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Short-Bite PNP Ligand-Supported Rare Tetranuclear [Cu_4I_4] Clusters: Structural and Photoluminescence Studies

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Ⓢ *Supporting Information*

ABSTRACT: The group 11 metal complexes of two short-bite PNP ligands, $C_6H_5N\{P(OC_6H_3(OMe\text{-}o)(C_3H_5\text{-}p))_2\}_2$ (**1**) and $C_6H_5N\{P(OC_6H_4C3H_5\text{-}o)_2\}_2$ (**2**), are described. Ligands **1** and **2** on treatment with copper(I) halides (CuX, X = Cl, Br, or I) yielded dimeric, tetranuclear complexes of the type $[(CuX)_4\{C_6H_5N(PR_2)_2\}]$ (R = $OC_6H_3(OMe\text{-}o)(C_3H_5\text{-}p)$, X = Cl (**3**), Br (**5**), I (**7**); R = $OC_6H_3(C_3H_5\text{-}o)$, X = Cl (**4**), Br (**6**), I (**8**)). The chloro-derivative **3** adopts the common “stair-step” geometry, whereas the bromo- and iodo-derivatives form Cu_4 square planes with two tetracoordinating μ_4-halides capping the axial positions to give octahedral geometry with two other μ_2-halides being in the plane. The iodo-derivative **8** with a very short Cu−Cu distance of 2.568 Å shows photoluminescence in the solid state.

INTRODUCTION

The chemistry of d^{10} metal systems has attracted considerable attention in last few decades due to their structural diversities, rich photophysical properties,[1−3] and catalytic applications.[4,5] The metallophilic interactions in these complexes, especially in the case of gold(I), resulted in the formation of several interesting macrocyclic molecules and supramolecular architectures via intra- and intermolecular aggregations.[6−8] The strong relativistic effects possessed by gold also make it unique.[9] Many studies have shown that the presence of Au···Au interactions plays an important role in governing the unique electronic absorption and emission features of these complexes. Similar to gold(I) complexes, polynuclear copper(I) complexes are also interesting due to their diverse structural, rich photoluminescence properties and wide applications in material science.[10−23] The structures of multinuclear copper(I) complexes depend on the metal-to-ligand ratios as well as the steric properties of the ligands employed. Treatment of Cu^I halides, in particular CuCl, with one equivalent of tertiary phosphines usually results in cubane-type structures,[24−26] whereas a tetranuclear, ladder-type structure was observed with bulky phosphines, especially in the case of CuBr and CuI. These ladder structure molecules usually dissociate in solution in the presence of bridging linkers to form different types of coordination polymers.[24−38] Combinations of copper(I) halides with bidentate, aromatic imino ligands generally produce 1-D chains or 2-D layer networks containing rhombic Cu_2X_2 units or $(CuX)_\infty$ chains. In contrast, ligands such as bis(dicyclohexylphosphino)methane (DCPM) and 2-{(diorganophosphino)methyl}pyridine (P^N) have produced coplanar, tetranuclear copper complexes with μ_4-bridging halides.[39,40] The different types of copper complexes formed by mono- and bidentate ligands are shown in Chart 1.

Among all copper(I) halide complexes, the iodide derivatives have been investigated extensively due to their peculiar photoluminescence properties. The cubane-like structures exhibit two distinct emission bands, one at higher energy around 400−450 nm arising from halide(X)-to-ligand charge transfer (^{3}XLCT) and a low-energy band around 550−600 nm arising from a cluster-centered excited state (^{3}CC). The relative intensities of these bands depend on the temperature and the Cu···Cu distance.[12,41,42] The high-energy band is dominant at low temperature, while the low-energy band is dominant at room temperature in clusters with Cu···Cu distances less than 2.8 Å. However, complexes with the stair-step structure exhibit luminescence only from the ^{3}XLCT excited state due to longer Cu···Cu distances.[43−47] The planar tetracopper(I) structures axially capped with tetrabridging halides have shown both types of bands depending upon the nature of the coordinating ligands and their substituents.[40] The aminobis(phosphonite) $C_6H_5N\{P(OC_6H_4OMe\text{-}o)_2\}_2$ reported earlier by our group on reactions with copper halides showed a preference to form only the ladder-step molecules without any photoluminiscent properties.[48] Herein we describe the copper(I) complexes of aminobis(phosphonites), $C_6H_5N\{P(OC_6H_3(OMe\text{-}o)(C_3H_5\text{-}p))_2\}_2$ (**1**) and $C_6H_5N\{P(OC_6H_4C_3H_5\text{-}o)_2\}_2$ (**2**), and their photophysical properties. Interestingly aminobis(phosphonites) **1** and **2** on reaction with CuBr and CuI yielded tetranuclear complexes with planar Cu_4 units axially capped by μ_4-halides

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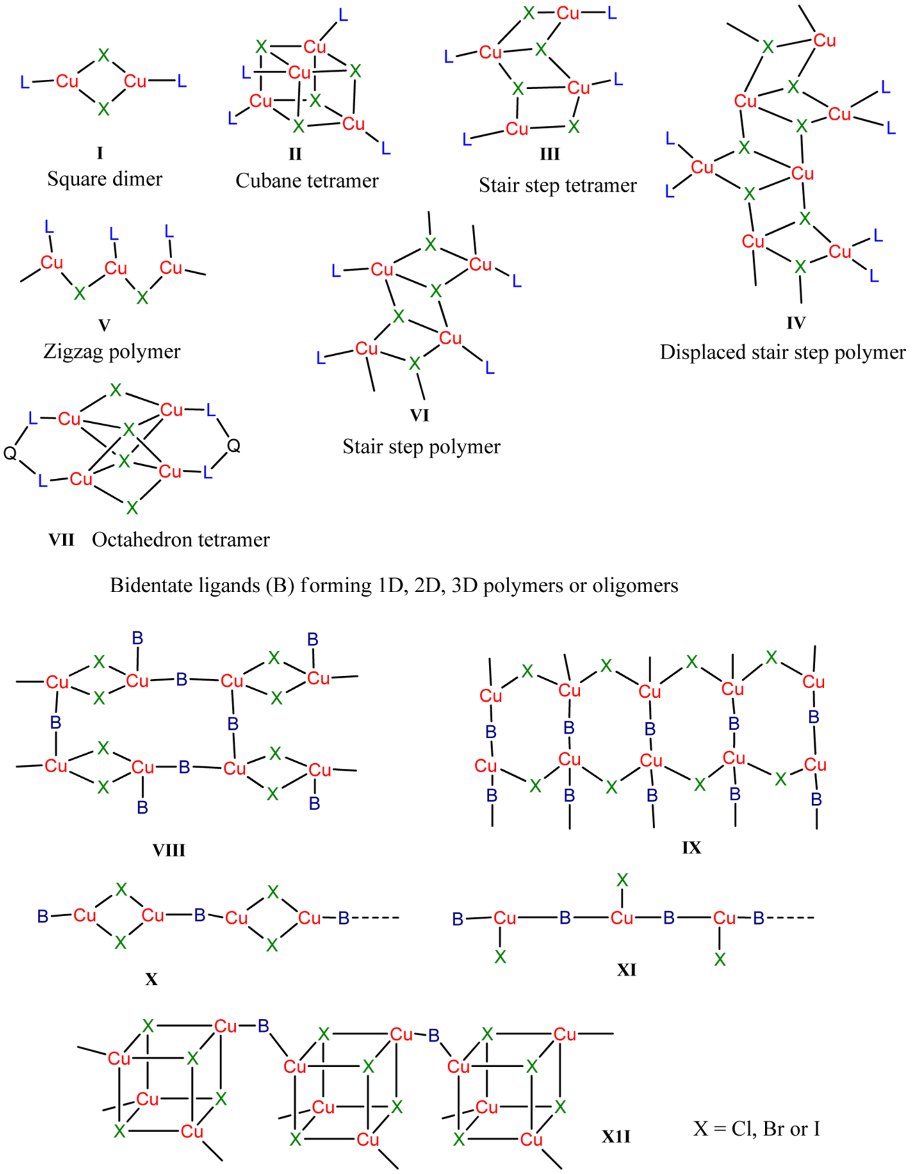
Chart 1. Monodentate (L) and Bidentate (LQL or 2L) Ligands



