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

Supporting information

Soft X-Ray Absorption and Fragmentation of Tin-oxo Cage Photoresists

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Data repository: https://doi.org/10.21942/uva.24994439

Table S1. Fit parameters NEXAFS spectra (eq. 1 main text)

	TinF film	±	TinOH film	±	dication gas phase	±
I0	0.0229	0.0001	0.0205	0.0001	0.0000	-
step_height	0.0794	0.0013	0.0803	0.0008	1.044	0.018
step_pos	288.79	1.36	288.94	0.74	294.00	0.05
step_width	0.744	0.647	0.593	0.147	0.550	0.028
step_decay	0.0113	0.0001	0.0125	0.0001	0.0128	0.0011
A0	0.0188	0.0008	0.0166	0.0005	0.505	0.011
pos0	285.38	0.02	285.43	0.01	285.22	0.02
w0	0.180	0.018	0.218	0.019	0.591	0.038
A1	0.0590	0.0134	0.0463	0.0169	0.900	0.082
pos1	287.33	0.07	287.25	0.03	287.59	0.06
w1	0.430	0.049	0.328	0.066	1.098	0.103
A2	0.0780	0.0648	0.1013	0.0248	0.551	0.134
pos2	288.31	0.07	288.19	0.14	289.76	0.35
w2	0.711	0.341	0.861	0.400	2.298	1.676
A3	0.0229	0.0007	0.0319	0.0003	0.357	0.153
pos3	292.67	0.05	292.61	0.02	292.00	0.67
w3	7.344	0.622	7.103	0.232	2.279	1.699
A4	0.0168	0.0004	0.0163	0.0002	0.119	0.015
pos4	299.72	0.19	299.91	0.07	297.15	0.26
w4	40.66	3.31	20.96	0.99	25.00	-

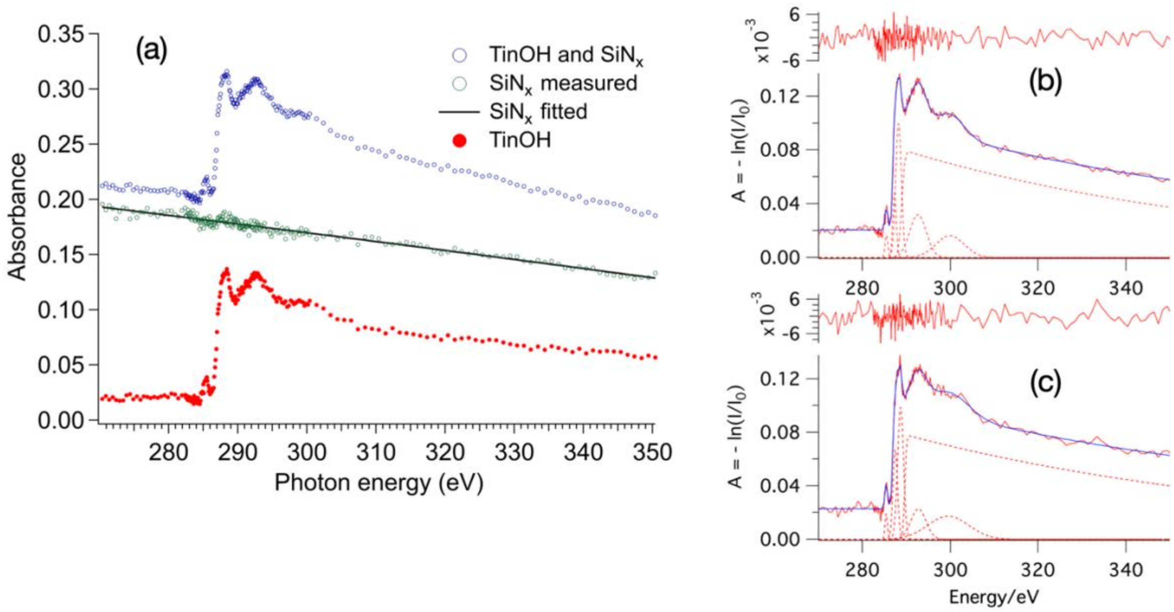

Figure S1. C K-edge absorption spectrum of TinOH. (a) raw data: absorbance of TinOH on 30 nm SiN membrane, absorbance of SiN membrane (average of three independent measurements) with polynomial fit ($ax^2 + bx + c$; $a = -4.4 \times 10^{-7}$, $b = -5.3 \times 10^{-4}$, $c = 0.36$), and absorbance of TinOH alone. (b) full spectrum of TinOH. (c) full spectrum of TinF.

