

Supporting Information for

Binary Ionic Porphyrin Nanosheets: Electronic and Light-harvesting Properties Regulated by Crystal Structure

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Zn/Sn nanosheet crystal (CCDC 833006): A dark red shard of dimensions 0.09 x 0.04 x 0.001 mm³ was mounted in the 250(2) K nitrogen cold stream provided by an Oxford Cryosystems Cryostream 700 Plus low temperature apparatus on the goniometer head of a Bruker D8 diffractometer equipped with a Platinum200 CCD detector on beamline 11.3.1 at the Advanced Light Source in Berkeley, CA. Diffraction data were collected using synchrotron radiation monochromated using silicon(111) to a wavelength of 0.77490(1) Å. An approximate full sphere of data to $2\theta_{\text{max}}=50.5^\circ$ was collected using 0.3° ω scans. A multi-scan correction for absorption was applied using the program SADABS-2008/1. A total of 78267 reflections were collected, of which 23249 were unique [$R(\text{int}) = 0.0555$], and 15932 were observed [$I > 2\sigma(I)$]. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares on F^2 (SHELXL-97) using 2036 parameters and 1062 restraints. The hydrogen atoms on carbon atoms were generated geometrically and refined as riding atoms with C-H = 0.95- 0.99 Å and $U_{\text{iso}}(\text{H}) = 1.2$ times $U_{\text{eq}}(\text{C})$ for CH and CH₂ groups and $U_{\text{iso}}(\text{H}) = 1.5$ times $U_{\text{eq}}(\text{C})$ for CH₃ groups. This structure was challenging on many crystallographic levels. There is a large amount of disorder present in the structure; in the solvent, and in the molecules of interest. Hydrogens could be only located for the axial water molecule for Zn1, which had to be refined as restrained with the thermal parameter $U(\text{H}) = 1.5 * U(\text{O})$. O1W and O2W, which are the two highest occupancy water sites, were the only water molecules with hydrogens that were found in the difference map. Those hydrogens were treated the same as the axial ligated water molecule on Zn1. No hydrogens could be located for the other Zn porphyrin or the hydroxides of the Sn porphyrins. Other disorder modeling is described below. The maximum and minimum peaks in the final difference Fourier map were 0.960 and -0.587 e.Å⁻³. Crystal Data: C₈₈ H_{89.45} N₁₂ O_{28.47} S₄ Zn Sn, Mw = 2082.98, triclinic, a = 17.1975(9) Å, b = 22.7109(11) Å, c = 23.2400(12) Å, $\alpha = 94.052(3)^\circ$, $\beta = 104.128(3)^\circ$, $\gamma = 106.292(3)^\circ$, V = 8353.9(7) Å³, T = 250(2) K, Z = 3, $R_1 [I > 2\sigma(I)] = 0.0821$, wR_2 (all data) = 0.2806, GOF (on F^2) = 0.977.

The contents of the asymmetric unit are as follows: one complete Zn porphyrin with 4-phenyl-sulfonyl groups at the meso positions, one half of the same Zn-porphyrin, and three half Sn porphyrins with 4-N-methyl-pyridines (4-map) at the meso positions. The Zn porphyrins, with their sulfonyl groups deprotonated have a total charge of 4⁻. The Sn porphyrins, with the 4-map groups, have a net 4⁺ charge, with Sn(IV) bonded as well to axial hydroxides. The charge balance is achieved. The asymmetric unit also contains 47 water molecule positions, which sum to 20.41 water molecules. The other axial water and the hydroxide ligands seem to be in free rotation. No hydrogen positions

could be determined and refined for these oxygen atoms.

There are some close contacts, but only with partially-occupied solvated water molecules. All attempts to refine hydrogen positions on these axial oxygens failed.

On the sulfonated porphyrin of Zn1, there is a wagging disorder of one of the sulfonyl groups. The sites were split, and refined using geometric and thermal parameter restraints. CifCheck is having a problem with there being duplicate named atoms in the file (which is common with disorder), so this is probably due to CifCheck not properly interpreting the disorder PART statements.

On the sulfonated porphyrin of Zn2, there is a rotational disorder of the oxygens in a sulfonyl group, these were also modeled as a split-site, and refined with geometric and thermal parameter restraints. CifCheck is also having a problem with these duplicate names in PART statements. Zn2 and its axial oxygen O401 have been refined as having 50 percent occupancy due to proximity to an inversion center, and the fact that Zn is five coordinate in these porphyrins. The fact that this was a Zn porphyrin was confirmed by the appearance of sulfonyls during the refinement.

The Sn porphyrins all appear in the asymmetric unit with the Sn atom on an inversion center. The porphyrins of Sn1 and Sn2 are mostly well behaved, with one 4-map ring split over two sites. Some of the other rings are waving within the plane of the ring, but splitting these rings further, and the introduction of more restraints and parameters was not balanced with a gain of chemical information.

The porphyrin containing Sn3 seems to be the most unhappy with the Sn placement on an inversion center. The whole porphyrin seems disordered, but refining the whole porphyrin as a split site model did not work. The current model was a success- splitting both rings dramatically. One ring required four positions to encompass the residual density. The other, only two. The thermal parameters within the planar porphyrin core are still larger than optimal, but this is the best model.

This structure contains many solvated water molecules. All the oxygen (water) positions found were restrained to

the same thermal parameter, and allowed to refine their occupancy. Once the occupancies converged, the thermal parameter was allowed to refine. All but one position refined to a partial occupancy. No hydrogens vectors could be reliably located for most of the solvated water molecules. There are close contacts between solvated water molecules and hydrogen acceptors, and certainly hydrogen bonding is occurring within this structure, however modeling hydrogen atoms on partially-occupied water molecules was not possible with this data.

