Assembly of Coordination Polymers Using Thioether-Functionalized Octasilsesquioxanes: Occurrence of (CuX) n Clusters (X=Br and I) within 3D-POSS Networks

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Assembly of Coordination Polymers using Thioether-Functionalized Octasilsesquioxanes. Occurrence of $(CuX)_n$ Clusters (X = Br and I) within 3D-POSS Networks

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This manuscript is dedicated in memory of our colleague Dr. Myriam Euvrard

Abstract: For the first time, POSS-based coordination polymers (CPs) have been structurally characterized. These CPs were obtained in high yield *via* self-assembly reactions of thioether-functionalized polysilsesquioxanes with Cu(I) salts under mild conditions. Single crystal analyses revealed the formation of 3D networks incorporating different secondary building units (SBUs) as connection nodes. The nature of the -SAr function allows a fine-tuning of the cluster nuclearity, *i.e.* butterfly-shaped Cu_2X_2 or closed cubane-type Cu_4I_4 cores. As such, the resulting hybrid materials exhibit a combination of high thermal stability arising from the inorganic POSS core along with interesting luminescent properties conferred by the cubane cluster core. Furthermore, the occurrence of channels has been crystallographically evidenced in the case of the Cu_4I_4 cluster containing CP.

Polyhedral oligomeric silsesquioxanes (POSS) refer to a class of cage-like organic–inorganic species of general formula $(RSiO_{1.5})_n$. POSS Si_8O_{12} cages with a cubic core and eight organic substituents on the vertices, or a T8 structure, are the most studied systems, mainly due to their symmetrical arrangement and easy synthesis. Further, the POSS core possesses interesting properties such as high thermal stability, rigidity and hydrophobicity.[1] The possibility to easily functionalize their organic arms makes these systems interesting for the design of functional hybrid materials.[2] Thus, these systems have found a lot of applications such as in the formation of liquid crystals,[3] porous materials,[4] ionic liquids,[5] catalysts,[6] biomaterials,[7] dielectric materials,[8] light-emitting diode materials,[2b-9] and nanocomposites.[2c] More recently, POSS have been used as building blocks for the formation of high-ordered structures driven by intermolecular interactions such as hydrophobic interactions,[10] hydrogen bonding[11] or metal coordination[12] to assemble coordination polymers (CPs).[13] These CPs have been obtained by reacting hard lanthanide (Eu^{3+}, Tb^{3+}) or transition metal ions (Cu^{2+}, Co^{2+}, Fe^{2+}, Zn^{2+}) with hard ligands. Examples are the coordination of CuX_2 by a 3-amino-1,2,4-triazole-modified silsesquioxane yielding a paramagnetic material characterized by electron spin resonance (ESR) and the use of a terpyridine-functionalized POSS to form coordination networks with Co(II) and Cu(II).[13c,f]

However, we are not aware of any POSS-based CPs with the combination soft donor-soft Lewis acid. Furthermore, to the best of our knowledge, the structural characterization of any coordination networks with functionalized-POSS ligands has never been reported. Only recently, the presence of long-range ordering in POSS-based CPs has been ascertained by microscopy and powder X-ray diffraction analysis.[14]

CPs containing Cu(I) have attracted much interest due to their ease of synthesis, the propensity of CuX salts to aggregate to higher-nuclear cluster cores, their rich structural diversity and their potential applications in photo(thermo)chromism,[15] photoluminescence,[16] catalysis[17] and gas sorption.[18] Several research groups, including ours, have investigated the formation of various CPs and MOFs by reacting copper(I) halides with different thioethers.[19] Though the results of self-assembly process are difficult to predict, it was found that the network architecture of these CPs largely depends on the metal-to-ligand ratio, flexibility of the ligand, the character of the SR substituents (alkyl *vs* aryl) and finally on the nature of halide ligands (Cl *vs* Br *vs* I). Thus, a wide range of networks (one, two and three-dimensional) containing, among others, Cu_2X_2 rhomboids, cubane-type (Cu_4X_4), hexanuclear (Cu_6I_6) and even octanuclear (Cu_8I_8) clusters as connecting nodes have been explored.[19a-b]

With the objective to design a novel class of functional materials combining the intrinsic advantageous properties of POSS building blocks with those of luminescent CuX-thioether CPs/MOFs, we prepared thioether-functionalized POSS bricks as polydentate assembling ligands for the rational build-up of stable coordination networks incorporating polynuclear $(CuX)_n$ cores as secondary building units (SBUs).

