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Cubane copper(I) iodide clusters with remotely functionalized phosphine ligands: synthesis, structural characterization and optical properties.

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Abstract: The synthesis, chemical and photophysical investigation of a series of three novel copper-halide derivatives is herein presented, 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 $\{\text{Cu}_4\text{X}_4\}$ 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**). X-ray diffraction analysis on single crystal was used to determine the molecular structure of the complexes. 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 to a $^3\text{CC}/^3\text{XLCT}$ excited state.

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

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 as 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-based systems 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 emission properties of copper-based complexes, primarily through design and synthesis of copper-specific ligands that can control and enhance its 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 ($^1,^3\text{MLCT}$) 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 $[\text{Cu}(\mu_3\text{-I})\text{L}]_4$, 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 demonstrated that phosphine ligands that differ only in small chemical modifications can induce profound effects on solid-state emission properties, highlighting the importance of 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 is 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. General Remarks

All the manipulations of the air- and moisture-sensitive compounds were carried out using standard Schlenk techniques under an argon atmosphere and the solvents were purified and degassed following standard procedures. All the reagents were purchased from commercial chemical suppliers (Acros (Illkirch, France), Alfa Aesar (Lancashire, UK), and TCI Europe (Paris, France)) and used without further purification. ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AVANCE 300 or Bruker AVANCE 500 spectrometer (Bruker, Wissembourg, France) using the residual solvent peak as a reference (CDCl_3 : $\delta_{\text{H}} = 7.26$ ppm; $\delta_{\text{C}} = 77.16$ ppm) at 295 K. Positive mode electrospray ionization mass spectra (ESI-HRMS) analyses were carried out on a microTOF Bruker Daltonics (Bruker, Wissembourg, France).

Steady-state emission spectra were recorded on a Horiba Jobin-Yvon IBH FL-322 Fluorolog 3 spectrometer equipped with a 450 W xenon arc lamp, double-grating excitation, and emission monochromators (2.1 nm mm^{-1} of dispersion; 1200 grooves mm^{-1}) and a Hamamatsu R13456 red sensitive Peltier-cooled PMT detector. Emission and excitation spectra were corrected for source intensity (lamp and grating) and emission spectral response (detector and grating) by standard correction curves. Time-resolved measurements were performed using the time-correlated single-photon counting (TCSPC) electronics option of the TimeHarp 260 board installed on a PicoQuant FluoTime 300 fluorimeter (PicoQuant GmbH, Germany), equipped with a PDL 820 laser pulse driver. A pulsed laser diode LDH-P-C-375 ($\lambda = 375$ nm, pulse full width at half maximum FWHM <50 ps, repetition rate 200 kHz– 40 MHz) was used to excite the sample and mounted directly on the sample chamber at 90° . The photons were collected by a PMA Hybrid-07 single photon counting detector. The data were acquired by using the commercially available software EasyTau II (PicoQuant GmbH, Germany), while data analysis was performed using the built-in software FluoFit (PicoQuant GmbH, Germany).

For time resolved measurements, data fitting was performed by employing the maximum likelihood estimation (MLE) methods and the quality of the fit was assessed by inspection of the reduced χ^2 function and of the weighted residuals. The absolute photoluminescence quantum yields (PLQY) were measured on a Hamamatsu Quantaurus-QY C11347-11 integrating sphere in air-equilibrated condition using an empty quartz tube as the reference upon excitation at $\lambda_{\text{exc}} = 320$ nm.

2.2. Synthesis of ethyl 3-(diphenylphosphanyl)propanoate **1a**

A mixture of 2.0 g (10.7 mmol) of diphenyl phosphine Ph₂PH, 1.15 g (11.5 mmol) of ethyl acrylate H₂C=CHCO₂Et and 2-MeTHF (4.3 mL) were placed under argon in a closed vessel. The mixture was stirred during 4 hours at 90°C. Excess of ethyl acrylate and MeTHF 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 colourless viscous liquid (95% yield).