All split site model refinements were accomplished using geometric and thermal parameter similarity restraints. The restraints used in the refinement are as follows:

SIMU 0.001 O1W > O47W

SADI_mmap 0.01 N204 C222

SADI_mmap 0.02 C222 C218 C222 C219

SADI_mmap 0.01 N203 C221 N3 C21

SADI_mmap 0.02 C221 C213 C221 C214 C21 C13 C21 C14

SADI_mmap 0.01 C216 C217 C216 C220 C11 C12 C11 C15

SADI_mmap 0.01 C217 C218 C220 C219 C12 C13 C14 C15

SADI_mmap 0.01 N204 C219 N204 C218 N3 C13 N3 C13

SADI_mmap 0.02 N204 C220 N204 C217 N3 c12 N3 C15

SADI_mmap 0.02 C216 C218 C216 C219 C11 C13 C11 C14

SIMU 0.01 C11_7 > C21_8

FLAT_mmap 0.01 C210_0 C216 c217 c218 n204 c219 c220

SIMU 0.01 C211_3 > C222_6

SIMU 0.01 S302 > O307

SADI 0.01 S302 O305 S302 O306 S302 O307 S401 O402 S401 O403 S401 O404

SADI 0.01 O305 O306 O305 O307 O306 O307 O402 O403 O402 O404 O403 O404

SIMU 0.01 O402 > O404

DFIX 0.854 0.01 O301 H301 O301 H302 O1w H1wa O1w H1wb O2w H2wa O2w H2wb

DFIX 1.367 0.02 H301 H302 H1wa H1wb H2wa H2wb

Table S1. Crystal data and structure refinement for 833006.

Identification code	833006	
Empirical formula	C ₈₈ H _{89.45} N ₁₂ O _{28.47} S ₄ Zn Sn	
Formula weight	2082.98	
Temperature	250(2) K	
Wavelength	0.77490 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 17.1975(9) Å	α = 94.052(3)°.
	b = 22.7109(11) Å	β = 104.128(3)°.
	c = 23.2400(12) Å	γ = 106.292(3)°.
Volume	8353.9(7) Å ³	
Z	3	
Density (calculated)	1.242 Mg/m ³	
Absorption coefficient	0.733 mm ⁻¹	
F(000)	3220	
Crystal size	0.09 x 0.04 x 0.001 mm ³	
θ range for data collection	2.10 to 25.25°.	
Index ranges	-18 ≤ h ≤ 18, -25 ≤ k ≤ 25, -25 ≤ l ≤ 24	
Reflections collected	78267	
Independent reflections	23249 [R(int) = 0.0555]	
Completeness to θ = 25.25°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.999 and 0.937	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	23249 / 1062 / 2036	
Goodness-of-fit on F ²	0.977	
Final R indices [I > 2σ(I)]	R1 = 0.0821, wR2 = 0.2550	
R indices (all data)	R1 = 0.1108, wR2 = 0.2806	
Largest diff. peak and hole	0.960 and -0.587 e.Å ⁻³	

Table S2. Bond distances for 833006.

Number	Atom1	Atom2	Length
1	Sn1	O1	2.037(4)
2	Sn1	N1	2.088(6)
3	Sn1	N2	2.095(5)
4	Sn1	N1	2.088(6)
5	Sn1	N2	2.095(5)
6	Sn1	O1	2.037(4)
7	N1	C1	1.369(9)
8	N1	C4	1.40(1)
9	N2	C6	1.38(1)
10	N2	C9	1.368(9)
11	N4	C18	1.35(1)
12	N4	C19	1.32(1)
13	N4	C22	1.51(1)
14	C1	C2	1.42(1)
15	C1	C10	1.41(1)
16	C2	H2A	0.940(7)
17	C2	C3	1.35(1)
18	C3	H3A	0.94(1)
19	C3	C4	1.46(1)
20	C4	C5	1.40(1)
21	C5	C6	1.38(1)
22	C5	C11_7	1.50(2)
23	C6	C7	1.43(1)
24	C7	H7A	0.940(8)
25	C7	C8	1.32(1)
26	C8	H8A	0.940(7)
27	C8	C9	1.44(1)
28	C9	C10	1.40(1)
29	C10	C16	1.47(1)
30	C10	C1	1.41(1)
31	C11_7	C12_7	1.39(1)
32	C11_7	C15_7	1.38(2)
33	C12_7	H12A_7	0.94(1)
34	C12_7	C13_7	1.39(2)
35	C13_7	H13A_7	0.94(1)
36	C13_7	N3_7	1.35(2)
37	N3_7	C14_7	1.33(2)
38	N3_7	C21_7	1.55(2)
39	C14_7	H14A_7	0.94(2)
40	C14_7	C15_7	1.40(2)
41	C15_7	H15A_7	0.94(1)
42	C21_7	H21A_7	0.97(1)
43	C21_7	H21B_7	0.97(2)
44	C21_7	H21C_7	0.97(2)
45	C16	C17	1.39(1)
46	C16	C20	1.380(9)
47	C17	H17A	0.941(8)
48	C17	C18	1.38(1)
49	C18	H18A	0.941(9)

50	C19	H19A	0.940(7)
51	C19	C20	1.38(1)
52	C20	H20A	0.940(8)
53	C22	H22A	0.970(8)
54	C22	H22B	0.97(1)
55	C22	H22C	0.97(1)
56	N1	C1	1.369(9)
57	N1	C4	1.40(1)
58	N2	C6	1.38(1)
59	N2	C9	1.368(9)
60	N4	C18	1.35(1)
61	N4	C19	1.32(1)
62	N4	C22	1.51(1)
63	C1	C2	1.42(1)
64	C2	H2A	0.940(7)
65	C2	C3	1.35(1)
66	C3	H3A	0.94(1)
67	C3	C4	1.46(1)
68	C4	C5	1.40(1)
69	C5	C6	1.38(1)
70	C5	C11_7	1.50(2)
71	C6	C7	1.43(1)
72	C7	H7A	0.940(8)
73	C7	C8	1.32(1)
74	C8	H8A	0.940(7)
75	C8	C9	1.44(1)
76	C9	C10	1.40(1)
77	C10	C16	1.47(1)
78	C11_7	C12_7	1.39(1)
79	C11_7	C15_7	1.38(2)
80	C12_7	H12A_7	0.94(1)
81	C12_7	C13_7	1.39(2)
82	C13_7	H13A_7	0.94(1)
83	C13_7	N3_7	1.35(2)
84	N3_7	C14_7	1.33(2)
85	N3_7	C21_7	1.55(2)
86	C14_7	H14A_7	0.94(2)
87	C14_7	C15_7	1.40(2)
88	C15_7	H15A_7	0.94(1)
89	C21_7	H21A_7	0.97(1)
90	C21_7	H21B_7	0.97(2)
91	C21_7	H21C_7	0.97(2)
92	C16	C17	1.39(1)
93	C16	C20	1.380(9)
94	C17	H17A	0.941(8)
95	C17	C18	1.38(1)
96	C18	H18A	0.941(9)
97	C19	H19A	0.940(7)
98	C19	C20	1.38(1)
99	C20	H20A	0.940(8)
100	C22	H22A	0.970(8)
101	C22	H22B	0.97(1)
102	C22	H22C	0.97(1)

