Supporting Information

Noncovalent interactions governing imatinib binding to MoS_2 sheets: a PXRD/DFT study

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Content

I. Assembling of imatinib-MoS_2 layered compound

Layered compound with alternating monolayers of imatinib cations ($ImaH^+$) and MoS_2 was obtained in a way similar to that previously used for preparation of various MoS_2-organic compounds [1]. Initially, the crystalline $LiMoS_2$ has been obtained by treating purified natural molybdenum disulfide (DM-1, Scopin Factory, Russia) with a particle size (95%) smaller than 7 μm with an excess of 1.6 M n-butyllithium solution in hexane (Aldrich) for 1 week, washing in hexane and drying in vacuum. This compound has been sonicated in bi-distilled water to prepare aqueous dispersions of the concentration $2 \cdot mg \cdot mL^{-1}$. Then, 70 ml of the MoS_2 dispersion have been mixed with 40 ml of the solution prepared by dissolution of imatinib mesylate (Sigma-Aldrich) in amount of 0.125 g (0.21 mmol) in water acidified by HCl. The visible formation of the particles in dispersion was observed shortly after mixing the components. After stirring the reaction mixture on a magnetic stirrer for 2 h, the precipitate was collected by centrifugation. The acidity of the first supernatant measured using a Hanna Instruments 8424 pH meter amounted to pH 4. The structure probed by powder X-ray diffraction (PXRD) just after precipitation looked nearly amorphous until the prolonged washing with water at pH 5, which yielded structurized layered compound with the interlayer distance (*c*) of approximately 11.3 Å.

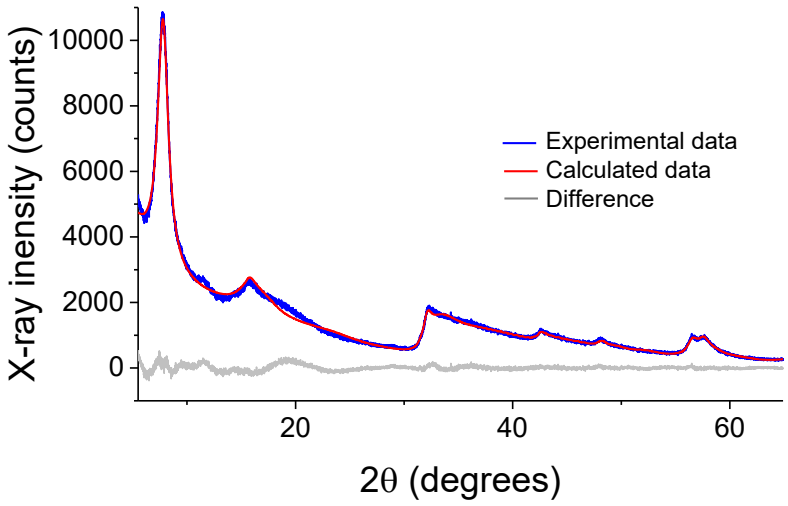

Fig. S1 X-ray diffraction pattern of **b**-ImaH-MoS_2 and its fit (Rwp=4.95 %). (The pattern of **p**-ImaH-MoS_2 is presented in the main text.)

II. Structure refinement

Табле S1 Selected structural parameters of (**p**-ImaH)$_{1/32}$MoS$_2$ obtained by PXRD pattern modeling and their relation with the parameters of the built periodic crystal structure

