Electronic Supplementary Information for

Ligand Geometry Directs the Packing and Symmetry of One-Dimensional Helical Motifs in Lead Oxide Naphthoates and Biphenylcarboxylates

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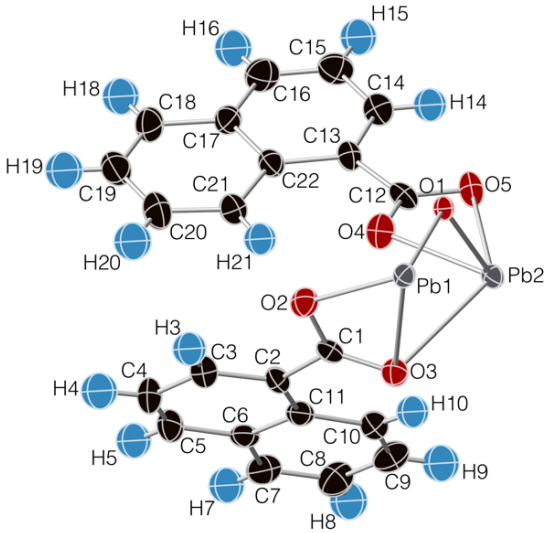

Figure S1. Asymmetric unit for **1**. Thermal ellipsoids for data collected at 150 K are shown at 50% probability.

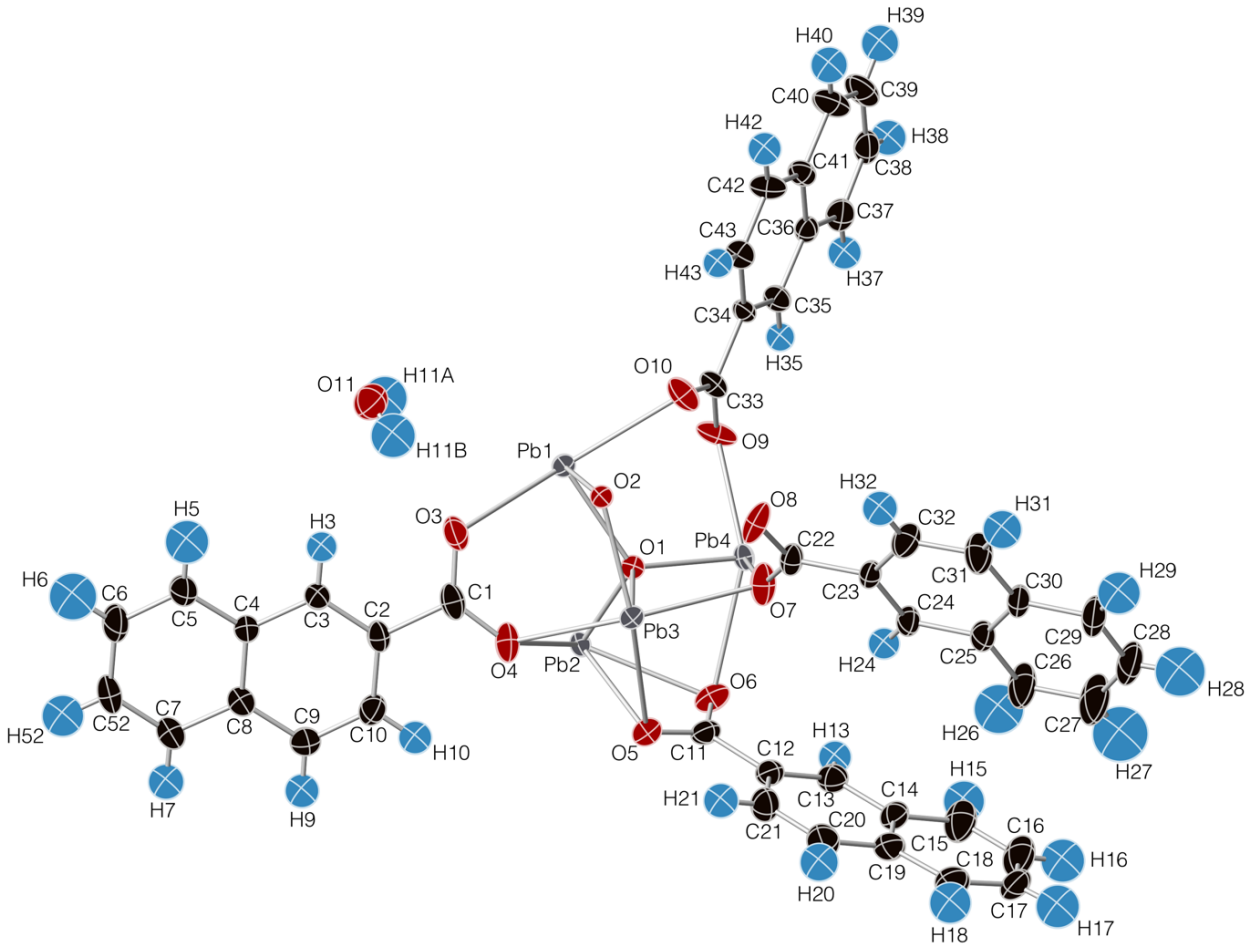

Figure S2. Asymmetric unit for **2**. Thermal ellipsoids for data collected at 150 K are shown at 50% probability.

