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# Homoleptic Copper(I), Silver(I), and Gold(I) Bisphosphine Complexes

Adrien Kaeser,<sup>[a,b]</sup> Omar Moudam,<sup>[a,b]</sup> Gianluca Accorsi,<sup>[c]</sup> Isabelle Séguy,<sup>\*[d,e]</sup> Jose Navarro,<sup>[d]</sup> Abdelhalim Belbakra,<sup>[c]</sup> Carine Duhayon,<sup>[b]</sup> Nicola Armaroli,<sup>\*[c]</sup> Béatrice Delavaux-Nicot,<sup>\*[b]</sup> and Jean-François Nierengarten<sup>\*[a,b]</sup>

Dedicated to Bruno Chaudret on the occasion of his 60th birthday

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A series of homoleptic copper(I), silver(I), and gold(I) complexes of two bisphosphine ligands {1,2-bis(diphenylphosphino)benzene, dppb; bis[2-(diphenylphosphino)phenyl]-ether, POP} have been prepared. Whilst all three [M(dppb)<sub>2</sub>]-BF<sub>4</sub> complexes are tetracoordinate, this geometry is found only for the silver(I) complex with POP. Instead,  $[Cu(POP)_2]^+$  and  $[Au(POP)_2]^+$  adopt a trigonal coordination geometry with an uncoordinated phosphorus atom. A close inspection of the P–M bond lengths reveals an interesting trend. From the copper to silver and gold complexes, a substantial elongation is found. On the other hand, from the silver to gold compounds, a decrease in the M–P bond length is found. Indeed, gold(I) has a smaller van der Waals radius than silver(I) as a result of its peculiar relativistic effects. Electrochemical in-

## Introduction

Bisphosphines are widely used chelating ligands, and the coordination properties of many commercially available

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vestigations revealed two oxidation processes for all of the  $[M(dppb)_2]BF_4$  and  $[M(POP)_2]BF_4$  complexes. The first oxidation is likely metal-centered, whereas the second one corresponds to ligand-centered processes in all cases. The emission properties of these compounds in solution, in frozen rigid matrices at 77 K, and in the solid state at room temperature have been systematically investigated. Although all of them are weak emitters in solution, remarkably high emission quantum yields were found in the solid state, in particular for  $[Cu(dppb)_2]BF_4$  and  $[Ag(dppb)_2]BF_4$ . Finally, these two compounds were used for the fabrication of light-emitting devices. Interestingly, both the copper(I) and the silver(I) complex afford quite broad electroluminescence spectra with white light emission.

bisphosphine derivatives have been systematically investigated with virtually all of the metallic elements.<sup>[1]</sup> In the particular case of the group 11 elements, a strong driving force for structural investigations of bisphosphine complexes is related to their relevance in the field of catalysis.<sup>[2]</sup> In contrast, their electronic properties have attracted attention only in recent years. The discovery of strongly luminescent copper(I) complexes incorporating bisphosphine ligands in their coordination sphere has been the starting point of this research. In particular, McMillin and coworkers have reported heteroleptic Cu<sup>I</sup> complexes prepared from 1,10-phenanthroline derivatives and bis[2-(diphenylphosphino)phenyl]ether (POP),<sup>[3,4]</sup> which are characterized by remarkably high emission quantum yields from their long lived metal-to-ligand charge-transfer (MLCT) excited states. Following this key finding, numerous examples of related heteroleptic Cu<sup>I</sup> complexes have been prepared from bisphosphine and aromatic diimine ligands.<sup>[5-7]</sup> Eventually, copper(I) compounds prepared exclusively from bisphosphine ligands were also reported.<sup>[8,9]</sup> Some of these compounds exhibit excellent emission properties, which have been exploited to fabricate efficient electroluminescent devices; therefore, inexpensive and earth-abundant copper(I)

<sup>[</sup>a] Laboratoire de Chimie des Matériaux Moléculaires, Université de Strasbourg et CNRS (UMR 7509), 25 rue Becquerel, 67087 Strasbourg Cedex 2, France E-mail: nierengarten@unistra.fr http://www-ecpm.u-strasbg.fr/umr7509/ WebLaboNierengarten.htm
[b] Laboratoire de Chimie de Coordination du CNRS (UPR 8241), Université de Toulouse (UPS, INPT), 205 Boute de Narbonne 21077 Toulouse France

<sup>205</sup> Route de Narbonne, 31077 Toulouse, France E-mail: beatrice.delavaux-nicot@lcc-toulouse.fr http://www.lcc-toulouse.fr/lcc/spip.php?article25
[c] Istituto per la Sintesi Organica e la Fotoreattività, Consiglio Nazionale delle Ricerche, Via Gobetti 101, 40129 Bologna, Italy

E-mail: nicola.armaroli@isof.cnr.it

http://www.isof.cnr.it/?q=content/armaroli-nicola [d] Laboratoire Plasma et Conversion d'Energie (LAPLACE), UPS-CNRS (UMR 5213),

<sup>118</sup> route de Narbonne, 31062 Toulouse Cedex 9, France[e] CNRS, LAAS,7 avenue du colonel Roche, 31400 Toulouse, France

E-mail: iseguy@laas.fr http://www.laas.fr/MICA/



is an attractive alternative to noble metal ions for such applications.<sup>[9–11]</sup> Investigations on luminescent bisphosphine copper(I) complexes have also been extended to analogous silver(I) and gold(I) derivatives.<sup>[12–17]</sup> Interesting vapochromic and mechanochromic properties have been reported for these silver(I) and gold(I) derivatives.<sup>[13,14]</sup> Luminescent gold(I) bisphosphine complexes have also been tested in light-emitting devices.<sup>[15a]</sup>

In the frame of this expanding research field, we prepared  $[Cu(PP)_2]^+$  complexes with various bisphosphine ligands and systematically investigated their electronic properties.<sup>[9]</sup> The emission properties of the copper(I) complex with 1,2-bis(diphenylphosphino)benzene (dppb) were particularly interesting. Although the emission quantum yield of this compound is quite low in solution, it exhibits bright luminescence in the solid state at room temperature as well as in rigid frozen CH<sub>2</sub>Cl<sub>2</sub> solutions at 77 K. Indeed, under these conditions, geometric distortions that prompt nonradiative deactivation of the MLCT excited states are prevented, as is often observed for copper(I) complexes.<sup>[18,19]</sup> The [Cu(dppb)<sub>2</sub>]<sup>+</sup> complex has also been used for the fabrication of an electroluminescent device.<sup>[9]</sup>

Following these earlier studies on copper(I) compounds, we became naturally interested in extending our investigations to analogous silver(I) and gold(I) complexes. In this paper, we now report homoleptic copper(I), silver(I), and gold(I) complexes prepared from two bisphosphine ligands, namely, dppb and POP. Although the three complexes obtained from dppb are tetracoordinate, this geometry is found only for the silver(I) compound with POP. Indeed, both [Cu(POP)<sub>2</sub>]<sup>+</sup> and [Au(POP)<sub>2</sub>]<sup>+</sup> adopt a trigonal coordination geometry with an uncoordinated phosphorus atom. The electrochemical and photophysical properties of the six compounds have been investigated and rationalized on the basis of their different coordination geometries. Finally, the potential for electroluminescence applications has been evaluated for the most promising compounds.

## **Results and Discussion**

#### Synthesis and Characterization

As shown in Scheme 1, the copper(I) complexes  $[Cu(dppb)_2]BF_4$  and  $[Cu(POP)_2]BF_4$  were obtained by treatment of the corresponding bisphosphine ligand (2 equiv.) with  $[Cu(CH_3CN)_4]BF_4$  (1 equiv.) in CH<sub>2</sub>Cl<sub>2</sub>. Both compounds were then isolated in pure form by recrystallization in CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O.  $[Cu(dppb)_2]^+$  has been reported previously as its PF<sub>6</sub><sup>-</sup> or C<sub>n</sub>F<sub>2n+2</sub>CO<sub>2</sub><sup>-</sup> (*n* = 2, 4, 6, 8 or 9) salts.<sup>[20,21]</sup> The homoleptic copper(I) complex obtained from POP has been reported previously by Balakrishna<sup>[22]</sup> and some of us<sup>[7]</sup> in independent studies.

