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Copper(I)/silver(I)-phosphine-*N*-{(2-pyridyl)methyliden}-6-coumarin complexes: Syntheses, structures, redox interconversion, photophysical properties and DFT computation

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ABSTRACT

Mixed ligand complexes of Cu(I) and Ag(I) with bis(diphenylphosphino)methane (dppm)/1,2-bis(diphenylphosphino)ethane (dppe) and *N*-{(2-pyridyl) methyliden}-6-coumarin (L) have been synthesized and characterized by elemental analyses, conductivity, ¹H NMR, UV–Vis and fluorescence spectral data. The coordination of dppm to M(I) forms a binuclear metallacycle, $[(L)M(\mu-dppm)_2M(L)](X)_2$ (X = NO₃ or ClO₄), and one of the complexes has been characterized by single crystal X-ray structure analysis. The dppe ligand is a bidentate chelator, which is supported by the X-ray structure of $[Cu(dppe)(L)]ClO_4$. In the Ag(I) complex, dppe is serving as a bridging agent to form the binuclear complex $[(L)Ag(\mu-dppe)Ag(L)](NO_3)_2$, and NO₃⁻ asymmetrically chelates Ag(I), which exhibits solvent polarity dependent coordination. In a coordinating polar solvent, like MeCN, the nitrate group dissociates and shows conductivity, while in nitrobenzene the complex is non-conducting and supports no dissociation. The complexes are more fluorescent than free L. Cyclic voltammetry shows a Cu(II)/Cu(I) quasireversible couple, while the Ag(I) complexes have isolated Cu(II) complexes that are established by spectroscopic and magnetic data. The electronic configuration of the complexes is assessed by DFT computation, and the spectral and redox properties are explained.

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1. Introduction

Use of natural products as synthetic precursors to design new molecules with various interests has been of long standing demand [1]. Coumarin, a natural product found in many plants, such as Tonka bean, lavender, sweet clover grass, licorice, strawberries, apricots, cherries, cinnamon, etc., has been used by many researchers to synthesize new derivatives [2-9]. Some of the coumarin derivatives and their metal complexes exhibit anticancer activity [10-14]. The Schiff bases of coumarin are well known for their fluorescent properties and usefulness as laser dyes [15]. This has inspired us to synthesize coumarinyl-azo (-N=N-) and imine (-C=N-) derivatives. We have synthesized N-[(2-pyridyl)methyliden]-6-coumarin (L) and have used it to synthesize copper(I) and silver(I) complexes [16]. In this article, we use dppm (bis-(diphenylphosphino)methane) and dppe (1,2-bis-(diphenylphosphino)ethane) as co-ligands to synthesize mixed ligand Cu(I) and Ag(I) complexes of L to examine the luminescence activity of the coumarin Schiff base in the presence of diphosphino ligands. Bis-(diphenylphosphino)methane (dppm) is a versatile ligand used to construct rigid M_2P_4 frameworks (M = Cu(I), Ag(I)) in the design of clusters [17]. 1,2-Bis(diphenylphosphino)ethane (dppe) chelates to constitute mononuclear MP₂ complexes and also bridges to generate a binuclear M_2P_4 framework [18]. Mixed ligand complexes of Cu(I) and Ag(I)-{*N*-[(2-pyridyl)methyliden]-6-coumarin (L)} and dppm/dppe are reported in this work. All these compounds are characterized by spectroscopic data. The structures of [(L)Cu(μ dppm)₂Cu(L)](ClO₄)₂ (**1**), [(L)Ag(μ -dppe)Ag(L)](NO₃)₂ (**4**) and [Cu(dppe)(L)]ClO₄ (**5**) have been confirmed by X-ray crystallography. Quantum chemical calculations using density functional theory (DFT) have been carried out to explain the electronic configuration, spectral and redox properties of the compounds.

2. Results and discussion

2.1. Synthesis and formulation

N-[(2-Pyridyl)methyliden]-6-coumarin (L) was synthesized by the condensation of pyridine-2-carboxaldehyde with 6-aminocoumarin. The condensation is supported by the elimination of $v(NH_2)$ (3329 and 3409 cm⁻¹) of 6-aminocoumarin, a new band



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at 1565 cm⁻¹ (assigned to v(C=N)) and lactone v(COO) at 1716 cm⁻¹. The electronic absorption spectrum of L in acetonitrile gives two intense bands at 325 and 278 nm, which are assigned to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. The ¹H NMR spectrum shows a singlet signal at 8.63 ppm for CH=N, the pyridyl protons appear at δ 7.8–8.7 ppm and the coumarin protons appear at δ 6.5 to 7.7 ppm [16].

The reaction of L, dppm and $[Cu(MeCN)_4]ClO_4$ (1:1:1 M ratio, respectively) in dry methanol under a N₂ environment for 2 h isolated a yellow precipitate of $[(L)Cu(\mu-dppm)_2Cu(L)](ClO_4)_2$ (1) (Scheme 1). A similar reaction using AgNO₃ under identical conditions separated $[(L)Ag(\mu-dppm)_2Ag(L)](NO_3)_2$ (2). The reaction product of dppe with L and $[Cu(MeCN)_4]ClO_4/AgNO_3$ is dependent on the composition of reactants; for the reaction with L:M:dppe (M refers to the metal salts used in the reaction) of 1:1:0.5 mol proportions, the products are $[(L)Cu(\mu-dppe)Cu(L)](ClO_4)_2$ (3) and $[(L)Ag(\mu-dppe)Ag(L)](NO_3)_2$ (4), while equimolar proportions (1:1:1 M ratio) of L:M:dppe has isolated products of the compositions $[Cu(dppe)(L)]ClO_4$ (5) and $[Ag(dppe)(L)]NO_3$ (6). The complexes were crystallized by slow diffusion of hexane into a dichloromethane solution of the complexes.

The molar conductance was measured in the polar solvent MeCN and the non-polar solvent nitrobenzene. The molar conductance (Λ_M) data of **1** and **2** in CH₃CN are 117 and 130 Ω^{-1} cm² mol⁻¹ and in nitrobenzene 24 and 28 Ω^{-1} cm² mol⁻¹, respectively. The Λ_M values support 1:1 electrolyte character. Complexes **5** and **6** also support 1:1 conductivity (Λ_M : 108 (MeCN) and 27 (nitrobenzene) for **5**; 126 (MeCN) and 33 (nitrobenzene) for **6**). A remarkable observation is that compounds **3** and **4** are non-conducting in nitrobenzene (($\Lambda_M < 5 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$) while they are 1:1 electrolytes in acetonitrile solution (Λ_M : 122 and 138 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ for **3** and **4**, respectively). This result signifies dissociation of the complex in a polar coordinating solvent whilst in a non-polar medium ClO₄⁻ or NO₃⁻ remains coordinated to metal ion center.

