Supplementary Information

Rhodium-Silver Superatomic Nanoclusters Stabilized by Diselenophosphate Ligands

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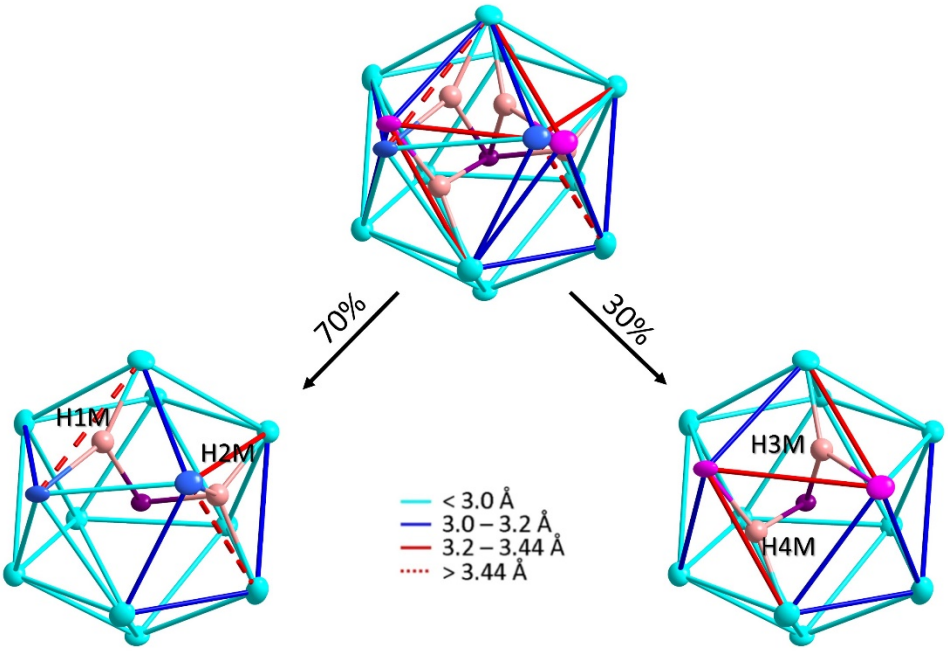

Figure S1. Possible positions of hydrides of **1** in the icosahedron. Color code: sky blue for Ag_{ico}, blue for Ag_{ico} with 70% occupancy, magenta for Ag_{ico} with 30% occupancy, purple for Rh, pink for H.

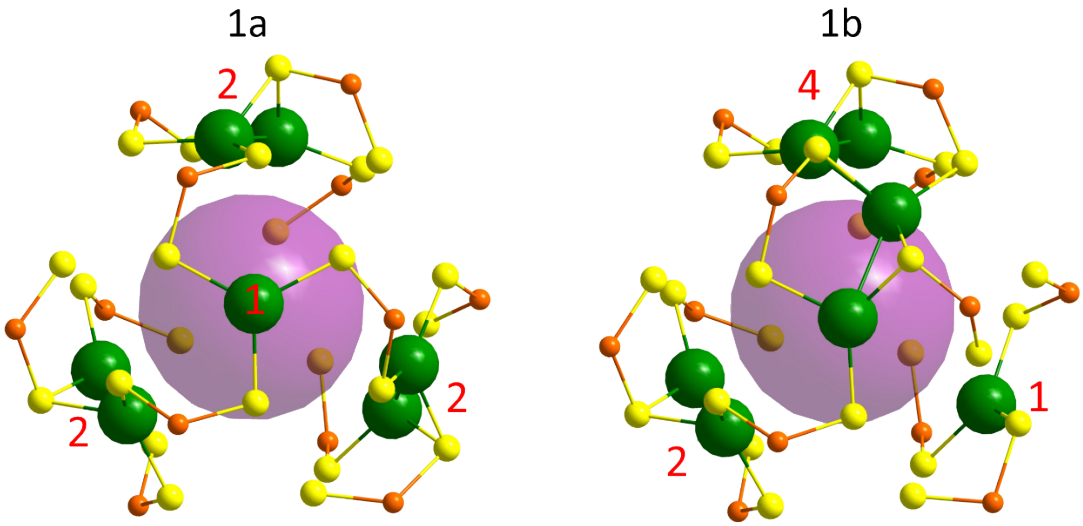

Figure S2. Top view of the metal-framework for **1a** and 1**b.** color code: purple for $RhH_2@Ag_{12}$; green for Ag_{cap}; yellow for Se; orange for P.