Here, we describe for the first time an easy to implement procedure for the high yield preparation of fully crystallographically characterized three-dimensional (3D) CPs obtained by simple reaction between a soft Cu(I) salt (according the HSAB principle) with POSS cages bearing soft and flexible $(CH_2)_3SAr$ arms. The preparation of these 3D materials occurs in a two steps procedure as shown in Scheme 1. In the first step, octakis(3-chloropropyl)octasilsesquioxane[20] is converted by nucleophilic substitution of the chlorine atoms using an excess of the respective arylthiolate in DMF into octakis(3-(*p*-tolylthio)propyl)octasilsesquioxane **L1** and octakis(3-(5-(*tert*-butyl)-2-methylphenyl)thio)propyl)octasilsesquioxane **L2**.[21] These new functionalized POSS ligands have been characterized by multinuclear NMR techniques (Figures S1-S6).

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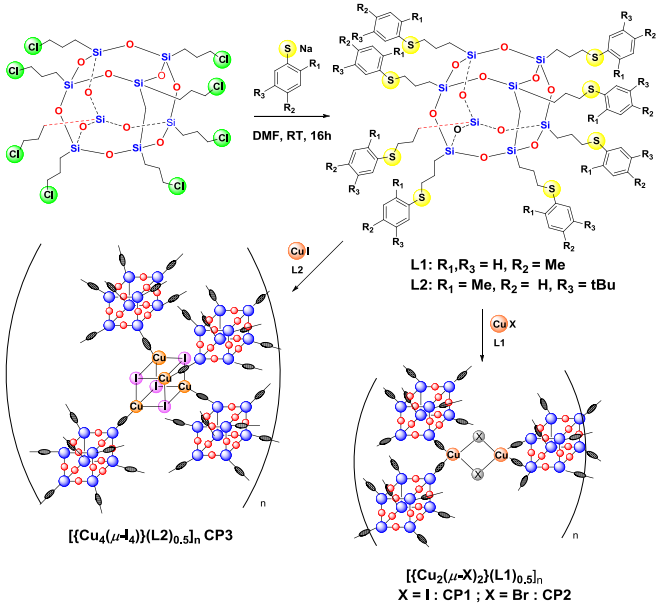
The $^{29}Si\{^{1}H\}$ NMR spectra of **L1** and **L2** present a singlet at -67.2 ppm, indicating a complete conservation of the T8 core. Furthermore, in the case of **L1**, single-crystals suitable for X-ray diffraction analysis were obtained confirming the spectroscopic data (See Fig. S7 ESI). **CP1** and **CP2** were then obtained as colorless materials of composition $[Cu_2(\mu\text{-}X)_2(\mu\text{-}\mathbf{L1})_{0.5}]_n$ by reacting **L1** with CuI or CuBr, respectively, in a mixture of dichloromethane and MeCN or EtCN in a 1:4 ratio at room temperature. Note that same compositions were obtained using a 1:8 ratio.