The reaction of  $AgBF_4$  with two equivalents of the appropriate bisphosphine ligand in  $CH_2Cl_2/MeOH$  (5:1) gave the corresponding homoleptic silver(I) complexes. [Ag(dppb)<sub>2</sub>]BF<sub>4</sub> was isolated in 93% yield by recrystallization in  $CH_2Cl_2/Et_2O$ , and [Ag(POP)<sub>2</sub>]BF<sub>4</sub> was obtained in 70% yield by recrystallization in  $CH_2Cl_2/hexane$ . Both



Scheme 1. Preparation of  $[M(dppb)_2]BF_4$  and  $[M(POP)_2]BF_4$  (M = Cu, Ag, or Au); all of the compounds were isolated in pure form by recrystallization in either CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O or CH<sub>2</sub>Cl<sub>2</sub>/hexane. Reagents and conditions: (i)  $[Cu(CH_3CN)_4]BF_4$ , CH<sub>2</sub>Cl<sub>2</sub> { $[Cu(dppb)_2]BF_4$ : 68%;  $[Cu(POP)_2]BF_4$ : 83%}; (ii) AgBF<sub>4</sub>, CH<sub>2</sub>Cl<sub>2</sub>/MeOH (5:1) { $[Ag(dppb)_2]BF_4$ : 93%;  $[Ag(POP)_2]BF_4$ : 70%}; (iii)  $[Au(SMe_2)]Cl$ , CH<sub>2</sub>Cl<sub>2</sub> then NaBF<sub>4</sub>, CH<sub>2</sub>Cl<sub>2</sub>/H<sub>2</sub>O { $[Au(dppb)_2]BF_4$ : 97%;  $[Au(POP)_2]BF_4$ : 91%}.

 $[Ag(dppb)_2]^+$  and  $[Ag(POP)_2]^+$  have been reported previously as their hexafluorophosphate<sup>[12]</sup> and triflate<sup>[23]</sup> salts, respectively.

Finally, the corresponding gold complexes were obtained by addition of the appropriate bisphosphine ligand (dppb or POP) to a suspension of  $[Au(SMe_2)]Cl$  in CH<sub>2</sub>Cl<sub>2</sub>. After 1 h, the resulting  $[Ag(PP)_2]Cl$  complexes<sup>[13,15c]</sup> were subjected to an anion-exchange reaction. Aqueous NaBF<sub>4</sub> solutions (1 M) were added to the reaction mixtures. After 1 h of vigorous stirring, the organic layers were evaporated, and the gold complexes were isolated as their tetrafluoroborate salts by recrystallization.

X-ray quality crystals were obtained for the six complexes, and X-ray crystal structure analyses were performed for the whole series. The structures are depicted in Figures 1 and 2; selected bond lengths and angles are summarized in Tables 1 and 2. Whatever the metal, the  $[M(dppb)_2]^+$  cations are all tetracoordinate and both dppb ligands chelate the metal center. The relative orientations of the two dppb ligands are very similar for the three  $[M(dppb)_2]^+$  cations. However, in contrast to that of  $[Cu(dppb)_2]BF_4$ , the structures of  $[Ag(dppb)_2]BF_4$  and  $[Au(dppb)_2]BF_4$  are not centrosymmetric. In these two cases, the two cocrystallized CH<sub>2</sub>Cl<sub>2</sub> molecules change substantially the packing of the



 $[M(dppb)_2]^+$  cations (M = Ag or Au) when compared to the packing of the corresponding copper complex, for which no cocrystallized solvent molecules are present. For this reason, the environment around the metal center cannot remain centrosymmetric for the silver and gold complexes. A close inspection of the P-M bond lengths reveals an interesting trend. From copper to silver or gold, a substantial increase is observed [Cu-P 2.291(1)-2.309(1) Å; Ag-P 2.478(4)-2.510(3) Å, Au-P 2.388(1)-2.432(1); see Table 1]. This is line with the larger size of silver or gold ions when compared with copper ions. In contrast, a comparison of the silver and gold complexes revealed a decrease in the M-P bond lengths when going down the column of the group 11 elements. Indeed, gold(I) has a smaller van der Waals radius than that of silver(I) as a result of its peculiar relativistic effects.<sup>[24]</sup> This size feature is also responsible for significant differences in the electrochemical properties of  $[Au(dppb)_2]BF_4$  when compared with those of the copper and silver analogues (vide infra).



Figure 1. Structure of the  $[M(dppb)_2]^+$  cations in the X-ray crystal structures of (A)  $[Cu(dppb)_2]BF_4$ , (B)  $[Ag(dppb)_2]BF_4$ ·2(CH<sub>2</sub>Cl<sub>2</sub>), and (C)  $[Au(dppb)_2]BF_4$ ·2(CH<sub>2</sub>Cl<sub>2</sub>). Thermal ellipsoids drawn at the 50% probability level, H atoms omitted for clarity. C: pale gray, P: gray, Cu: dark gray, Ag: dark gray, Au: dark gray.

As shown in Figure 2, both POP ligands chelate the silver(I) cation, which is in a distorted tetrahedral  $AgP_4$  coordination environment. In contrast, for both copper and gold, one POP ligand behaves as a chelating unit, but only one P atom of the second POP ligand coordinates effectively to the metal center. The other P atom of the latter ligand is clearly located at a nonbonding distance from the metal center [Cu(1)–P(4) 3.958(2) Å and Au(1)–P(4) 3.9788(8) Å]. As a result, both the copper(I) and the gold(I) center adopt a trigonal coordination geometry with P–M–P bond angles close to 120° (see Table 2). In both cases, the metal ions lie almost in the center of the P(1)–P(2)–P(3) plane (deviation of 0.21 Å for the copper complex and 0.16 Å for the gold complex). Whatever the metal, the ether



Figure 2. Structure of the  $[M(POP)_2]^+$  cations in the X-ray crystal structures of (A)  $[Cu(POP)_2]BF_4$ , (B)  $[Ag(POP)_2]BF_4$ ·1.5 $(CH_2Cl_2)$ ·2.5 $(H_2O)$ , and (C)  $[Au(POP)_2]BF_4$ . Thermal ellipsoids drawn at the 50% probability level, H atoms omitted for clarity. C: pale gray, P: gray, O: black, Cu: dark gray, Ag: dark gray, Au: dark gray.

Table 1. Bond lengths [Å] and angles [°] within the coordination spheres of  $[Cu(dppb)_2]^+$ ,  $[Ag(dppb)_2]^+$ , and  $[Au(dppb)_2]^+$  (see Figure 1 for the numbering).

	[Cu(dppb) <sub>2</sub> ] <sup>+[a]</sup>	[Ag(dppb) <sub>2</sub> ] <sup>+</sup>	[Au(dppb) <sub>2</sub> ] <sup>+</sup>
M(1)–P(1)	2.309(1)	2.510(3)	2.432(1)
M(1) - P(2)	2.291(1)	2.478(4)	2.3931(1)
M(1) - P(3)		2.508(3)	2.388(1)
M(1) - P(4)		2.495(4)	2.414(1)
P(1)-M(1)-P(2)	84.72(3)	82.27(11)	83.60(2)
P(1)-M(1)-P(3)		80.05(11)	84.25(2)
P(1)-M(1)-P(4)		122.96(11)	120.30(2)
P(2)-M(1)-P(3)		123.10(12)	121.70(2)
P(2)-M(1)-P(4)		121.26(12)	130.17(2)
P(3)-M(1)-P(4)		130.93(12)	121.84(2)
P(1)-M(1)-P(1')	122.59(5)		
P(1)-M(1)-P(2')	120.94(3)		
P(2)-M(1)-P(2')	127.85(5)		

[a] From ref.<sup>[9]</sup>

Table 2. Bond lengths [Å] and angles [°] within the coordination spheres of  $[Cu(POP)_2]^+$ ,  $[Ag(POP)_2]^+$ , and  $[Au(POP)_2]^+$  (see Figure 2 for the numbering).