103	Zn1	O301	2.177(6)
104	Zn1	N301	2.044(5)
105	Zn1	N302	2.062(6)
106	Zn1	N303	2.036(5)
107	Zn1	N304	2.041(6)
108	S301	O302	1.407(9)
109	S301	O303	1.474(7)
110	S301	O304	1.35(1)
111	S301	C324	1.749(9)
112	S302	O305	1.45(1)
113	S302	O306	1.42(1)
114	S302	O307	1.42(1)
115	S302	C330	1.75(2)
116	S303	O308	1.399(7)
117	S303	O309	1.398(9)
118	S303	O310	1.453(9)
119	S303	C336	1.77(1)
120	S304	O311	1.41(1)
121	S304	O312	1.38(1)
122	S304	O313	1.41(1)
123	S304	C342	1.755(9)
124	O301	H301	0.9(1)
125	O301	H302	0.86(7)
126	N301	C301	1.379(8)
127	N301	C304	1.366(9)
128	N302	C316	1.373(9)
129	N302	C319	1.372(9)
130	N303	C311	1.341(8)
131	N303	C314	1.35(1)
132	N304	C306	1.37(1)
133	N304	C309	1.369(9)
134	C301	C303	1.44(1)
135	C301	C320	1.385(9)
136	C302	H30A	0.939(7)
137	C302	C303	1.34(1)
138	C302	C304	1.44(1)
139	C303	H30B	0.940(7)
140	C304	C305	1.398(8)
141	C305	C306	1.41(1)
142	C305	C321	1.48(1)
143	C306	C307	1.458(9)
144	C307	H30C	0.939(9)
145	C307	C308	1.30(1)
146	C308	H30D	0.940(8)
147	C308	C309	1.46(1)
148	C309	C310	1.39(1)
149	C310	C311	1.42(1)
150	C310	C327	1.51(1)
151	C311	C312	1.45(1)
152	C312	H31A	0.940(8)
153	C312	C313	1.33(1)
154	C313	H31B	0.941(8)
155	C313	C314	1.45(1)

156	C314	C315	1.41(1)
157	C315	C316	1.38(1)
158	C315	C333	1.51(1)
159	C316	C317	1.44(1)
160	C317	H31C	0.940(9)
161	C317	C318	1.34(1)
162	C318	H31D	0.939(9)
163	C318	C319	1.44(1)
164	C319	C320	1.42(1)
165	C320	C339	1.491(9)
166	C321	C322	1.39(1)
167	C321	C326	1.39(1)
168	C322	H32A	0.94(1)
169	C322	C323	1.37(1)
170	C323	H32B	0.940(9)
171	C323	C324	1.38(1)
172	C324	C325	1.40(1)
173	C325	H32C	0.94(1)
174	C325	C326	1.39(1)
175	C326	H32D	0.94(1)
176	C327	C328	1.42(2)
177	C327	C332	1.34(1)
178	C328	H32E	0.94(1)
179	C328	C329	1.37(2)
180	C329	H32F	0.94(2)
181	C329	C330	1.43(2)
182	C330	C331	1.32(2)
183	C331	H33A	0.94(1)
184	C331	C332	1.36(2)
185	C332	H33B	0.94(1)
186	C333	C334	1.36(1)
187	C333	C338	1.36(1)
188	C334	H33C	0.94(1)
189	C334	C335	1.37(1)
190	C335	H33D	0.939(9)
191	C335	C336	1.40(1)
192	C336	C337	1.36(1)
193	C337	H33E	0.94(1)
194	C337	C338	1.40(1)
195	C338	H33F	0.939(9)
196	C339	C340	1.38(1)
197	C339	C344	1.39(1)
198	C340	H34A	0.942(9)
199	C340	C341	1.41(1)
200	C341	H34B	0.940(8)
201	C341	C342	1.37(2)
202	C342	C343	1.39(1)
203	C343	H34C	0.94(1)
204	C343	C344	1.37(1)
205	C344	H34D	0.940(7)
206	Sn2	O101	2.025(7)
207	Sn2	N101	2.097(7)
208	Sn2	N102	2.092(7)

209	Sn2	N101	2.097(7)
210	Sn2	N102	2.092(7)
211	Sn2	O101	2.025(7)
212	N101	C101	1.354(9)
213	N101	C104	1.38(1)
214	N102	C106	1.37(1)
215	N102	C109	1.391(9)
216	N103	C113	1.24(2)
217	N103	C114	1.36(2)
218	N103	C121	1.53(2)
219	N104	C118	1.31(1)
220	N104	C119	1.31(1)
221	N104	C122	1.48(1)
222	C101	C102	1.45(1)
223	C101	C110	1.40(1)
224	C102	H10B	0.940(7)
225	C102	C103	1.34(1)
226	C103	H10C	0.94(1)
227	C103	C104	1.42(1)
228	C104	C105	1.42(1)
229	C105	C106	1.40(1)
230	C105	C111	1.49(1)
231	C106	C107	1.45(1)
232	C107	H10D	0.94(1)
233	C107	C108	1.33(1)
234	C108	H10E	0.940(7)
235	C108	C109	1.43(1)
236	C109	C110	1.39(1)
237	C110	C116	1.500(9)
238	C110	C101	1.40(1)
239	C111	C112	1.37(1)
240	C111	C115	1.37(1)
241	C112	H11B	0.94(1)
242	C112	C113	1.37(2)
243	C113	H11C	0.94(1)
244	C114	H11D	0.94(1)
245	C114	C115	1.37(2)
246	C115	H11E	0.94(1)
247	C116	C117	1.41(1)
248	C116	C120	1.35(1)
249	C117	H11F	0.941(9)
250	C117	C118	1.37(1)
251	C118	H11G	0.940(8)
252	C119	H11H	0.94(1)
253	C119	C120	1.39(1)
254	C120	H12B	0.938(9)
255	C121	H12C	0.97(2)
256	C121	H12D	0.97(1)
257	C121	H12E	0.97(2)
258	C122	H12F	0.97(1)
259	C122	H12G	0.97(1)
260	C122	H12H	0.97(1)
261	N101	C101	1.354(9)