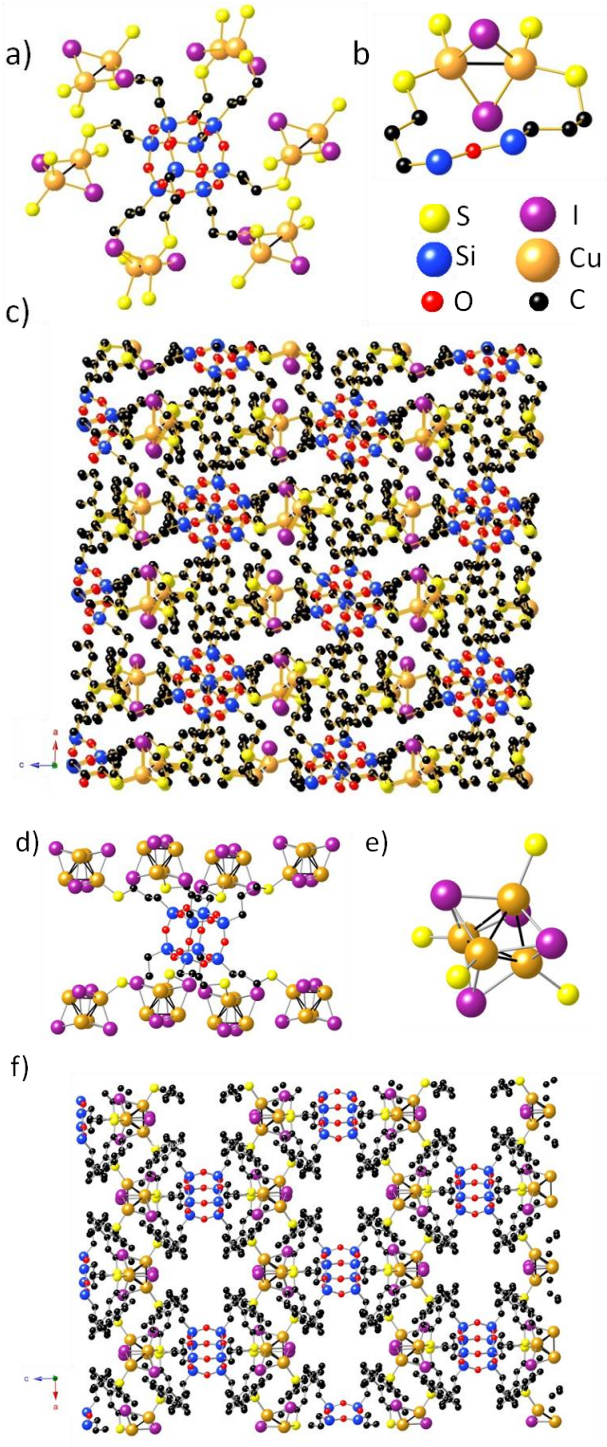


Scheme 1. Synthesis routes to POSS **L1** and **L2** and their corresponding **CP1**, **CP2** and **CP3**.

Single X-ray structure determination of **CP1** and **CP2** revealed generation of 3D networks built upon dinuclear $Cu_2(\mu\text{-}X)_2$ secondary building units (SBUs) and **L1** in the 4:1 stoichiometry (Figures 1a, S8 and S9 in the Supporting Information). **CP1** and **CP2** are isomorph and isostructural (monoclinic, $P2_1/n$). Two adjacent sulfur atoms of **L1** span as bridging ligand of two copper atoms of the same $Cu(\mu_2\text{-}X)_2Cu$ SBU, thus forming 13-membered macrocycles (Figure 1b). This coordination mode is also found for two sulfur atoms located opposite in the POSS core. The four remaining sulfur atoms are coordinated each to one copper atom of a $Cu(\mu_2\text{-}X)_2Cu$ core. Noteworthy, these SBUs do not adopt the common rhomboid geometry featuring a coplanar arrangement of the 4 atoms as encountered for 3D material $[Cu(\mu_2\text{-}I)_2Cu(\mu\text{-}\mathbf{L})]_n$ (L = 1,5,9,13-tetrathiacyclohexadecane),[22] but belong rather to the butterfly type, the two Cu atoms forming the hinge and the X atoms the wing tips. To the best of our knowledge, **CP1** represents the first

Figure 1. Different views on the networks and SBUs of **CP1** (a-c) and **CP3** (d-f).