2.2. Molecular structures

The molecular structures of **1**. **4** and **5** are shown in Fig. 1a–c. The bond parameters are listed in Table 1. The structures of 1 (Fig. 1a) and **4** (Fig. 1b) consist of binuclear $M_2N_4P_4$ and $M_2N_4P_2O_2$ coordination types, respectively, while the structure of **5** (Fig. 1c) has an MN_2P_2 coordination. M(I) is present at the center of a distorted tetrahedron. The charges of the cationic complexes $[(L)Cu(\mu-dppm)_2Cu(L)]^{2+}$ (1) and $[Cu(dppe)(L)]^+$ (5) are satisfied by ClO_4^{-} , and in complex 4 (Fig. 1b) the charge is balanced by NO_3^- . The ligand L acts as an N,N'-chelator (N refers to N(pyridine) and N' refers to N(imine)) end capping agent. The pendant coumarinyl ring makes dihedral angles of $10.1(4)^{\circ}$ (1), $12.1(5)^{\circ}$ (4) and 34.6(12)° (5) with chelated diimine ring, $|| \ | \ (M-N=C-C=N-)$, and may assist in the distortion from an ideal platonic geometry. The chelate angles. M(N. N'), of 78.7(3)° (1), 71.2(3)° (4) and $80.55(10)^{\circ}$ (**5**) are extended by L on coordination to M(I) and they are comparable with reported results in the series of chelated Cu(I) and Ag(I) complexes [19]. The small chelate angle may be one of the reasons for the geometrical distortion. The P(1)-M(1)-P(2) angle is 133.67(8)° for 1, which supports this structural deviation from an ideal tetrahedral geometry. The distortion may be due to steric demand of the pendant coumarinyl group of the chelating N,N'-unit. The M-N(pyridine) distances (2.133(7) (1), 2.320(8) (4) and 2.054(2) (**5**) Å) are shorter than the M(I)–N(imine) distances (2.215(6) (1), 2.405(8) (4) and 2.082(2) Å (5)), which reflects the preferentially stronger interaction of M(I) with N(pyridine) compared to exocyclic N(imine) of L. The M–P distances (M(1)-P(1)): 2.282(2) (1), 2.361(3) (4), 2.266(9) Å (5); M(1)-P(2): 2.344(2) (1), 2.340(3) (4), 2.271(9) Å (5)) are comparable with the reported results [20]. In **4**, NO_3^- acts as a weakly chelating agent and the unsymmetrical binding is estimated from the unequal Ag-O bond lengths: Ag(1)–O(5), 2.631 and Ag(1)–O(6), 2.803 Å, which are



Scheme 1. The ligands and the complexes.



Fig. 1. The molecular structure of (a) $[(L)Cu(\mu-dppm)_2Cu(L)]^{2+} (1^{2+})$, (b) $[(L)Ag(\mu-dppe)Ag(L)](NO_3)_2 (4)$ and (c) $[Cu(dppe)(L)]^+ (5^+)$ with the atom numbering schemes. The ClO_4^- , hydrogen and solvent molecules are omitted for figure clarity.

Table 1 Selected bond lengths and bond angles of $[(L)Cu(\mu-dppm)_2Cu(L)](ClO_4)_2$ (1), $[(L)Ag(\mu-dppe)Ag(L)](NO_3)_2$ (4) and $[Cu(dppe)(L)]ClO_4$ (5).

	(M = Cu)(1)	(M = Ag) (4)	(M = Cu) (5)
Bond lengths (Å)			
M(1)-N(1)	2.133(7)	2.320(8)	2.054(2)
M(1)-N(2)	2.215(6)	2.405(8)	2.082(2)
M(1) - P(1)	2.282(2)	2.361(3)	2.2663(9)
M(1)-P(2)	2.344(2)	-	2.2714(9)
M(1)-C(1)	1.350(11)	1.331(13)	1.345(4)
M(1)-C(5)	1.367(10)	1.328(12)	1.350(4)
M(2)-C(6)	1.287(10)	1.281(11)	1.283(4)
M(2)-C(7)	1.462(10)	1.422(11)	1.425(4)
Bond angles (°)			
N(1)-M(1)-N(2)	78.7(3)	71.2(3)	80.5(10)
P(1)-M(1)-P(2)	133.6(8)	-	91.1(3)
N(1)-M(1)-P(1)	121.4(19)	137.7(2)	121.5(7)
N(1)-M(1)-P(2)	97.8(19)	-	122.1(7)
N(2)-M(1)-P(1)	109.1(2)	133.5(2)	120.8(7)
N(2)-M(1)-P(2)	101.2(18)	_	124.6(7)

shorter than the sum of the van der Waals radii of silver and oxygen but are longer than the sum of the covalent radii (van der Waals radii: Ag = 1.72, O = 1.52 Å, covalent radii: Ag = 1.53, O = 0.73 Å). In the same way the Ag(2)–O(8) and Ag(2)–O(9) distances are 2.743 and 2.758 Å, respectively. Such a long Ag–O(NO₃) distance may be responsible for solvent assisted ionization in polar coordinating media. The conductance measurements of the compound in CH₃CN show it is a 1:1 electrolyte, whilst it is non-conducting in nitrobenzene. The chelate angles of NO₃⁻ bonded to Ag(I) are $\angle O(5)$ –Ag(1)–O(6), 44.0(3)° and $\angle O(8)$ –Ag(2)–O(9), 45.1(4)°.

Different weak interactions are observed in these molecules. The intramolecular $\pi \cdots \pi$ interactions in [(L)Cu(μ -dppm)₂Cu(L)](ClO₄)₂ (1) are $Cg(4) \cdots Cg(5)$ (Cg(4): C(7)-C(8)-C(9)-C(13)-C(14)-C(14)) C(15); Cg(5): C(16)-C(17)-C(18)-C(19)-C(20)-C(21); distance, 3.823(6) Å; symmetry, x, y, z), Cg(6)...Cg(7) (Cg(6): C(22)-C(23)-C(24)-C(25)-C(26)-C(27); Cg(7):C(29)-C(30)-C(31)-C(32)-C(33)-C(34); distance, 3.723(6)Å; symmetry: x, y, z) and $Cg(3) \cdots Cg(8)$ (Cg(3): N(1)-C(1)-C(2)-C(3)-C(4)-C(5); Cg(8): C(35)-C(36)-C(37)-C(38)-C(39)-C(40); distance, 3.927(6) Å; symmetry, 3 - x, -y, 2 - z) (Fig. 2a). The intermolecular interactions are $C(12)-O(2)\cdots Cg(11)$ ($O(2)\cdots Cg(11)$, 3.275(9) Å; $C(12)\cdots$ Cg(11), 3.815(14) Å and $\angle C - O \cdots Cg(11)$, 107.0(7)°; symmetry: x, y, z) and Cg(10) \cdot Cg(16) (3.909(5) Å; symmetry: 1 + x, y, z) (Cg(10) is the phenyl ring of the coumarinyl ring and Cg(16) is the phenyl ring of the PPh₂ unit of a neighboring molecule). The weak interactions $\pi \cdots \pi$, C-H $\cdots \pi$ and hydrogen bonding exist in [Cu(dppe)(L)]ClO₄ (5). The Cg(4)···Cg(4) distance of 3.669(2) Å (Cg(4): N(1)-C(1)-C(2)-C(3)-C(4)-C(5); symmetry -1-x, 1-y, 1-z) is strong in the unit cell packing of two molecular units (Fig. 2b). A C-H $\cdots\pi$ interaction is observed between H(4) and Cg(8) (Cg(8): C(30)-C(31)-C(32)-C(33)-C(34)-C(35); $H(4)\cdots Cg(8),$ 2.84 Å; $C(4)\cdots$ Cg(8), 3.618(5) Å and $\angle C-H\cdots \pi$, 143°). There are also weak interactions between C(1)-H(1)···O(3) (symmetry, 1 - x, 1 - y, 1 - z; $H(1) \cdots O(3)$, 2.58 Å; $C(1) \cdots O(3)$, 3.472(5) Å; $\angle C - H \cdots \pi$, 160°), C(6) - H = -100 $H(6) \cdots O(6)$ ($H(6) \cdots O(6)$, 2.53 Å; $C(6) \cdots O(6)$, 3.328(5) Å; $\angle C - H \cdots$ π , 144°) and C(8)–H(8)···O(6) (H(8)···O(6), 2.52 Å; C(8)···O(6), 3.397(5) Å; $\angle C - H \cdots \pi$, 158°), that is the ClO₄⁻ ion is weakly interacting with the C-H's of the coumarinyl and chelate rings. The solvent of crystallization, CH₂Cl₂, in compound **1** forms a weak bond with ClO₄⁻, the coumarinyl COO group binds through hydrogen bonding to form a supramolecular structure (Fig. 2c); the distances are H(82A)–O(4) (Coumarin), 2.343 Å; H(83A)–O(9) (ClO₄⁻), 2.469 Å; H(84A)–O(2) (Coumarin), 2.484 Å; H(84B)–O(11) (ClO₄⁻), 2.716 Å and H(85A)–O(12) (ClO₄⁻), 2.428 Å.