262	N101	C104	1.38(1)
263	N102	C106	1.37(1)
264	N102	C109	1.391(9)
265	N103	C113	1.24(2)
266	N103	C114	1.36(2)
267	N103	C121	1.53(2)
268	N104	C118	1.31(1)
269	N104	C119	1.31(1)
270	N104	C122	1.48(1)
271	C101	C102	1.45(1)
272	C102	H10B	0.940(7)
273	C102	C103	1.34(1)
274	C103	H10C	0.94(1)
275	C103	C104	1.42(1)
276	C104	C105	1.42(1)
277	C105	C106	1.40(1)
278	C105	C111	1.49(1)
279	C106	C107	1.45(1)
280	C107	H10D	0.94(1)
281	C107	C108	1.33(1)
282	C108	H10E	0.940(7)
283	C108	C109	1.43(1)
284	C109	C110	1.39(1)
285	C110	C116	1.500(9)
286	C111	C112	1.37(1)
287	C111	C115	1.37(1)
288	C112	H11B	0.94(1)
289	C112	C113	1.37(2)
290	C113	H11C	0.94(1)
291	C114	H11D	0.94(1)
292	C114	C115	1.37(2)
293	C115	H11E	0.94(1)
294	C116	C117	1.41(1)
295	C116	C120	1.35(1)
296	C117	H11F	0.941(9)
297	C117	C118	1.37(1)
298	C118	H11G	0.940(8)
299	C119	H11H	0.94(1)
300	C119	C120	1.39(1)
301	C120	H12B	0.938(9)
302	C121	H12C	0.97(2)
303	C121	H12D	0.97(1)
304	C121	H12E	0.97(2)
305	C122	H12F	0.97(1)
306	C122	H12G	0.97(1)
307	C122	H12H	0.97(1)
308	Zn2	O401	2.11(1)
309	Zn2	N401	2.080(8)
310	Zn2	N402	2.055(8)
311	Zn2	N401	2.046(8)
312	Zn2	N402	2.062(8)
313	Zn2	Zn2	0.611(5)
314	S401	O402	1.45(1)

315	S401	O403	1.42(1)
316	S401	O404	1.439(9)
317	S401	C414	1.777(6)
318	S402	O405	1.43(1)
319	S402	O406	1.421(8)
320	S402	O407	1.439(9)
321	S402	C420	1.778(9)
322	N401	C401	1.37(1)
323	N401	C404	1.374(8)
324	N401	Zn2	2.046(8)
325	N402	C406	1.380(7)
326	N402	C409	1.36(1)
327	N402	Zn2	2.062(8)
328	C401	C402	1.449(9)
329	C401	C410	1.379(9)
330	C402	H40B	0.940(8)
331	C402	C403	1.34(1)
332	C403	H40C	0.939(6)
333	C403	C404	1.44(1)
334	C404	C405	1.39(1)
335	C405	C406	1.41(1)
336	C405	C411	1.498(8)
337	C406	C407	1.43(1)
338	C407	H40D	0.941(6)
339	C407	C408	1.34(1)
340	C408	H40E	0.938(9)
341	C408	C409	1.43(1)
342	C409	C410	1.415(9)
343	C410	C417	1.50(1)
344	C410	C401	1.379(9)
345	C411	C412	1.38(1)
346	C411	C416	1.41(1)
347	C412	H41B	0.939(9)
348	C412	C413	1.396(9)
349	C413	H41C	0.941(7)
350	C413	C414	1.36(1)
351	C414	C415	1.37(1)
352	C415	H41D	0.940(9)
353	C415	C416	1.41(1)
354	C416	H41E	0.940(8)
355	C417	C418	1.37(1)
356	C417	C422	1.35(1)
357	C418	H41F	0.940(9)
358	C418	C419	1.39(1)
359	C419	H41G	0.939(8)
360	C419	C420	1.35(1)
361	C420	C421	1.36(1)
362	C421	H42A	0.940(9)
363	C421	C422	1.38(2)
364	C422	H42B	0.94(1)
365	S401	O402	1.45(1)
366	S401	O403	1.42(1)
367	S401	O404	1.439(9)

368	S401	C414	1.777(6)
369	S402	O405	1.43(1)
370	S402	O406	1.421(8)
371	S402	O407	1.439(9)
372	S402	C420	1.778(9)
373	N401	C401	1.37(1)
374	N401	C404	1.374(8)
375	N401	Zn2	2.080(8)
376	N402	C406	1.380(7)
377	N402	C409	1.36(1)
378	N402	Zn2	2.055(8)
379	C401	C402	1.449(9)
380	C402	H40B	0.940(8)
381	C402	C403	1.34(1)
382	C403	H40C	0.939(6)
383	C403	C404	1.44(1)
384	C404	C405	1.39(1)
385	C405	C406	1.41(1)
386	C405	C411	1.498(8)
387	C406	C407	1.43(1)
388	C407	H40D	0.941(6)
389	C407	C408	1.34(1)
390	C408	H40E	0.938(9)
391	C408	C409	1.43(1)
392	C409	C410	1.415(9)
393	C410	C417	1.50(1)
394	C411	C412	1.38(1)
395	C411	C416	1.41(1)
396	C412	H41B	0.939(9)
397	C412	C413	1.396(9)
398	C413	H41C	0.941(7)
399	C413	C414	1.36(1)
400	C414	C415	1.37(1)
401	C415	H41D	0.940(9)
402	C415	C416	1.41(1)
403	C416	H41E	0.940(8)
404	C417	C418	1.37(1)
405	C417	C422	1.35(1)
406	C418	H41F	0.940(9)
407	C418	C419	1.39(1)
408	C419	H41G	0.939(8)
409	C419	C420	1.35(1)
410	C420	C421	1.36(1)
411	C421	H42A	0.940(9)
412	C421	C422	1.38(2)
413	C422	H42B	0.94(1)
414	Zn2	O401	2.11(1)
415	Sn3	O201	2.023(7)
416	Sn3	N201	2.090(9)
417	Sn3	N202	2.057(8)
418	Sn3	N201	2.090(9)
419	Sn3	N202	2.057(8)
420	Sn3	O201	2.023(7)

