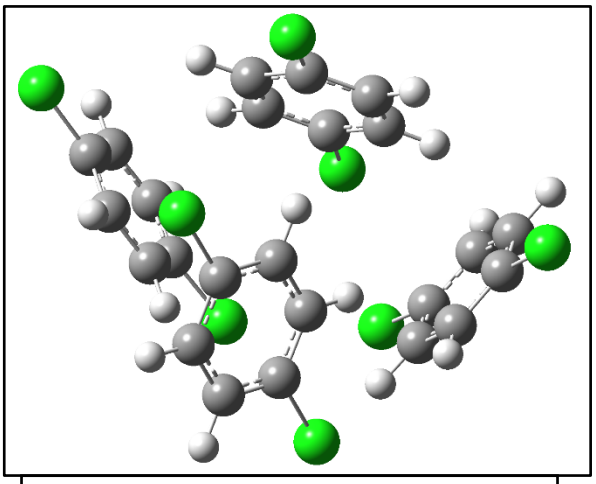
4merC (+3.2 kJ/mol)



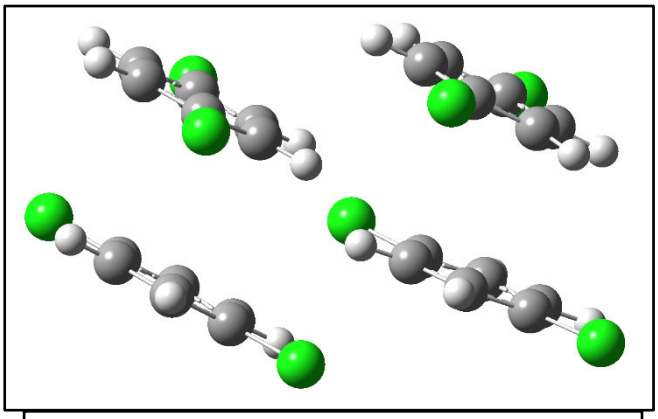
4merD (+3.6 kJ/mol)



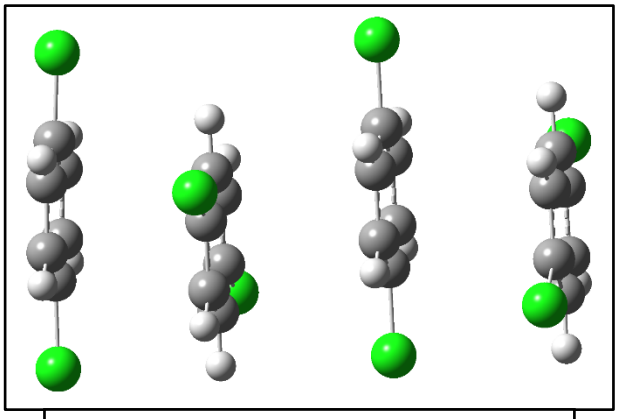
4merE (+5.5 kJ/mol)



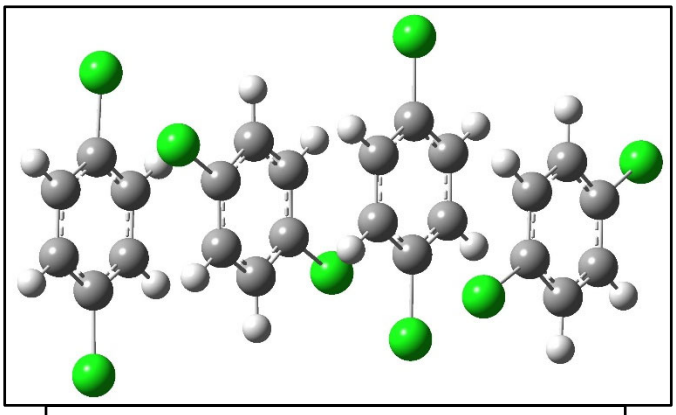
4merF (+5.9 kJ/mol)



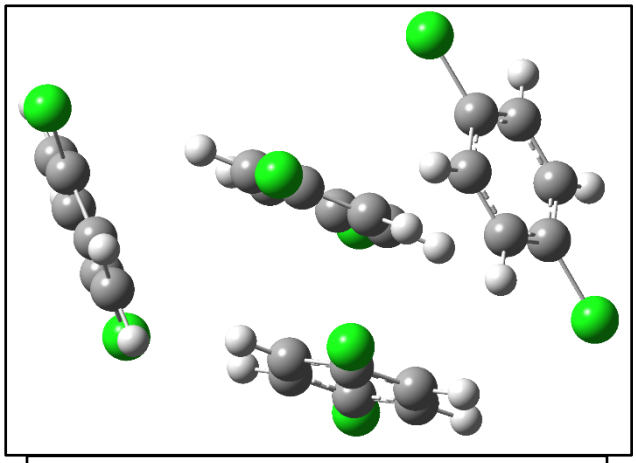
4merG (+8.2 kJ/mol)



