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Introduction

Copper complexes form a class of coordination compounds with very rich photochemical and photophysical behavior. In particular, numerous copper-based complexes have been found to show bright photoluminescence (PL).^{1–7} Depending on the specific complex structure, the PL (typically phosphorescence or delayed fluorescence) has been observed across the whole visible range from blue to deep-red and it can demonstrate various electronic relaxation and decay patterns in the solid state and solution. Based on the abundant materials, several types of mononuclear Cu(1) complexes with a high

Optical properties of trinuclear metal chalcogenolate complexes – room temperature NIR fluorescence in [Cu₂Ti(SPh)₆(PPh₃)₂]†

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The optical properties of four isostructural trinuclear chalcogenolato bridged metal complexes [Cu₂Sn (SPh)₆(PPh₃)₂], [Cu₂Sn(SePh)₆(PPh₃)₂], [Ag₂Sn(SPh)₆(PPh₃)₂] and [Cu₂Ti(SPh)₆(PPh₃)₂] have been investigated by absorption and photoluminescence spectroscopy and time-dependent density functional theory (TDDFT) calculations. All copper–tin compounds demonstrate near-infrared (NIR) phosphorescence at ~900–1100 nm in the solid state at low temperature, which is nearly absent at ambient temperature. Stokes shifts of these emissions are found to be unusually large with values of about 1.5 eV. The copper–titanium complex [Cu₂Ti(SPh)₆(PPh₃)₂] also shows luminescence in the NIR at 1090 nm but with a much faster decay ($\tau \sim 10$ ns at 150 K) and a much smaller Stokes shift (*ca.* 0.3 eV). Even at 295 K this fluorescence is found to the spectra simulated from the calculated singlet transitions. In line with the large Stokes shifts of the emission spectra the calculations reveal for the copper–tin complexes strong structural relaxation of the excited triplet states whereas those effects are found to be much smaller in the case of the copper–titanium complex.

emission efficiency (up to ~90% in the solid state at ambient temperature) are considered as promising candidates for future economical and mass-producible organic light-emitting diodes (OLEDs)^{8,9} and light-emitting electrochemical cells (LECs).^{10,11} Additional diversity of photophysical properties can be introduced by polynuclear structures. For instance, we have recently demonstrated that the polynuclear copper complexes $[Cu_{12}S_6(dpppt)_4]$ and $[Cu_{12}S_6(dppo)_4]$ attain PL efficiency at ambient temperature larger than 48%, which is complemented by high photostability.^{12,13} Consequently, these compounds may be a valuable addition to the line of copperbased luminophors. Furthermore, introduction of another type of metal provides supplementary structural and photophysical variability. In this respect, it has been shown recently that ternary metal chalcogenide and chalcogenolato complexes which comprise additional tin atoms in the copper chalcogen framework exhibit interesting luminescent properties in the solid state. The heteroheptanuclear Sn(IV)-Cu(I) oxosulphur complex $[Sn_3Cu_4(S_2C_2H_4)_6(\mu_3-O)(PPh_3)_4](ClO_4)_2$ generates, for example, a blue-green light at 495 nm,¹⁴ whereas [Cu₂SnS $(edt)_2(PPh_3)_2$ (edt = $(SCH_2CH_2S)^{2-}$) and $[Cu_2Sn(SPh)_6(PPh_3)_2]$ emit at 568 and 696 nm, respectively.¹⁵ The large cluster complex (NBu₄)[Cu₁₉S₂₈(SnPh)₁₂(PEt₂Ph)₃] was found to display deep-red, temperature-dependent photoluminescence at ~820-930 nm, which is especially bright at temperatures below ~100 K.16 Despite the great diversity of luminescence



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Scheme 1 Structures of the trinuclear metal chalcogenolato complexes 1-4.

properties found for copper-based complexes, to our knowledge, no examples were found with the NIR emission beyond ~950 nm – in the spectral region which is of interest, for instance, for bioanalytical applications. In fact, such emitters, especially those with relatively high PL quantum yields, are extremely rare among other metal complexes as well (NIR emission is ubiquitous for lanthanide complexes, but is usually of poor efficiency).¹⁷

In the following we report on the four isostructural trinuclear complexes $[M_2M'(EPh)_6(PPh_3)_2]$ 1–4 (Scheme 1), which luminesce at as long wavelengths as ~900–1100 nm. We describe in detail the synthesis of 1 and 2, crystallographic data for 1–4, their absorption and emission spectra, as well as the results of modelling these spectra *via* time-dependent density functional theory (TDDFT) calculations.