¹H NMR (400 MHz, CDCl₃): δ 1.26 (t, *J* = 7.1 Hz, 3H, CH₃), 2.28 (m, 4H, CH₂CH₂P), 4.01 (q, *J* = 7.1 Hz, 2H, CH₂O), 7.33-7.43 (m, 6H, CH_{arom}), 7.43-7.50 (m, 4H, CH_{arom}) ppm; ¹³C NMR (CDCl₃, 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; ³¹P NMR (162 MHz, CDCl₃) δ: -15.64 ppm. MS (positive ESI) 287.12 *m/z* (%): [M+H]⁺; FTIR: ν = 3072, 2980, 2872, 1731 (CO), 1480, 1431, 1371, 1348, 1216, 1165, 1026, 732, 691 cm⁻¹.

2.3. Synthesis of diethyl 3,3'-(phenylphosphanediyl)dipropionate **1b**

A mixture of 2.00 g (18.2 mmol) of phenyl phosphine PhPH₂, 4.00 g (39.9 mmol) of ethyl acrylate H₂C=CHCO₂Et and 2-MeTHF (7.3 mL) were placed under argon in a closed vessel. The mixture was stirred during 6 hours at 90°C. Excess of ethyl acrylate and MeTHF 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 colourless viscous liquid (61% yield). [21]

¹H NMR (500 MHz, CDCl₃): 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; ¹³C NMR (CDCl₃, 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; ³¹P NMR (202 MHz, CDCl₃) δ: -22.71 ppm; MS (positive ESI) 317.14 *m/z* (%): [M+Li]⁺; FTIR: ν : 3067, 2978, 2905, 1730 (C=O), 1431, 1344, 1371, 1215 (C-O), 1159 (C-O), 1040, 737, 696 cm⁻¹.

2.4. 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 Ph₂PH, 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 during 8 hours 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, CDCl₃): 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; ¹³C NMR (CDCl₃, 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; ³¹P NMR (162 MHz, CDCl₃) δ: -15.8 ppm HRMS (positive ESI): *m/z* calcd. for C₃₅H₃₈O₄P₂ 584.2200, found 584.2207; FTIR: ν = 3052, 2967, 2860, 1731 (CO), 1476, 1433, 1373, 1214, 1148, 1047, 735, 693 cm⁻¹.

2.5. Synthesis of cluster [Cu(μ₃-I)(**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. 5 mL of dry toluene were added and the solution was heated at 110°C during 24 hours. 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 CH₂Cl₂, filtered through a pad of silica and the solution was poured into Et₂O. The complex precipitates directly and was filtered and washed several times with Et₂O and *n*-hexane. The product was dried under vacuum giving a colourless solid (173 mg, 70%).

¹H NMR (500 MHz, CD₃CN) δ: 7.68 – 7.56 (m, 16H), 7.53 – 7.17 (m, 24H), 4.01 (q, ³*J*_{H-H} = 7.1 Hz, 8H), 2.61 – 2.39 (m, 16H), 1.15 (t, ³*J*_{H-H} = 7.1 Hz, 12H). ¹³C NMR (126 MHz, CD₃CN) δ 173.2 (d, 4C, ³*J*_{C-P} = 18.3 Hz), 134.2 (d, 8C, ¹*J*_{C-P} = 27.8 Hz), 133.9 (d, 16C, ²*J*_{C-P} = 13.8 Hz),

131.0 (s, 8C), 129.6 (d, 16C, $^3J_{C-P} = 9.0$ Hz), 61.4 (4C), 30.5 (d, 4C, $^2J_{C-P} = 9.4$ Hz), 23.0 (d, 4C, $^1J_{C-P} = 19.5$ 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.

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

Copper iodide CuI (100 mg, 0.52 mmol) and diethyl 3,3'-(phenylphosphanediy)-dipropionate **1** (171 mg, 0.55 mmol, 1.05 eq.) were placed in a flame-dried Schlenk tube under argon. 5 mL of dry toluene were added and the solution was heated at 110°C during 24 hours. 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 bed 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 colourless 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, $^3J_{H-H} = 7.1$ Hz, 16H), 2.72 – 2.44 (m, 8H), 2.48 – 2.13 (m, 24H), 1.18 (t, $^3J_{H-H} = 7.1$ Hz, 24H). ^{13}C NMR (126 MHz, CD_3CN) δ : 173.3 (d, 8C, $^3J_{C-P} = 15.9$ Hz), 133.8 (d, 8C, $^2J_{C-P} = 13.7$ Hz), 132.4 (d, 4C, $^1J_{C-P} = 25.3$ Hz), 131.4 (s, 4C), 129.7 (d, 8C, $^3J_{C-P} = 9.0$ Hz), 61.3 (s, 8C), 30.3 (d, 8C, $^2J_{C-P} = 6.8$ Hz), 22.5 (d, 8C, $^1J_{C-P} = 18.4$ 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.

