

Article

Cubane Copper(I) Iodide Clusters with Remotely Functionalized Phosphine Ligands: Synthesis, Structural Characterization and Optical Properties

Damien Bissessar ¹, Thibault Thierry ¹, Julien Egly ¹, Valerio Giuso ¹ , Thierry Achard ¹ , Pascal Steffanut ², Matteo Mauro ^{1,*}  and Stéphane Bellemin-Laponnaz ^{1,*} 

¹ Institut de Physique et Chimie des Matériaux de Strasbourg, Université de Strasbourg-CNRS UMR7504, 23 Rue du Loess, BP 43, CEDEX 2, 67034 Strasbourg, France

² CLARIANT Plastics and Coatings AG, Rothausstrasse 61, 4132 Muttenz, Switzerland

* Correspondence: mauro@unistra.fr (M.M.); bellemin@unistra.fr (S.B.-L.)

Abstract: We present here the synthesis, chemical, and photophysical study of a series of three new copper halide derivatives, namely **2a–c**. They are all tetranuclear copper-iodide clusters of general formula $[\text{Cu}(\mu_3\text{-I})\text{P}]_4$ consisting of a cubane-like $\{\text{Cu}_4\text{I}_4\}$ motif and P = phosphine. They differ in the type of the phosphines used as ligands: a monophosphine with a single pendant ester unit (complex **2a**), two pendant ester units (**2b**), and a diphosphine containing two esters in the linker (**2c**). The molecular structure of the complexes was determined by single-crystal X-ray diffraction analysis. All the investigated derivatives were found to be photo- and thermally-stable luminescent species. In the solid state, the complexes display intense and long-lived photoluminescence in the orange region with PLQY values of 0.43–0.84 at room temperature associated mainly with a ³CC excited state with mixed ³XMCT character.

Keywords: copper complexes; phosphine ligands; cuprophilic interactions; photophysics; luminescence



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1. Introduction

Earth-abundant photo-active transition metal complexes are currently the subject of intensive research in inorganic photochemistry because of their potential applications in photocatalysis, solar energy conversion, and light emitting devices [1–5]. Among the metals studied, copper(I)-based emitters are certainly the ones that attract the most attention because of their many advantages. They are considered an attractive alternative to emitters containing platinum group metals for the development of (electro)luminescent materials [6–10] since copper is less toxic and cheaper than the latter.

However, the photophysical properties of Cu(I)-based emitters remain inferior to those of platinum group based complexes mainly due to the smaller spin-orbit coupling exerted by the lighter metal elements, which scales roughly with the fourth power of the atomic number. Hence, increasing efforts are being made to improve the emission properties of copper-based complexes, primarily through the design and synthesis of copper-specific ligands that can control and enhance their photophysical properties. Thus, depending on the geometry, nuclearity, and electronic properties of the ligand surrounding the metal, copper complexes can exhibit emissions derived from different excited states, namely metal-ligand charge transfer (MLCT), halide-to-ligand charge transfer (XLCT) and cluster-centered (CC) [11]. Among all the recent developments, some Cu(I) complexes possess close-lying singlet and triplet manifolds with MLCT character (^{1,3}MLCT) that enables thermally activated delayed fluorescence (TADF) mechanism with interesting application in organic light-emitting diodes (OLEDs) [12–17]. This prompts the study of the coordination chemistry of Cu(I) with the design of new ligands that can provide enhanced photophysical properties.

Multinuclear copper compounds bearing nitrogen or phosphorus ligands are also widely studied [11]. They present a polymeric or discrete structure typically formed by the assembling of $\{\text{Cu}_2\text{X}_2\}$ or $\{\text{Cu}_4\text{X}_4\}$ subunits. Copper-iodide tetranuclear clusters of the general formula $[\text{Cu}(\mu_3\text{-I})\text{P}]_4$, consisting of a $\{\text{Cu}_4\text{X}_4\}$ core and apically located ligands, have attracted major attention due to their novel photophysics, including double emission from two electronically decoupled excited states, namely a high-energy (HE) $^3\text{XLCT}$ state and a low-energy ^3CC state (LE) [18].

In the search for new copper complexes of interest, we have recently shown that phosphine ligands, which differ only in minor chemical modifications can induce profound effects on solid-state emission properties, highlighting the importance of the microenvironment for the emitters in the aggregated phase [19,20]. In continuity, we studied the coordination chemistry of three phosphine ligands. Herein, the synthesis of a phenylphosphine- and a diphenylphosphine ligand functionalized by ester moieties are reported along with their coordination on Cu(I) yielding photoactive cubane clusters. The ligands were easily obtained in one step through hydrophosphination reaction, and the corresponding copper-iodide tetranuclear clusters featuring $\{\text{Cu}_4\text{X}_4\}$ core were obtained by direct reaction with CuI and characterized by single crystal X-ray diffraction. The photophysical properties in the solid state were also studied and hereafter presented.

2. Materials and Methods

2.1. Synthesis of Ethyl 3-(Diphenylphosphanyl)propanoate 1a

A mixture of 2.0 g (10.7 mmol) of diphenyl phosphine Ph_2PH , 1.15 g (11.5 mmol) of ethyl acrylate $\text{H}_2\text{C}=\text{CHCO}_2\text{Et}$ and 2-MeTHF (4.3 mL) were placed under argon in a closed vessel. The mixture was stirred for 4 h at 90 °C. Excess of ethyl acrylate and Me-THF was then removed under reduced pressure and the remaining residue was purified by flash chromatography on silica gel (gradient from cyclohexane to cyclohexane/ethyl acetate 8:2) giving 2.9 g of colorless viscous liquid (95% yield).

^1H NMR (400 MHz, CDCl_3): δ 1.26 (t, $J = 7.1$ Hz, 3H, CH_3), 2.28 (m, 4H, $\text{CH}_2\text{CH}_2\text{P}$), 4.01 (q, $J = 7.1$ Hz, 2H, CH_2O), 7.33–7.43 (m, 6H, CH_{arom}), 7.43–7.50 (m, 4H, CH_{arom}) ppm; ^{13}C NMR (CDCl_3 , 101 MHz): δ 14.25, 23.04 (d, $J = 12$ Hz), 31.87 (d, $J = 19$ Hz), 60.64, 128.54 (d, $J = 6.5$ Hz), 128.84, 132.86 (d, $J = 19$ Hz), 137.84 (d, $J = 12.5$ Hz), 173.23 (d, $J = 15$ Hz) ppm; ^{31}P NMR (162 MHz, CDCl_3) δ : –15.64 ppm. MS (positive ESI) 287.12 m/z (%): $[\text{M}+\text{H}]^+$; FTIR: $\nu = 3072, 2980, 2872, 1731$ (CO), 1480, 1431, 1371, 1348, 1216, 1165, 1026, 732, 691 cm^{-1} .

2.2. Synthesis of Diethyl 3,3'-(Phenylphosphanediy) dipropionate 1b

A mixture of 2.00 g (18.2 mmol) of phenyl phosphine PhPH_2 , 4.00 g (39.9 mmol) of ethyl acrylate $\text{H}_2\text{C}=\text{CHCO}_2\text{Et}$ and 2-MeTHF (7.3 mL) was placed under argon in a closed vessel. The mixture was stirred for 6 h at 90 °C. Excess of ethyl acrylate and Me-THF is then removed under reduced pressure and the remaining residue was purified by flash chromatography on silica gel (gradient from cyclohexane to cyclohexane/ethyl acetate 8:2) giving 3.45 g of colorless viscous liquid (61% yield) [21].