Results and discussion

Syntheses and structures

The synthesis and structural data have already been published for 3¹⁵ and 4.¹⁸ From reaction solutions of CuCl and $[SnCl_4(thf)_2]$ with PhSeSiMe₃ in the presence of PPh₃, 1 can be obtained in the form of dark red crystals according to Scheme 2. Yellow crystals of 2 can be obtained from a similar reaction of AgCl, $[SnCl_4(thf)_2]$, PhSSiMe₃ and PPh₃.

Single crystal X-ray analysis reveals that compound **1** crystallizes in the trigonal space group $R\overline{3}$ (Table S1[†]). There is an inversion centre at the tin atom and a threefold rotation axis runs through the linear chain formed by the copper, tin and



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

Scheme 2 Synthesis of the trinuclear metal chalcogenolato complexes 1 and 2.

phosphorus atoms (Scheme 1 and Fig. S1, ESI[†]). The molecular structure of 1 can be viewed as consisting of a distorted octahedrally coordinated tin atom sharing parallel trigonal faces with two copper centred 'CuSe₃P' tetrahedra. This structural motif can also be found in complexes 2 (Table S1 and Fig. S2, ESI[†]), 3¹⁵ and 4¹⁸ although with differing geometrical parameters due to an exchange of the metal and chalcogen atoms. Assuming the phenyl-chalcogenolato ligands to be singly negatively charged we assign, in agreement with previous papers on 3 and 4, the formal oxidation states +iv to the tin atoms and +1 to the coinage metal atoms in 1 and 2. For a comparison of the structural parameters of 1-4 see Table S2, ESI.[†] In the literature, several other heterobimetallic trinuclear complexes can be found, which comprise a similar linear metal skeleton, including $[Cu_2Nb(SePh)_6(PR_3)_2]$ (R = org. group),¹⁹ [Co₂V(SPh)₈]²⁻, [Ni₂V(SPh)₈]²⁻,²⁰ [Cu₂M(SAr)₆(PPh₃)₂] $(M = W, Mo, U; Ar = Ph, p-C_6H_4Me, p-C_6H_4F, p-C_6H_4Cl,$ $p-C_6H_4Br$,^{21–23} and [LFeMFeL]ⁿ⁺ (M = Ge, Sn; n = 2, 3; L =1,4,7-(4-tert-butyl-2-mercaptobenzyl)-1,4,7triazacyclononane).24

Absorption spectra

Absorption spectra of **1–4** have been measured for powdered crystals in a mineral oil layer between two quartz plates and in solution (Fig. 1, 2 and S3, ESI[†]). Additionally, singlet transition energies were calculated using the experimental structure parameters within time-dependent density functional theory (TDDFT). Calculations were done with TURBOMOLE^{25,26} employing Becke's three parameter hybrid functional with Lee-Yang-Parr correlation (B3LYP),^{27,28} and polarized double-zeta valence basis sets def2-SV(P),²⁹ throughout. In Table 1 (compd 1 and 4) and Table S3[†] (compd 2 and 3), the calculated energies for excitations with significant oscillator strengths



Fig. 1 Comparison of measured electronic spectra (powdered crystals in mineral oil) of 1 with calculated singlet excitation energies and oscillator strengths plotted as vertical lines (green) as well as with super-imposed Gaussians of FWHM = 0.3 eV (black curve) to simulate the spectrum (see also Table 1).



Fig. 2 Comparison of measured electronic spectra (powdered crystals in mineral oil and in toluene) of 4 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 1).