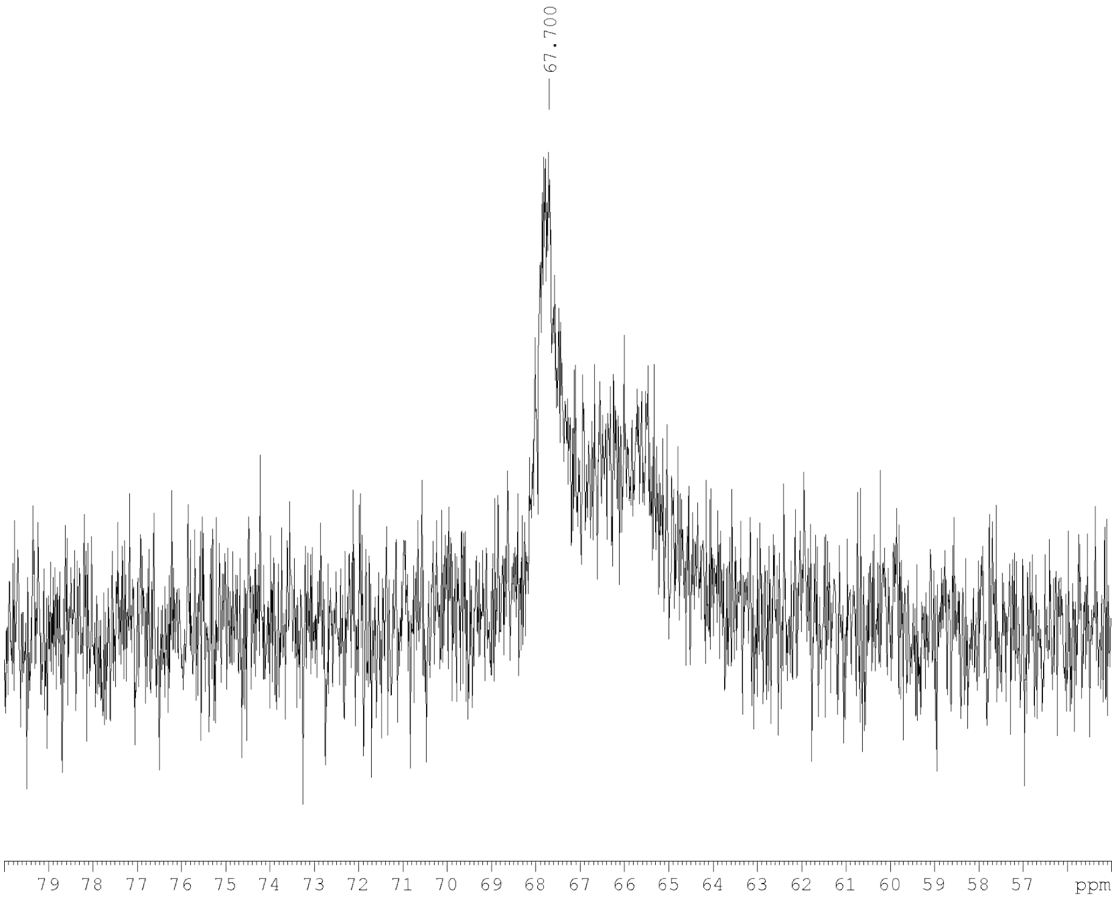

Figure S3. ^{31}P NMR spectrum ($CDCl_3$) of **2**.

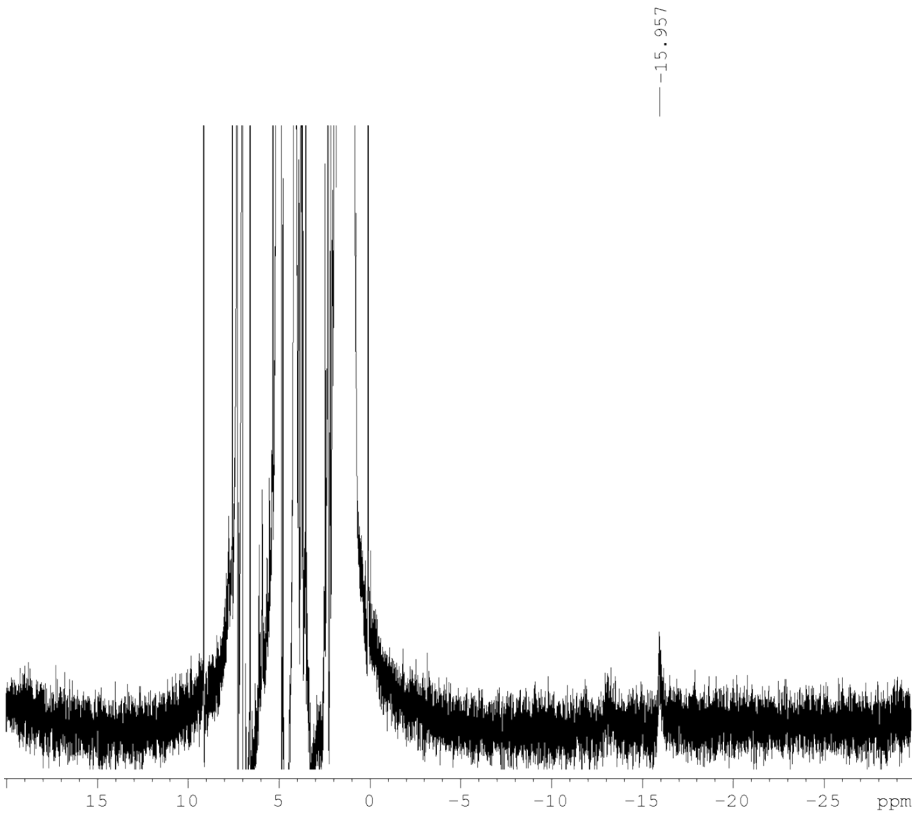

Figure S4. ^{1}H NMR spectrum ($CDCl_3$) of **2**.

