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Article

Preparation and Solid-State Characterization of Mixed-Ligand Coordination/Organometallic Oligomers and Polymers of Copper(I) and Silver(I) Using Diphosphine and Mono- and Diisocyanide Ligands

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The dimers $[Cu_2(dppm)_2(CN\text{-}t\text{-}Bu)_3](BF_4)_2$ and $[Ag_2(dppm)_2(CN\text{-}t\text{-}Bu)_2](X)_2$ ($X^- = BF_4^-$, ClO_4^-) and the coordination polymers $\{[M(diphos)(CN\text{-}t\text{-}Bu)_2]BF_4\}_n$ (M = Cu, Ag; diphos = bis(diphenylphosphino)butane (dppb), bis-(diphenylphosphino)pentane (dpppen), bis(diphenylphosphino)hexane (dpph)), $\{[Ag_2(dppb)_3(CN\text{-}t\text{-}Bu)_2](BF_4)_2\}_n$, and $\{[Ag(dpppen)(CN\text{-}t\text{-}Bu)]BF_4\}_n$ have been synthesized and fully characterized as model materials for the mixed bridging ligand polymers which exhibit the general formula $\{[M(diphos)(dmb)]BF_4\}_n$ (M = Cu, Ag; dmb = 1,8-diisocyano-*p*-menthane) and $\{[Ag(dppm)(dmb)]ClO_4\}_n$. The identity of four polymers ($\{[Ag(dppb)(CN\text{-}t\text{-}Bu)_x]BF_4\}_n$ (x = 1, 2), $\{[Ag_2(dppb)_3(CN\text{-}t\text{-}Bu)_2](BF_4)_2\}_n$, $\{[Ag(dppm)(dmb)]ClO_4\}_n$) and the two dimers has been confirmed by X-ray crystallography. The structure of $\{[Ag(dppm)(dmb)]ClO_4\}_n$ exhibits an unprecedented 1-D chain of the type "$\{Ag(dmb)_2Ag(dppm)_2^{2+}\}_n$", where $d(Ag\cdots Ag)$ values between tetrahedral Ag atoms are 4.028(1) and 9.609(1) Å for the dppm and dmb bridged units, respectively. The $\{[Ag(dppb)(CN\text{-}t\text{-}Bu)_x]BF_4\}_n$ polymers (x = 1, 2) form zigzag chains in which the Ag atoms are tri- and tetracoordinated, respectively. The $\{[Ag_2(dppb)_3(CN\text{-}t\text{-}Bu)_2](BF_4)_2\}_n$ polymer, which is produced from the rearrangement of $\{[Ag(dppb)(CN\text{-}t\text{-}Bu)_2]BF_4\}_n$, forms a 2-D structure described as a "honeycomb" pattern, where large $\{Ag(dppb)^+\}_6$ macrocycles each hosting two counterions and two acetonitrile guest molecules are observed. Properties such as glass transition temperature, morphology, thermal decomposition, and luminescence in the solid state at 293 K are reported. The luminescence bands exhibit maxima between 475 and 500 nm with emission lifetimes ranging between 6 and 55 μs. These emissions are assigned to a metal-to-ligand charge transfer (MLCT) of the type $M(I) \rightarrow \pi^*(NC)/\pi^*(PPh_2)$.

Introduction

1-, 2-, and 3-D polymeric networks constructed from polydentate ligands and transition metals comprise an area that has experienced a tremendous increase in interest in recent years.[2] The field is overwhelmingly dominated by the use of N-containing bridging ligands.[3] The use of P- or CNR-donor-containing assembling groups is far less extensive,[4] and examples of mixed-ligand polymers of Cu(I) and Ag(I) where the bridging ligands are both neutral are rather limited. Recent related examples of this work provided by this group include the 1-D $\{M(dmb)_2^+\}_n$ (M = Cu, Ag; dmb = 1,8-diisocyano-*p*-menthane) and the mixed-metal $\{Cu_xAg_{1-x}$-(dmb)_2^+\}_n$ polymers ($0 \leq x \leq 1$)[5] and the "polymers of clusters" $\{Pd_4(dmb)_4(dmb)^{2+}\}_n$ and $\{Pt_4(dmb)_4(diphos)^{2+}\}_n$ (Charts 1 and 2).[5i,j] The use of two neutral ligands provides a new and interesting strategy for the design of coordination networks and deserves to be explored.

We now wish to report the syntheses and characterization of a series of mixed-ligand Cu(I) and Ag(I) diphosphine-

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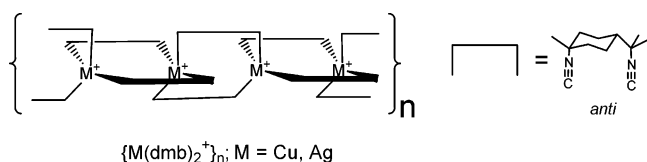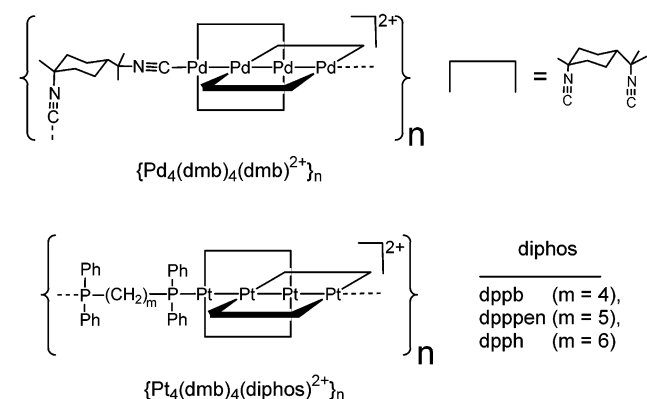
Chart 1

$\{M(dmb)_2{}^+\}_n$; M = Cu, Ag

Chart 2

$\{Pd_4(dmb)_4(dmb)^{2+}\}_n$

$\{Pt_4(dmb)_4(diphos)^{2+}\}_n$

diphos
dppb (m = 4),
dpppen (m = 5),
dpph (m = 6)

Table 1. List of Investigated Compounds and Numbering

formula	code	formula	code
[Cu$_2$(dppm)$_2$(CN-t-Bu)$_3$](BF$_4$)$_2$	1	[Ag$_2$(dppm)$_2$(CN-t-Bu)$_2$](BF$_4$)$_2$	2a
		[Ag$_2$(dppm)$_2$(CN-t-Bu)$_2$](ClO$_4$)$_2$	2b
{[Cu(dppb)(CN-t-Bu)$_2$]BF$_4$}$_n$	3	{[Ag(dppb)(CN-t-Bu)$_2$]BF$_4$}$_n$	4
		{[Ag$_2$(dppb)$_3$(CN-t-Bu)$_2$]BF$_4$}$_n$	5
{[Cu(dpppen)(CN-t-Bu)$_2$]BF$_4$}$_n$	6	{[Ag(dpppen)(CN-t-Bu)$_2$]BF$_4$}$_n$	7
		{[Ag(dpppen)(CN-t-Bu)$_2$]BF$_4$}$_n$	8
{[Cu(dpph)(CN-t-Bu)$_2$]BF$_4$}$_n$	9	{[Ag(dpph)(CN-t-Bu)$_2$]BF$_4$}$_n$	10
{[Cu(dppm)(dmb)]BF$_4$}$_n$	11	{[Ag(dppm)(dmb)]BF$_4$}$_n$	12a
		{[Ag(dppm)(dmb)]ClO$_4$}$_n$	12b
{[Cu(dppb)(dmb)]BF$_4$}$_n$	13	{[Ag(dppb)(dmb)]BF$_4$}$_n$	14
{[Cu(dpppen)(dmb)]BF$_4$}$_n$	15	{[Ag(dpppen)(dmb)]BF$_4$}$_n$	16
{[Cu(dpph)(dmb)]BF$_4$}$_n$	17	{[Ag(dpph)(dmb)]BF$_4$}$_n$	18

dmb coordination polymers, using the bridging diphosphine ligands dppm, dppb, dpppen, and dpph (Table 1). The highly crystalline model compounds in which dmb is replaced by two t-BuNC ligands have been investigated and provide ideal material for X-ray structure analysis. Properties such as glass

transition temperature (when it applies), morphology, thermal decomposition, and luminescence in the solid state are reported.

