Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information

A Ternary Cu–Sn–S Cluster Complex

—

$(NBu_4)[(PEt_2Ph)_3Cu_{19}S_{28}(SnPh)_{12}]$

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Table S1. Selected bond lengths [pm] and angles [deg] for $(NBu_4)[(PEt_2Ph)_3Cu_{19}S_{28}(SnPh)_{12}]$ (**2**).

Sn(1)-S(14)	238.55(18)
Sn(1)-S(2)	238.74(13)
Sn(1)-S(15)	243.24(14)
Sn(2)-S(3)	237.91(16)
Sn(2)-S(15)	239.10(15)
Sn(2)-S(16)	243.61(17)
Sn(3)-S(4)	238.30(15)
Sn(3)-S(17)	239.24(16)
Sn(3)-S(18)	244.75(14)
Sn(4)-S(19)	238.36(16)
Sn(4)-S(5)	238.69(14)
Sn(4)-S(17)	242.81(16)
Sn(5)-S(6)	238.93(15)
Sn(5)-S(20)	239.45(16)
Sn(5)-S(16)	245.63(14)
Sn(6)-S(7)	238.33(15)
Sn(6)-S(21)	238.72(14)
Sn(6)-S(20)	243.64(14)
Sn(7)-S(22)	238.23(14)
Sn(7)-S(8)	239.93(14)
Sn(7)-S(23)	243.45(16)
Sn(8)-S(9)	238.34(13)
Sn(8)-S(23)	238.36(17)
Sn(8)-S(24)	244.55(15)
Sn(9)-S(10)	237.79(14)
Sn(9)-S(25)	238.69(16)
Sn(9)-S(26)	243.37(16)
Sn(10)-S(11)	238.56(14)
Sn(10)-S(26)	238.69(15)
Sn(10)-S(24)	244.33(17)
Sn(11)-S(28)	237.77(15)
Sn(11)-S(12)	239.65(17)
Sn(11)-S(27)	242.26(16)
Sn(12)-S(27)	238.18(15)
Sn(12)-S(13)	238.67(15)
Sn(12)-S(18)	245.90(15)
Cu(1)-S(2)	229.34(15)
Cu(1)-S(1)	231.29(14)
Cu(1)-S(3)	236.19(16)
Cu(2)-S(5)	230.55(15)
Cu(2)-S(1)	231.25(14)
Cu(2)-S(4)	233.60(15)
Cu(3)-S(7)	230.18(15)
Cu(3)-S(1)	230.84(18)
Cu(3)-S(6)	233.46(15)
Cu(4)-S(8)	229.18(18)
Cu(4)-S(1)	232.69(14)
Cu(4)-S(9)	238.14(16)
Cu(5)-S(1)	230.55(14)
Cu(5)-S(11)	231.92(18)
Cu(5)-S(10)	232.05(17)
Cu(6)-S(12)	229.36(15)
Cu(6)-S(1)	231.47(18)
Cu(6)-S(13)	234.24(17)
Cu(7)-S(22)	219.27(18)
Cu(7)-S(2)	223.50(15)

Cu(7)-S(9)	229.07(15)
Cu(8)-P(3)	222.15(17)
Cu(8)-S(7)	231.75(14)
Cu(8)-S(16)	234.19(15)
Cu(8)-S(2)	240.95(19)
Cu(9)-S(3)	219.96(14)
Cu(9)-S(6)	222.48(17)
Cu(9)-S(5)	225.97(15)
Cu(10)-S(14)	220.26(15)
Cu(10)-S(12)	224.32(15)
Cu(10)-S(3)	231.65(17)
Cu(11)-S(19)	223.00(16)
Cu(11)-S(25)	224.42(16)
Cu(11)-S(4)	231.6(2)
Cu(12)-S(13)	219.92(16)
Cu(12)-S(4)	222.62(16)
Cu(12)-S(10)	225.31(16)
Cu(13)-P(1)	224.18(16)
Cu(13)-S(5)	233.40(18)
Cu(13)-S(18)	236.41(16)
Cu(13)-S(12)	243.74(15)
Cu(14)-S(21)	224.62(16)
Cu(14)-S(19)	225.56(15)
Cu(14)-S(6)	231.78(14)
Cu(15)-S(9)	219.46(16)
Cu(15)-S(11)	221.01(15)
Cu(15)-S(7)	225.28(14)
Cu(16)-P(2)	223.23(19)
Cu(16)-S(10)	234.83(16)
Cu(16)-S(8)	238.41(15)
Cu(16)-S(24)	239.02(18)
Cu(17)-S(28)	220.86(15)
Cu(17)-S(8)	224.46(16)
Cu(17)-S(13)	231.10(15)
Cu(18)-S(25)	223.23(16)
Cu(18)-S(21)	225.20(18)
Cu(18)-S(11)	229.92(16)
Cu(19)-S(28)	227.13(18)
Cu(19)-S(22)	227.22(16)
Cu(19)-S(14)	228.58(15)