2.3. Spectroscopic studies

2.3.1. The infrared and ¹H NMR spectral characterization

The main vibrational bands are v(COO) at 1709–1731 cm⁻¹ and v(C=N) at 1565–1571 cm⁻¹. The presence of ionic ClO_4^- in **1** and **5** is supported by a strong single stretch at 1090–1095 cm⁻¹, with a weak stretch at 625 cm⁻¹. Ionic NO₃⁻ in **2** and **6** is supported by a strong single stretch at 1383 and 1385 cm⁻¹, respectively. The coordinated $OClO_3$ in **3** and ONO_2 in **4** are confirmed by the multiple peaks due to the reduced symmetry of the functions. The peaks at 1150, 1093 and 621 cm⁻¹ ($v(ClO_4)$) confirm the presence of a coordinated perchlorate ion, and the peaks at 1434, 1383 and 1312 cm⁻¹ ($v(NO_3)$) are assigned to the coordinated nitrate [21].

The ¹H NMR spectra were recorded in CDCl₃ for [(L)Cu (μ -dppm)₂Cu(L)](ClO₄)₂ (**1**) and [Cu(dppe)(L)]ClO₄ (**5**), while DMSO-d₆ was used to record the NMR spectra of [(L)Ag(μ -dppm)₂-Ag(L)](NO₃)₂ (**2**), [(L)Cu(μ -dppe)Cu(L)](ClO₄)₂ (**3**), [(L)Ag(μ -dppe)Ag(L)](NO₃)₂ (**4**) and [Ag(dppe)(L)]NO₃ (**6**). The spectra are analyzed by a comparison with the free ligand values (Table 2). The pyridine protons (13-H to 16-H) experience a significant downfield shift by 0.1–0.2 ppm, while the coumarin protons (3-H, 4-H, 5-H, 7-H, 8-H) are perturbed by 0.07–0.5 ppm. The immine proton (-CH=N–) appears a singlet in the lowest field of >9.5 ppm. The proton movement is in association with coordination of L to the metal ion(s). The P-CH₂-CH₂-P/P-CH₂-P protons appear at 2.69–3.93 ppm and -PPh₂ protons at 7.11–7.43 ppm.

2.3.2. Absorption and emission spectroscopy

The electronic spectra of the complexes are recorded in CH₃CN solution in the wavelength range 200–800 nm (Fig. 3 and Table 3). The electronic transitions have been assigned based on TD DFT calculations in acetonitrile for complex **5**. The complexes exhibit a transition below 400 nm corresponding to intraligand and interligand charge transfer transitions. The transitions are red shifted by 10–20 nm compared to those of L, which is in support of coordination to the metal ions. A weak broad band is observed at >400 nm. This transition remains absent in the free ligand L and is assigned to the admixture of MLCT and LLCT transitions, $Cu(d\pi)/L \rightarrow L(\pi^*)$, on comparing with reported copper(1) complexes, and this is a characteristic feature of copper complexes when bonded with a conjugated organic chromophore [22–24]. No such bands are observed in the case of the silver complexes **2**, **4** and **6**.

Transition metal complexes of a d¹⁰ electronic configuration (Cu(I), Ag(I), etc.) with the appropriate N-heterocyclic chelating ligands with additional auxiliary ligands such as halide or phosphine are of considerable interest for their intriguing photophysical properties and luminescence behavior [25-27]. The emission properties of the compounds were explored at room temperature in CH₃CN (Table 3 and Fig. 4) solution. Ligand L exhibits an emission at 516 nm at 298 K upon excitation at 325 nm. The complexes 1-6 do not emit significantly when they are excited at the MLCT band, whilst an emission is observed upon excitation at the near UV region, 328–349 nm, at the π – π * band (334 (1), 328 (2), 349 (3), 333 (4), 339 (5) and 336 nm (6) (Table 3)). The MLCT transition is not sufficient to excite the molecule to show emission activity. The emission refers to the ligand centered excitation (ILCT/LLCT or both, where ILCT is intraligand charge transfer and LLCT is ligand-to-ligand charge transfer). The fluorescence quantum yield (ϕ) of complexes **1–6** vary in the range 0.019–0.032 and for L it is 0.018. The emission efficiencies of the present series of copper complexes (1, 3 and 5) are better than that of $[Cu(L)(PPh_3)_2](ClO_4)$ [16] reported earlier. The mechanism of the enhancement of quantum yields for the complexes may be due to the structural rigidity attributed to the organic frame via chelation or formation of a



Fig. 2. (a) The π - π interaction in [(L)Cu(μ -dppm)₂Cu(L)]ClO₄ (1), (b) π ··· π , C-H··· π and hydrogen bonded ClO₄⁻ in [Cu(dppe)(L)]ClO₄ (5) and (c) solvent (CH₂Cl₂) interaction in [(L)Cu(μ -dppm)₂Cu(L)]ClO₄ (1).

Table 2									
¹ H NMR	spectral	data	of t	he	ligand	and	the	comp	lexes.

Compound	δ ppm (J, Hz)											
	3-H ^d	4-H ^d	5-H ^c	7-H ^d	8-H ^d	10-Н ^с	13-H ^d	14-H ^e	15-Н ^е	16-H ^d	PCH ₂ CH ₂ P/PCH ₂ P	-PPh ₂
L ^a (Ref. [16])	6.48 (9.6)	7.75 (9.5)	7.37	7.38 (8.6)	7.51 (8.7)	8.63	8.74 (6.8)	7.87	7.87	8.20 (7.9)		
1 ^a	6.36 (6.1)	7.70 (9.6)	8.11	6.87 (8.7)	7.24 (6.9)	9.97	8.80 (7.8)	7.85	7.93	8.71 (5.3)	3.22 ^c	7.11-7.37
2 ^b	6.36 (6.3)	7.73 (9.6)	8.05	6.86 (8.7)	7.31 (6.9)	9.99	8.87 (7.9)	7.89	7.95	8.84 (5.4)	3.93 ^c	7.29-7.43
3 ^b	6.33 (5.9)	7.65 (9.5)	7.86	6.76 (8.6)	7.11 (6.8)	9.59	8.63 (7.7)	7.62	8.21	8.33 (4.9)	3.76 ^f	7.24-7.43
4 ^b	6.35 (6.1)	7.71 (9.6)	7.92	6.83 (8.6)	7.25 (6.9)	9.64	8.59 (7.6)	7.65	8.15	8.43 (5.1)	3.62 ^f	7.25-7.37
5 ^a	6.37 (6.2)	7.68 (9.6)	7.89	6.85 (8.8)	7.22 (8.0)	9.54	8.55 (7.6)	7.57	8.12	8.37 (4.0)	2.69 ^f	7.19-7.31
6 ^b	6.32 (6.1)	7.59 (9.5)	7.84	6.78 (8.7)	7.08 (6.9)	9.97	8.64 (7.6)	7.56	8.17	8.22 (3.9)	2.86 ^f	7.18-7.43

^a In CDCl₃.

^b In DMSO-d₆.

^c Singlet.

^d Doublet.

e Multiplet.

f Quartet.

metallacycle with L and dppm/dppe that eliminates vibrational relaxation, referred to as the chelation enhancement quantum yield (CEQ). Heteroatom containing fluorophores develop partial charges due to internal charge transfer (ICT) and their interaction with charged groups can affect the energy of transition [28]. The fluorescence study of the ligand and the complexes in the solid state show emissions at longer wavelengths (λ_{em}) compared to

solution phase emissions (Fig. 5 and Table 3). In general, there is a distortion of the tetrahedral coordination towards square-planar in the excited state of Cu(I) complexes (flattening). Therefore, the reason for the difference between the solid and solution phases is usually the rigidity of the environment which influences the extent of flattening [26]. Besides, the restriction to vibrational relaxation in the solid state relative to the solution phase may enhance



Fig. 3. UV–Vis spectra of (a) L, (b) [(L)Cu(µ-dppm)₂Cu(L)](ClO₄)₂ (1), (c) [(L)Ag(µ-dppm)₂Ag(L)](NO₃)₂ (2), (d) [(L)Cu(µ-dppe)Cu(L)](ClO₄)₂ (3), (e) [(L)Ag(µ-dppe)Ag(L)](NO₃)₂ (4), (f) [Cu(dppe)(L)]ClO₄ (5) and (g) [Ag(dppe)(L)]NO₃ (6) in CH₃CN.

the emissivity. Since all the metal ions present in the complexes have a d¹⁰ electronic configuration, they quench less retarding intersystem crossing processes via magnetic interactions [29,30].