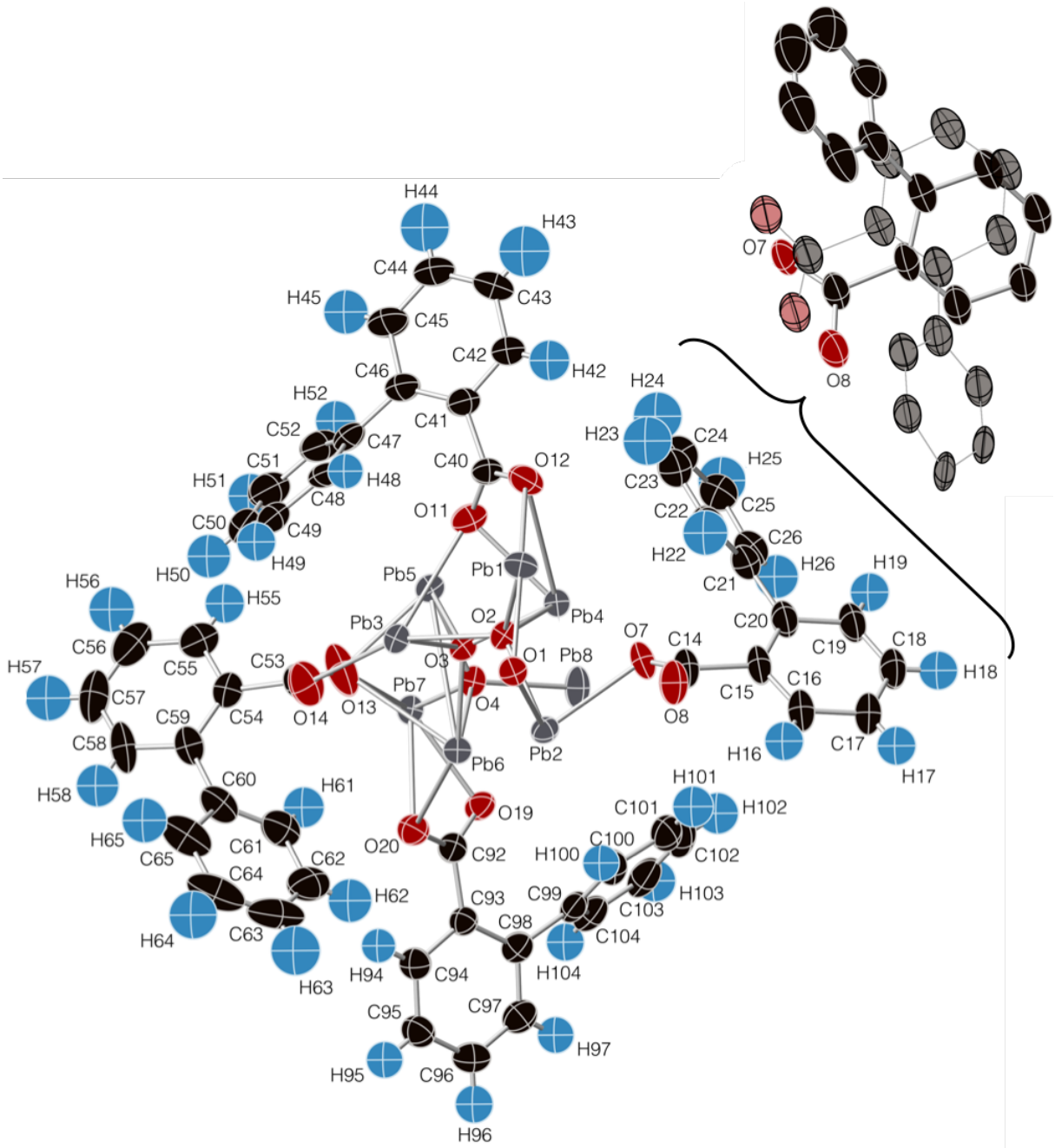

Figure S3a. Asymmetric unit for **3**. Four of the eight crystallographically independent ligands are shown with the inorganic substructure. Insets show 0.722 occupancy (opaque) and 0.278 occupancy (translucent) positions of disordered atoms, excluding hydrogen atoms. Thermal ellipsoids for data collected at 150 K are shown at 50% probability.

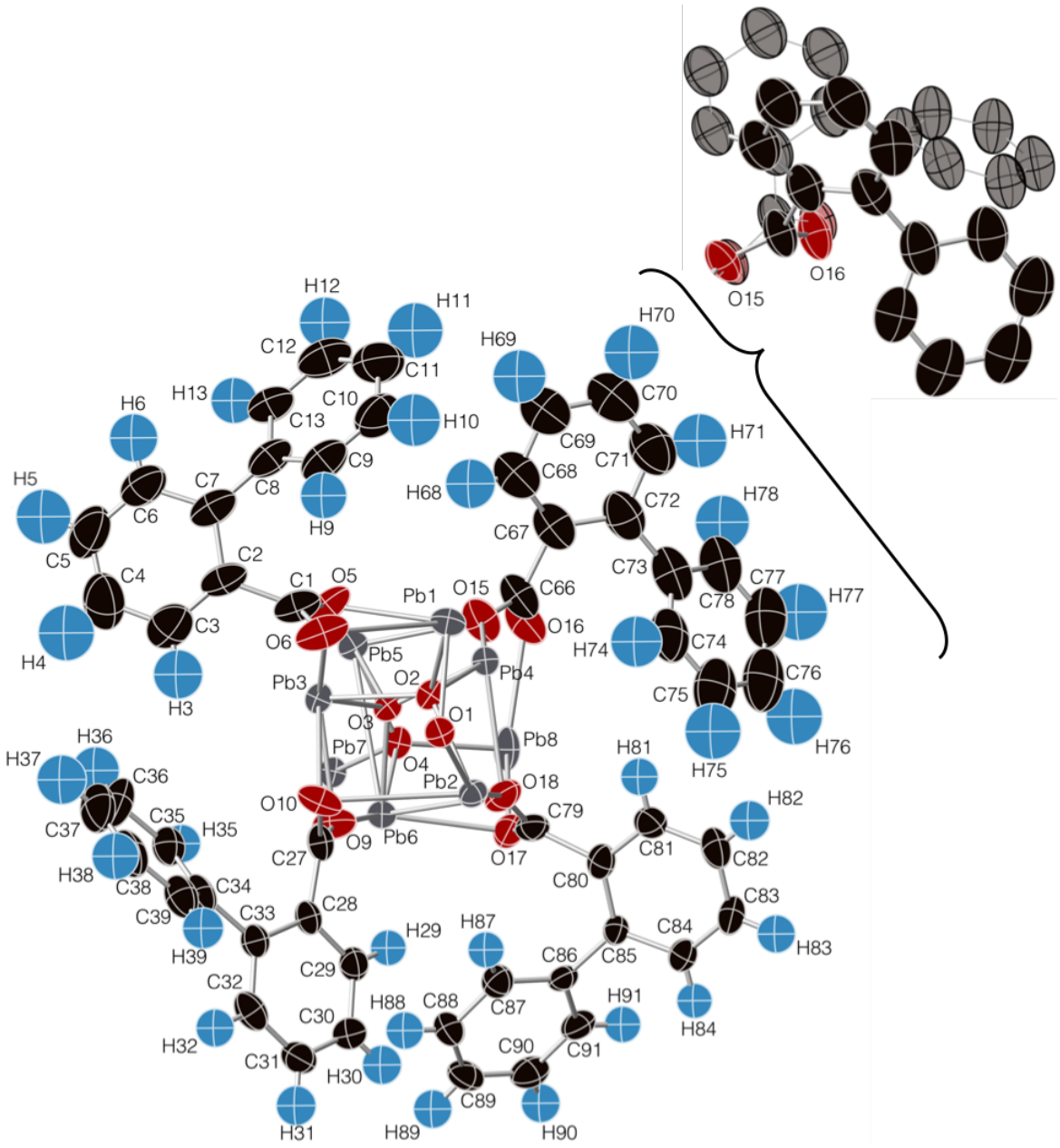

Figure S3b. Asymmetric unit for **3**. Four of the eight crystallographically independent ligands are shown with the inorganic substructure. Insets show 0.722 occupancy (opaque) and 0.278 occupancy (translucent) positions of disordered atoms, excluding hydrogen atoms. Thermal ellipsoids for data collected at 150 K are shown at 50% probability.