Table 1 Observed and calculated (TDDFT) electronic excitation energies in 1 and $4^{a,b}$

	Exp. ΔE	Theory			
		ΔE	f	Character	
1		2.39	0.0050	$e_{\rm u}({\rm HOMO-2}) \rightarrow a_{\rm g}({\rm LUMO})$	
	2.57	2.60	0.1852	$a_{u}(HOMO-1) \rightarrow a_{g}(LUMO)$	
	3.65	3.52	0.2688	$e_{\rm u}({\rm HOMO}-5) \rightarrow a_{\rm g}({\rm LUMO})$	
4	1.43	1.59	$2.6 imes 10^{-5}$	$a(\text{HOMO}) \rightarrow e(\text{LUMO})$	
		2.01	0.0086	$0.5 \ e(\text{HOMO}) \rightarrow e(\text{LUMO+1})$	
				$0.5 a(\text{HOMO}-1) \rightarrow a(\text{LUMO})$	
	1.96	2.19	0.0757	$0.5 \ e(\text{HOMO}) \rightarrow e(\text{LUMO+1})$	
				$0.5 a(\text{HOMO}-1) \rightarrow a(\text{LUMO})$	
		2.24	0.0075	$e(\text{HOMO}-2) \rightarrow e(\text{LUMO})$	
	2.43	2.57	0.0489	$e(\text{HOMO}-3) \rightarrow e(\text{LUMO})$	
		2.70	0.0142	$e(HOMO-5) \rightarrow e(LUMO)$	

^{*a*} Parameters: transition energy ΔE [eV], corresponding oscillator strength *f*. For the spectra, see Fig. 1 and 2. ^{*b*} In the case of *e* representations the notation of the HOMOs/LUMOs counts for two degenerate orbitals.

 $(>5 \times 10^{-3})$ are listed together with the respective molecular orbitals involved and the corresponding values determined in the experiment. From these transitions the spectra were simulated by superimposing Gaussians with a full width at half maximum of (FWHM) 0.3 eV. Fig. 1, 2 and Tables 1, S3 (ESI[†]) demonstrate a very good agreement within ~0.2 eV between the calculated singlet excitations and measured solid state spectra of 1–4.‡

Note that the solid state spectra overemphasize the intensity of weak bands due to the non-validity of Lambert-Beer law for this kind of sample preparation. This is especially well seen for the first absorption maximum of 4 at 1.43 eV, whereas the relative band intensities in the spectrum of 4 in toluene display a better agreement with the calculated excitations. For complexes 1-3, absorption measurements in solution were not possible due to decomposition as indicated either by strong shifts of the absorption maxima of 1 and 3 (Fig. S4, ESI[†]) or by formation of a white precipitate by 2. Respective characteristics of excitations listed in Table 1 (Table S3, ESI[†]) are very similar for compounds 1–3, which all exhibit S_6 symmetry: they all are transitions from HOMO-1/HOMO-2/HOMO-5 to the LUMO. The reason for this similarity is found in the similarity of the MO schemes of compounds 1-3 (Fig. 3 and S5, ESI⁺). The LUMO is energetically well separated from the higher lying unoccupied MOs (by more than 1 eV) and thus is the only unoccupied orbital in reach for the lowest excitations. It is of a_{g} symmetry, therefore only transitions from occupied orbitals of a_u or e_u symmetry are dipole-allowed. For compounds 1–3, these are the three orbitals mentioned above. One might note that for instance for 1 the energetically lowest excitation corresponds to a transition from HOMO-2 to LUMO, whereas that from HOMO-1 to LUMO is slightly higher in energy. This can happen, as excitations in TDDFT are calculated as the response of the electron density on a time-dependent external electric field. Thus not always an excitation is dominated by a pair of a



Fig. 3 Calculated molecular orbital diagrams of **1** and **4**. The dashed line separates occupied orbitals from unoccupied ones $(e_g/e_u$ denotes two levels, thus four near-degenerate orbitals).

[‡]Excitation spectra of **1–4** for the DFT-optimized structures qualitatively agree with those for the experimental structures, but are shifted to lower energies by *ca.* 0.5 eV. They are shown in the supplement together with the relevant bond distances (Fig. S13 and Table S9, ESI†). Respective optimized Cartesian coordinates are available (ESI†).