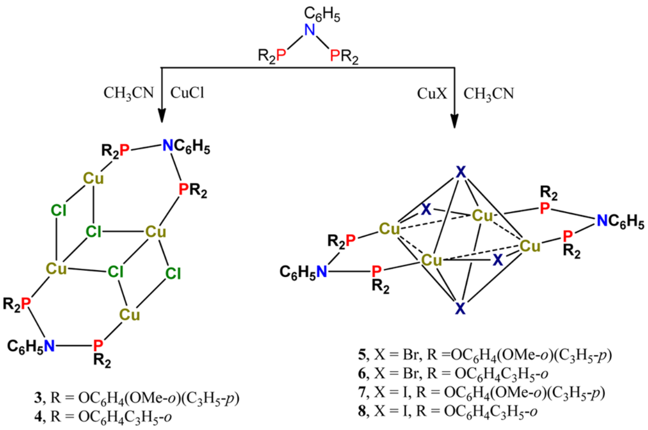
and with two additional μ_2-halides being almost coplanar with the Cu_4 array.

■ RESULTS AND DISCUSSION

The short-bite PNP ligands **1** and **2** were synthesized by reacting phenylaminobis(dichlorophosphine) with four equivalents of ArOH in the presence of a base using our previously reported literature procedure.[49] The primary objectives of incorporating dangling olefinic groups at *ortho* and *para* positions on the phosphorus substituents are to involve them in either inter-[50] or intramolecular[51] coordination with the transition metals in addition to those of the trivalent phosphorus centers as well as to enhance the solubility of the metal complexes in organic solvents. The present study includes synthesis, structural characterization, and photoluminescence studies of copper(I) complexes containing the ligands **1** and **2**.

Copper(I) Complexes. The reactions of **1** and **2** with one or two equivalents of CuX (X = Cl, Br, or I) in acetonitrile resulted in the formation of the tetranuclear complexes $[(CuX)_2\{C_6H_5N(PR_2)_2\}]_2$ (R = $OC_6H_4(OMe\text{-}o)(C_3H_5\text{-}p)$; X = Cl, **3**; Br, **5**; I, **7** and R = $OC_6H_4(C_3H_5\text{-}o)$; X = Cl, **4**; Br, **6**; I, **8**). The analogous reactions of $C_6H_5N(P(OC_6H_4OMe\text{-}o)_2)_2$ with copper halides (CuX, X = Cl, Br, or I) resulted in the formation of exclusively "stair-step"-type clusters.[48] Interestingly, in the present study, the ligands **1** and **2** with allylic groups in *para* and *ortho* position, respectively, yielded "stair-step"-type complexes in the case of CuCl. But the similar reactions with CuBr and CuI resulted in the formation of bicapped "octahedron"-type complexes in which two of the halide ions are μ_2-bridged and the other two halides display μ_4-coordination. The "stair-step"-type complex consists of two bis(phosphonite)s each bridging a pair of copper(I) centers along with two μ_2-bridged and two μ_3-bridged chloride ions as shown in Scheme 1. All the copper complexes (**3**–**8**) are moderately stable to air and moisture and are soluble in polar solvents such as dichloromethane, chloroform, and acetonitrile and insoluble in nonpolar solvents. The $^{31}P\{^1H\}$ NMR spectra of all the complexes consist of broad single resonances in the range 89–103 ppm.

Scheme 1. Synthesis of Copper(I) Complexes of PNP Ligands 1 and 2



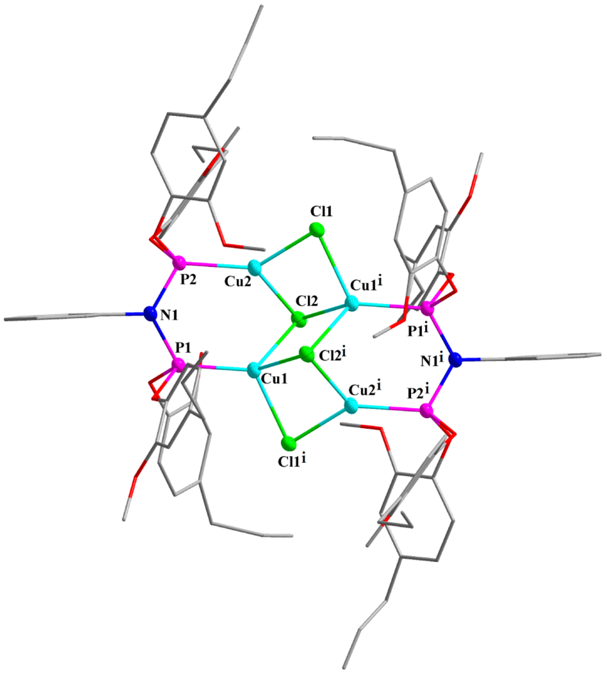
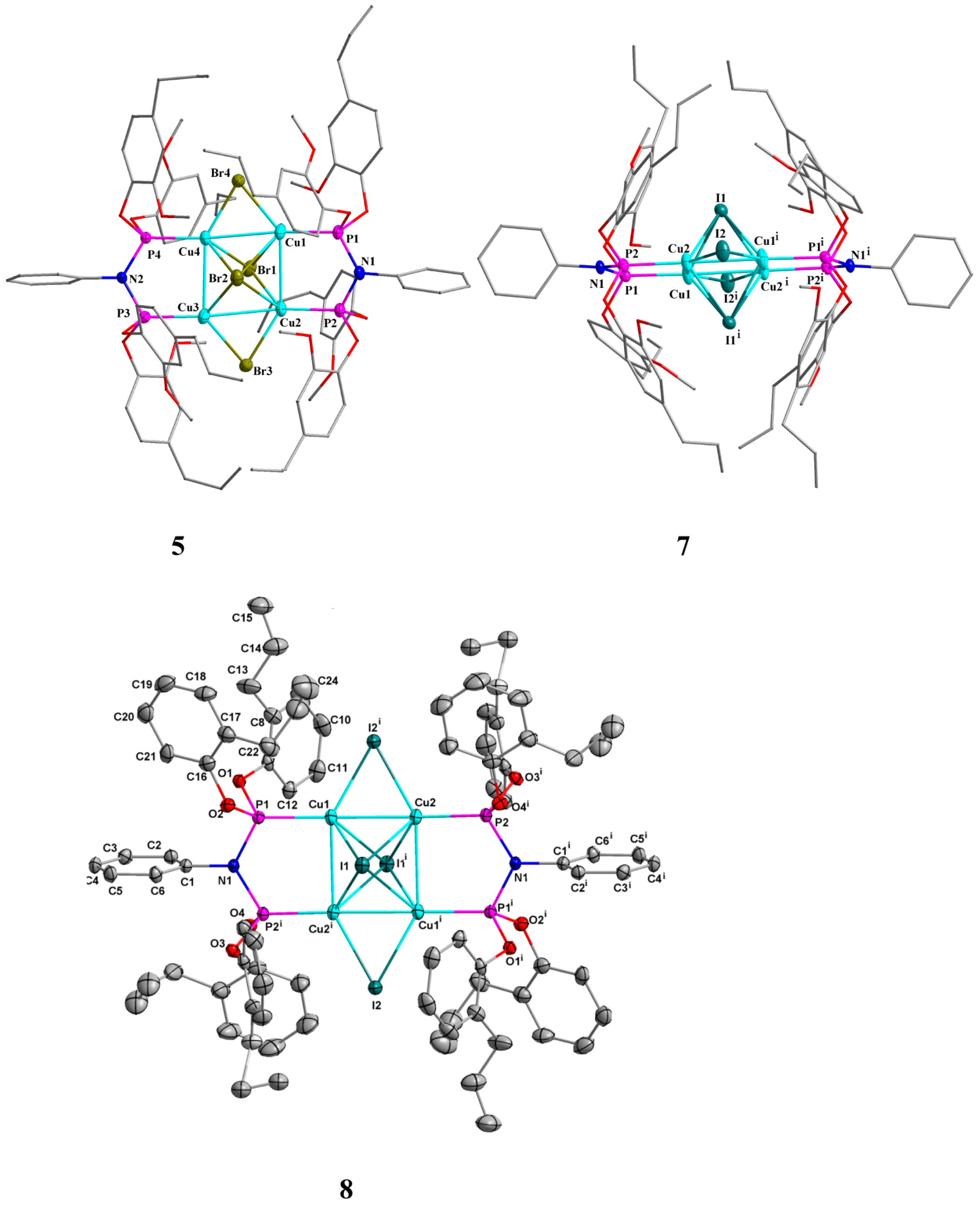


