DOI: 10.1002/ejic.200900711

One-Dimensional Coordination Polymers Containing Polynuclear (Selenolato)copper Complexes Linked by Bipyridine Ligands

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Dedicated to Prof. Rüdiger Kniep on the occasion of his 65th birthday

Keywords: Copper / Selenium / Coordination polymers / X-ray diffraction / UV/Vis spectroscopy

Three one-dimensional coordination polymers $[Cu_6(SePh)_6(PPh_3)_3(4,4'\text{-bpy})]$ (**1**) (4,4′-bpy = 4,4′-bipyridine), $[Cu_2(SePh)_2(dppm)(4,4'\text{-bpy})]$ (**2**), and $[Cu_2(SePh)_2(dppe)(4,4'\text{-bpy})]$ (**3**), containing polynuclear (selenolato)copper complexes and linear cross-linking bipyridine ligands, and one isolated dinuclear complex, $[Cu_2(SeC_6H_4SMe)_2(PPh_3)_2(4,4'\text{-bpy})_2]$ (**4**), have been prepared. The four complexes show optical transitions with HOMO–LUMO gaps of ca. 1.76 eV (**1**), 1.83 eV (**2**), 1.76 eV (**3**), and 2.12 eV (**4**), respectively.

Introduction

Over the last few years a great deal of attention has been paid to the rich chemistry of inorganic cluster compounds.[1–3] Among these the metal chalcogenide clusters play a prominent role.[4–8] In contrast to the oxides the syntheses of clusters containing the heavier chalcogenes pose special experimental challenges due to the oxidation and moisture sensitivity of the starting materials as well as the resulting compounds.[9,10] These compounds could serve as model systems giving information about formation, structure, and properties of larger colloidal nanoparticles and their superlattices. Such nanoparticles normally have less well-defined compositions and sizes; also the periodicity of superlattices of nanoparticles is less accurate compared to crystals consisting of precise cluster compounds.[11] The properties of such crystalline cluster compounds depend on the nature of the individual clusters, their spatial arrangement, and the properties of cross-linking ligands.[10,12] For example Schmid et al. could demonstrate that the electron-transfer between Au_{55} clusters occurs in two different ways: in the case of noncovalent linkage electron-transport mainly depends on the cluster–cluster distance, whereas covalently cluster-linking species with delocalized π-electrons enable electron-transfers at low activation energies.[13]

Previous work includes a series of tetrahedral chalcogenide clusters {e.g., $[In_{10}S_{18}]^{6-}$, $[In_{16}Cd_4S_{33}]^{10-}$, and $[Cd_{17}S_4(SCH_2CH_2OH)_{26}]$} that are linked through corner-sharing chalcogene atoms (e.g., S^{2-}, SPh^-, and $S_3{}^{2-}$) to form rigid covalent superlattices.[10] In addition Feng et al. used various bifunctional organic ligands as the organizing force to stabilize and assemble clusters into crystallographically ordered networks.[14–17] Recently, Vaqueiro et al. reported on gallium sulfide supertetrahedral clusters linked through an organic moiety.[18,19]

On the other hand, for some years there has been increasing interest in the synthesis of so-called metal–organic frameworks (MOFs) where single metal ions[20] or polynuclear complexes[21–23] are used as knots to build rigid frameworks. Common linkers in this area are polycarboxylates and multidentate N-donor ligands or a combination of both.

In this paper we report on the use of 4,4′-bipyridine (4,4′-bpy) as a cross-linking ligand between (selenolato)copper complexes. We describe the synthesis, structural characterization, and absorption spectra of three 1-D polymers of (selenolato)copper(I) complexes and one isolated dinuclear complex.

Results and Discussion

According to Scheme 1 the reactions of solutions of copper(I) acetate, phosphane ligands, and 4,4′-bipyridine in dme with the addition of $PhSe(SiMe_3)$ or $MeSPhSe(SiMe_3)$ lead to crystalline compounds $[Cu_6(SePh)_6(PPh_3)_3(4,4'\text{-bpy})]$ (**1**), $[Cu_2(SePh)_2(dppm)(4,4'\text{-bpy})]$ (**2**), $[Cu_2(SePh)_2(dppe)(4,4'\text{-bpy})]$ (**3**), and $[Cu_2(SeC_6H_4SMe)_2(PPh_3)_2(4,4'\text{-bpy})_2]$ (**4**). Their crystallographic data are summarized in Table 1.