Fig. 4 Molecular frontier orbitals involved in the relevant (lowest energy) electronic transitions of 1. Contours are drawn at 0.05 (white) and -0.05 (black) atomic units [a.u.].

single occupied and a single virtual molecular orbital, and even if this is the case, the difference of the respective orbital energies is only a rough approximation to the excitation energy. As a consequence, the sequence of excitations (Tables 1 and S3, ESI[†]) is not necessarily the same as the sequence of orbital energy differences depicted in Fig. 3 and S5 in the ESI.[†] Visualization of these orbitals, as shown in Fig. 4 exemplarily for compound 1, reveals that the LUMO is an antibonding combination of the 5s orbital of the central tin atom and the 4p orbitals of the neighboring sulfur atoms, whereas the occupied orbitals do not involve the tin atom but copper d, sulfur p and - for HOMO-1 - also phosphorus p orbitals. For compound 4 (C_3 symmetry) matters are somewhat different. LUMO (of e symmetry) and LUMO+1 (of a symmetry) are quite close in energy (~0.4 eV, see Fig. 3) and thus both are involved in the transitions listed in Table 1. In contrast to 1-3 they show contributions predominantly of the d orbitals of the central titanium atom and almost no contributions of the neighboring sulphur atoms (Fig. 5). Furthermore, all occupied orbitals of high energy are involved in the transitions, as no symmetry applies.

Emission spectra

Solid (crystalline) complexes **1–4** display relatively strong NIR emission centered between 920 and 1110 nm at low temperatures (Fig. 6, Table 2, and Fig. S6, S7, ESI[†]). However, the PL intensity of **1–3** decreases significantly by increasing the temperature over ~100 K. In these compounds the PL decays on the time scale of sub-microseconds to tens of microseconds as extracted from bi-exponential fits. Consequently, the PL can be



Fig. 5 Molecular frontier orbitals involved in the relevant (lowest energy) electronic transitions of 4. Contours are drawn at 0.05 (white) and -0.05 (black) atomic units [a.u.].



Fig. 6 Photoluminescence excitation (PLE, solid line) and emission (PL, dashed line) spectra of 1 and 4 (powdered crystals in mineral oil) at different temperatures.

Table 2 Photoluminescence wavelength λ_{PL} [nm] at 150 and 20 K and decay times τ [µs] for $1{-}4$

	$\lambda_{ m PL}$, 150 K	$\lambda_{ m PL}$, 20 K	τ, 150 K ^{<i>a</i>}	τ, 20 K ^{<i>a</i>}
1	1090, 715	1110, 600	0.59, 0.17 (34 : 66) 54, 8.4 (50 : 50)	1.7, 0.32 (49:51) 63, 7.7 (60:40)
2	930	930		35, 7.9 (55:45)
3	1020, 700	1020, 685		10, 1.5(76:24)
4	1090^{b}	1063	$\sim 0.01^b$	115, 25 (40 : 60) 0.04

 a Biexponential decay parameters for 1–3 with relative amplitudes of two exponential components in brackets. b Parameters at 295 K.

attributed to phosphorescence. In contrast to 1–3, complex 4 remains an efficient emitter also at ambient temperature, with the emission maximum at ~1090 nm and a relatively high quantum efficiency of 9.5% – comparable to that of NIR-emitting quantum dot nanoparticles.³⁰

Referring to the last value, the PL efficiency of ~30% is estimated for 4 below ~50 K. The NIR emission of 4 proceeds unusually fast, with a lifetime of ~40 ns at 20 K, which decreases to ~10 ns at ambient temperature - close to the time resolution limit of our apparatus. Consequently, the PL of 4 can be ascribed to fluorescence. In addition the following details of the experimental luminescence spectra are noteworthy. Although PL excitation (PLE) spectra (Fig. 6, S5 and S7, ESI[†]) agree well with the corresponding absorption spectra (Fig. 1 and 2) with regard to the onsets of the lowest-energy bands, the 'saturation' effect for PLE features is even more pronounced than that in the solid state absorption (see above) due to optically 'thick' sample preparations for PL measurements. We also remark that the NIR emission of 4 at ~1150 nm was also detected in toluene solution (Fig. S8, ESI†), however with a much weaker intensity as from the solid samples. We note in passing that 3 demonstrates a second minor emission band at 685 nm at low temperatures. A dual emission is also observed for 1 under UV excitation (Fig. S9, ESI[†]). The higher-energy emission bands decay significantly slower as compared to the NIR bands (Table 2). Combined theoretical and time-resolved photoluminescence investigations of [Mo₆Br₁₄]²⁻ metal cluster units have recently evidenced the existence of multiple competitive de-excitation processes in these compounds - in contrast to a 'simple' relaxation pathway as described by Kasha's rule.³¹ The origin of the dual emission in these complexes needs to be clarified in future work.