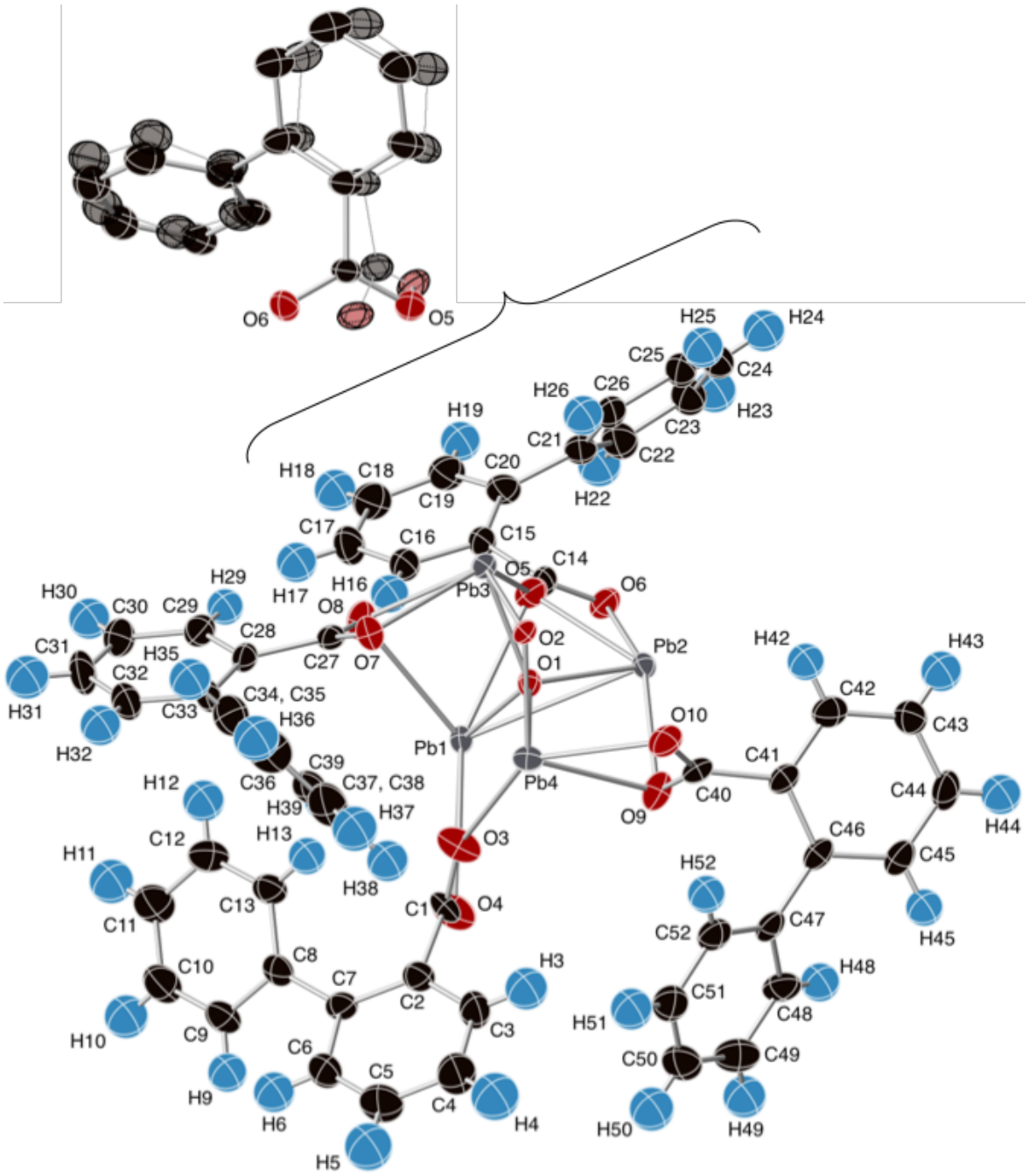

Figure S4a. Asymmetric unit for **4**. One of the two crystallographically unique hybrid chains. The inset shows the 0.688 occupancy (opaque) and 0.312 occupancy (translucent) positions of disordered atoms, excluding hydrogen atoms. Thermal ellipsoids for data collected at 150 K are shown at 50% probability.

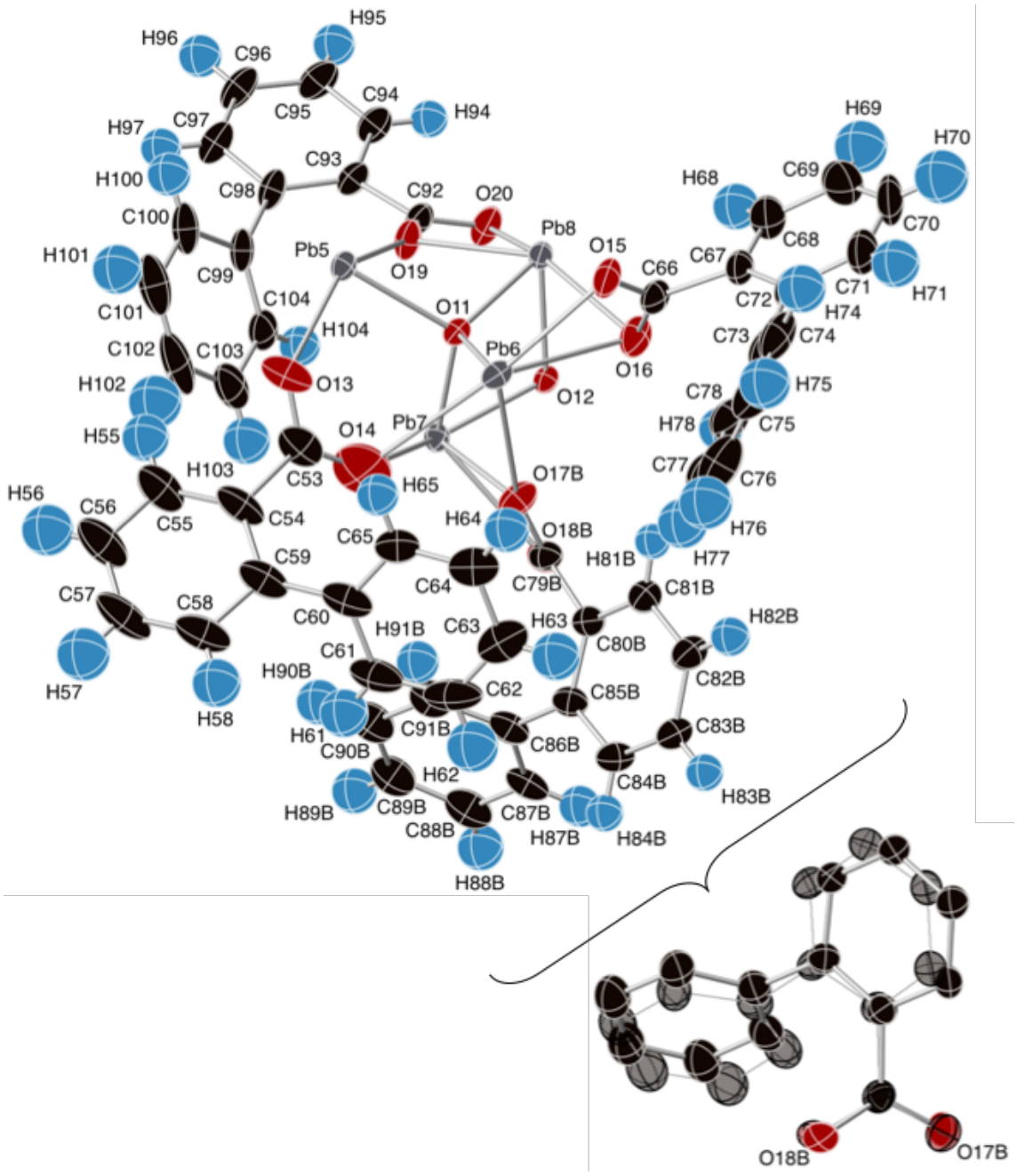

Figure S4b. Asymmetric unit for **4**. The second of two crystallographically unique hybrid chains. The inset shows 0.586 occupancy (opaque) and 0.414 occupancy (translucent) positions of disordered atoms, excluding hydrogen atoms. Thermal ellipsoids for data collected at 150 K are shown at 50% probability.

a)

b)