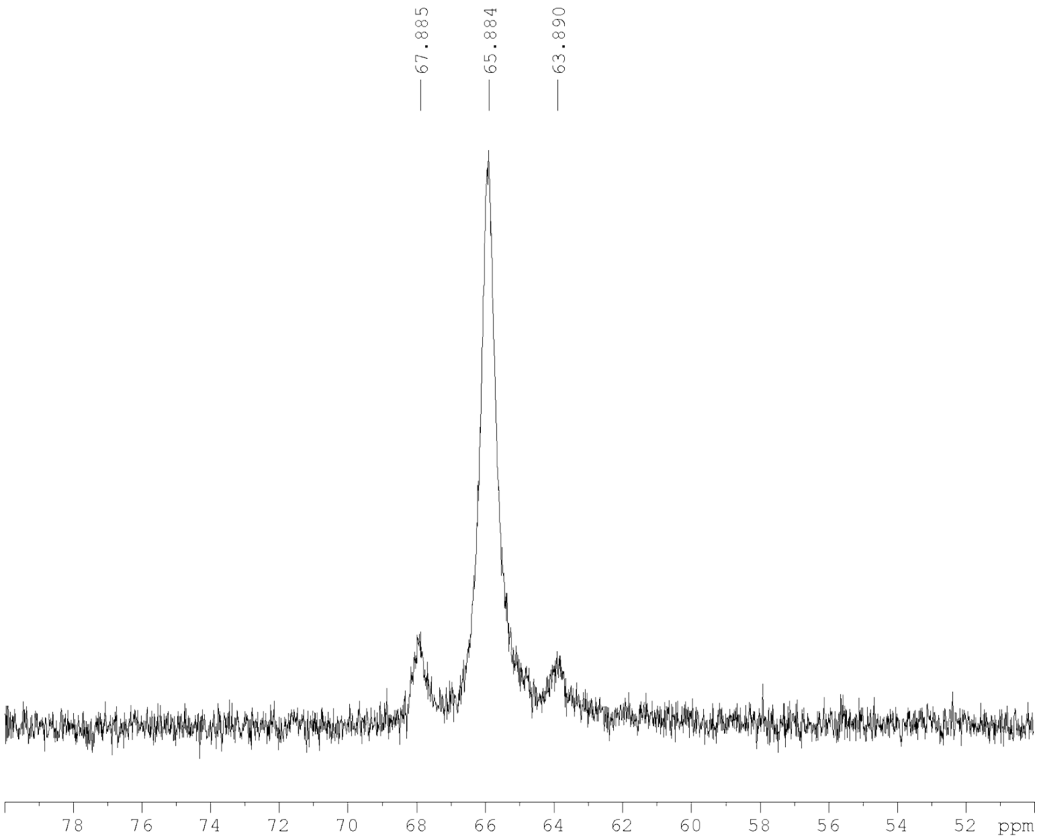

Figure S5. ^{31}P NMR spectrum ($CDCl_3$) of **3**.