	$[Cu(POP)_2]^{+[a]}$	$[Ag(POP)_2]^+$	[Au(POP) <sub>2</sub> ] <sup>+</sup>
M(1) - P(1)	2.273(2)	2.610(2)	2.3748(6)
M(1) - P(2)	2.261(2)	2.611(2)	2.3849(7)
M(1) - P(3)	2.263(2)	2.539(2)	2.3419(6)
M(1) - P(4)	3.958(2)	2.524(2)	3.9788(8)
P(1)-M(1)-P(2)	114.03(6)	111.46(6)	111.78(2)
P(1)-M(1)-P(3)	121.49(5)	104.48(6)	123.34(2)
P(1)-M(1)-P(4)		111.94(6)	
P(2)-M(1)-P(3)	121.90(5)	108.16(6)	123.49(2)
P(2)-M(1)-P(4)		111.75(6)	
P(3)-M(1)-P(4)		108.71(6)	

[a] From ref.<sup>[7]</sup>

O atoms of the POP ligands are always at a nonbonding distance from the metal centers (>3.2 Å). In the case of the



smallest cations, that is, copper and gold, it appears that the metal center is unable to accommodate two POP chelating ligands. This is most probably the result of steric crowding, which forces one of the four P atoms out of the coordination sphere and results in tricoordinate complexes. In contrast, the silver cation is larger than the copper and gold cations; therefore, the M–P bonds are longer (Table 2) and allow the system to accommodate a tetrahedral geometry with two chelating POP ligands.

The compounds  $[M(dppb)_2]BF_4$  and  $[M(POP)_2]BF_4$  (M = Cu, Ag, or Au) were also characterized in solution by NMR spectroscopy. Their structures were further confirmed by mass spectrometry. The NMR spectra for all of the dppb derivatives in CD<sub>2</sub>Cl<sub>2</sub> are fully consistent with their X-ray crystal structures. Their <sup>31</sup>P{<sup>1</sup>H} NMR spectra  $(CD_2Cl_2)$  revealed that the four P atoms are equivalent for all of the  $[M(dppb)_2]BF_4$  derivatives. Effectively, a single resonance is observed at  $\delta = 8.12$  and 21.43 ppm for [Cu(dppb)<sub>2</sub>]BF<sub>4</sub> and [Au(dppb)<sub>2</sub>]BF<sub>4</sub>, respectively. For  $[Ag(dppb)_2]BF_4$ , the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum displays two doublets centered at  $\delta = 0.28$  ppm because of the coupling of the equivalent phosphorus atoms with both the  $^{107}$ Ag ( $^{1}J$ = 230 Hz) and  $^{109}$ Ag ( $^{1}J$  = 265 Hz) nuclei (for  $^{107}$ Ag and <sup>109</sup>Ag, the natural abundances are 48.2 and 51.8%, respectively).<sup>[12,25]</sup> Similarly, the <sup>31</sup>P{<sup>1</sup>H} NMR spectra of [Cu(POP)<sub>2</sub>]BF<sub>4</sub>, [Ag(POP)<sub>2</sub>]BF<sub>4</sub>, and [Au(POP)<sub>2</sub>]BF<sub>4</sub> in  $CD_2Cl_2$  at room temperature show single resonances, which suggests that the four P atoms of the POP ligands are also equivalent for all of the complexes (Figure 3). This is in perfect agreement with the solid-state structure of  $[Ag(POP)_2]BF_4$ . However, the apparent equivalence of the four P atoms contradicts the solid-state structures of [Cu(POP)<sub>2</sub>]BF<sub>4</sub> and [Au(POP)<sub>2</sub>]BF<sub>4</sub>, for which three resonances are expected for the different P atoms. Indeed, the P atoms of the two POP ligands may exchange their position inside and outside the coordination sphere in solution. In other words, this dynamic exchange is fast on the NMR



Figure 3.  ${}^{31}P{}^{1}H$  NMR (202 MHz, CD<sub>2</sub>Cl<sub>2</sub>) spectra of [Cu-(POP)<sub>2</sub>]BF<sub>4</sub>, [Ag(POP)<sub>2</sub>]BF<sub>4</sub>, and [Au(POP)<sub>2</sub>]BF<sub>4</sub> at 298 and 198 K.

timescale, and the four P atoms appear as equivalent in the room-temperature <sup>31</sup>P{<sup>1</sup>H} NMR spectra. To confirm this hypothesis, the <sup>31</sup>P{<sup>1</sup>H} NMR spectra of  $[Cu(POP)_2]BF_4$ ,  $[Ag(POP)_2]BF_4$ , and  $[Au(POP)_2]BF_4$  were recorded at different temperatures. As shown in Figure 3, as the solution is cooled, the exchange between the different conformers becomes slower on the NMR timescale, as attested by the broadening of the <sup>31</sup>P NMR resonances for both  $[Cu(POP)_2]BF_4$  and  $[Au(POP)_2]BF_4$ . In contrast, no changes were observed for  $[Ag(POP)_2]BF_4$ . These observations are in perfect agreement with the difference in the coordination environments observed in their X-ray crystal structures, that is, tetrahedral for  $[Ag(POP)_2]BF_4$ .

#### Electrochemistry

The electrochemical properties of  $[M(dppb)_2]BF_4$  and  $[M(POP)_2]BF_4$  (M = Cu, Ag or Au) were determined by cyclic voltammetry (CV) and Osteryoung square wave voltammetry (OSWV). For comparison, the ligands dppb and POP were also investigated under the same experimental conditions. All of the experiments were performed at room temperature in CH<sub>2</sub>Cl<sub>2</sub> solutions containing tetra-*n*-butyl-ammonium tetrafluoroborate (0.1 M) as the supporting electrolyte, a Pt wire as the working electrode, and a saturated calomel electrode (SCE) as the reference electrode. The potential data for all of the compounds are collected in Table 3, and typical examples of the OSVW voltammograms are depicted in Figure 4.

Table 3. Electrochemical data of dppb, POP,  $[M(dppb)_2]BF_4$ , and  $[M(POP)_2]BF_4$  (M = Cu, Ag or Au) determined by OSWV with a Pt working electrode in CH<sub>2</sub>Cl<sub>2</sub> and 0.1 M *n*Bu<sub>4</sub>NBF<sub>4</sub> at room temperature.<sup>[a]</sup>

	Oxidation $E_{ox1}^{[b]}$	$E_{\mathrm{ox2}}^{[\mathrm{b}]}$	Reduction $E_{\rm red1}^{[b]}$
dppb	+1.04	+1.69	[d]
[Cu(dppb) <sub>2</sub> ]BF <sub>4</sub>	$+1.19^{[c]}$	+1.66	-2.20
$[Ag(dppb)_2]BF_4$	$+0.99^{[c]}$	broad	-2.14
$[Au(dppb)_2]BF_4$	+0.70	broad	[d]
POP	+1.31	+1.54	[d]
$[Cu(POP)_2]BF_4$	+1.46	+1.70	[d]
$[Ag(POP)_2]BF_4$	+1.68	broad	[d]
$[Au(POP)_2]BF_4$	+1.42	+1.60	[d]

[a] The OSWV data were obtained with a sweep width of 20 mV, a frequency of 10 Hz, and a step potential of 5 mV. [b] Values in V vs. SCE. [c] Quasi-reversible process in CV. [d] No signals observed in the available potential windows (> -2.20 V vs. SCE) under our experimental conditions.