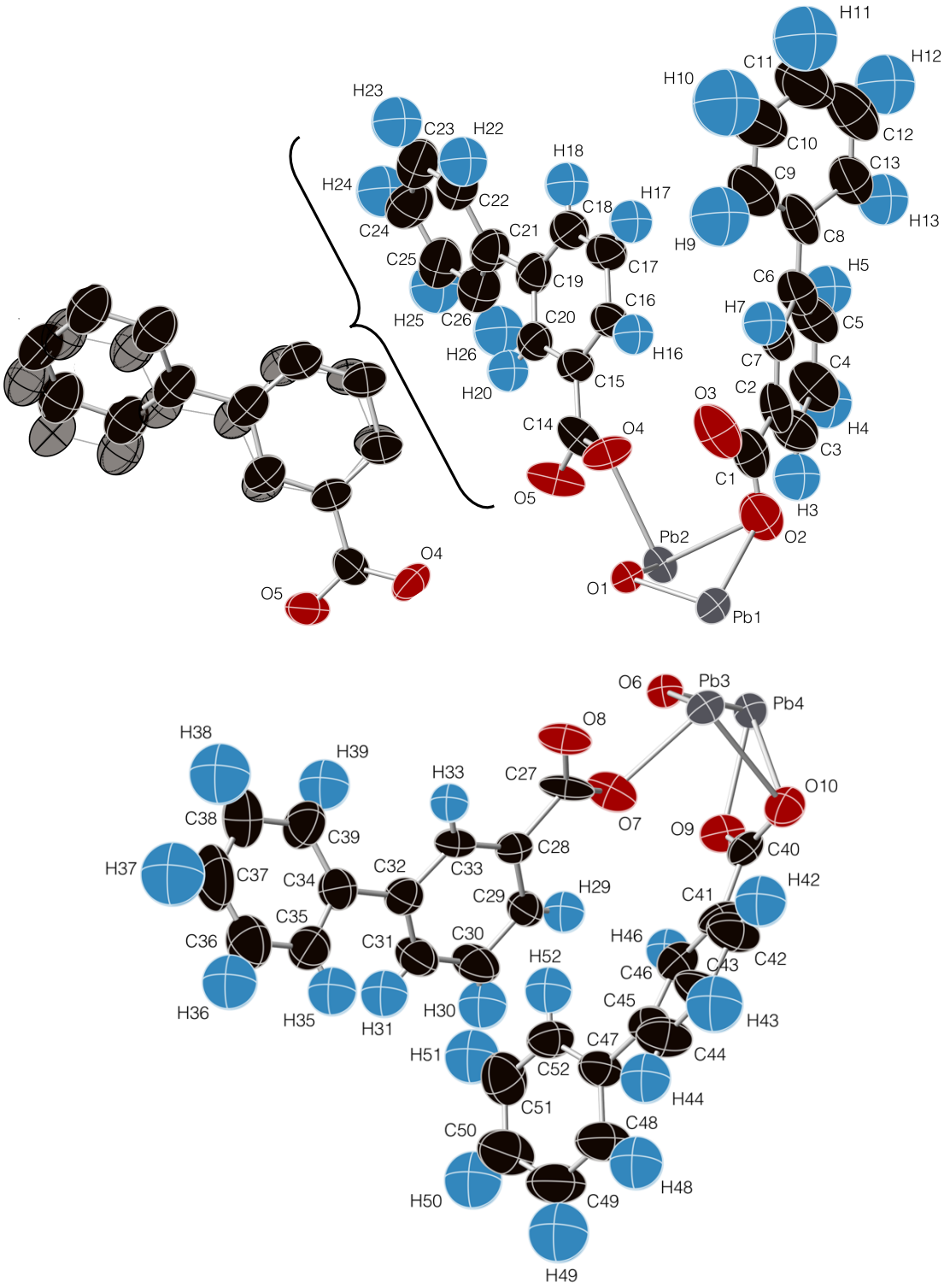

Figure S5. Asymmetric unit for **5**. Two crystallographically unique hybrid chains (**a**,**b**). The inset shows the 0.64 occupancy (opaque) and 0.36 occupancy (translucent) positions of disordered atoms, excluding hydrogen atoms. Thermal ellipsoids for data collected at 296 K are shown at 50% probability.

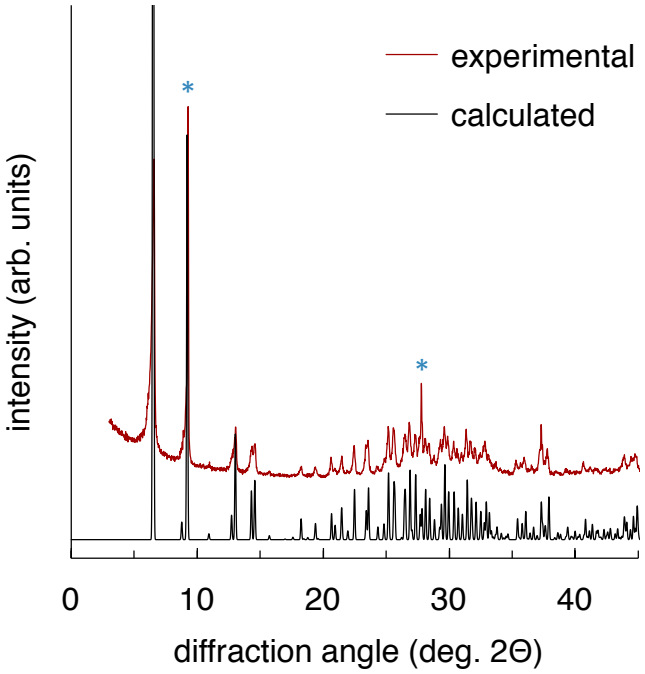

Figure S6. Comparison of PXRD collected at room temperature for **1** with pattern calculated from 150 K single crystal structure. Peaks designated by asterisks were identified as (220) and (660). Their high intensity in the experimental pattern is likely due to preferred orientation.

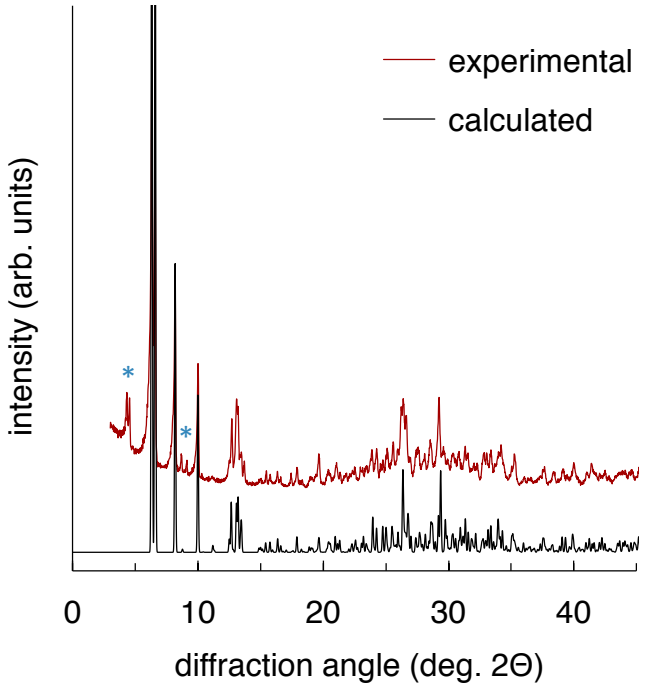

Figure S7. Comparison of PXRD pattern collected at room temperature for **2** with pattern calculated from 150 K single crystal structure. The two peaks designated by asterisks belong to impurities, likely including lead 2-naphthoate.