^1H NMR (500 MHz, CDCl_3): δ 1.13 (t, $J = 7.0$ Hz, 6H), 1.94 (m, 4H), 2.25 (m, 4H), 4.01 (q, $J = 7.4$ Hz, 4H), 7.27 (m, 3H), 7.44 (m, 2H) ppm; ^{13}C NMR (CDCl_3 , 125 MHz): δ 14.19, 22.8 (d, $J = 11.0$ Hz), 30.69 (d, $J = 17.0$ Hz), 60.59, 128.63 (d, $J = 6.5$ Hz), 129.48, 132.63 (d, $J = 19$ Hz), 136.06 (d, $J = 12.5$ Hz), 173.17 (d, $J = 13.6$ Hz) ppm; ^{31}P NMR (202 MHz, CDCl_3) δ : –22.71 ppm; MS (positive ESI) 317.14 m/z (%): $[\text{M}+\text{Li}]^+$; FTIR: ν : 3067, 2978, 2905, 1730 (C=O), 1431, 1344, 1371, 1215 (C-O), 1159 (C-O), 1040, 737, 696 cm^{-1} .

2.3. Synthesis of 2,2-Dimethylpropane-1,3-diyl Bis(3-(diphenylphosphanyl)propanoate) 1c

A mixture of 2.00 g (10.7 mmol) of diphenyl phosphine Ph_2PH , 1.1 g (5.2 mmol) of diacrylate 2,2-dimethyl-1,3-propanediol and 2-MeTHF (4.3 mL) were placed under argon in a closed vessel. The mixture was stirred for 8 h at 90 °C. Excess of ethyl acrylate and Me-THF is then removed under reduced pressure and the remaining residue was purified

by flash chromatography on silica gel (cyclohexane/ethyl acetate 8:2) giving 2.6 g of white solid (84% yield).

^1H NMR (400 MHz, CDCl_3): δ 0.85 (s, 6H), 2.23–2.37 (m, 8H), 3.77 (s, 4H), 7.20–7.30 (m, 12H), 7.30–7.38 (m, 8H) ppm; ^{13}C NMR (CDCl_3 , 101 MHz): δ 21.90, 23.04 (d, $J = 12.1$ Hz), 30.76 (d, $J = 19.4$ Hz), 34.78, 69.45, 128.69 (d, $J = 6.7$ Hz), 128.96, 132.84 (d, $J = 18.7$ Hz), 137.81 (d, $J = 12.5$ Hz), 173.15 (d, $J = 15.0$ Hz) ppm; ^{31}P NMR (162 MHz, CDCl_3) δ : -15.8 ppm HRMS (positive ESI): m/z calcd. for $\text{C}_{35}\text{H}_{38}\text{O}_4\text{P}_2$ 584.2200, found 584.2207; FTIR: $\nu = 3052$, 2967, 2860, 1731 (CO), 1476, 1433, 1373, 1214, 1148, 1047, 735, 693 cm^{-1} .

2.4. Synthesis of Cluster $[\text{Cu}(\mu_3\text{-I})(\mathbf{1a})]_4$ **2a**

Copper iodide CuI (100 mg, 0.52 mmol) and ethyl 3-(diphenylphosphanyl)propanoate **1a** (141 mg, 0.55 mmol, 1.05 eq.) were placed in a flame-dried Schlenk tube under argon. A total of 5 mL of dry toluene was added and the solution was heated at 110 °C for 24 h. Then the mixture was cooled down to room temperature and the solvent was removed under vacuum. The solid residue was dissolved in a minimum of CH_2Cl_2 , filtered through a pad of silica, and the solution was poured into Et_2O . The complex precipitates directly and was filtered and washed several times with Et_2O and *n*-hexane. The product was dried under vacuum giving a colorless solid (173 mg, 70%).

^1H NMR (500 MHz, CD_3CN) δ : 7.68–7.56 (m, 16H), 7.53–7.17 (m, 24H), 4.01 (q, $^3J_{\text{H-H}} = 7.1$ Hz, 8H), 2.61–2.39 (m, 16H), 1.15 (t, $^3J_{\text{H-H}} = 7.1$ Hz, 12H). ^{13}C NMR (126 MHz, CD_3CN) δ 173.2 (d, 4C, $^3J_{\text{C-P}} = 18.3$ Hz), 134.2 (d, 8C, $^1J_{\text{C-P}} = 27.8$ Hz), 133.9 (d, 16C, $^2J_{\text{C-P}} = 13.8$ Hz), 131.0 (s, 8C), 129.6 (d, 16C, $^3J_{\text{C-P}} = 9.0$ Hz), 61.4 (4C), 30.5 (d, 4C, $^2J_{\text{C-P}} = 9.4$ Hz), 23.0 (d, 4C, $^1J_{\text{C-P}} = 19.5$ Hz), 14.5 (4C). ^{31}P NMR (202 MHz, CD_3CN) δ : -29.74 (br. s). HRMS (ESI+, m/z) $[\text{M}+\text{Na}]^+$ calculated 1928.77338 found 1928.7934. TGA: 5% weight loss at $T_{5\%} = 253$ °C. CCDC Deposition Number 2256486.

2.5. Synthesis of Cluster $[\text{Cu}(\mu_3\text{-I})(\mathbf{1b})]_4$ **2b**

Copper iodide CuI (100 mg, 0.52 mmol) and diethyl 3,3'-(phenylphosphanediy)l-dipropionate **1** (171 mg, 0.55 mmol, 1.05 eq.) were placed in a flame-dried Schlenk tube under argon. A total of 5 mL of dry toluene was added and the solution was heated at 110 °C for 24 h. Then the mixture was cooled down to the room temperature and the solvent was removed under vacuum. The solid residue was dissolved in a minimum of CH_2Cl_2 , filtered through a pad of silica and the solution was poured into Et_2O . The complex precipitates directly and was filtered and washed several times with Et_2O and *n*-hexane. The product was dried under vacuum giving a colorless solid (177 mg, 68%).

^1H NMR (500 MHz, CD_3CN) δ : 7.90–7.73 (m, 8H), 7.63–7.23 (m, 12H), 4.03 (q, $^3J_{\text{H-H}} = 7.1$ Hz, 16H), 2.72–2.44 (m, 8H), 2.48–2.13 (m, 24H), 1.18 (t, $^3J_{\text{H-H}} = 7.1$ Hz, 24H). ^{13}C NMR (126 MHz, CD_3CN) δ : 173.3 (d, 8C, $^3J_{\text{C-P}} = 15.9$ Hz), 133.8 (d, 8C, $^2J_{\text{C-P}} = 13.7$ Hz), 132.4 (d, 4C, $^1J_{\text{C-P}} = 25.3$ Hz), 131.4 (s, 4C), 129.7 (d, 8C, $^3J_{\text{C-P}} = 9.0$ Hz), 61.3 (s, 8C), 30.3 (d, 8C, $^2J_{\text{C-P}} = 6.8$ Hz), 22.5 (d, 8C, $^1J_{\text{C-P}} = 18.4$ Hz), 14.48 (s, 8C). ^{31}P NMR (202 MHz, CD_3CN) δ : -35.06 (br.s). HRMS (ESI+, m/z) $[(\text{M-Ph})+\text{Na}]^+$ calculated 1947.81882 found 1947.8169. TGA: 5% weight loss at $T_{5\%} = 252$ °C. CCDC Deposition Number 2256487.