In the cathodic region, no reduction process could be observed for most of the studied compounds under our experimental conditions. In contrast, two main oxidation processes are observed for the six complexes. In all of the cases, the first oxidation is likely metal-centered, whereas the second one corresponds to ligand-centered processes.<sup>[6]</sup> In the particular cases of  $[Cu(dppb)_2]BF_4$  and  $[Ag(dppb)_2]BF_4$ , the first one-electron oxidation process is quasi-reversible and is assigned to the  $M^{2+}/M^+$  redox couple. In both cases,



Figure 4. OSWV voltammograms (anodic scan) of  $[Cu(dppb)_2]BF_4$ ,  $[Ag(dppb)_2]BF_4$ , and  $[Au(dppb)_2]BF_4$  with a Pt electrode in  $CH_2Cl_2$  and 0.1 M  $nBu_4NBF_4$  at room temperature.

the second oxidation is chemically irreversible and, as already reported for analogous phosphine-containing complexes,<sup>[6]</sup> chemical reactions occur with ligand-centered oxidations. For [Au(dppb)<sub>2</sub>]BF<sub>4</sub>, the first oxidation is observed at a lower potential than those of its copper and silver analogues. This oxidation is indeed a two-electron process that leads to the formation of a gold(III) complex. As already mentioned, gold exhibits a large relativistic effect, and higher oxidation states are more accessible in gold than in silver. Indeed, the gold s electrons are more strongly bound, and their orbitals are smaller as a consequence of the relativistic effect; simultaneously, the d and f electrons are more loosely bound owing to an increased shielding of the nuclear charge. As a result, oxidation to gold(III) is energetically less disfavored when compared to oxidation of the related Cu or Ag complexes.<sup>[24]</sup> It can be added that the electrochemistry of [Au(dppb)<sub>2</sub>]<sup>+</sup> has already been investigated in detail by McArdle and Bossard.<sup>[26]</sup> On the basis of spectroelectrochemical investigations performed in CH<sub>3</sub>CN, they have proposed a change from a tetrahedral coordination geometry for  $[Au(dppb)_2]^+$  to a square-planar structure for the  $[Au(dppb)_2]^{3+}$  complex obtained upon oxidation. Under their conditions (CH<sub>3</sub>CN), the oxidation process is perfectly reversible. In contrast, we used a non-coordinating solvent (CH<sub>2</sub>Cl<sub>2</sub>), and this oxidation is irreversible. Moreover, in the CV experiments, additional reduction waves appear when scanning back towards cathodic potentials (see Supporting Information). The intensity of these new signals is scan-rate dependent, which suggests that they result from a chemical reaction of the [Au(dppb)<sub>2</sub>]<sup>3+</sup> complex. Indeed, the high stability of [Au(dppb)<sub>2</sub>]<sup>3+</sup> in CH<sub>3</sub>CN suggests that the coordinating solvent may also contribute to the stabilization of the gold(III) complex.<sup>[26]</sup> Under our conditions, such stabilization is not possible, and the new signals observed could be partly due to Au<sup>III</sup> chlorine adducts formed in CH<sub>2</sub>Cl<sub>2</sub>, in agreement with the previous studies.<sup>[26]</sup>

For the POP complexes, the metal-centered oxidation process is more difficult than those of their dppb analogues. This results from a combination of effects, one of which is the difference in the electronic properties of the two bisphosphine ligands as deduced from the difference in the first oxidation potentials of POP and dppb (Table 3). For  $[Ag(POP)_2]BF_4$ , the metal center adopts a tetrahedral coordination geometry, and the larger P-Ag-P bite angle, compared to that of dppb, hinders the formation of a flatter structure (i.e., square planar), which would be more appropriate for the silver(II) oxidation state. As a result,  $[Ag(POP)_2]^{2+}$  is destabilized, and oxidation of the silver(I) complex is more difficult. For both [Cu(POP)<sub>2</sub>]BF<sub>4</sub> and  $[Au(POP)_2]BF_4$ , the situation is more complex. As shown by CV, their first oxidation process is also irreversible. However, the metal centers are now in a trigonal environment, and their oxidation potential is probably closer to that of the mono-coordinated diphosphine. Upon oxidation, the three P ligands are not sufficient to stabilize the higher oxidation states and, simultaneously, rearrangement and decoordination process may easily occur. Finally, it is noteworthy that substitution of the dppb ligand by the POP ligand has a dramatic effect for the gold compound, as the first oxidation potential is shifted by 720 mV toward anodic potential.

## **Photophysical Properties**

The absorption spectra of  $[M(dppb)_2]BF_4$  and  $[M(POP)_2]BF_4$  (M = Cu, Ag or Au) as well as those of dppb and POP have been recorded in both tetrahydrofuran (THF) and CH<sub>2</sub>Cl<sub>2</sub> (see Supporting Information). As a typical example, the absorption spectrum of [Ag(dppb)<sub>2</sub>]-BF<sub>4</sub> in THF is depicted in Figure 5. For the free ligands, several photostability tests have been made by exciting them at 300 nm in both solvents because of the well-known photoreactivity of phosphine molecules.<sup>[27]</sup> All of the samples were unstable in solution under light irradiation, especially in CH<sub>2</sub>Cl<sub>2</sub>;<sup>[12]</sup> changes in the absorption spectra were systematically observed after a couple of hours. To minimize irreversible photochemical degradation, solutions of all of the compounds were always kept in the dark and investigated immediately after dissolution. The electronic absorption of the complexes is mainly localized in the UV region down to ca. 350 and 400 nm for [M(POP)<sub>2</sub>]BF<sub>4</sub> and [M(dppb)<sub>2</sub>]BF<sub>4</sub>, respectively. For the latter family of complexes, a comparison with the absorption spectrum of dppb reveals an additional absorption tail above 350 nm that is likely due to charge-transfer transitions, which, for Cu<sup>I</sup> and Ag<sup>I</sup>, are attributed to metal-to-ligand charge-transfer (MLCT) states (vide infra), in line with previous reports.<sup>[9,12]</sup> By contrast, absorption tails above 350 nm are not observed for the [M(POP)<sub>2</sub>]BF<sub>4</sub> complexes; this sug-

1349



gests that the lowest electronic transitions are ligand-centered. This interpretation is supported by the electrochemical data. Metal-centered oxidations of  $[M(POP)_2]BF_4$  compounds occur at higher potentials than those of the analogous dppb derivatives, therefore the MLCT transitions occur at higher energy.



Figure 5. Left: electronic absorption spectra of  $[Ag(dppb)_2]BF_4$  in CH<sub>2</sub>Cl<sub>2</sub> (black) and THF (grey) at room temperature. Right: normalized emission spectra ( $\lambda_{exc} = 300$  nm) of  $[Ag(dppb)_2]BF_4$  in CH<sub>2</sub>Cl<sub>2</sub> (full squares) and THF (empty circles) at room temp., as powder (10% in KBr) at room temp. (empty squares), and in rigid THF matrix at 77 K (full circles).

The photoluminescence properties of the whole series of compounds were investigated in THF and CH<sub>2</sub>Cl<sub>2</sub> (see Supporting Information). They were further investigated in rigid THF matrices at 77 K and in the solid state at room temperature (KBr disks). The data in THF are summarized in Tables 4 and 5. On the basis of the large Stokes shift and the sensitivity of the excited-state lifetime towards oxygen, the weak emission of [Ag(dppb)<sub>2</sub>]BF<sub>4</sub> in THF is assigned to a triplet MLCT excited state.<sup>[12]</sup> The compound is substantially influenced by conformational changes from a pseudotetrahedral coordination geometry (ground state) to a flattened structure in the excited state, which leads to a stabilized excited state exhibiting a formally silver(II) center. This is in line with the results obtained by Osawa and Hoshino with  $[Ag(dppb)_2]PF_6$ .<sup>[12]</sup> The same rationale can be applied to the emission behavior of [Cu(dppb)<sub>2</sub>]BF<sub>4</sub> in solution, though its excited-state lifetime in oxygen-free THF (26 ns) is much shorter than that of the Ag<sup>I</sup> analogue (8400 ns). THF is a coordinating solvent, and the flattened square-planar structure of the MLCT excited state may facilitate the formation of a pentacoordinate exciplex with an incoming solvent molecule, as is often observed for copper(I) complexes, which may exhibit triplet lifetimes as short as a few ns.<sup>[18,19]</sup> This view is supported by the excited-state lifetimes recorded in non-coordinating CH<sub>2</sub>Cl<sub>2</sub>, for which  $\tau = 1.5$  ns was found in air-equilibrated solution, whereas  $\tau = 244$  ns was measured in oxygen-free solution. Accordingly, it appears that copper complexes are more prone to form pentacoordinate exciplexes than their silver analogues. Interestingly, the emission of the Ag<sup>I</sup> complex occurs at lower energy than that of the Cu<sup>1</sup> analogue. This is attributed to a stronger excited-state distortion of the former in the MLCT excited state when  $M^{II}$  ions are formally generated. This hypothesis is in line with the lower oxidation potential of  $[Ag(dppb)_2]BF_4$  compared with that of  $[Cu(dppb)_2]BF_4$  (Table 3).