S(14)-Sn(1)-S(2)	110.38(5)
S(14)-Sn(1)-S(15)	112.89(6)
S(2)-Sn(1)-S(15)	105.39(6)
S(3)-Sn(2)-S(15)	109.60(6)
S(3)-Sn(2)-S(16)	116.11(5)
S(15)-Sn(2)-S(16)	106.94(5)
S(4)-Sn(3)-S(17)	111.06(6)
S(4)-Sn(3)-S(18)	117.42(5)
S(17)-Sn(3)-S(18)	104.61(6)
S(19)-Sn(4)-S(5)	112.44(5)
S(19)-Sn(4)-S(17)	111.22(6)
S(5)-Sn(4)-S(17)	103.24(6)
S(6)-Sn(5)-S(20)	113.70(5)
S(6)-Sn(5)-S(16)	115.77(5)
S(20)-Sn(5)-S(16)	103.34(5)
S(7)-Sn(6)-S(21)	112.33(6)
S(7)-Sn(6)-S(20)	104.00(5)
S(21)-Sn(6)-S(20)	110.15(5)
S(22)-Sn(7)-S(8)	109.37(5)
S(22)-Sn(7)-S(23)	115.18(6)
S(8)-Sn(7)-S(23)	104.10(5)
S(9)-Sn(8)-S(23)	110.58(5)

S(9)-Sn(8)-S(24)	115.41(5)
S(23)-Sn(8)-S(24)	107.60(6)
S(10)-Sn(9)-S(25)	115.39(5)
S(10)-Sn(9)-S(26)	105.48(5)
S(25)-Sn(9)-S(26)	105.77(6)
S(11)-Sn(10)-S(26)	110.88(5)
S(11)-Sn(10)-S(24)	114.32(5)
S(26)-Sn(10)-S(24)	107.86(6)
S(28)-Sn(11)-S(12)	112.58(5)
S(28)-Sn(11)-S(27)	113.92(5)
S(12)-Sn(11)-S(27)	105.89(6)
S(27)-Sn(12)-S(13)	110.33(5)
S(27)-Sn(12)-S(18)	106.72(6)
S(13)-Sn(12)-S(18)	111.37(6)
S(2)-Cu(1)-S(1)	120.88(5)
S(2)-Cu(1)-S(3)	116.12(5)
S(1)-Cu(1)-S(3)	122.99(5)
S(5)-Cu(2)-S(1)	107.45(5)
S(5)-Cu(2)-S(4)	113.95(5)
S(1)-Cu(2)-S(4)	135.94(5)
S(7)-Cu(3)-S(1)	106.93(6)
S(7)-Cu(3)-S(6)	112.95(6)
S(1)-Cu(3)-S(6)	137.34(5)
S(8)-Cu(4)-S(1)	118.35(5)
S(8)-Cu(4)-S(9)	117.01(6)
S(1)-Cu(4)-S(9)	124.63(6)
S(1)-Cu(5)-S(11)	133.22(6)
S(1)-Cu(5)-S(10)	109.34(6)
S(11)-Cu(5)-S(10)	114.96(6)
S(12)-Cu(6)-S(1)	120.88(6)
S(12)-Cu(6)-S(13)	116.32(6)
S(1)-Cu(6)-S(13)	122.76(6)
S(22)-Cu(7)-S(2)	131.06(6)
S(22)-Cu(7)-S(9)	125.93(6)
S(2)-Cu(7)-S(9)	102.97(6)
P(3)-Cu(8)-S(7)	120.27(6)
P(3)-Cu(8)-S(16)	119.20(7)
S(7)-Cu(8)-S(16)	105.91(5)
P(3)-Cu(8)-S(2)	105.01(7)
S(7)-Cu(8)-S(2)	94.26(5)
S(16)-Cu(8)-S(2)	108.82(6)
S(3)-Cu(9)-S(6)	133.35(6)
S(3)-Cu(9)-S(5)	118.16(6)
S(6)-Cu(9)-S(5)	108.47(6)
S(14)-Cu(10)-S(12)	135.08(6)
S(14)-Cu(10)-S(3)	124.84(6)
S(12)-Cu(10)-S(3)	99.99(6)
S(19)-Cu(11)-S(25)	127.61(6)
S(19)-Cu(11)-S(4)	123.21(6)
S(25)-Cu(11)-S(4)	107.18(6)
S(13)-Cu(12)-S(4)	133.34(6)
S(13)-Cu(12)-S(10)	117.02(6)
S(4)-Cu(12)-S(10)	109.61(6)
P(1)-Cu(13)-S(5)	113.49(6)
P(1)-Cu(13)-S(18)	121.56(6)
S(5)-Cu(13)-S(18)	107.98(6)
P(1)-Cu(13)-S(12)	105.93(6)
S(5)-Cu(13)-S(12)	95.20(5)
S(18)-Cu(13)-S(12)	109.36(5)
S(21)-Cu(14)-S(19)	128.18(6)
S(21)-Cu(14)-S(6)	119.02(6)
S(19)-Cu(14)-S(6)	110.18(6)
S(9)-Cu(15)-S(11)	134.00(6)