Figure 1. Molecular structure of $[Cu_2(\mu\text{-}Cl)(\mu_3\text{-}Cl)\{C_6H_5N\{P(OC_6H_3(OMe\text{-}o)(C_3H_5\text{-}p))_2\}_2\}]_2$ (**3**). All hydrogen atoms and lattice solvent have been omitted for clarity.

The molecular structures of complexes **3**, **5**, **7**, and **8** with atom-numbering schemes are shown in Figures 1 and 2. Crystal data and the details of the structure determinations are given in Table 1, while selected bond lengths and bond angles are given in Tables 2 and 3. For comparison, Cu−Cu bond distances in di-, tri-, and teranuclear complexes are presented in Table 4, whereas Table 5 includes Cu−Cu bond distances for typical octahedron-type complexes. The molecular structure of **3** consists of a $[\{Cu_4(\mu\text{-}Cl)_2(\mu_3\text{-}Cl)_2\}]$ core containing two bis(phosphonites) and having crystallographically imposed centrosymmetry. The Cu_4Cl_4 unit resembles "stair-step" geometry with each of the 10 edges defined by a Cu−Cl bond. The Cu1 atom adopts a distorted tetrahedral geometry coordinated by one phosphorus and three chlorine atoms, whereas Cu2 is in a distorted trigonal planar environment with one phosphorus and two chlorine atoms. The Cu−P distances are equivalent within experimental error (2.1530(8) to 2.1541(8) Å), while the Cu−Cl bond lengths vary appreciably, ranging from 2.3375(8) Å (Cu1−Cl1) to 2.2565(8) Å (Cu2−Cl1^i). As expected, the Cu−Cl distances involving the triply bridging chlorine atoms (Cl2 and Cl2^i) are longer than those to the doubly bridging chlorine atoms (Cl1 and Cl1^i). The four copper atoms are precisely coplanar, with Cu···Cu distances Cu1···Cu2^i = Cu1^i···Cu2 = 3.0058(5) Å, and Cu1···Cu2 = Cu1^i···Cu2^i = 2.9163(6) Å. The Cl−Cu−Cl angles (Cl1−Cu1−Cl2 = 90.06(3)° and Cl2−Cu2−Cl1^i = 91.10(2)°) are larger than the Cu−Cl−Cu angles, which range from 75.94(2)° to 81.71(3)°. The CuCl complexes of analogous short-bite PNP ligands such $C_6H_5N\{PPh_2\}_2$ and $CH_3N\{P(2\text{-}C_6H_4Me)_2\}_2$ are reported to have distorted octahedral geometry with Cu···Cu distances ranging from 2.75 to 2.89 Å.[52,53]

The molecular structures of **5**, **7**, and **8** contain similar $[\{Cu_4(\mu_2\text{-}X)_2(\mu_4\text{-}X)_2\}]$ (X = Br or I) cores analogous to that in complex **3** with two diphosphonites, but possess a different geometry due to the differences in the Cu−Cu and Cu−X bond lengths. The complexes **5**, **7**, and **8**, with the Cu_4X_4 core, are isostructural with the complexes containing bisphosphines such as bis(dicyclohexylphosphino)methane and 2-(diorganophosphino)methylpyridine.[39,40] All copper atoms are tetracoordinated and are arranged in a distorted rectangular shape. The capping halides are bonded to four copper atoms in a μ_4-fashion and are placed in axial positions above and below the Cu_4-plane, whereas the other two halides are bonded to two copper atoms in a μ_2-fashion. Complex **5** exhibits four different types of Cu−Cu atom distances ranging from 2.7561 to 2.8484 Å (Cu1−Cu2 = 2.8362(7) Å, Cu1−Cu4 = 2.7561(6) Å, Cu2−Cu3 = 2.8128(6) Å, Cu3−Cu4 = 2.8485(7) Å). In contrast, complexes **7** and **8** exhibit two unique Cu−Cu atom distances (Cu1−Cu2 = 2.6406(11); Cu1−Cu2^i = 2.8883(12) Å for **7** and Cu1−Cu2 = 2.5680(4); Cu1−Cu2^i = 2.8327(5) Å for **8**) because of the crystallographically imposed centrosymmetry. The Cu1−Cu2 distance in **8** is shorter than the same in complex **7** but is comparable with the equivalent Cu−Cu distances found in analogous complexes reported in the literature (see Table 5). The Cu−Cu bond length in complex **8** (2.5680(4) Å) is shorter than those found in the stair-step structure and Cu_2I_2 clusters coordinated with bisphosphine ligands (2.898 Å)[54] as well as monodentate N-heteroaromatic ligands (2.872−3.303 Å)[55] but is comparable with those in bimetallic complexes containing bulky pyridyl ligands (2.557 Å),[56] benzimidazoles (2.546 Å),[57] imidazolyl pyridines (2.592 Å),[58] phenanthroline (2.609 Å),[59] 1,2,3-triazole (2.530 Å),[60] and related nitrogen donor ligands (see Table 4). The steric crowding imposed by the bridging bis(phosphonite) ligands in complexes **7** and **8** also influences the separation between the two fragments in the Cu_4I_4 cores. The Cu−X bond lengths involved in the μ_4-bridging [2.4906(6)−2.7318(6) Å for **5**; 2.7652(10)−2.8636(10) Å for **7**; and 2.7035(4)−2.8751(4) Å for **8**] are significantly longer than those participating in μ_2-bridging [2.3780(6) and 2.4350(6) Å for **5**; 2.6016(9) and 2.6397(9) Å for **7**; 2.5965(4) and 2.6074(4) Å for **8**]. The P−N−P bond angles in all these complexes are in the range 118−120°.

Photoluminescence Study of Complex 8. The absorption spectra of **8** recorded in 10^{-5} M solution of dichloromethane, acetonitrile, THF, and acetone are shown in Figure 5. The spectra are characterized by sharp absorption bands in the region 220−230 nm and a broad absorption band at 280 nm, which are assigned to ligand-centered n→π* and π→π*



5

7

8

Figure 2. Molecular structures of $[Cu_2(\mu\text{-Br})(\mu_4\text{-Br})\{C_6H_5N\{P(OC_6H_3(OMe\text{-}o)(C_3H_5\text{-}p))_2\}_2\}]_2$ (**5**), $[\{[Cu_2(\mu\text{-I})(\mu_4\text{-I})\{C_6H_5N\{P(OC_6H_3(OMe\text{-}o)(C_3H_5\text{-}p))_2\}_2\}]_2$ (**7**), and $[Cu_2(\mu\text{-I})(\mu_4\text{-I})\{C_6H_5N\{P(OC_6H_4C_3H_5\text{-}o)_2\}_2\}]_2$ (**8**). All hydrogen atoms and lattice solvent have been omitted for clarity.

transitions, respectively. The featureless transitions observed at longer wavelengths (>300 nm) that gradually decrease in intensity are assigned to halide-to-ligand charge transfer transitions except in the case of the acetone solution, which showed an absorption maximum at 320 nm, but due to the poor solubility in acetone, this solution showed a maximum absorbance of only about 0.1. The low-energy transitions in complex **8** can be observed down to 330 nm in the excitation spectra recorded from neat solids.