Table 4. Luminescence data in air-equilibrated and air-free THF solutions at room temperature.

	$\lambda_{\max} \ [nm]^{[a]}$	$\varPhi_{\mathrm{em}}  [\%]^{\mathrm{[b]}}$	$\tau \ [ns]^{[c]}$
dppb	[d]	[d]	[d]
$[Cu(dppb)_2]BF_4$	560	< 0.01 (0.04)	<sup>[d]</sup> (26)
[Ag(dppb) <sub>2</sub> ]BF <sub>4</sub>	608	< 0.01 (0.5)	<sup>[d]</sup> (8400)
[Au(dppb) <sub>2</sub> ]BF <sub>4</sub>	[d]	[d]	[d]
POP	430	0.03 (0.8)	$^{[d]}(1.5)$
$[Cu(POP)_2]BF_4$	423	0.05 (0.1)	1.4 (2.0)
$[Ag(POP)_2]BF_4$	462	0.04 (0.04)	[d]
$[Au(POP)_2]BF_4$	490	0.2 (1.5)	126 (2200)

[a] Emission maxima from uncorrected spectra,  $\lambda_{exc} = 300$  (complexes) and 280 nm (free ligands). [b] Emission quantum yields in air-equilibrated and air-purged solutions (in brackets). [c] Excited-state lifetimes in air-equilibrated and air-purged solutions (in brackets). [d] Weak signal. In particular, for lifetime measurements, hours of accumulation are required with the time-correlated single photon counting (TCSPC) spectrometer; hence, the signal-to-noise ratios are too low for a reliable appraisal.

Table 5. Luminescence data in a frozen THF rigid matrix (77 K) and in the solid state (KBr disks, room temperature).

	Rigid matrix 77 K		Solid state (KBr disk, 298 K)		
	λ <sub>max</sub> [nm] <sup>[a]</sup>	τ [ms]	λ <sub>max</sub> [nm] <sup>[a]</sup>	$\Phi_{ m em}$ [%]	τ [µs]
dppb	500	17.6	[b]	[b]	[b]
[Cu(dppb) <sub>2</sub> ]BF <sub>4</sub>	455	1.9	497	56	2.5
[Ag(dppb) <sub>2</sub> ]BF <sub>4</sub>	448	3.4	505	22	6.8
[Au(dppb) <sub>2</sub> ]BF <sub>4</sub>	503	0.14, 12.5	529	28	2.9
POP	480	16.5	445	4	[b]
$[Cu(POP)_2]BF_4$	401	2.3	469	2	[b]
$[Ag(POP)_2]BF_4$	405	9.0	458	1	[b]
[Au(POP) <sub>2</sub> ]BF <sub>4</sub>	445	1.3, 8.4	494	5	6.9

[a] Emission maxima from uncorrected spectra,  $\lambda_{exc} = 325$  (complexes) and 280 nm (free ligands). [b] Weak signal. In particular, for lifetime measurements, hours of accumulation are required with the TCSPC spectrometer; hence, the signal-to-noise ratio results are too low for a reliable appraisal.

Whereas the emission quantum yields of both  $[Cu(dppb)_2]$ -BF<sub>4</sub> and  $[Ag(dppb)_2]BF_4$  are very low in solution, they both exhibit a bright luminescence in the solid state at room temperature as well as in rigid frozen THF matrices at 77 K. Under these conditions, geometric distortions that prompt nonradiative deactivation of the MLCT excited states are prevented.<sup>[12,13]</sup> This is further confirmed by the large blueshifted emission maxima when going from room temperature to 77 K in THF for both  $[Cu(dppb)_2]BF_4$  and  $[Ag(dppb)_2]BF_4$  (Tables 4 and 5).<sup>[12,13]</sup>

Although emission was detected for  $[Cu(dppb)_2]BF_4$  and  $[Ag(dppb)_2]BF_4$  in solution, the corresponding gold(I) derivative is nonemissive under these conditions (Table 4). However, as reported by Osawa,<sup>[13]</sup> a strong emission is observed for this compound at 77 K in a frozen THF rigid matrix or at room temperature in the solid state (Table 5). It must be highlighted that the excited state is rather different in this case when compared to those of the analogous

1350



copper and silver complexes. Indeed, as deduced from DFT calculations on  $[Au(PP)_2]^+$  systems,<sup>[13,15,28]</sup> the lowest emitting state is mainly a charge-transfer state from a P atom to the phenylene or phenyl groups of the dppb ligand. The nature of the lowest excited state in Au<sup>I</sup> bisphosphine complexes is highly sensitive to small conformational changes, that is, symmetry reduction caused by change of the counteranion and the occurrence of intramolecular CH– $\pi$  interactions in one conformation, which affects the localization of the lowest unoccupied molecular orbital (LUMO) level.<sup>[13]</sup> Thus, emission maxima are observed over quite a large spectral window (478–596 nm) depending on the symmetry of the [Au(PP)<sub>2</sub>]<sup>+</sup> cation.<sup>[13]</sup>

For the POP-based complexes, the situation appears to be rather different. As already mentioned, in this case, the lowest electronic transitions are likely to be ligand-centered. This has already been discussed by McCleskey and Gray for a three-coordinate monomeric AuP<sub>3</sub> complex.<sup>[17]</sup> The electronic transition involves the promotion of an electron from the lone pair of a phosphorus atom to an empty antibonding  $\pi^*$  orbital of a phenyl subunit attached to the P atom. Depopulation of the lone pair of one P atom should in principle strengthen the Au-P bonds by a retrodonation mechanism. As a result, a substantial contraction of the AuP<sub>3</sub> core may explain the rather large Stokes shift observed for [Au(POP)2]BF4. As for the AuP3 complex reported by McCleskey and Gray,<sup>[17]</sup> the AuP<sub>3</sub> monomeric unit in [Au(POP)<sub>2</sub>]BF<sub>4</sub> is also sterically protected, which seems to be a key prerequisite for the observation of emission in solution for AuP<sub>3</sub> units that retain their integrity in solution. It is likely that similar excited states are involved in the emission of [(CuPOP)<sub>2</sub>]BF<sub>4</sub> and [Ag(POP)<sub>2</sub>]BF<sub>4</sub>. Along the series, the Stokes shift increases from copper to silver and finally to gold. The retrodonation, which can strengthen the M-P bonds leading to a deformation of the coordination sphere around the metal center, is expected to be increasingly pronounced as group 11 is descended. Indeed, the excited-state properties of [(CuPOP)<sub>2</sub>]BF<sub>4</sub> in solution are almost identical to those of the uncoordinated POP ligand. For the three  $[M(POP)_2]BF_4$  complexes, significant blueshifts are observed for the emission spectra recorded in the frozen THF matrices at 77 K relative to those recorded at room temperature in solution. Indeed, changes in the coordination sphere are more limited under such conditions. However, the differences observed between the emission maxima at 298 and 77 K are less pronounced for the POPbased complexes (ca. 20-60 nm) when compared to those for the dppb derivatives (ca. 100-160 nm). This is in agreement with the different nature of the excited states involved in the emission of the different compounds.