Experimental Section

Materials. 1,8-Diisocyano-p-menthane (dmb),[6] [Cu$_2$(dppm)$_2$-(NCCH$_3$)$_4$](BF$_4$)$_2$,[7] and [Ag$_2$(dppm)$_2$](X)$_2$ (X$^-$ = BF$_4{}^-$, ClO$_4{}^-$)[8] were prepared according to literature procedures. The [M$_2$(diphos)$_2$]-(BF$_4$)$_2$ dimers (M = Cu, Ag; diphos = dppb, dpppen, dpph) were also prepared according to published methods except that, for [Ag$_2$-(dppp)$_2$](NO$_3$)$_2$ (dppp = bis(diphenylphosphino)methane),[9] [Ag$_2$-(dppb)$_2$](ClO$_4$)$_2$, and [M$_2$(dpph)$_2$](ClO$_4$)$_2$ (M = Cu, Ag),[10] AgBF$_4$ and [Cu(NCMe)$_4$]BF$_4$ were used instead of AgNO$_3$, AgClO$_4$, and [Cu(NCMe)$_4$]ClO$_4$. Their identity of the dimers was verified by ^{1}H, ^{31}P NMR, and IR spectroscopy. The solvents used in the syntheses (acetone (Fisher), dichloromethane (ACP), and diethyl ether (ACP)) were purified according to established procedures.[11] AgBF$_4$, AgClO$_4$, Cu(BF$_4$)$_2$·xH$_2$O, t-BuNC, dppm, dppb, dpppen, and dpph (Aldrich Chemical Co.) and Cu(m) (Anachemia) were used as received. All air- or moisture-sensitive materials were handled inside an inert-atmosphere glovebox, and all reactions were performed using standard Schlenk techniques or a high-vacuum manifold system.

[Cu$_2$(dppm)$_2$(CN-t-Bu)$_3$](BF$_4$)$_2$ (1). [Cu$_2$(dppm)$_2$(NCCH$_3$)$_4$]-(BF$_4$)$_2$ (272 mg, 0.254 mmol) was dissolved in 100 mL of degassed acetonitrile. A 115 μL (1.02 mmol) volume of t-BuNC was added dropwise using a microsyringe. The colorless solution was stirred for 2 h prior to concentrating it in vacuo until a volume of 20 mL was obtained. A 100 mL volume of diethyl ether was added to the remaining solution to precipitate a white solid, which was filtered off and dried. Yield: 95% (319 mg). ^{1}H NMR (CD$_2$Cl$_2$): δ 7.30−

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7.14 (m, 40H, Ph), 3.32 (m, 4H, *CH$_2$*P), 1.48 (s, 32H, CH$_3$). ^{31}P-$\{^1$H$\}$ NMR (CD$_2$Cl$_2$): δ −2.13. ^{13}C$\{^1$H$\}$ NMR (CD$_2$Cl$_2$): δ 138.5, 132.3, 130.9, 129.2, 58.4, 30.0. IR (KBr): ν 2176 (C≡N), 1061 cm^{-1} (BF$_4$). Raman (neat solid): ν 2175 cm^{-1} (C≡N). Anal. Calcd for Cu$_2$C$_{65}$H$_{71}$N$_3$P$_4$B$_2$F$_8$: C, 59.19; H, 5.43; N, 3.19. Calcd for Cu$_2$C$_{65}$H$_{71}$N$_3$P$_4$B$_2$F$_8$ + 0.5 C$_5$H$_9$N: C, 59.59; H, 5.59; N, 3.60. Found: C, 59.68; H, 5.93; N, 3.68. Crystals suitable for X-ray analysis were obtained by slow evaporation of an acetonitrile solution. The X-ray data confirmed the indentity of **1**, and the ^{1}H NMR spectroscopic signature was identical with that described above, except that the integration for *t*-BuNC corresponds with the structure.

[Ag$_2$(dppm)$_2$(CN-*t*-Bu)$_2$](BF$_4$)$_2$ (2a). The complex was prepared in the same manner as **1**, except [Cu$_2$(dppm)$_2$(NCCH$_3$)$_4$](BF$_4$)$_2$ was replaced by [Ag$_2$(dppm)$_2$](BF$_4$)$_2$. Yield: 75%. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.42−7.23 (m, 40H, Ph), 3.42 (m, 4H, *CH$_2$*P), 1.46 (s, 18H, CH$_3$). ^{31}P$\{^1$H$\}$ NMR (CD$_2$Cl$_2$): δ 6.2. ^{13}C$\{^1$H$\}$ NMR (CD$_2$Cl$_2$): δ 141.1, 132.7, 131.4, 129.4, 58.0, 30.0, 26.2. IR (KBr): ν 2181 (C≡N), 1056 cm^{-1} (BF$_4{}^-$). Raman (neat solid): ν 2178 cm^{-1} (C≡N). Mass-FAB: *m/z* 1071 (Ag$_2$(dppm)$_2$, *m/z* 1071.4). Anal. Calcd for Ag$_2$C$_{60}$H$_{62}$N$_2$P$_4$B$_2$F$_8$: C, 54.41; H, 4.72; N, 2.12. Found: C, 54.40; H, 5.00; N, 2.17.

[Ag$_2$(dppm)$_2$(CN-*t*-Bu)$_2$](ClO$_4$)$_2$ (2b). The complex is prepared in the same manner as **2a**, except that [Ag$_2$(dppm)$_2$](ClO$_4$)$_2$ was used instead of [Ag$_2$(dppm)$_2$](BF$_4$)$_2$. Crystals were obtained by slow vapor diffusion of *tert*-butyl methyl ether in an acetonitrile solution. Yield: 80%. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.40−7.35 (m, 40H, Ph), 3.59 (m, 4H, *CH$_2$*P), 1.46 (s, 18H, CH$_3$). ^{31}P$\{^1$H$\}$ NMR (CD$_2$Cl$_2$): δ 6.2. ^{13}C$\{^1$H$\}$ NMR (CD$_2$Cl$_2$): δ 142.3, 133.1, 131.5, 130.9, 129.5, 57.9, 29.7, 24.9. IR (KBr): ν 2178 (C≡N), 1090 cm^{-1} (ClO$_4{}^-$). Raman (neat solid): ν 2178 cm^{-1} (C≡N).