2.7. Synthesis of cluster $[\text{Cu}(\mu_3\text{-I})(\mathbf{1c})_4] \mathbf{2c}$

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. 5 mL of dry toluene were added and the solution was heated at 110°C during 24 hours. 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 bed 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 colourless 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, $^3J_{C-P} = 20.7$ Hz), 133.4 (d, 16C, $^2J_{C-P} = 12.8$ Hz), 133.1 (d, 8C, $^1J_{C-P} = 27.5$ Hz), 129.7 (s, 8C), 128.6 (d, 16C, $^3J_{C-P} = 9.0$ Hz), 72.3 (s, 4C), 35.1 (s, 2C), 29.6 (d, 4C, $^2J_{C-P} = 9.4$ Hz), 22.8 (d, 4C, $^1J_{C-P} = 18.8$ 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.

2.8. X-ray analyses

For complexes **2a** and **2b**, X-ray diffraction data collection was carried out on a Nonius Kappa-CCD diffractometer equipped with an Oxford Cryosystem liquid N_2 device, using Mo-K α radiation ($\lambda = 0.71073$ Å). The crystal-detector distance was 36 mm. The cell parameters were determined (Denzo software) from reflections taken from one set of 10 frames (1.0° steps in phi angle), each at 20 seconds exposure [22]. The structures were solved by direct methods using the program SHELXS-2013 [23]. The refinement and all further calculations were carried out using SHELXL-2013 [24]. 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 . A semi-empirical absorption correction was applied using the MULscanABS routine in 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 N_2

device, using Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). The crystal-detector distance was 38 mm. The cell parameters were determined (APEX2 software) from reflections taken from three sets of 12 frames, each at 10 seconds exposure. The structure was solved by direct methods using the program SHELXS-97 [26]. The refinement and all further calculations were 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 F². A semi-empirical absorption correction was applied using SADABS in APEX2.

3. Results

3.1. Synthesis of the phosphine ligands **1a-c**

Phosphines **1a-c** were easily synthesized in 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 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).

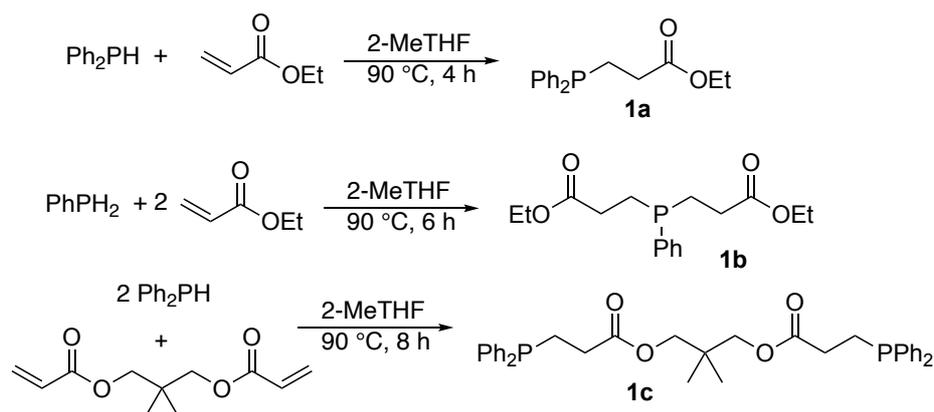
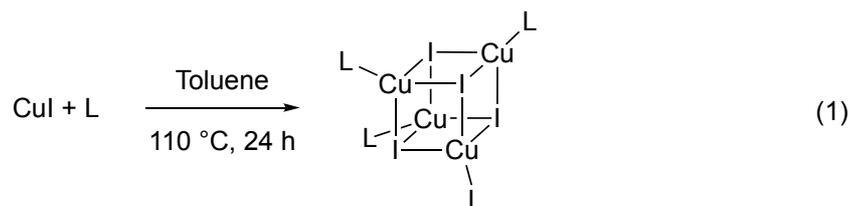


Figure 1. Catalyst-free hydrophosphination of alkenes in the presence of 4 equiv. of 2-MeTHF: synthesis of phosphine ligands **1a-c**.