example where this geometry is encountered for a $S_2Cu(\mu_2I)_2CuS_2$ motif.[23]The Cu···Cu separation in **CP1** is 2.7394(5) Å at 100 K, a value close to the sum of the van der Waals radii of two Cu atoms (2.8 Å) and reaches 2.7855(6) Å for **CP2**. When the POSS ligand **L2** bearing bulkier aryl substituents



was reacted with CuI in an 1:8 ratio, single crystal X-ray analysis (tetragonal, I4/m) of the colorless material of composition $[Cu_4(\mu\text{-}I)_4(\mu\text{-}\mathbf{L2})_{0.5}]_n$ revealed that the 3D **CP3** contains Cu_4I_4 clusters of the closed-cubane type as SBUs (Figures S10 and S11).[19a-g] Each of the four crystallographically identical Cu atoms of the centrosymmetric tetranuclear $(Cu_4\text{-}\mu_3\text{-}I)_4$ core within **CP3** is ligated by one S-POSS group. Thus, each POSS is surrounded by eight $Cu_4(\mu_3\text{-}I)_4$ cores (Fig. 1d and 1e). A mean Cu···Cu distance of 2.731 Å was found at 290 K. This value is lower than those found for **CP1** and **CP2** (despite being registered at room temperature) and compares well with that of other examples described in the literature such as the 3D diamond-like network $[Cu_4(\mu\text{-}I)_4(\mu\text{-}\mathbf{L})_{0.5}]_n$ (L = 1,10-dithia-18-crown-6), displaying a

mean Cu···Cu distance of 2.734 Å.[24] Comparison of the experimental PXRD data with those calculated from single X-ray diffraction confirmed the homogeneity of the samples (Figure 2 and Figures S12-S13 in the Supporting Information). In contrast to **CP1** and **CP2**, where no voids are present (Figure 1c), **CP3** exhibits a more porous character with an estimated void of 20% as shown in Figure 1f. The approximate dimensions of a channel present in **CP3** are illustrated in Fig S11**.**

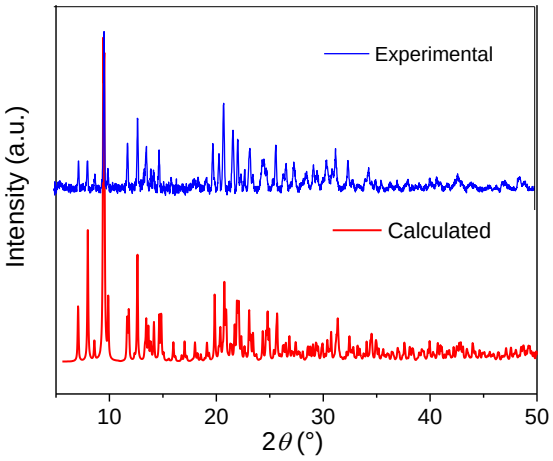


Figure 2. Experimental (top) and calculated (bottom) PXRD patterns of **CP1**.

TGA measurements were carried out under air at a rate of 10 °C.min^{-1}. TGA curve (Figure 3) of **L1** revealed a total weight loss of 73.2 % corresponding to 26.8 % remaining SiO_2, a value close to the theoretical one (27.6 %). As shown in Figure 3, the 3D CPs exhibit high thermal stabilities up to 350 °C, much higher than previously reported CPs connected by thioethers ligands.[25] Decomposition of **L1** occurs in two main steps. The first step can be attributed to the partial decomposition of the organic ligands while the second step occurring at 430 °C is due to the decomposition of the Si-O-Si cage. The thermal behavior of **CP1** and **CP3** are rather similar to **L1** with a more important mass loss occurring in the second step due to the decomposition of iodide fragments. The final residue yields are very close for **CP1** (31.9 %) and **CP3** (30.5 %) indicating similar decomposition mechanism and the formation of CuO and SiO_2 (theoretical values: 32.3% for **CP1** and 30.1 % for **CP3**).[26] However, **CP2** containing bromide ligand undergoes different decomposition mechanism as seen from the absence of a well-defined plateau at 800 °C. This thermal difference between CuBr and CuI cluster cores has already been observed with other thioether-based CPs but has not been yet rationnalized.[25c] Note that all CPs are also stable under ambient conditions and can be stored several weeks without degradation.