{[Cu(dppb)(CN-*t*-Bu)$_2$]BF$_4$}$_n$ (3). The complex was prepared in the same manner as **1**, except [Cu$_2$(dppm)$_2$(NCCH$_3$)$_4$](BF$_4$)$_2$ was replaced by [Cu$_2$(dppb)$_2$](BF$_4$)$_2$. Yield: 55%. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.50−7.42 (m, 20H, Ph), 2.36 (m, 4H, *CH$_2$*P), 1.81 (m, 4H, *CH$_2$*CH$_2$P), 1.29 (s, 18H, CH$_3$). ^{31}P$\{^1$H$\}$ NMR (CD$_2$Cl$_2$): δ −0.63. ^{13}C$\{^1$H$\}$ NMR (CD$_2$Cl$_2$): δ 134.83, 132.55, 130.53, 129.25, 57.48, 30.05, 25.27, 23.97. IR (KBr): ν 1061 (BF$_4$), 2174 cm^{-1} (C≡N). Raman (neat solid): ν 2178 cm^{-1} (C≡N). Anal. Calcd for CuC$_{38}$H$_{46}$N$_2$P$_2$BF$_4$: C, 61.42; H, 6.24; N, 3.77. Found: C, 61.03; H, 6.37; N, 3.81.

{[Ag(dppb)(CN-*t*-Bu)$_2$]BF$_4$}$_n$ (4). The complex was prepared in the same manner as **1**, except [Cu$_2$(dppm)$_2$(NCCH$_3$)$_4$](BF$_4$)$_2$ was replaced by [Ag$_2$(dppb)$_2$](BF$_4$)$_2$. Yield: 91%. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.42−7.35 (m, 20H, Ph), 2.05 (m, 4H, *CH$_2$*P), 1.42 (m, 4H, *CH$_2$*CH$_2$P), 1.38 (s, 18H, CH$_3$). ^{31}P$\{^1$H$\}$ NMR (CD$_2$Cl$_2$): δ 3.24. ^{13}C$\{^1$H$\}$ NMR (CD$_2$Cl$_2$): δ 142.6, 132.6, 130.5, 129.1, 57.0, 30.0, 27.0, 26.7. IR (KBr): ν 2184 (C≡N), 1057 cm^{-1} (BF$_4$). Raman (neat solid): ν 2187 cm^{-1} (C≡N). Anal. Calcd for AgC$_{38}$H$_{46}$N$_2$P$_2$BF$_4$: C, 57.96; H, 5.89; N, 3.56. Found: C, 58.06; H, 5.88; N, 3.47.

{[Ag$_2$(dppb)$_3$(CN-*t*-Bu)$_2$]BF$_4$}$_n$ (5). Polymer **4** was dissolved in a minimum amount of acetonitrile and exposed to *tert*-butyl methyl ether by slow diffusion for a few months. Colorless and irregular shaped crystals were obtained which were characterized by X-ray crystallography. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.42−7.28 (m, 60H, Ph), 2.21 (m, 12H, *CH$_2$*P), 1.58 (m 12H, *CH$_2$*CH$_2$P), 1.41 (s, 18H,CH$_3$).

{[Cu(dpppen)(CN-*t*-Bu)$_2$]BF$_4$}$_n$ (6). The complex was prepared in the same manner as **1**, except [Cu$_2$(dppm)$_2$(NCCH$_3$)$_4$](BF$_4$)$_2$ was replaced by [Cu$_2$(dpppen)$_2$](BF$_4$)$_2$. Yield: 89%. ^{1}H NMR (CD$_2$-Cl$_2$): δ 7.48−7.33 (m, 20H, Ph), 2.31 (m, 4H, *CH$_2$*P), 1.36 (m, 4H, *CH$_2$*CH$_2$P), 1.29 (s, 18H, CH$_3$), 1.23 (m, 2H, *CH$_2$*CH$_2$CH$_2$P).

^{31}P$\{^1$H$\}$ NMR (CD$_2$Cl$_2$): δ −3.69. ^{13}C$\{^1$H$\}$ NMR (CD$_2$Cl$_2$): δ 134.71, 132.65, 130.47, 129.18, 57.43, 30.00, 26.30, 29.97, 25.72, 21.82. IR (KBr): ν 1059 (BF$_4$), 2172 cm^{-1} (C≡N). Raman (neat solid): ν 2173 cm^{-1} (C≡N). Anal. Calcd for CuC$_{39}$H$_{48}$N$_2$P$_2$BF$_4$: C, 61.87; H, 6.39; N, 3.70. Found: C, 61.72; H, 6.52; N, 3.70.

{[Ag(dpppen)(CN-*t*-Bu)$_2$]BF$_4$}$_n$ (7). The complex was prepared in the same manner as **1**, except [Cu$_2$(dppm)$_2$(NCCH$_3$)$_4$](BF$_4$)$_2$ was replaced by [Ag$_2$(dpppen)$_2$](BF$_4$)$_2$. Yield: 72%. ^{1}H NMR (CD$_2$-Cl$_2$): δ 7.47−7.35 (m, 20H, Ph), 2.22 (m, 4H, *CH$_2$*P), 1.62 (m, 2H, *CH$_2$*CH$_2$CH$_2$P), 1.49 (m, 4H, *CH$_2$*CH$_2$P), 1.34 (s, 18H, CH$_3$). ^{31}P$\{^1$H$\}$ NMR (CD$_2$Cl$_2$): δ 2.45. ^{13}C$\{^1$H$\}$ NMR (CD$_2$Cl$_2$): δ 142.3, 132.7, 130.7, 129.3, 57.3, 30.0, 26.8, 24.4. IR (KBr): ν 1056 (BF$_4{}^-$), 2178 cm^{-1} (C≡N). Raman (neat solid): ν 2178 cm^{-1} (C≡N). Anal. Calcd for CuC$_{39}$H$_{48}$N$_2$P$_2$BF$_4$: C, 58.45; H, 6.04; N, 3.50. Found: C, 58.11; H, 5.95; N, 4.07.

{[Ag(dpppen)(CN-*t*-Bu)]BF$_4$}$_n$ (8). Polymer **7** was dissolved in a minimal amount of acetone, and the solution was exposed to *tert*-butyl methyl ether by slow diffusion over a few months. Colorless and irregular shaped crystals were obtained which were characterized from X-ray crystallography. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.50−7.37 (m, 20H, Ph), 2.31 (m, 4H, *CH$_2$*P), 1.71−1.46 (m, 15H, *CH$_2$*CH$_2$P, *CH$_2$*CH$_2$CH$_2$P, CCH$_3$).