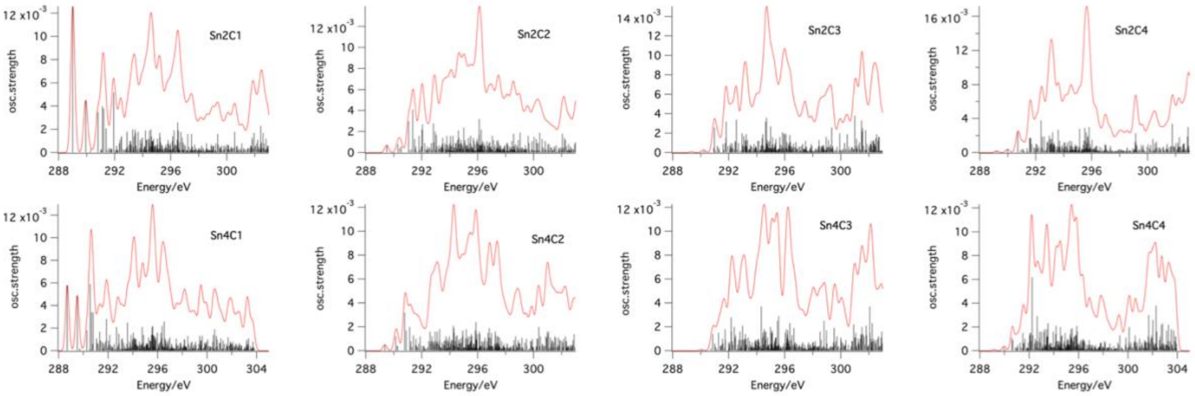

Figure S2. Representative XAS spectra calculated with the Transition Potential method for the bare tin cage. Computed energies and oscillator strengths are shown by the stick diagram in black. The red curves are the convolution of the stick diagram with a Gaussian (FWHM 0.33 eV).

The codes C1, C2, C3, C4 refer to the number of the carbon atom in a butyl chain, C1 being bonded to Sn. Sn2 is one of the six 5-coordinated Sn atoms in the molecule, Sn4 is one of the six 6-coordinated Sn atoms. The graphs clearly show that the carbon atoms further away from the tin atoms contribute less to the absorption at low energies.

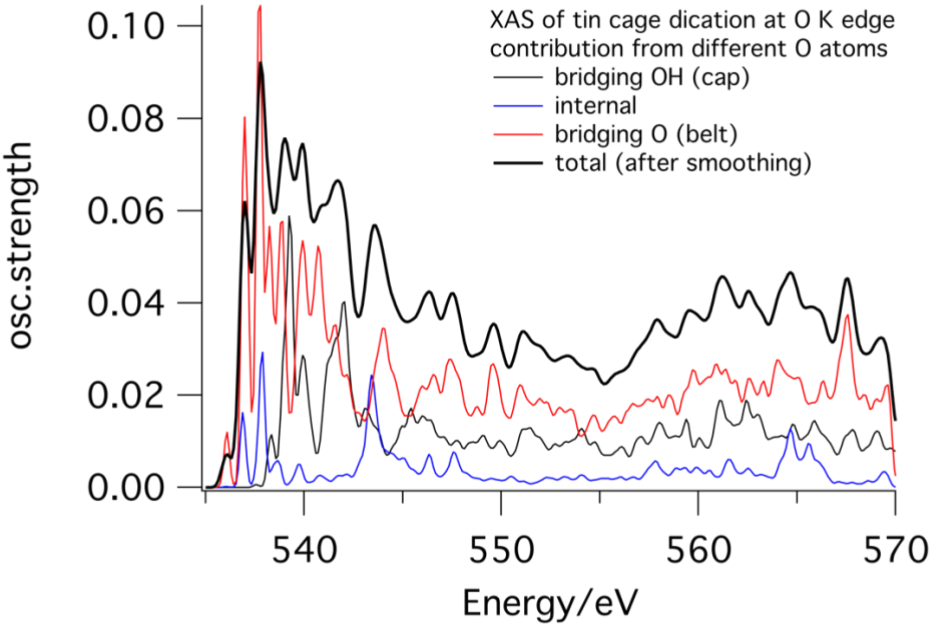

Figure S3. Calculated XAS of the bare tin cage dication at the O K-edge with the contributions of the different types of O: 6 bridging OH groups in the caps of the ion, 12 O atoms in the four-membered rings that form the central belt, and the two central O atoms of the caps that are on the inside of the cage.