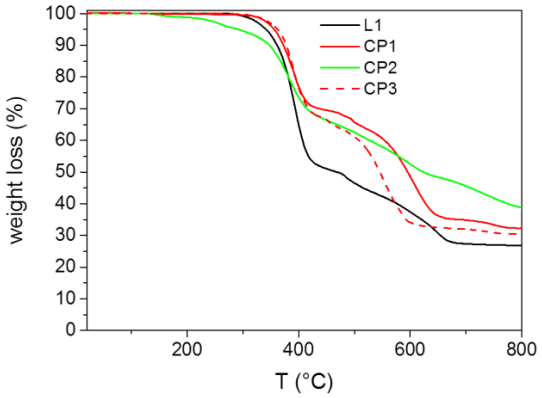


Figure 3. TGA traces of **L1**, **CP1**, **CP2** and **CP3** under air flow (rate: 10 °C.min^{-1}).

High-nuclear $(CuI)_n$ (n = 4, 6, 8) aggregates exhibit often intense luminescence and feature intriguing photophysical properties.[19] It is also known that Cu···Cu distances are temperature-dependent affecting the photophysical properties of these materials.[19f,25,27-29] We therefore recorded the solid-state emission and excitation spectra of **CP3** at 298 and 77 K (Figure 4 and S14). The luminescence spectrum recorded at 298 K exhibits two emission bands with maxima at λ_{max} = 384 and 535 nm attributed to high- and low-energy bands characteristic of a closed-cubane Cu_4I_4 motif. The low-energy emission has been attributed to a combination of halide to copper charge transfer (XMCT) transition and cluster-centered transition (CC*) and depends essentially on the Cu-Cu distances. The high-energy band was assigned to a ^{3}XLCT/^{3}MLCT mixed transition.[25,28,29] A red shift of the maxima of the emission band from 535 to 550 nm was observed upon cooling with a narrowing of the bandwidth. This is in accordance with the shortening of the Cu···Cu distance that reinforces the bonding character and thus, lowers the energy levels.[27] We also noticed no decay in the luminescence intensity of **CP3** after exposure to air, ruling out any significant aging processes.

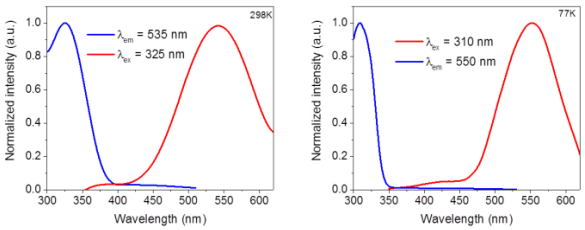


Figure 4. Emission (red) and excitation (blue) spectra of **CP3** at 298K (left) and 77K (right).

In conclusion, we have reported a simple procedure to construct, under mild reaction conditions, 3D CPs based on CuX salts and thioether-functionalized POSS ligands, representing the first examples of structurally characterized CPs bearing POSS. These materials incorporate SBUs of different nuclearity depending on the substitution pattern of the -SAr thioether functions. They all present high thermal stability and **CP3**

featuring closed-cubane Cu_4I_4 SBUs is moreover strongly luminescent even at room temperature. More advanced photophysical studies are intended. We anticipate that this approach can be easily extended to other soft metal ions and even harder ones permitting to fine-tune the physico-chemical (electrochemical, optical…) properties of these high-ordered POSS-based 3D networks. Also, variation of the $(CH_2)_n$ spacer length may allow to modulate the flexibility in order to vary the dimensionality/ $(CuX)_n$ cluster nuclearity and may provide an access to more porous frameworks.[19h,30] An increase of the porosity could open future prospects of these materials to solvochromism and their use as MOF for gas sorption, solvent "guest" inclusion and other applications requiring the presence of voids.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: Coordination polymers • copper halide • luminescence • POSS • self-assembly

[1] D. B. Cordes, P. D. Lickiss, F. Rataboul, *Chem. Rev*. **2010**, *110*, 2081-2173.

