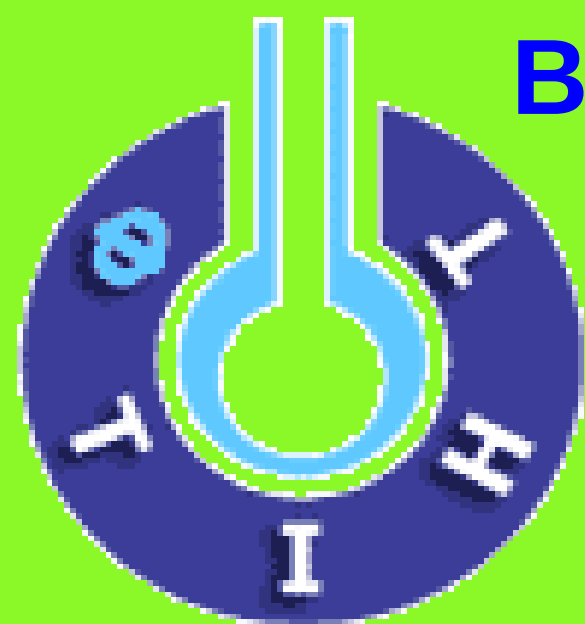




BINDING OF NATIVE DNA TO MoS₂ NANOFLLAKES: EXPERIMENTAL AND THEORETICAL STUDIES

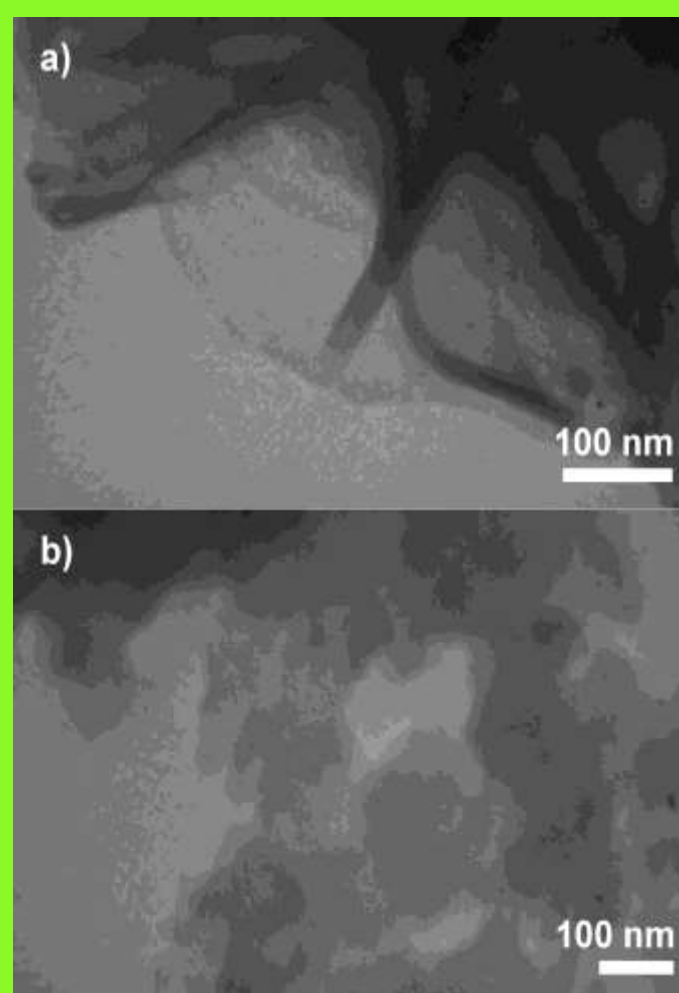
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Currently, the study of the optical and physicochemical properties of 2D materials is of great interest. Such materials include MoS₂, which is currently considered as a promising candidate for use in the field of nanobiosensing (for the development of sensitive nanobiosensors) and nanomedicine (as a theranostic agent). In the present work, we study whether native DNA would bind to MoS₂ flakes (FLs) at relatively low ionic force (10⁻³ M Na⁺, pH7) using experimental (differential UV spectroscopy and thermal denaturation method) and theoretical (DFT) methods.



