Supporting Information

Optical Properties of Trinuclear Metal Chalcogenolate Complexes – Room Temperature NIR Fluorescence in $[Cu_2Ti(SPh)_6(PPh_3)_2]$

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Content

List of Compounds

$[Cu_2Sn(SePh)_6(PPh_3)_2]$ (**1**)

$[Ag_2Sn(SPh)_6(PPh_3)_2]$ (**2**)

$[Cu_2Sn(SPh)_6(PPh_3)_2]$ (**3**)

$[Cu_2Ti(SPh)_6(PPh_3)_2]$ (**4**)

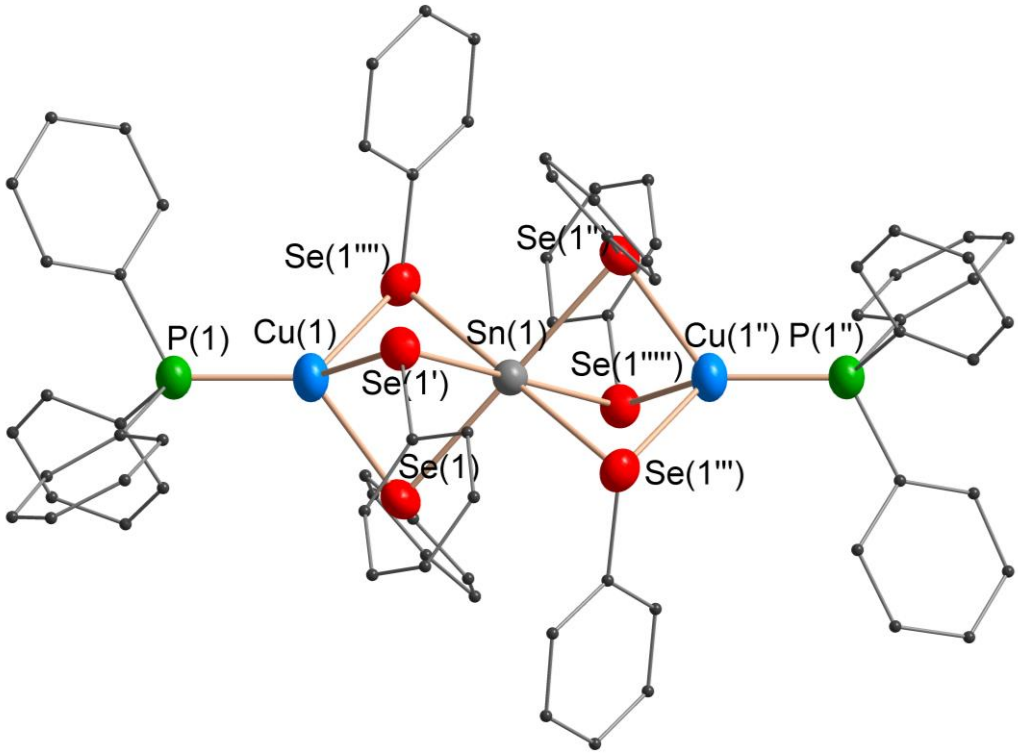

Figure S1. Molecular structure of $[Cu_2Sn(SePh)_6(PPh_3)_2]$ (**1**) (disordered C and all H atoms are omitted for clarity). Thermal ellipsoid plots at 50 % probability. For selected bond lengths and angles see Table S2. Symmetry transformation for generation of equivalent atoms: ’ –y, x–y , z; ’’ –x, –y, –z; ’’’ x–y, x, –z; ’’’’ –x+y, –x, z; ’’’’’ y, –x+y, –z.

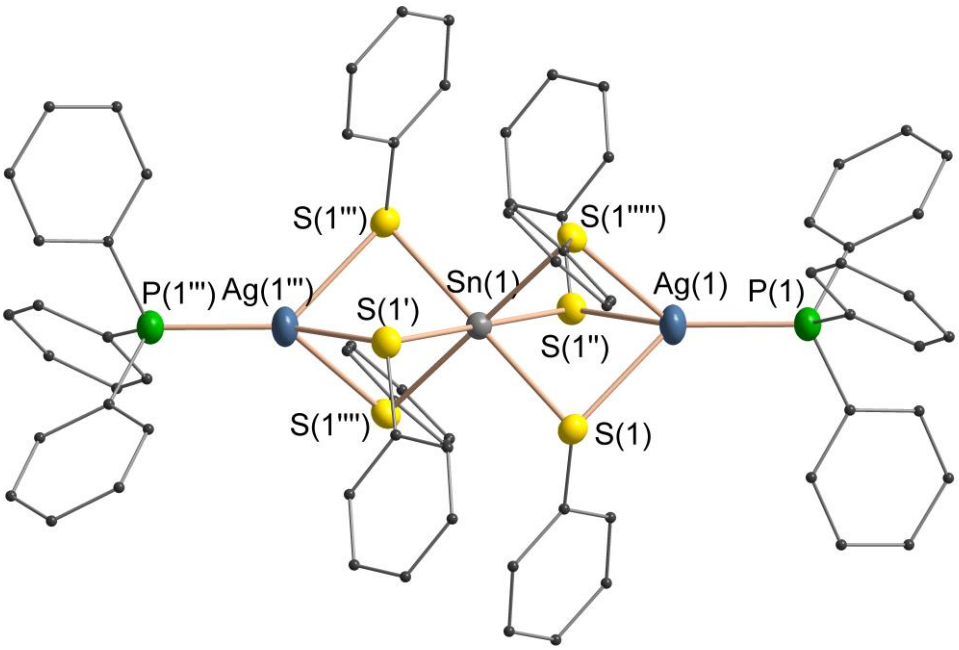

Figure S2. Molecular structure of $[Ag_2Sn(SPh)_6(PPh_3)_2]$ (**2**) (H atoms are omitted for clarity). Thermal ellipsoid plots at 50 % probability. For selected bond lengths and angles see Table S2. Symmetry transformation for generation of equivalent atoms: ’ y, –x+y, –z; ’’ –y, x–y , z; ’’’ –x, –y, –z; ’’’’ x–y, x, –z; ’’’’’ –x+y, –x, z.

Table S1. Crystallographic data for $[Cu_2Sn(SePh)_6(PPh_3)_2]$ (**1**) and $[Ag_2Sn(SPh)_6(PPh_3)_2]$ (**2**).