421	N201	C201	1.36(2)
422	N201	C204	1.36(1)
423	N202	C206	1.41(1)
424	N202	C209	1.38(2)
425	C201	C202	1.47(2)
426	C201	C210	1.42(2)
427	C202	H20C	0.94(2)
428	C202	C203	1.30(2)
429	C203	H20D	0.94(1)
430	C203	C204	1.43(2)
431	C204	C205	1.39(2)
432	C205	C206	1.39(2)
433	C205	C211_3	1.65(3)
434	C206	C207	1.42(2)
435	C207	H20E	0.94(1)
436	C207	C208	1.36(2)
437	C208	H20F	0.94(2)
438	C208	C209	1.41(2)
439	C209	C210	1.37(2)
440	C210	C216_1	1.61(4)
441	C210	C201	1.42(2)
442	C211_3	C212_3	1.35(5)
443	C211_3	C215_3	1.39(6)
444	C212_3	H21D_3	0.94(3)
445	C212_3	C213_3	1.39(3)
446	C213_3	H21E_3	0.94(3)
447	C213_3	N203_3	1.42(4)
448	N203_3	C214_3	1.32(3)
449	N203_3	C221_3	1.55(2)
450	C214_3	H21F_3	0.94(3)
451	C214_3	C215_3	1.47(3)
452	C215_3	H21G_3	0.94(4)
453	C221_3	H22L_3	0.97(3)
454	C221_3	H22M_3	0.97(3)
455	C221_3	H22N_3	0.97(2)
456	C216_1	C217_1	1.39(5)
457	C216_1	C220_1	1.38(5)
458	C217_1	H21W_1	0.94(4)
459	C217_1	C218_1	1.39(6)
460	C218_1	H21S_1	0.94(4)
461	C218_1	N204_1	1.34(5)
462	N204_1	C219_1	1.35(5)
463	N204_1	C222_1	1.57(8)
464	C219_1	H21K_1	0.94(4)
465	C219_1	C220_1	1.40(6)
466	C220_1	H22D_1	0.94(3)
467	C222_1	H22K_1	0.97(7)
468	C222_1	H22O_1	0.97(5)
469	C222_1	H22P_1	0.97(7)
470	N201	C201	1.36(2)
471	N201	C204	1.36(1)
472	N202	C206	1.41(1)
473	N202	C209	1.38(2)

474	C201	C202	1.47(2)
475	C202	H20C	0.94(2)
476	C202	C203	1.30(2)
477	C203	H20D	0.94(1)
478	C203	C204	1.43(2)
479	C204	C205	1.39(2)
480	C205	C206	1.39(2)
481	C205	C211_3	1.65(3)
482	C206	C207	1.42(2)
483	C207	H20E	0.94(1)
484	C207	C208	1.36(2)
485	C208	H20F	0.94(2)
486	C208	C209	1.41(2)
487	C209	C210	1.37(2)
488	C210	C216_1	1.61(4)
489	C211_3	C212_3	1.35(5)
490	C211_3	C215_3	1.39(6)
491	C212_3	H21D_3	0.94(3)
492	C212_3	C213_3	1.39(3)
493	C213_3	H21E_3	0.94(3)
494	C213_3	N203_3	1.42(4)
495	N203_3	C214_3	1.32(3)
496	N203_3	C221_3	1.55(2)
497	C214_3	H21F_3	0.94(3)
498	C214_3	C215_3	1.47(3)
499	C215_3	H21G_3	0.94(4)
500	C221_3	H22L_3	0.97(3)
501	C221_3	H22M_3	0.97(3)
502	C221_3	H22N_3	0.97(2)
503	C216_1	C217_1	1.39(5)
504	C216_1	C220_1	1.38(5)
505	C217_1	H21W_1	0.94(4)
506	C217_1	C218_1	1.39(6)
507	C218_1	H21S_1	0.94(4)
508	C218_1	N204_1	1.34(5)
509	N204_1	C219_1	1.35(5)
510	N204_1	C222_1	1.57(8)
511	C219_1	H21K_1	0.94(4)
512	C219_1	C220_1	1.40(6)
513	C220_1	H22D_1	0.94(3)
514	C222_1	H22K_1	0.97(7)
515	C222_1	H22O_1	0.97(5)
516	C222_1	H22P_1	0.97(7)
517	O1W	H1WA	0.86(8)
518	O1W	H1WB	0.9(1)
519	O2W	H2WA	0.85(7)
520	O2W	H2WB	0.84(8)

Table S3. Normal coordinate Structural Decomposition results for the five-coordinate ZnTPPS molecule in the crystal structure of the Zn/Sn nanosheets. Both in-plane and out-of-plane deformations are given.

basis	Dip	dip	B2g	B1g	Eu(x)	Eu(y)	A1g	A2g
min.	0.0813	0.0181	-0.0382	-0.0431	0.0019	-0.0007	0.0574	-0.0005
ext.	0.0952	0.0157	-0.0383	-0.0422	0.0026	-0.0005	0.0608	-0.0005
			-0.0318	-0.0024	0.0036	0.0120	-0.0197	-0.0290
			-0.0008	0.0168	-0.0030	-0.0148	0.0623	0.0124
			-0.0001	0.0122	0.0008	0.0079	-0.0346	-0.0063
			-0.0068	0.0009	0.0106	0.0039	0.0095	-0.0106
			0.0019	-0.0114	-0.0088	-0.0006	0.0257	
					-0.0083	-0.0094		
					0.0086	-0.0075		
					0.0158	0.0114		
					0.0043	0.0035		
					-0.0154	0.0119		
comp.	0.1314	0.0000	0.0502	0.0492	0.0293	0.0297	0.0971	0.0340
basis	Doop	doop	B2u	B1u	A2u	Eg(x)	Eg(y)	A1u
min.	1.2106	0.0156	-1.1702	0.2607	0.0731	-0.0543	0.1413	-0.0009
ext.	1.2148	0.0049	-1.1683	0.2607	0.0733	-0.0549	0.1390	-0.0009
			0.0790	0.0205	0.0134	-0.0150	-0.0585	-0.0096
			0.0255	0.0079	-0.0068	0.0018	-0.0072	
						-0.0015	0.0046	
						-0.0028	-0.0031	
comp.	1.2152	0.0000	1.1730	0.2616	0.0746	0.0564	0.1531	0.0096