[2] a) H. Zhou, Q.Yea, J. Xu, *Mater. Chem. Front.*, **2017**, *1*, 212-230; b) Z. Li, J. Kong, F. Wang, C. He, *J. Mater. Chem. C* **2017**, *5*, 5283-5298; c) Q. Ye, H. Zhou, J. Xu, *Chem. Asian J.* **2016**, *11*, 1322-1337; d) K. Tanaka, Y. Chujo, *J. Mater. Chem*. **2012**, *22*, 1733-1746.

[3] a) X. Wang, C. M. Cho, W. Y. Say, A. Y. X. Tan, C. He, H. S. O. Chan, J. Xu, *J. Mater. Chem.* **2011**, *21*, 5248-5257; b) D. Y. Kim, S. Kim, S. A. Lee, Y. E. Choi, W. J. Yoon, S. W. Kuo, C. H. Hsu, M. Huang, S. H. Lee, K. U. Jeong, *J. Phys. Chem. C* **2014**, *118*, 6300-6306; c) N. Kim, D. Y. Kim, M. Park, Y. J. Choi, S. Kim, S. H. Lee, K. U. Jeong, *J. Phys. Chem. C* **2015**, *119*, 766-774.

[4] a) P. Sangtrirutnugul, T. Chaiprasert, W. Hunsiri, T. Jitjaroendee, P. Songkhum, K. Laohhasurayotin, T. Osotchan, V. Ervithayasuporn, *ACS Appl. Mater. Interfaces* **2017**, *9*, 12812-12822; b) W. Chaikittisilp, M. Kubo, T. Moteki, A. Sugawara-Narutaki, A. Shimojima, T. Okubo, *J. Am. Chem. Soc.* **2011**, *133*, 13832-13835; c) H. Zhou, Q. Ye, X. Wu, J. Song, C. M. Cho, Y. Zong, B. Z. Tang, T. S. A. Hor, E. K. L. Yeow, J. Xu, *J. Mater. Chem. C* **2015**, *3*, 11874-11880.

[5] a) K. Tanaka, F. Ishiguro, Y. Chujo, *J. Am. Chem. Soc*. **2010**, *132*, 17649-17651. T. b) Ishii, T. Enoki, T. Mizumo, J. Ohshita, Y. Kaneko, *RSV Adv*. **2015**, *5*, 15226-15232. c) J. H. Leon, K. Tanaka, Y. Chujo, *J. Mater. Chem. A* **2014**, *2*, 624-630.

[6] a) E. A. Quadrelli, J. M. Basset, *Coord. Chem. Rev.* **2010**, *254*, 707-728; b) M. C. Hung, M. V. Riofski, M. N. Minasghi, H. H. Kung, *Chem. Commun*. **2014**, *50*, 3262–3276.

[7] a) K. Tanaka, Y. Chujo, *J. Mater. Chem.* **2012**, *22*, 1733-1746; b) Tanaka, K.; Chujo, Y. *Bull. Chem. Soc. Jpn* **2013**, *86*, 1231-1239.

[8] Y. Kim, J. Roh, J. H. Kim, C. Kang-Mo, I. N. Kang, B. J. Jung, C. Lee, D. H. Hwang, *Org. Electron*. **2013**, *14*, 2315-2323.

[9] K. L. Chan, P. Sonar, A. Sellinger, *J. Mater. Chem*. **2009**, *19*, 9103-9120.

[10] Z. Wang, Y. Li, X.-H. Dong, X. Yu, K. Guo, H. Su, K. Yue, C. Wesdemiotis, S. Z. D. Cheng, W.-B. Zhang, *Chem. Sci.* **2013**, *4*, 1345–1352; b) M. J. Huang, C. H. Hsu, J. Wang, S. Mei, X. H. Dong, Y. W. Li, M. X. Li, H. Liu, W. Zhang, T. Z. Aida, W. B. Zhang, K. Yue, S. Z. D. Cheng, *Science* **2015**, *348*, 424–428; c) A. Shimojima, R. Goto, N. Atsumi, K. Kuroda, *Chem. Eur. J*. **2008**, *14*, 8500–8506.