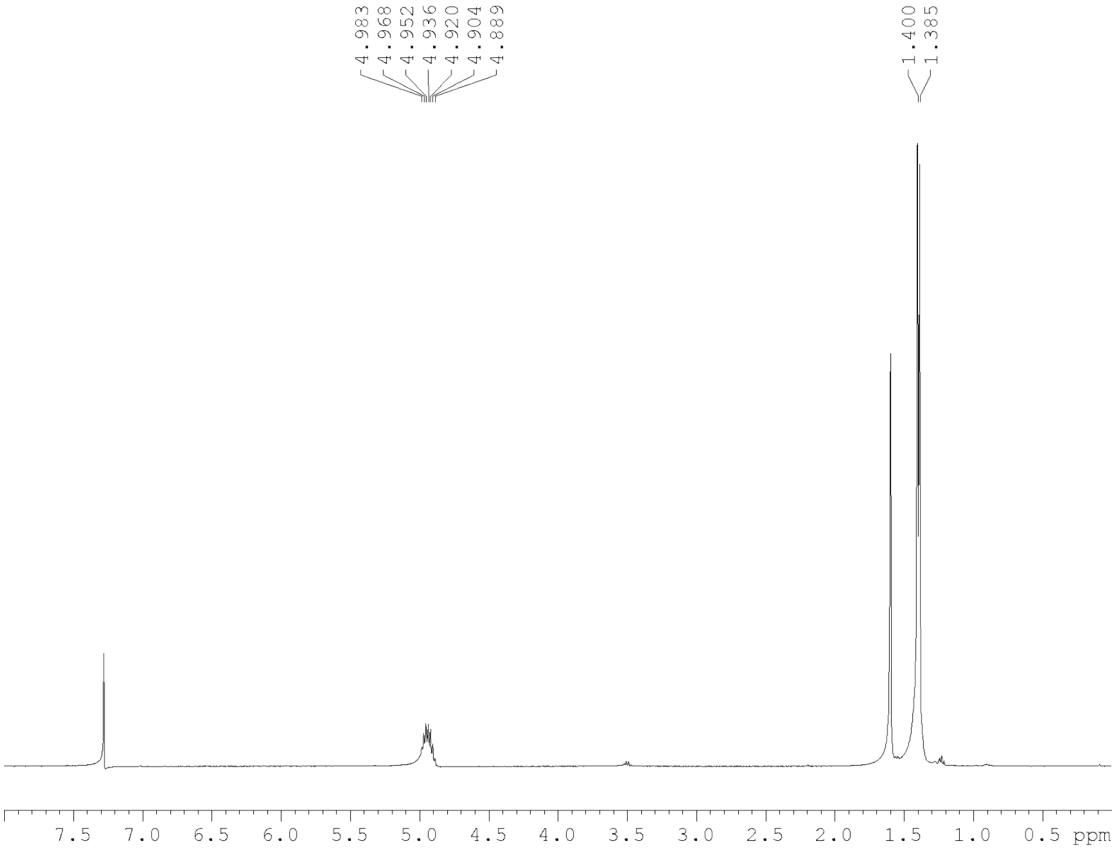

Figure S6. ^{1}H NMR spectrum ($CDCl_3$) of **3**.

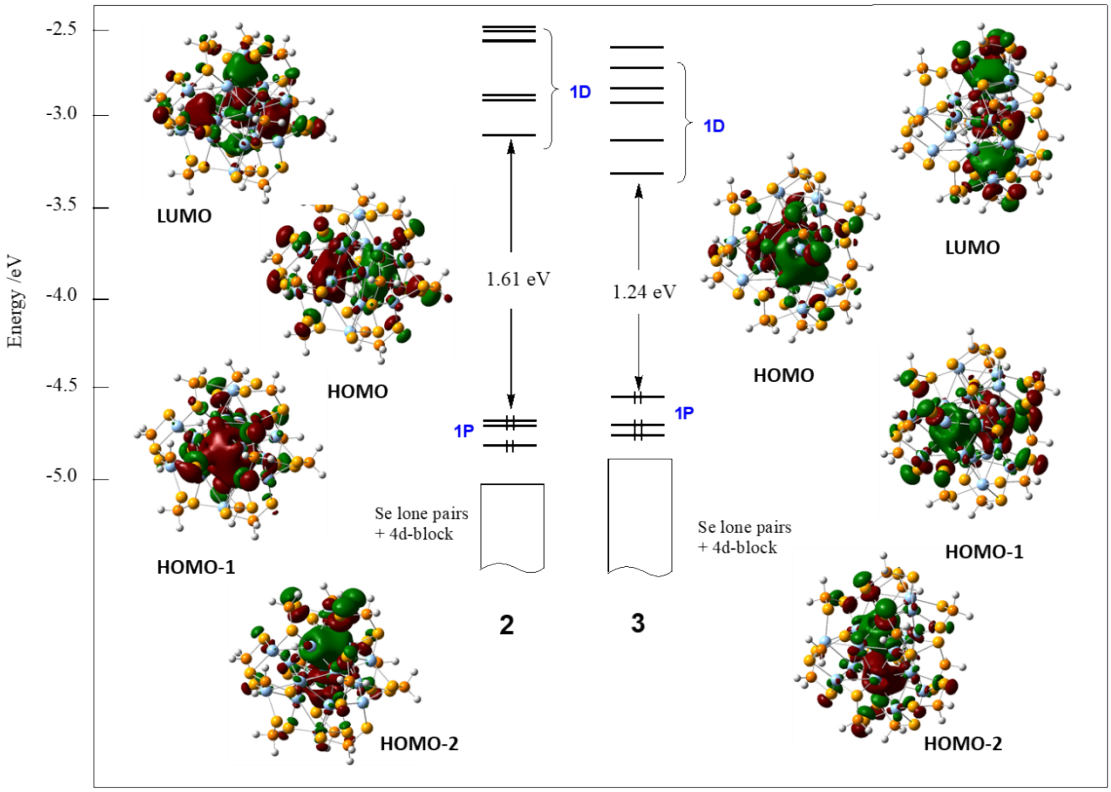

Figure S7. Kohn-Sham frontier orbital diagram of **2** and **3**.

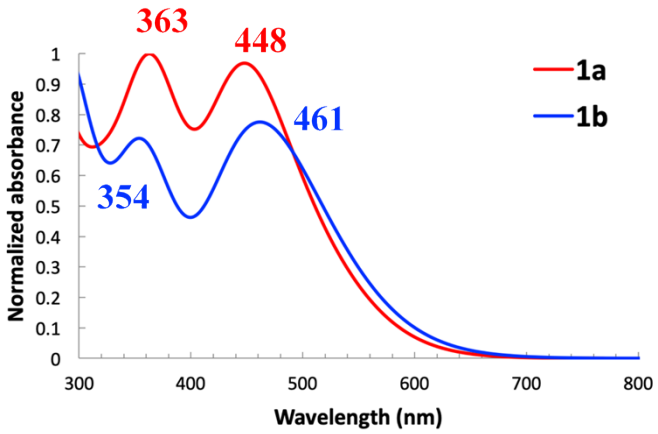

Figure S8. TD-DFT simulated spectra of **1a** and **1b**.