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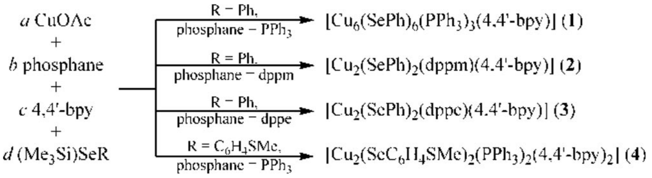
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.200900711.

Table 1. Crystallographic data of **1**–**4**.

	1·3dme	**2**·dme	**3**·2dme	**4**
Empirical formula	$C_{112}H_{113}Cu_6N_2O_6P_3Se_6$	$C_{51}H_{50}Cu_2N_2O_2P_2Se_2$	$C_{56}H_{62}Cu_2N_2O_4P_2Se_2$	$C_{70}H_{60}Cu_2N_4P_2S_2Se_2$
Formula mass	2530.95	1069.87	1174.02	1368.28
T [K]	180	200	180	180
Crystal system	triclinic	monoclinic	monoclinic	triclinic
Space group	$P\bar{1}$	$P2_1/c$	$C2/c$	$P\bar{1}$
a [pm]	1471.7(3)	2585.9(5)	2577.5(5)	935.6(3)
b [pm]	2040.3(4)	1352.0(3)	1057.6(2)	1309.8(4)
c [pm]	2071.4(4)	2667.1(5)	2299.0(5)	1365.9(3)
α [°]	82.17(2)	90	90	110.52(3)
β [°]	74.31(3)	96.82(3)	121.24(3)	106.89(3)
γ [°]	86.66(3)	90	90	90.17(3)
V [10^6 pm^3]	5931(2)	9259(3)	5358.3(19)	1489.5(9)
Z	2	8	4	1
$\rho_{calcd.}$ [g cm^{-1}]	1.417	1.535	1.455	1.525
μ [mm^{-1}]	2.986	2.603	2.258	2.107
F(000)	2540	4336	2400	696
2θ range [°]	2.9–51	5.1–50	3.7–51	5.3–51
Reflections collected	70661	31207	11269	10872
Independent reflections	22311 (R_{int} = 0.0673)	16533 (R_{int} = 0.0717)	4986 (R_{int} = 0.0923)	5466 (R_{int} = 0.0294)
Reflections with $I > 2\sigma(I)$	18631	9474	2808	4757
Parameters/restraints	1183/40	961/13	305/1	371/0
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0579, $wR2$ = 0.1564	R_1 = 0.0805, $wR2$ = 0.1698	R_1 = 0.0632, $wR2$ = 0.0868	R_1 = 0.0361, $wR2$ = 0.0900
Final R indices (all data)	R_1 = 0.0708, $wR2$ = 0.1647	R_1 = 0.1402, $wR2$ = 0.1934	R_1 = 0.1308, $wR2$ = 0.1001	R_1 = 0.0 37, $wR2$ = 0.0936
GoF	1.065	1.012	0.949	1.028
Max./min. residual electron density [e Å^{-3}]	1.523/–0.852	0.882/–0.666	0.504/–0.447	0.753/–0.833
CCDC	731104	731105	731106	731107



Scheme 1. Reactions yielding the compounds **1**–**4** (molar ratios *a*/*b*/*c*/*d* in the reaction mixture: **1**, **4**: 1:1:2:1; **2**, **3**: 1:0.5:2:1).

X-ray analysis of single crystals reveals that **1** consists of 1-D zigzag chains along the crystallographic *b*-axis, with repeating $[Cu_6(SePh)_6(PPh_3)_3]$ clusters and 4,4′-bpy bridges arranged in an alternating fashion. Complex **1** crystallizes in the triclinic space group $P\bar{1}$ with two formula units per unit cell and six additional molecules of dme per cell. As shown in Figure 1, the constitution of the cluster can be described as a distorted Se_6 octahedron with the copper ions occupying different sites of this polyhedron. Two copper ions (Cu4 and Cu5) are located in the center of two opposite faces of the octahedron in a trigonal-planar coordination mode. Three copper ions (Cu1, Cu2, and Cu6) are capping three faces of the Se polyhedron and are additionally coordinated by either a phosphorus atom of a PPh_3 ligand (P1, P2) or a nitrogen atom of the 4,4′-bpy ligand (N1) in a distorted tetrahedral coordination sphere. The sixth copper ion (Cu3) acts as a μ_2-bridge over one edge of the octahedron with additional bonds to one phosphane ligand (P3) and the nitrogen atom N2 of the 4,4′-bpy bridge. Some of the Cu–Cu distances in **1** are relatively short compared to twice the van der Waals radius of Cu^I (280 pm) or the inter-atomic distance in bulk copper (256 pm): Cu1–Cu5 246.8 pm, Cu2–Cu5 253.5 pm, Cu5–Cu6 254.4 pm. Within the literature these distances fall in the range where dispersion-type d^{10}–d^{10} interactions are discussed.[24]