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 (eq. 1). In all cases, the reaction was performed in dry toluene at 110 °C under controlled atmosphere (N_2) for 24 hours. All products were isolated as air stable off-white solids. All compounds were characterized using classical analytical methods. $^{31}\text{P}\{^1\text{H}\}$ 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 $\text{CH}_2\text{Cl}_2/n$ -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 $[\text{Cu}_4\text{I}_4\text{L}_4]$ 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 type of compound containing phosphorus-based ligands.[28–34] The copper cluster has a mean $\text{Cu}\cdots\text{Cu}$ 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 $\text{C}=\text{O}\cdots\text{H}-\text{C}$ 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.

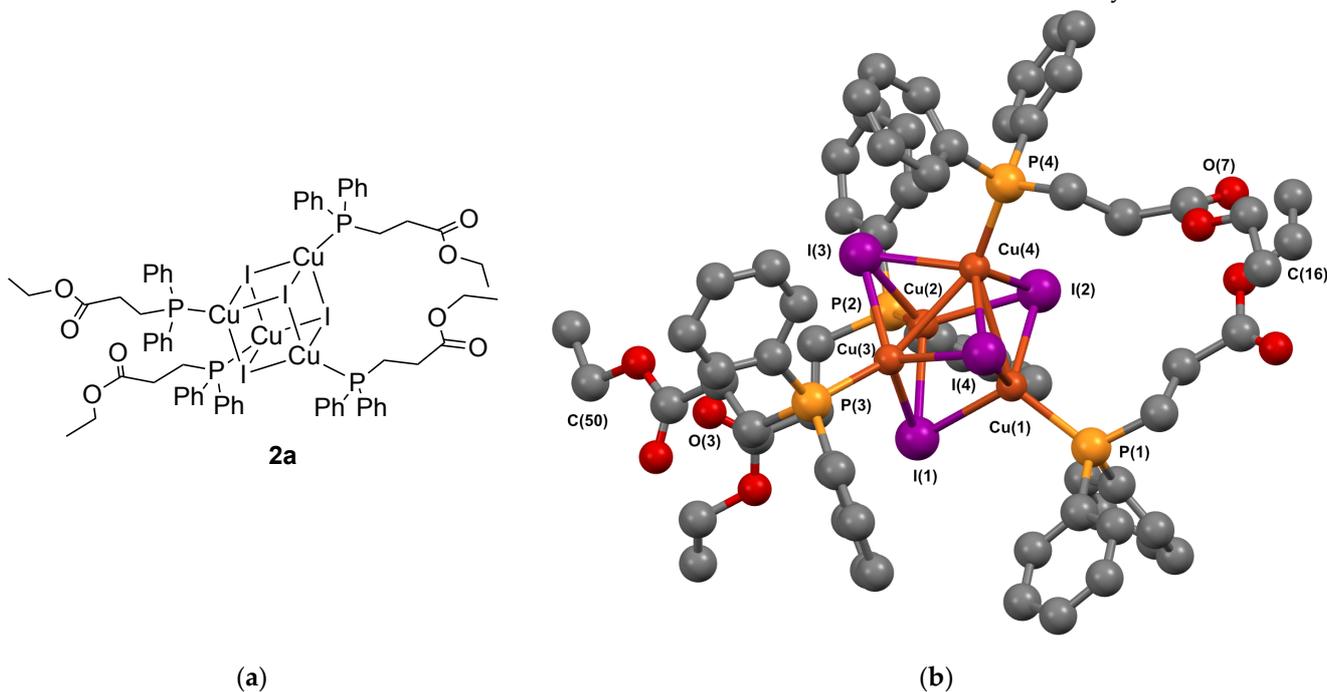


Figure 2. (a) Molecular structure of **2a**; (b) Single-crystal X-ray molecular structure of copper complex **2a**. Selected bond distances (Å) and angles (deg): Cu(1)-P(1), 2.254(2); Cu(2)-P(2), 2.256(2); Cu(3)-P(3), 2.247(2); Cu(4)-P(4), 2.253(2); Cu(1)-I(1), 2.6569(12); Cu(1)-I(4), 2.6897(11); Cu(1)-I(2), 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 CH₂Cl₂/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 ¼ 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. Figures 4a and 4b provide 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: a O(3)-C(11) atom distance of 2.904 Å is indicative of a C=O···H₃C- interaction.