One general discrepancy evident by comparison of the absorption and emission spectra of 1-4 is the distinctly different Stokes shifts of 1-3 *versus* 4. In order to identify possible reasons for this behaviour, we made an attempt to simulate the respective processes with TDDFT – similar to the route followed by Costuas *et al.*³¹ – in the following manner. At first, the structure parameters of 1-4 were optimized. For the resulting structures triplet and singlet excitation energies were calculated for 1-3 and 4, respectively, in order to simulate the respective excitation process (Table S8, ESI⁺). Next, structure

parameters were optimized for the respective excited states, accounting for geometric relaxation after excitation. Finally, emission energies for the respective excited state were obtained as excitation energies from a ground-state determinant calculated for the relaxed structure (Table S8, ESI†). For **1–3** this method was applied to the four lowest triplet transitions and for **4** to the two lowest singlet transitions. The calculations predict large Stokes shifts of 0.72–1.55 eV for **1–3** and small ones (0.09–0.27 eV) for **4**. Both trends are in fact also observed in the experiments: Stokes shifts of *ca*. 1.4–1.6 eV are estimated for **1–3**, whereas for **4** the shift is *ca*. 0.3 eV.§

This difference in Stokes shifts between compounds 1-3 (with tin in the central position) and 4 (with titanium in the central position) can be related to the emission character (phosphorescence vs. fluorescence for 1-3 and 4, respectively), but also to the degree of the distortion in the excited state (Table S9, ESI[†]), in particular to the changes in distances between the central atom and its neighbors upon electronic excitation. For 4, only comparably small structure relaxation effects upon electronic excitation are observed: the Ti-S bonds are elongated by ca. 5 pm. Much more pronounced elongation upon excitation is calculated for the Sn-E (E = S, Se) distances in 1-3: 12-20 pm, depending on the elements and the number of the excited state. These observations might be rationalized with the character of the LUMO (Fig. 4), which is occupied for all excited states discussed. For the excited state structures of 1-3 it is anti-bonding with respect to the central atom and its neighbors, so distances will increase if it is occupied. On the other hand, for elongated distances, the anti-bonding character of respective orbitals is reduced, which in turn lowers the orbital energy and thus also the energy of the respective excited state resulting in $\Delta E_{\rm em} \ll \Delta E_{\rm ex}$.¶ For 4, in contrast, the LUMO (Fig. 5) is essentially non-bonding (3d orbitals of titanium), which leads both to only moderate deviations in the structural parameters upon excitation and to smaller changes in the orbital energies. Such large structural relaxations accompanied by energy lowering for excited states are not uncommon. For instance, Costuas et al.³¹ calculated an elongation of Mo-Mo distances for the first excited triplet state of $[Mo_6Br_{14}]^{2-}$ by ca. 12 pm, accompanied by an energetic lowering of 0.4 eV. As explicitly noted in their work, consideration of these relaxation effects is essential for the match of the calculated and measured emission energies.

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[§] Stokes shifts were estimated for 1–3 and 4 from the PLE and PL spectra at low and ambient temperatures, respectively. At cryogenic temperatures, the Stokes shift of 4 slightly decreases to *ca*. 0.27 eV. Note also that the low-energy PLE bands of 1, 2 (recorded at 17–20 K) and 4 (both at 20 and 295 K), well correspond to their counterparts in the Nujol absorption spectra measured at ambient temperature; solid 3 shows a ~0.25 eV upshift of the absorption at 295 K *vs*. the PLE onset at 17 K (see Fig. 1, 2, 6, S6 and S7†).

[¶]According to a Mulliken population analysis for the spin density of the excited triplet state in 1–3, the unpaired electrons are mainly located at the chalcogenide atoms, 0.20 to 0.31 electrons per atom (R. S. Mulliken, Electronic Population Analysis on LCAO–MO Molecular Wave Functions. I. *J. Chem. Phys.*, 1955, 23(10), 1833–1840).