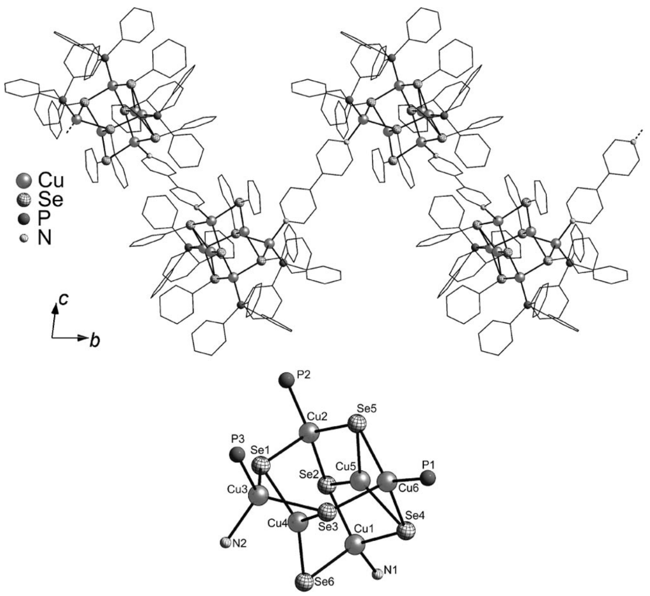


Figure 1. Top: Arrangement of the 1-D zigzag chains in $[Cu_6(SePh)_6(PPh_3)_3(4,4'\text{-bpy})]$ (**1**) viewed along the *a*-axis; bottom: heavy-atom skeleton of the basic building unit of $[Cu_6(SePh)_6(PPh_3)_3(4,4'\text{-bpy})]$ in **1** (hydrogen atoms omitted for clarity).

Compounds **2** and **3** are both composed of 1-D $[Cu_2(SePh)_2L(4,4'\text{-bpy})]_\infty$ [L = dppm (**2**), dppe (**3**)] chains with repeating $[Cu_2(SePh)_2L]$ units and 4,4′-bpy ligands arranged in an alternating fashion (Figures 2 and 3). In **2** (crystallizing in the monoclinic space group $P2_1/c$) one finds two crystallographically independent linear chains along the *b*-axis (Figure 2). The main difference between these two chains is the orientation of the phenyl rings of the PhSe⁻ groups. In chain A they adopt a *trans* orientation with respect to the Cu_2Se_2 rings, whereas in chain B the phenyl rings are *cis*-oriented. The Cu_2Se_2 rings themselves are folded with torsion angles of 131.53° (Se1–Cu1–Cu2–Se2) in chain A and 139.67° (Se3–Cu3–Cu4–Se4) in chain B. The Cu–Cu distances are: Cu1–Cu2 264.5 pm and Cu3–Cu4 257.9 pm, respectively. All copper atoms have distorted tetrahedral coordination spheres of two selenium, one phosphorus, and one nitrogen atom.

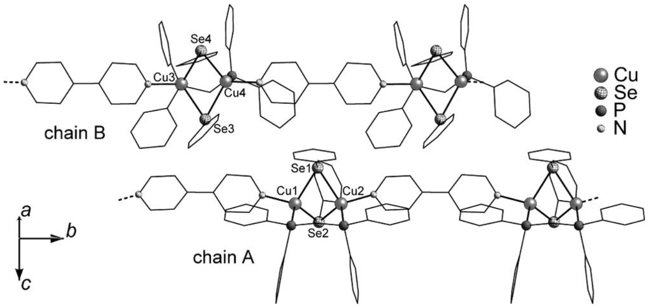


Figure 2. Arrangement of the two crystallographically independent linear chains in $[Cu_2(SePh)_2(dppm)(4,4'\text{-bpy})]$ (**2**) viewed along [201] (hydrogen atoms omitted for clarity).