[11] a) D. Voisin, D. Flot, A. Van der Lee, O. J. Dautel, J. J. E Moreau,. *Cryst. Eng. Comm.* **2017**, *19*, 492-502; b) Y.-C. Wu, S.-W. Kuo, *J. Mater. Chem.* **2012**, *22*, 2982-2991; c) R.-S. Shih, C.-H. Lu, S.-W. Kuo, F.-C. Chang, *J. Phys. Chem. C* **2010**, *114*, 12855-12862; d) W.-H. Hu, K.-W. Huang, C.-W. Chiou, S.-W. Kuo, *Macromolecules* **2012**, *45*, 9020-9028; e) N. Sato, Y. Kuroda, T. Abe, H. Wada, A. Shimojima, K. Kuroda, *Chem. Commun*. **2015**, *5*1, 10034-11037.

[12] A. Boullanger, G. Gracy, N. Bibent, S. Devautour-Vinot, S. Clément, A. Mehdi, *Eur. J. Inorg. Chem.* **2012**, 143-150.

[13] a) L. Li, S. Feng, H. Liu, *RSC Adv*. **2014**, *4*, 39132-39139; b) F. Du, H. Wang, Y. Bao, B. Liu, H. Zheng, R. Bai, *J. Mater. Chem*. **2011**, *21*, 10859-10864; c) S. Köytepe, V. Demirel, V. Gültek, T. Seçkin, *Polym. Int*. **2014**, *6*3, 778-787; d) Q. Xu, Z. Li, H. Li, *Cryst. Eng. Comm*. **2016**, *18*, 177-182; e) V. Carbonell, V. Binova, V. Fusaro, C. Aprile, *Inorg. Chem*. **2017**, *56*, 6393-6403; f) N. L. Dias Filho, R. M. Costa, M. S. Schultz, *Inorg. Chim. Acta* **2008,** *361*, 2314-2320.

[14] S. Banerjee, S. Kataoka, T. Takahashi, Y. Kamimura, K. Suzuki, K. Sato, A. Endo, *Dalton Trans*. **2016**, *45*, 17082-17086.

[15] a) A. Kobayashi, K. Komatsu, H. Ohara, W. Kamada, Y. Chishina, K. Tsuge, H.-C. Chang, M. Kato, *Inorg. Chem*. **2015**, *52*, 13188-13198; b) E. Cariati, E. Lucenti, C. Botta, U. Giovanella, D. Marinotto, S. Righetto, *Coord. Chem. Rev*. **2016**, *306*, 566-614.

[16] a) A. Barbieri, G. Accorsi, N.Armaroli, *Chem. Commun*. **2008**, 2185-2193; b) P. C. Ford, E. Cariati, J. Bourassa, *Chem. Rev*. **1999**, *99*, 3625-3648.

[17] L. Jiang, Z. Wang, S.-Q. Bai, T. S. Andy Hor, *Dalton Trans*. **2013**, *42*, 9437-9443.

[18] P.-Q. Liao, A.-X. Zhu, W.-X. Zhang, J.-P. Zhang, X.-M. Chen, *Nat. Commun*. **2015**, *6*, 6350.

[19] a) P. D. Harvey, M. Knorr, *J. Clust. Sci*. **2015**, *26*, 411-459; b) P. D. Harvey, M. Knorr, *J. Inorg. Organomet. Polym*. *Mat.* **2016**, *26*, 1174-1197; c) A. Raghuvanshi, N. J. Hamad; M. Knorr, L. Viau, C. Strohmann, L.Knauer, *J. Inorg. Organomet. Polym*. *Mat.* **2017**, *27*, 1501-1513; d) S. Cho, Y. Jeon, S. Lee, J. Kim, T. H. Kim, *Chem Eur. J.* **2015,** *21*, 1439-1443; e) T. H. Kim, H. Yang, G. Park, K. Y. Lee, J. Kim, *Chem. Asian J.* **2010,** *5*, 252-255; f) J. Y. Lee, S. Y. Lee, W. Sim, K.-M. Park, J. Kim, S. S Lee,. *J. Am. Chem. Soc.* **2008,** *130*, 6902-6903; g) P. R. Martinez-Alanis, V. M. Ugalde-Saldivar, I. Castillo, *Eur. J. Inorg. Chem.* **2011**, 212–220; h) S. Q. Liu, H. Konaka, T. Kuroda-Sowa, Y. Suenaga, H. Ito, G. L. Ning, M. Munakata, *Inorg. Chim. Acta* **2004,** *357*, 3621-3631.