2.6. Synthesis of Cluster $[\text{Cu}(\mu_3\text{-I})]_4(\mathbf{1c})_2$ **2c**

Copper iodide CuI (100 mg, 0.52 mmol) and 2,2-dimethylpropane–1,3-diyl bis(3-(diphenylphosphanyl)propanoate) **1c** (161 mg, 0.275 mmol, 0.5 eq.) were placed in a flame-dried Schlenk tube under argon. A total of 5 mL of dry toluene was added and the solution was heated at 110 °C for 24 h. Then the mixture was cooled down to the room temperature and the solvent was removed under vacuum. The solid residue was dissolved in a minimum of CH_2Cl_2 , filtered through a pad of silica and the solution was poured into Et_2O . The complex precipitates directly and was filtered and washed several times with Et_2O and *n*-hexane. The product was dried under vacuum giving a colorless solid (163 mg, 65%).

^1H NMR (500 MHz, CDCl_3) δ : 7.73–7.47 (m, 16H), 7.47–7.35 (m, 8H), 7.36–7.04 (m, 16H), 3.90 (s, 8H), 2.79–2.40 (m, 16H), 0.91 (s, 12H). ^{13}C NMR (126 MHz, CDCl_3) δ : 173.1 (d, 4C, $^3J_{\text{C-P}} = 20.7$ Hz), 133.4 (d, 16C, $^2J_{\text{C-P}} = 12.8$ Hz), 133.1 (d, 8C, $^1J_{\text{C-P}} = 27.5$ Hz), 129.7 (s, 8C), 128.6 (d, 16C, $^3J_{\text{C-P}} = 9.0$ Hz), 72.3 (s, 4C), 35.1 (s, 2C), 29.6 (d, 4C, $^2J_{\text{C-P}} = 9.4$ Hz), 22.8 (d, 4C, $^1J_{\text{C-P}} = 18.8$ Hz), 22.2 (s, 4C). ^{31}P NMR (202 MHz, CDCl_3) δ : –31.68 (br.s). HRMS (ESI+, m/z) $[\text{M}+\text{H}]^+$ calculated 1930.79144 found 1930.7937. TGA: 5% weight loss at $T_{5\%} = 307$ °C. CCDC Deposition Number 2256488.

2.7. X-ray Analyses

For complexes **2a** and **2b**, X-ray diffraction data collection were collected on a Nonius Kappa-CCD diffractometer, using Mo-K α radiation ($\lambda = 0.71073$ Å). The apparatus was equipped with an Oxford Cryosystem liquid N₂ device. The crystal-detector distance was 36 mm and the cell parameters were determined from reflections taken from one set of 10 frames (1.0° steps in phi angle), each at 20 s exposure (Denzo software) [22]. The structures have been solved by direct methods using the program SHELXS-2013 [23] and the refinement and all further calculations were carried out using SHELXL-2013 [24]. The H-atoms were included in the calculated positions. They were treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2 . A semi-empirical absorption correction has been applied by means of the MULscanABS routine in the PLATON [25].

For complexes **2c**, X-ray diffraction data collection was carried out on a Bruker APEX II DUO Kappa-CCD diffractometer equipped with an Oxford Cryosystem liquid N₂ device, using Mo-K α radiation ($\lambda = 0.71073$ Å). The crystal-detector distance was 38 mm. The cell parameters were determined from reflections taken from three sets of 12 frames, each at 10 s exposure (APEX2 software). The structure has been solved by direct methods using the program SHELXS-97 [26] and the refinement and all further calculations have been carried out using SHELXL-97. The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F_2 . SADABS in APEX2 was used to apply a semi-empirical absorption correction.

3. Results

3.1. Synthesis of the Phosphine Ligands **1a–c**

Phosphines **1a–c** were easily synthesized in a one-step procedure starting from diphenylphosphine (Ph_2PH) or phenylphosphine (PhPH_2) and the corresponding alkene derivative (i.e., ethyl acrylate or ethylene glycol diacrylate), according to our previously reported procedure [27]. They were prepared by hydrophosphination of the corresponding alkene compounds over the phosphine in the presence of 2-MeTHF (4 eq.) under an argon atmosphere in a closed vessel. The product was then purified by flash chromatography on silica gel using cyclohexane/ethyl acetate as eluent, with reaction yield ranging from 61% to 95% (Figure 1).

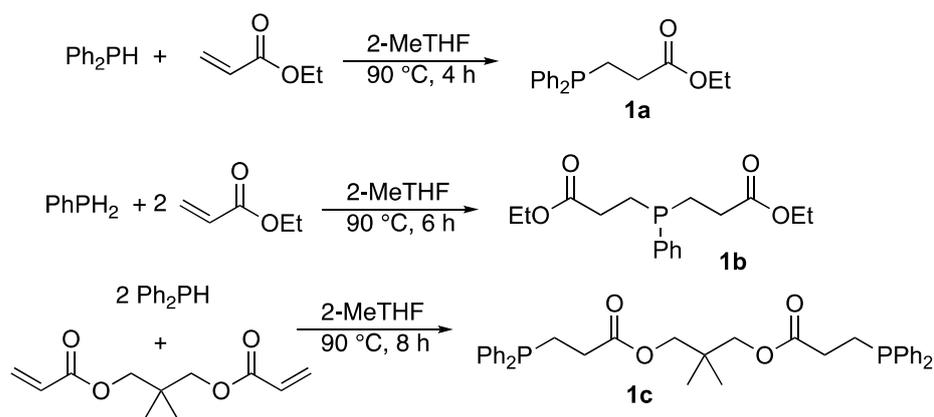
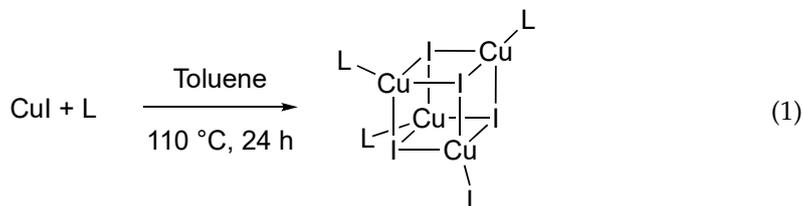


Figure 1. Synthesis of phosphine ligands **1a–c** by direct hydrophosphination of alkenes (2-MeTHF as solvent).

3.2. Synthesis and Characterization of the Cubane-like Copper Cluster **2a–c**

3.2.1. Synthesis

By reacting copper iodide with a stoichiometric amount of phosphine (**1a** or **1b**) or half an equivalent of diphosphine (**1c**), the tetrameric copper cluster was formed (Equation (1)). In all cases, the reaction was performed in dry toluene at 110 °C under controlled atmosphere (N_2) for 24 h. All products were isolated as air stable off-white solids. All compounds were characterized using classical analytical methods (Figures S1–S9 in Supplementary Materials). $^{31}P\{^1H\}$ NMR spectra showed a broad signal slightly shifted to downfield with respect to the free ligand confirming the successful formation of the copper cluster.