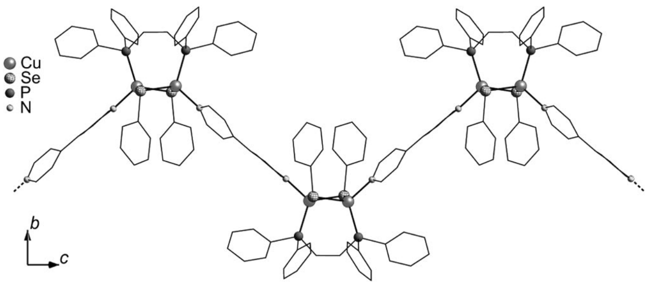


Figure 3. Zigzag chain in $[Cu_2(SePh)_2(dppe)(4,4'\text{-bpy})]$ (**3**) viewed along the *a*-axis (hydrogen atoms omitted for clarity).

Compound **3** (crystallizing in the monoclinic space group $C2/c$) consists of 1-D zigzag chains along the *c*-direction (Figure 3). A twofold rotational axis parallel to *b* is running through the Cu_2Se_2 unit in which the phenyl rings of the PhSe⁻ groups are *cis*-oriented. Compared to **2** the Cu_2Se_2 ring is less folded (torsion angle Se1–Cu1–Cu1′–Se1′ 163.55°) with a Cu–Cu distance of 268.7 pm. The coordination of the copper atoms is distorted tetrahedral consisting of two selenium, one phosphorus, and one nitrogen atom.

In contrast to the previously described polymers **1**–**3** compound **4** (crystallizing in the triclinic space group $P\bar{1}$) forms isolated, inversion-symmetrical, dinuclear complexes (Figure 4). Like in **2** and **3** two copper and two selenium atoms form a four-membered ring. With 308.5 pm the Cu–Cu distance is significantly longer than for **2** and **3**. This is a clear hint that the short distances in those compounds mainly result from the bite size of the bidentate ligands and not from metal–metal interactions.[24,25] As shown in Figure 4 the copper atoms in **4** are additionally coordinated by one phosphane and one 4,4′-bipyridine molecule each with these ligands taking a *trans* arrangement with respect to the planar Cu_2Se_2 ring. Also, the phenyl rings of the MeS–C_6H_4–Se part are *trans*-oriented. Surprisingly neither the sulfur atom nor the second nitrogen atom of the 4,4′-bipyridine is coordinating to any metal atom.

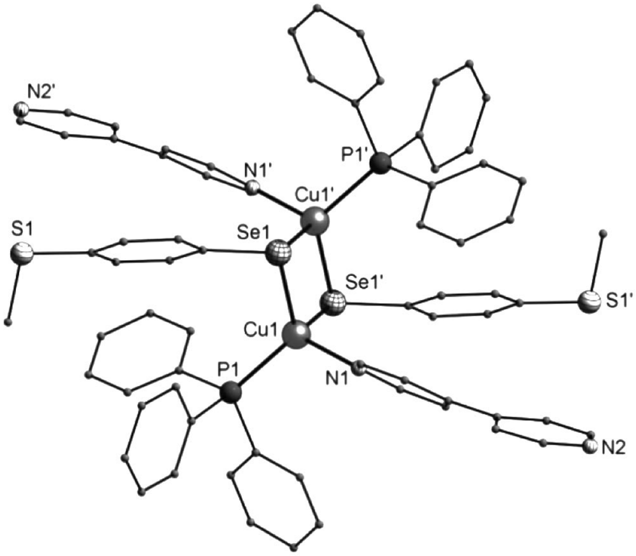


Figure 4. Molecular structure of $[Cu_2(SeC_6H_4SMe)_2(PPh_3)_2(4,4'\text{-bpy})_2]$ (**4**) (hydrogen atoms omitted for clarity).