S(9)-Cu(15)-S(7)	116.99(6)
S(11)-Cu(15)-S(7)	109.01(6)
P(2)-Cu(16)-S(10)	121.36(6)
P(2)-Cu(16)-S(8)	117.82(7)
S(10)-Cu(16)-S(8)	93.51(5)
P(2)-Cu(16)-S(24)	108.00(7)
S(10)-Cu(16)-S(24)	104.11(6)
S(8)-Cu(16)-S(24)	110.78(6)
S(28)-Cu(17)-S(8)	133.69(6)
S(28)-Cu(17)-S(13)	123.40(6)
S(8)-Cu(17)-S(13)	102.89(5)
S(28)-Cu(17)-Cu(6)	105.20(5)
S(8)-Cu(17)-Cu(6)	102.40(6)
S(13)-Cu(17)-Cu(6)	54.52(5)
S(25)-Cu(18)-S(21)	129.21(6)
S(25)-Cu(18)-S(11)	118.09(6)
S(21)-Cu(18)-S(11)	110.18(6)
S(28)-Cu(19)-S(22)	120.47(6)
S(28)-Cu(19)-S(14)	120.69(6)
S(22)-Cu(19)-S(14)	116.51(6)
Cu(5)-S(1)-Cu(3)	86.44(5)
Cu(5)-S(1)-Cu(2)	83.55(5)
Cu(3)-S(1)-Cu(2)	84.03(5)
Cu(5)-S(1)-Cu(1)	140.98(6)
Cu(3)-S(1)-Cu(1)	70.00(5)
Cu(2)-S(1)-Cu(1)	122.50(6)
Cu(5)-S(1)-Cu(6)	121.00(6)
Cu(3)-S(1)-Cu(6)	138.29(6)
Cu(2)-S(1)-Cu(6)	70.21(5)
Cu(1)-S(1)-Cu(6)	96.46(5)
Cu(5)-S(1)-Cu(4)	69.34(5)
Cu(3)-S(1)-Cu(4)	121.00(6)
Cu(2)-S(1)-Cu(4)	140.32(6)
Cu(1)-S(1)-Cu(4)	96.13(5)
Cu(6)-S(1)-Cu(4)	99.05(6)
Cu(7)-S(2)-Cu(1)	98.42(6)
Cu(7)-S(2)-Sn(1)	98.66(6)
Cu(1)-S(2)-Sn(1)	99.45(6)
Cu(7)-S(2)-Cu(8)	130.71(6)
Cu(1)-S(2)-Cu(8)	97.09(6)
Sn(1)-S(2)-Cu(8)	124.32(6)
Cu(9)-S(3)-Cu(10)	120.22(6)
Cu(9)-S(3)-Cu(1)	77.52(5)
Cu(10)-S(3)-Cu(1)	70.71(5)
Cu(9)-S(3)-Sn(2)	110.26(6)
Cu(10)-S(3)-Sn(2)	122.80(6)
Cu(1)-S(3)-Sn(2)	97.41(5)
Cu(12)-S(4)-Cu(11)	120.80(6)
Cu(12)-S(4)-Cu(2)	71.22(5)
Cu(11)-S(4)-Cu(2)	72.59(5)
Cu(12)-S(4)-Sn(3)	110.19(6)
Cu(11)-S(4)-Sn(3)	121.26(6)
Cu(2)-S(4)-Sn(3)	100.36(5)
Cu(9)-S(5)-Cu(2)	95.06(5)
Cu(9)-S(5)-Cu(13)	118.35(6)
Cu(2)-S(5)-Cu(13)	111.14(6)
Cu(9)-S(5)-Sn(4)	110.18(6)
Cu(2)-S(5)-Sn(4)	97.13(5)
Cu(13)-S(5)-Sn(4)	119.81(6)
Cu(9)-S(6)-Cu(14)	118.47(6)
Cu(9)-S(6)-Cu(3)	70.28(5)
Cu(14)-S(6)-Cu(3)	73.27(5)
Cu(9)-S(6)-Sn(5)	112.73(6)