4merH (+11.6 kJ/mol)



4merI (+11.7 kJ/mol)*



4merJ (+12.2 kJ/mol)

Fig. S6: Calculated gas phase tetramer structures indicating the CCSD(T)//B3LYP-D3BJ/6-31G(d) energy of the global minimum (relative to the constituent monomers), and energies of other structures relative to the global minimum. *Indicates the structure from fitting of the diffraction pattern.

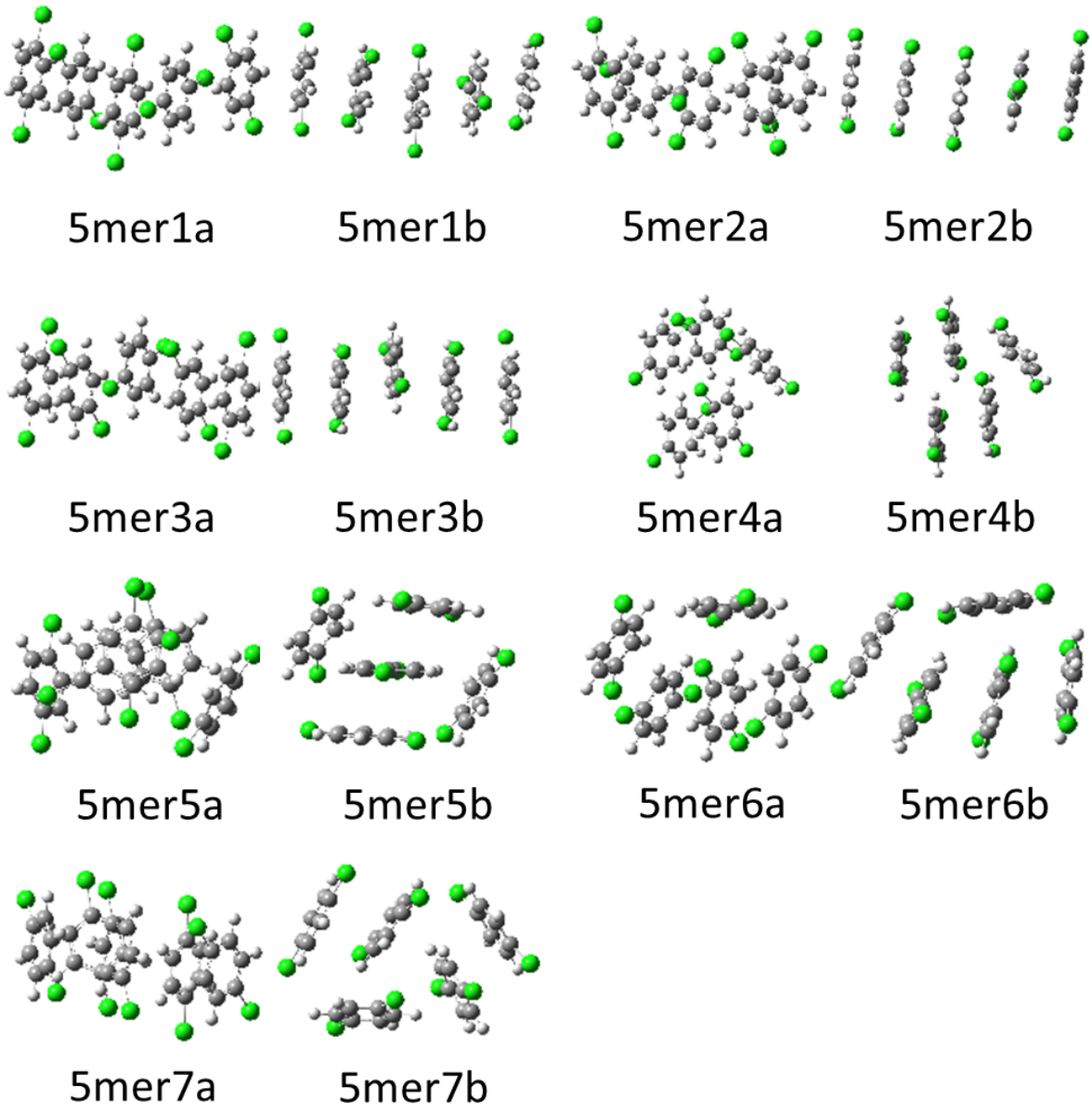


Fig. S7: The B3LYP-D3BJ/6-31G(d) optimized structures of the 2ClB pentamers (5mer) each presented from two perspectives (labeled a and b). 5mer6 is the global minimum at the B3LYP-D3BJ/6-31G(d) level.

