Supporting Information Available. ESI-MS spectra; ^{29}Si NMR and infrared transmission spectra of AP_2IO_6 and U_2IO_6 POSS; AFM measurements of U_2IO_6 POSS corrosion inhibition layers.

ESI-MS spectra. The ESI-MS spectra presented in Figure S1 revealed peaks attributed to the various POSS products outlined in Table S1.

Table S1. Molecular masses of possible POSS cage-like structures present in the synthesized AP2IO6 POSS (1st synthesis step). The corresponding peaks observed in the ESI-MS spectra (Figure S1) are marked in bold.

substituent amino	substituent isobutyl	mass	POSS
0	8	1322.5	
1	**7**	**1267.4**	T_8 AP_1IO_7
2	**6**	**1212.2**	T_8 AP_2IO_6
3	5	1157.1	
4	4	1102.0	
5	3	1046.0	
6	2	991.7	
7	1	936.6	
8	0	881.4	
0	12	1983.7	
12	0	1322.2	
10	0	1101.8	
0	10	1653.1	
2	**8**	**1542.8 (771.9)**	T_{10} AP_2IO_8
1	9	1598.0	
3	7	1487.7	
2	7	1432.6	
2	**7 (OH)**	**1386.5 (693.9)**	$T_9(OH)$ AP_2IO_7

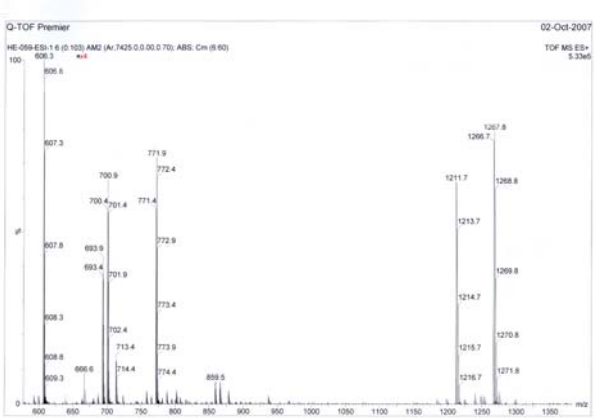


Figure S1. ESI-MS spectra of AP_2IO_6 POSS obtained after hydrolysis and condensation of APTMS and IOTMS (1st synthesis step).

^{29}Si NMR and IR transmission spectra of AP_2IO_6 POSS (1st step). The structure of AP_2IO_6 was established from the ^{29}Si NMR, IR transmission and ^{1}H NMR spectra (Figures S2-S4). ^{29}Si NMR spectra did not reveal any T^1 and T^2 signals around -50 and -59 ppm [14,50,51], which implied the absence of unwanted condensation species like dimers ($T_2(OH)_4$), cyclic trimers and other cyclic species ($T_4(OH)_4$) [17]. The signals observed in the region from -67 to -69 ppm were attributed to T^3 resonances stemming from cube-like (T_8) polyhedral condensation products [16,17]. The appearance of two signals at -67.3 and -69.2 ppm in the spectrum of AP_2IO_6 POSS (Figure S2) reflected the differences in the groups substituted on the octasilsesquioxane cube [52].

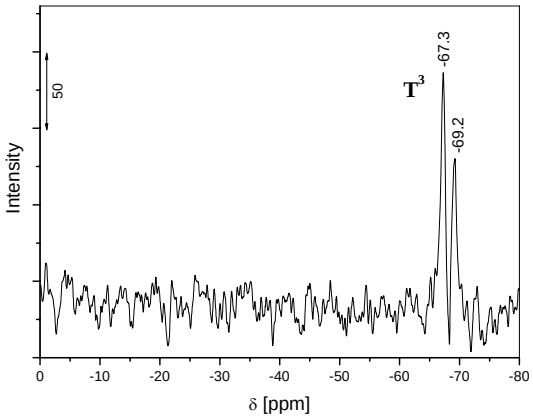


Figure S2. ^{29}Si NMR spectra of AP_2IO_6 POSS prepared in the 1st synthesis step.

IR transmission spectra (Figure S3) independently confirmed the formation of AP_2IO_6 cube-like species. Namely, cube-like species exhibit just one IR band in the region from 1122-1128 cm^{-1}, contrary to ladder-like condensation products which are characterized by two bands at 1155 and 1040-1050 cm^{-1}, respectively [15-17]. It should be noted that the ^{29}Si NMR spectra do not give sufficient evidence for differentiation between cube- and ladder-like species since both showed just a single T^3 signal [14]. Therefore, the decisive argument for identification of the cube-like structure of AP_2IO_6 was obtained from the IR spectra (Figure S3). The band at 1118 cm^{-1} (asymmetric Si-O-Si stretching mode of the T_8 cube), together with the band at 486 cm^{-1} (symmetric stretching mode of the $(SiO_{3/2})_8$ cube) [15,53], unquestionably confirmed the presence of the AP_2IO_6 cubes. Amino groups expected to be present in AP_2IO_6 POSS were also identified from the band at 1585 cm^{-1} (Figure S3) and additionally confirmed from the ^1H NMR spectra (Figure S4).