#### **Light-Emitting Devices**

On the basis of their electrochemical properties and the photoluminescence data,  $[Cu(dppb)_2]BF_4$  and  $[Ag(dppb)_2]-BF_4$  were selected for the fabrication of light-emitting devices. Indeed, these two compounds combine a quasi-re-

versible metal-centered oxidation process and a high emission quantum yield in the solid state. Poly(vinyl carbazole) (PVK) was chosen as the host material because of its good hole-transport ability, broad band-gap, and the overlap of its emission spectra with the absorption spectra of [Cu(dppb)<sub>2</sub>]BF<sub>4</sub> and [Ag(dppb)<sub>2</sub>]BF<sub>4</sub>. The light-emitting devices were prepared by spin coating a thin film of a [Cu(dppb)<sub>2</sub>]BF<sub>4</sub>:PVK<sup>[9]</sup> or a [Ag(dppb)<sub>2</sub>]BF<sub>4</sub>:PVK blend (ca. 120 nm) on an indium tin oxide (ITO) substrate. The concentration of [Cu(dppb)<sub>2</sub>]BF<sub>4</sub> and [Ag(dppb)<sub>2</sub>]BF<sub>4</sub> in the PVK matrix was 12.5 wt.-%. After the film had been dried under vacuum at room temperature for 2 h, the cathode was fabricated by thermal evaporation of an Al layer (100 nm). A typical example electroluminescence (EL) spectrum of [Ag(dppb)<sub>2</sub>]BF<sub>4</sub> in PVK films is displayed in Figure 6.



Figure 6. I-V-B characteristics of the device obtained from  $[Ag(dppb)_2]BF_4$ . Inset: EL spectra of  $[Ag(dppb)_2]BF_4$  at a concentration of 12.5 wt.-% in a PVK matrix.

The electroluminescence spectrum of  $[Ag(dppb)_2]BF_4$  is significantly broader when compared to the photoluminescence spectrum recorded in THF solution. As a result, almost white light was produced by the device. Similar results were obtained with [Cu(dppb)<sub>2</sub>]BF<sub>4</sub>.<sup>[9]</sup> The current-voltage-brightness (I-V-B) characteristics (Figure 6) of the device prepared from  $[Ag(dppb)_2]BF_4$  indicate that it has a turn-on voltage of ca. 15 V and maximum brightness of 365 cd m<sup>-2</sup> at 20 V (measured with a Minolta LS 110 luminance meter). To the best of our knowledge, this is the first example of a light-emitting device that incorporates a silver(I) complex as a triplet emitter in its active layer. The I-V-B characteristics obtained with the corresponding copper(I) complex are similar<sup>[9]</sup> (turn-on voltage of ca. 15 V and a maximum brightness of 490 cd m<sup>-2</sup> at 20 V); therefore, silver(I) complexes are also attractive candidates for light-emitting applications. However, it is clear that the device efficiencies have not been yet optimized. They should be improved through the use of appropriate hole-blocking and electron-transfer layers in the device configuration.

1351



# Conclusions

We have prepared homoleptic copper(I), silver(I), and gold(I) complexes with two bisphosphine ligands, namely, dppb and POP. Whereas the three complexes obtained from dppb are tetracoordinate, in the case of POP, only the silver(I) complex exhibits such a geometry. Indeed, both [Cu(POP)<sub>2</sub>]<sup>+</sup> and [Au(POP)<sub>2</sub>]<sup>+</sup> adopt a trigonal coordination geometry with an uncoordinated phosphorus atom both in the solid state and in solution. Owing to steric hindrance caused by the large bite angle of the POP ligand, the Cu<sup>I</sup> and Au<sup>I</sup> cations are unable to accommodate two chelating POP moieties in a tetrahedral complex. This is only possible for the largest Ag<sup>I</sup> cation. The electrochemical properties of the six complexes have been investigated, and two oxidation processes have been observed in all cases. The first one is likely metal-centered, and the second one is ligand-centered. However, major differences have been observed for both series of compounds. The POP-based derivatives are more difficult to oxidize than their dppb analogues. This observation is explained by a combination of steric and electronic effects as well as by the difference in their coordination geometries. For similar reasons, the photophysical properties of  $[M(dppb)_2]BF_4$  and  $[M(POP)_2]BF_4$ complexes are rather different. Whereas the emissions of [Cu(dppb)<sub>2</sub>]BF<sub>4</sub> and [Ag(dppb)<sub>2</sub>]BF<sub>4</sub> are attributed to triplet MLCT excited states, their POP analogues are characterized by ligand-centered triplet excited states. The gold complexes [Au(dppb)<sub>2</sub>]BF<sub>4</sub> and [Au(POP)<sub>2</sub>]BF<sub>4</sub> have similar excited states that result from the promotion of an electron from the lone pair of a phosphorus atom to an empty antibonding  $\pi^*$  orbital of a phenyl subunit attached to the P atom; however, their behavior is substantially different as a result of their particular coordination geometries (i.e., AuP<sub>3</sub> vs. AuP<sub>4</sub>). Finally, the two compounds that combine reversible metal-centered oxidation processes with high emission quantum yields in the solid state, namely, [Cu(dppb)2]BF4 and  $[Ag(dppb)_2]BF_4$ , have been selected for the fabrication of light-emitting devices. Interesting electroluminescence properties have been observed for both compounds, which highlights the potential of the group 11 ions for such applications.

This work paves the way towards the design of new copper, silver, and gold complexes with improved emission properties. This will require the design of PP ligands with appropriate chelate bite angles, optimized donating abilities, and suitable steric hindrance to isolate the metallic center without compromising the tetrahedral coordination geometry. Work in this direction is under way in our laboratories.

# **Experimental Section**

**General Procedures:** Reagents were purchased as reagent grade and used without further purification. Et<sub>2</sub>O was distilled from Na/ benzophenone under Ar. Dichloromethane was distilled from CaH<sub>2</sub> under Ar. All reactions were performed in standard glass-ware under an argon atmosphere by using Schlenk and vacuum-line techniques. Evaporations and concentrations were performed

by using a water aspirator and drying in vacuo at  $10^{-2}\,\mathrm{Torr.}\;\mathrm{NMR}$ spectra were recorded with Bruker ARX 250, Bruker DPX 300, Avance 300, and Avance 500 spectrometers equipped with a 5 mm triple-resonance inverse probe with a dedicated <sup>31</sup>P channel operating at 500.33 for <sup>1</sup>H NMR spectroscopy. Chemical shifts ( $\delta$ ) are in ppm relative to an external tetramethylsilane reference for <sup>1</sup>H and <sup>13</sup>C, 85% H<sub>3</sub>PO<sub>4</sub> for <sup>31</sup>P, and AgNO<sub>3</sub> for <sup>109</sup>Ag; coupling constants (J) are in Hz. The temperature was calibrated by using a methanol chemical shift thermometer. <sup>109</sup>Ag NMR resonances were obtained by using 2D <sup>31</sup>P-<sup>109</sup>Ag proton-decoupled heteronuclear multiple quantum correlation (HMQC-{<sup>1</sup>H}). Elemental analyses were performed with a Perkin-Elmer 2400 B analyzer (flash combustion and detection by catharometry) at the Microanalytical Laboratory (LCC, Toulouse, France). Mass spectra were obtained at the Service Commun de Spectrométrie de Masse (Université Paul Sabatier and CNRS, Toulouse, France). Spectra were recorded with a triple quadrupole mass spectrometer (Perkin-ElmerSciex API 365) by using electrospray ionization.

**[Cu(dppb)<sub>2</sub>]BF<sub>4</sub>:** A mixture of Cu(CNCH<sub>3</sub>)BF<sub>4</sub> (80 mg, 0.18 mmol) and dppb (170 mg, 0.37 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was stirred for 1 h under Ar at room temperature. The resulting solution was concentrated to ca. 5 mL. Crystals of [Cu(dppb)<sub>2</sub>]BF<sub>4</sub> were obtained by vapor diffusion of Et<sub>2</sub>O into this CH<sub>2</sub>Cl<sub>2</sub> solution. Compound [Cu(dppb)<sub>2</sub>]BF<sub>4</sub> was thus isolated as colorless crystals in 68% yield. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 6.98 (m, 16 H), 7.09 (m, 16 H), 7.34 (m, 8 H), 7.54 (m, 8 H) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.12 ppm. <sup>13</sup>C{<sup>31</sup>P}{<sup>1</sup>H} NMR (62 MHz, CDCl<sub>3</sub>):  $\delta$  = 129.0, 130.2, 131.2, 131.7, 132.4, 134.0, 141.6 ppm. ES-MS: *m/z* = 955.2 [M – BF<sub>4</sub><sup>-</sup>]<sup>+</sup>. C<sub>60</sub>H<sub>48</sub>BCuF<sub>4</sub>P<sub>4</sub>·H<sub>2</sub>O: C 67.90, H 4.75; found C 67.85, H 4.40.