	1	**2**
sum formula	$C_{72}H_{60}Cu_2P_2Se_6Sn$	$C_{72}H_{60}Ag_2P_2S_6Sn$
fw [g/mol]	1706.67	1513.93
crystal system	trigonal	trigonal
space group	$R\bar{3}$	$R\bar{3}$
Cell *a* [Å]	13.4969(4)	13.2373(19)
b		
c	33.8779(11)	34.644(7)
α [°]		
β		
γ		
V [Å^3]	5334.6(4)	5257.2(18)
Z	3	3
T [K]	180(2)	180(2)
d_c [g cm^{-3}]	1.591	1.435
$\mu(\lambda)$ [mm^{-1}]	4.087	1.170
F[000]	2502	2286
$2\theta_{max}$ [°]	56	66
meas reflns	6671	17659
unique reflns	2831	4174
R_{int}	0.0384	0.0553
reflns with $I > 2\sigma(I)$.	2300	3294
refined params	132	162
$R1(I > 2\sigma(I))$[a]	0.0367	0.0298
*wR*2(all data)[b]	0.0983	0.0689

Table S2. Selected bond distances [pm] and angles [°] of $[Cu_2Sn(SePh)_6(PPh_3)_2]$ (**1**), $[Ag_2Sn(SPh)_6(PPh_3)_2]$ (**2**), $[Cu_2Sn(SPh)_6(PPh_3)_2]$ (**3**) [1] and $[Cu_2Ti(SPh)_6(PPh_3)_2]$ (**4**).[2]

	M	M'	E	M–E–M' [°]	M–E [pm]	M'–E [pm]	M–M' [pm]
3	Cu^{+}	Sn^{4+}	S	78.15(6)	242.1(2)	256.57(17)	314.52(16)
1	Cu^{+}	Sn^{4+}	Se	76.18(2)	249.86(5)	268.97(3)	320.4
2	Ag^{+}	Sn^{4+}	S	81.85(2)	265.22(6)	256.44(5)	341.8
4	Cu^{+}	Ti^{4+}	S	70.54(13), 70.88(12)	234.6(3), 235.4(4)	242.8(4), 248.6(4)	276.2(5), 280.4(5)

Table S3. Observed and calculated (TDDFT) electronic excitation energies in $[Cu_2Sn(SePh)_6(PPh_3)_2]$ (**1**), $[Ag_2Sn(SPh)_6(PPh_3)_2]$ (**2**), $[Cu_2Sn(SPh)_6(PPh_3)_2]$ (**3**) and $[Cu_2Ti(SPh)_6(PPh_3)_2]$ (**4**).[a,b]

	exp.	theory		
	ΔE	ΔE	f	character
1		2.39	0.0050	e_u(HOMO–2) → a_g(LUMO)
	2.57	2.60	0.1852	a_u(HOMO–1) → a_g(LUMO)
	3.65	3.52	0.2688	e_u(HOMO–5) → a_g(LUMO)
2		2.94	0.0186	e_u(HOMO–2) → a_g(LUMO)
	2.97	3.41	0.2047	a_u(HOMO–1) → a_g(LUMO)
	3.84	3.73	0.3538	e_u(HOMO–5) → a_g(LUMO)
3		2.68	0.0046	e_u(HOMO–2) → a_g(LUMO)
	2.97	2.80	0.1833	a_u(HOMO–1) → a_g(LUMO)
	3.79	3.62	0.2888	e_u(HOMO–5) → a_g(LUMO)
4	1.43	1.59	$2.6 \cdot 10^{-5}$	a(HOMO) → e(LUMO)
		2.01	0.0086	0.5 e(HOMO) → e(LUMO+1) 0.5 a(HOMO–1) → a(LUMO)
	1.96	2.19	0.0757	0.5 e(HOMO) → e(LUMO+1) 0.5 a(HOMO–1) → a(LUMO)
		2.24	0.0075	e(HOMO–2) → e(LUMO)
	2.43	2.57	0.0489	e(HOMO–3) → e(LUMO)
		2.70	0.0142	e(HOMO–5) → e(LUMO)

[a] Parameters: transition energy ΔE [eV], corresponding oscillator strength f. For the spectra, see Figures 1 and 2 in the main paper.

[b] in the case of e representations the notation of the HOMOs / LUMOs counts for two degenerate orbitals.

Table S4. Calculated (B3LYP/def2-SV(P)) singlet excitation energies [eV] and oscillator strengths up to 4.5 eV for the X-ray structure parameters of $[Cu_2Sn(SePh)(PPh_3)_2]$ (**1**).

Exc. energy	oscillator strength
2.3914	0.00250952
2.3914	0.00250952
2.6034	0.18519295
3.5169	0.13435884
3.5169	0.13435884
3.7184	0.0203584
3.8363	0.00292854
3.8525	0.00319653
3.8525	0.00319653
3.8818	0.02412452
3.9745	0.00309808
3.9745	0.00309808
4.0454	0.01376861
4.0454	0.01376861
4.0704	0.0085812
4.0704	0.0085812
4.0718	0.01328463
4.1166	0.01336919
4.1166	0.01336919
4.1175	0.00365227
4.1273	0.01462059
4.1273	0.01462059
4.1414	0.05475726
4.2449	0.00000144
4.297	0.00462648
4.3248	0.01417489
4.328	0.0017858
4.328	0.0017858
4.3323	0.03478801
4.3323	0.03478801
4.3335	0.00012091
4.3424	0.00330516
4.3424	0.00330516
4.3431	0.01016643
4.3453	0.06218534
4.3691	0.01527335
4.3691	0.01527335
4.3931	0.0003627
4.4136	0.01677058
4.4136	0.01677058
4.4366	0.01724249
4.4389	0.04469734
4.4389	0.04469734
4.4671	0.01891963
4.4671	0.01891963
4.4796	0.00002264

Table S5. Calculated (B3LYP/def2-SV(P)) singlet excitation energies [eV] and oscillator strengths up to 4.5 eV for the X-ray structure parameters of $[Ag_2Sn(SePh)(PPh_3)_2]$ (**2**).

Exc. energy	oscillator strength
2.9422	0.0092529
2.9422	0.0092529
3.4085	0.2046865
3.7282	0.17685693
3.7282	0.17685693
3.7452	0.00108085
3.7561	0.00620501
3.7561	0.00620501
3.768	0.00188794
3.8507	0.0014759
4.021	0.00026169
4.0339	0.00472121
4.0339	0.00472121
4.0574	0.07494474
4.0717	0.00184009
4.0717	0.00184009
4.1916	0.00271238
4.1927	0.00006686
4.1927	0.00006686
4.1964	0.0006401
4.2238	0.00407915
4.2238	0.00407915
4.2425	0.03490168
4.2425	0.03490168
4.2898	0.02438271
4.2898	0.02438271
4.2927	0.00381271
4.3525	0.01512808
4.3616	0.00065502
4.3616	0.00065502
4.3724	0.00385374
4.3724	0.00385374
4.3815	0.00349968

Table S6. Calculated (B3LYP/def2-SV(P)) singlet excitation energies [eV] and oscillator strengths up to 4.5 eV for the X-ray structure parameters of $[Cu_2Sn(SPh)(PPh_3)_2]$ (**3**).