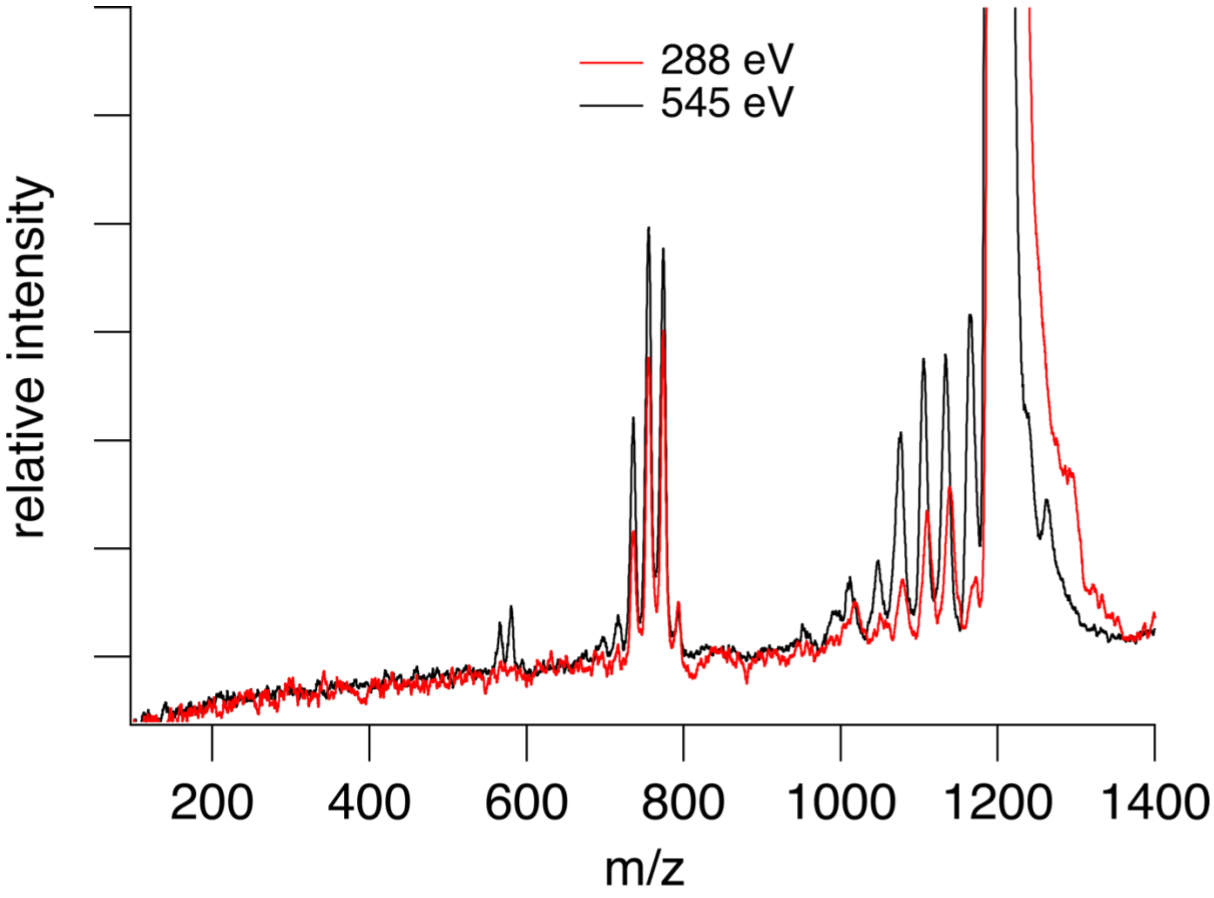

Figure S4. Full photofragmentation mass spectra of butyltin-oxo cage dication (m/z 1218) at the C K-edge (red) and the O K-edge (black). **Important note**: the ion extraction was optimized for the 3+ ions around m/z 750. In other ranges both the intensity and the m/z scale are *not reliable*.