In all compounds the bond lengths are in the expected range for ligand-stabilized (selenolato)copper complexes/clusters.[7]

Compared to other (selenolato)copper complexes of similar nuclearity **1**–**4** are significantly colored. Crystals of **1**–**3** are deep orange to red, **4** is bright orange. In contrast, $[Cu_2(SePh)_2(PPh_3)_3]$,[26] $[Cu_3(SeMes)_3(dppm)]$,[27] and even $[Cu_9(SePh)_6(O_2PPh_2)_3]$[28] are yellow. Figure 5 displays the UV/Vis/NIR absorption spectra of **1**–**4** in the solid state at room temperature. The estimated HOMO–LUMO gaps are ca. 1.76 eV (703 nm) for **1**, 1.83 eV (676 nm) for **2**, 1.76 eV (703 nm) for **3**, and 2.12 eV (615 nm) for **4**, respectively.[29] The transition likely originates from metal-to-ligand charge transfer (MLCT) between Cu^+-dominated to 4,4′-bpy-dominated orbitals. The absorption onsets of the 1-D polymers **1**–**3** are redshifted compared with that of the isolated complex **4**. Similar change in color is also observed for example for copper(I) bromide. Binary CuBr and its phosphane complexes are colorless, whereas the polymeric $[CuBr(4,4'\text{-bpy})]$ is red.[30] The latter consists of dinuclear Cu_2Br_2 units that are 2D-linked through bipyridine bridges.

Whereas **1**–**3** do not show any fluorescence at room temperature, **4** emits at 640 nm when excited with 500 nm (Figure S9).

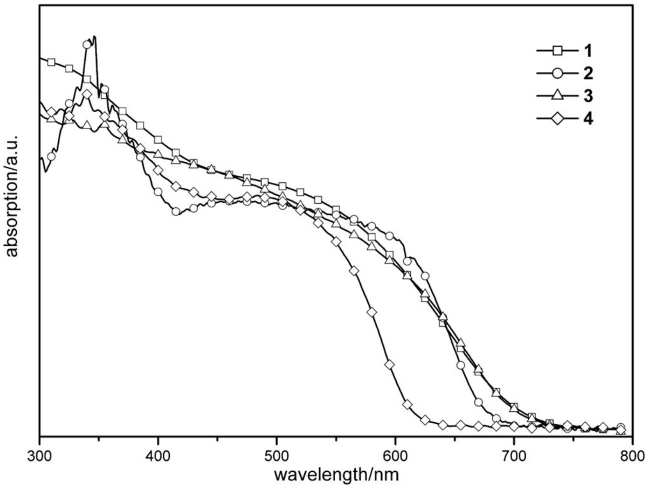


Figure 5. The absorption spectra of polycrystalline samples of **1**–**4**.

Conclusions

Four polynuclear (selenolato)copper compounds protected by phosphane ligands and 4,4′-bipyridine were synthesized and structurally and optically characterized. The use of the linear ligand 4,4′-bipyridine reported here, offers an efficient route for the connection of polynuclear copper complexes or clusters to crystallographically ordered superlattices as demonstrated in **1**–**3** where the (selenolato)copper subunits show 1-D polymeric arrangements. The absorption spectra of **1**–**4** are dominated by MLCT transitions between copper(I) ions and bipyridine ligands.

Experimental Section

General: Because of the high oxygen and moisture sensitivity of the compounds used, all reactions were performed under dry, oxygen-free nitrogen by using standard Schlenk techniques. Solvents were dried with sodium/benzophenone and freshly distilled. Copper(I) acetate (CuOAc)[31] and PhSeSiMe$_3$[32] were synthesized according to literature procedures. Solid-state reflection spectra were measured as micron-sized crystalline powders between quartz plates with a Labsphere integration sphere attached to a Varian Cary 500 spectrophotometer; NMR spectra were recorded with a Bruker DPX Avance 300 spectrometer.

X-ray Structure Determination: Data were collected with a STOE IPDS II diffractometer by using Mo-K_α radiation (λ = 0.71073 Å). Structure solution and refinement against F^2 were carried out with SHELXS and SHELXL software.[33] CCDC-731104 to -731107 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The purity of the compounds **1**–**4** was proved by X-ray power diffraction. Measured and calculated diffraction patterns can be found in the Supporting Information in Figures S10–S13.

Synthesis of MeSC$_6$H$_4$SeSiMe$_3$: 4-Bromothioanisole (20.7 g, 0.1 mol) was treated with magnesium (2.44 g, 0.1 mol) in thf (200 mL) to give the corresponding Grignard compound. After cooling to –60 °C, selenium (7.9 g, 0.1 mol) was added. Slow warming to room temperature over 6 h and stirring for another 12 h yielded a yellow solution to which Me$_3$SiCl (14 mL, 0.11 mol) was added dropwise. The reaction mixture was refluxed for 2 h. After cooling, toluene (50 mL) was added to complete the precipitation of the magnesium halides. These were filtered off, and the precipitate was washed with toluene. The solvents were removed in vacuo, and the product was purified by distillation (b.p. 123 °C at 10^{-3} mbar). Yield: 11 g (40%). ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C, TMS): δ = 7.51 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H), 6.99 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H), 2.08 (s, 3 H, SMe), 0.34 (s, 9 H, SiMe$_3$) ppm.