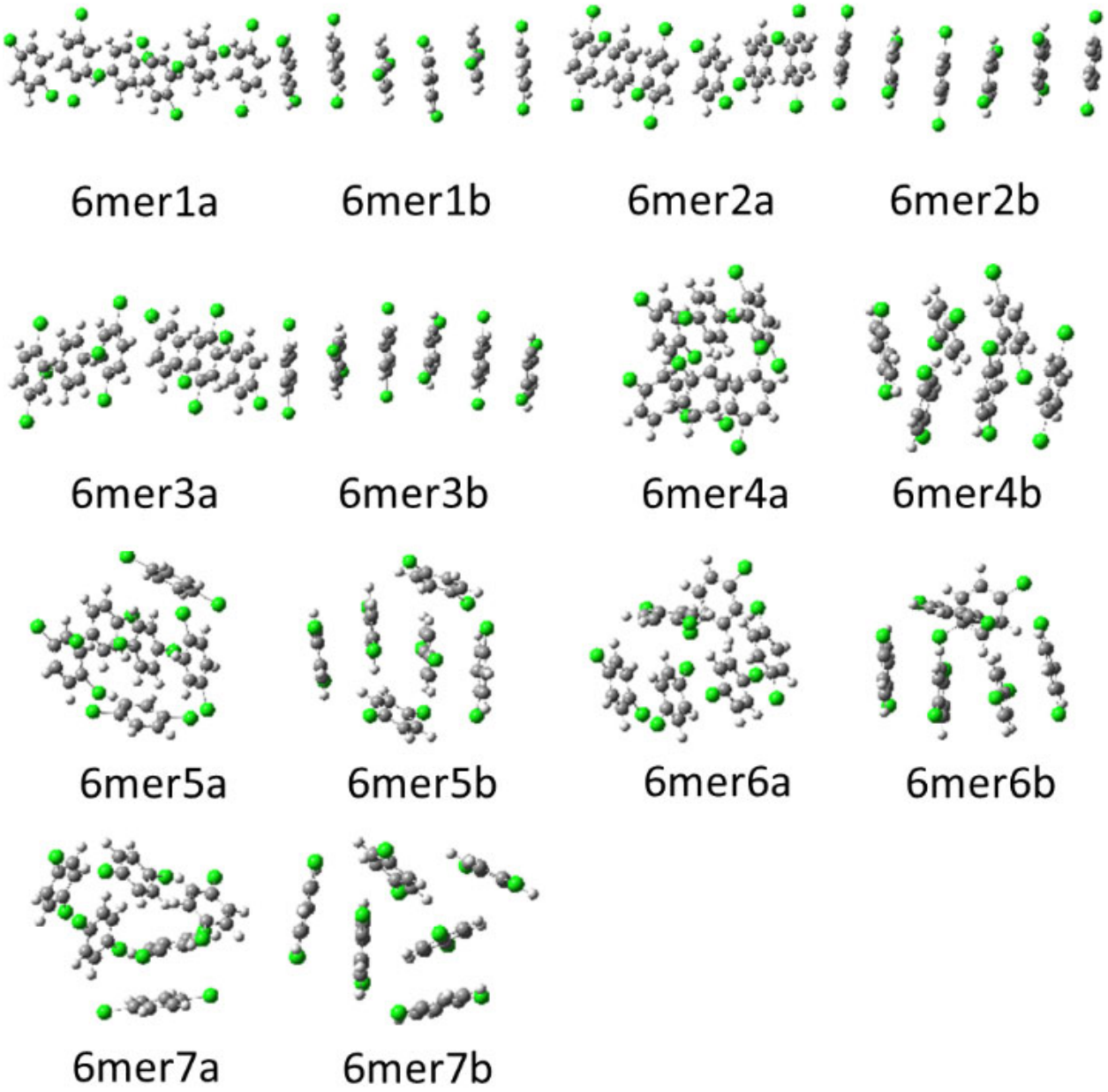


Fig. S8: The B3LYP-D3BJ/6-31G(d) optimized structures of the 2ClB hexamers (6mer) each presented from two perspectives (labeled a and b). 6mer6 is the global minimum at the B3LYP-D3BJ/6-31G(d) level.