{[Cu(dpph)(CN-*t*-Bu)$_2$]BF$_4$}$_n$ (9). The complex was prepared in the same manner as **1**, except [Cu$_2$(dppm)$_2$(NCCH$_3$)$_4$](BF$_4$)$_2$ was replaced by [Cu$_2$(dpph)$_2$](BF$_4$)$_2$. Yield: 73%. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.50−7.29 (m, 20H, Ph), 2.18 (m, 4H, *CH$_2$*P), 1.75 (m, 4H, *CH$_2$*CH$_2$P), 1.41 (m, 4H, *CH$_2$*CH$_2$CH$_2$P), 1.34 (s, 18H, CH$_3$). ^{31}P$\{^1$H$\}$ NMR (CD$_2$Cl$_2$): δ −1.61. ^{13}C$\{^1$H$\}$ NMR (CD$_2$Cl$_2$): δ 140.22, 134.03, 132.49, 130.47, 129.16, 57.60, 32.66, 30.06, 28.24, 26.09. IR (KBr): ν 1060 (BF$_4$), 2174 cm^{-1} (C≡N). Raman (neat solid): ν 2178 cm^{-1} (C≡N). Anal. Calcd for CuC$_{40}$H$_{50}$N$_2$P$_2$BF$_4$: C, 62.30; H, 6.54; N, 3.63. Found: C, 62.18; H, 6.64; N, 3.60.

{[Ag(dpph)(CN-*t*-Bu)$_2$]BF$_4$}$_n$ (10). The complex was prepared in the same manner as **1**, except [Cu$_2$(dppm)$_2$(NCCH$_3$)$_4$](BF$_4$)$_2$ was replaced by [Ag$_2$(dpph)$_2$](BF$_4$)$_2$. Yield: 84%. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.42−7.33 (m, 20H, Ph), 2.10 (m, 4H, *CH$_2$*P), 1.40 (s, 18H, CH$_3$), 1.26−1.25 (m, 8H, *CH$_2$*CH$_2$P + *CH$_2$*CH$_2$CH$_2$P). ^{31}P$\{^1$H$\}$ NMR (CD$_2$Cl$_2$): δ 2.80. ^{13}C$\{^1$H$\}$ NMR (CD$_2$Cl$_2$): δ 143.15, 132.60, 130.53, 129.13, 57.0, 30.78, 30.12, 27.68, 25.68. IR (KBr): ν 2174, 2135 (C≡N), 1055 cm^{-1} (BF$_4$). Raman (neat solid): ν 2181 cm^{-1} (C≡N). Anal. Calcd for CuC$_{40}$H$_{50}$N$_2$P$_2$BF$_4$: C, 58.92; H, 6.18; N, 3.44. Found: C, 59.07; H, 6.18; N, 3.48.

{[Cu(dppm)(dmb)]BF$_4$}$_n$ (11). [Cu$_2$(dppm)$_2$(NCMe)$_4$](BF$_4$)$_2$ (222.1 mg, 0.18 mmol) was dissolved in 30 mL of acetonitrile. A 69.0 mg (0.36 mmol) amount of dmb was dissolved separately in a round flask containing 60 mL of acetonitrile. This latter colorless solution was slowly added dropwise to the former. The mixture was stirred for 2 h prior to being reduced to 15 mL in vacuo. A 150 mL volume of diethyl ether was added to the reaction mixture precipitating the white product, which was filtered off and dried in vacuo. Yield: 74% (260.2 mg). ^{1}H NMR (CD$_2$Cl$_2$): δ 7.31−7.14 (m, 40H, Ph), 3.26 (m, 4H, *CH$_2$*P), 1.96−0.93 (m, 36H dmb). ^{31}P-$\{^1$H$\}$ NMR (CD$_2$Cl$_2$): δ −4.50. ^{13}C$\{^1$H$\}$ NMR (CD$_2$Cl$_2$): δ 140.58, 132.60, 131.20, 129.41, 66.00, 60.54, 44.20, 36.23, 28.45, 27.41, 22.72, 15.43. IR (KBr): ν 1103 (BF$_4$), 2181 cm^{-1} (C≡N). Raman (neat solid): ν 2171 cm^{-1} (C≡N). Anal. Calcd for CuC$_{37}$H$_{40}$N$_2$P$_2$BF$_4$: C, 61.29; H, 5.56; N, 3.86. Found: C, 61.31; H, 5.61; N, 3.96.

{[Ag(dppm)(dmb)]BF$_4$}$_n$ (12a). This polymer was prepared in the same manner as **11**, except [Cu$_2$(dppm)$_2$(NCCH$_3$)$_4$](BF$_4$)$_2$ was replaced by [Ag$_2$(dppm)$_2$](BF$_4$)$_2$. Yield: 54%. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.42−7.21 (m, 40H, Ph), 3.36 (m, 4H, *CH$_2$*P), 1.84 (m, 8H, dmb), 1.48−1.34 (m, 28H, dmb). ^{31}P$\{^1$H$\}$ NMR (CD$_2$Cl$_2$): δ 5.71. ^{13}C-

{^{1}H} NMR (CD$_2$Cl$_2$): δ 146.59, 144.95, 132.78, 131.51, 129.56, 63.90, 60.72, 43.19, 36.50, 28.34, 26.76, 22.39. IR (KBr): ν 1059 (BF$_4$), 2180, 2134 cm^{-1} (C≡N). Raman (neat solid): ν 2178 cm^{-1} (C≡N). Anal. Calcd for AgC$_{37}$H$_{40}$N$_2$P$_2$BF$_4$: C, 57.76; H, 5.24; N, 3.64. Found: C, 57.23; H, 5.28; N, 3.64. Mass-FAB: m/z 1071 (Ag$_2$(dppm)$_2$(BF$_4$), m/z 1071.4).

{[Ag(dppm)(dmb)]ClO$_4$}$_n$ (12b). This polymer was prepared in the same manner as **11**, except [Cu$_2$(dppm)$_2$(NCCH$_3$)$_4$](BF$_4$)$_2$ was replaced by [Ag$_2$(dppm)$_2$](ClO$_4$)$_2$. Yield: 93%. ^{1}H NMR (CD$_3$-CN): δ 7.45−7.10 (m, 40H, Ph), 3.55 (s, 4H, *CH$_2$*P), 2.20−1.97 (m, 12H, dmb), 1.64−1.40 (m, 24H, dmb). ^{31}P{^{1}H} NMR (CD$_3$-CN): δ 9.85. ^{13}C{^{1}H} NMR (CD$_3$CN): δ 145.8, 144.3, 133.1, 131.6, 129.4, 65.8, 65.0, 61.6, 42.3, 36.0, 27.4, 26.6, 25.4, 22.4, 15.1. IR (KBr): ν 1090 (ClO$_4$), 2178 cm^{-1} (C≡N). Anal. Calcd for AgC$_{31}$H$_{31}$N$_2$P$_2$ClO$_4$: C, 54.21; H, 4.55; N, 2.04. Found: C, 54.24; H, 4.76; N, 2.24. Mass-FAB: m/z 1274 (Ag$_2$(dppm)$_2$(dmb)-(ClO$_4$), m/z 1274.3).

{[Cu(dppb)(dmb)]BF$_4$}$_n$ (13). This polymer was prepared in the same manner as **11**, except [Cu$_2$(dppm)$_2$(NCCH$_3$)$_4$](BF$_4$)$_2$ was replaced by [Cu$_2$(dppb)$_2$](BF$_4$)$_2$. Yield: 70%. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.43 (m, 20H, Ph), 2.35 (m, 4H, *CH$_2$*P), 2.10−1.07 (m, 22H, *CH$_2$CH$_2$*P + dmb). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ −0.38, −2.78. ^{13}C-{^{1}H} NMR (CD$_2$Cl$_2$): δ 134.60, 132.50, 130.67, 129.35, 63.18, 61.14, 43.90, 37.11, 29.34, 28.04, 26.06, 22.91. IR (KBr): ν 2170 (C≡N), 1061 cm^{-1} (BF$_4$). Raman (neat solid): ν 2171 cm^{-1} (C≡N).