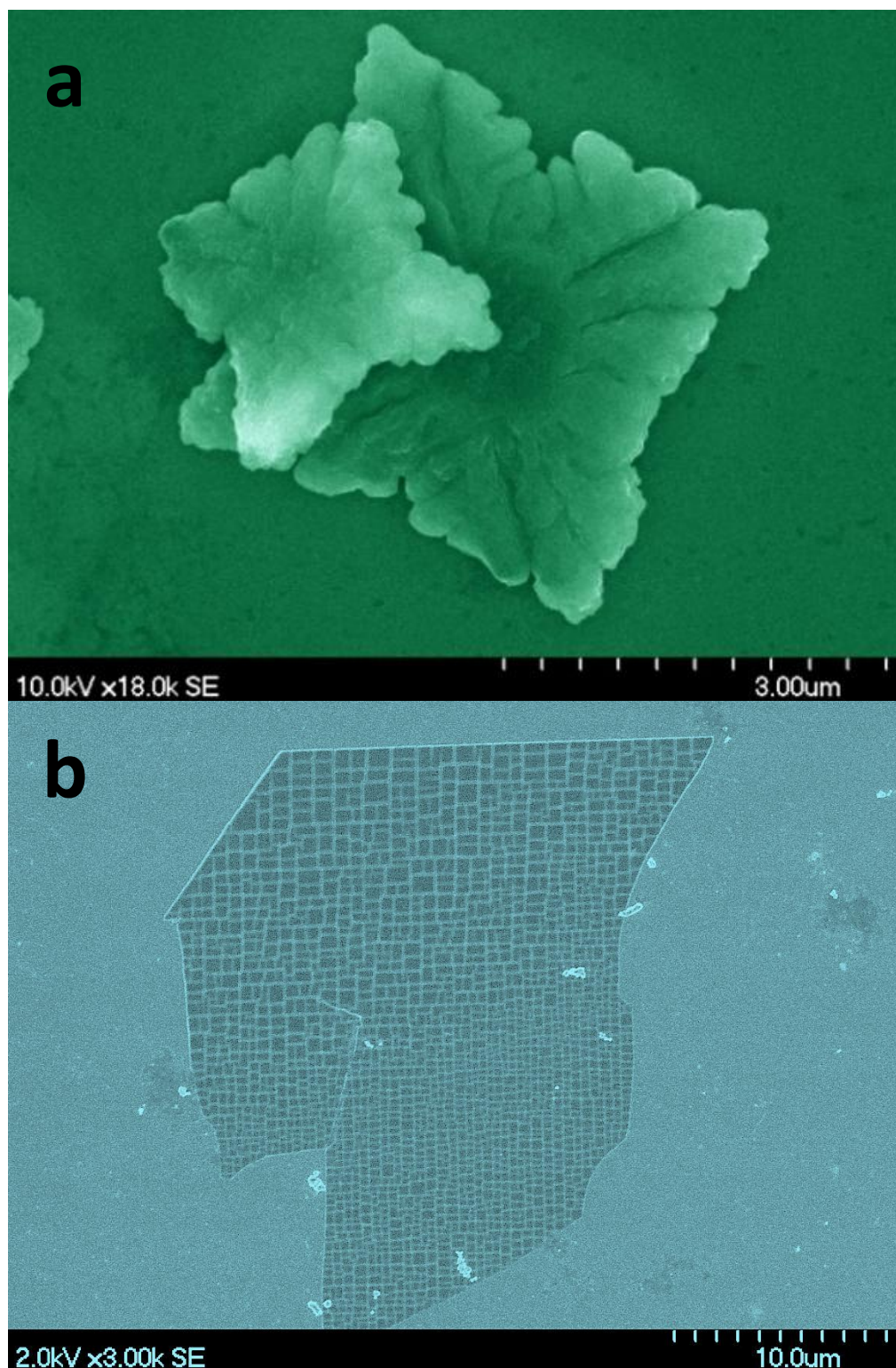


Figure S1. SEM images of the Zn/Sn clovers (a) and the Zn/Sn nanosheets (b) prepared at 23° C with 210 μM initial total concentrations of ZnTPPS and SnTNEtOHPyP or SnTNMePyP, respectively, in equal proportion.