Exc. energy	oscillator strength
2.6833	0.00233166
2.6833	0.00233166
2.7978	0.18325601
3.6199	0.1444532
3.6199	0.1444532
3.8829	0.01772761
3.9516	0.00090125
3.9704	0.00456294
3.9704	0.00456294
4.0125	0.04008712
4.0165	0.03899321
4.0165	0.03899321
4.0928	0.00401359
4.0928	0.00401359
4.1678	0.03565834
4.1678	0.03565834
4.1872	0.00488577
4.1872	0.00488577
4.2008	0.00093333
4.2088	0.0123517
4.2121	0.01302054
4.2121	0.01302054
4.2263	0.05068478
4.2391	0.01663516
4.3983	0.00253231
4.4008	0.00238319
4.4008	0.00238319
4.4042	0.00529952
4.4142	0.00076352
4.4142	0.00076352
4.4529	0.00232241
4.4566	0.01283008
4.4566	0.01283008

Table S7. Calculated (B3LYP/def2-SV(P)) singlet excitation energies [eV] and oscillator strengths up to 4.5 eV for the X-ray structure parameters of [$Cu_2Ti(SPh)(PPh_3)_2$] (**4**).

Exc. energy	oscillator strength
1.5900	0.00001306
1.5900	0.00001306
1.9999	0.00196596
2.0067	0.00860254
2.0531	0.00175833
2.0531	0.00175833
2.1861	0.07571081
2.2384	0.00745552
2.3023	0.00105309
2.3023	0.00105309
2.3073	0.00129176
2.3857	0.00317842
2.3857	0.00317842
2.4534	0.00081384
2.4808	0.00083617
2.4808	0.00083617
2.5061	0.00033623
2.5061	0.00033623
2.5684	0.04886358
2.6229	0.00110697
2.6229	0.00110697
2.6997	0.01414943
2.7258	0.0000888
2.7258	0.0000888
2.8666	0.00615146
2.8666	0.00615146
2.8844	0.00041694
3.0441	0.00075305
3.0441	0.00075305
3.0799	0.00144029
3.1479	0.00014252
3.1479	0.00014252
3.2161	0.00139542
3.2194	0.00003153
3.2194	0.00003153
3.2295	0.00000258
3.2584	0.04555494
3.2584	0.04555494
3.3194	0.01194426
3.3194	0.01194426
3.4315	0.02778912
3.5822	0.00010731
3.5822	0.00010731
3.5989	0.00023151
3.5989	0.00023151
3.6032	0.00096233
3.621	0.00153616

3.621	0.00153616
3.6265	0.00322513
3.6265	0.00322513
3.6373	0.02057443
3.6373	0.02057443
3.6681	0.04441775
3.6958	0.00881697
3.6958	0.00881697
3.7018	0.0320492
3.8052	0.00009446
3.809	0.00015784
3.809	0.00015784
3.8179	0.00118851
3.8241	0.0004506
3.8592	0.01807902
3.8688	0.00673125
3.8688	0.00673125
3.9126	0.02630274
3.915	0.00040057
3.915	0.00040057
3.9182	0.00032274
3.9287	0.01005998
3.9287	0.01005998
3.9352	0.02482826
3.9508	0.0144786
3.981	0.00000747
3.9939	0.00034967
3.9939	0.00034967
4.0172	0.00006153
4.0241	0.00245443
4.0286	0.00207042
4.0286	0.00207042
4.0367	0.00002137
4.0367	0.00002137
4.0402	0.00010219
4.0559	0.00163921
4.0607	0.00006306
4.0607	0.00006306
4.0646	0.06056736
4.0732	0.00413487
4.0785	0.00114617
4.0785	0.00114617
4.1114	0.02604674
4.1196	0.02506236
4.1196	0.02506236
4.1308	0.00339507
4.1308	0.00339507
4.1386	0.00475134
4.142	0.00321342
4.142	0.00321342
4.1512	0.00681745

4.1514	0.07642983
4.1514	0.07642983
4.1600	0.06426561
4.1738	0.00683347
4.1738	0.00683347
4.1771	0.07831398
4.1895	0.00928739
4.1895	0.00928739
4.1915	0.00000194
4.1943	0.00955625
4.1943	0.00955625
4.1961	0.01608585
4.2301	0.00007187
4.2301	0.00007187
4.2433	0.00503639
4.2477	0.00001049
4.2477	0.00001049
4.2578	0.00005181
4.2693	0.02657475
4.2696	0.0138371
4.2696	0.0138371
4.2756	0.00120327
4.2756	0.00120327
4.2887	0.00156401
4.2967	0.00233629
4.2967	0.00233629
4.3169	0.00478792
4.3215	0.0061088
4.332	0.00348246
4.332	0.00348246
4.3395	0.00085128
4.3441	0.00057495
4.3444	0.00539334
4.3444	0.00539334
4.3514	0.02493845
4.3588	0.01454802
4.3621	0.0001669
4.3621	0.0001669
4.3685	0.00180699
4.3685	0.00180699
4.3761	0.00137122
4.3835	0.00318429
4.3835	0.00318429
4.3987	0.00047193
4.4041	0.00366143
4.4041	0.00366143
4.4114	0.01305887
4.4222	0.0006741
4.4222	0.0006741
4.4243	0.00116849
4.4439	0.00223673

4.4507	0.00112055
4.4507	0.00112055
4.4522	0.00022855
4.4541	0.00057903
4.4541	0.00057903
4.4541	0.00000747
4.4588	0.00412908
4.4627	0.00136173
4.4627	0.00136173
4.4685	0.00434687
4.4685	0.00434687
4.4702	0.00234378
4.477	0.0055228
4.477	0.0055228
4.4806	0.00438961
4.4854	0.00508467
4.4854	0.00508467
4.4896	0.00874154
4.4936	0.02437459