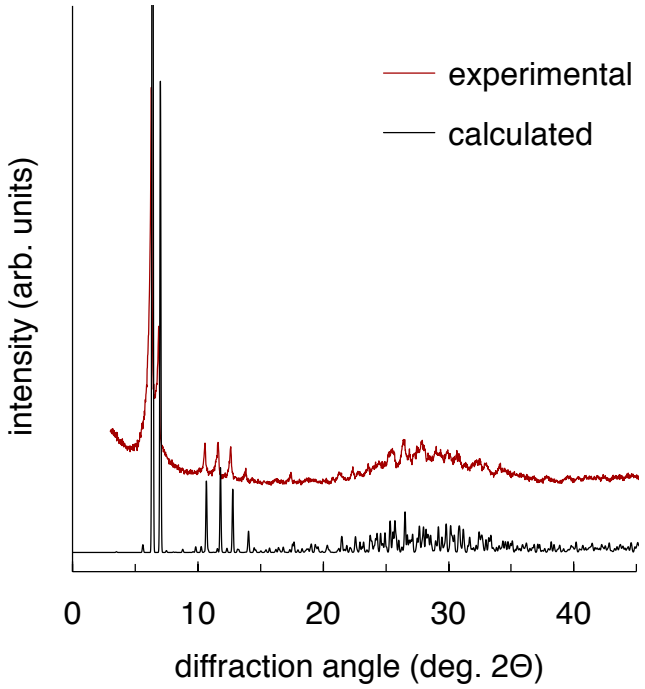

Figure S8. Comparison of PXRD pattern collected at room temperature for **3** with pattern calculated from 150 K single crystal structure.

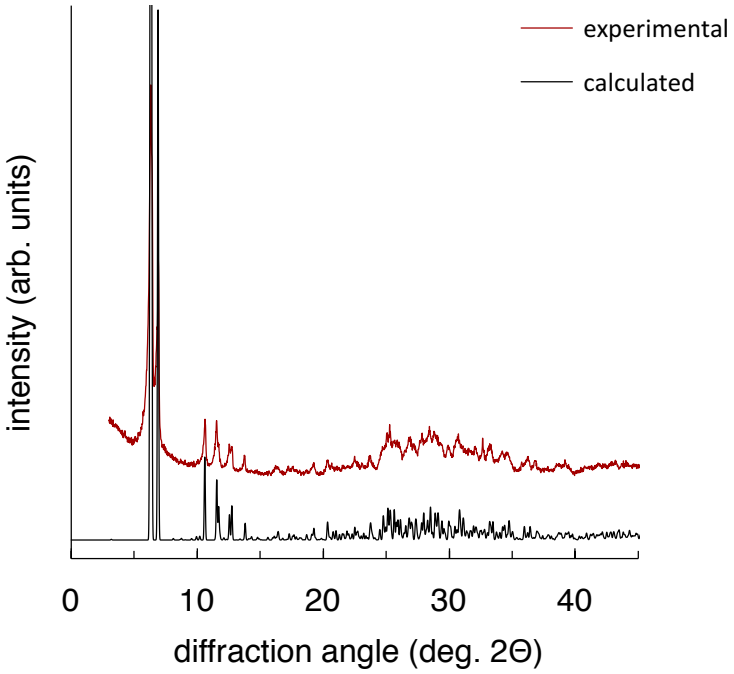

Figure S9. Comparison of PXRD pattern collected at room temperature for **4** with pattern calculated from 150 K single crystal structure.

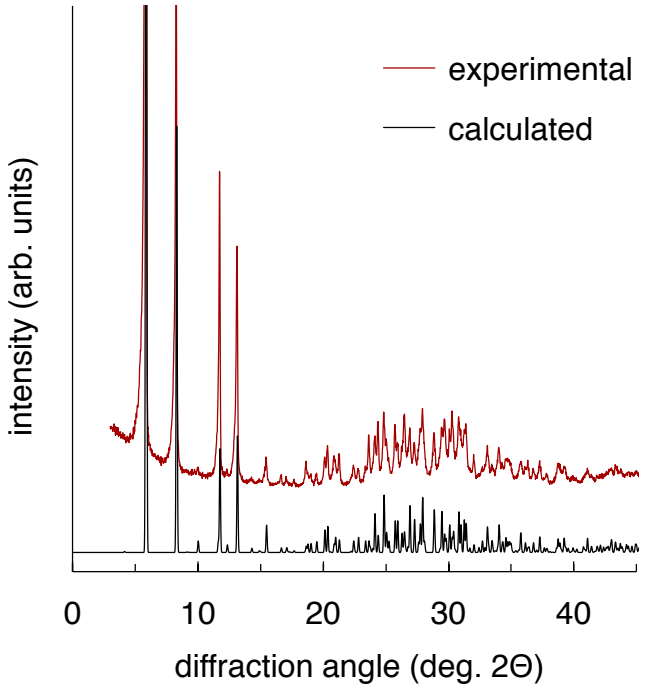

Figure S10. Comparison of PXRD pattern collected at room temperature for **5** with pattern calculated from 296 K single crystal structure.

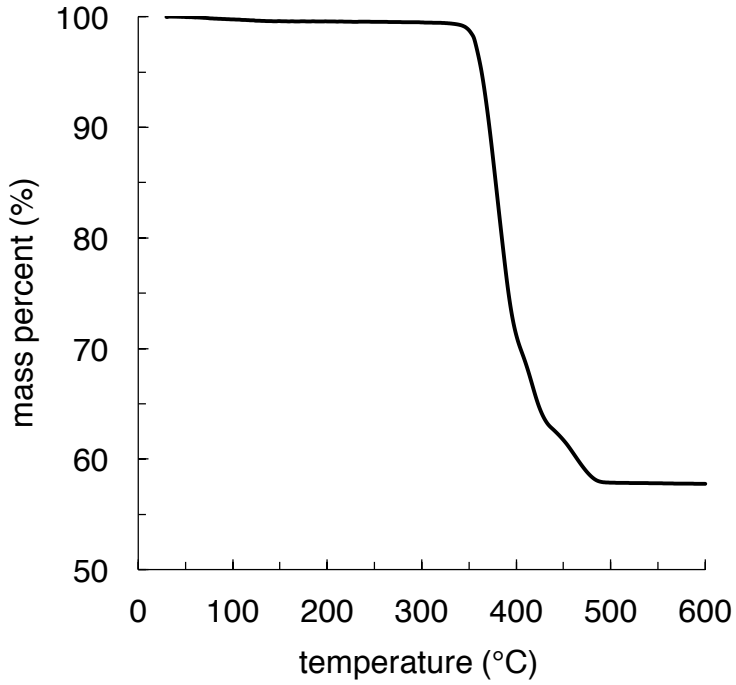

Figure S11. Thermogravimetric analysis trace for **1** heated to 600 °C under flowing air.

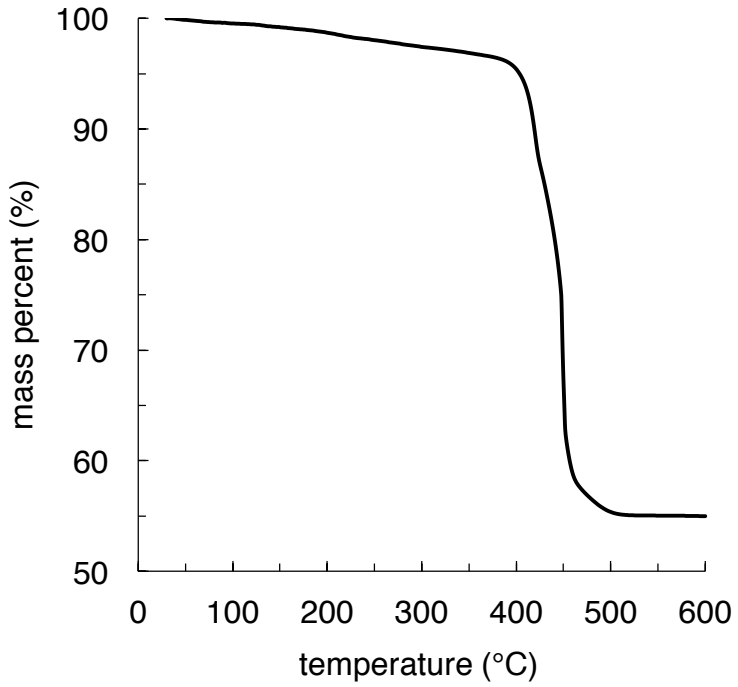

Figure S12. Thermogravimetric analysis trace for **2** heated to 600 °C under flowing air.