3.2.2. Crystal Structure of the Cubane Clusters

• Complex **2a**

Crystals of **2a** suitable for X-ray crystallography were obtained from CH_2Cl_2/n -pentane. The molecular structure of the cubane is depicted in Figure 2. Complex **2a** was crystallized in the triclinic P-1 space group and has the general formula $[Cu_4I_4L_4]$ with L being **1a**: the compound presents the classical cubane-like structure formed by 4 copper atoms and 4 iodine atoms and the phosphine ligands are coordinated to each copper atom. Therefore, all copper atoms present a pseudo-tetrahedral $PCuI_3$ geometric environment. In the structure, the Cu-I bond distances and I-Cu-I angle values are within the range of reported values for such types of compounds containing phosphorus-based ligands [28–34]. The copper cluster has a mean $Cu \cdots Cu$ distance of 2.95 Å, which is much greater than the sum of the van der Waals radii of 2.80 Å, implying weak or no cuprophilic interaction in such system [35]. We note the presence of a non-covalent inter-ligand interaction of type $C=O \cdots H-C$ between C(16) and O(7) of 2.89 Å and on the other side between C(50) and O(3) of 3.36 Å. Therefore, the ester chains interact with each other, two by two.

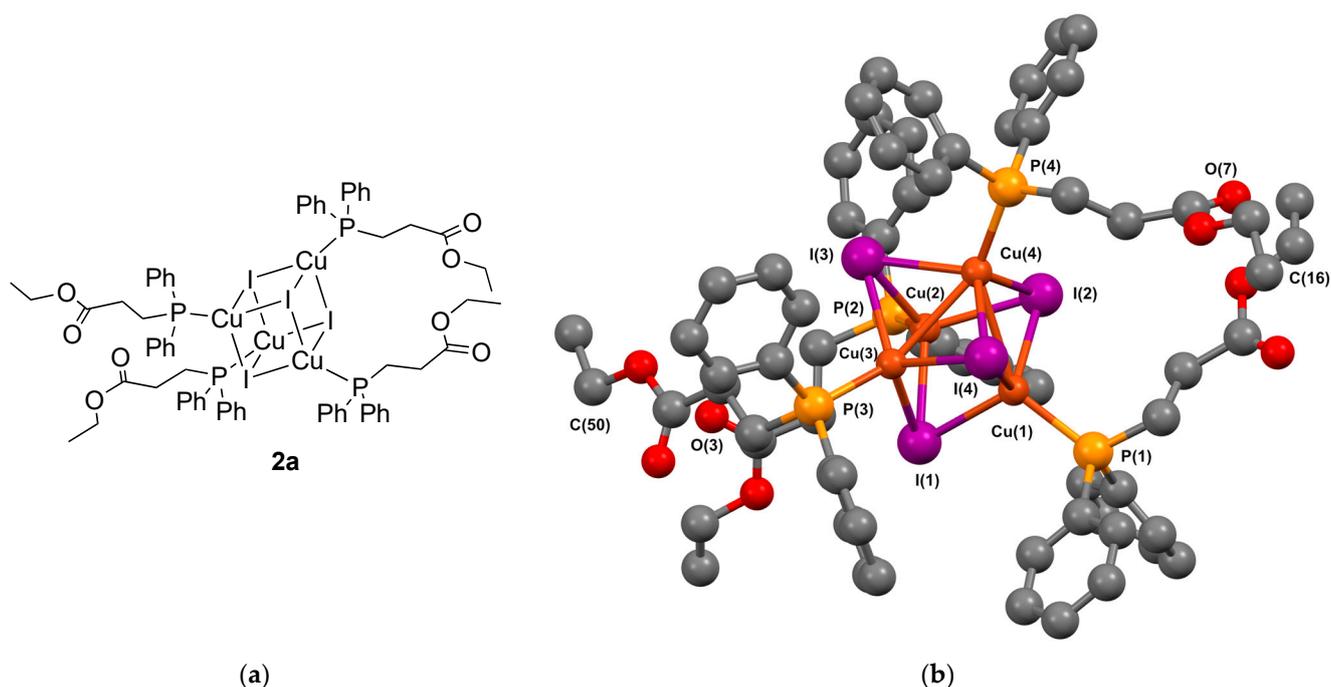


Figure 2. (a) Molecular structure of **2a**; (b) Single-crystal X-ray molecular structure of copper complex **2a**. Selected bond distances (Å) and angles (deg): Cu(1)-P(1), 2.254(2); Cu(2)-P(2), 2.256(2); Cu(3)-P(3), 2.247(2); Cu(4)-P(4), 2.253(2); Cu(1)-I(1), 2.6569(12); Cu(1)-I(4), 2.6897(11); Cu(1)-I(2), 2.7005(11); Cu(1)-I(1)-Cu(3), 65.65(3); Cu(1)-I(2)-Cu(2), 69.03(3); Cu(3)-Cu(4)-Cu(1), 61.80(4); P(1)-Cu(1)-I(1), 112.66(7); P(1)-Cu(1)-I(4), 105.63(7); I(1)-Cu(1)-I(4), 109.51(4); P(1)-Cu(1)-Cu(4)-P(4), 0.18(3).

- **Complex 2b**

Crystals of **2b** suitable for X-ray crystallography were obtained from CH_2Cl_2 /diethyl ether. The molecular structure of the cluster is depicted in Figure 3, as well as selected bond lengths and angles. Complex **2a** was crystallized in the tetragonal $P-4c2$ space group and there is $\frac{1}{4}$ molecule in the asymmetric unit. The four phosphine ligands form a highly symmetric intermolecular network forming a square in which the copper cluster is embedded. The alternating arrangement of the phosphine ligands confers an overall D_{2d} symmetry to the tetramer. Figure 4a,b provides a better visualization of the alternative entanglement of the 4 ligands with two 90° offset views. We also note weak inter-ligand interactions that should enhance the molecular rigidity of the system: an O(3)-C(11) atom distance of 2.904 Å is indicative of a $\text{C}=\text{O} \cdots \text{H}_3\text{C}$ - interaction.

Regarding the metal cluster, the Cu–I bond distances (2.70 Å) and the I–Cu–I angle mean values are comparable and within the range of reported values for this type of compound. The Cu–Cu distances are at 2.97 Å, which is also identical to the previous copper cubane **2a** and the P–Cu bond distance is 2.244 Å.