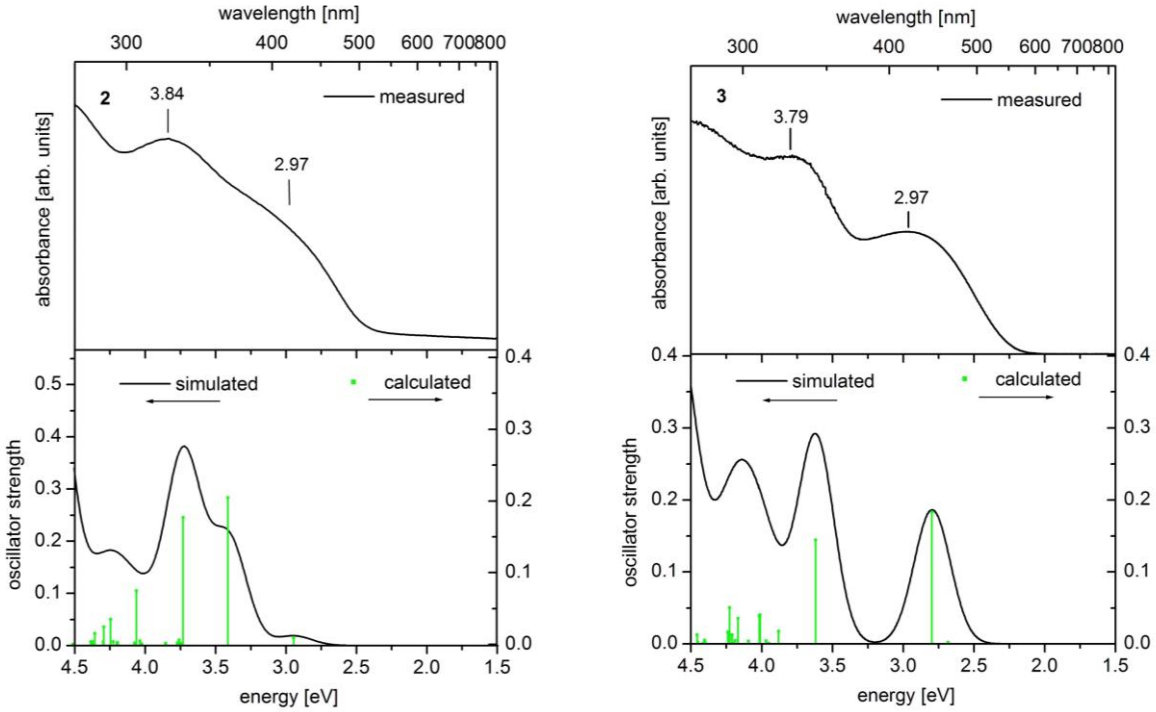

Figure S3. Comparison of measured electronic spectra (powdered crystals in mineral oil) of $[Ag_2Sn(SePh)(PPh_3)_2]$ (**2**) and $[Cu_2Sn(SPh)(PPh_3)_2]$ (**3**) (from left to right) with calculated singlet excitation energies and oscillator strengths plotted as vertical lines (green) as well as with superimposed Gaussians of FWHM = 0.3 eV (black curve) to simulate the spectrum (see also Table S3).

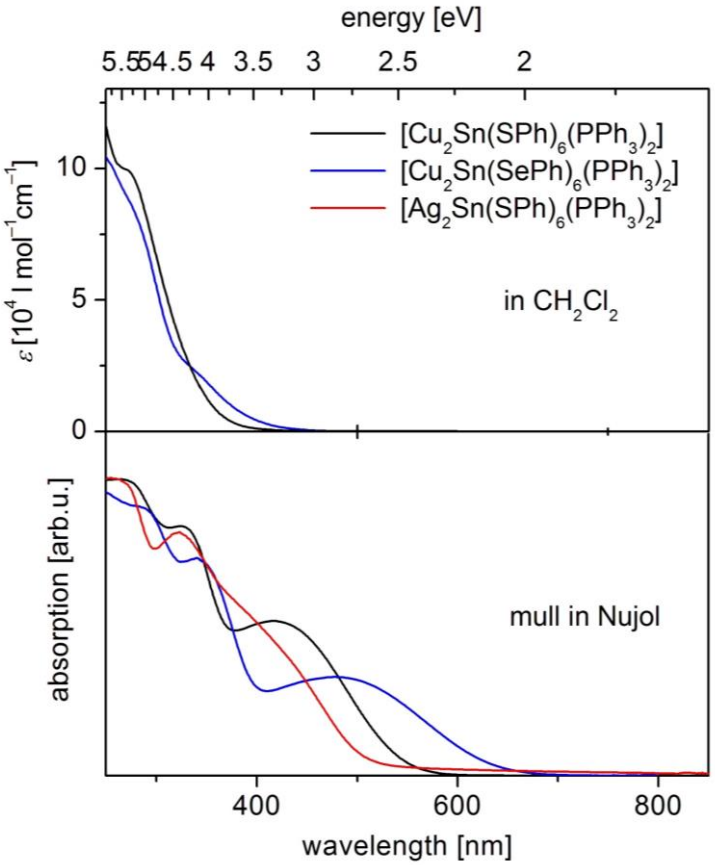

Figure S4. Comparison of UV-vis absorption spectra of $[Cu_2Sn(SePh)_6(PPh_3)_2]$ (**1**), $[Ag_2Sn(SPh)_6(PPh_3)_2]$ (**2**) and $[Cu_2Sn(SPh)_6(PPh_3)_2]$ (**3**) measured in dichloromethane and as powdered crystals in mineral oil.

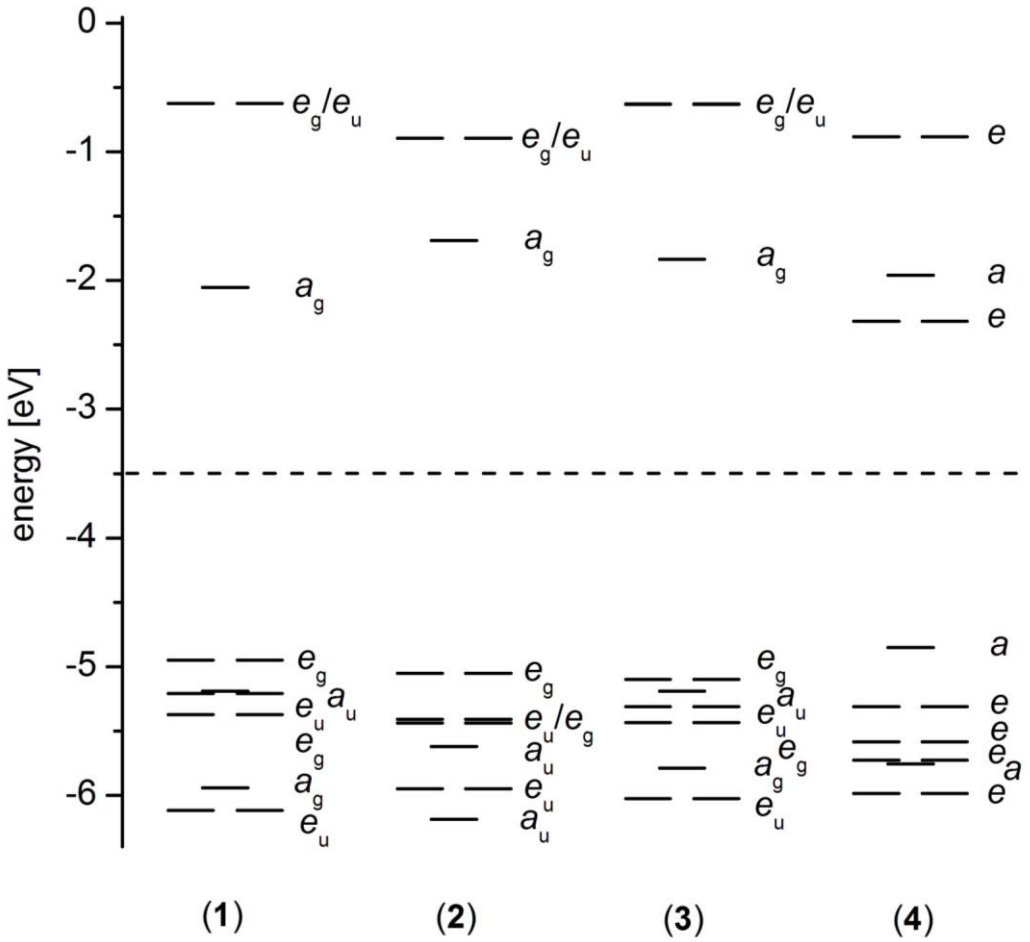

Figure S5. Calculated molecular orbital diagrams of $[Cu_2Sn(SePh)_6(PPh_3)_2]$ (**1**), $[Ag_2Sn(SPh)_6(PPh_3)_2]$ (**2**), $[Cu_2Sn(SPh)_6(PPh_3)_2]$ (**3**) and $[Cu_2Ti(SPh)_6(PPh_3)_2]$ (**4**). The dashed line separates occupied orbitals from unoccupied ones (e_g/e_u denotes two levels, thus four near-degenerate orbitals).