{[Ag(dppb)(dmb)]BF$_4$}$_n$ (14). This polymer was prepared in the same manner as **11**, except [Cu$_2$(dppm)$_2$(NCCH$_3$)$_4$](BF$_4$)$_2$ was replaced by [Ag$_2$(dppb)$_2$](BF$_4$)$_2$. Yield: 85%. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.40−7.28 (m, 20H, Ph), 2.22 (m, 4H, *CH$_2$*P), 1.88−1.81 (m, 4H, dmb), 1.61−1.42 (m, 18H, dmb + *CH$_2$CH$_2$*P). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ 4.42. ^{31}P{^{1}H} NMR (DMF-d_7): δ 7.62. ^{13}C{^{1}H} NMR (DMF-d_7): δ 151.47, 137.15, 134.86, 133.42, 66.8, 64.12, 48.14, 40.82, 32.68, 30.67, 29.51, 26.79. ^{13}C{^{1}H} NMR (DMSO-d_6): δ 147.29, 146.75, 132.49, 130.36, 128.87, 61.76, 59.29, 43.25, 36.07, 28.44, 26.30, 24.91, 22.03. IR (KBr): ν 2167, 2132 (C≡N), 1060 cm^{-1} (BF$_4$). Raman (neat solid): ν 2172 cm^{-1} (C≡N). Anal. Calcd for C$_{40}$H$_{46}$N$_2$P$_2$BF$_4$Ag: C, 59.21; H, 5.71; N, 3.45. Found: C, 58.95; H, 5.90; N, 3.31. Mass-FAB: m/z 1238 (Ag(dppb)$_2$(dmb)(BF$_4$), m/z 1238.0).

{[Cu(dpppen)(dmb)]BF$_4$}$_n$ (15). This polymer was prepared in the same manner as **11**, except [Cu$_2$(dppm)$_2$(NCCH$_3$)$_4$](BF$_4$)$_2$ was replaced by [Cu$_2$(dpppen)$_2$](BF$_4$)$_2$. Yield: 67%. IR (KBr): ν 1061 (BF$_4$), 2168 cm^{-1} (C≡N). Raman (neat solid): ν 2173 cm^{-1} (C≡N). Anal. Calcd for CuC$_{41}$H$_{48}$N$_2$P$_2$BF$_4$: C, 63.04; H, 6.19; N, 3.59. Found: C, 62.97; H, 6.30; N, 3.61.

{[Ag(dpppen)(dmb)]BF$_4$}$_n$ (16). This polymer was prepared as for **11**, except [Cu$_2$(dppm)$_2$(NCCH$_3$)$_4$](BF$_4$)$_2$ was replaced by [Ag$_2$-(dpppen)$_2$](BF$_4$)$_2$. Yield: 64%. IR (KBr): ν 1056 (BF$_4$), 2176, 2130 cm^{-1} (C≡N). Raman (neat solid): ν 2178 cm^{-1} (C≡N). Anal. Calcd for AgC$_{41}$H$_{48}$N$_2$P$_2$BF$_4$: C, 59.66; H, 5.86; N, 3.39. Found: C, 59.18; H, 6.05; N, 3.43. Mass-FAB: m/z 1183 (Ag$_2$(dpppen)$_2$](BF$_4$), m/z 1183.6).

{[Cu(dpph)(dmb)]BF$_4$}$_n$ (17). This polymer was prepared in the same manner as **11**, except [Cu$_2$(dppm)$_2$(NCCH$_3$)$_4$](BF$_4$)$_2$ was replaced by [Cu$_2$(dpph)$_2$](BF$_4$)$_2$. Yield: 85%. IR (KBr): ν 2170 (C≡N), 1057 cm^{-1} (BF$_4$). Raman (neat solid): ν 2172 cm^{-1} (C≡N).

{[Ag(dpph)(dmb)]BF$_4$}$_n$ (18). This polymer was prepared in the same manner as **11**, except [Cu$_2$(dppm)$_2$(NCCH$_3$)$_4$](BF$_4$)$_2$ was replaced by [Ag$_2$(dpph)$_2$](BF$_4$)$_2$. Yield: 65%. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.41−7.33 (m, 20H, Ph), 2.18 (m, 4H, *CH$_2$*P), 1.88−1.73 (m, 4H, dmb), 1.51−1.23 (m, 24H, dmb + *CH$_2$CH$_2$*P). ^{31}P{^{1}H} NMR

(CD$_2$Cl$_2$): δ 3.63. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 146.26, 145.55, 132.74, 130.72, 129.32, 63.31, 60.60, 44.17, 36.98, 30.47, 28.95, 27.61, 26.55, 25.45, 22.77. IR (KBr): ν 2169, 2130 (C≡N), 1057 cm^{-1} (BF$_4$). Raman (neat solid): ν 2172 cm^{-1} (C≡N). Anal. Calcd for C$_{42}$H$_{50}$N$_2$P$_2$BF$_4$Ag: C, 60.09; H, 6.00; N, 3.34. Found: C, 59.89; H, 6.20; N, 3.36. Mass-FAB: m/z 1277 (Ag$_2$(dpph)(dmb)$_2$(CN)$_2$-(BF$_4$)$_2$, m/z 1276.5).

Apparatus. NMR spectra were acquired using a Bruker AC-300 spectrometer (^{1}H, 300.15 MHz; ^{13}C, 75.48 MHz; ^{31}P, 121.50 MHz) using the solvent as chemical shift standard, except in ^{31}P NMR, where the chemical shifts are referenced to D$_3$PO$_4$ (85% in D$_2$O). All chemical shifts (δ) and coupling constants (*J*) are given in ppm and Hertz, respectively. IR spectra were acquired using a Bomem FT-IR MB series spectrometer equipped with a baseline-diffused reflectance. Emission spectra and emission lifetimes were measured using a nanosecond N$_2$ laser system from PTI (model GL-3300 pumping a dye laser model GL-302) with an excitation wavelength of 311 nm. Emission spectra were also measured using a SPEX Fluorolog II. Glass transition temperatures (T_g) were measured using a Perkin-Elmer 5A DSC7 equipped with a thermal controller 5B TAC 7/DS, employing water and indium as calibration standards. FT-Raman spectra were acquired using a Bruker RFS 100/S spectrometer. XRD were acquired using a Rigaku/USA Inc. diffractometer with a copper lamp operating under a 30 mA current and a 40 kV tension. TGA were obtained under N$_2$ using a TGA 7 Perkin-Elmer instrument, with a temperature range of 50−650 °C increasing by at 3°/min. Chemical analyses were performed at the Université de Montréal and the University of Toronto.