The emission spectra of similar bare tetragonal complexes $Cu_4I_4(R_2\hat{P}N)_2$ recorded in the solid state at room temperature have shown both dual emission (HE band at 450−470 nm and LE band at 560−580 nm, R = C_6H_5, C_2H_5, or Cy) and only the high energy emission band (R = ^{t}Bu or ^{i}Pr).[40] However, $Cu_4I_4(dcpm)_2$ (dcpm = bis(dicyclohexylphosphino)methane) has shown only a low-energy emission band at 596 nm.[39] Excitation of dichloromethane solution of **8** at 340 nm displayed a high-energy emission band at 419 nm corresponding to the halide-to-ligand charge transfer transition (XLCT).[61−64] The emission lifetime is calculated using three-exponential calculations. The average lifetime of the excited-state species is around 178 ps. Similar to the complex $Cu_4I_4(dcpm)_2$, the emission spectrum of **8** recorded in the solid state at room temperature showed only a low-energy emission band at 596 nm when excited at 340 nm. The emission lifetime is calculated using monoexponential calculations to be 6.22 μs, implying that the emission is from the triplet excited state. Complex **8** displayed an orange emission

Table 1. Crystallographic Information for Compounds 3, 5, 7, and 8

	3	5	7	8
emp formula	$C_{92}H_{98}Cl_4Cu_4N_2O_{16}P_4$	$C_{92}H_{98}Br_4Cu_4N_2O_{16}P_4$	$C_{92}H_{98}Cu_4I_4N_2O_{16}P_4$	$C_{84}H_{82}Cu_4I_4N_2O_8P_4$
fw	2009.62	2193.47	2373.41	2133.16
cryst syst	triclinic	monoclinic	monoclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
a, Å	11.8854(3)	16.6114(4)	16.5661(8)	10.3109(6)
b, Å	14.2961(4)	17.5727(4)	15.8160(6)	14.3055(9)
c, Å	15.0486(4)	32.0136(6)	18.4637(9)	14.8135(9)
α, deg	111.404(2)	90	90	94.458(1)
β, deg	92.821(2)	102.268(2)	91.059(5)	99.793(1)
γ, deg	100.448(2)	90	90	101.868(1)
V, Å^3	2322.49(11	9131.6(4)	4836.8(4)	2092.7(2)
Z	1	4	2	1
D_{calc}, g cm^{-3}	1.437	1.595	1.630	1.693
μ(Mo Kα), mm^{-1}	1.152	2.805	2.273	2.609
F(000)	1038	4464	2360	1052
cryst size, mm	0.24 × 0.29 × 0.32	0.16 × 0.21 × 0.28	0.14 × 0.18 × 0.23	0.10 × 0.11 × 0.18
T (K)	150	150	150	100
2θ range, deg	3.1, 25.0	3.0, 25.0	3.0, 25.0	2.1, 28.3
total no. reflns	19 014	70 165	33 532	37 087
no. of indep reflns	8111 [R_{int} = 0.018]	15 992 [R_{int} = 0.038]	8501 [R_{int} = 0.086]	10 220[R_{int} = 0.031]
S	1.13	0.91	1.12	1.04
R_1	0.0392	0.0342	0.0634	0.0253
wR_2	0.1246	0.0787	0.1777	0.0601

under UV excitation at room temperature analogous to cubane-type complexes, which are reported to show green to orange emission under similar conditions. It is reported that, in the case of octahedral Cu_4I_4 clusters, the HOMO is composed primarily of iodide 6p and Cu 3d orbitals, whereas the LUMO consists of iodide (6s, 6p) and Cu (4s, 4p, 3d) orbitals and the halide-to-ligand charge transfer transition is the lowest energy band observed when the complexes are in the ground state.[39] However, both ^{3}XLCT and ^{3}CC states can be populated upon irradiation at room temperature according to DFT calculations on the cubane $Cu_4I_4L_4$ clusters.[18,65] Excitation to the ^{3}XLCT state leaves the C_4I_4 cluster unperturbed. The excitation to the ^{3}CC state, which involves transfer of electrons from an antibonding 3d orbital to the bonding combination of 4s orbitals, leads to the distortion of the Cu_4I_4 core compared to the ground-state geometry, causing a large Stokes shift. Thus the low-energy emission band is assigned to a cluster centered excited state. The usual Cu−Cu distances of cubane derivatives with pyridyl- or phosphine-based ligands are in the range 2.56−2.90 Å. The octahedron complexes $[(CuI)_4(Py\text{-}2\text{-}CH_2P^tBu_2)_2]$ and $[(CuI)_4(Py\text{-}2\text{-}CH_2P^iPr_2)_2]$, having short Cu−Cu distances of 2.630(1) and 2.620(1) Å, respectively, have shown only a high-energy emission band at 460 nm, although the band separation falls within the range of the ^{3}CC transition. Surprisingly, complexes **5** and **7**, having Cu−Cu distances of 2.7561(6) and 2.6406(11) Å, respectively, are nonemissive at room temperature. It is clear that the Cu−Cu interactions in cubane as well as octahedron $Cu_4I_4L_4$ clusters are the key parameters that influence the luminescence properties of the ^{3}CC transition, and the range of Cu−Cu distances in octahedron clusters is found to be less (probably <2.60 Å) than the cubane derivatives. To our knowledge, the maximum Cu−Cu distance reported for the ^{3}CC transition in octahedron copper clusters is 2.5760(8) Å.[39] As reported, the LE emission is associated with some kind of structural relaxation, so the photoluminescence properties of complexes **7** and **8** appear to be controlled by the steric bulk of the substituents on the phosphorus atoms.

CONCLUSIONS

The reactions of **1** and **2** with copper(I) halides (CuX, X = Cl, Br, or I) afforded tetranuclear cluster complexes of the type $[(CuX)_4\{C_6H_5N(PR_2)_2\}_2]$ (**3**−**8**) irrespective of the stoichiometry. The chloro complex adopts the common "stair-step" geometry, whereas the bromo and iodo complexes of these two ligands crystallized in a rare octahedron-type structure. The iodo cluster **8** of ligand **2** has a short Cu−Cu distance of 2.5680(4) Å, due to which it shows a cluster-centered photoluminescence in the solid state. Although complex **7** has a Cu···Cu distance of 2.6406(11) Å, surprisingly it is nonfluorescent at room temperature and also at low temperature. The solid-state emission has a lifetime of 6 μs, implying that the emission is from the triplet excited state. It is interesting to note that in some papers authors have used Cu−Cu, whereas the recent papers have referred it as Cu···Cu for copper−copper interactions in their studies. From the discussion and the data provided in Tables 4 and 5, the copper−copper distances below 2.7 Å may be considered as Cu−Cu bonding interactions, and those with bond distances more than 2.7 Å may be treated as Cu···Cu nonbonding interactions. In the present study, these interactions are considered as Cu−Cu bonding interactions aided by the photophysical studies.