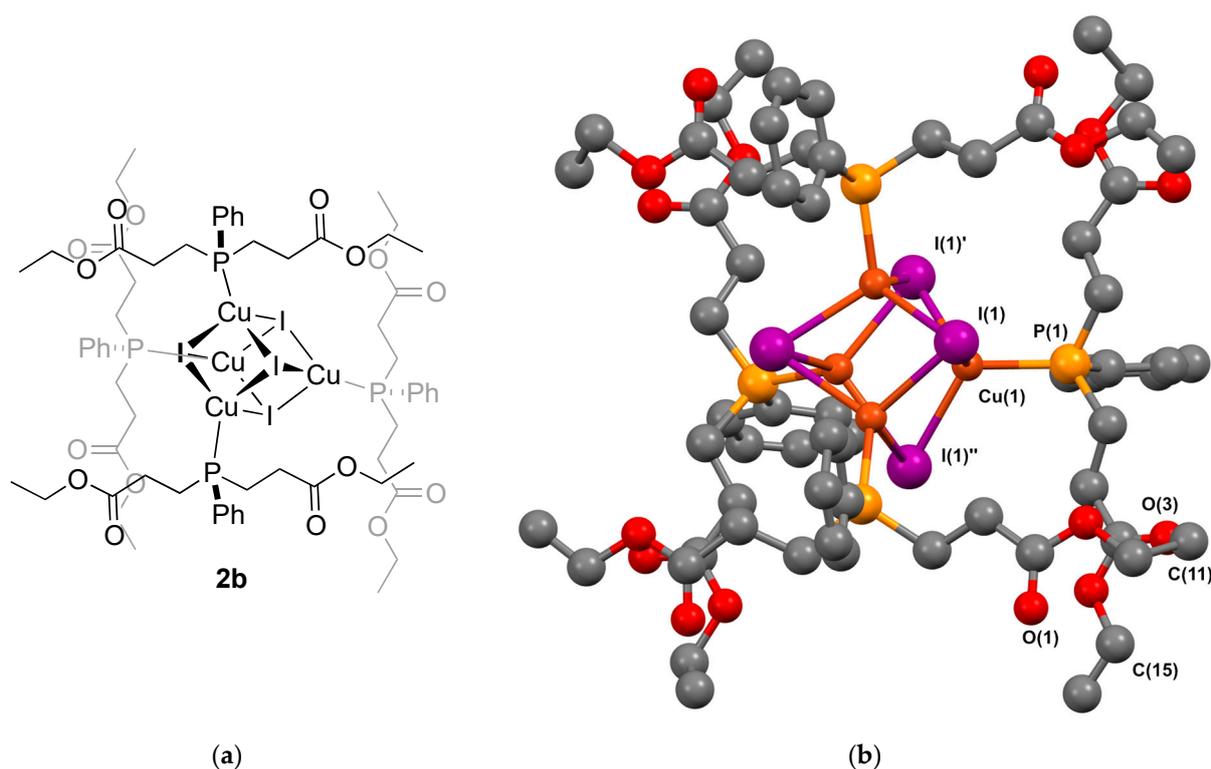


Figure 3. (a) Molecular structure of **2b**; (b) Single-crystal X-ray molecular structure of copper complex **2a**. Selected bond distances (Å) and angles (deg): Cu(1)–P(1), 2.244(2); Cu(1)–I(1), 2.7589(12); Cu(1)–I(1)', 2.6770(10); Cu(1)–I(1)'', 2.6547(10); C(11)–O(3), 2.904(10); C(15)–O(1), 3.598(13); P(1)–Cu(1)–I(1), 98.44(6); P(1)–Cu(1)–I(1)', 113.62(7); P(1)–Cu(1)–I(1)'', 118.20(7); I(1)–Cu(1)–I(1)', 110.29(4); I(1)–Cu(1)–I(1)'', 110.97(4); I(1)'–Cu(1)–I(1)'', 105.26(4); P(1)–Cu(1)–Cu(1)'–P(1)', $-33.74(3)$.

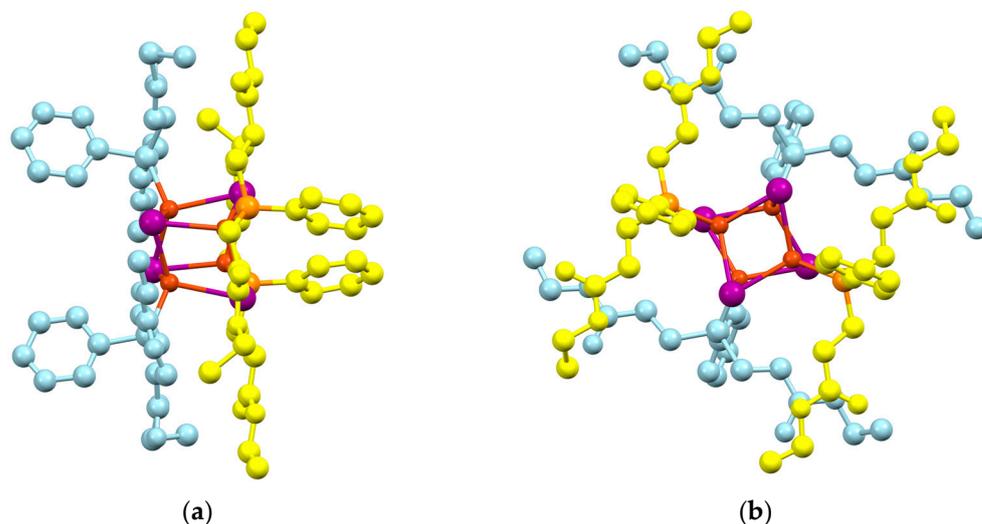


Figure 4. Single-crystal X-ray molecular structure of **2b**: (a) View through b axis; (b) View through c axis.

- **Complex 2c**

Single crystals of complex **2c** were obtained from CH_2Cl_2 /n-pentane. The molecular structure of the cubane is depicted in Figure 5. Complex **2c** was crystallized in the triclinic $P\bar{1}$ space group and shows characteristics close to the previous compounds. The diphosphine is coordinated on two adjacent copper atoms, thus forming a 16-membered cycle. The metal cluster contains an average distance between Cu–I atoms of 2.69 Å and the I–Cu–I

angle mean values are comparable and within the range of reported values for this type of compound. The Cu-Cu distances are at ca. 2.95 Å, and the P-Cu mean bond distance is 2.254 Å.