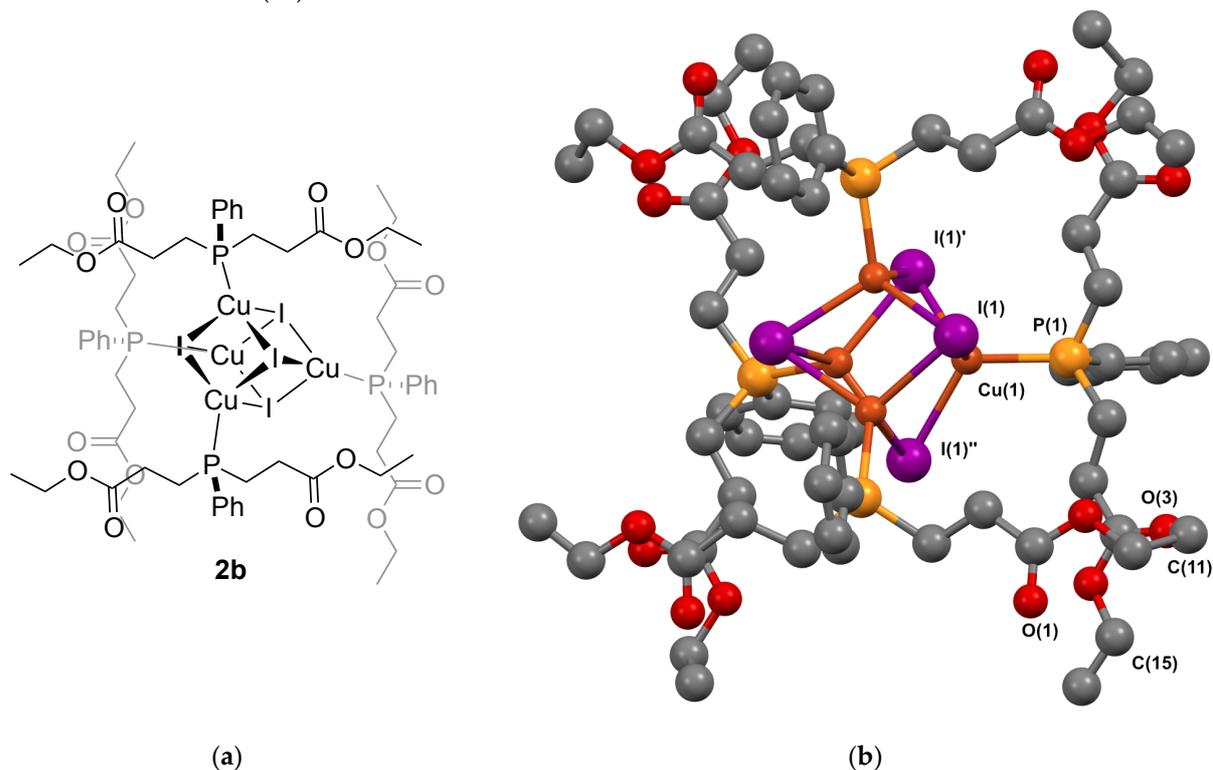


Figure 3. (a) Molecular structure of **2b**; (b) Single-crystal X-ray molecular structure of copper complex **2a**. Selected bond distances (Å) and angles (deg): Cu(1)-P(1), 2.244(2); Cu(1)-I(1), 2.7589(12); Cu(1)-I(1)', 2.6770(10); Cu(1)-I(1)'', 2.6547(10); C(11)-O(3), 2.904(10); C(15)-O(1), 3.598(13);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

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 bond 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.