EXPERIMENTAL SECTION

General Considerations. All experimental manipulations were performed under an inert atmosphere of dry nitrogen or argon, using standard Schlenk techniques. All the solvents were purified by conventional procedures and distilled prior to use. $C_6H_5N(PCl_2)_2$,[66] ligand **1**,[49] and CuX (X = Cl or Br)[67] were prepared according to the published procedures. Other reagents were obtained from commercial sources and used after purification. The ^{1}H and ^{31}P{^{1}H} NMR (δ in ppm) spectra were obtained with a Varian VRX 400 spectrometer

Table 2. Selected Bond Distances and Bond Angles for Complexes 3 and 5

bond distances (Å)		bond angles (deg)	
$[\{Cu_2(\mu\text{-}Cl)(\mu_3\text{-}Cl)\}\{C_6H_5N\{P(OC_6H_3(OMe\text{-}o)(C_3H_5\text{-}p))_2\}_2\}]_2$ (**3**)			
P1−N1	1.691(2)	P2−N1−P1	119.86(15)
P2−N1	1.677(2)	N1−P1−Cu1	122.38(9)
Cu1−P1	2.1541(8)	N1−P2−Cu2	116.14(9)
Cu2−P2	2.1530(8)	P1−Cu1−Cl1	119.18(3)
Cu1−Cl1	2.3375(8)	P1−Cu1−Cl2	121.08(3)
Cu1−Cl2	2.3732(8)	P1−Cu1−Cl2^{i}	123.97(3)
Cu1−Cl2^{i}	2.5124(7)	P2−Cu2−Cl2	127.85(3)
Cu2−Cl2	2.3665(8)	P2−Cu2−Cl1^{i}	136.23(3)
Cu2−Cl1^{i}	2.2565(8)	Cl1−Cu1−Cl2	104.48(3)
Cu1−Cu2^{i}	3.0058(5)	Cl1−Cu1−Cl2^{i}	90.06(3)
Cu2−Cu1^{i}	3.0058(5)	Cl2−Cu1−Cl2^{i}	91.10(2)
Cl1−Cu2^{i}	2.2565(8)	Cu2−Cl2−Cu1	75.94(2)
Cl2−Cu1^{i}	2.5124(7)	Cu2^{i}−Cl1−Cu1	81.71(3)
$[\{Cu_2(\mu\text{-}Br)(\mu_4\text{-}Br)\}\{C_6H_5N\{P(OC_6H_3(OMe\text{-}o)(C_3H_5\text{-}p))_2\}_2\}]_2$ (**5**)			
P1−N1	1.680(3)	P1−N1−P2	118.70(15)
P2−N1	1.685(3)	N1−P1−Cu1	118.41(10)
P3−N2	1.676(3)	N1−P2−Cu2	118.43(11)
P4−N2	1.691(3)	N2−P3−Cu3	118.80(9)
Cu1−P1	2.1626(9)	N2−P4−Cu4	120.17(10)
Cu2−P2	2.1610(9)	P1−Cu1−Br4	128.45(4)
Cu3−P3	2.1597(10)	P1−Cu1−Br1	125.94(4)
Cu4−P4	2.1653(9)	P1−Cu1−Br2	114.14(3)
Cu1−Br1	2.7094(6)	P2−Cu2−Br3	120.49(3)
Cu1−Br2	2.7304(6)	P2−Cu2−Br1	125.39(3)
Cu1−Br4	2.3915(6)	P2−Cu2−Br2	117.34(3)
Cu2−Br1	2.4906(6)	P3−Cu3−Br3	128.25(3)
Cu2−Br2	2.7318(6)	P3−Cu3−Br2	122.11(3)
Cu2−Br3	2.4169(6)	P4−Cu4−Br4	120.34(3)
Cu3−Br3	2.3780(6)	P4−Cu4−Br1	122.67(3)
Cu3−Br2	2.5101(6)	Cu1−Cu4−Cu3	95.19(2)
Cu4−Br4	2.4350(6)	Cu2−Cu3−Cu4	83.258(18)
Cu4−Br1	2.5669(6)	Cu3−Cu2−Cu1	94.22(2)
Cu4−Br2	2.6476(6)	Cu4−Cu1−Cu2	84.510(18)
Cu1−Cu2	2.8362(7)		
Cu1−Cu4	2.7561(6)		
Cu2−Cu3	2.8128(6)		
Cu3−Cu4	2.8485(7)		

operating at frequencies of 400 and 162 MHz, respectively. The spectra were recorded in $CDCl_3$ (or DMSO-d_6) solutions with $CDCl_3$ (or DMSO-d_6) as an internal lock; TMS and 85% H_3PO_4 were used as internal and external standards for ^1H and $^{31}P\{^1H\}$ NMR, respectively. Positive values indicate downfield shifts. Microanalyses were carried out on a Carlo Erba (model 1106) elemental analyzer. Melting points of all compounds were determined with a Veego melting point apparatus and are uncorrected.

Synthesis of $C_6H_5N\{P(OC_6H_4C_3H_5\text{-}o)_2\}_2$ (2). To a solution of $C_6H_5N(PCl_2)_2$ (2.72 g, 9.23 mmol) in diethyl ether (20 mL) was added dropwise a mixture of 2-allyl phenol (4.96 g, 37.8 mmol) and triethyl amine (3.294 g, 38.7 mmol) in diethyl ether (15 mL) at 0 °C. The reaction mixture was warmed to room temperature and stirred overnight. Triethyl amine hydrochloride formed was filtered through a frit layered with activated Celite, and the solvent was evaporated under reduced pressure to give an analytically pure product of **2** as a colorless oil. Yield: 85% (5.4 g). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 128.2 (s). ^1H NMR ($CDCl_3$) δ: 3.10 (d, CH_2, 8H, $^3J_{HH}$ = 3.6 Hz), 4.81−4.91 (m, CH_2, 8H), 5.69−5.76 (m, CH, 4H), 7.0−7.34 (m, ArH, 21H). Anal. Calcd for $C_{42}H_{41}NO_4P_2$: C, 73.55; H, 6.03; N, 2.04. Found: C, 73.35; H, 5.58; N, 1.89.

Table 3. Selected Bond Distances and Bond Angles for Complexes 7 and 8

bond distances (Å)		bond angles (deg)	
$[\{Cu_2(\mu\text{-}I)(\mu_4\text{-}I)\}\{C_6H_5N\{P(OC_6H_3(OMe\text{-}o)(C_3H_5\text{-}p))_2\}_2\}]_2$ (7)			
P1−N1^{i}	1.685(5)	P1^{i}−N1−P2	120.1(3)
P2−N1	1.702(5)	N1^{i}−P1−Cu1	118.19(18)
Cu1−P1	2.1891(18)	N1−P2−Cu2	119.61(18)
Cu1−I2	2.6016(9)	P1−Cu1−I2	119.58(5)
Cu1−Cu2	2.6406(11)	P1−Cu1−I1^{i}	116.99(6)
Cu1−I1^{i}	2.7652(10)	P1−Cu1−I1	120.94(6)
Cu1−I1	2.8636(10)	P2−Cu2−I2	119.72(5)
Cu1−Cu2^{i}	2.8883(12)	P2−Cu2−I1	116.92(6)
Cu2−P2	2.1977(17)	P2−Cu2−I1^{i}	119.32(6)
Cu2−I1	2.7684(10)	Cu1−Cu2−Cu1^{i}	91.79(3)
Cu2−I2	2.6397(9)	Cu2−Cu1−Cu2^{i}	88.21(3)
Cu2−I1^{i}	2.776(1)		
Cu2−Cu1^{i}	2.8883(12)		
I1−Cu1^{i}	2.7652(10)		
I1−Cu2^{i}	2.776(1)		
$[\{Cu_2(\mu\text{-}I)(\mu_4\text{-}I)\}\{C_6H_5N\{P(OC_6H_4C_3H_5\text{-}o)_2\}_2\}]_2$ (**8**)			
P1−N1	1.683(2)	P1−N1−P2^{i}	120.83(12)
P2−N1^{i}	1.687(2)	N1^{i}−P2−Cu2	117.61(7)
Cu1−P1	2.1837(6)	N1−P1−Cu1	118.16(7)
I1−Cu1	2.8751(4)	P1−Cu1−I2	119.38(2)
I1−Cu1^{i}	2.7035(4)	P1−Cu1−I1^{i}	115.34(2)
Cu2−P2	2.1878(7)	P1−Cu1−I1	120.22(2)
I1−Cu2	2.8142(4)	P2−Cu2−I2	119.11(2)
I1−Cu2^{i}	2.7470(4)	P2−Cu2−I1^{i}	113.43(2)
I2−Cu1	2.5965(4)	P2−Cu2−I1	122.43(2)
I2−Cu2	2.6074(4)	Cu1−Cu2−Cu1^{i}	90.430(13)
Cu1−I1^{i}	2.7034(4)	Cu2−Cu1−Cu2^{i}	89.569(13)
Cu2−I1^{i}	2.7469(4)		
Cu1−Cu2	2.5680(4)		
Cu2−Cu1^{i}	2.8327(5)		