Table S2. Absorption cross sections (σ_X) at different photon energies of elements that are present in the tin-oxo cage dication. The relative cross section ($\sigma_{X,rel}$), given as the fraction of the total absorption, is calculated by multiplying the cross section with the number of atoms of each element (12 × Sn, 20 × O, 48 × C) in the tin-oxo cage dication. It gives the relative probability that a photon is absorbed by the element. Values were calculated using tabulated data by Henke et al.[1]

	300 eV	550 eV
σ_C (cm^2/mol)	5.5×10^5	1.3×10^5
$\sigma_{C,rel}$ (48 atoms)	0.69	0.18
σ_O (cm^2/mol)	7.9×10^4	3.3×10^5
$\sigma_{O,rel}$ (20 atoms)	0.04	0.19
σ_{Sn} (cm^2/mol)	8.5×10^5	1.9×10^6
$\sigma_{Sn,rel}$ (12 atoms)	0.27	0.64

The Density of States (orbital energy density) was calculated using AMS2022[2] for the bare tin cage dication using PBE(D3BJ)/TZP with a small-core basis, which includes 4d and higher energy orbitals on Sn and 2s and higher on C and O. The DOS can be calculated per atom and per orbital type, as shown in Figure S5. The individual spectra are given in the data repository on figshare at doi:10.21942/uva.24994439.

The results show the Sn 4d levels just below the valence band. The orbitals on the top of the valence band are mostly built from 2p AOs on C and O, and H 1s. The Sn 5p orbitals contribute particularly to the lowest vacant MO's. The 2s electrons on O are more strongly bound than those on C, which leads to a higher energy content after the KVV or KL_1L_1 Auger process in O than in C.

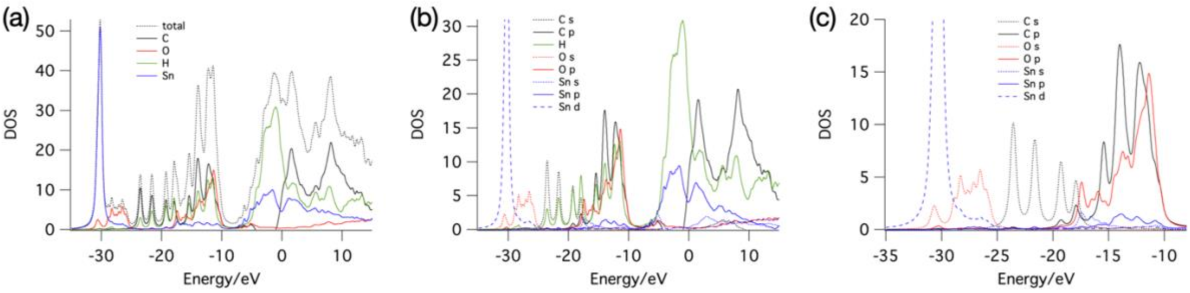

Figure S5. Density of states of bare tin cage dication. (a) totals per element. (b) separated by angular momentum. (c) zoom in on s, p, and d contributions to the occupied orbitals.

Table S3. Results of computations. Structures optimized at the B3LYP/Def2SVP level, zero-point vibrational energies, and single point energies at the B3LYP/Def2TZVP level. Energies in atomic units (Hartree). Energies of subsequent butyl loss in eV (see fig. 7 in main text).

species	E(Def2SVP) (Ha)	ZPE (Ha)	E(Def2TZVP) (Ha)	Def2TZVP+ZPE (Ha)	E(butyl loss) (eV)
SnBu12_2p	-5972.68850	1.59521	-5976.73306	-5975.13785	
SnBu12_3p	-5972.26528	1.59262	-5976.31235	-5974.71973	
SnBu11_1_3p	-5814.55756	1.47417	-5818.43323	-5816.95906	0.79
SnBu10_1-5_3p	-5656.78877	1.35079	-5660.49097	-5659.14018	2.38
SnBu10_1-2_3p	-5656.78711	1.35080	-5660.48933	-5659.13853	2.42
SnBu9_1-2-3_3p	-5499.07246	1.22936	-5502.61221	-5501.38285	0.66
SnBu8_1-2-3-5_3p	-5341.30304	1.10697	-5344.66886	-5343.56189	2.43

References

1 B. L. Henke, E. M. Gullikson, and J. C. Davis. X-ray interactions: photoabsorption, scattering, transmission and reflection at E = 50-30,000 eV, Z = 1-92. *At. Data Nucl. Data Tables,* 1993, **55**, 181-342.

2 AMS2022, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com.