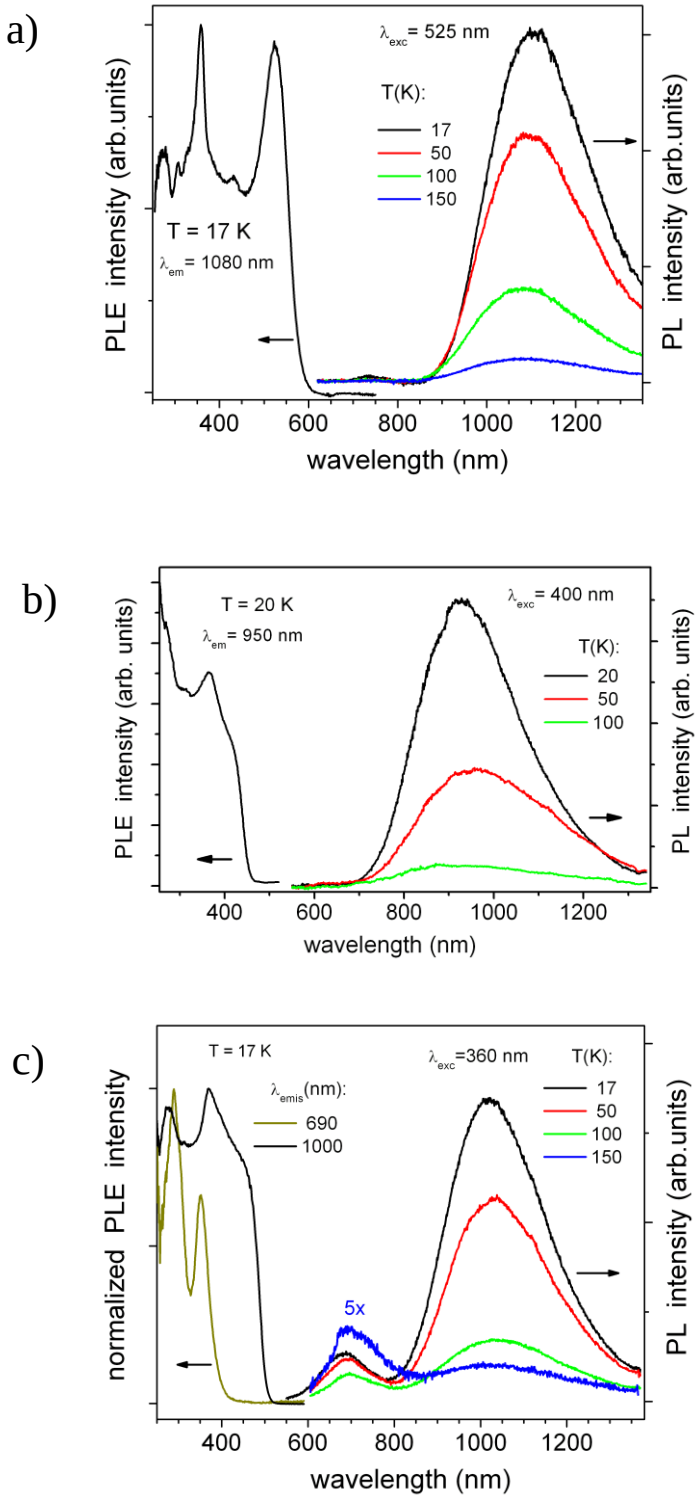

Figure S6. Photoluminescence excitation (PLE, solid line) and emission (PL, dashed line) spectra of a) $[Cu_2Sn(SePh)_6(PPh_3)_2]$ (**1**), b) $[Ag_2Sn(SPh)_6(PPh_3)_2]$ (**2**) and c) $[Cu_2Sn(SPh)_6(PPh_3)_2]$ (**3**) (powdered crystals in mineral oil) at different temperatures.

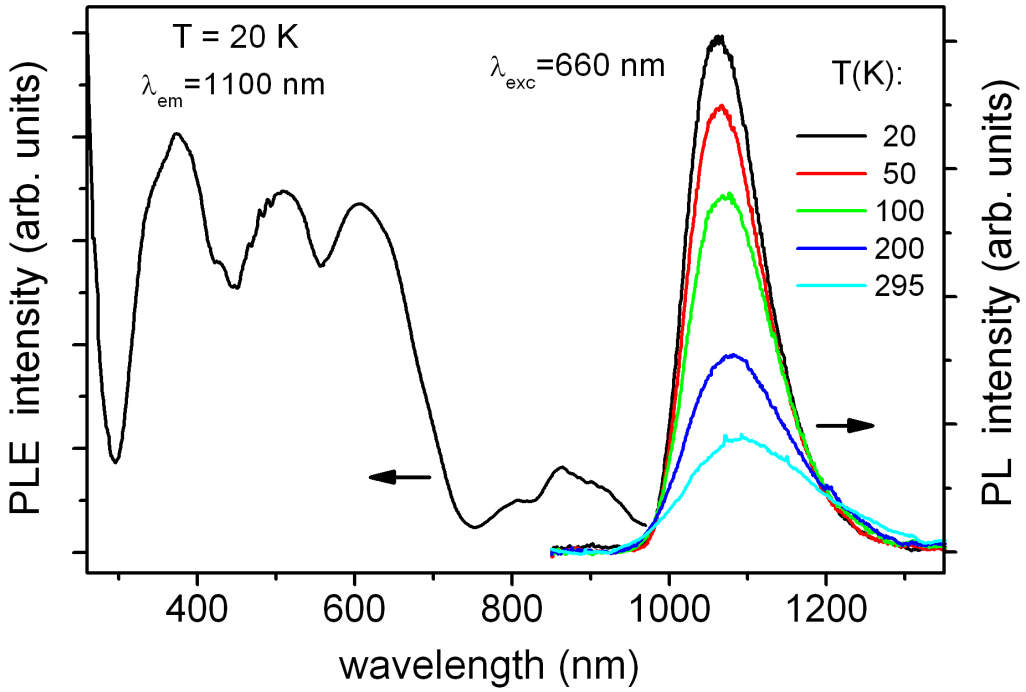

Figure S7. Photoluminescence excitation (PLE, solid line) and emission (PL, dashed line) spectra of **4** (powdered crystals in mineral oil) at different temperatures.