Lifetime data are obtained upon excitation at 370 nm and are summarized in Table 3. The observed decay of the excited states of $[(L)Cu(\mu-dppm)_2Cu(L)](ClO_4)_2$ (1), $[(L)Ag(\mu-dppm)_2Ag(L)](NO_3)_2$ (2), $[(L)Cu(\mu-dppe)Cu(L)](ClO_4)_2$ (3) and $[(L)Ag(\mu-dppe)Ag(L)]$ $(NO_3)_2$ (4) fit with a single exponential decay curve (Fig. 6), whereas $[Cu(dppe)(L)]ClO_4$ (5) and $[Ag(dppe)(L)]NO_3$ (6) fit with a bi-exponential decay, which may be due to decay through both high energy and MLCT states. The average lifetime values for the complexes are higher than the free ligand value. The metal-ligand orbital mixing in the complexes (as supported by DFT computations) may be the reason for the longer lifetimes of the complexes and the lower k_{nr} .

2.4. Redox properties

Copper(I) complexes show a quasi-reversible oxidation–reduction Cu(II)/Cu(I) couple at *ca*. 0.7–0.8 V. The quasi-reversible character is accounted for from the $\Delta E_p(E_{pa} - E_{pc})$ (160–170 mV) values

under the conditions of measurements (Fig. 7 and Table 3). A small dihedral angle of the chelate plane with the pendant coumarinyl group in the complexes may assist better delocalization. So a less negative reduction potential value is feasible. The electrochemistry of the silver complexes is not very informative. The cathodic progress followed by scan reversal on the anodic side gives an irreversible sharp oxidative response (Fig. 7b) on the positive side to Ag/AgCl, which may be due to oxidation of adsorbed silver on the electrode bed produced on the cathodic scan [31]. The reductive responses at -0.65 to -0.8 V and -1.40 to -1.65 V may be assigned to the reduction of the diimine group of the chelated ligand. The free ligand does not show any oxidation, but irreversible reductive responses appear at < -1.5 V.

A brown–red solution of Cu(II) species has been generated upon coulometric oxidation of the corresponding Cu(I) complexes (**1**, **3** and **5**) in CH₃CN solution. The oxidation of the metal center is supported by UV–Vis (Fig. 3) and EPR (Fig. 8) spectral measurements. The absorption spectra of the coulometrically oxidized complexes show a weak broad band at 650 to 600 nm which is absent in the parent Cu(I) complexes. This band is assigned to a *d*–*d* transition of the Cu(II) complex (d⁹ confign.). The EPR spectra of the

Table 3

UV-Vis, fluorescence, lifetime and cyclic voltammetric data of L, and the copper(I) and silver(I) complexes.

Compound UV-Vis spectral data λ_{max} (nm), $10^{-3} \varepsilon$		Fluorescence data in				Fluorescence decay data in CH ₃ CN				Cyclic	
	$(dm^3 mol^{-1} cm^{-1})$ in CH ₃ CN	CH ₃ CN	I		Solid state	Solid state			voltammogram $0^{a} E$ (V) (ΔE_{P} , mV)		
		λ_{ex} (nm)	λ _{em} (nm)	Φ	$\lambda_{\rm em} ({\rm nm})$	χ^2	τ (ns)	$k_{\rm r} imes 10^{-9}$	$k_{ m nr} imes 10^{-9}$	E _M	EL
L	278(20.2), 326(8.8)	326	526	0.018	431, 455, 492, 537	0.99	8.37	0.0022	0.1173		
1	222(83.0), 277(72.6), 330(26.8), 453(1.6)	330	521	0.024	486, 531	1.1	10.2	0.0023	0.0957	0.80 (170)	-0.75 (160), -1.4
2	222(92.9), 276(93.4), 328(35.3)	328	525	0.032	481, 526	0.97	10.42	0.0031	0.0929	0.5 ^b 1.22 ^c	-0.65 (160), -1.55
3	223(42.8), 268(25.8), 334(6.5), 422(3.1)	334	496	0.025	488, 522	1.1	10.3	0.0024	0.0947	0.75 (165)	-0.77 (165), -1.42
4	222(73.6),276(74.5), 328(26.8)	328	520	0.021	484, 490	1.09	10.16	0.0021	0.0963	0.4 1.18 ^c	-0.7 (165), -1.65
5	223(58.5), 277(47.6), 335(15.9), 452(1.9)	335	520	0.026	495, 529	1.08	9.4	0.0026	0.1025	0.7 (160)	-0.8 (170), -1.45
6	224(52.8), 267(36.7), 332(5.5)	332	518	0.019	529	1.03	9.1	0.0025	0.1083	0.45 ^b 1.2 ^c	-0.67 (163), -1.60

^a Solvent, MeCN Pt-working electrode, SCE reference electrode, Pt-auxiliary electrode; [*n*-Bu₄N](ClO₄) supporting electrolyte, scan rate 50 mV/s; metal oxidation E_{M} = 0.5 ($E_{pa} + E_{pc}$), V, $\Delta E_{p} = |E_{pa} - E_{pc}|$, mV; E_{L} refers to ligand reduction.

^b *E*_{pa} (anodic-peak-potential).

^c *E*_{pc} (cathodic-peak-potential).



Cu(II) complexes provide information about the hyperfine and superhyperfine structures which helps define the geometry and distortion of the complexes. The spectra show the usual four line $(^{63}$ Cu, I = 3/2) EPR spectra and are anisotropic at higher magnetic fields (Fig. 8). Three peaks of low intensity in the weaker field are considered to originate from the g_{\parallel} component and A_{\parallel} lies at 150–160 × 10⁻⁴ cm⁻¹. The calculated g_{\parallel} and g_{\perp} values for these complexes were 2.18-2.22 and 2.02-2.05, respectively. The relation $g_{\parallel} > g_{\perp} > 2.0023$ agrees with the ground state configuration of $d_{x^2-y^2}$. The axial symmetry parameter, G > 4 $[G = (g_{11} - 2)/$ $(g_{\perp} - 2)$], supports no exchange interaction between the copper centers [32,33]. The presence of a weak broad spectral transition also supports the d-d transition in Cu(II) compounds [34]. Upon a one-electron reduction of the oxidized solutions the original Cu(I) complex was not regenerated, which is evident from spectral shifting and its structure pattern.

2.5. Redox interconversion, $Cu^{II} \leftrightarrow Cu^{I}$

 $[(L)Cu(\mu\text{-}dppm)_2Cu(L)](ClO_4)_2$ (1) and $[Cu(dppe)(L)]ClO_4$ (5) are oxidized to brown–red Cu(II) complexes by Cl₂ in CH₃CN solution

(Scheme 2) and the products are characterized by microanalytical, FT-IR, UV–Vis and mass spectroscopic, redox and magnetic moment data to $[(L)Cl_2Cu(\mu-dppm)_2CuCl_2(L)]$ (7) and $[Cu(dppe)(L)Cl_2]$ (8) (*vide* Section 4). These complexes (7 and 8) are reduced by Naascorbate to their Cu(I) precursor complexes and have been isolated as perchlorate salts upon adding NaClO₄. A similar oxidation of 2, 4 and 6 by Cl₂ and has precipitated quantitative AgCl.