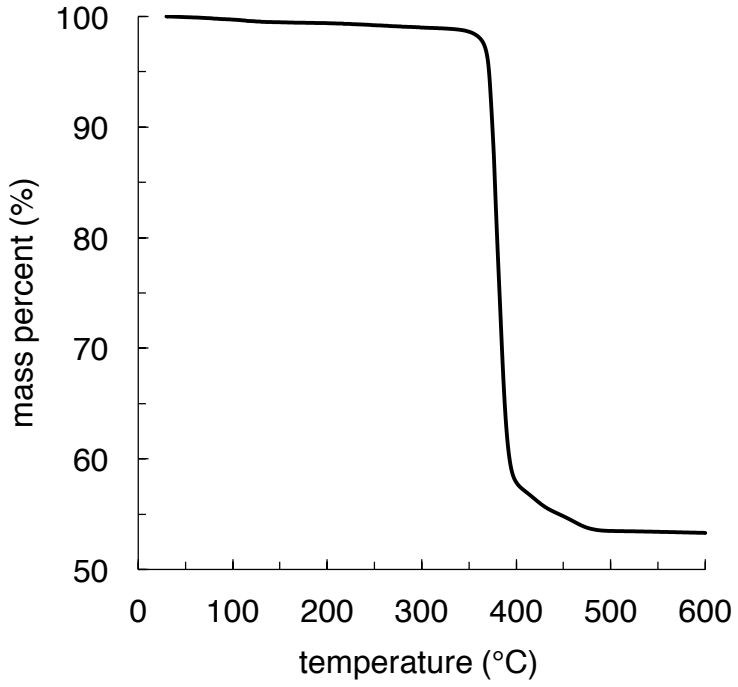

Figure S13. Thermogravimetric analysis trace for **3** heated to 600 °C under flowing air.

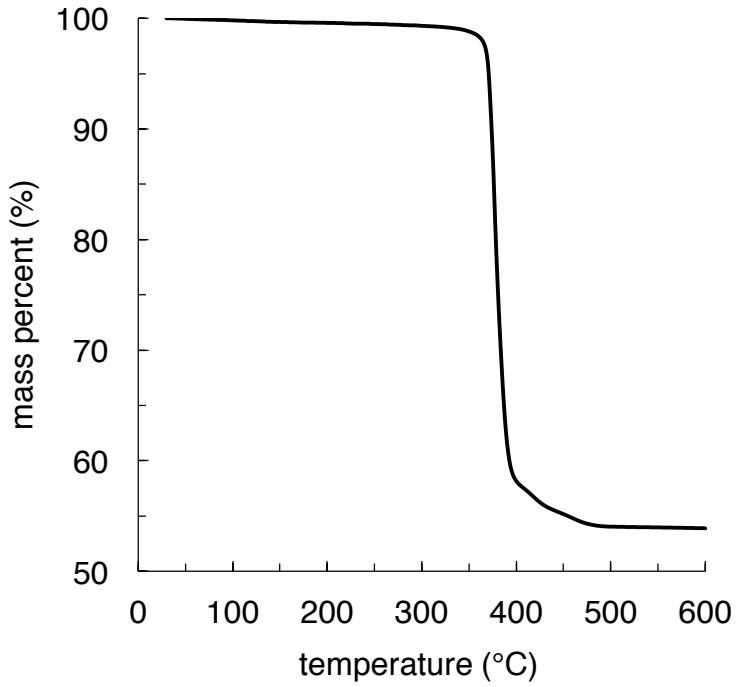

Figure S14. Thermogravimetric analysis trace for **4** heated to 600 °C under flowing air.

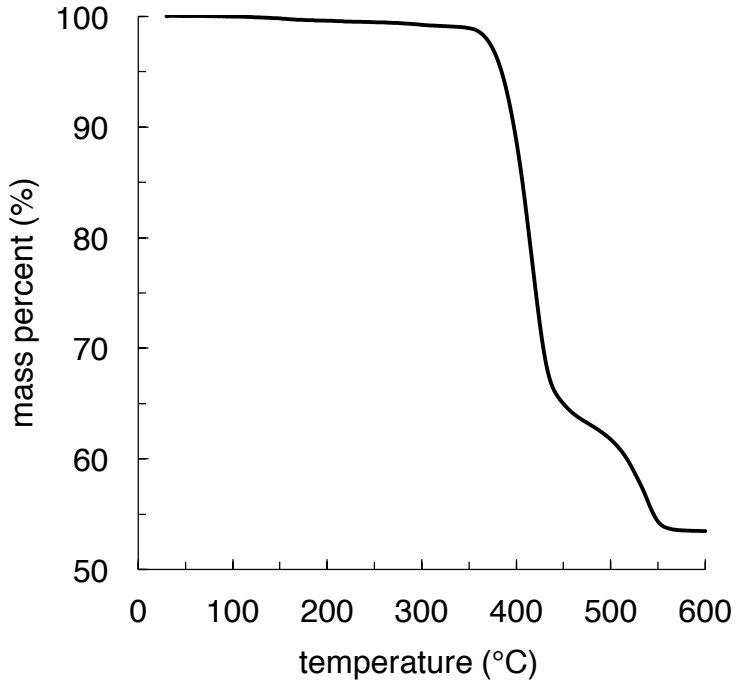

Figure S15. Thermogravimetric analysis trace for **5** heated to 600 °C under flowing air.

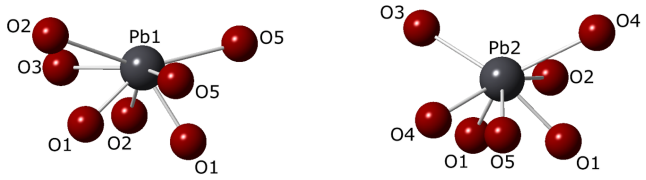

Figure S16. Asymmetric coordination environments of Pb atoms in **1** indicating stereoactive $6s^2$ lone pairs.

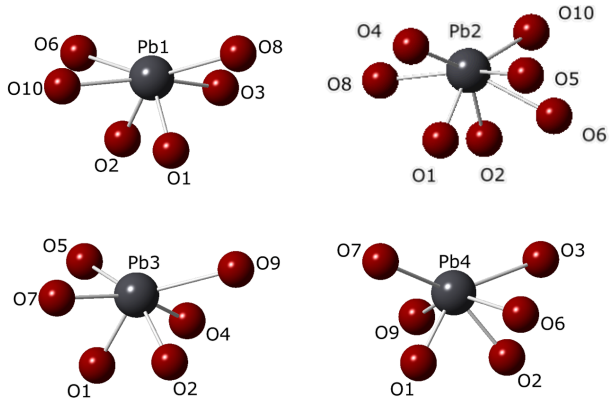

Figure S17. Asymmetric coordination environments of Pb atoms in **2** indicating stereoactive $6s^2$ lone pairs.