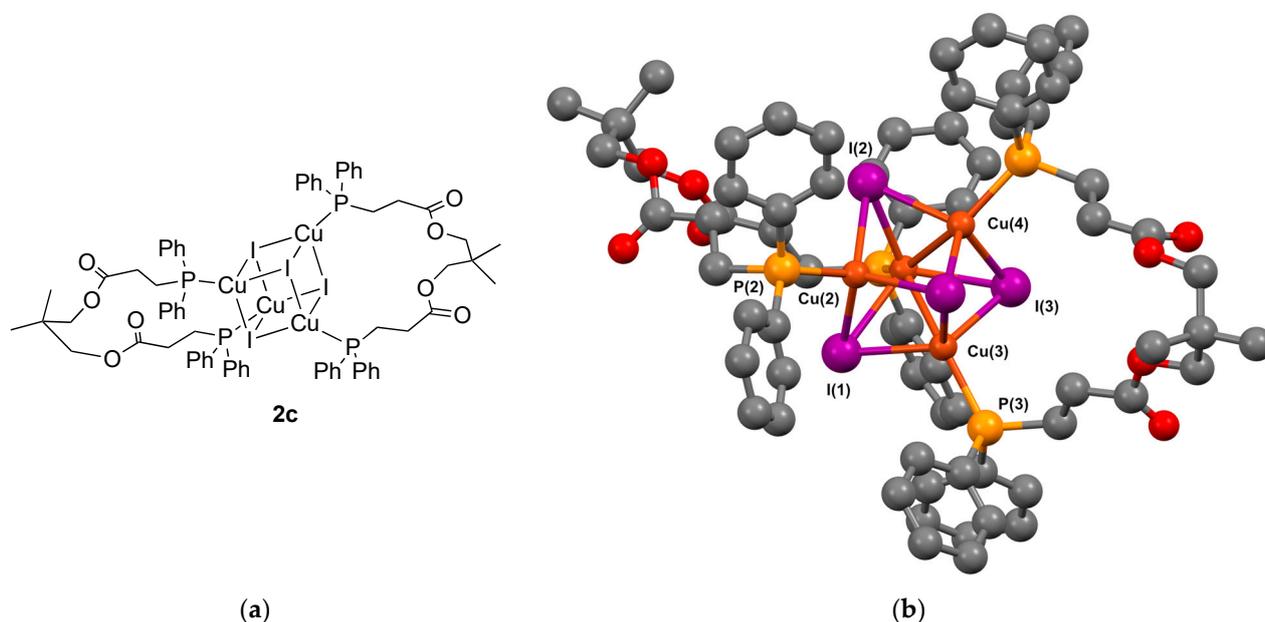


Figure 5. (a) Molecular structure of **2c**; (b) Single-crystal X-ray molecular structure of copper complex **2c**. Selected bond distances (Å) and angles (deg): Cu(2)-P(2), 2.2594(16); Cu(2)-I(1), 2.7065(8); Cu(2)-I(1), 2.6891(10); Cu(3)-P(3), 2.2565(17); Cu(1)-I(3), 2.6674(7); I(1)-Cu(3)-I(3), 113,13(3); I(1)-Cu(3)-P(3), 113,39(3); I(3)-Cu(3)-P(3), 103.47(2); P(2)-Cu(2)-I(2), 11,60(3); P(2)-Cu(2)-Cu(3)-P(3), -2.26(2).

3.3. Photophysical Characterization

No emission was detected for solution samples at room temperature, as expected, owing to the flexible nature of the overall cubane Cu-I scaffold and dynamic ligand dissociation in such conditions [8,36].

In the solid state, all three complexes show one intense and structureless yellow-orange photoluminescence with emission maximum centered at $\lambda_{em} = 569, 575,$ and 578 nm for **2a**, **2b**, and **2c**, respectively. Complex **2a** is the most emissive amongst the series with photoluminescence quantum yield (PLQY) as high as 84% in neat powder (see Table 1 and Figure 6). Compounds **2b** and **2c** have slightly lower PLQY values of 43% and 50%, respectively. Despite the absence of cuprophilic interaction, no higher energy (HE) band is observed in the region at ca. 400–480 nm surprisingly, as often observed for related cubane $[\text{Cu}_4\text{I}_4\text{L}_4]$ derivatives, where L is a either N- or P-based coordinated ligand, such as for instance substituted pyridine or phosphine [37,38]. Interestingly, time-resolved emission traces can be nicely fitted with mono-exponential decays providing an excited state lifetime in the range $\tau = 5.11\text{--}5.89$ μs . Closer analysis of the excited-state kinetic parameters yields an estimated radiative kinetic constant, k_r , of $8.4\text{--}16.2 \times 10^4 \text{ s}^{-1}$. The smaller value of the non-radiative rate constant, k_{nr} , was observed for derivative **2a** and was $3.1 \times 10^4 \text{ s}^{-1}$, giving rise to the compound with the highest PLQY value amongst the series. The linear nature of the phosphine ligand in **2a** seems to provide a less flexible and better packing motif in the solid state reducing the radiationless deexcitation pathways compared, for instance, to the compound bearing the bidentate diphosphine ligand, complex **2c**. Overall, these findings allow us to ascribe the radiative process as originating from a single excited state with main triplet cluster-centered (^3CC) with mixed copper-centered and triplet halide-to-metal charge transfer ($^3\text{XMCT}$) character in accordance with previously reported derivatives [8,36–38].

Table 1. Photophysical data of compounds **2a–c** in the solid state at room temperature.

Compound	λ_{em} [nm]	PLQY	CIE Chromaticity (<i>x</i> , <i>y</i>)	τ_{obs} [μ s]	k_r [a] [$10^4 s^{-1}$]	k_{nr} [a]
2a	569	0.84	0.40, 0.51	5.17	16.24	3.09
2b	575	0.43	0.39, 0.44	5.11	8.42	11.16
2c	578	0.50	0.42, 0.47	5.89	8.49	8.49

[a] k_r and k_{nr} were estimated by using the following equations: $k_r = PLQY/\tau$ and $k_{nr} = (1 - PLQY)/\tau$.

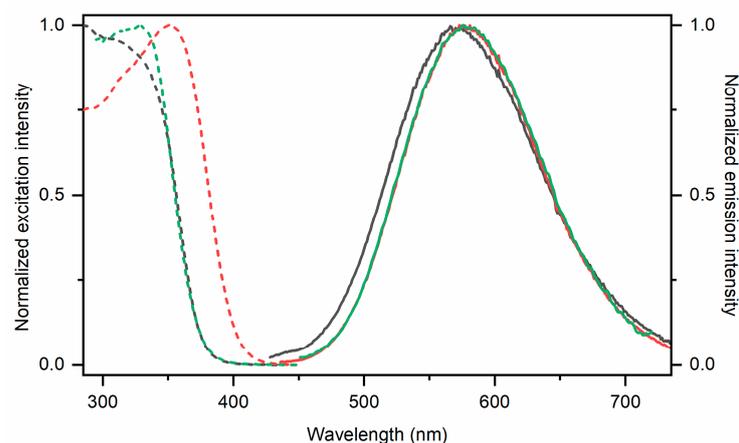


Figure 6. Excitation (dashed traces) and emission (solid traces) photoluminescence spectra of compounds **2a** (black), **2b** (red) and **2c** (green) in the solid state as neat powders. The samples were excited at $\lambda_{ex} = 380$ nm.

4. Discussion

We describe here the synthesis of three copper cubanes containing the subunit $[Cu_4I_4]$ and stabilized by phosphine ligands. The phosphines used are either monodentate or bidentate ligands and are characterized by the presence of ester functions [39]. The three complexes were fully characterized, including the determination of their molecular structure by single-crystal X-ray diffraction. Of the three molecular structures, that of complex **2b** is particularly remarkable, with the ligands arranged in high symmetry to give an overall D_{2d} symmetry to the tetramer. Interestingly, compounds **2a** and **2c** crystallize in the low-symmetry space group $P-1$ (with apparently no relation to the molecular symmetry), while compound **2b** crystallizes in the highly symmetric tetragonal space group $P-4c2$. In all three cases, the Cu-Cu intramolecular distance is greater than 2.95 Å, which is greater than the sum of the van der Waals radii of 2.80 Å. Thermogravimetric analyses (TGA) revealed that they are highly robust (Figures S10–S12 in Supplementary Materials). The monodentate phosphine-stabilized complexes **2a** and **2b** show a weight loss of 5% at 253 and 252 °C, respectively, while complex **2c** requires a temperature of 307 °C for the same weight loss, which could be correlated with the chelate effect of the diphosphine.

All three cubanes are highly luminescent in the solid state but not in solution, which is typical for this class of Cu(I) compounds, with emission that is found to be relatively independent of the nature of the phosphine capping ligand ($\lambda_{em} = ca. 570–580$ nm) and with high PLQY values ranging from 43% (**2b**) to 84% for complex **2a** (see Figure S1 in Supplementary Materials for CIE coordinates of compound **2a–2c**). Our studies also allow us to attribute the radiative process as originating from a single excited state with a mixed $^3CC/{}^3XLCT$ character. The presence of ester functions on the ligands could allow good formulation compatibility in organic polymers such as polyacrylates or polyurethanes, which can be a relevant strategy to design materials with enhanced functionalities [40–42].