The Cu(II)–Cu(I) interconversion has been established in both these complexes. Magnetic moment (room temperature) data (**7**, 2.88 BM; **8**, 1.65 BM) indicate the Cu(II) (d⁹) electronic state of the oxidized products **7** and **8**. Mass spectra of these compounds also support the molecular composition (Supplementary material, Fig. S4). Although complex **7** is a dimer, no significant metal–metal interaction is observed in the room temperature magnetic moment. The EPR spectra of **7** and **8** are recorded at liquid N₂ temperature (77 K) and show similar characteristics to Cu(II) complexes, as shown in the case of the coulometrically oxidized products. The solution spectra also show an additional weak band at 600– 650 nm corresponding to a d–d transition of the Cu(II) complexes.

The copper(II) complexes **7** and **8** are reduced by Na-ascorbate, followed by the precipitation of the perchlorate salt, and have been identified by matching the spectroscopic and cyclic voltammetric results of the Cu(I) precursor (Scheme 3). The compounds are diamagnetic. The structure of the coordinated Cu(I) compound has been established by its ¹H NMR spectrum and a comparison with the spectrum of the directly synthesized complexes. Microanalytical data (C, H, N) also confirm the composition of the compound.

2.6. DFT computations: explanation of the spectral and redox properties

The structural agreement has been verified by comparing the bond distances and angles between the DFT optimized and X-ray determined structure of **5**. The orbital energies, along with contributions from the ligands and metal, are given in the Supplementary material and Fig. 9 depicts some of the selected occupied and unoccupied MOs. To assign the electronic transitions, TD-DFT calculations were carried out for **5**.

In case of **1**, the HOMO is constituted of 47% dppm and 46% copper characteristics, and the LUMO has 96% contribution from L. So, the HOMO to LUMO transition may be assigned to the admixture of dppm \rightarrow L and Cu(d π) \rightarrow L(π *). In the case of **5**, the HOMO-1 is constituted by >90% contribution from L, whereas the HOMO has 67% dppe and 29% Cu(1) character. The LUMO, LUMO+1 and LUMO+2 are composed of L function (>95%). Thus, the HOMO to



Fig. 5. Emission spectra of (a) L, (b) $[(L)Cu(\mu-dppm)_2Cu(L)](CIO_4)_2$ (1), (c) $[(L)Ag(\mu-dppm)_2Ag(L)](NO_3)_2$ (2), (d) $[(L)Cu(\mu-dppe)Cu(L)](CIO_4)_2$ (3), (e) $[(L)Ag(\mu-dppe)Ag(L)](NO_3)_2$ (4), (f) $[Cu(dppe)(L)]CIO_4$ (5) and (g) $[Ag(dppe)(L)]NO_3$ (6) in the solid state.



Fig. 6. Exponential decay profiles (\bullet) and fitting curves (-) of (a) L, (b) [(L)Cu(μ -dppm)₂Cu(L)](ClO₄)₂ (1), (c) [(L)Ag(μ -dppe)Ag(L)](NO₃)₂ (4) and (d) [Cu(dppe)(L)]ClO₄ (5) in CH₃CN. Excitation is carried out at 370 nm.



Fig. 7. Cyclic voltammograms of (a) [(L)Cu(µ-dppm)₂Cu(L)](ClO₄)₂ (1) and (b) [(L)Ag(µ-dppm)₂Ag(L)](NO₃)₂ (2) in acetonitrile using Pt-bead, SCE reference and Pt-auxiliary electrodes in the presence of [*n*-Bu₄N]ClO₄ supporting electrolyte in MeCN solution at 100 mV scan rate.

LUMO transition is considered as the major transition which is $L(\pi) \rightarrow L(\pi^*)$ and dppe $\rightarrow L$ charge transfers. HOMO–3 has 40% L and 42% Cu(I) contribution. The transition HOMO–3 \rightarrow LUMO is described as a mixture of $L(\pi) \rightarrow L(\pi^*)$ and $Cu(d\pi) \rightarrow L(\pi^*)$ charge transfers.

In L, the electronic transitions at 325 and 278 nm are due to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions, respectively. The polar solvent stabilizes the occupied MOs more efficiently than those of unoccupied MOs. Thus, the energy separation (ΔE) between the HOMO and LUMO increase on going from the gas phase to the MeCN phase.



Fig. 8. EPR spectrum of a frozen oxidized solution of $[(L)Cu(\mu-dppm)_2Cu(L)](ClO_4)_2$ (1) at 77 K in CH_2Cl_2 .

The occupied MOs have significantly contributions from metal (29% of Cu(I) in **5** and 46% of Cu(I) in **1**); dppe contributes 67% to HOMO and 85% to HOMO–2 but only 2% to LUMO in complex **5**, whereas dppm contributes 47% to HOMO, 44% to HOMO–1 and only 2% to LUMO in **1**. The ligand L, in general, is the main constituent of the unoccupied MOs: LUMO, LUMO+1, LUMO+2 (**5**: LUMO to LUMO+2, 96–99% and **1**: LUMO to LUMO+2, 96–98%). The calculated transitions of **5** are grouped in Table 4. The intensity of these transitions has been assessed from the oscillator strength (*f*). In CH₃CN the calculated transition appears at ~487 nm (*f*, 0.0726) for **5**, along with a large number of transitions in the UV region

(<400 nm). The observed transitions (Fig 3 and Table 3) are more or less close to the calculated one in **5**. The charge transfer may not be assigned only to a pure MLCT, rather an admixture of $d(Cu) \rightarrow \pi^*(L)$ and $\pi(L) \rightarrow \pi^*(L)$ transitions involving HOMO- $-3 \rightarrow$ LUMO (in complex **5**).

The cyclic voltammetric behaviors of **4** and **5** are readily accountable from the DFT calculations. Because of the higher metal (Cu) contribution in the occupied MOs, the complexes show metal oxidation, which is indeed observed. The unoccupied MOs are significantly dominated by the diimine function (>90%), thus reduction may refer to electron accommodation at the diimine dominated orbital of the ligand. So the assignment of diimine reductions are justified.

3. Conclusion

Copper(I) and silver(I) complexes of N-[(2-pyridyl)methyliden]-6-coumarine (L) and with the auxiliary ligands dppm/dppe have been prepared and characterized by spectroscopic techniques. Complexes of the formula $[(L)Cu(\mu-dppm)_2Cu(L)](ClO_4)_2$ (1), $[(L)Ag(\mu-dppm)_2Ag(L)](NO_3)_2$ (2), $[(L)Cu(\mu-dppe)Cu(L)](ClO_4)_2$ (3), $[(L)Ag(\mu-dppe)Ag(L)](NO_3)_2$ (4), $[Cu(dppe)(L)]ClO_4$ (5) and [Ag(dppe)(L)]NO₃ (6) are reported in this work. In the cases of 1, 4 and 5, the structures have been confirmed by X-ray crystallography. The structure of the complex is distorted tetrahedral, in which the coumarin ligand coordinates in a bidentate fashion and the other two coordination sites are occupied by dppm (bridging)/ dppe in a chelating or bridging manner. The ligand and the complexes are fluorescent and the quantum yields of the complexes are higher than that of the ligand. The Cu(I) complexes show Cu(II)/Cu(I) redox responses, while the Ag(I) complexes exhibit deposition of Ag(0) on the electrode surface. The redox



Scheme 2. Oxidation of Cu(I) complexes 1 and 5 by Cl₂ in MeCN.



Scheme 3. Cu(II)/Cu(I) interconversion.



Fig. 9. Contour plots of some selected MOs of [(L)Cu(µ-dppm)₂Cu(L)](ClO₄)₂ (1), [(L)Ag(µ-dppe)Ag(L)](NO₃)₂ (4) and [Cu(dppe)(L)]ClO₄ (5).

interconversion Cu(II)–Cu(I) shows the structural flexibility of the copper complexes.