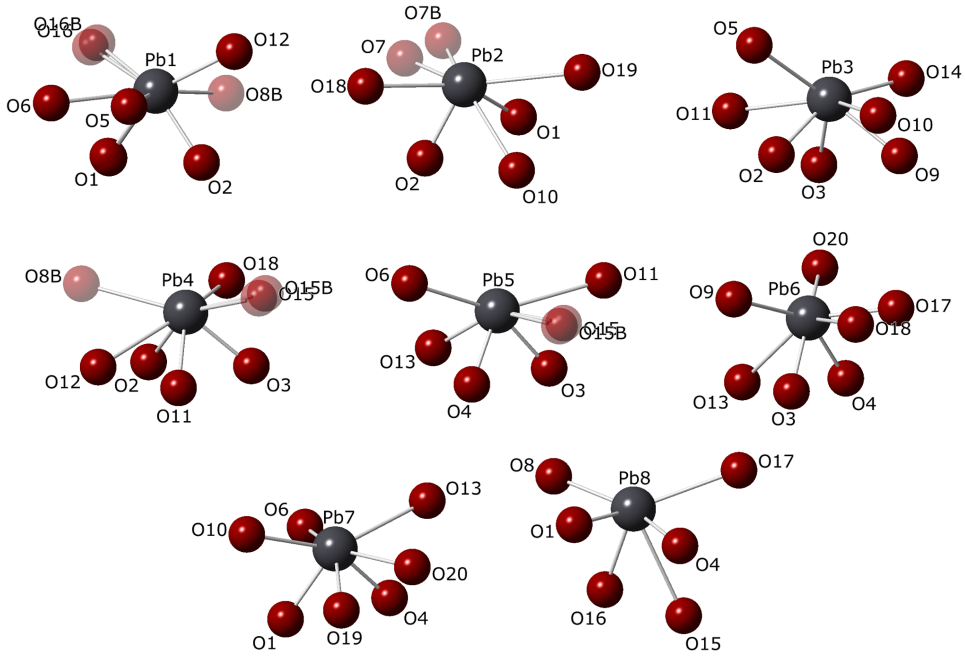

Figure S18. Asymmetric coordination environments of Pb atoms in **3** indicating stereoactive $6s^2$ lone pairs. Transparent atoms are part of refined disorder and have partial occupancy. For Pb8, the metal as well as several oxygen atoms are disordered. Shown here are the major contributors.

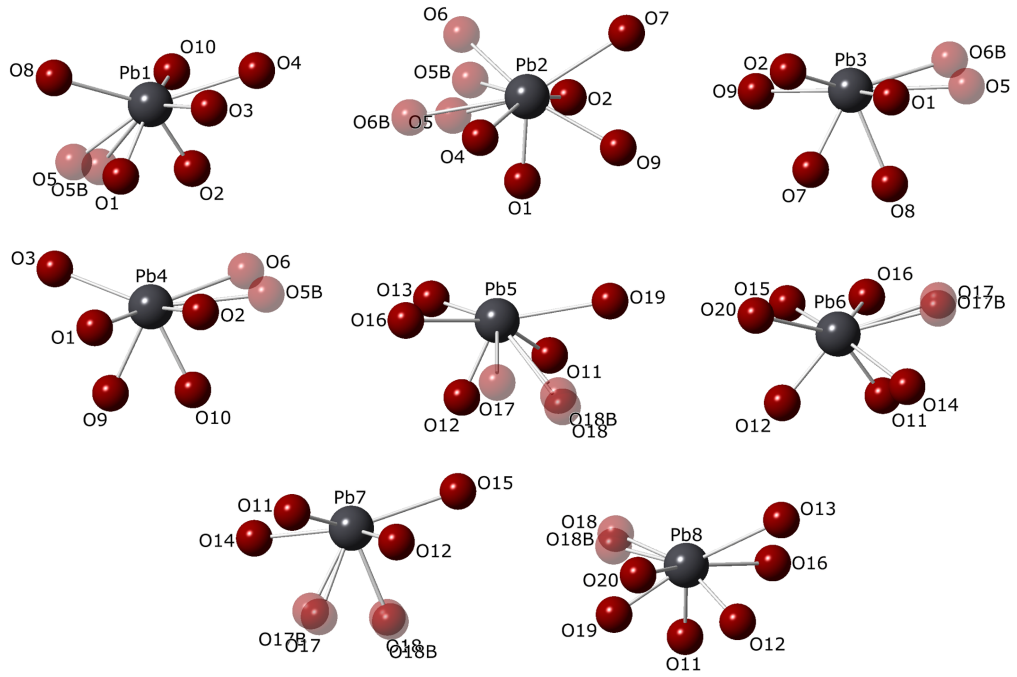

Figure S19. Asymmetric coordination environments of Pb atoms in **4** indicating stereoactive $6s^2$ lone pairs. Transparent atoms are part of refined disorder and have partial occupancy.

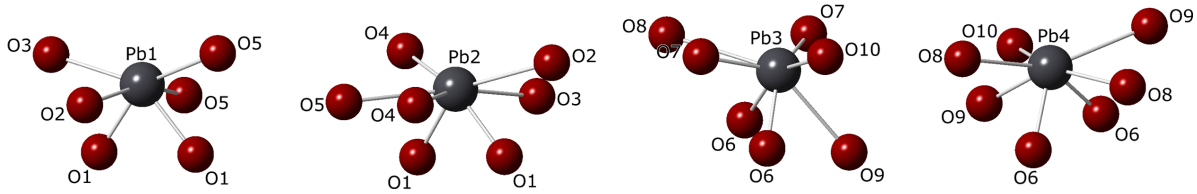

Figure S20. Asymmetric coordination environments of Pb atoms in **5** indicating stereoactive $6s^2$ lone pairs.

Table S1. Pb-O bond lengths and resulting bond valence sums for **1**-**5**. Maximum contact distances to be considered in the calculations were determined by looking for gaps in histograms of Pb-O contacts, through comparison among this group of compounds as well as with previously reported lead oxide carboxylates, and through the bond valence sum calculations themselves. Contact up to 3.20 Å were used in final calculations of sums for **1**, **2, 3**, and **5**, with distances up to 3.22 Å included for two of the eight sites in **4**.

compound	bond	bond length (Å)	bond valence contribution (v.u.)
1	Pb1-O1	2.2597	0.546
	Pb1-O1	2.2937	0.509
	Pb1-O2	2.4316	0.384
	Pb1-O5	2.7399	0.205
	Pb1-O3	2.8902	0.151
	Pb1-O5	2.8941	0.150
	Pb1-O2	3.1932	0.081
			total 2.026
	Pb2-O1	2.3059	0.497
	Pb2-O1	2.3131	0.489
	Pb2-O4	2.4524	0.368
	Pb2-O3	2.7803	0.189
	Pb2-O4	2.8396	0.167
	Pb2-O5	2.8421	0.166
	Pb2-O2	2.9109	0.144
			total 2.021

compound	bond	bond length (Å)	bond valence contribution (v.u.)
2	Pb1-O2	2.2559	0.550
	Pb1-O1	2.2892	0.514
	Pb1-O3	2.5520	0.301
	Pb1-O10	2.5575	0.297
	Pb1-O8	2.8521	0.163
	Pb1-O6	3.1462	0.089
			total 1.914