**[Cu(POP)<sub>2</sub>]BF<sub>4</sub>:** As described for [Cu(dppb)<sub>2</sub>]BF<sub>4</sub> from Cu(CNCH<sub>3</sub>)BF<sub>4</sub> (50 mg, 0.16 mmol) and POP (171 mg, 0.32 mmol). Recrystallization (CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O) gave [Cu(POP)<sub>2</sub>]BF<sub>4</sub> as colorless crystals in 83% yield. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$ = 6.49 (dd, *J* = 8 and 1 Hz, 4 H), 6.79 (m, 20 H), 7.00 (m, 20 H), 7.16 (m, 4 H), 7.26 (t, *J* = 7 Hz, 8 H) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = -13.57 ppm. <sup>13</sup>C{<sup>31</sup>P}{<sup>1</sup>H} NMR (63 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 119.6, 125.0, 125.05, 129.0, 130.5, 131.5, 132.4, 134.1, 134.7, 158.5 ppm. ES-MS: *m*/*z* = 1139.7 [M – BF<sub>4</sub><sup>-</sup>]<sup>+</sup>. C<sub>72</sub>H<sub>56</sub>P<sub>4</sub>O<sub>2</sub>CuBF<sub>4</sub>: C 70.46, H 4.60; found C 70.57, H 4.74.

**[Ag(dppb)<sub>2</sub>]BF<sub>4</sub>:** A mixture of AgBF<sub>4</sub> (22 mg, 0.11 mmol) and dppb (100 mg, 0.22 mmol) in CH<sub>2</sub>Cl<sub>2</sub>/MeOH (5:1, 20 mL) was stirred for 1 h under Ar at room temperature. The resulting solution was evaporated. Recrystallization (CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O) gave [Ag(dppb)<sub>2</sub>]BF<sub>4</sub> as colorless crystals in 93% yield. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 7.11 (m, 32 H), 7.34 (m, 8 H), 7.54 (m, 8 H) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 0.28 (2d, <sup>1</sup>J<sub>31P,109Ag</sub> = 265 Hz, <sup>1</sup>J<sub>31P,107Ag</sub> 230 Hz) ppm. <sup>109</sup>Ag NMR (23 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 1052 ppm. ES-MS: *m*/*z* = 999.4 [M - BF<sub>4</sub>-]<sup>+</sup>. C<sub>60</sub>H<sub>48</sub>P<sub>4</sub>AgBF<sub>4</sub>·(CH<sub>2</sub>Cl<sub>2</sub>)<sub>2/3</sub>: C 63.68, H 4.35; found C 67.47, H 4.32.

[Ag(POP)<sub>2</sub>]BF<sub>4</sub>: As described for [Ag(dpp)<sub>2</sub>]BF<sub>4</sub> from AgBF<sub>4</sub> (50 mg, 0.26 mmol) and POP (277 mg, 0.51 mmol). Recrystallization (CH<sub>2</sub>Cl<sub>2</sub>/hexane) gave [Ag(POP)<sub>2</sub>]BF<sub>4</sub> as colorless crystals in 70% yield. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = 6.71$  (m, 4 H), 6.85 (m, 16 H), 6.94 (m, 20 H), 7.04 (m, 4 H), 7.19 (m, 12 H) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = -9.58$  (2d, <sup>1</sup>J<sub>31P,107Ag</sub> = 268 Hz, <sup>1</sup>J<sub>31P,107Ag</sub> 234 Hz) ppm. <sup>13</sup>C{<sup>31</sup>P}{<sup>1</sup>H} NMR (63 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = 119.2$ , 124.7, 125.0, 128.9, 130.4, 131.8, 132.4, 134.2, 134.6, 157.5. <sup>109</sup>Ag NMR (23 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = 1192$  ppm. ES-MS: m/z = 1183.7 [M – BF<sub>4</sub><sup>-</sup>]<sup>+</sup>. C<sub>72</sub>H<sub>56</sub>AgBF<sub>4</sub>O<sub>2</sub>P<sub>4</sub> (1271.80): calcd. C 68.00, H 4.44; found C 67.89, H 4.56.



[Au(dppb)<sub>2</sub>]BF<sub>4</sub>: A mixture of [Au(SMe<sub>2</sub>)]Cl (100 mg, 0.34 mmol) and dppb (303 mg, 0.68 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was stirred for 1 h under Ar at room temperature. A 1 M aqueous NaBF<sub>4</sub> solution (10 mL) was then added, and the resulting mixture was vigorously stirred for 1 h. The organic layer was decanted, and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2×). The combined organic layers were dried (MgSO<sub>4</sub>) and filtered, and the solvent was evaporated. Recrystallization (CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O) gave [Au(dppb)<sub>2</sub>]BF<sub>4</sub> as colorless crystals in 97% yield. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 7.05 (m, 32 H), 7.33 (m, 8 H), 7.46 (m, 8 H) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 21.43 ppm. ES-MS: *m*/*z* = 1089.6 [M – BF<sub>4</sub>–]<sup>+</sup>. C<sub>60</sub>H<sub>48</sub>AuBF<sub>4</sub>P<sub>4</sub> (1176.70): calcd. C 61.24, H 4.11; found C 61.05, H 3.65.

[Au(POP)<sub>2</sub>]BF<sub>4</sub>: As described for [Au(dppb)<sub>2</sub>]BF<sub>4</sub> from [Au-(SMe<sub>2</sub>)]Cl (100 mg, 0.34 mmol) and POP (366 mg, 0.68 mmol). Recrystallization (CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O) gave [Au(POP)<sub>2</sub>]BF<sub>4</sub> as colorless crystals in 83% yield. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = 6.36$  (d, J = 8 Hz, 4 H), 6.72 (d, J = 7 Hz, 4 H), 6.96 (m, 20 H), 7.09 (m, 20 H), 7.32 (t, J = 7 Hz, 8 H) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = 17.00$  ppm. <sup>13</sup>C{<sup>31</sup>P}{<sup>1</sup>H} NMR (63 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = 119.6$ , 124.7, 125.2, 129.1, 130.8, 132.4, 134.1, 134.8, 158.4 ppm. ES-MS: *m*/*z* = 1273.4 [M – BF<sub>4</sub>–]<sup>+</sup>. C<sub>72</sub>H<sub>56</sub>AuBF<sub>4</sub>O<sub>2</sub>P<sub>4</sub> (1360.90): calcd. C 63.55, H 4.15; found C 63.41, H 3.89.

**X-ray Crystal Structures:** The data were collected at low temperature with an Oxford Xcalibur, STOE IPDS, or Bruker APEX2 diffractometer by using graphite-monochromated Mo- $K_a$  radiation ( $\lambda = 0.71073$  Å) and an Oxford Cryosystems Cryostream cooling device. The structures were solved by direct methods by using SIR92<sup>[29]</sup> and refined by full-matrix least-squares procedures by using the programs of the PC version of CRYSTALS.<sup>[30]</sup> Atomic scattering factors were taken from the International Tables for Xray Crystallography.<sup>[31]</sup> For [Au(dppb)<sub>2</sub>]BF<sub>4</sub>, all non-hydrogen atoms were refined anisotropically. Solvent molecules and counteranions were refined isotropically for  $[Ag(POP)_2]BF_4$  and  $[Au(POP)_2]BF_4$ . For  $[Ag(dppb)_2]BF_4$ , only the heaviest atoms were refined anisotropically owing to the lack of data. Hydrogen atoms were refined by using a riding model. Absorption corrections were introduced by using the MULTISCAN program.<sup>[32]</sup> The X-ray crystal structures of  $[Cu(dppb)_2]BF_4^{[9]}$  (CCDC-645318) and  $[Cu(POP)_2]BF_4^{[7]}$  (CCDC-952429) have been reported previously. The colorless crystal used for the diffraction studies were produced by either slow diffusion of Et<sub>2</sub>O into a CH<sub>2</sub>Cl<sub>2</sub> solution of the appropriate complex { $[Ag(dppb)_2]BF_4$  and  $[Au(dppb)_2]BF_4$ } or slow diffusion of hexane into a CH<sub>2</sub>Cl<sub>2</sub> solution of the appropriate complex { $[Ag(POP)_2]BF_4$  and  $[Au(POP)_2]BF_4$ }. The crystallographic data are reported in Table 6.