Cu(14)-S(6)-Sn(5)	121.72(6)
Cu(3)-S(6)-Sn(5)	100.97(6)
Cu(15)-S(7)-Cu(3)	94.78(6)
Cu(15)-S(7)-Cu(8)	118.80(6)
Cu(3)-S(7)-Cu(8)	113.48(6)
Cu(15)-S(7)-Sn(6)	108.22(6)
Cu(3)-S(7)-Sn(6)	97.44(6)
Cu(8)-S(7)-Sn(6)	119.39(6)
Cu(17)-S(8)-Cu(4)	100.02(6)
Cu(17)-S(8)-Cu(16)	132.66(6)
Cu(4)-S(8)-Cu(16)	98.23(6)
Cu(17)-S(8)-Sn(7)	97.34(5)
Cu(4)-S(8)-Sn(7)	98.79(6)
Cu(16)-S(8)-Sn(7)	122.39(6)
Cu(15)-S(9)-Cu(7)	117.45(6)
Cu(15)-S(9)-Cu(4)	75.03(6)
Cu(7)-S(9)-Cu(4)	69.82(5)
Cu(15)-S(9)-Sn(8)	111.16(6)
Cu(7)-S(9)-Sn(8)	122.63(7)
Cu(4)-S(9)-Sn(8)	96.50(6)
Cu(12)-S(10)-Cu(5)	92.32(6)
Cu(12)-S(10)-Cu(16)	121.00(6)
Cu(5)-S(10)-Cu(16)	110.93(6)
Cu(12)-S(10)-Sn(9)	106.34(6)
Cu(5)-S(10)-Sn(9)	93.87(6)
Cu(16)-S(10)-Sn(9)	124.11(6)
Cu(15)-S(11)-Cu(18)	119.48(6)
Cu(15)-S(11)-Cu(5)	72.76(5)
Cu(18)-S(11)-Cu(5)	75.16(5)
Cu(15)-S(11)-Sn(10)	113.29(6)
Cu(18)-S(11)-Sn(10)	122.17(6)
Cu(5)-S(11)-Sn(10)	100.58(7)
Cu(10)-S(12)-Cu(6)	97.96(6)
Cu(10)-S(12)-Sn(11)	96.64(6)
Cu(6)-S(12)-Sn(11)	97.68(5)
Cu(10)-S(12)-Cu(13)	134.76(6)
Cu(6)-S(12)-Cu(13)	94.53(5)
Sn(11)-S(12)-Cu(13)	124.50(6)
Cu(12)-S(13)-Cu(17)	119.05(6)
Cu(12)-S(13)-Cu(6)	78.48(6)
Cu(17)-S(13)-Cu(6)	72.03(5)
Cu(12)-S(13)-Sn(12)	113.31(6)
Cu(17)-S(13)-Sn(12)	123.56(6)
Cu(6)-S(13)-Sn(12)	100.30(6)
Cu(10)-S(14)-Cu(19)	88.94(5)
Cu(10)-S(14)-Sn(1)	98.87(6)
Cu(19)-S(14)-Sn(1)	106.12(6)
Sn(2)-S(15)-Sn(1)	102.00(5)
Cu(8)-S(16)-Sn(2)	108.27(6)
Cu(8)-S(16)-Sn(5)	107.67(5)
Sn(2)-S(16)-Sn(5)	107.76(5)
Sn(3)-S(17)-Sn(4)	101.66(6)
Cu(13)-S(18)-Sn(3)	106.07(6)
Cu(13)-S(18)-Sn(12)	109.01(6)
Sn(3)-S(18)-Sn(12)	109.32(6)
Cu(11)-S(19)-Cu(14)	81.23(6)
Cu(11)-S(19)-Sn(4)	101.86(7)
Cu(14)-S(19)-Sn(4)	108.91(6)
Sn(5)-S(20)-Sn(6)	99.36(6)
Cu(14)-S(21)-Cu(18)	79.60(6)
Cu(14)-S(21)-Sn(6)	104.80(5)
Cu(18)-S(21)-Sn(6)	108.35(6)
Cu(7)-S(22)-Cu(19)	93.16(6)