The performed analysis of TEM image in Fig. 1a reveals well-defined 2D multilayer lateral FLs, as well as folded edges. A noticeable contrast between one FL and a few flaked aggregates can be observed. As shown in Fig. 1b, the DNA:MoS₂ FL nanocomposites exhibit agglomerated functionalized nanostructures. Polymer covers of MoS₂ FLs blurs their outlines.

Fig.1 . TEM images of a) MoS₂ FLs and b) DNA:MoS₂ FL nanoassemblies.

The spectra (Fig. 2) show that the absorption intensity increases as the MoS₂ FL concentration increases, indicating that there are no the aggregation processes with the MoS₂ FLs concentration. An analysis of our sample gives the average lateral size of MoS₂ FLs are about 125 nm and the number of the MoS₂ layers per FL is about 12.

Fig. 2. Absorption spectra of MoS₂ FLs obtained at different concentrations.

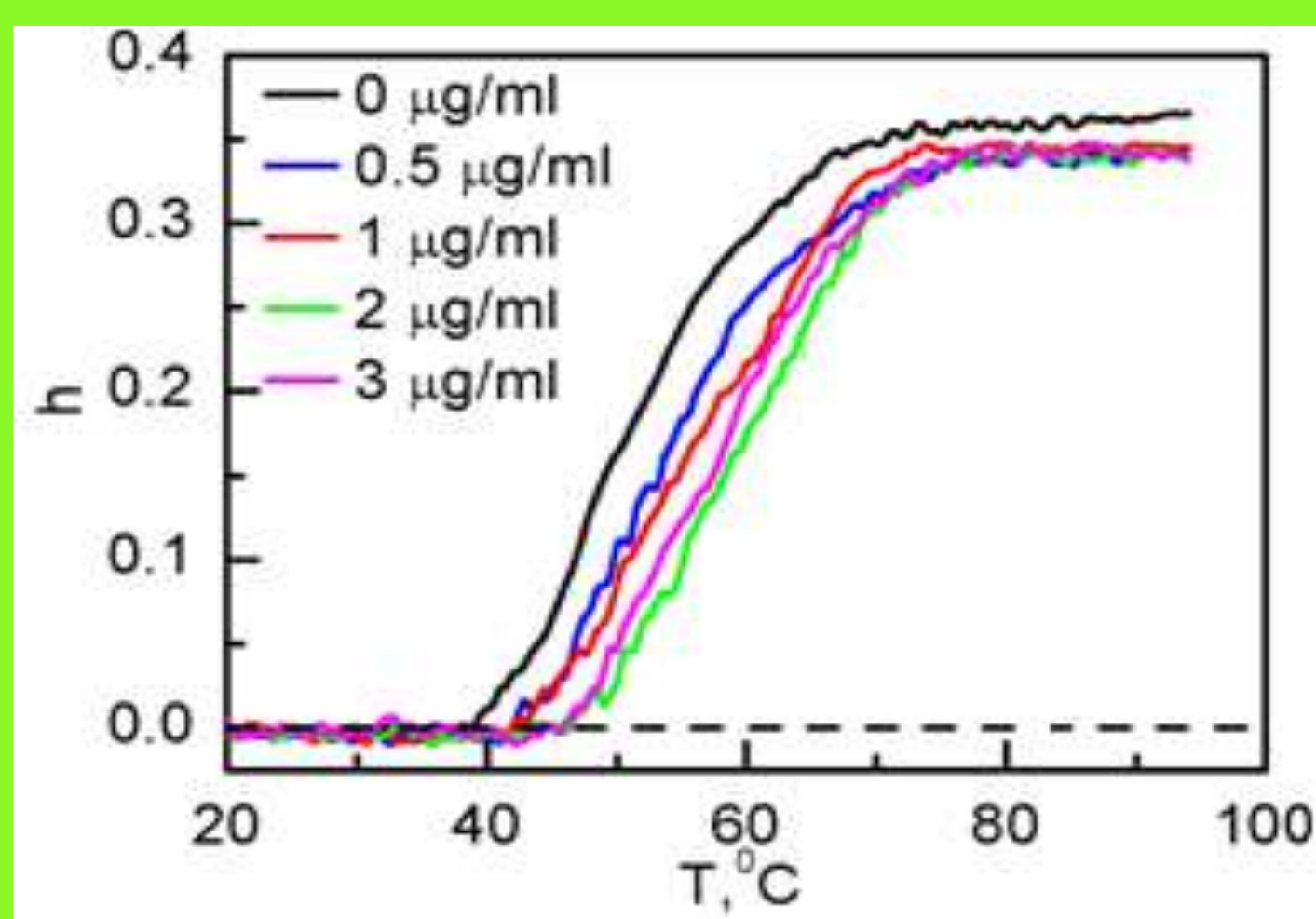
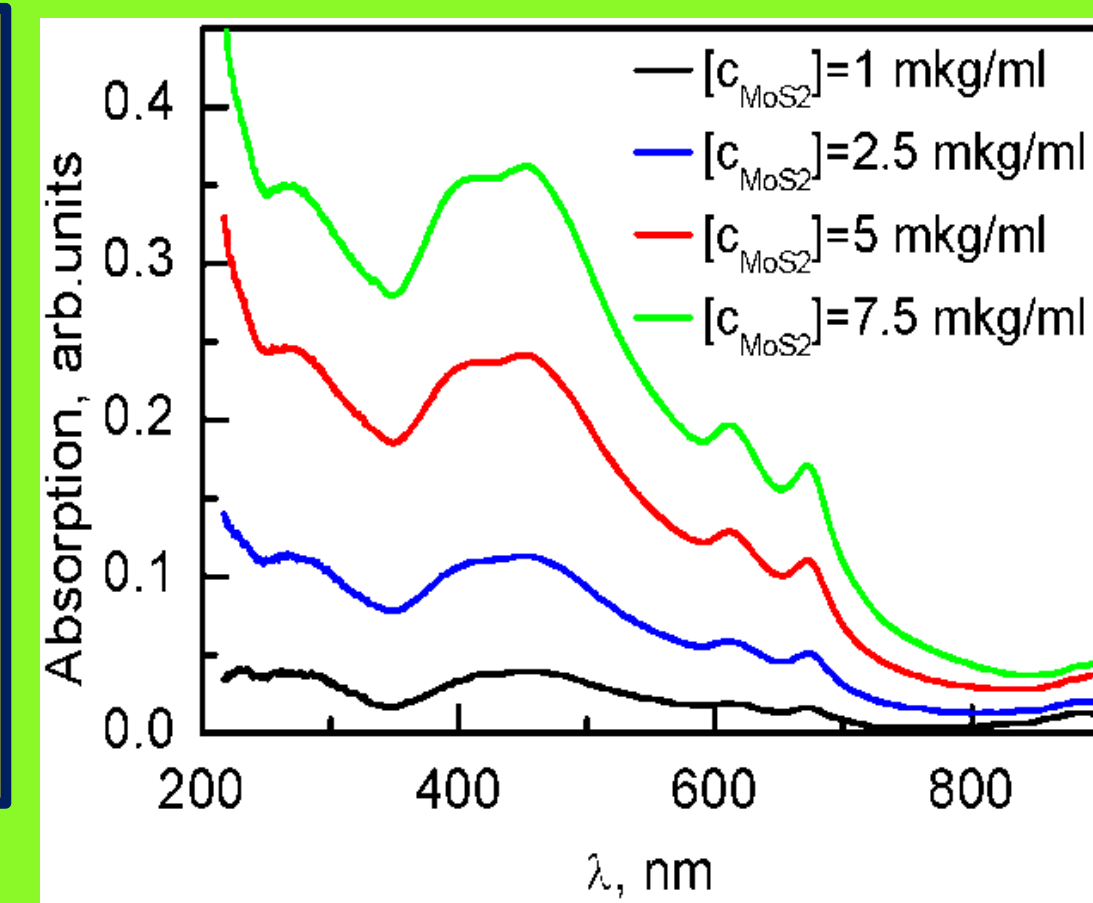