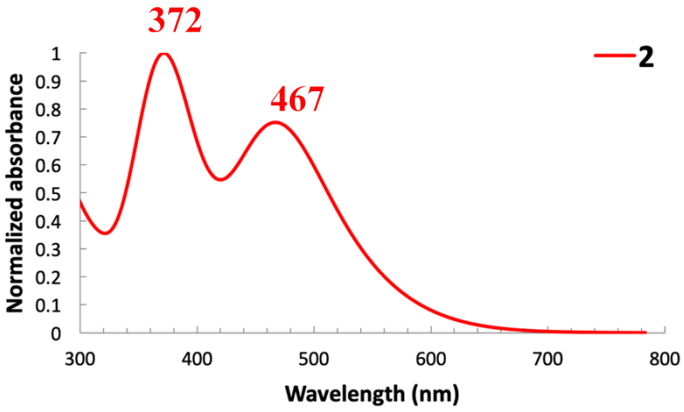

Figure S9. TD-DFT simulated spectrum of **2**.

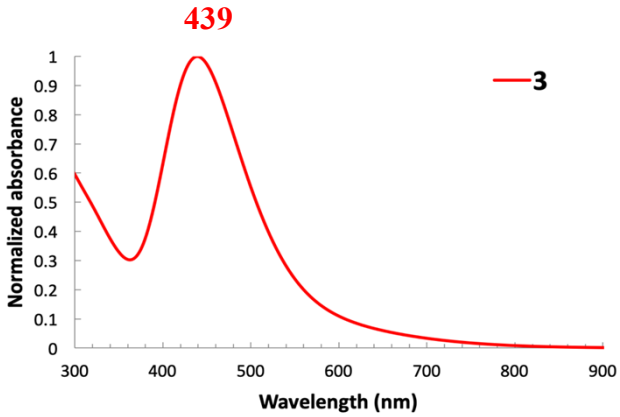

Figure S10. TD-DFT simulated spectrum of **3**.

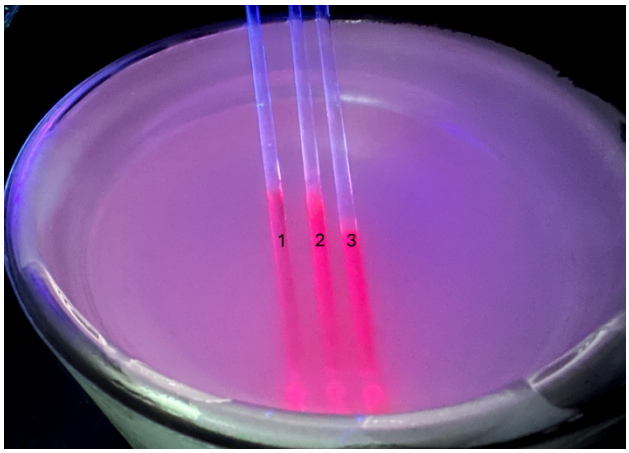

Figure S11. Image of emission recorded in Me-THF, in liquid Nitrogen (*ca.* 77 K).

Table S1. Selected X-ray crystallographic data of **1**, **2,** and **3**.

Compound	**1**	**2**	**3**
CCDC no.	2432601	2432602	2432603
Chemical formula	$C_{76}H_{186}Ag_{19}O_{28}P_{12}RhSe_{24}$	$C_{72}H_{169}Ag_{20}O_{24}P_{12}RhSe_{24}$	$C_{72}H_{168}Ag_{21}O_{24}P_{12}RhSe_{24}$
Formula weight	5967.36	5946.054	6052.91
Wavelength, Å	0.71073	0.71073	0.71073
Crystal System	Monoclinic	Cubic	Triclinic
Space group	$P2_1/n$	$I23$	$P\bar{1}$
a, Å	30.227(4)	32.578(2)	16.0696(11)
b, Å	17.3463(19)	32.578(2)	18.3134(17)
c, Å	33.229(4)	32.578(2)	29.837(2)
α, deg.	90	90	81.936(2)
β, deg.	112.607(3)	90	76.8308(16)
γ, deg.	90	90	64.9124(15)
V, Å^3	16084(3)	34577(8)	7733.6(11)
Z	4	8	2
Temperature, K	100(2)	100(2)	100(2)
ρ_{calcd}, g/cm^3	2.464	2.284	2.599
μ, mm^{-1}	7.955	7.507	8.514
θ_{max}, deg.	25.056	25.062	25.000
Completeness, %	99.5	99.9	98.9
Reflection collected / unique	95965 / 28358 [R(int) = 0.0869]	112089 / 10242 [R(int) = 0.0856]	58572 / 26937 [R(int) = 0.0538]
Restraints / parameters	573 / 1556	145 / 477	498 / 1477
[a] $R1$, [b] $wR2$ [I > 2σ(I)]	0.0767, 0.1552	0.0592, 0.1234	0.0576, 0.1197
[a] $R1$, [b] $wR2$ (all data)	0.1146, 0.1709	0.0906, 0.1469	0.0938, 0.1396
GOF	1.122	1.078	1.023
Absolute structure parameter	-	0.00(2)	-
Largest diff. peak and hole, e/Å^3	2.846 and -1.736	1.910 and -1.191	2.532 and -2.476

Table S2. Computed natural atomic charges for **1**, **2** and **3** and their dtp analogs.