4. Experimental

4.1. Materials

AgNO₃, bis-(diphenylphosphino)methane (dppm), 1,2-bis (diphenylphosphino)ethane (dppe) and pyridine-2-carboxaldehyde were purchased from Aldrich Chemical Co. Coumarin was available from S.D. Fine Chem. Ltd., Boisar. [Cu(MeCN)₄]ClO₄ was prepared by standard procedures [22]. All the solvents were dried and purified by standard methods [35]. The acetonitrile used for electrochemical studies was dried with CaH₂ and distilled prior to use. Dinitrogen was purified by bubbling through an alkaline pyrogallol solution. All other chemicals and solvents were of reagent grade and were used without further purification.

4.2. Physical measurements

Microanalytical data (C, H, N) were collected on a Perkin-Elmer 2400 CHNS/O elemental analyzer. Spectroscopic data were obtained using the following instruments: UV–Vis spectra on a Perkin

Elmer UV-Vis spectrophotometer model Lambda 25; FT-IR spectra (KBr disk, 4000 to 400 cm⁻¹) on a Perkin Elmer FT-IR spectrophotometer model RX-1; ¹H NMR spectra on a Bruker (AC) 300 MHz FTNMR spectrometer. Mass spectra were collected from a JEOL MStation, JMS 700. Electrochemical measurements were performed using a computer-controlled CH-Instruments, Electrochemical workstation, Model No. CHI 600D (SPL) with Pt-disk electrodes. All measurements were carried out under a nitrogen environment at 298 K with reference to Ag/AgCl at 50 mV s⁻¹ scan rate using a Pt-bead working electrode in acetonitrile and [nBu₄₋ N]ClO₄ as the supporting electrolyte. The reported potentials are uncorrected for junction potential. Controlled potential coulometry was performed to know the number of electrons involved in the oxidation of Cu(I) in CH₃CN medium. It was carried out in an electrochemical cell using a suitable platinum wire gauge electrode, Ptcounter and Ag/AgCl reference electrodes. In the case of coulometry, a CH₃CN solution of the Cu(I) complex was electrolyzed against a constant potential of 1.0 V for 1 h. The total charge (C) provided during electrolysis of the Cu(I) complex was monitored against time in seconds and the results were analyzed. 0.1 M tetrabutylammonium perchlorate (TBAP) was used for CH₃CN media. Nitrogen gas was used to maintain an inert atmosphere and proper stirring was ensured. Emission was examined by an LS 55 Perkin

 Table 4

 Selected electronic excitation for [Cu(dppe)(L)]ClO₄ (5).

Excitation energy (eV)	Excitation wavelength(nm)	Osc. strength (f)	Key transitions	Character
2.4021	516.15	0.0223	(59%) HOMO $-2 \rightarrow$ LUMO	$Cu/dppe \rightarrow L$
25440	107.20	0.0700	(25%) HOMO $-3 \rightarrow$ LUMO	$Cu/L \rightarrow L$
2.5440	487.36	0.0726	$(65\%)HOMO-3 \rightarrow LOMO$	$Cu/L \rightarrow L$
2.8032	442.31	0.0248	$(75\%)HOMO-2 \rightarrow LUMO+1$	$Cu/dppe \rightarrow L$
3.1328	395.76	0.0258	(67%) HOMO $-10 \rightarrow$ LUMO+2	$Cu/dppe \rightarrow L$
3.4974	354.50	0.0259	$(92\%)HOMO \rightarrow LUMO+4$	$L \rightarrow dppe$
3.5987	344.52	0.0692	(53%) HOMO \rightarrow LUMO+5	$L \rightarrow dppe$
			(29%) HOMO \rightarrow LUMO+6	$L \rightarrow L$
3.6061	343.82	0.0399	(77%) HOMO $-7 \rightarrow$ LUMO+2	$L/dppe \rightarrow L$
3.6321	341.36	0.0779	(71%) HOMO \rightarrow LUMO+7	$L \rightarrow L$
3.6812	336.81	0.0349	(68%)HOMO \rightarrow LUMO+8	$L \rightarrow L$

Table 5

Summarized crystallographic data of 1, 4 and 5.

Crystal parameters	(1)	(4)	(5)
Empirical formula	C84H72Cl10Cu2N4O12P4	C ₅₇ H ₄₆ Ag ₂ Cl ₂ N ₆ O ₁₀ P ₂	C41H34ClCuN2O6P2
Formula weight	1934.92	1323.58	811.64
Temperature (K)	293(2)	293(2)	293(2)
Crystal system	triclinic	monoclinic	triclinic
Space group	ΡĪ	P2/c	ΡĪ
Unit cell dimensions			
a (Å)	13.041(5)	20.918(8)	10.4175(7)
b (Å)	15.066(5)	13.209(5)	13.9283(9)
c (Å)	23.657(5)	20.599(8)	14.3541(9)
α (°)	85.900(5)	90.00	96.819(2)
β (°)	85.608(5)	95.147(5)	104.294(2)
γ (°)	78.716(5)	90.00	105.001(2)
$V(Å)^3$	4537(2)	5669(4)	1912.0(2)
Ζ	2	4	2
λ (Å)	0.71073	0.71073	0.71073
μ (mm $^{-1}$)	0.893	0.905	0.775
D_{calc} (Mg m ⁻³)	1.416	1.551	1.410
Refine parameters	1030	713	478
Total reflection	15047	9842	7464
Unique data $[I > 2\sigma(I)]$	6340	4526	5420
$R_1^{a} \left[I > 2\sigma(I) \right]$	0.0873	0.0907	0.0478
wR_2^{b}	0.2031	0.1743	0.1262
Goodness of fit (GOF)	1.037	1.091	1.036

^a $R = \Sigma |F_0 - F_c| / \Sigma F_0$.

 $\int_{0}^{1} w_{R} \left[\sum w(F_{0}^{2} - F_{c}^{2}) / \sum wF_{0}^{4} \right]^{1/2} \text{ are general but } w \text{ are different, } w = 1/[\sigma^{2}(F_{0}^{2}) + (0.0780P)^{2} + 0.4301P] \text{ for (1); } w = [\sigma^{2}(-F_{0})^{2} + (0.0615P)^{2} + 10.2546P]^{-1} \text{ for (4); } w = [\sigma^{2}(F_{0})^{2} + (0.0961P)^{2} + 0.000P]^{-1} \text{ for (5) where } P = (F_{0}^{2} + 2F_{c}^{2}) / 3.$

Elmer spectrofluorimeter at room temperature (298 K) in CH₃CN solution under degassed conditions. The EPR spectra were recorded in CH₃CN solution at room temperature (298 K) and liquid nitrogen temperature (77 K) using a Bruker EPR spectrometer model EMX 10/12, X-band ER 4119 HS cylindrical resonator.

The fluorescence quantum yield of the complexes was determined using carbazole as a reference with a known ϕ_R value of 0.42 in benzene [36]. Carbazole was used as we do not have a more accurate fluorophore to compare the emission data of the present series of complexes. The complex and the reference dye were excited at the same wavelength, maintaining nearly equal absorbance (~0.1), and the emission spectra were recorded. The area of the emission spectrum was integrated using the software available in the instrument and the quantum yield was calculated according to the following equation:

$$\phi_S/\phi_R = [A_S/A_R] \times [(Abs)_R/(Abs)_S] \times [\eta_S^2/\eta_R^2]$$
(1)

Here, ϕ_S and ϕ_R are the fluorescence quantum yields of the sample and reference, respectively. A_S and A_R are the areas under the fluorescence spectra of the sample and the reference, respectively, (Abs)_S and (Abs)_R are the respective optical densities of the sample and the reference solution at the wavelength of excitation, and η_S and η_R are the values of the refractive index for the respective solvents used for the sample and reference.