Scheme 3 Schematic representation of the electronic processes in 1–3 (left) and 4 (right), representatively shown for the energetically lowest transition (ISC \equiv intersystem crossing). $\Delta E_{\rm exc} - \Delta E_{\rm em}$ depicts the calculated Stokes shift listed in Table S7, ESI.†

A schematic overview of the electronic processes in 1–4 is shown in Scheme 3. For 1–3 the molecules are excited from the ground state S_0 to the lowest excited singlet state S_1^* (ΔE_{exc}) which then converts by intersystem crossing to an excited triplet state T^{*}.

Distinct geometric relaxation of this excited state structure results in the relaxed excited triplet state T from which, at low temperature, phosphorescence ($\Delta E_{\rm em}$) with a strong Stokes shift ($\Delta E_{\rm exc} - \Delta E_{\rm em}$) can be observed. In 4 there is no intersystem crossing to a triplet state and only a moderate relaxation of the excited state structure S₁* to S₁ comprising a fluorescence with a small Stokes shift.

We note that calculations for **1–4** were done in gas phase. Distinct differences in bond lengths (about 10 pm) between the optimized and experimentally determined ground state structures to a certain degree indicate deficits of this simplification compared to a treatment of the solid state. The latter might give a more reliable picture but lies outside the scope of present technologies.

Conclusions

We conclude that the experimental optical absorption spectra of the trinuclear complexes studied in this work are well described by the TDDFT calculations. This is in line with our previous results that the TDDFT method can generally well describe the absorption spectra of various polynuclear copper(1) complexes. At temperatures below ~100 K, solid compounds 1-3 demonstrate bright near-infrared (NIR) microsecond-long phosphorescence at ~900-1100 nm. Its intensity decreases strongly by increasing the temperature. Complex 4 also shows NIR emission at ~1100 nm, but with an unusually high, practically relevant efficiency of 9.5% at ambient temperature comparable to that of NIR-emitting quantum dot nanoparticles. The decay is fast (<10 ns), *i.e.* the emission is fluorescence. The trends in the experimental Stokes shifts of 1-4 correlate with the amount/size of the calculated geometrical relaxation in the respective excited states (*i.e.* lowering of the orbital energies) and can be rationalized by the qualitative difference of the LUMOs of 1-3 compared to 4. However, the lowest-energy

singlet transitions in **4**, both in excitation and emission, are predicted with low oscillator strength. This is consistent with the weak red-NIR absorption of **4**, but in discrepancy with its efficient NIR fluorescence, which remains to be clarified by future investigations.

Experimental section

Synthesis

Standard Schlenk techniques were employed throughout the syntheses using a double manifold vacuum line with high purity dry nitrogen (99.9994%) and a MBraun glovebox with high purity dry argon (99.9990%). The solvents Et₂O (diethylether), thf (tetrahydrofuran) and toluene were dried over sodium-benzophenone, distilled and under nitrogen. Anhydrous dimethylenchlorine (CH_2Cl_2) $(H_2O < 0.005\%)$ obtained from Aldrich was degassed, freshly distilled and stored over molecular sieves under nitrogen. CuCl obtained from Sigma-Aldrich was subsequently washed with HCl, CH₃OH, and diethylether to remove traces of CuCl₂, and dried under vacuum. [SnCl₄(thf)₂],³² [AgCl(PPh₃)₃]³³ and LiSPh³⁴ were prepared according to literature procedures. PPh3 obtained from Sigma-Aldrich was recrystallized in ethanol before use.