[20] U. Dittmar, B. J. Hendan, U. Flörke, H. C. Marsmann, *J. Organomet. Chem*. **1995**, *489*, 185-194.

[21] V. Ervithayasuporn, T. Tomeechai, N. Takeda, M. Unno, A. Chaiyanurakkul, R. Hamkool, T. Osotchan, *Organometallics,* **2011***, 30,* 4475-4478.

[22] N. R. Brooks, A. J. Blake, N. R. Champness, P. A. Cooke, P. Hubberstey, D. M. Proserpio, C. Wilson, M. Schröder, *J. Chem. Soc., Dalton Trans.* **2001**, 456-465.

[23] A butterfly-shaped $S_2Cu(\mu_2\text{-}Br)_2CuS_2$ core has been encountered as SBU in the 1D CP $[\{Cu(\mu_2\text{-}Br)_2Cu\}(\mu\text{-}p\text{-}MeSC_6H_4SCH_2SC_6H_4SMe\text{-}p)_2]_n$ M. Chaabéne, A. Khatyr, M. Knorr, M. Askri, Y. Rousselin, M. M. Kubicki, *Inorg. Chim. Acta* **2016**, *451,* 177–186.

[24] M. *Z.* Heller, *Anorg, Allg. Chem.* **2006,** *632*, 441-444.

[25] a) M. Knorr*,* A. Khatyr*,* A. Dini Aleo*,* A. El Yaagoubi*,* C. Strohmann*,* M. M. Kubicki*,* Y. Rousselin*,* S. M. Aly*,* D. Fortin*,* A. Lapprand*,* P. D. Harvey*, Cryst. Growth Des*. **2014***, 14,* 5373–5387; b) M. Knorr, A. Bonnot, A. Lapprand, A. Khatyr, C. Strohmann, M. M. Kubicki, Y. Rousselin, P. D. Harvey, *Inorg. Chem*. **2015**, *54*, 4076-4093; c) A. Bonnot, M. Knorr, F. Guyon, M. M. Kubicki, Y. Rousselin, K. Strohmann, D. Fortin, P. D. Harvey, *Cryst. Growth Des*. **2016***, 16,* 774-788.

[26] R.-Y. Wang, X. Zhang, Q.- F. Yang, Q.-S. Huo, J.- H. Yu, J.- N. Xu, *J. Solid State Chem.* **2017**, *251*, 176–185.

[27] We have also recorded the X-ray structure of **CP3** at 100 K. Unfortunately, the data are of poor quality, but a mean Cu···Cu distance of 2.711 Å has been determined indicating a slight shrinkage of the Cu_4I_4 cluster.

[28] a) K. Tsuge, Y. Chishina, H. Hashiguchi, Y. Sasaki, M. Kato, S. Ishizaka, N. Kitamura, *Coord. Chem. Rev*. **2016**, 306, 636–651; b) E. Cariati, E. Lucenti, C. Botta, U. Giovanella, D. Marinotto, S. Righetto, *Coord. Chem. Rev.* **2016,** *306*, 566–614; c) A. Kobayashi, M. Kato, *Chem. Lett*. **2017**, *46*, 154-162.

[29] a) S.; Perruchas, C. Tard, X.F. Le Goff, A. Fargues, A. Garcia, S. Kahlal, J.-Y. Saillard, T. Gacoin, J.-P. Boilot, *Inorg. Chem*. **2011**, *50*, 10682-10692; b) F. D. Angelis, S. Fantacci, A. Sgamellotti, E. Cariati; R. Ugo, P. C. Ford, *Inorg. Chem.* **2006,** *45*, 10576-10584.

[30] J. J. Morrison, C. J. Love, B. W. Manson, I. J. Shannon, R. E. Morris, *J. Mat. Chem.* **2002,** *12*, 3208-3212.