Cu(7)-S(22)-Sn(7)	98.92(6)
Cu(19)-S(22)-Sn(7)	104.47(6)
Sn(8)-S(23)-Sn(7)	102.43(6)
Cu(16)-S(24)-Sn(10)	109.54(6)
Cu(16)-S(24)-Sn(8)	105.32(5)
Sn(10)-S(24)-Sn(8)	110.59(6)
Cu(18)-S(25)-Cu(11)	81.78(6)
Cu(18)-S(25)-Sn(9)	105.53(6)
Cu(11)-S(25)-Sn(9)	109.06(6)
Sn(10)-S(26)-Sn(9)	99.91(5)
Sn(12)-S(27)-Sn(11)	102.07(6)
Cu(17)-S(28)-Cu(19)	89.26(6)
Cu(17)-S(28)-Sn(11)	98.16(6)
Cu(19)-S(28)-Sn(11)	103.59(6)

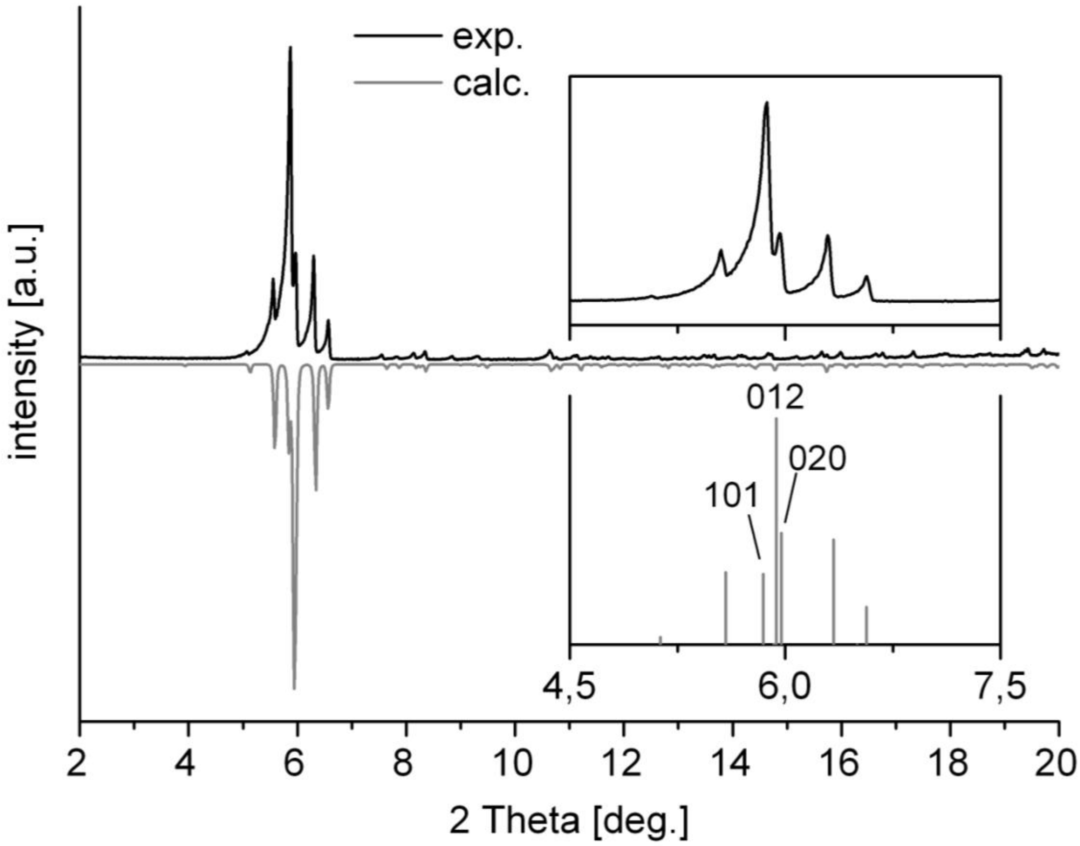

Figure S1. Measured (black) and simulated (grey) X-ray powder patterns for $[Li(thf)_4][(PEt_2Ph)_3Cu_{19}S_{28}(SnPh)_{12}]$ (**1**).