Crystallography. Crystals were obtained by slow evaporation (**12b**) from acetonitrile solution or by vapor diffusion using acetonitrile−*tert*-butyl methyl ether at 23 °C (**1, 5, 7**). Data for **12b** and **1** were collected at 293(2) K on an Enraf-Nonius CAD-4 automatic diffractometer at the Université de Sherbrooke. The NRCCAD program was used for centering, indexing, and data collection.[12] Two standard reflections were measured every 60 min, and no significant decay was observed during data collection. The NRCVAX programs were used for crystal structure solution by application of direct methods.[13] The SHELX-97 program was used for refinement by full-matrix least squares of F^2.[14] Empirical absorption corrections were made on the basis of a ψ scan. Isotropic extinction coefficients were included in the refinement to account for secondary extinction effects.[15] Hydrogen atoms were geometrically placed, and the respective final refinements included anisotropic thermal parameters for non-hydrogen atoms and isotropic thermal parameter for the hydrogen atoms. Single crystals of **5, 7**, and **8** were coated with Paratone-N oil, mounted using a glass fiber, and frozen in the cold nitrogen stream of the goniometer. A hemisphere of data was collected on a Bruker AXS P4/SMART 1000 diffractometer (University of New Brunswick) using ω and θ scans with a scan width of 0.3° and 30 (**7, 8**) or 25 s (**5**) exposure times. The detector distance was 6 (**7, 8**) or 5 cm (**5**). The data were reduced and corrected for absorption.[16,17] The structure was solved by direct methods and refined by full-matrix least squares on F.[18] For **7**, the space group was checked using MISSYM in

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Table 2. Crystal Data for **1, 4, 7, 8,** and **12b**

	[Cu₂(dppm)₂(CN-*t*-Bu)₃]-(BF₄)₂ (**1**)	{[Ag₂(dppb)₃(CN-*t*-Bu)₂]-(BF₄)₄}ₙ (**5**)	{[Ag(dpppen)(CN-*t*-Bu)₂]-(BF₄)}ₙ (**7**)	{[Ag(dpppen)(CN-*t*-Bu)]-(BF₄)}ₙ (**8**)	{[Ag(dppm)(dmb)]-ClO₄}ₙ (**12b**)
empirical formula	$C_{65}H_{71}B_2Cu_2F_8N_3P_4$	$C_{98}H_{108}Ag_2B_2F_8N_4\,P_6$	$C_{39}H_{48}AgBF_4N_2P_2$	$C_{68}H_{69}Ag_2B_2F_8N_2P_4$	$C_{74}H_{80}Ag_2Cl_2N_4O_8P_4$
fw	1318.83	1917.06	801.41	1427.49	1563.94
description	colorless, parall	colorless, irregular	colorless, irregular	colorless, irregular	colorless, needle
cryst size (mm)	0.40 × 0.35 × 0.30	0.20 × 0.30 × 0.35	0.18 × 0.18 × 0.33	0.20 × 0.30 × 0.30	0.20 × 0.20 × 0.20
temp (K)	293(2)	173(1)	198(1)	173(1)	293(2)
cryst system	monoclinic	triclinic	triclinic	monoclinic	triclinic
space group	$P2_1/a$	$P\bar{1}$	$P1$	$P2_1$	$P\bar{1}$
a (Å)	20.395(3)	11.4175(12)	8.7574(9)	11.147(1)	13.1321(19)
b (Å)	15.287(2)	17.7558(19)	14.8390(16)	18.423(2)	13.3093(18)
c (Å)	21.022(4)	23.465(3)	16.7222(18)	16.169(2)	13.4611(16)
α (deg)	90	90.565(2)	86.462(2)	90	103.780(12)
β (deg)	92.347(14)	92.498(2)	77.099(2)	91.619(2)	107.349(11)
γ (deg)	90	94.076(2)	73.170(2)	90	115.764(11)
V (Å³)	6548.6(18)	4740.0(9)	2027.5(4)	3319.0(7)	1828.0(4)
Z	4	2	2	2	1
radiatn	Cu Kα	Mo Kα	Mo Kα	Mo Kα	Cu Kα
wavelength (Å)	1.540 60	0.710 73	0.710 73	0.710 73	1.540 60
calcd density (Mg/m³)	1.338	1.343	1.313	1.428	1.421
scan mode	$\omega/2\theta$	ω and ϕ	ω and ϕ	ω and ϕ	$\omega/2\theta$
$F(000)$	2728	1980	828	1454	804
abs coeff (mm⁻¹)	2.256	0.577	0.622	0.75	6.249
θ range (deg)	2.10−71.98	0.87−27.50	1.25−25.00	1.26−25.00	3.80−69.93
limiting indices	−25 ≤ h ≤ 18	−14 ≤ h ≤ 13	−10 ≤ h ≤ 10	−13 ≤ h ≤ 13	−16 ≤ h ≤ 13
	0 ≤ k ≤ 18	−23 ≤ k ≤ 22	−15 ≤ k ≤ 17	−21 ≤ k ≤ 20	0 ≤ k ≤ 16
	0 ≤ l ≤ 25	−29 ≤ l ≤ 30	−19 ≤ l ≤ 19	−18 ≤ l ≤ 19	−16 ≤ l ≤ 15
reflcns collcd	12 096	31 368	10 516	17 191	6931
indpndnt reflcns	12 096	20 217	9001	9324	5990
data/restraints/params	12 096/0/758	20 217/0/1117	9001/3/922	9324/1/803	6931/0/425
goodness-of-fit on F^2	1.051	1.056	1.036	1.113	1.062
final R indices [$I > 2\sigma(I)$]ᵃ	R1 = 0.0669	R1 = 0.0582	R1 = 0.0402	R1 = 0.0593	R1 = 0.0484
	wR2 = 0.1997	wR2 = 0.1901	wR2 = 0.1053	wR2 = 0.1571	wR2 = 0.1542
R indices (all data)ᵃ	R1 = 0.0822	R1 = 0.0879	R1 = 0.0415	R1 = 0.0618	R1 = 0.0625
	wR2 = 0.2159	wR2 = 0.2092	wR2 = 0.1068	wR2 = 0.1583	wR2 = 0.2051
largest diff peak and hole (e Å⁻³)	1.142	2.983	1.906	1.471	1.017
	−1.305	−1.170	−0.458	−0.78	−1.210

ᵃ R1 = $\sum||F_o| - |F_c||/\sum|F_o|$; wR2 = $(\sum[w(F_o^2 - F_c^2)^2]/\sum[F_o^4])^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (AP)^2 + (BP)]$, where $P = (\max(F_o^2, 0) + 2F_c^2)/3$: **1**, $A = 0.1617$, $B = 4.7121$; **4**, $A = 0.1342$, $B = 0.000$; **7**, $A = 0.0657$, $B = 1.600$; **8**, $A = 0.0557$, $B = 19.3282$, **12b**, $A = 0.1478$, $B = 1.9468$.

PLATON97 included in WINGX.[13b] No extra crystallographic symmetry was detected. The space group is *P*1. One of the BF₄ anions exhibited disorder, and the site occupancy was determined using an isotropic model by fixing 0.65 (F(6)−F(8)) and 0.35 (F(6a)−F(8a)) in subsequent refinement cycles. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions and refined using a riding model. For **5**, one of the solvent molecules and one butyl bridge exhibited disorder and the site occupancy was determined using an isotropic model by fixing 0.65 (C(73)−C(74)), 0.35 (C(73A)−C(74A)), 0.5 (C(97)−C(98)), and 0.5 (C(97A)−C(98A)) in subsequent refinement cycles. Hydrogen atoms were included in calculated positions and refined using a riding model. Hydrogen atoms for the solvent molecules were omitted. For **8**, one of the *tert*-butyl groups exhibited disorder and the site occupancy was determined using an isotropic model by fixing 0.55 (C(3)−C(5)) and 0.45 (C(3A)−C(5A)) in subsequent refinement cycles. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions and refined using a riding model.