Fig. 3. Temperature dependence of the hyperchromic coefficient (*h*) of DNA without and with MoS₂ FLs.

DNA melting curves (Fig. 3) maintains the S-shape for the biopolymer in the nanoassembly indicating that the duplex structure of the DNA is preserved.

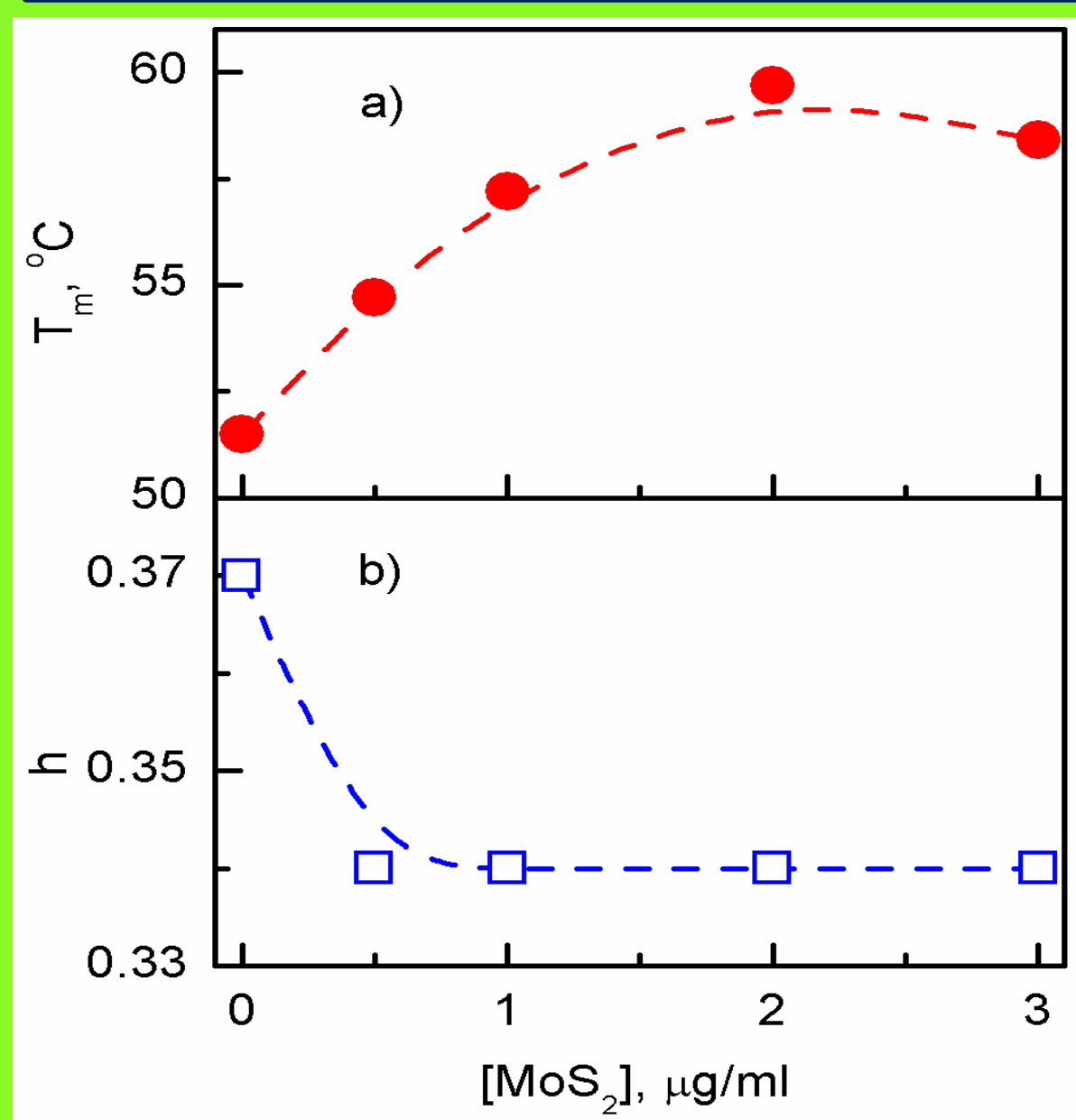


Fig. 4. (a) The melting temperature dependence of DNA (*T_m*) as a function of [*c_{MoS2}*]. (b) The concentration dependence of hyperchromic coefficient (*h*) of DNA with MoS₂ FLs.

An increase in the melting temperature of DNA and a decrease in the hyperchromic coefficient at binding with MoS₂ FLs (Fig.4) indicates the formation of the DNA:MoS₂ FL nanoassemblies due primarily to the covalent interaction of the oxygen atoms of the phosphate groups of DNA with the MoS₂ FLs.

The weakest interaction is observed for the stacked MoS₂-dMP S complexes in which the adsorbed molecule is only in contact with the surface of the sulfur atoms (IE are about -23.3 kcal/mol). Much stronger interaction is observed for the bonded MoS₂-dMP B complexes where the adsorbed molecule interacts with the edge of the MoS₂ nanolayer fragment (IE is -162.5 kcal/mol). An aqueous environment significantly reduces the interaction energies in all complexes (Table 1). At the same time, in the covalently bonded complexes, the interaction energy exceeds 50 kcal/mol in absolute value when taking into account the aqueous environment. This indicates that the complexes are stable in water. In the dMP complex with a disulfur-vacancies V_{2S} defect (MoS₂(V_{2S})-dMP B, Fig. 5) the interaction energy is -100.7 kcal/mol. The interaction energy in the dMP complex with the vacancy complex of Mo and its nearest three disulfur pairs (MoS₂(Mo_S)-dMP B, Fig. 5) is -101.6 kcal/mol.