Synthesis of $[Cu_2(\mu\text{-}Cl)(\mu_3\text{-}Cl)\{C_6H_5N\{P(OC_6H_3(OMe\text{-}o)(C_3H_5\text{-}p))_2\}_2\}]_2$ (3). A solution of cuprous chloride (0.0153 g, 0.156 mmol) in acetonitrile (5 mL) was added to the solution of **1** (0.063 g, 0.078 mmol) in acetonitrile (5 mL). After stirring for 4 h the solvent was evaporated under vacuum to yield an oily residue, which, on washing several times with petroleum ether and drying under vacuum, gave **13** as a white solid. Yield: 87% (0.0681 g). Mp: 123−124 °C. $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 98.4 (br s). ^1H NMR ($CDCl_3$) δ: 3.31 (d, CH_2, 8H, $^3J_{HH}$ = 8 Hz), 3.63 (s, OCH_3, 12H), 5.04−5.10 (m, CH_2, 8H), 5.88−5.98 (m, CH, 4H), 6.51−7.74 (m, ArH, 17H). Anal. Calcd for $C_{92}H_{98}N_2P_4O_{16}Cl_4Cu_4$: C, 55.04; H, 4.92; N, 1.39. Found: C, 54.86; H, 4.71; N, 1.58.

Synthesis of $[Cu_2(\mu\text{-}Cl)(\mu_3\text{-}Cl)\{C_6H_5N\{P(OC_6H_4C_3H_5\text{-}o)_2\}_2\}]_2$ (4). This compound was prepared analogously to **3** by adding a solution of CuCl (0.015 g, 0.1604 mmol) in acetonitrile (5 mL) to the solution of ligand **2** (0.055 g, 0. 0802 mmol) in the same solvent (5 mL). Yield: 87% (0.061 g). Mp: >200 °C. $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 102.9 (br s). ^1H NMR ($CDCl_3$) δ: 2.59 (s, CH_2, 8H), 4.76 (d, CH_2, *trans*-H, 4H, $^3J_{HH}$ = 17.2 Hz), 4.89 (d, CH_2, *cis*-H, 4H, $^3J_{HH}$ = 9.5 Hz), 5.56−5.64 (m, CH, 4H), 7.0−7.6 (m, ArH, 21H). Anal. Calcd for $C_{84}H_{82}Cu_4Cl_4N_2O_8P_4$: C, 57.08; H, 4.68; N, 1.58. Found: C, 57.35; H, 4.58; N, 1.69.

Synthesis of $[Cu_2(\mu\text{-}Br)(\mu_4\text{-}Br)\{C_6H_5N\{P(OC_6H_3(OMe\text{-}o)(C_3H_5\text{-}p))_2\}_2\}]_2$ (5). This compound was prepared analogous to **3** by adding a solution of cuprous bromide (0.008 g, 0.055 mmol) in acetonitrile (3 mL) to the solution of **1** (0.022 g, 0.027 mmol) also in acetonitrile (5 mL). Yield: 86% (0.0254 g). Mp: 128−130 °C. $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 95.4 (br s). ^1H NMR ($CDCl_3$) δ: 3.31 (d, CH_2, 8H, $^3J_{HH}$ = 6.4 Hz), 3.63 (s, OCH_3, 12H), 5.04−5.09 (m, CH_2, 8H), 5.88−5.96 (m, CH, 4H), 6.6 (m, C_6H_3, 4H), 6.95 (d, C_6H_3, 4H, $^3J_{HH}$ = 7.94 Hz),

Table 4. Cu···Cu Distances in Di-, Tri-, and Tetranuclear Copper(I) Complexes[a]

complex	Cu···Cu distances (Å)	ref
$[Cu_2(\mu\text{-}I)_2(\mu\text{-}C_6H_4(o\text{-N-Bn-triazole})_2]$	2.5303(7)	60
$[Cu_2(\mu\text{-}I)_2(\text{benzimidazole})_2]$	2.546	57
$[Cu_2(\mu\text{-}I)_2(\text{2-benzolylpyridine})_2]$	2.587	58
$[Cu_2(\mu\text{-}I)_2(\text{imidazolyl pyridine})_2]$	2.592	58
$[Cu_2(\mu\text{-}I)_2(\text{phenanthrolene})_2]$	2.609	59
$[Cu_2(\mu\text{-}I)_2(\text{FecP})_2\text{NHC})]$	2.356	73
$[Cu_2(\mu\text{-}Cl)_2(\text{dppf})_2]$	3.216(2)	74
$[Cu_2(\mu\text{-}Br)_2(\text{dppf})_2]$	3.331	74
$[Cu_2(\mu\text{-}I)_2(\text{dppf})_2]$	2.5298	74
$[Cu_2(\text{napy})_2(ClO_4)_2]$	2.506(2)	75
$[Cu_2(\mu\text{-}Cl)_2(\text{dppb})_2]$	2.866	54
$[Cu_2(\mu\text{-}Br)_2(\text{dppb})_2]$	2.837	54
$[Cu_2(\mu\text{-}I)_2(\text{dppb})_2]$	2.898	54
$[Cu_2(\mu\text{-}Br)_2(\mu\text{-1,8-naph})(PPh_3)_2]$	2.6271(4)	76
$[Cu_2(\mu\text{-}I)_2(\mu\text{-1,8-naph})(PPh_3)_2]$	2.6123(5)	76
$[CuBr(PPh_3)_2(\text{pym})]$	2.8193(16)	77
$[CuCl(PPh_3)_2(\text{pdz})]$	2.303	77
$[CuBr(PPh_3)_2(\text{Trz})]$	2.8545(8)	77
$[(PCy_3)_2Cu_2(\mu\text{-}Br)_2]$	3.098(1)	78
$[(PCy_3)_2Cu_2(\mu\text{-}Cl)_2]$	3.066(1)	79
$[(PBn_3)_2Cu_2(\mu\text{-}Br)_2]$	3.065(1)	80
$[(P(\text{o-tol})_3)_2Cu_2(\mu\text{-}Cl)_2]$	3.103(1)	81
$[(P(\text{o-tol})_3)_2Cu_2(\mu\text{-}Br)_2]$	3.109(1)	81
$[(P(\text{o-tol})_3)_2Cu_2(\mu\text{-}I)_2]$	3.122(1)	81
$[(PPh_3)_2Cu_2(\mu\text{-}Cl)_2(\text{pyrazine})]_n$	3.059(1)	82
$[Cu_2(\mu\text{-}I)_2(\mu\text{-phz})]_n$	2.525	83
$[Cu_2(\mu\text{-}Br)_2(\mu\text{-phz})]_n$	3.141	83
$[Cu_2(\mu\text{-}Cl)_2(\mu\text{-phz})]_n$	3.049	83
$[Cu_3(\text{dppm})_3(\mu\text{-}Br)_2]ClO_4$	3.005(3)−3.128(3)	84
$[Cu_2(\text{dppm})_2(\text{dmcn})Cl_2]_2(\text{dmcn})$	3.293(1)	84
$[Cu_3(\text{dppm})_3(\mu_3\text{-}I)_2I]$	3.111(3)−3.199	84
$[Cu_2(\mu\text{-}I)_2(NCCH_3)_2(\mu\text{-PNP})]$	2.721(1)	48
$[Cu_4(\mu\text{-}I)_2(NCCH_3)_2(\mu\text{-PNP})_2]$	2.721(1)	48
$[Cu_4(\mu\text{-}Br)_2(\mu_3\text{-}Br)_2(\mu\text{-PNP})_2]$	2.819(1)-2.939(1)	48
$[Cu_4(\mu\text{-}Cl)_2(\mu_3\text{-}Cl)_2(\mu\text{-PNP})_2]$	2.931(1)-2.980(2)	48
$[Cu_2(\mu\text{-}I)_2(C_5H_5N)_2(\mu\text{-PNP})]$	2.708(1)	48
$[Cu_2(\mu\text{-}I)I(C_{10}H_8N_2)(\mu\text{-PNP})]$	2.877(1)	48
$[Cu_2(\mu\text{-}Br)_2(\mu\text{-PNP})(C_{10}H_8N_2)]_n$	2.695(1)	48
$[Cu_2(\mu\text{-}Cl)(\mu_3\text{-}Cl)\{\mathbf{1}\}]_2$	2.9163(6)−3.0058(5)	this work