Results and Discussion

dppm-Containing Dimers. 1 (Chart 3) is prepared from [Cu₂(dppm)₂(NCCH₃)₄](BF₄)₂ in the presence of an excess of *t*-BuNC. Both the ¹H NMR and elemental analysis of the crude product indicate a nonstoichiometric formulation (∼"[Cu₂(dppm)₂(CN-*t*-Bu)₃.₅](BF₄)₂") suggesting the presence of a mixture of dimers containing either 4 or 3 *t*-BuNC

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Chart 3
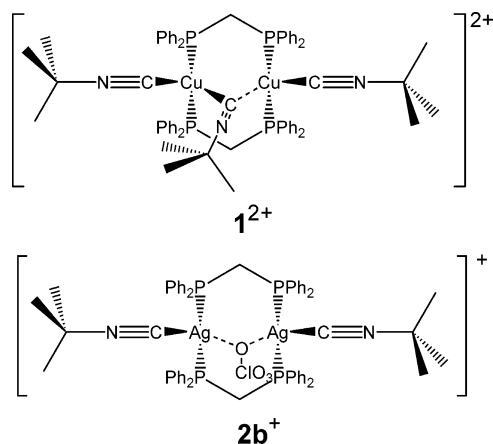
groups. The former is consistent with the structure of the starting materials, and there is precedence for complexes of the type "Cu₂(dppm)₂(L)₃" or "Cu₂(dppm)₂(L)₂(L′)".[19] The structure of **1** was confirmed by X-ray crystallography (Tables 2 and 3; Figure 1). The structure consists of two Cu atoms, separated by 3.1003(9) Å, bridged by two dppm ligands and one *t*-BuNC group. The ligand sphere of the metal centers is completed by two terminal *t*-BuNC groups. The Cu−C distances are 2.059(4) and 2.376(4) Å, indicating

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Table 3. Selected Bond Lengths (Å) and Angles (deg) for **1**, **5**, **7**, **8**, and **12b**

[Cu₂(dppm)₂(CN-*t*-Bu)₃](BF₄)₂ (**1**)		{[Ag₂(dppb)₃(CN-*t*-Bu)₂]BF₄}ₙ (**5**)	
Cu(1)−P(1)	2.2810(10)	Ag(1)−P(1)	2.5190(11)
Cu(1)−P(4)	2.2631(10)	Ag(1)−P(2)	2.5000(11)
Cu(2)−P(2)	2.2528(9)	Ag(1)−P(3)	2.4814(11)
Cu(2)−P(3)	2.2639(10)	Ag(2)−P(4)	2.4670(11)
Cu(1)−C(61)	1.969(4)	Ag(2)−P(5)	2.5022(11)
Cu(1)−C(56)	2.059(4)	Ag(2)−P(6)	2.5141(12)
Cu(2)−C(51)	1.953(4)	Ag(1)−C(1)	2.243(5)
Cu(2)−C(56)	2.376(5)	Ag(2)−C(90)	2.255(5)
P(4)−Cu(1)−P(1)	117.74(4)	P(3)−Ag(1)−P(2)	123.07(4)
C(61)−Cu(1)−P(4)	104.25(12)	P(3)−Ag(1)−P(1)	113.87(4)
C(56)−Cu(1)−P(4)	114.08(11)	P(2)−Ag(1)−P(1)	98.88(4)
C(61)−Cu(1)−P(1)	103.27(11)	C(1)−Ag(1)−P(2)	105.51(12)
C(56)−Cu(1)−P(1)	111.01(12)	C(1)−Ag(1)−P(3)	110.20(12)
C(61)−Cu(1)−C(56)	104.71(18)	C(1)−Ag(1)−P(1)	103.09(13)
P(2)−Cu(2)−P(3)	121.75(4)	P(4)−Ag(2)−P(5)	122.89(4)
C(51)−Cu(2)−P(2)	109.53(11)	P(4)−Ag(2)−P(6)	114.48(4)
C(51)−Cu(2)−P(3)	105.25(11)	P(5)−Ag(2)−P(6)	99.49(4)
P(2)−Cu(2)−C(56)	112.10(10)	C(90)−Ag(2)−P(4)	112.69(12)
P(3)−Cu(2)−C(56)	103.69(10)	C(90)−Ag(2)−P(5)	101.51(12)
C(51)−Cu(2)−C(56)	102.70(15)	C(90)−Ag(2)−P(6)	103.14(13)

{[Ag(dpppen)(CN-*t*-Bu)₂]BF₄}ₙ (**7**)		{[Ag(dppm)(dmb)]ClO₄}ₙ (**12b**)	
Ag(1)−C(6)	2.189(7)	Ag−C(9)	2.251(6)
Ag(1)−C(1)	2.335(8)	Ag−C(1)	2.331(6)
Ag(1)−P(1)	2.4706(15)	Ag−P(1)	2.4672(14)
Ag(1)−P(2)	2.5136(16)	Ag−P(2)	2.4921(15)
C(6)−Ag(1)−C(1)	109.0(3)	C(9)−Ag−C(1)	99.0(2)
C(6)−Ag(1)−P(1)	114.30(17)	C(9)−Ag−P(1)	118.58(17)
C(1)−Ag(1)−P(1)	117.6(2)	C(1)−Ag−P(1)	97.57(18)
C(6)−Ag(1)−P(2)	112.69(19)	C(9)−Ag−P(2)	98.14(18)
C(1)−Ag(1)−P(2)	96.2(2)	C(1)−Ag−P(2)	98.90(18)
P(1)−Ag(1)−P(2)	105.56(5)	P(1)−Ag−P(2)	136.48(4)

{[Ag(dpppen)(CN-*t*-Bu)]BF₄}ₙ (**8**)			
Ag(1)−C(35)	2.178(11)	Ag(1)−P(2)	2.454(3)
Ag(1)−C(1)	2.195(13)	Ag(2)−P(3)	2.458(2)
Ag(1)−P(1)	2.425(2)	Ag(2)−P(4)	2.453(3)
P(1)−Ag(1)−P(2)	128.01(8)	P(3)−Ag(2)−P(4)	125.85(8)
P(1)−Ag(1)−C(1)	120.0(3)	P(3)−Ag(2)−C(35)	113.9(3)
P(2)−Ag(1)−C(1)	107.2(4)	P(4)−Ag(2)−C(35)	119.3(3)

Figure 1. ORTEP diagram of the structure of for [Cu₂(dppm)₂(NCCH₃)₃]-(BF₄)₂ (**1**) using 50% probability ellipsoids. The H atoms and counterions are omitted for clarity.
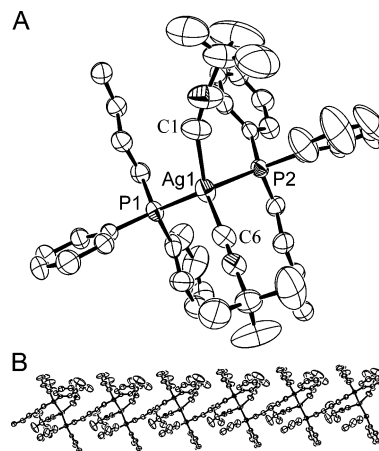
Figure 2. (A) ORTEP diagram of one Ag(dpppent)(CN-*t*-Bu)₂⁺ unit of polymer **7**. The H atoms and counterions are not shown for clarity. (B) ORTEP diagram of a segment of polymer **7**. The H atoms and counterions are omitted for clarity. The ellipsoids are shown in 50% probability.