Fluorescence lifetimes were measured using a time-resolved spectrofluorometer from IBH, UK. The instrument uses a picoseconds diode laser (NanoLed-07, 370 nm) as the excitation source and works on the principle of time-correlated single photon counting [37]. The instrument responses function is \sim 230 ps at FWHM. To eliminate depolarization effects on the fluorescence decays. measurements were done with magic angle geometry (54.7°) for the excitation and emission polarizers. The observed decays of $[(L)Cu(\mu-dppm)_2Cu(L)](ClO_4)_2$ (1), $[(L)Ag(\mu-dppm)_2Ag(L)](NO_3)_2$ (2), $[(L)Cu(\mu-dppe)Cu(L)](ClO_4)_2$ (3) and $[(L)Ag(\mu-dppe)Ag(L)]$ $(NO_3)_2$ (4) fit with a single exponential decay, whereas [(L) Cu(dppe) [ClO₄ (**5**) and [(L)Ag(dppe)]NO₃ (**6**) fit with a bi-exponential decay as in the following equation where τ 's are the fluorescence lifetimes and α is the pre-exponential factor. For the fits, the reduced χ^2 values were within 0.97–1.1 and the distributions of the weighted residuals were random among the data channels. τ_f is the mean fluorescence lifetime (the meanings of the symbols are as usual) [38].

$$I(t) = [a_1 \exp(-t/\tau_1) - a_2 \exp(-t/\tau_2)]$$
(2)

$$\tau_f = a_1 \tau_1 + a_2 \tau_2 \tag{3}$$

4.3. Synthesis

4.3.1. Synthesis of N-[(2-pyridyl)methyliden]-6-coumarine (L)

Nitration of coumarin by mixed acid has synthesized 6-nitro coumarine. It is reduced by Fe powder/NH₄Cl to 6-aminocoumarine. The reaction of pyridine-2-carboxaldehyde and 6-aminocoumarin has synthesized N-[(2-pyridyl)methyliden]-6-coumarin (L). Detailed characterization is reported elsewhere [16].

4.3.2. Synthesis of the complexes

4.3.2.1. $[(L)Cu(\mu-dppm)_2Cu(L)](ClO_4)_2$ (1). [Cu(MeCN)₄]ClO₄ (0.025 g, 0.076 mmol) was taken in a double neck round bottom flask dissolved in dry MeOH, with magnetic stirring under N₂ atmosphere. Then bis-(diphenylphosphino)methane (0.0293 g, 0.076 mmol) was added to this solution and stirred magnetically. After half an hour, L (0.019 g, 0.076 mmol) was added to the reaction mixture and stirred for another 2 h. A vellow precipitate was obtained. It was collected by filtration and dried. The compound in CH₂Cl₂ solution was layered with hexane to get single crystals by the diffusion technique. The complex was obtained in 0.11 g (75%) yield; decomposition temperature >192 °C. FT-IR (KBr, cm⁻¹): v(COO) 1730; v(C=N) 1591; v(ClO₄) 1095 (s), 625 (w). $[(L)Cu(\mu-dppm)_2Cu(L)](ClO_4)_2$ (1): $C_{80}H_{64}Cl_2Cu_2$ N₄O₁₂P₄: Anal. Calc.: C, 54.8; H, 4.17; N, 3.65. Found: C, 54.85; H, 4.15; N, 3.62%.

4.3.2.2. $[(L)Ag(\mu-dppm)_2Ag(L)](NO_3)_2$ (**2**). To an AgNO₃ (0.025 g, 0.15 mmol) solution in MeOH (20 ml) in the dark with stirring, bis(diphenylphosphino)methane (0.0565 g, 0.15 mmol) was added and stirred for one hour. Then L (0.0368 g, 0.15 mmol) was added to this solution and was magnetically stirred for 2 h. A light yellow precipitate was obtained. It was collected by filtration and dried. The complex was obtained in 0.16 g (70%) yield; decomposition temperature >264 °C. FT-IR (KBr, cm⁻¹): v(COO) 1731; v(C=N) 1590; $v(NO_3)$ 1385. $[(L)Ag(\mu-dppm)_2Ag(L)](NO_3)_2$ (**2**): C₈₀H₆₄Ag₂ N₆O₁₀P₄: *Anal.* Calc.: C, 59.7; H, 3.98; N, 5.22. Found: C, 59.68; H, 3.96; N, 5.25%.

4.3.2.3. $[(L)Cu(\mu-dppe)Cu(L)](ClO_4)_2$ (**3**). $[Cu(MeCN)_4]ClO_4$ (0.025 g, 0.076 mmol) was dissolved in dry MeOH (20 ml) by magnetic stirring under N₂ atmosphere. Then 1,2-bis(diphenylphosphino)ethane (0.015 g, 0.038 mmol) was added to this solution and stirred magnetically. After half an hour L (0.019 g, 0.076 mmol) was added to the reaction mixture and stirred for another 2 h. Red colored precipitate was obtained. It was filtered and collected. The complex was obtained in 0.075 g (80%) yield; decomposition temperature >230 °C. FT-IR (KBr, cm⁻¹): v(COO), 1708; v(C=N), 1588; $v(ClO_4)$ 1093(s), 1150(m), 621(w). $[(L)Cu(\mu-dppe)Cu(L)](ClO_4)_2$ (**3**): C₅₆H₄₄. Cl₂Cu₂ N₄O₁₂P₂: *Anal.* Calc.: C, 54.9; H, 3.6; N, 4.6. Found: C, 54.8; H, 3.7; N, 4.7%.

4.3.2.4. $[(L)Ag(\mu-dppe)Ag(L)](NO_3)_2$ (**4**). To an AgNO₃ (0.025 g, 0.15 mmol) solution in MeOH (20 ml) in the dark with stirring, 1,2-bis(diphenylphosphino)ethane (0.029 g, 0.075 mmol) was added and stirred for 1 h. Then L (0.0368 g, 0.15 mmol) was added to this solution and magnetically stirred for 2 h. A yellow colored precipitate was obtained. It was collected by filtration and dried. This yellow compound was dissolved in CH₂Cl₂ and layered with hexane to get single crystals. The complex was obtained in 0.15 g (85%) yield; decomposition temperature >250 °C. FT-IR (KBr, cm⁻¹): v(COO) 1709; v(C=N) 1590; $v(NO_3)$ 1434, 1383, 1312. [(L)Ag(dppe)Ag(L)](NO_3)_2 (**3**): C₅₆H₄A₄Ag₂N₆O₁₀P₂: Anal. Calc.: C, 54.28; H, 3.55; N, 6.78. Found: C, 54.3; H, 3.5; N, 6.8%.

4.3.2.5. $[Cu(dppe)(L)]ClO_4$ (**5**). $[Cu(MeCN)_4]ClO_4$ (0.025 g, 0.076 mmol) was dissolved in dry MeOH (20 ml) by magnetic stirring under a N₂ atmosphere. Then 1,2-bis-(diphenylphosphino)ethane

(0.030 g, 0.076 mmol) was added to this solution and stirred magnetically. After half an hour L (0.019 g, 0.076 mmol) was added to the reaction mixture and stirred for another two hours. Then the solution was refluxed for two further hours. The solution color changed to deep red. It was cooled, filtered and kept undisturbed. After 15 days, red single crystals were obtained and collected. The complex was obtained in 0.049 g (80%) yield; decomposition temperature >210 °C. FT-IR (KBr, cm⁻¹): ν (COO) 1731; ν (C=N) 1566; ν (ClO₄) 1090 (s), 620 (w). [Cu(dppe)(L)]ClO₄ (**5**): C₄₁H₃₄ClCu N₂O₆P₂: *Anal.* Calc.: C, 60.6; H, 4.2; N, 3.4. Found: C, 60.65; H, 4.18; N, 3.2%.