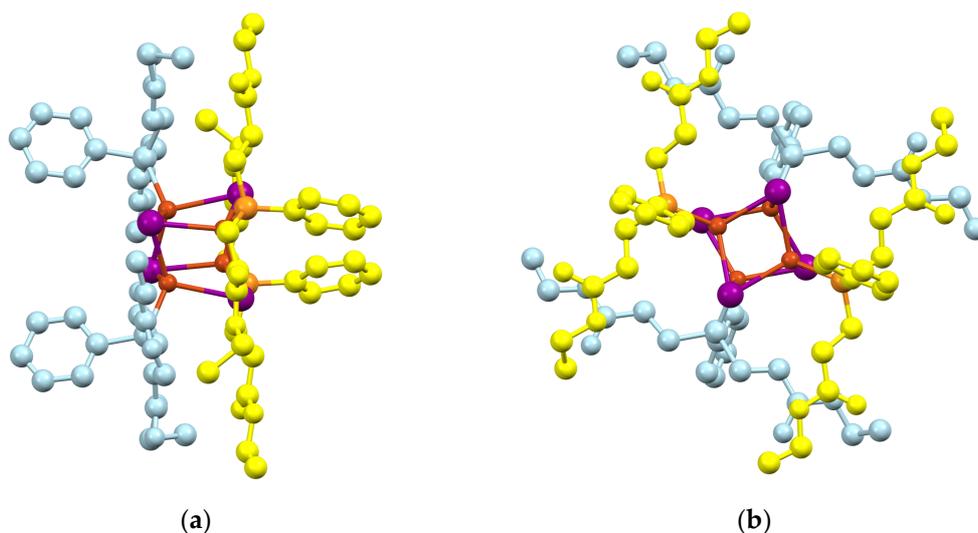


Figure 4. Single-crystal X-ray molecular structure of **2b**: (a) View through b axis; (b) View through c axis.

- Complex **2c**

Single crystals of complex **2c** were obtained from $\text{CH}_2\text{Cl}_2/n$ -pentane. The molecular structure of the cubane is depicted in Figure 5. Complex **2a** was crystallized in the triclinic P-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 bond distances are at ca. 2.95 Å, and the P-Cu mean bond distance is 2.254 Å.