PhSSiMe₃. LiSPh (67.3 mmol, 7.82 g) was suspended in 200 mL of thf in a 1 L flask and Me₃SiCl (7.39 g, 68 mmol), diluted with 50 mL of thf, was added dropwise to the solution upon stirring. The reaction mixture was then heated for 8 h under reflux after which thf was removed by distillation and then the product was removed from the remaining wet, solid residue by vacuum distillation (1 mbar) into a flask connected with a knee. This raw product (turbid liquid) was then further purified by a vacuum distillation (8 mbar) with a vigreux column to yield PhSSiMe₃ as a colourless liquid (b.p. 70 °C). Yield: 10.6 g (86.4%). C₉H₁₄SSi (182.36): ¹H (500 MHz, C₆D₆): 7.38 (m, 2H, *ortho*-CH), 6.95 (m, 3H, *meta*, *para*-CH); 0.12(s, 3H, SiCH₃); ¹³C{¹H}-NMR (126 MHz, C₆D₆): 134.6 (s, *ortho*-CH), 131.2 (s, CSSi), 128.1 (s, *meta*-CH), 126.1 (s, *para*-CH) ppm, 0.0 (s, SiCH₃); ²⁹Si (99 MHz, C₆D₆): 16.6 ppm.

 $[Cu_2Sn(SePh)_6(PPh_3)_2]$ (1). $[SnCl_4(thf)_2]$ (0.31 g, 0.77 mmol) and CuCl (0.152 g, 1.53 mmol) were dissolved with PPh₃ (0.5 g, 1.91 mmol) in 30 mL of thf to give a light yellow solution. Upon addition of PhSeSiMe₃ (0.91 mL, 4.75 mmol) the colour of the solution turned quickly to orange red. After 3 h stirring at room temperature thf was removed by vaccum condensation and the residue dissolved in 15 mL of CH₂Cl₂. After addition of 10 ml of Et₂O dark red crystals of 1 started to grow after one night in the fridge at -42 °C. After four days the crystals were filtered cold and were washed three times with 10 mL of Et₂O to give a final yield of 1.24 g (80.0%). $C_{72}H_{60}Cu_2P_2Se_6Sn$ (1706.76): calcd C 50.7, H 3.5 found C 50.5, H 3.8%.

 $[Ag_2Sn(SPh)_6(PPh_3)_2]$ (2). $[SnCl_4(thf)_2]$ (0.31 g, 0.77 mmol) and $[AgCl(PPh_3)_3]$ (1.42 g, 1.52 mmol) were suspended in 30 mL of thf. Upon addition of PhSSiMe₃ (0.91 mL, 4.75 mmol) the colour of the solution turned to pale yellow but remains turbid. After 3 h stirring at room temperature thf was removed by vacuum condensation and the residue dissolved in 15 mL of CH_2Cl_2 to give a clear yellow solution. This was 'layered' with diethylether through slow diffusion by evaporation *via* a connected flask to give pale yellow crystals of 2 which were filtered after four days and washed three times with 10 mL of Et₂O to give a final yield of 0.82 g (71.3%). $C_{72}H_{60}Ag_2P_2S_6Sn$ (1514.03): calcd C 57.1, H 4, S 12.7 found C 56.4, H 4.5, S 12%. The reduced experimental values for C and S (enhanced for H) are indicative for remaining lattice solvent molecules of CH_2Cl_2 and $(C_2H_5)_2O$. The single crystal X-ray analysis also reveals the exsistence of solvent accessible voids although no such molecules could be properly refined due to disorder.

 $[Cu_2Sn(SPh)_6(PPh_3)_2]$ (3). $SnCl_4(thf)_2$ (0.31 g, 0.77 mmol) and CuCl (0.152 g, 1.53 mmol) were dissolved with PPh₃ (0.5 g, 1.91 mmol) in 30 mL of CH₂Cl₂ to give a pale yellow solution. Upon addition of PhSSiMe₃ (0.91 mL, 4.75 mmol) the colour of the solution intensified and went to orange. Stirring was stopped and crystallization of 3 started. After four days the supernatant solution was decanted and the crystals washed three times with 10 mL of thf to give a final yield of 0.88 g (80.0%). C₇₂H₆₀Cu₂P₂S₆Sn (1425.39): calcd C 60.7, H 4.2, S 13.5 found C 61.2, H 4.1, S 12.7%.

 $[Cu_2Ti(SPh)_6(PPh_3)_2]$ (4) was prepared according to ref. 18.