4.3.2.6. $[Ag(dppe)(L)]NO_3$ (**6**). To an AgNO₃ (0.025 g, 0.15 mmol) solution in MeOH (20 ml) in the dark with stirring, 1,2-bis(diphenylphosphino)ethane (0.058 g, 0.15 mmol) was added and stirred for 1 h. Then L (0.0368 g, 0.15 mmol) was added to this solution and magnetically stirred for 2 h. After that the solution was refluxed for nearly two hours. A yellow colored precipitate was obtained. The solution was cooled, collected by filtration and dried. The complex was obtained in 0.104 g (85%) yield; decomposition temperature >230 °C. FT-IR (KBr, cm⁻¹): v(COO) 1733; v(C=N) 1571; $v(NO_3)$ 1383. [Ag(dppe)(L)]NO₃ (**6**) C₄₁H₃₄AgN₃O₅P₂: Anal. Calc.: C, 60.1; H, 4.2; N, 5.1. Found: C, 59.9; H, 4.3; N, 5.2%.

4.4. Cu(II) ··· Cu(I) interconversion

 $[(L)Cu(\mu-dppm)_2Cu(L)](ClO_4)_2$ (1)

 $\times \overset{Cl_2}{\rightarrow} \overset{solution}{=} [(L)Cl_2Cu(\mu\text{-}dppm)_2CuCl_2(L)] \ \textbf{(7)}$

 $[(L)Cu(\mu-dppm)_2Cu(L)](ClO_4)_2$ (1) (120 mg, 0.075 mmol) was dissolved in CH₃CN and chlorine saturated in acetonitrile was added in drops. The resultant brown–red solution was stirred for 6 h at room temperature with time-to-time addition of drops of chlorine in acetonitrile. The solution color turned permanently to deep brown–red. A solution of LiCl in acetonitrile (2 ml, 0.2 mmol) was added and stirred for few minutes. The resulting solution was then filtered and allowed to evaporate in air. The solid mass so obtained was washed with a profuse amount of water, recrystallised from methanol and then dried in a CaCl₂ desiccator. Yield 69 mg (60%).

$$\begin{split} & [(L)Cl_2Cu(\mu\text{-}dppm)_2CuCl_2(L)] \ \textbf{(7)} \xrightarrow[(ii)]{NaScc}_{(ii) NaClO_4} [(L)Cu(\mu\text{-}dppm)_2Cu(L)] \\ & \times (ClO_4)_2 \ \textbf{(1)} \end{split}$$

To a stirred solution of $[(L)Cl_2Cu(\mu-dppm)_2CuCl_2(L)]$ (7) (50 mg, 0.033 mmol), Na-ascorbate (Na-Asc) (10.5 mg, 0.053 mmol) was added pinchwise in excess. The resultant dark brown-red solution was stirred for 3 h at room temperature and then filtered. The filtrate was left for slow evaporation at room temperature in a beaker to reduce its volume to half, followed by the addition of NaClO₄ (aqueous). A dark crystalline compound was deposited on the wall of container after a week. The product was then washed with water and dried in a CaCl₂ desiccator. Recrystallisation was carried out by diffusion of a CH₂Cl₂ solution of the compound into hexane. Yield 34 mg (64%).

[(L)Cl₂Cu(μ-dppm)₂CuCl₂(L)] (7): Decomposition temperature >214 °C; FT-IR(KBr, ν cm⁻¹): ν(COO) 1734; ν(C=N) 1590; UV (λ_{max} , nm (ε , 10³ M⁻¹ cm⁻¹) in CH₃CN): 650 (0.18), 494 (0.35), 354 (7.5), 287 (14.8); Magnetic moment (room temperature) data: 2.88 BM; EPR data: $g_{||}$, 2.18; g_{\perp} , 2.02; $A_{||}$, 150 × 10⁻⁴ cm⁻¹; *m/z*: 1535.8; C₈₀₋H₆₄Cl₄Cu₂N₄O₄P₄: *Anal.* Calc.: C, 62.43; H, 4.16; N, 3.64. Found: C, 62.45; H, 4.12; N, 3.61%.

[*Cu*(*dppe*)(*L*)*Cl2*] (**8**): 0.034 g (70%) yield; decomposition temperature >224 °C; FT-IR (KBr, cm⁻¹): v(COO) 1734; v(C=N) 1571;

UV (λ_{max} , nm (ϵ , 103 M⁻¹ cm⁻¹) in CH3CN): 654 (0.25), 491 (0.51), 355 (7.8), 285 (14.3); Magnetic moment (room temperature) data: 1.65 BM; EPR data: g_{\parallel} , 2.2; g_{\perp} , 2.04; A_{\parallel} , 155 \times 10⁻⁴ cm⁻¹; m/z: 780.7; C41H34Cl2CuN2O2P2: Anal. Calc.: C, 62.88; H, 4.35; N, 3.58. Found: C, 62.85; H, 4.36; N, 3.61%.

4.5. X-ray crystallography

 $[(L)Cu(\mu-dppm)_2Cu(L)](ClO_4)_2$ (1) (0.28 × 0.24 × 0.22 mm) and $[(L)Ag(dppe)Ag(L)](NO_3)_2$ (4) $(0.24 \times 0.18 \times 0.15 \text{ mm})$ were crystallized by slow diffusion of a CH₂Cl₂ solution of the complexes into hexane and $[Cu(dppe)(L)]ClO_4$ (5) $(0.33 \times 0.29 \times 0.26 \text{ mm})$ was crystallized by slow evaporation of a methanol solution of the complex. Data were collected on a Bruker Smart Apex II CCD Area Detector at 293(2) K. Diffractions were recorded with 2θ in the range $3.18 \le 2\theta \le 49.22$ (1), $3.66 \le 2\theta \le 50$ (4) and $2.98 \leq 2\theta \leq 52$ (**5**). A fine-focus sealed tube was used as the radiation source of the graphite-monochromatized Mo K α radiation $(\lambda = 0.71073 \text{ Å})$. Data were corrected for Lorentz and polarization effects and an empirical absorption correction in the *hkl* range: $-15 \leq h \leq 15$; $-17 \leq k \leq 17$; $-27 \leq l \leq 27$ for **1**, $-24 \leq h \leq 24$; $-15 \le k \le 15$; $-24 \le l \le 24$ for **4** and $-12 \le h \le 12$; $-17 \le k \le 16$; $-18 \le l \le 18$ for **5**. The structures were solved and refined by fullmatrix least-squares techniques on F^2 using the SHELX-97 program with anisotropic displacement parameters for all non-hydrogen atoms [39,40]. Crystallographic refinement data and selected geometric parameters are collected in Table 5. Hydrogen atoms were constrained to ride on the respective carbon atoms with isotropic displacement parameters equal to 1.2 times the equivalent isotropic displacement of their parent atom for all the aromatic units.

4.6. Theoretical calculations

Full geometry optimization of $[Cu(dppe)(L)]ClO_4$ (5) and single point calculations of $[(L)Cu(\mu-dppm)_2Cu(L)](ClO_4)_2$ (1) and $[(L)Ag(dppe)Ag(L)](NO_3)_2$ (4) were carried out using density functional theory (DFT) at the B3LYP level [41-43]. All calculations were carried out using the GAUSSIAN 03 program package [44] with the aid of the GAUSS VIEW visualization program [45]. For C, H, N, O and P atoms the 6-31G(d) basis sets were assigned, while for Cu and Ag the LanL2DZ basis sets with effective core potential were employed [46]. The vibrational frequency calculations were performed to ensure that the optimized geometries represent the local minima and there are only positive eigen values. Vertical electronic excitations based on B3LYP optimized geometries were computed for [Cu(dppe)(L)]ClO₄ (5) using the time-dependent density functional theory (TD-DFT) formalism [47-49] in acetonitrile using a conductor-like polarizable continuum model (CPCM) [50-52]. GAUSS SUM was used to calculate the fractional contributions of various groups to each molecular orbital [53].

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Appendix A. Supplementary material

CCDC 847595, 847596 and 847594 contain the supplementary crystallographic data for for $[(L)Cu(\mu-dppm)_2Cu(L)](ClO_4)_2$ (1), $[(L)Ag(\mu-dppe)Ag(L)](NO_3)_2$ (4) and for Cu(dppe)(L)]ClO₄ (5). These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/ conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccpadc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2012.11.050.

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