Electrochemistry: The cyclic voltammetric measurements were performed with an Autolab PGSTAT100 potentiostat. The experiments were performed at room temperature in a homemade airtight three-electrode cell connected to a vacuum/argon line. The reference electrode consisted of a saturated calomel electrode (SCE) separated from the solution by a bridge compartment. The counter electrode was a platinum wire of ca  $1 \text{ cm}^2$  apparent surface area. The working electrode was a Pt microdisk (0.5 mm diameter). The supporting electrolyte [nBu<sub>4</sub>N][BF<sub>4</sub>] (Fluka, 99% electrochemical grade) was used as received and simply degassed under argon. Dichloromethane was freshly distilled from CaH<sub>2</sub> prior to use. The concentrations of the solutions used during the electrochemical studies were typically 10<sup>-3</sup> M in complex and 0.1 M in supporting electrolyte. Before each measurement, the solutions were degassed by bubbling Ar through them, and the working electrode was polished with a polishing machine (Presi P230).

Photophysical Measurements: The absorption spectra were recorded with a Perkin–Elmer  $\lambda 9$  spectrophotometer. For lumines-

	[Ag(dppb) <sub>2</sub> ]BF <sub>4</sub>	[Au(POP) <sub>2</sub> ]BF <sub>4</sub>	[Au(dppb) <sub>2</sub> ]BF <sub>4</sub>	[Ag(POP) <sub>2</sub> ]BF <sub>4</sub>
Chemical formula	$C_{60}H_{48}AgBF_4P_4\cdot 2(CH_2Cl_2)$	C72H56AuBF4O2P4	$C_{60}H_{48}AuBF_4P_4\cdot 2(CH_2Cl_2)$	C <sub>72</sub> H <sub>56</sub> AgBF <sub>4</sub> O <sub>2</sub> P <sub>4</sub> ·1.5(CH <sub>2</sub> Cl <sub>2</sub> )· 2.5(H <sub>2</sub> O)
Formula weight	1257.47	1360.90	1346.57	1444.24
Crystal system	monoclinic	orthorhombic	monoclinic	monoclinic
Space group	P2 <sub>1</sub> / <i>n</i>	Pbcn	$P2_1/n$	$P2_{1}/c$
a [Å]	16.7320(10)	20.2099(5)	16.6179(8)	12.8583(5)
<i>b</i> [Å]	19.407(2)	24.6442(6)	19.3178(9)	16.5170(7)
c [Å]	18.601(2)	24.7354(6)	18.5362(9)	33.6578(13)
a [°]	90	90	90	90
β [°]	107.656(9)	90	107.502(2)	90.193(4)
γ [°]	90	90	90	90
$V [Å]^3$	5755.6(10)	12319.6(5)	5675.0(5)	7148.2(5)
Ζ	4	8	4	4
Density	1.451	1.467	1.576	1.342
$\mu$ (Mo- $K_{\alpha}$ ) [mm <sup>-1</sup> ]	0.700	2.551	2.947	0.542
F(000)	2560	5472	2688	2940
T [K]	180	180	180	180
Reflections collected	57391	244744	181443	76241
Unique reflections	11135	21485	19515	18996
R <sub>int</sub>	0. 125	0.041	0.046	0.109
Reflections used	3377, <i>n</i> = 1.6	11970, $n = 3$	12289, $n = 3$	7687, $n = 1.2$
in the calculations				
$[I > n\sigma(I)]$				
Parameters	330	731	685	764
Goodness- of-fit on $F$	1.001	1.029	1.130	1.078
R	0.0605	0.0306	0.0202	0.0787
wR	0.0672	0.0328	0.0241	0.0808

Table 6. Crystallographic and structure refinement data for [Ag(dppb)<sub>2</sub>]BF<sub>4</sub>, [Au(POP)<sub>2</sub>]BF<sub>4</sub>, [Au(dppb)<sub>2</sub>]BF<sub>4</sub>, and [Ag(POP)<sub>2</sub>]BF<sub>4</sub>.



cence experiments, the samples (with optical densities between 0.1 and 0.4) were placed in 1 cm path fluorimetric cuvettes and, when necessary, purged of oxygen by bubbling argon through them. Uncorrected emission spectra were obtained with an Edinburgh FLS920 spectrometer equipped with a Peltier-cooled Hamamatsu R928 photomultiplayer tube (PMT; 185–850 nm). An Edinburgh Xe900 450 W Xenon arc lamp was used as the excitation light source. Corrected spectra were obtained by using a calibration curve supplied with the instrument. The luminescence quantum yields ( $\Phi_{\rm em}$ ) in solution were obtained from spectra corrected for the instrumental response on a wavelength scale [nm] and were determined according to the approach described by Demas and Crosby<sup>[33]</sup> by using air-equilibrated [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> in water [ $\Phi_{\rm em} = 0.028$ ]<sup>[34]</sup> as the standard.

The emission lifetimes were determined by the single-photon counting technique with the same Edinburgh FLS920 spectrometer by using a laser diode as the excitation source (1 MHz,  $\lambda_{exc}$  = 407 nm, 200 ps time resolution after deconvolution) and the abovementioned PMT as the detector. For the emission in the visible region, the luminescence lifetimes in the microsecond-millisecond scales were measured by using a Perkin-Elmer LS-50B spectrofluorometer equipped with a pulsed xenon lamp with variable repetition rate and elaborated with standard software fitting procedures. To record the 77 K luminescence spectra in THF, the samples were placed in glass tubes (2 mm diameter) and inserted into a special quartz Dewar filled with liquid nitrogen. For solid samples, the  $\Phi_{\rm em}$ values were calculated from corrected emission spectra obtained by following the procedure described by De Mello et al. with an apparatus consisting of a barium sulfate coated integrating sphere (6 inches), a He–Cd laser ( $\lambda_{exc}$ : 325 nm, 5 mW) as the light source, and an AVA-Spec2048 CCD (or R928 photomultiplayer tube) as the signal detector;<sup>[35]</sup> suitable attenuation filters were used when needed, in particular to record the signal of the laser excitation source. Experimental uncertainties are estimated to be 8% for lifetime determinations, 20% for emission quantum yields, and 2 and 5 nm for the absorption and emission peaks, respectively.

The devices were fabricated as sandwich structures between an Al cathode and an ITO anode. The ITO-coated glass substrates were cleaned sequentially in ultrasonic baths of detergent, a 2-propanol/ deionized water (1:1 volume) mixture, toluene, deionized water, and acetone. The appropriate complex mixed with PVK was then spin-coated from CHCl<sub>3</sub> solutions onto the poly(3,4-ethylenedioxythiophene) (PEDOT) layer and dried at 80 °C in vacuo. Finally, 100 nm Al electrodes were deposited through a shadow mask onto the polymer films by thermal evaporation by using an Auto 306 vacuum coater (BOC Edwards, Wilmington, MA). The current–voltage characteristics of the diodes were measured by using a Keithley 2400 source meter, and the brightness was measured with a Minolta LS 110 luminance meter.

CCDC-959657 {for  $[Ag(dppb)_2]BF_4$ }, -959658 {for  $[Au(POP)_2]-BF_4$ }, -959659 {for  $[Au(dppb)_2]BF_4$ }, and -959660 {for  $[Ag(POP)_2]-BF_4$ } contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/ data\_request/cif.

**Supporting Information** (see footnote on the first page of this article): NMR spectra of the new compounds, CV and OSWV voltammograms of  $[M(dppb)_2]BF_4$  and  $[M(POP)_2]BF_4$  (M = Cu, Ag or Au), absorption and emission spectra of  $[M(dppb)_2]BF_4$  and  $[M(POP)_2]BF_4$  (M = Cu, Ag or Au), emission data in CH<sub>2</sub>Cl<sub>2</sub>, *I*-*V*-*B* characteristics and EL spectrum of the device obtained from  $[Cu(dppb)_2]BF_4$ .

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