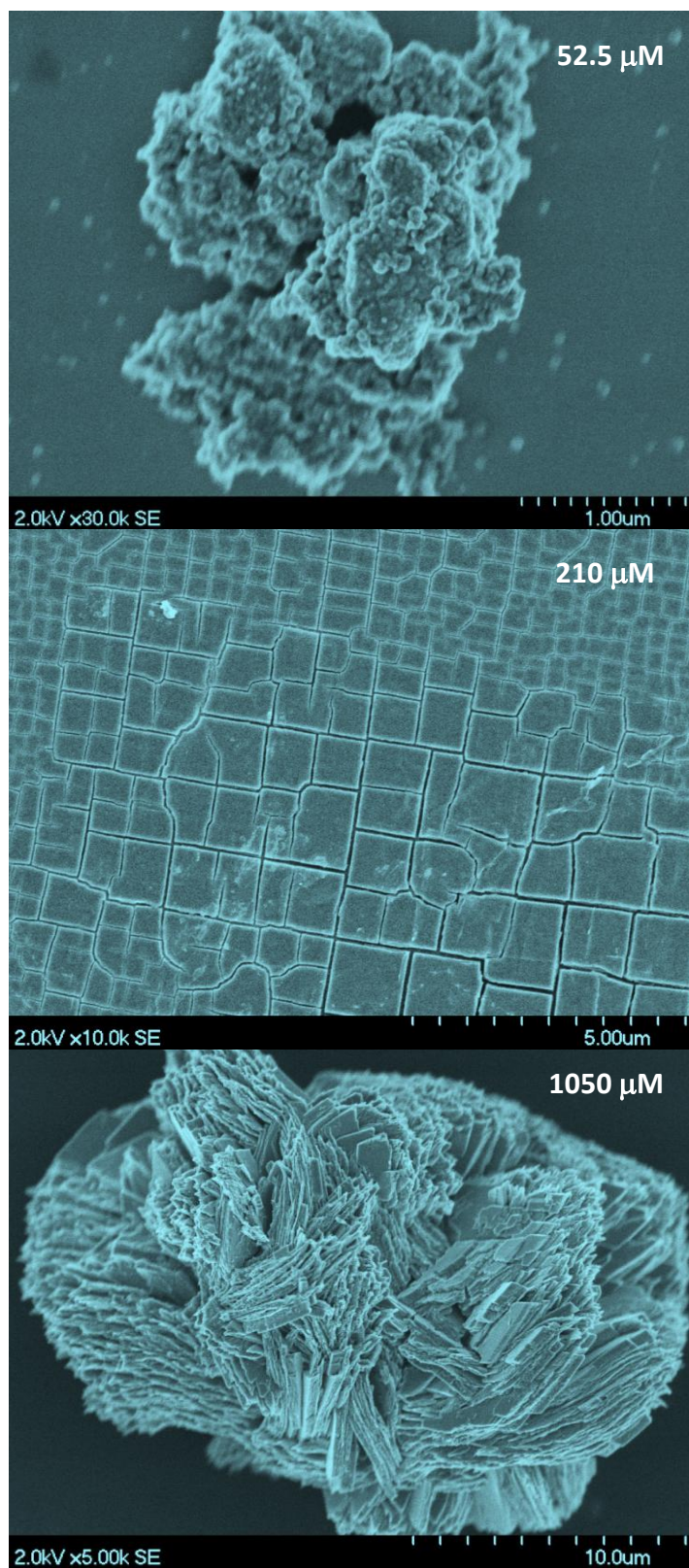


Figure S2. SEM images of structures obtained for the Zn/Sn nanosheets prepared at 23° C with different initial total concentrations of ZnTPPS and SnTNMePyP in equal proportion.

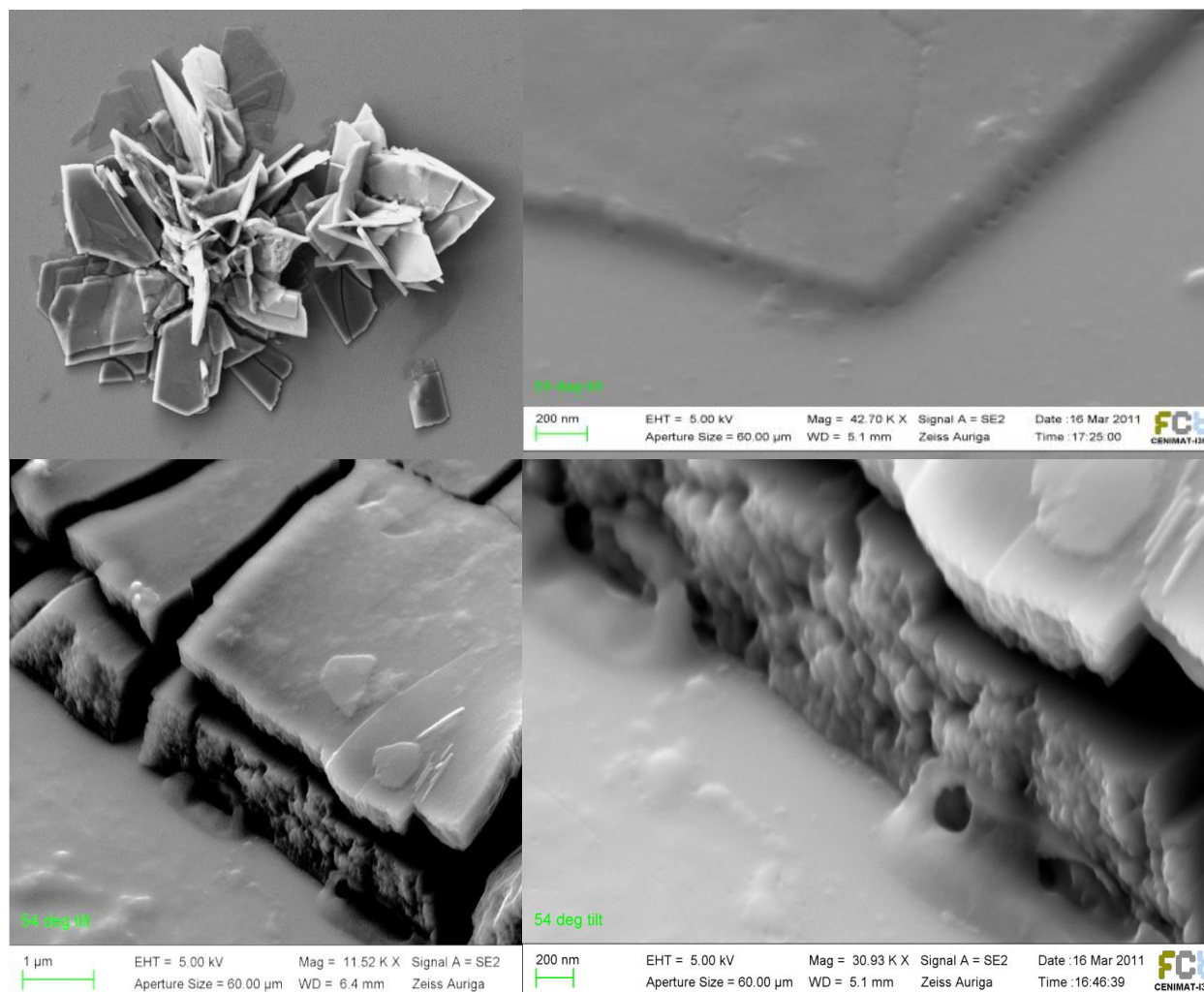


Figure S3. SEM images of Zn/Sn nanosheets at low (top) and high (bottom) magnification.