Parameter	Refined cell	Calculated model crystal
a (Å)	a_0 = 5.69(3)	a = 11.2627 ($\vec{a} = 2\overrightarrow{a_0}$)
b (Å)	b_0 = 3.205(18)	b = 25.0320 ($\vec{b} = 8\overrightarrow{b_0}$)
c (Å)	c_0 = 11.31(6) *	*c* = 11.4584 ($\vec{c} = \vec{c}_0 + \vec{\Delta}_a + \vec{\Delta}_b$)
α (°)	90	86.776
β (°)	90	81.304
γ (°)	90	90
V, A^3	2063(19)	3188.129
Mo-Mo (Å)	2.831(11), 3.205(18), 3.732(16)	2.737, 3.122, 3.735
Mo-Mo-Mo (deg)	68.9(4)	69.49
S-S $\Delta\chi 1$, $\Delta\chi 2$ (Å)	3.47(2), 2.515(16)	3.484, 2.735
Height variation in S positions on the sheet surface (Å)	0.477(12)	0.372

In Ufer supercell c=10c_0

Табле S2 Selected structural parameters of (**b**-ImaH) $_{1/32}MoS_2$ obtained by PXRD pattern modeling and their relation with the parameters of the built periodic crystal structure

Parameter	Refined cell	Calculated model crystal
a (Å)	a_0 = 5.70(4)	a = 14.6616 ($\vec{a} = 2\overrightarrow{a_0} + 3\overrightarrow{b_0}$)
b (Å)	b_0 = 3.22(2)	b = 25.0320 ($\vec{b} = 8\overrightarrow{b_0}$)
c (Å)	c_0 = 113.1(8) *	*c* = 11.4584 ($\vec{c} = \vec{c}_0 + \vec{\Delta}_a + \vec{\Delta}_b$)
α (°)	90	86.776
β (°)	90	81.349
γ (°)	90	50.128
V, A^3	2076(24)	3186.3
Mo-Mo (Å)	2.839(15), 3.22(2), 3.74(2)	2.734, 3.140, 3.722
Mo-Mo-Mo (deg)	69.1(5)	69.95
S-S $\Delta z1$, $\Delta z2$ (Å)	3.47(3), 2.52(2)	3.499, 2.735
Height variation in S positions on the sheet surface (Å)	0.477(16)	0.390

In Ufer supercell $c=10c_0$

Table S3 Torsion angles Q1-Q8 (degrees) of **p**-ImaH molecule (**p**) in the free state (**fr**), in the assembled (**as**) and exfoliated (**exf**) ImaH-MoS_2 structure

Angle	**fr-p ***	**as-p**	**Δ_{as-p}****	**exf-p**	**Δ_{exf} ****
Q1	-160.688	158.70	**40.61**	-174.18	**13.49**
Q2	-179.37	-178.67	**-0.7**	-173.61	**-5.76**
Q3	-0.42	5.89	**-6.31**	0.63	**-1.05**
Q4	175.76	-177.15	**-7.09**	169.42	**6.34**
Q5	179.07	176.97	**2.1**	-179.90	**-1.03**
Q6	154.01	152.36	**1.65**	144.98	**9.03**
Q7	54.86	27.44	**27.42**	57.14	**-2.28**
Q8	-169.72	-176.68	**6.96**	177.21	**13.07**

* According to ref. [2]

** Δ_{as-p} or Δ_{exf} is the difference between the angles in **fr-p** and **as-p** or **exf-p**, respectively. The conjugate angle reversed in sign is given for the angles approaching +/-360°.

Table S4 Torsion angles (degrees) of **b**-ImaH molecule (**b**) in the free state (**fr**) and in the assembled (**as**) ImaH-MoS_2 structure

Angle	**fr-b ***	**as-b**	**Δ_{as-b}****
Q1	-30.04	23.52	**-53.56**
Q2	-5.82	-1.65	**-4.17**
Q3	-9.85	2.29	**-12.14**
Q4	177.79	-175.65	**-6.56**
Q5	177.38	-179.19	**-3.43**
Q6	154.96	-155.49	**-49.55**
Q7	55.89	-10.57	**66.46**
Q8	-169.94	167.57	**22.49**

* According to ref. [2].

** Δ_{as-b} is the difference between the angles in **fr-b** and **as-b**, respectively. The conjugate angle reversed in sign is given for the angles approaching +/-360°.