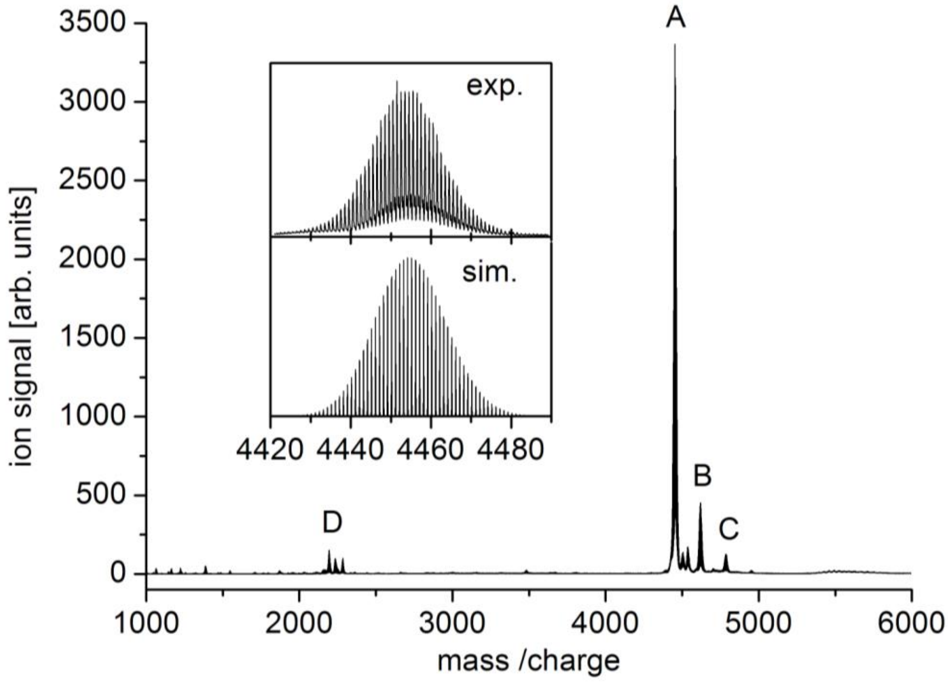

Figure S2. Negative-ion ESI-TOF mass spectrum from a DMF/THF solution of $[Li(thf)_4][Cu_{19}S_{28}(SnPh)_{12}(PEt_2Ph)_3]$ (**1**). The inset shows a comparison of isotopomere–resolved peaks from experiment and simulation (For assignment of the peaks see table S2).

Table S2. Assignment of the observed negative ions in the ESI-TOF Mass Spectrum of $[Li(thf)_4][Cu_{19}S_{28}(SnPh)_{12}(PEt_2Ph)_3]$ (**1**) (as shown in Fig. S2).

	exp.	calc.	composition
A	**4454.52**	**4454.2**	$\mathbf{[Cu_{19}(SnC_6H_5)_{12}S_{28}]^-}$
B	4619.55	4620.8	$[Cu_{19}(SnC_6H_5)_{12}S_{28}(PEt_2Ph)]^-$
C	4786.57	4787.0	$[Cu_{19}(SnC_6H_5)_{12}S_{28}(PEt_2Ph)_2]^-$
D	2195.27	2195.6	$[Cu_{18}(SnC_6H_5)_{12}S_{28}]^{2-}$