[a] (FecP)$_2$NHC) = (*SP*-4)-[*í*-1,3-Bis[(*R*)-1-((*S*)-2-diphenylphosphino-*P*-ferrocenyl)ethyl] imidazole-2-*í*-ylidene]; dppf = 1,1′-bis-(diphenylphosphine)ferrocene; naph =1,8-naphthyridine; dppb = 1,2-bis(diphenylphosphino)benzene; PNP = $C_6H_5N(P(OC_6H_4OMe\text{-}o)_2)_2$; pym = pyrimidine; pdz = pyridazine; Trz = triazine; phz = phthalazine; dmcn = dimethylcyanamide.

Table 5. Cu···Cu Distances in Octahedron-Type Complexes[a]

complex	Cu···Cu distances (Å)	ref
$[(CuI)_4(\text{dcpm})_2]$	2.475(1)−2.9846(1)	39
$[(CuI)_2(\text{dcpm})]_2$	2.5760(8)−3.005(1)	39
$[(CuI)_2(\text{Py-2-}CH_2PPh_2)]_2$	2.525(2)−2.943(2)	40
$[(CuI)_2(\text{Py-2-}CH_2PCy_2)]_2$	2.574(1)−2.930(1)	40
$[(CuI)_2(\text{Py-2-}CH_2P^tBu_2)]_2$	2.630(1)−2.839(3)	40
$[(CuI)_2(\text{Py-2-}CH_2P^iPr_2)]_2$	2.620(1)−2.880(1)	40
$[(CuI)_2(\text{Py-2-}CH_2PEt_2)]_2$	2.562(2)−3.035(2)	40
$[Cu_2(\mu\text{-}I)(\mu_4\text{-}I)(\mu\text{-L})]_2$	2.5516(9)−2.848(1)	85
$[Cu_4(\text{dppa})_2Cl_4]$	2.7861(9)−2.8892(8)	52
$[\{(2\text{-}C_6H_4Me)_2P\}_2NMe)Cu_2Cl_2]_2$	2.7526(13)−2.8726(9)	53
$[Cu_2(\mu\text{-}Br)(\mu_4\text{-}Br)C_6H_5N\{P(OC_6H_3(OMe\text{-}o)(C_3H_5\text{-}p))_2\}_2]_2$	2.7561(6)−2.8485(7)	this work
$[Cu_2(\mu\text{-}I)(\mu_4\text{-}I)\{C_6H_5N\{P(OC_6H_3(OMe\text{-}o)(C_3H_5\text{-}p))_2\}_2\}]_2$	2.6406(11)−2.8883(12)	this work
$[Cu_2(\mu\text{-}I)(\mu_4\text{-}I)\{C_6H_5N\{P(OC_6H_4C_3H_5\text{-}o)_2\}_2\}]_2$	2.5680(4)−2.8327(5)	this work

[a] Dcpm = bis(dicyclohexylphosphanyl)methane; L = 2-diphenylphosphino-3-methylphosphinine; dppa = bis(diphenylphosphine)aniline.

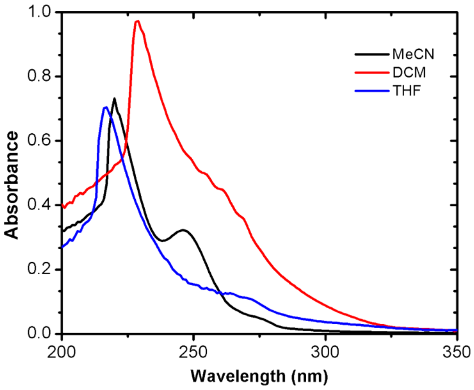


Figure 5. UV−visible spectra of complex **8** in different solvents.

6.67 (s, C_6H_3, 4H), 7.32−7.57 (m, C_6H_5, 5H). Anal. Calcd for $C_{92}H_{98}N_2P_4O_{16}Br_4Cu_4$: C, 50.56; H, 4.51; N, 1.28. Found: C, 51.06; H, 4.46; N, 1.61.

Synthesis of $[Cu_2(\mu\text{-}Br)(\mu_4\text{-}Br)\{C_6H_5N\{P(OC_6H_4C_3H_5\text{-}o)_2\}_2\}]_2$ (6). This compound was prepared similarly to **3** by adding CuBr (0.021 g, 0.145 mmol) (in 5 mL) to the solution of ligand **2** (0.050 g, 0. 073 mmol) in the same solvent (5 mL). Yield: 89% (0.0573 g). Mp: >200 °C. $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 97.1 (br s). ^1H NMR ($CDCl_3$) δ: 2.94 (d, CH_2, 8H, $^3J_{HH}$ = 5.2 Hz), 4.77 (d, CH_2, *trans*-H, 4H, $^3J_{HH}$ = 16.8 Hz), 4.9 (d, CH_2, *cis*-H, 4H, $^3J_{HH}$ = 9.6 Hz), 5.6 (m, CH, 4H), 7.09−7.45 (m, ArH, 21H). Anal. Calcd for $C_{84}H_{82}Cu_4Br_4N_2O_8P_4$: C, 51.86; H, 4.25; N, 1.44. Found: C, 51.46; H, 4.57; N, 1.43.

Synthesis of $[Cu_2(\mu\text{-}I)(\mu_4\text{-}I)\{C_6H_5N\{P(OC_6H_3(OMe\text{-}o)(C_3H_5\text{-}p))_2\}_2\}]_2$ (7). This compound was synthesized by a procedure similar to that for **3** using cuprous iodide (0.014 g, 0.074 mmol) and **1** (0.03 g, 0.037 mmol). Yield: 89% (0.0391 g). Mp: 123−125 °C. $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 86.3 (br s). ^1H NMR ($CDCl_3$) δ: 3.30 (d, CH_2, 8H, $^3J_{HH}$ = 8 Hz), 3.63 (s, OCH_3, 12H), 5.04−5.10 (m, CH_2, 8H), 5.9−5.97 (m, CH, 4H), 6.52 (d, C_6H_3, 4H, $^3J_{HH}$ = 6.4 Hz), 6.58 (s, C_6H_3, 4H), 6.73 (d, C_6H_3, 4H, $^3J_{HH}$ = 7.99 Hz), 7.30−7.74 (m, C_6H_5, 5H). Anal. Calcd for $C_{92}H_{98}N_2P_4O_{16}I_4Cu_4$: C, 46.56; H, 4.16; N, 1.18. Found: C, 46.13; H, 4.01; N, 1.19.