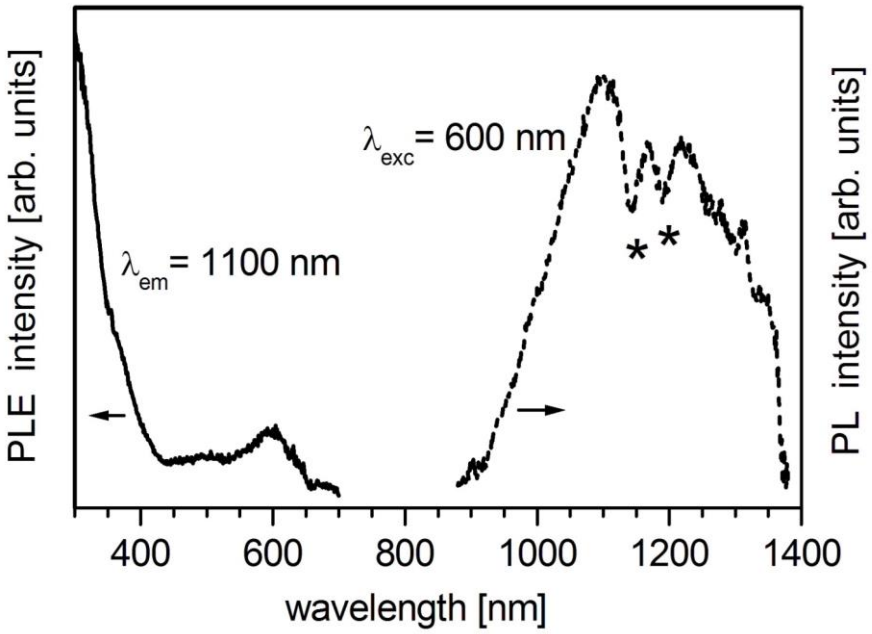

Figure S8. Photoluminescence excitation (PLE, solid line) and emission (PL, dashed line) spectra of $[Cu_2Ti(SPh)_6(PPh_3)_2]$ (**4**) (solution in toluene) at room temperature. Discontinuities marked with an asterisk result from vibrational absorptions of toluene.

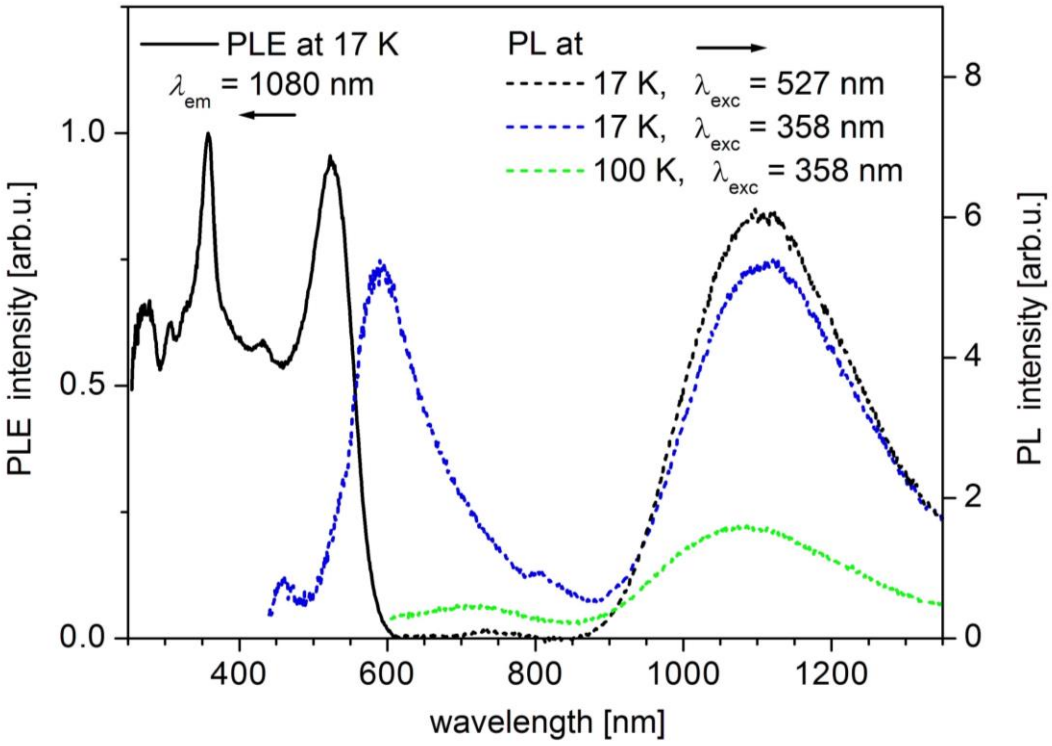

Figure S9. Photoluminescence excitation (PLE, solid line) and emission (PL, dashed line) spectra of $[Cu_2Sn(SePh)_6(PPh_3)_2]$ (**1**) (powdered crystals in mineral oil) at different excitation wavelengths.

Table S8. Calculated lowest triplet (**1** – **3**) and singlet (**4**) excitation and emission energies for $[Cu_2Sn(SePh)_6(PPh_3)_2]$ (**1**), $[Ag_2Sn(SPh)_6(PPh_3)_2]$ (**2**), $[Cu_2Sn(SPh)_6(PPh_3)_2]$ (**3**) and $[Cu_2Ti(SPh)_6(PPh_3)_2]$ (**4**).[a,b,c]

		ΔE_{exc} [eV]	f	ΔE_{em} [eV]	f	ΔE_{exc}–ΔE_{em} [eV]
1	$1\,^3E_u$	1.72	0.021	1.00	0.030	0.72
	$1\,^3A_u$	1.76	0.601	0.53	0.458	1.23
	$2\,^3E_u$	2.53	0.849	1.61	0.707	0.92
	$2\,^3A_u$	2.97	0.092	1.57	0.148	1.40
2	$1\,^3E_u$	2.23	0.102	1.20	0.177	1.03
	$1\,^3A_u$	2.50	0.620	0.95	0.445	1.55
	$2\,^3E_u$	2.73	0.902	1.64	0.824	1.09
	$2\,^3A_u$	3.11	0.008	1.89	0.018	1.22
3	$1\,^3E_u$	2.04	0.049	1.08	0.061	1.06
	$1\,^3A_u$	2.08	0.555	[d]	[d]	[d]
	$2\,^3E_u$	2.67	0.790	1.62	0.679	1.05
	$2\,^3A_u$	3.07	0.022	1.86	0.027	1.21
4	$1\,^1E$	1.56	0	1.47	0	0.09
	$1\,^1A$	1.89	0	1.62	0	0.27

[a] at level B3LYP/def2-SV(P). Excitation energies were calculated for the structure parameters optimized for the ground state; emission energies as excitation energies for the structure parameters optimized for the respective excited state. For further details of the theoretical methods, see text.
[b] parameters: excitation energy ΔE_{exc}, `emission´ energy ΔE_{em}, oscillator strength f, Stokes shift ΔE_{exc}–ΔE_{em}
[c] e.g. $1\,^3E_u$ denotes here the first (i.e. energetically lowest) excited triplet state of E_u symmetry.
[d] optimization failed.