5. Patents

A patent application has been filed on these results: Bissessar, D.; Bellemin-Laponnaz, S.; Steffanut, P. Tetra-nuclear copper (I) complexes with diarylphosphine ligands. 2021, US2021253611.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/sym15061210/s1>, Figures S1–S9: NMR spectra of the compounds. Figures S10–S12: TGA analyses and Figure S13: CIE coordinates of complexes **2a–c**.

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References

1. Wenger, O.S. Photoactive Complexes with Earth-Abundant Metals. *J. Am. Chem. Soc.* **2018**, *140*, 13522–13533. [[CrossRef](#)]
2. Larsen, C.B.; Wenger, O.S. Photoredox Catalysis with Metal Complexes Made from Earth-Abundant Elements. *Chem. Eur. J.* **2018**, *24*, 2039–2058. [[CrossRef](#)] [[PubMed](#)]
3. Förster, C.; Heinze, K. Photophysics and Photochemistry with Earth-Abundant Metals—Fundamentals and Concepts. *Chem. Soc. Rev.* **2020**, *49*, 1057–1070. [[CrossRef](#)] [[PubMed](#)]
4. Twilton, J.; Le, C.; Zhang, P.; Shaw, M.H.; Evans, R.W.; MacMillan, D.W.C. The Merger of Transition Metal and Photocatalysis. *Nat. Rev. Chem.* **2017**, *1*, 0052. [[CrossRef](#)]
5. Barbieri, A.; Accorsi, G.; Armaroli, N. Luminescent Complexes beyond the Platinum Group: The D10 Avenue. *Chem. Commun.* **2008**, 2185–2193. [[CrossRef](#)]
6. Armaroli, N. Photoactive Mono- and Polynuclear Cu(I)–Phenanthrolines. A Viable Alternative to Ru(II)–Polypyridines? *Chem. Soc. Rev.* **2001**, *30*, 113–124. [[CrossRef](#)]
7. Wallesch, M.; Volz, D.; Zink, D.M.; Schepers, U.; Nieger, M.; Baumann, T.; Bräse, S. Bright Coppertunities: Multinuclear Cu^I Complexes with N-P Ligands and Their Applications. *Chem. Eur. J.* **2014**, *20*, 6578–6590. [[CrossRef](#)]
8. Ford, P.C.; Cariati, E.; Bourassa, J. Photoluminescence Properties of Multinuclear Copper(I) Compounds. *Chem. Rev.* **1999**, *99*, 3625–3648. [[CrossRef](#)]
9. Kobayashi, A.; Kato, M. Stimuli-Responsive Luminescent Copper(I) Complexes for Intelligent Emissive Devices. *Chem. Lett.* **2017**, *46*, 154–162. [[CrossRef](#)]
10. Czerwieniec, R.; Leitl, M.J.; Homeier, H.H.H.; Yersin, H. Cu(I) Complexes—Thermally Activated Delayed Fluorescence. Photo-physical Approach and Material Design. *Coord. Chem. Rev.* **2016**, *325*, 2–28. [[CrossRef](#)]
11. Troyano, J.; Zamora, F.; Delgado, S. Copper(I)–Iodide Cluster Structures as Functional and Processable Platform Materials. *Chem. Soc. Rev.* **2021**, *50*, 4606–4628. [[CrossRef](#)] [[PubMed](#)]
12. Hamze, R.; Peltier, J.L.; Sylvinson, D.; Jung, M.; Cardenas, J.; Haiges, R.; Soleilhavoup, M.; Jazzar, R.; Djurovich, P.I.; Bertrand, G.; et al. Eliminating Nonradiative Decay in Cu(I) Emitters: >99% Quantum Efficiency and Microsecond Lifetime. *Science* **2019**, *363*, 601–606. [[CrossRef](#)] [[PubMed](#)]
13. Zhang, J.; Duan, C.; Han, C.; Yang, H.; Wei, Y.; Xu, H. Balanced Dual Emissions from Tridentate Phosphine-Coordinate Copper(I) Complexes toward Highly Efficient Yellow OLEDs. *Adv. Mater.* **2016**, *28*, 5975–5979. [[CrossRef](#)]
14. Shi, S.; Jung, M.C.; Coburn, C.; Tadde, A.; Daniel Sylvinson, M.R.; Djurovich, P.I.; Forrest, S.R.; Thompson, M.E. Highly Efficient Photo- and Electroluminescence from Two-Coordinate Cu(I) Complexes Featuring Nonconventional N-Heterocyclic Carbenes. *J. Am. Chem. Soc.* **2019**, *141*, 3576–3588. [[CrossRef](#)]
15. Elie, M.; Sguerra, F.; Di Meo, F.; Weber, M.D.; Marion, R.; Grimault, A.; Lohier, J.-F.; Stallivieri, A.; Brosseau, A.; Pansu, R.B.; et al. Designing NHC–Copper(I) Dipyriddyamine Complexes for Blue Light-Emitting Electrochemical Cells. *ACS Appl. Mater. Interfaces* **2016**, *8*, 14678–14691. [[CrossRef](#)] [[PubMed](#)]