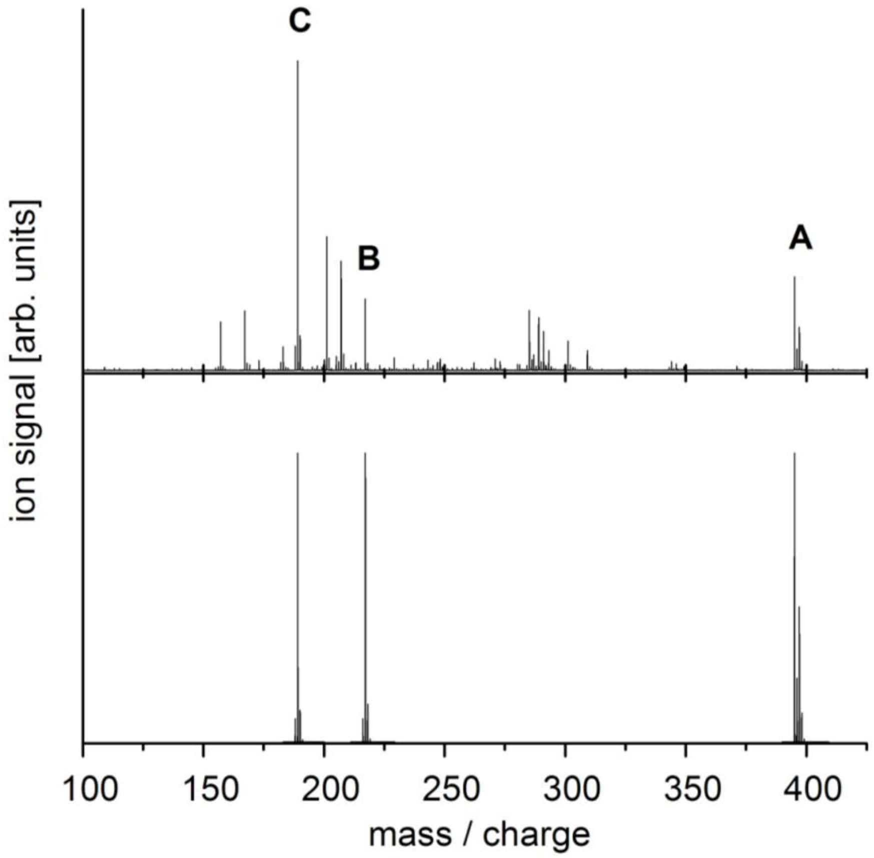

Figure S3. positive-ion ESI-TOF mass spectrum from a DMF/THF solution of $[Li(thf)_4][Cu_{19}S_{28}(SnPh)_{12}(PEt_2Ph)_3]$ (**1**) (upper spectrum). Below are shown a simulation of identifiable peaks (For assignment of the peaks see table S3).

Table S3. Assignment of the observed positive ions in the ESI-TOF Mass Spectrum of $[Li(thf)_4][Cu_{19}S_{28}(SnPh)_{12}(PEt_2Ph)_3]$ (**1**) (as shown in Fig. S2).

	exp.	calc.	composition
A	395.13	395.1	$[Cu(P(C_2H_5)_2C_6H_5)_2]^+$
B	217.12	217.1	$[Li(HP(C_2H_5)C_6H_5)(C_4H_8O)]^+$
C	189.10	189.1	$[Li(H_2PC_6H_5)(C_4H_8O)]^+$