Synthesis of $[Cu_2(\mu\text{-}I)(\mu_4\text{-}I)\{C_6H_5N\{P(OC_6H_4C_3H_5\text{-}o)_2\}_2\}]_2$ (8). This compound was prepared similarly to **3** by adding a solution of CuI (0.039 g, 0.2052 mmol) in acetonitrile (5 mL) to the solution of **2** (0.0704 g, 0.1026 mmol) also in acetonitrile (5 mL). Yield: 79% (0.0864 g). Mp: 190−192 °C. $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 89.7 (s). ^1H NMR ($CDCl_3$) δ: 2.8 (br s, CH_2, 8H), 4.78 (d, CH_2, *trans*-H, 4H, $^3J_{HH}$ = 17.2 Hz), 4.9 (d, CH_2, *cis*-H, 4H, $^3J_{HH}$ = 9.6 Hz), 5.61−5.66 (m, CH, 4H), 7.0−7.5 (m, ArH, 21H). Anal. Calcd for $C_{84}H_{82}Cu_4I_4N_2O_8P_4$: C, 47.29; H, 3.87; N, 1.31. Found: C, 47.68; H, 3.70; N, 1.69.

Photophysical Studies. The absorption spectra of **8** were recorded at 298 K on a Perkin-Elmer UV−vis spectrometer in a 10^{-5} M solution in dichloromethane, acetonitrile, THF, and acetone using a quartz cell of 1 cm width. The emission spectra of **8** in a solid as well as the solution in dichloromethane were recorded at 298 K with a Perkin-Elmer fluoroscence spectrometer using a quartz cell (1 cm width). The time-resolved fluorescence decay measurements of the solid and solution were carried out at a magic angle using a picoseconds diode laser based time-correlated single photon counting (TCSPC) fluorescence spectrometer from IBH, UK. The emission

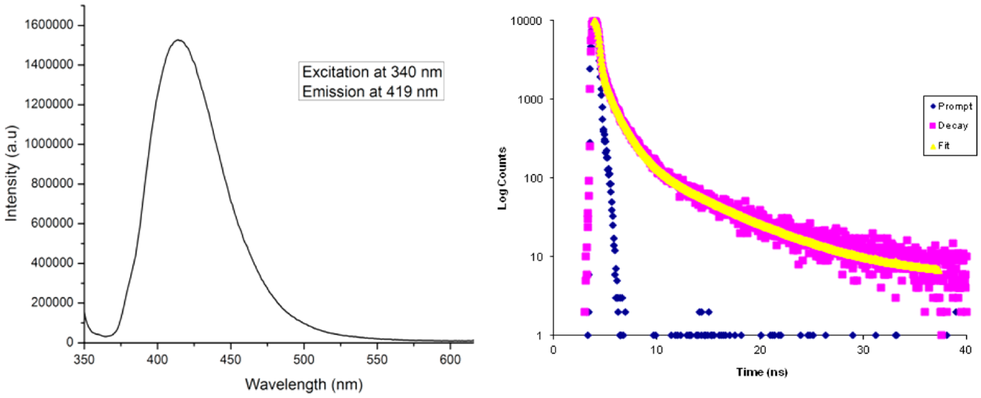


Figure 6. Emission spectra and decay lifetime measurement of copper complex **8** in dichloromethane.

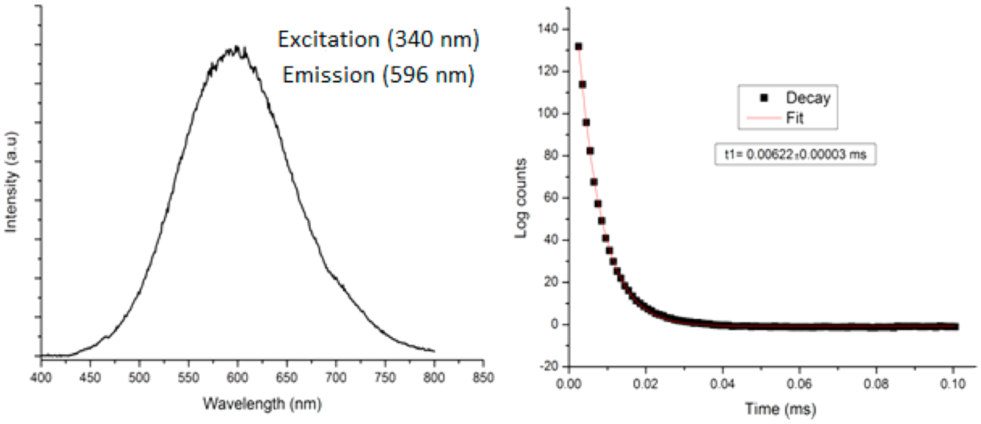


Figure 7. Solid-state emission spectra and decay lifetime measurement of copper complex **8**.

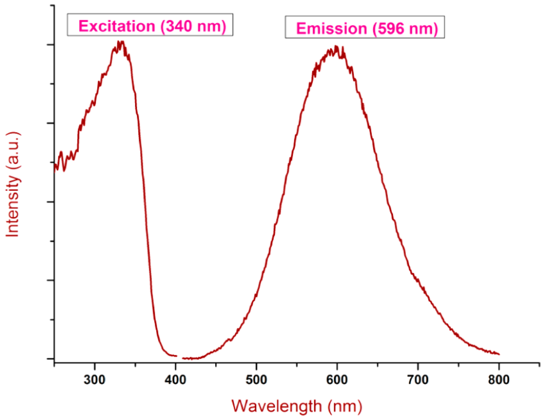


Figure 8. Excitation and emission spectra of copper complex **8** (solid sample).

lifetime of complex **8** in dichloromethane was calculated using a three exponential, whereas that of the solid sample was calculated using a monoexponential. The good fit criteria were low chi-square (1.0) and random distributions of residuals.

X-ray Diffraction Studies. A crystal of each of the compounds in the present work suitable for single-crystal X-ray diffraction studies was mounted in a cryoloop with a drop of paratone oil and placed in the cold nitrogen stream of the kryoflex attachment of the CCD Oxford Diffraction XCALIBUR-S diffractometer for complexes **3**, **5**, and **7** and Bruker APEX CCD diffractometer for complex **8**. The data were collected by the standard "phi-omega scan technique" using the CrysAlisPro CCD software for complexes **3**, **5**, and **7**, and for complex **8**, a full sphere of data was collected using a combination of three sets of 400 scans in ω (0.5° per scan) at φ = 0°, 90°, and 180° plus two sets of 800 scans in φ (0.45° per scan) at ω = −30° and 210° under the control of the APEX2 program suite.[68] The raw data were reduced to F^2 values using the CrysAlisPro RED (**3**, **5**, and **7**) and SAINT+ (**8**) software.[69] Multiple measurements of equivalent reflections provided the basis for empirical absorption corrections as well as corrections for any crystal deterioration during the data collection (SADABS).[70] The structure of **8** was solved by the Patterson method, whereas the rest of the structures were solved by direct methods, and all were refined by full-matrix least-squares procedures using the SHELXL-97 program package.[71,72] Hydrogen atoms were placed in calculated positions and included as riding contributions with isotropic displacement parameters tied to those of the attached non-hydrogen atoms.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallogrpahic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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