Averaged NPA charges	1a	1b	2	3	1(dtp) [a]	2(dtp) [a]	3(dtp) [a]
Rh	-1.32	-1.31	-1.50	-1.66	-1.40	-1.53	-1.67
Ag_{ico}	0.37	0.38	0.32	0.26	0.40	0.33	0.27
Ag_{cap}	0.65	0.65	0.65	0.64	0.70	0.70	0.68
H	-0.32	-0.36	-0.33	-	-0.33	-0.34	-

[a] From: T. H. Chiu, J. H. Liao, Y. Y. Wu, J. Y. Chen, Y. J. Chen, X. Wang, S. Kahlal, J. Y. Saillard and C. W. Liu, *J. Am. Chem. Soc.*, 2023, **145**, 16739–16747.

Table S3. Atomic coordinates of the DFT-optimized structure of **1a**, **1b**, **2** and **3**

1a

Rh	-0.006326	-0.082747	0.313804
Ag	-0.998348	-2.740926	-0.182669
Ag	-2.839809	-0.407438	0.564704
Ag	-1.767368	2.029211	-0.672249
Ag	-1.572052	-0.554270	-2.094743
Ag	1.217555	-1.554417	-1.837962
Ag	1.991007	-2.106876	0.937588
Ag	1.900749	0.490869	2.525653
Ag	0.884450	2.600460	0.559559
Ag	0.709846	1.359823	-2.129366
Ag	2.803874	0.476706	-0.278568
Ag	-1.081280	-1.247234	2.800910
Ag	-1.532829	1.722875	2.257123
Ag	-3.510303	-3.073185	1.907865
Ag	-3.748787	-2.620338	-1.475157
Ag	-1.377947	4.652185	1.195588
Ag	4.607252	-0.920226	2.053781
Ag	4.212056	-2.133247	-1.161461
Ag	0.270858	-0.515184	-4.561247
Ag	-0.109792	4.311188	-1.886151
H	0.017388	0.572157	1.843821
H	0.041958	-1.512810	1.156097
Se	-2.380605	-0.022203	-4.732141
Se	-2.414910	-3.650169	-3.605497
Se	1.151569	-3.050005	-4.205361
Se	-4.111051	3.193063	-1.369594
Se	2.496194	4.690141	-1.276166
Se	1.115345	4.810047	2.261730
Se	5.022570	1.980068	-0.695327
Se	6.502890	-1.470437	0.201325
Se	3.204603	-4.545886	-0.376586
Se	3.479466	-3.165109	3.115699
Se	4.561566	1.504482	3.183834
Se	1.887894	-0.088008	5.255780
Se	-1.697244	-4.113328	3.564812
Se	-1.987434	-0.809289	5.309610

Se	-5.034358	-0.849461	2.302143
Se	-5.361105	-0.446065	-1.448550
Se	-4.643585	-4.716651	0.057171
Se	-0.854702	-5.403444	-0.005870
Se	-0.806157	2.707516	4.840454
Se	-3.532382	3.726943	2.513174
Se	4.345285	-1.064395	-3.632012
Se	2.040111	1.521461	-4.616567
Se	-1.236751	3.366634	-4.166905
Se	-1.798569	6.258969	-0.938535
P	-3.024509	-2.121357	-5.025817
P	3.283562	-2.656792	-4.659815
P	-3.660853	5.297010	-1.651356
P	2.174200	5.787305	0.587195
P	6.652160	0.551582	-0.693203
P	4.150313	-4.607834	1.597616
P	3.796133	0.931272	5.180106
P	-2.190258	-2.974743	5.391779
P	-6.276224	-0.882101	0.485474
P	-2.902209	-6.001247	-0.391347
P	-2.656779	3.784202	4.550552
P	0.609238	3.074745	-5.284685
H	-2.640399	-2.547134	-6.325191
H	-4.436919	-2.097024	-5.171859
H	3.417176	-2.448240	-6.058209
H	3.962031	-3.896670	-4.521531
H	-3.755705	5.646498	-3.024732
H	-4.725287	6.072382	-1.120022
H	3.447921	6.192467	1.064929
H	1.586610	7.053202	0.319158
H	7.137374	0.330261	-2.009915
H	7.795384	1.151456	-0.101623
H	3.973829	-5.916959	2.118548
H	5.564941	-4.571492	1.467479
H	4.805069	0.219443	5.887845
H	3.776593	2.130561	5.943194
H	-1.385681	-3.525147	6.426732
H	-3.475137	-3.360438	5.866353

H	-7.334441	0.042674	0.685032
H	-7.005469	-2.100048	0.423394
H	-3.066561	-6.394428	-1.746172
H	-3.137449	-7.237871	0.265156
H	-3.679997	3.321262	5.421779
H	-2.571940	5.137832	4.982132
H	0.278537	2.849345	-6.647660
H	1.340243	4.287164	-5.398756