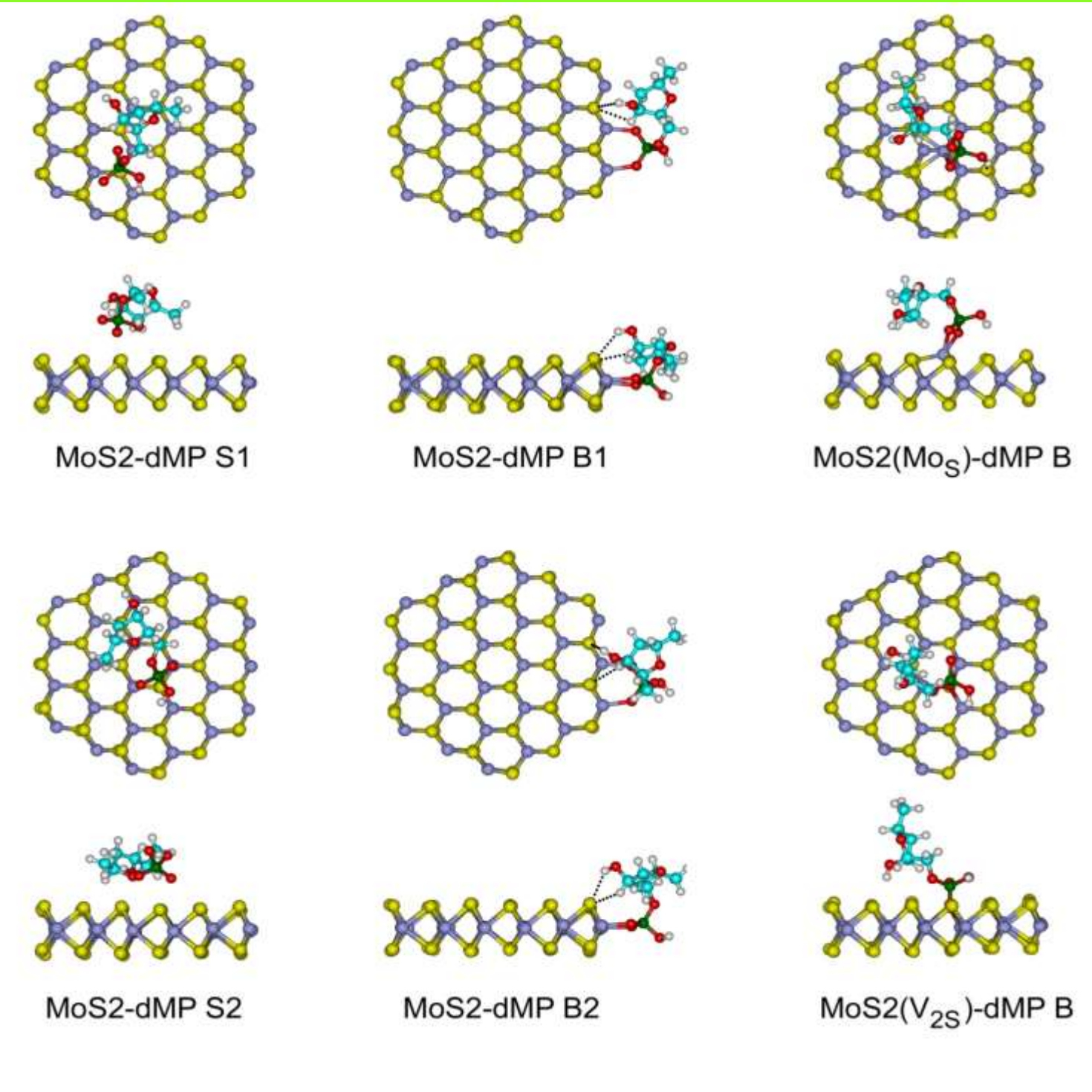


Fig. 5. Calculated structure of the MoS₂ (pristine layered fragment)-dMP and MoS₂ (defects)-dMP complexes (top view and side view): S – stacked complexes; B – covalently bonded complexes. Complexes with pristine MoS₂ are numbered according to their relative stabilities.

Conclusion

Thus, the results obtained indicate the critical role of defects and edge atoms of MoS₂ FLs in their biofunctionalization and can be used in biosensing and elaboration of new drug delivery systems.

Table 1

Calculated ZPVE and BSSE corrected interaction energies (IE, kcal/mol) of the deoxyribose monophosphate-MoS₂ complexes. The interaction energies calculated with accounting for water environment (using the PCM approach) are shown in parentheses.

Complex	MoS ₂	Description ^a	IE
MoS ₂ -dMP S1	pristine	stacked	-23.3 (-1.2)
MoS ₂ -dMP S2	pristine	stacked	-22.4 (-0.9)
MoS ₂ -dMP B1	pristine	bonded	-162.5 (-54.2)
MoS ₂ -dMP B2	pristine	bonded	-160.9 (-53.7)
MoS ₂ (Mo _S)-dMP B	Mo _S	bonded (O-Mo*)	-101.6 (-19.6)
MoS ₂ (V _{2S})-dMP B	V _{2S}	bonded (O-Mo**)	-100.7(-44.3)

^a, Mo* - molybdenum atom replacing a surface sulfur atom in the MoS₂ fragment. Mo** - inner molybdenum atoms available for interaction after the formation of a V_{2S} vacancy.