Table S9. Experimental and calculated (B3LYP/def2-SV(P)) atom distances [pm] for ground and excited state structures of $[Cu_2Sn(SePh)_6(PPh_3)_2]$ (**1**), $[Ag_2Sn(SPh)_6(PPh_3)_2]$ (**2**), $[Cu_2Sn(SPh)_6(PPh_3)_2]$ (**3**) [1] and $[Cu_2Ti(SPh)_6(PPh_3)_2]$ (**4**).[2]

		ground state structure		excited state structure			
		experimental	optimized	$1\,^3E_u$	$1\,^3A_u$	$2\,^3E_u$	$2\,^3A_u$
1	Cu···Cu	640.8	665.5	677.7	636.0	668.4	724.1
	Cu–Se	249.9	258.1	254.4	252.7	257.1	256.3
	Sn–Se	269.0	280.5	296.7	301.7	300.6	296.0
	Cu–Se–Sn	76.18	76.19	75.45	69.35	73.15	81.58
2	Ag···Ag	683.6	702.4	714.5	661.3	703.0	710.3
	Ag–S	265.2	266.5	269.0	268.8	272.4	271.8
	Sn–S	256.4	272.7	285.2	287.7	286.9	284.1
	Ag–S–Sn	81.85	81.26	80.22	72.81	77.83	79.39
3	Cu···Cu	629.1	650.6	658.5	[a]	658.6	684.7
	Cu–S	242.1	248.8	243.6	[a]	247.4	247.7
	Sn–S	256.6	265.7	283.3	[a]	285.6	281.9
	Cu–S–Sn	78.15	78.36	76.93	[a]	75.93	80.27
				$1\,^1A$		$1\,^1E$	
4	Cu···Cu	556.6	579.8	603.8		574.2	
	Cu–S	234.6, 235.4	242.8, 243.0	237.9, 244.4		241.5, 241.7	
	Ti–S	242.8, 248.6	250.3, 250.4	245.9, 266.5		253.6, 254.0	
	Cu–S–Ti	70.88, 70.54	71.74, 72.21	70.49, 78.80		70.81, 70.75	

[a] optimization failed

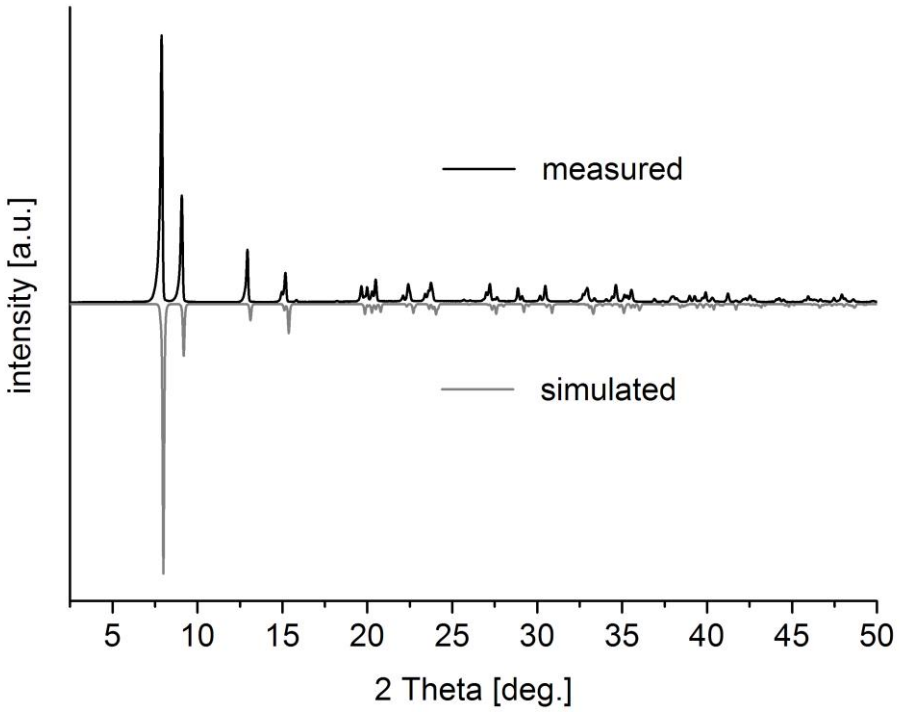

Figure S10. Measured (black) and simulated (grey) X–ray powder pattern for $[Cu_2Sn(SePh)_8(PPh_3)_2]$ (**1**) as a dried crystalline powder.

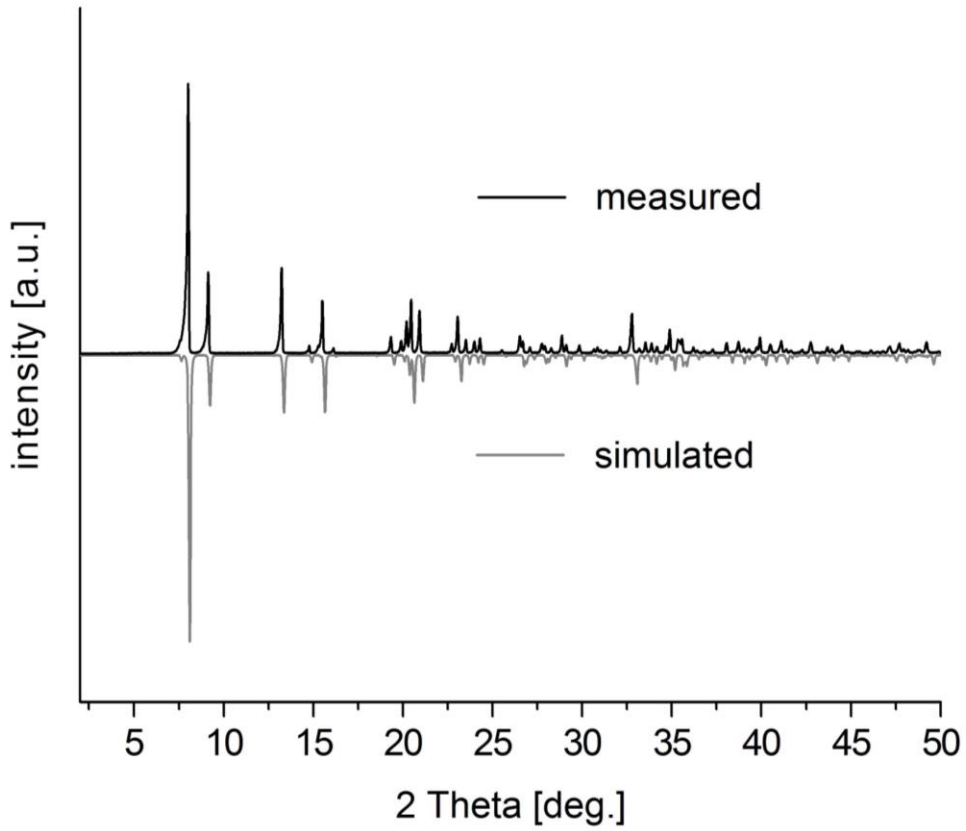

Figure S11. Measured (black) and simulated (grey) X–ray powder pattern for $[Ag_2Sn(SPh)_8(PPh_3)_2]$ (**2**) as a dried crystalline powder.