1b

Rh	0.213639	0.263808	-0.208490
Ag	1.232369	-2.191274	-1.183784
Ag	3.010852	-0.213453	0.267248
Ag	1.465250	1.212821	2.307747
Ag	1.005097	-1.692854	1.796838
Ag	-1.432770	-2.024119	0.144712
Ag	-1.278018	-0.764479	-2.524255
Ag	-0.373670	2.097811	-2.299581
Ag	-0.859892	2.791523	1.156378
Ag	-1.265166	0.098187	2.277662
Ag	-2.572201	0.816380	-0.285293
Ag	2.241195	0.552930	-2.479039
Ag	2.050360	2.602177	-0.300621
Ag	4.298171	-1.779741	-2.077240
Ag	3.333466	-3.331206	0.714606
Ag	1.517665	4.382924	2.241370
Ag	-3.669547	1.328754	-3.047758
Ag	-3.921604	-1.707339	-1.626608
Ag	-1.697647	-2.976630	2.990655
Ag	-4.018030	-1.130498	1.471823
H	0.063071	1.926468	-0.322731
H	0.505393	-0.076149	-1.833072
Se	0.677406	-2.909025	4.287541
Se	1.536561	-5.251065	1.418975
Se	-1.833857	-4.717753	0.851969
Se	3.613864	0.983797	4.017454
Se	-2.545347	3.875253	3.015117
Se	-0.245828	5.699052	0.679596

Se	-5.091347	1.381393	0.942983
Se	-5.966602	-0.070328	-2.542539
Se	-2.604998	-2.976682	-3.718739
Se	-2.222928	0.499410	-5.140485
Se	-3.538801	3.581078	-1.592877
Se	-0.803507	3.813511	-4.243693
Se	3.334138	-1.327705	-4.533046
Se	3.962787	2.262595	-3.692550
Se	5.657502	0.041929	-0.596392
Se	4.859353	-2.000405	2.497987
Se	4.752861	-4.372649	-1.404148
Se	1.266751	-4.155183	-3.014134
Se	2.430307	4.972222	-1.784575
Se	4.025870	3.916327	1.415907
Se	-5.364002	-3.204995	0.139887
Se	-4.120160	-2.272278	3.951635
Se	-1.739293	0.608954	4.884888
Se	0.663398	3.256662	4.508568
P	1.477777	-4.824255	3.546631
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P	2.620363	2.498966	5.221897
P	-2.027673	5.725051	1.996889
P	-6.523426	0.870862	-0.630558
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P	-2.243393	4.778745	-2.927328
P	4.423225	0.548719	-4.956921
P	6.314813	-1.262741	1.059325
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P	4.001079	5.278495	-0.327845
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H	2.767573	-4.963612	4.122967
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H	-4.220491	-5.850767	-0.459158
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H	-4.383624	-1.542583	-5.647212
H	-3.060292	5.642516	-3.707253
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H	5.821313	0.288769	-5.011260
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H	7.094876	-2.324839	0.527304
H	2.611637	-6.364327	-1.524618
H	3.487168	-6.021820	-3.492229
H	5.286401	5.177871	-0.926183
H	4.045784	6.630862	0.112227
H	-3.325910	-1.241750	6.587392
H	-4.620429	0.142946	5.522066

2

Rh	-0.000027	-0.000112	0.076645
Ag	-1.978960	-0.143509	2.221785
Ag	-1.533790	2.351404	0.508393
Ag	-2.780100	-0.211134	-0.556214
Ag	-0.972922	1.429778	-2.221997
Ag	1.109373	-1.652754	2.216135
Ag	-1.270614	-2.506119	0.493979
Ag	1.574168	-2.299092	-0.563784
Ag	-0.746700	-1.546777	-2.230887
Ag	0.871321	1.776362	2.226880
Ag	2.804484	0.150574	0.500915
Ag	1.205162	2.515707	-0.548783
Ag	1.717878	0.137554	-2.226257
Ag	-4.277384	1.705651	1.603096
Ag	-3.969792	2.244222	-1.706240
Ag	0.000842	-0.015187	4.730671
Ag	-0.000770	0.014524	-4.719302
Ag	0.657490	-4.563975	1.583883
Ag	0.044319	-4.551433	-1.726575

Ag	3.621005	2.843436	1.605791
Ag	3.922703	2.323881	-1.706442
H	0.000680	-0.005485	1.716039
Se	-2.551390	-0.898435	4.793051
Se	-3.115493	2.743348	3.834353
Se	-5.526273	-0.684460	1.569107
Se	-5.013338	-0.264809	-2.199240
Se	-5.432005	3.663944	0.059664
Se	-1.939835	4.980608	1.015529
Se	1.201994	2.428738	-5.074968
Se	4.105296	0.424902	-3.641239
Se	2.042449	-1.783382	4.789378
Se	-0.827739	-4.087586	3.813826
Se	3.351940	-4.448785	1.556903
Se	2.740539	-4.199089	-2.212032
Se	-0.457319	-6.536060	0.029011
Se	-3.346339	-4.173970	0.987584
Se	-2.691442	-0.150291	-5.082572
Se	-2.411568	3.359644	-3.632511
Se	0.512690	2.636580	4.803780
Se	3.944737	1.306744	3.827766
Se	2.175294	5.119999	1.587190
Se	2.270352	4.484866	-2.184877
Se	5.889591	2.871949	0.055480
Se	5.285960	-0.815112	0.995459
Se	1.488836	-2.231615	-5.088164
Se	-1.694910	-3.751291	-3.654604
P	-3.506846	1.072700	5.175979
P	-6.340934	-0.478437	-0.441705
P	-3.971602	5.305570	0.349511
P	3.196844	1.596362	-5.278664
P	0.811416	-3.597463	5.161642
P	3.586499	-5.248460	-0.456927
P	-2.609781	-6.093878	0.317614
P	-2.968418	1.994300	-5.277108
P	2.698438	2.474864	5.179141
P	2.754714	5.732377	-0.422497
P	6.580940	0.784338	0.330660