III. Quantum-chemical optimization and bonding interaction analysis

To fulfill the requirement of strictly ordered structure for periodic calculations, we constructed the hypothetical 3D models of the structures under consideration, in which the turbostratic disorder in sheet stacking was ignored. The protonated imatinib molecules were placed at the positions obtained in structure refinement with Ufer's supercell and regularly distributed on the sulfide sheets according to the ratio which provides full filling of the interlayer: $(ImaH)_{1/32}MoS_2$. Upon constructing the models, the unreasonably short intermolecular contacts were avoided. These 3D structural models were described with the triclinic cells with the parameters derived from the Ufer's supercell as indicated in Tables S1 and S2.

To optimize the structural model and to reveal the interactions between inorganic and organic components, periodic DFT calculations were carried out using the plane wave (PW) basis set and PBE functional (see Experimental).

Table S5. Calculated energies for different models of $(ImaH)_{1/32}MoS_2$

Model	Energy, eV
as-p	-1124.228
as-b	-1123.93
exf-p	-1122.75

Table S6 Summary of average critical point properties (a.u. if not given) in the hypothetical ordered $(\mathbf{p}\text{-}ImaH)_{1/32}MoS_2$

Atom1	Atom2	Count	d, Å	$\rho(\mathbf{r})$	$\nabla^2\rho(\mathbf{r})$	$g_e(\mathbf{r})$	$v_e(\mathbf{r})$	$h_e(\mathbf{r})$	Energy, kcal/mol
Mo	Mo	32	2.735-2.740	0,060934	0,074555	0,039518	-0,060400	-0,020880	-18.93
Mo	S	96	2.384-2.416	0,088315	0,142308	0,074031	-0,11248	-0,038450	-35.25
Mo	S	96	2.463-2.497	0,077212	0,108358	0,058270	-0,089450	-0,031180	-28.03
NH	S	1	3.729	0,009976	0,021891	0,004976	-0,004480	0,000497	-1.40
CH	S	21	3.487-4.630	0.004172	0.012206	0.002405	-0.001760	0.000647	-0.6
C	S	13	3.796-4.275	0.002436	0.007350	0.001358	-0.000879	0.000479	-0.28
N	S	4	4,056-4,103	0.002068	0.006879	0.001243	-0.000767	0.000476	-0.24

Table S7 Summary of average critical point properties (a.u. if not given) in the hypothetical ordered **exf-(p-**$(ImaH)_{1/32}MoS_2$

Atom1	Atom2	Count	d, Å	$\rho(\mathbf{r})$	$\nabla^2\rho(\mathbf{r})$	$g_e(\mathbf{r})$	$v_e(\mathbf{r})$	$h_e(\mathbf{r})$	Energy, kcal/mol
Mo	Mo	32	2.737-2.743	0.060953	0.074522	0.039526	-0.060422	-0.020895	-18.93
Mo	S	96	2.385-2.416	0.088289	0.142218	0.073992	-0.112429	-0.038437	-35.23
Mo	S	96	2.462-2.497	0.077189	0.108473	0.058268	-0.089418	-0.031150	-28.02
CH	S	15	3.709-4.715	0.003846	0.010703	0.002121	-0.001566	0.000554	-0.49
C	S	2	4.164-4.260	0.001795	0.005244	0.000950	-0.000590	0.000360	-0.18
NH	S	1	3.599	0.012838	0.026438	0.006427	-0.006245	0.000182	-1.96
N	S	2	4.037-4.196	0.001853	0.005732	0.001036	-0.000640	0.000396	-0.20

References

1 A. S. Golub, Y. V. Zubavichus, Y. L. Slovokhotov, Y. N. Novikov and M. Danot, *Solid State Ion.*, 2000, **128**, 151–160.

2 A. V. Vologzhanina, I. E. Ushakov and A. A. Korlyukov, *Int. J. Mol. Sci.*, 2020, **21**, 8970.