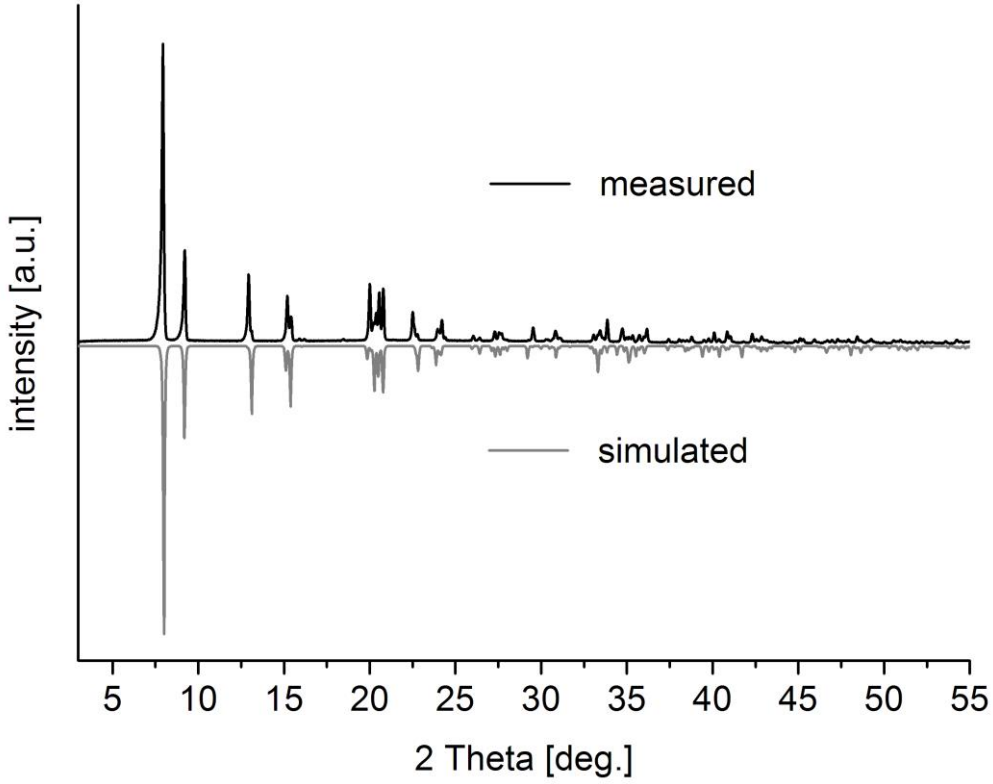

Figure S12. Measured (black) and simulated (grey) X–ray powder pattern for $[Cu_2Sn(SPh)_8(PPh_3)_2]$ (**3**) as a dried crystalline powder.

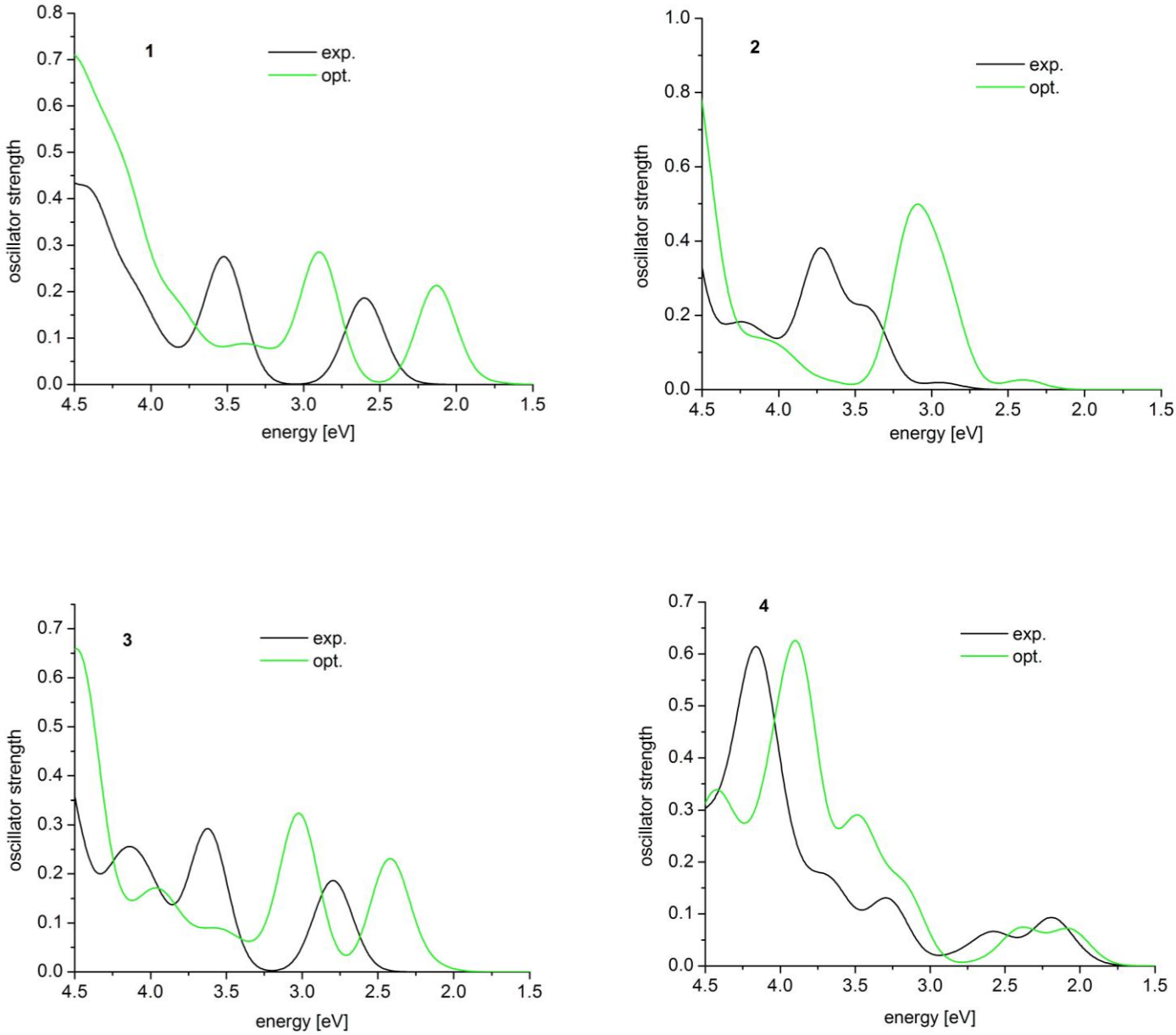

Figure S13. Comparison of the calculated excitation spectra for the experimental (black) and optimized (green) structures of $[Cu_2Sn(SePh)_6(PPh_3)_2]$ (**1**), $[Ag_2Sn(SPh)_6(PPh_3)_2]$ (**2**), $[Cu_2Sn(SPh)_6(PPh_3)_2]$ (**3**) and $[Cu_2Ti(SPh)_6(PPh_3)_2]$ (**4**).

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