Pb2-O1	2.2949		0.508
Pb2-O2	2.3182		0.484
Pb2-O8	2.5646		0.293
Pb2-O6	2.6145		0.265
Pb2-O5	2.7689		0.193
Pb2-O10	2.8727		0.156
Pb2-O4	2.9454		0.135
		total	2.034
Pb3-O1	2.3040		0.499
Pb3-O2	2.3066		0.496
Pb3-O7	2.4975		0.336
Pb3-O4	2.5464		0.304
Pb3-O5	2.7500		0.201
Pb3-O9	2.8226		0.173
		total	2.008
Pb4-O2	2.2772		0.527
Pb4-O1	2.2918		0.511
Pb4-O9	2.3962		0.413
Pb4-O6	2.6684		0.237
Pb4-O7	2.9431		0.135
Pb4-O3	2.9762		0.126
		total	1.950

compound	bond	bond length (Å)	fractional contribution (if other than unity)	bond valence contribution (v.u.)
3	Pb1-O2	2.2766		0.527
	Pb1-O5	2.3399		0.463
	Pb1-O1	2.3467		0.457
	Pb1-O8B	2.4714	0.278	0.099
	Pb1-O12	2.6429		0.250
	Pb1-O16B	2.8843	0.278	0.042
	Pb1-O16	3.0775	0.722	0.074
	Pb1-O6	3.0803		0.102
			total	2.014

Pb2-O1	2.2718			0.532
Pb2-O2	2.2787			0.525
Pb2-O7B	2.3061	0.278		0.138
Pb2-O7	2.4407	0.722		0.272
Pb2-O18	2.8739			0.156
Pb2-O10	2.9604			0.131
Pb2-O19	3.1610			0.087
			total	1.841
Pb3-O3	2.3097			0.493
Pb3-O2	2.3389			0.464
Pb3-O9	2.4497			0.370
Pb3-O14	2.6764			0.233
Pb3-O10	2.7428			0.204
Pb3-O11	3.0035			0.120
Pb3-O5	3.0052			0.119
			total	2.003
Pb4-O2	2.2526			0.554
Pb4-O3	2.2852			0.518
Pb4-O11	2.4484			0.371
Pb4-O18	2.6200			0.262
Pb4-O15	2.7891	0.722		0.134
Pb4-O15B	2.9472	0.278		0.037
Pb4-O8B	2.9692	0.278		0.036
Pb4-O12	3.0316			0.113
			total	2.024
Pb5-O3	2.2642			0.541
Pb5-O4	2.2662			0.539
Pb5-O13	2.4226			0.391
Pb5-O15	2.5258	0.722		0.229
Pb5-O6	2.8710			0.157
Pb5-O15B	2.5866	0.278		0.078
Pb5-O11	3.1055			0.097
			total	2.032

	Pb6-O3	2.2743		0.530
	Pb6-O4	2.2938		0.509
	Pb6-O17	2.4816		0.347
	Pb6-O9	2.7840		0.187
	Pb6-O20	2.9029		0.147
	Pb6-O13	2.9991		0.121
	Pb6-O18	3.0082		0.118
			total	1.959
	Pb7-O4	2.3014		0.501
	Pb7-O1	2.3717		0.434
	Pb7-O19	2.4049		0.406
	Pb7-O6	2.7154		0.215
	Pb7-O10	2.7225		0.212
	Pb7-O20	2.7857		0.187
	Pb7-O13	3.0997		0.098
			total	2.054
	Pb8-O1	2.2385		0.570
	Pb8-O4	2.3192		0.483
	Pb8-O16	2.4709		0.355
	Pb8-O8	2.6639		0.239
	Pb8-O17	2.9769		0.126
	Pb8-O15	3.1949		0.081
			total	1.854

compound	bond	bond length (Å)	fractional contribution (if other than unity)	bond valence contribution (v.u.)
4	Pb1-O2	2.2637		0.541
	Pb1-O1	2.3314		0.471
	Pb1-O3	2.3884		0.420
	Pb1-O10	2.7927		0.184
	Pb1-O5	2.7970	0.688	0.125
	Pb1-O8	2.8902		0.151
	Pb1-O5B	2.9444	0.312	0.042
	Pb1-O4	2.9544		0.132
			total	2.067

Pb2-O2	2.2579			0.548
Pb2-O1	2.3108			0.492
Pb2-O5B	2.3834	0.312		0.132
Pb2-O5	2.4933	0.688		0.233
Pb2-O9	2.8128			0.177
Pb2-O4	3.0029			0.120
Pb2-O6	3.0298	0.688		0.078
Pb2-O7	3.1240			0.094
Pb2-O6B	3.2161	0.312		0.024
			total	1.897
Pb3-O1	2.2716			0.533
Pb3-O2	2.3468			0.457
Pb3-O7	2.3912			0.417
Pb3-O8	2.6848			0.229
Pb3-O6B	2.8572	0.312		0.161
Pb3-O5	2.8769	0.688		0.048
Pb3-O4	3.0701			0.072
			total	1.988
Pb4-O1	2.2863			0.517
Pb4-O2	2.3104			0.492
Pb4-O10	2.4788			0.349
Pb4-O9	2.6028			0.271
Pb4-O3	2.8140			0.176
Pb4-O6	2.8494	0.688		0.113
Pb4-O5B	3.0648	0.312		0.033
			total	1.951
Pb5-O12	2.2686			0.536
Pb5-O11	2.2794			0.524
Pb5-O13	2.3963			0.413
Pb5-O18B	2.8775	0.586		0.091
Pb5-O16	2.9614			0.130
Pb5-O19	3.0369			0.112
Pb5-O17	3.0603	0.414		0.107
Pb5-O18	3.2062	0.414		0.033
			total	1.945

Pb6-O11	2.2840		0.519
Pb6-O12	2.3444		0.459
Pb6-O15	2.4848		0.345
Pb6-O17B	2.7305	0.586	0.122
Pb6-O17	2.8034	0.414	0.074
Pb6-O16	2.8679		0.158
Pb6-O14	2.9303		0.139
Pb6-O20	2.9733		0.127
			total 1.944
Pb7-O12	2.2703		0.534
Pb7-O11	2.2855		0.518
Pb7-O17B	2.4409	0.586	0.221
Pb7-O17	2.5490	0.414	0.125
Pb7-O18	2.6171	0.414	0.109
Pb7-O18B	2.6890	0.586	0.133
Pb7-O14	2.8067		0.179
Pb7-O15	3.0142		0.117
			total 1.936
Pb8-O12	2.3037		0.499
Pb8-O11	2.3351		0.468
Pb8-O19	2.4004		0.410
Pb8-O18B	2.6666	0.586	0.139
Pb8-O18	2.7445	0.414	0.084
Pb8-O16	2.8007		0.181
Pb8-O20	2.8015		0.181
Pb8-O13	3.1878		0.082
			total 2.044

compound	bond	bond length (Å)	bond valence contribution (v.u.)
5	Pb1-O1	2.2581	0.548
	Pb1-O1	2.3518	0.452
	Pb1-O2	2.4592	0.363
	Pb1-O5	2.6190	0.262
	Pb1-O3	2.7714	0.192
	Pb1-O5	2.8675	0.158
			total 1.975

Pb2-O1	2.2782		0.526
Pb2-O1	2.2888		0.514
Pb2-O4	2.4822		0.347
Pb2-O3	2.6996		0.222
Pb2-O4	2.8943		0.149
Pb2-O2	3.0881		0.101
Pb2-O5	3.1398		0.091
		total	1.950
Pb3-O6	2.2986		0.504
Pb3-O6	2.3099		0.493
Pb3-O7	2.3753		0.431
Pb3-O10	2.7940		0.183
Pb3-O7	2.8821		0.153
Pb3-O9	2.9059		0.146
Pb3-O8	3.1992		0.080
		total	1.991
Pb4-O6	2.2754		0.529
Pb4-O6	2.3073		0.495
Pb4-O9	2.4106		0.401
Pb4-O8	2.6816		0.231
Pb4-O8	2.7823		0.188
Pb4-O10	2.9863		0.124
Pb4-O9	3.0278		0.114
		total	2.081