P	-0.229106	-3.543226	-5.293773
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H	-3.206152	1.466331	6.507142
H	-7.158296	-1.611816	-0.691815
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H	-3.994631	6.046329	-0.862093
H	-4.612164	6.230225	1.217111
H	3.299867	0.775672	-6.432812
H	4.089856	2.645624	-5.621042
H	1.731604	-4.672959	5.279573
H	0.316650	-3.539005	6.491728
H	3.185939	-6.611382	-0.497135
H	4.977474	-5.386754	-0.704391
H	-3.238056	-6.481349	-0.895795
H	-3.090797	-7.113503	1.181923
H	-4.323118	2.243967	-5.620743
H	-2.307374	2.499312	-6.427855
H	3.170101	3.808738	5.304485
H	2.892638	2.010375	6.507238
H	2.181240	7.008251	-0.664253
H	4.135871	6.065080	-0.458827
H	7.226920	0.439602	-0.886301
H	7.706834	0.871097	1.192573
H	-0.993499	-3.218281	-6.445438
H	0.233407	-4.839594	-5.641813

3

Rh	-0.030618	0.121569	0.136579
Ag	-1.654200	-0.658251	2.351552
Ag	1.060097	-1.883823	1.835139
Ag	0.796578	0.873798	2.781933
Ag	-1.518177	2.157215	1.441870
Ag	-2.766449	0.109288	-0.381774
Ag	-1.179504	-2.412629	0.026674
Ag	1.410276	-1.839296	-1.258106
Ag	2.777123	0.180129	0.574114
Ag	1.190493	2.663655	0.466523
Ag	1.602333	0.986681	-2.044595

Ag	-1.008881	2.193132	-1.539013
Ag	-0.904992	-0.598334	-2.516401
Ag	-4.315642	0.993574	2.005049
Ag	-3.919234	-2.242486	1.297389
Ag	-3.462820	-2.304058	-1.981106
Ag	-0.641724	-3.759373	-2.505859
Ag	-1.137044	4.832347	-0.182966
Ag	1.447750	4.024001	-2.232699
Ag	3.649699	-1.042691	3.246642
Ag	3.605083	-2.794100	0.503713
Ag	4.230830	-0.793809	-1.878940
Se	5.824574	-2.310496	2.120208
Se	5.440273	0.893439	-0.071467
Se	2.413867	-5.083377	1.441799
Se	1.879131	-2.733336	4.401885
Se	0.954330	1.089859	5.464065
Se	4.099371	1.597709	3.433260
Se	-4.938601	3.190488	0.526380
Se	-2.008354	4.717104	2.390462
Se	-6.316764	-0.872778	1.424218
Se	-4.983522	0.027490	-2.088381
Se	-4.702337	-4.249667	-0.408013
Se	-0.978848	-5.222523	-0.154596
Se	5.008651	-3.434775	-1.835313
Se	1.751361	-3.185008	-3.748012
Se	3.380115	0.479065	-4.134728
Se	4.094691	3.492721	-1.935580
Se	2.804722	4.513172	1.583572
Se	0.817714	6.457848	-1.084231
Se	-2.967997	-2.662588	3.867112
Se	-3.635089	0.991710	4.615602
Se	0.084096	3.501329	-4.512245
Se	-2.880930	4.152413	-2.209475
Se	-2.789767	-3.834879	-4.176115
Se	-1.457205	-0.356593	-5.147487
P	6.622454	-0.485230	1.192739
P	2.589852	-4.644719	3.562074
P	2.920851	1.971796	5.256116

P	-4.162748	4.657039	1.922518
P	-6.620774	-0.389519	-0.695630
P	-3.086400	-5.740496	-0.458432
P	3.392104	-4.399821	-2.962214
P	4.393464	2.413259	-3.801849
P	2.062599	6.372021	0.745728
P	-4.087370	-1.107497	4.944395
P	-1.656070	4.694281	-3.974752
P	-2.016617	-2.375364	-5.660616
H	7.200503	0.305216	2.219517
H	7.785699	-0.868225	0.474090
H	1.928276	-5.677196	4.277557
H	3.927261	-4.856730	3.993131
H	3.706111	1.664970	6.402042
H	2.858615	3.386245	5.373966
H	-4.830144	4.584244	3.173575
H	-4.561858	5.948767	1.488218
H	-7.447270	-1.407848	-1.238667
H	-7.503157	0.720158	-0.751632
H	-3.404898	-6.728363	0.508877
H	-3.239489	-6.491604	-1.653894
H	3.986894	-5.107440	-4.040484
H	2.878710	-5.476739	-2.194517
H	5.787237	2.231608	-4.005863
H	4.070992	3.220705	-4.924542
H	1.352711	7.124411	1.719310
H	3.152513	7.251086	0.504896
H	-3.929296	-1.382174	6.328246
H	-5.477980	-1.358408	4.792664
H	-1.314276	6.071912	-3.898143
H	-2.534962	4.716553	-5.089859
H	-2.995163	-2.356251	-6.689987
H	-0.962577	-3.048473	-6.334381