16. Zink, D.M.; Volz, D.; Baumann, T.; Mydlak, M.; Flügge, H.; Friedrichs, J.; Nieger, M.; Bräse, S. Heteroleptic, Dinuclear Copper(I) Complexes for Application in Organic Light-Emitting Diodes. *Chem. Mater.* **2013**, *25*, 4471–4486. [[CrossRef](#)]
17. Au, V.K.-M. Organic Light-Emitting Diodes Based on Luminescent Self-Assembled Materials of Copper(I). *Energy Fuels* **2021**, *35*, 18982–18999. [[CrossRef](#)]
18. Perruchas, S. Molecular Copper Iodide Clusters: A Distinguishing Family of Mechanochromic Luminescent Compounds. *Dalton Trans.* **2021**, *50*, 12031–12044. [[CrossRef](#)]
19. Egly, J.; Bissessar, D.; Achard, T.; Heinrich, B.; Steffanut, P.; Mauro, M.; Bellemin-Laponnaz, S. Copper(I) Complexes with Remotely Functionalized Phosphine Ligands: Synthesis, Structural Variety, Photophysics and Effect onto the Optical Properties. *Inorg. Chim. Acta* **2021**, *514*, 119971. [[CrossRef](#)]
20. Bissessar, D.; Egly, J.; Achard, T.; Steffanut, P.; Mauro, M.; Bellemin-Laponnaz, S. A Stable and Photoreactive Copper-Iodide Cubane Suitable for Direct Post-Functionalization. *Eur. J. Inorg. Chem.* **2022**, *2022*, e202200101. [[CrossRef](#)]
21. Wolfsberger, W.; Bank, J.; Werner, H. Synthese Dreizähliger Phosphanliganden $RP[(CH_2)_n]_2$ ($Y = OR'$ Oder CO_2R' , $n = 1$ Oder 2) Sowie Einiger Zweizähliger Chiraler Phosphane $R_2PCH(CH_3)CO_2Me$ /Synthesis of Tridentate Phosphine Ligands $RP[(CH_2)_nY]_2$ ($Y = OR'$ or CO_2R' , $n = 1$ or 2) and Some Bidentate Chiral Phosphines $R_2PCH(CH_3)CO_2Me$. *Z. Nat. B* **1995**, *50*, 1319–1328. [[CrossRef](#)]
22. *Kappa CCD Operation Manual*; Nonius B.V.: Delft, The Netherlands, 1997.
23. Sheldrick, G.M. Phase Annealing in SHELX-90: Direct Methods for Larger Structures. *Acta Crystallogr. Sect. A Found. Crystallogr.* **1990**, *46*, 467–473. [[CrossRef](#)]
24. Sheldrick, G.M. A Short History of SHELX. *Acta Crystallogr. Sect. A Found. Crystallogr.* **2008**, *64*, 112–122. [[CrossRef](#)] [[PubMed](#)]
25. Spek, A.L. Single-Crystal Structure Validation with the Program PLATON. *J. Appl. Crystallogr.* **2003**, *36*, 7–13. [[CrossRef](#)]
26. Sheldrick, G. *SHELXL-97*; Universität Göttingen: Göttingen, Germany, 1999.
27. Bissessar, D.; Egly, J.; Achard, T.; Steffanut, P.; Bellemin-Laponnaz, S. Catalyst-Free Hydrophosphination of Alkenes in Presence of 2-Methyltetrahydrofuran: A Green and Easy Access to a Wide Range of Tertiary Phosphines. *RSC Adv.* **2019**, *9*, 27250–27256. [[CrossRef](#)]
28. Huitorel, B.; El Moll, H.; Utrera-Melero, R.; Cordier, M.; Fargues, A.; Garcia, A.; Massuyeau, F.; Martineau-Corcoc, C.; Fayon, F.; Rakhmatullin, A.; et al. Evaluation of Ligands Effect on the Photophysical Properties of Copper Iodide Clusters. *Inorg. Chem.* **2018**, *57*, 4328–4339. [[CrossRef](#)]
29. Utrera-Melero, R.; Massuyeau, F.; Latouche, C.; Camerel, F.; Perruchas, S. Copper Iodide Clusters Coordinated by Emissive Cyanobiphenyl-Based Ligands. *Inorg. Chem.* **2022**, *61*, 4080–4091. [[CrossRef](#)]
30. Kitagawa, H.; Ozawa, Y.; Toriumi, K. Flexibility of Cubane-like Cu_4I_4 Framework: Temperature Dependence of Molecular Structure and Luminescence Thermochromism of $[Cu_4I_4(PPh_3)_4]$ in Two Polymorphic Crystalline States. *Chem. Commun.* **2010**, *46*, 6302. [[CrossRef](#)]
31. Benito, Q.; Fargues, A.; Garcia, A.; Maron, S.; Gacoin, T.; Boilot, J.-P.; Perruchas, S.; Camerel, F. Photoactive Hybrid Gelators Based on a Luminescent Inorganic $[Cu_4I_4]$ Cluster Core. *Chem. Eur. J.* **2013**, *19*, 15831–15835. [[CrossRef](#)]
32. Benito, Q.; Maurin, I.; Cheisson, T.; Nocton, G.; Fargues, A.; Garcia, A.; Martineau, C.; Gacoin, T.; Boilot, J.-P.; Perruchas, S. Mechanochromic Luminescence of Copper Iodide Clusters. *Chem. Eur. J.* **2015**, *21*, 5892–5897. [[CrossRef](#)]
33. Cariati, E.; Lucenti, E.; Botta, C.; Giovanella, U.; Marinotto, D.; Righetto, S. Cu(I) Hybrid Inorganic–Organic Materials with Intriguing Stimuli Responsive and Optoelectronic Properties. *Coord. Chem. Rev.* **2016**, *306*, 566–614. [[CrossRef](#)]
34. Perruchas, S.; Le Goff, X.F.; Maron, S.; Maurin, I.; Guillen, F.; Garcia, A.; Gacoin, T.; Boilot, J.-P. Mechanochromic and Thermochromic Luminescence of a Copper Iodide Cluster. *J. Am. Chem. Soc.* **2010**, *132*, 10967–10969. [[CrossRef](#)] [[PubMed](#)]
35. Bondi, A. Van Der Waals Volumes and Radii. *J. Phys. Chem.* **1964**, *68*, 441–451. [[CrossRef](#)]
36. Tsuge, K.; Chishina, Y.; Hashiguchi, H.; Sasaki, Y.; Kato, M.; Ishizaka, S.; Kitamura, N. Luminescent Copper(I) Complexes with Halogenido-Bridged Dimeric Core. *Coord. Chem. Rev.* **2016**, *306*, 636–651. [[CrossRef](#)]
37. Perruchas, S.; Tard, C.; Le Goff, X.F.; Fargues, A.; Garcia, A.; Kahlal, S.; Saillard, J.-Y.; Gacoin, T.; Boilot, J.-P. Thermochromic Luminescence of Copper Iodide Clusters: The Case of Phosphine Ligands. *Inorg. Chem.* **2011**, *50*, 10682–10692. [[CrossRef](#)] [[PubMed](#)]
38. Kyle, K.R.; Ryu, C.K.; Ford, P.C.; DiBenedetto, J.A. Photophysical Studies in Solution of the Tetranuclear Copper(I) Clusters $Cu_4I_4L_4$ ($L =$ Pyridine or Substituted Pyridine). *J. Am. Chem. Soc.* **1991**, *113*, 2954–2965. [[CrossRef](#)]
39. Yin, S.-Y.; Wang, Z.; Liu, Z.-M.; Yu, H.-J.; Zhang, J.-H.; Wang, Y.; Mao, R.; Pan, M.; Su, C.-Y. Multiresponsive UV-One-Photon Absorption, Near-Infrared-Two-Photon Absorption, and X/ γ -Photoelectric Absorption Luminescence in One $[Cu_4I_4]$ Compound. *Inorg. Chem.* **2019**, *58*, 10736–10742. [[CrossRef](#)]
40. Liu, W.; Fang, Y.; Li, J. Copper Iodide Based Hybrid Phosphors for Energy-Efficient General Lighting Technologies. *Adv. Funct. Mater.* **2018**, *28*, 1705593. [[CrossRef](#)]

41. Baranov, A.Y.; Pritchina, E.A.; Berezin, A.S.; Samsonenko, D.G.; Fedin, V.P.; Belogorlova, N.A.; Gritsan, N.P.; Artem'ev, A.V. Beyond Classical Coordination Chemistry: The First Case of a Triply Bridging Phosphine Ligand. *Angew. Chem. Int. Ed.* **2021**, *60*, 12577–12584. [[CrossRef](#)]
42. Baranov, A.Y.; Rakhmanova, M.I.; Hei, X.; Samsonenko, D.G.; Stass, D.V.; Bagryanskaya, I.Y.; Ryzhikov, M.R.; Fedin, V.P.; Li, J.; Artem'ev, A.V. A New Subclass of Copper(I) Hybrid Emitters Showing TADF with near-Unity Quantum Yields and a Strong Solvatochromic Effect. *Chem. Commun.* **2023**, *59*, 2923–2926. [[CrossRef](#)]

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