Synthesis of [Cu$_6$(SePh)$_6$(PPh$_3$)$_3$(4,4′-bpy)] (1): At room temperature, copper(I) acetate (0.060 g, 0.49 mmol), PPh$_3$ (0.128 g, 0.49 mmol), and 4,4′-bipyridine (4,4′-bpy) (0.152 g, 0.98 mmol) were suspended in dme (20 mL). After stirring for 3 h, PhSeSiMe$_3$ (0.094 mL, 0.49 mmol) was added. The mixture was stirred for another 1 h to give a clear orange solution. At 0 °C **1** crystallized within 1–2 weeks. Yield: 0.121 g (62%). $C_{112}H_{113}Cu_6N_2O_6P_3Se_6$ (2531.0): calcd. C 53.15, H 4.50, N 1.11; found C 53.04, H 4.42, N 1.15.

Synthesis of [Cu$_2$(SePh)$_2$(dppm)(4,4′-bpy)] (2): At room temperature copper(I) acetate (0.108 g, 0.88 mmol), dppm (0.169 g, 0.44 mmol), and 4,4′-bpy (0.274 g, 1.76 mmol) were suspended in dme (30 mL). After the suspension was stirred for 14 h, PhSeSiMe$_3$ (0.17 mL, 0.088 mmol) was added. The red solution was stirred for an additional 1 h. At 0 °C **2** crystallized within 1 week. Yield: 0.264 g (56%). $C_{51}H_{50}Cu_2N_2O_2P_2Se_2$ (1069.9): calcd. C 57.25, H 4.71, N 2.62; found C 57.02, H 4.42, N 2.86.

Synthesis of [Cu$_2$(SePh)$_2$(dppe)(4,4′-bpy)] (3): At room temperature copper(I) acetate (0.085 g, 0.69 mmol), dppe (0.138 g, 0.35 mmol), and 4,4′-bpy (0.216 g, 1.38 mmol) were suspended in dme (30 mL). After stirring for 3 h, PhSeSiMe$_3$ (0.13 mL, 0.69 mmol) was added. The resulting yellow mixture was stirred for another 2 h to give a clear orange solution. At 0 °C **3** crystallized within 1–2 weeks. Yield: 0.262 g (70%). $C_{56}H_{62}Cu_2N_2O_4P_2Se_2$ (1174.0): calcd. C 57.29, H 5.32, N 2.39; found C 57.48, H 5.15, N 2.46.

Synthesis of [Cu$_2$(SeC$_6$H$_4$SMe)$_2$(PPh$_3$)$_2$(4,4′-bpy)$_2$] (4): At room temperature copper(I) acetate (0.037 g, 0.30 mmol), PPh$_3$ (0.079 g, 0.30 mmol), and 4,4′-bpy (0.094 g, 0.60 mmol) were suspended in dme (15 mL). After stirring for 3 h, MeSC$_6$H$_4$SeSiMe$_3$ (0.068 mL, 0.030 mmol) was added. The red solution was stirred for another 1 h. Within several days **4** crystallized. Yield: 0.147 g (72%). $C_{70}H_{60}Cu_2N_4P_2S_2Se_2$ (1368.3): calcd. C 61.44, H 4.42, N 4.09, S 4.69; found C 61.22, H 4.29, N 4.15, S 4.53.

Supporting Information (see footnote on the first page of this article): ORTEP representations with selected bond lengths and angels, powder diffraction patters, IR spectra and UV/Vis absorption of the compounds **1**–**4** as well as the luminescence spectrum of **4**.

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft (Center for Functional Nanostructures – CFN). The authors are grateful to S. Leuthner for his assistance with the practical work.

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[29] The absorption wavelength for the HOMO–LUMO gaps were calculated by laying the tangent line through the inflection point of the first increase of the curves. The intersection point of the tangent with the abscissa was considered as wavelength of the HOMO–LUMO gap. For more information see Figures S5–S8.

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Received: July 24, 2009