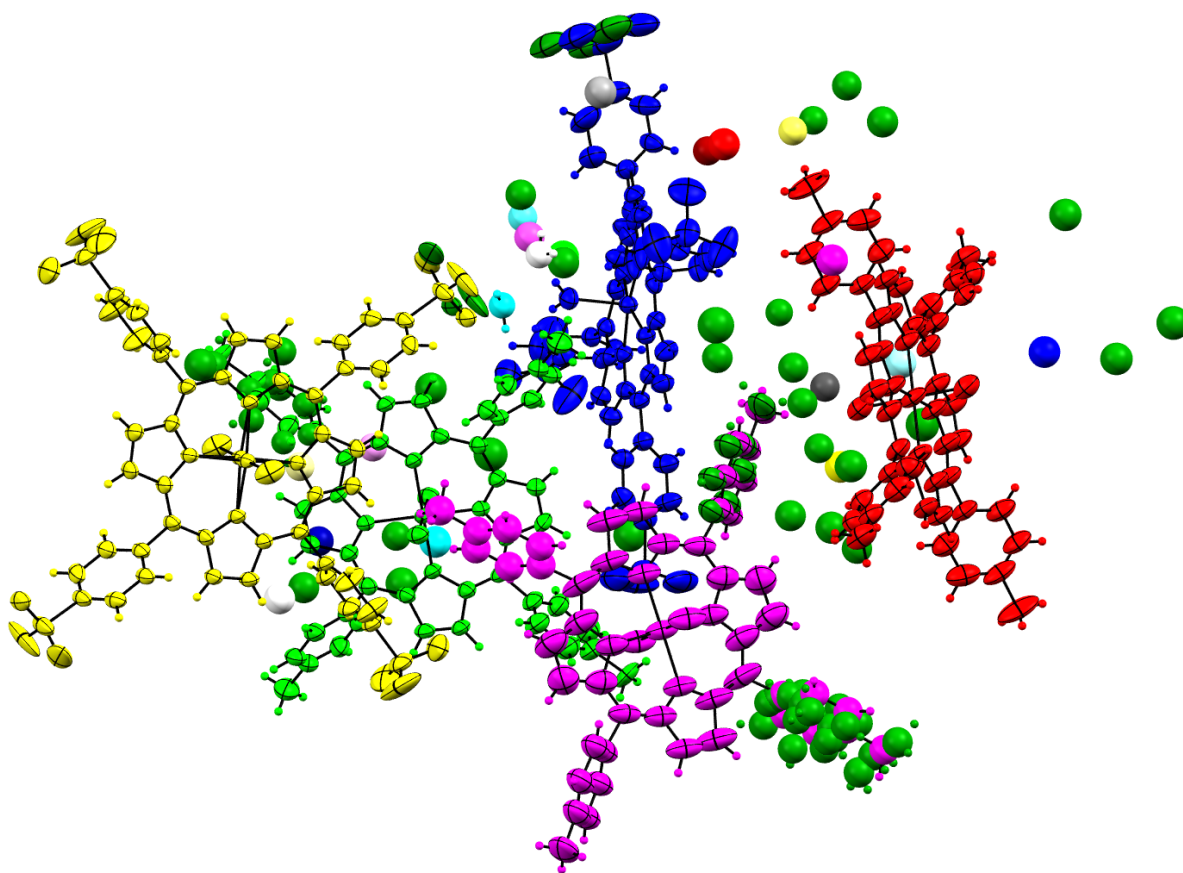


Figure S4. ORTEP image of the unit cell of the Zn/Sn nanosheet crystal structure showing the associated water molecules (colored by symmetry). Alternate positions of some of the atoms of the porphyrins indicate the disorder seen in the crystal.

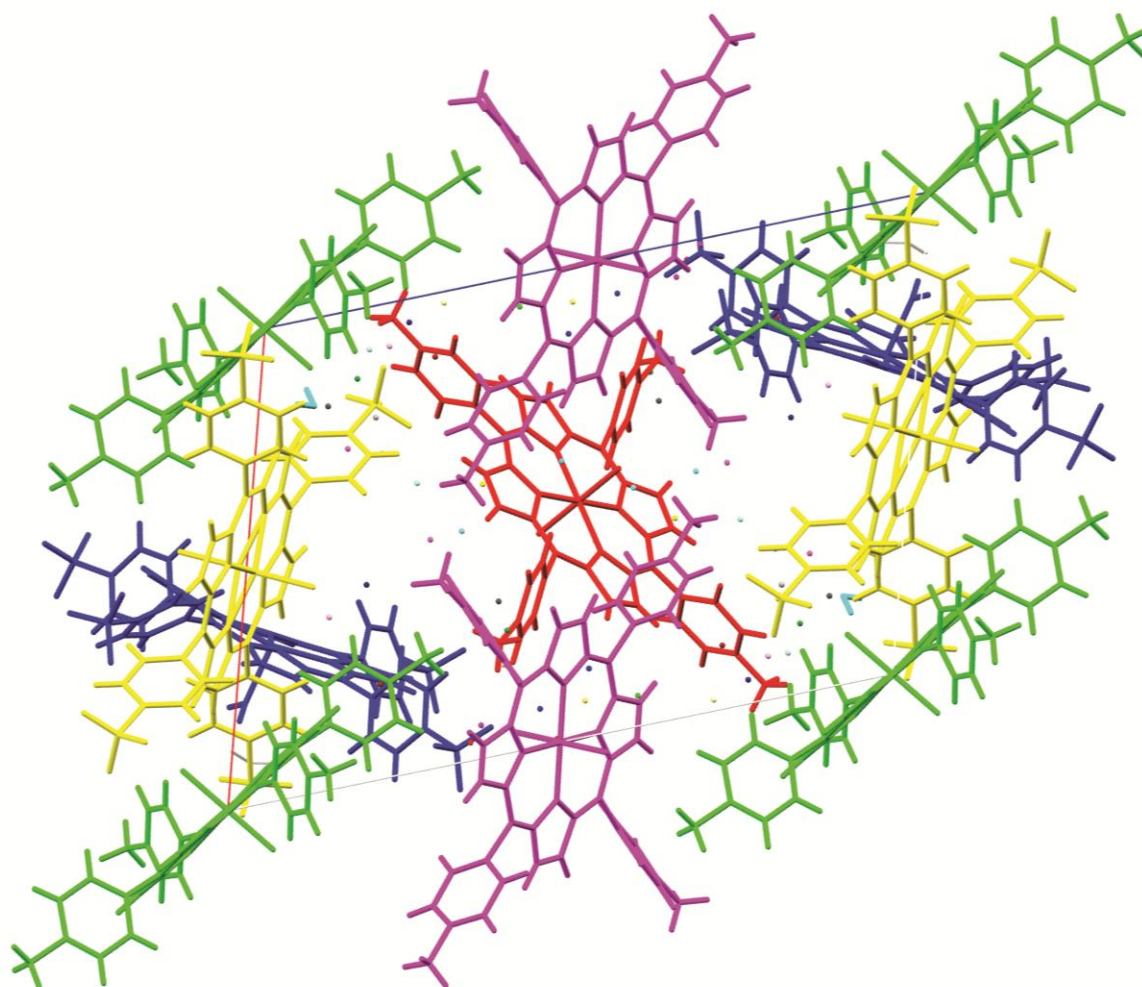


Figure S5. Unit cell of the Zn/Sn nanosheet crystal looking down the *b* axis with the *c* axis to the right.