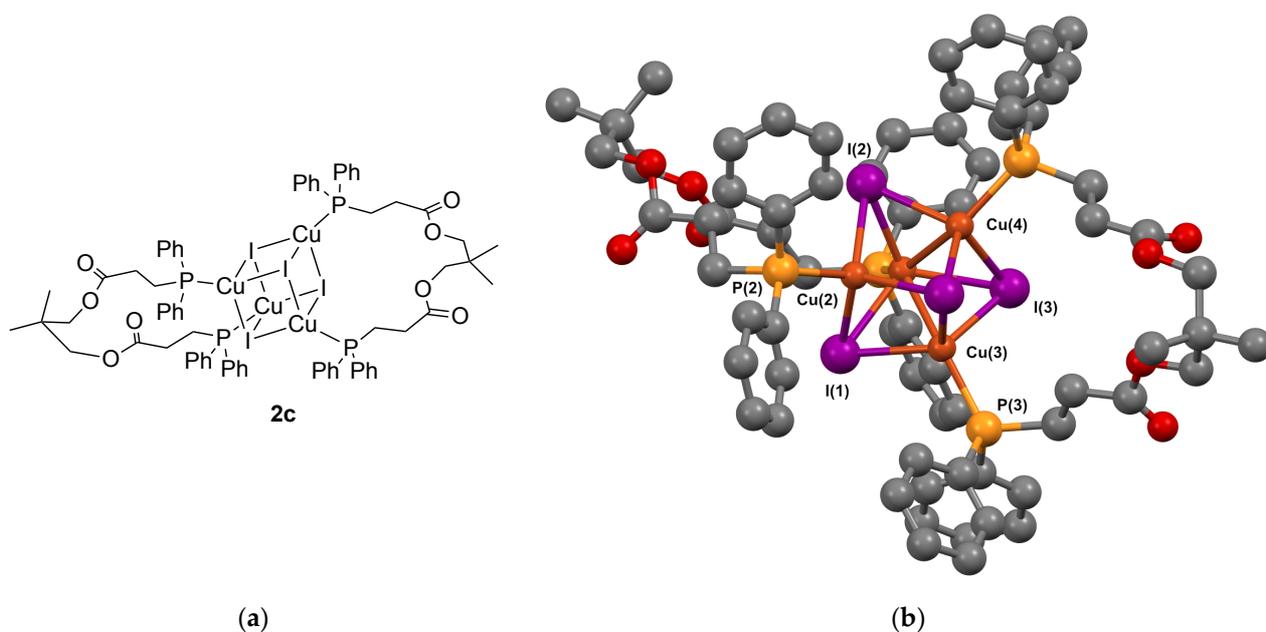


Figure 5. (a) Molecular structure of **2c**; (b) Single-crystal X-ray molecular structure of copper complex **2c**. Selected bond distances (Å) and angles (deg): Cu(2)-P(2), 2.2594(16); Cu(2)-I(1), 2.7065(8); Cu(2)-I(1), .6891(10); Cu(3)-P(3), 2.2565(17); Cu(1)-I(3), 2.6674(7); I(1)-Cu(3)-I(3), 113,13(3); 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 condition [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 2 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 excited state lifetime in the range $\tau = 5.11\text{--}5.89$ μs . Closer analysis of the excited-state kinetic parameters yields estimated radiative kinetic constant, k_r , of $8.4\text{--}16.2 \times 10^4 \text{ s}^{-1}$. The smaller value of 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 admixed ${}^3\text{CC}/{}^3\text{XLCT}$ character in accordance with previously reported derivatives [8, 36–38].

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

Compound	λ_{em} [nm]	PLQY	CIE chromaticity (x, y)	τ_{obs} [μs]	$k_r^{[a]}$ [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: $k_r = \text{PLQY} / \tau$ and $k_{nr} = (1 - \text{PLQY}) / \tau$

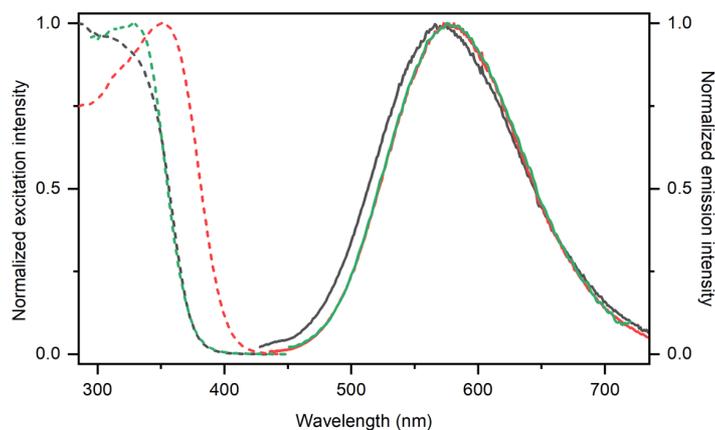


Figure 6. Excitation (dashed traces) and emission (solid traces) photoluminescence spectra of compounds **2a** (black), **2b** (red) and **2c** (green) in the solid state as neat powders. The samples were excited at $\lambda_{ex} = 380$ nm.

4. Discussion

We describe here the synthesis of three copper cubanes containing the subunit {Cu₄I₄} and stabilised by phosphine ligands. The phosphines used are either monodentate or bidentate ligands and are characterised by the presence of ester functions. The three complexes were fully characterised, including the determination of their molecular structure by single crystal X-ray diffraction. Of the three molecular structures, that of complex **3b** is particularly remarkable, with the ligands arranged in high symmetry to give an overall *D*_{2d} symmetry to the tetramer. In all three cases, the Cu-Cu intermolecular 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. 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 (λ_{em} = ca. 570–580 nm) and with high PLQY values ranging from 43% (**2b**) to 84% for complex **2a**. 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.

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: www.mdpi.com/xxx/s1, Figure S1-9: NMR spectra of the compounds. Figures S10-12: TGA analyses and Figure S13: CIE coordinates of complexes **2a-c**.

Author Contributions:

Conceptualization and methodology, D.B. and S.B.-L.; investigation, D.B., T.T., J.E., V.G., and T.A.; writing—original draft preparation M.M. and S.B.-L.; writing—review and editing, T.T., M.M., V.G. and S.B.-L.; supervision, S.B.-L.; project administration, S.B.-L.; funding acquisition, S.B.-L. All authors have read and agreed to the published version of the manuscript.

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