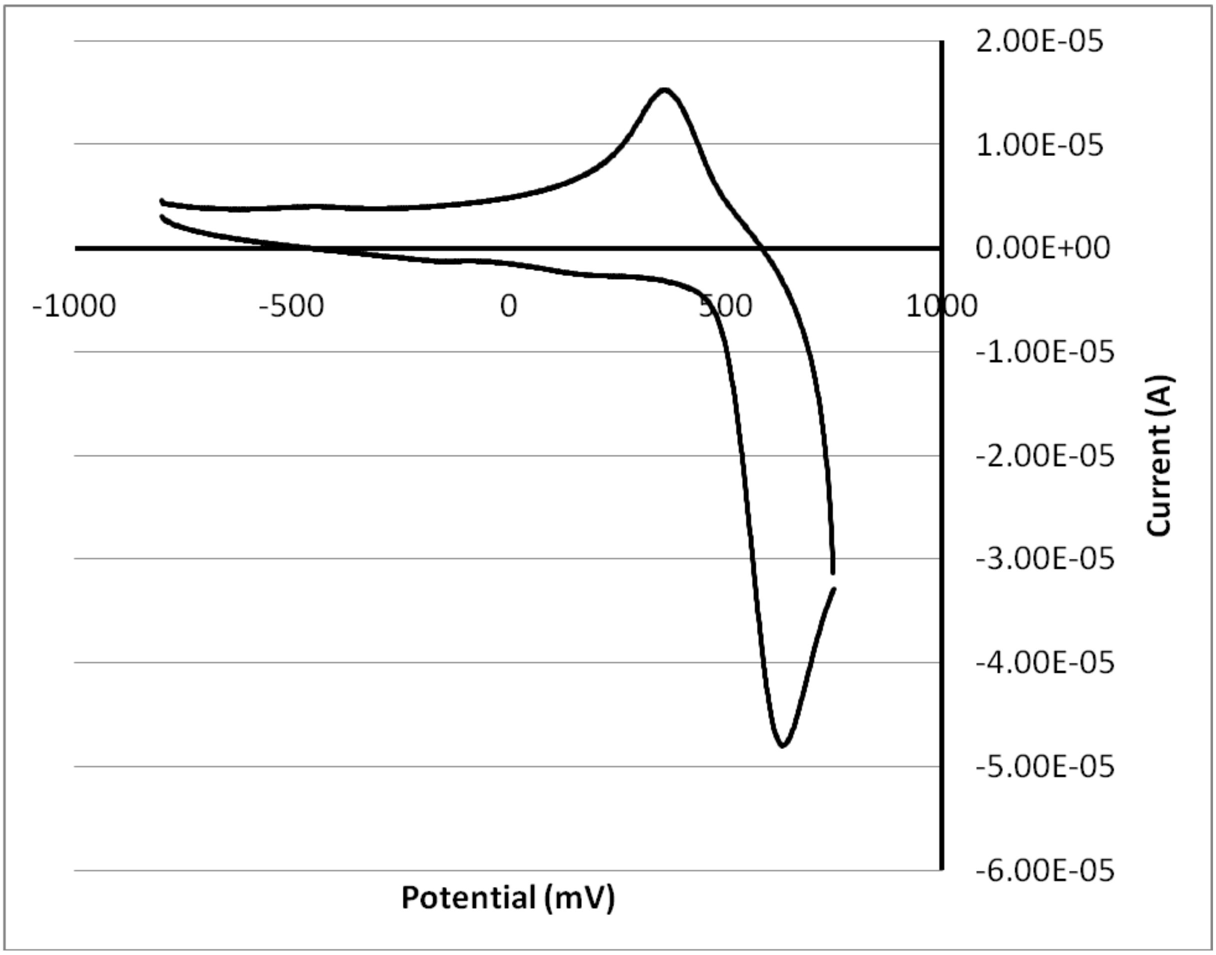

Figure S4.Cyclic voltammogram of $(NBu_4)[(PEt_2Ph)_3Cu_{19}S_{28}(SnPh)_{12}]$ (**2**) in DMF.

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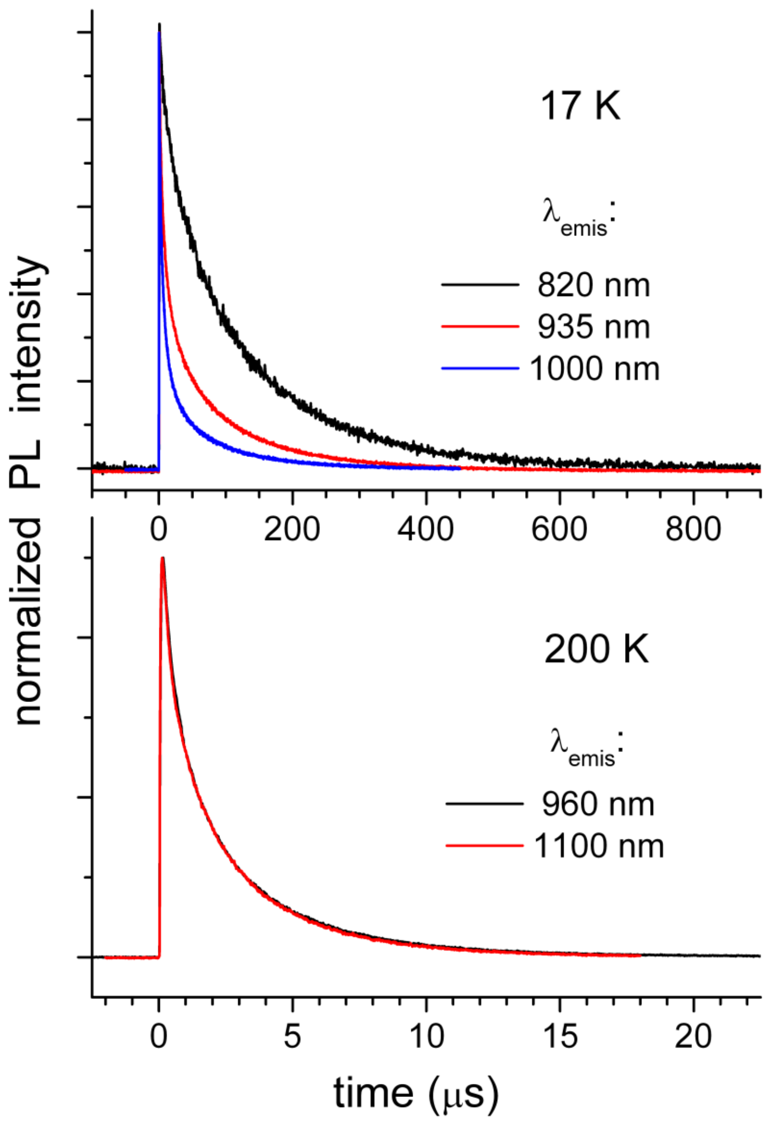

Figure S5. Normalized photoluminescence (PL) decay curves measured for solid complex **2** at temperatures of 17 and 200 K and at different emission wavelengths. PL was excited at 337 nm by using a N_2-laser (~2 ns pulses, 10 Hz pulse repetition rate, ~50 μW power on the sample). Typically 500-800 decay traces were acquired and averaged at specific temperature and emission wavelength.