Crystallography

Crystals suitable for single crystal X-ray diffraction were selected in perfluoroalkylether oil and mounted on a diffractometer equipped with an Oxford Cryosystem. Single-crystal X-ray diffraction data of 1 were collected using graphite-monochromatised MoK α radiation ($\lambda = 0.71073$ Å) on a STOE IPDS 2T (Imaging Plate Diffraction System). Single-crystal X-ray diffraction data of 2 were collected using MoK α radiation (λ = 0.71073 Å) generated by a multilayer optic on a STOE STADI Vari (Pilatus Hybrid Pixel Detector 300K). Raw intensity data were collected and treated with the STOE X-Area software Version 1.64. Interframe Scaling of the STADI Vari dataset of 2 was done with the implemented program LANA. Data were corrected for Lorentz and polarization effects. Based on a crystal description a numerical absorption correction was applied.³⁵ All structures were solved with the direct methods program SHELXS of the SHELXTL PC suite programs,³⁶ and were refined with the use of the full-matrix least-squares program SHELXL. Molecular diagrams were prepared using Diamond.³⁷ In 1 and 2 all Cu, Ag, S, Se, P and C atoms were refined with anisotropic displacement parameters whilst H atoms were computed and refined, using a riding model, with an isotropic temperature factor equal to 1.2 times the equivalent temperature factor of the atom which they are linked to. In 2 phenyl rings of the phosphine ligands are disordered and C atoms were refined with a split model of site disorder. Lattice solvent molecules were identified within both structures. These were located on a threefold axis and could not be adequately refined due to disorder. The data were therefore corrected for these using the SQUEEZE option within the PLATON³⁸

program package finding a total of 75 (1) and 120 (2) electrons in a potential solvent accessible area of 471 (1) and 445 (2) Å.

CCDC 1487085 (1) and 1487086 (2) contain the supplementary crystallographic data for this paper.

X-ray powder diffraction patterns (XRD) for 1-3 were measured on a STOE STADI P diffractometer (Cu-K_{a1} radiation, Germanium monochromator, Debye-Scherrer geometry, Mythen 1K detector) in sealed glass capillaries both as a suspension of crystals in the mother liquor and as a powder of crystals. The theoretical powder diffraction patterns were calculated on the basis of the atom coordinates obtained from single crystal X-ray analysis by using the program package STOE WinXPOW.³⁹ A comparison of the measured and calculated X-ray powder diffraction patterns for 1-3 reveals the crystalline purity with respect to the formation of other crystalline compounds (Fig. S10-S12, ESI[†]). Slightly increasing differences in the position of the peaks with increasing detection angle arise from the temperature difference of the data collections (single crystal XRD at 180 K and powder XRD at room temperature).

Physical measurements

C, H, S elemental analyses were performed on an 'Elementar vario Micro cube' instrument.

UV-vis absorption spectra were measured on a Perkin Elmer Lambda 900 spectrophotometer. Solid state spectra were measured in transmission for samples which were prepared as micron-sized crystalline powders dispersed in a nujol layer between two quartz plates. These were placed in front of a Labsphere integrating sphere.

Photoluminescence (PL) measurements were performed on a Horiba JobinYvon Fluorolog-3 spectrometer equipped with a Hamamatsu R5509 vis-NIR photomultiplier (~300-1400 nm) and an optical close-cycle cryostat (Leybold) for measurements at cryogenic temperatures down to ca. 17 K. The emission spectra were corrected for the wavelength-dependent response of the spectrometer and detector (in relative photon flux units). Emission decay traces were recorded by connecting the photomultiplier to an oscilloscope (typically with a 500 or 50 Ohm load) and using a N2-laser for pulsed excitation at 337 nm (~2 ns, ~5 μ J per pulse). PL quantum yield of 4, φ_{PL} , was measured at ambient temperature using a 10 cm integrating sphere out of optical PTFE with low auto-luminescence (Berghof GmbH), which was installed in the sample chamber of the Fluorolog-3. A powdered sample of 4 between quartz plates (see above) was placed into the sphere and excited at 500 nm. The $\varphi_{\rm PL}$ value was determined according to the method of de Mello et al.40 The accuracy was estimated to be ±10%.

Author contributions

A. E. was responsible for synthesis and characterization, S. L. for PL/PLE measurements, M. K. and F. W. for DFT and TDDFT calculations. Published on 05 January 2017. Downloaded by Hacettepe Universitesi on 18/01/2017 16:04:05.

Conflict of interests

The authors declare no financial interests.

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