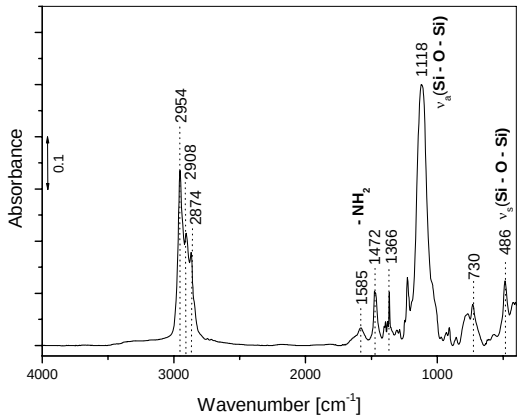


Figure S3. IR transmission spectrum of AP_2IO_6 POSS deposited on a silicon wafer.

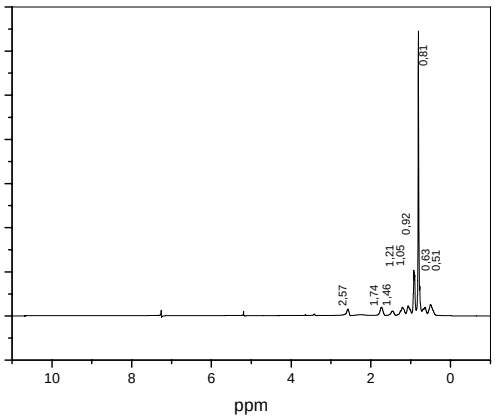


Figure S4. ^{1}H NMR spectra of AP_2IO_6 POSS.

The presentation of the corresponding ^{1}H NMR spectrum clearly showed the presence of protons of the propylene groups on which the amino groups are linked (signals at 2.57, 1.46 and 0.51 ppm). Other signals in this area originated from isooctyl groups (1.74, 1.25, 1.05, 1.21, 0.92, 0.81 and 0.63 ppm). However, the protons of the amino groups could not be detected in the spectrum. These protons could not be seen even in the spectrum of aminopropyltriethoxy silane**.**

^{29}Si NMR and IR transmission spectra of U_2IO_6 POSS

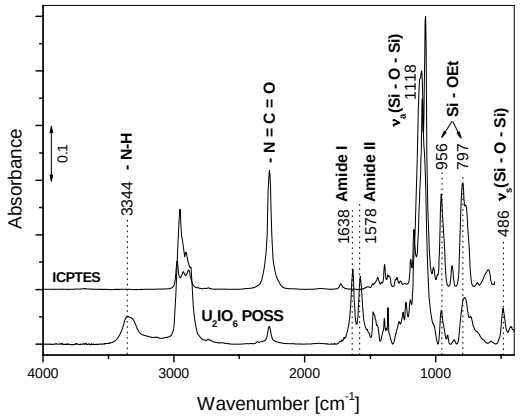


Figure S5. IR transmission spectra of ICPTES and U_2IO_6 POSS used for the preparation of corrosion inhibition coatings.

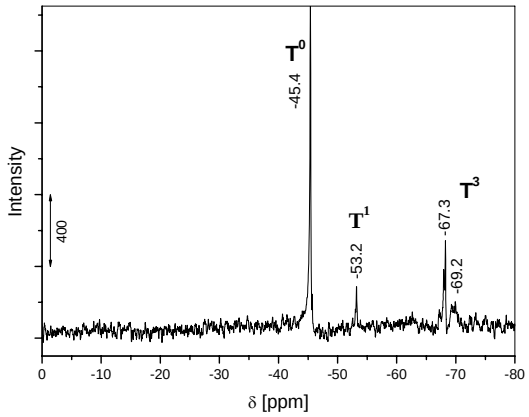
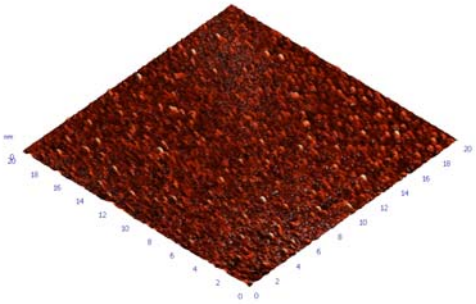
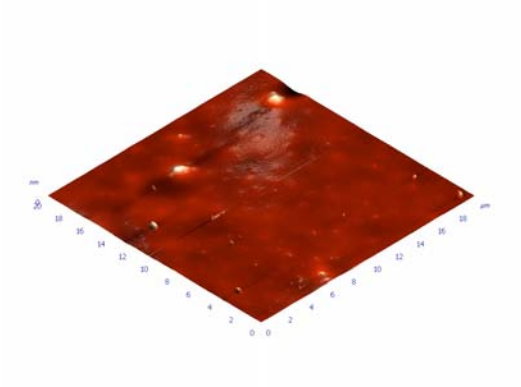


Figure S6. ^{29}Si NMR spectrum of U_2IO_6 POSS.

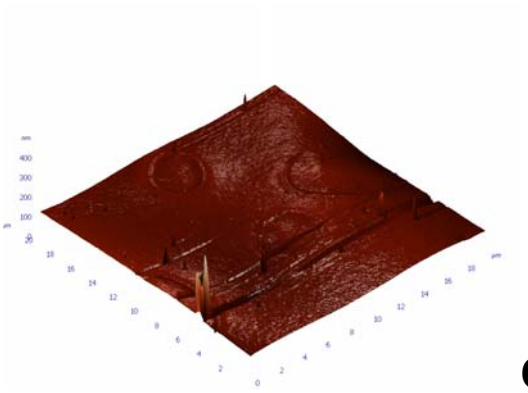
AFM measurements of U_2IO_6 POSS



A



B



C

Figure S7. AFM measurements of: A) Al (evaporated) substrate, B) thin U_2IO_6 POSS (2%) coating and C) thick U_2IO_6 POSS (10%) coating.

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