ligands. The Cu−C≡N angles strongly deviate from linearity (147.8 and 162.9° for the tetra- and tricoordinate metals, respectively), where the *tert*-butyl groups are directed away from each other, providing evidence for intramolecular steric hindrance. In comparison with the more symmetrically bridged [Cu₂(dppm)₂(NCNMe₂)₂(μ-ClO₄)]⁺ (3.424(5) Å), [Cu₂(dppm)₂(NCNMe₂)(Cl)(μ-Cl)] (3.293(1) Å), and Cu₂-(dppm)₂(NCNMe₂)₃²⁺ (3.143(2) Å) species, the observed Cu···Cu distance in **1** is the shortest of its kind.[19] We propose that, despite the presence of an excess of *t*-BuNC in the reaction, the presence of the unsaturated complex **1** in the crude mixture is due to ligand lability.

2a,**b** are synthesized in the same manner as **1**, but even in the presence of excess *t*-BuNC, these complexes are the sole products observed. Poor quality crystals, though suitable for X-ray analysis (40% of all reflections were observed), were obtained for **2b** (Chart 2 and Supporting Information). The structure shows similarities to that of [Cu₂(dppm)₂(NCNMe₂)₂-(μ-ClO₄)]⁺,[19] where two tricoordinate metal atoms are held almost face-to-face with a Ag···Ag separation of 3.2227-(13) Å, both interacting with an O atom of one of the ClO₄⁻ anions. The Ag−O distances (~2.61 Å) are indicative of important ionic interactions. The fact that no other *t*-BuNC groups is found in the coordination sphere of Ag strongly contrasts with the structures of the {Ag(dppm)(dmb)⁺}ₙ (described below) and {M(dmb)₂⁺}ₙ polymers shown in Chart 1.

t-**BuNC Polymers.** Compounds **3**, **4**, **6**, **7**, **9**, and **10** are prepared in reasonable yields from the reaction between the starting materials [M₂(diphos)₂](BF₄)₂ (M = Cu, Ag; diphos = dppb, dpppen, dpph) and an excess of *t*-BuNC. Crystals suitable for X-ray analysis were obtained for **7** (Tables 2 and 3; Figure 2). The X-ray structure reveals two crystallographically independent zigzag {Ag(dpppen)⁺}ₙ chains/asymmetric unit. These chains differ slightly by the orientation of the Ph and *t*-BuNC groups. The Ag atoms are placed in a zigzag geometry and describe a plane, where the P and C (CNR) atoms are located above and below the plane, respectively. *d*(Ag···Ag) is 8.757(1) Å, and ∠P₃ is 87.5°. This structure is not unprecedented as a similar polymer has been
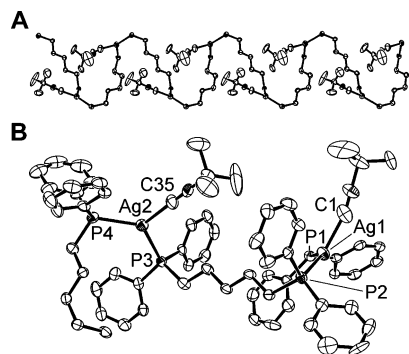
an unprecedented Cu−CNR semibridging coordination. The complex is best described as a dimer containing distorted tetra- and tricoordinate metal centers bridged by two dppm
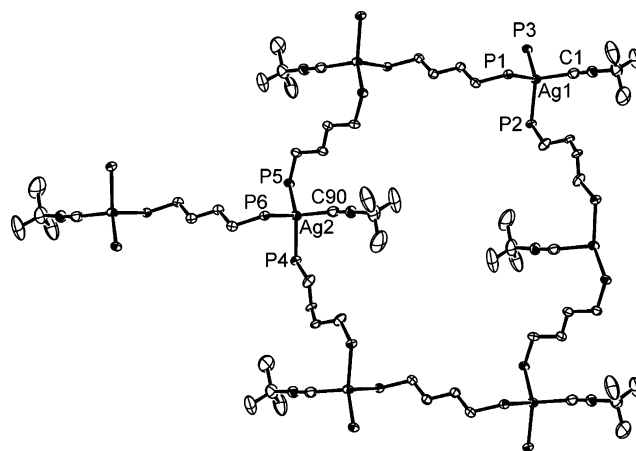
Figure 3. (A) ORTEP diagram of a segment of polymer **8** showing the skeleton of the chain. The H atoms, counterions, and *tert*-butyl and phenyl groups are omitted for clarity. (B) ORTEP diagram of a segment of **8** showing the tricoordinate Ag atoms. The H atoms and counterions are omitted for clarity. The ellipsoids are shown in 50% probability.
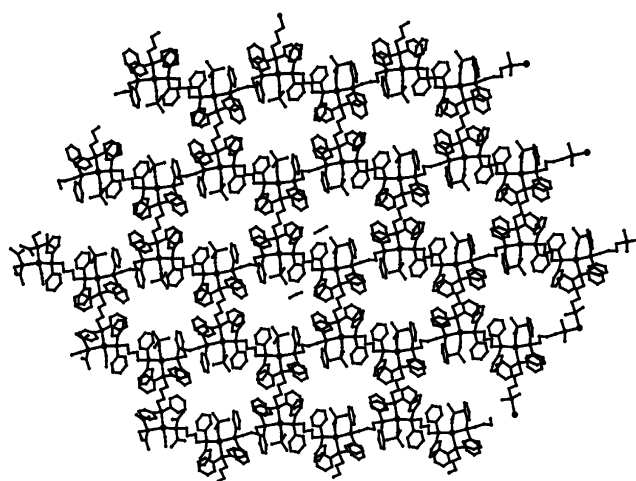
reported for {Hg(dpppen)I$_2$}$_n$.[20] On the basis of the characterization data (Experimental Section) and the physical properties described below, it is assumed that **3**, **4**, **6**, **9**, and **10** are polymeric as well, with similar structures.

When **7** is redissolved and left to recrystallize for several months, new crystals are obtained. Despite the poor quality of the crystals, the data again reveal a zigzag polymeric Ag—dpppen structure, but **7** has lost a *t*-BuNC ligand to form **8** (Figure 3; Tables 2 and 3).[21] The 1:1 dpppen/*t*-BuNC ratio is consistent with the ^{1}H NMR data. The repetitive unit contains two dpppen ligands exhibiting different alkyl chain conformations and two planar tricoordinate Ag atoms. The *d*(Ag···Ag) values for the Ag—dpppen—Ag units are 7.721-(1) and 8.997(1) Å. The ∠Ag$_3$ value is 83.3°. This zigzag structure exhibits some similarities with the polymer {Ag-(dpph)O$_2$CCF$_3$}$_n$ (dpph = bis(diphenylphosphino)hexane), recently reported by Brandys and Puddephatt.[22]
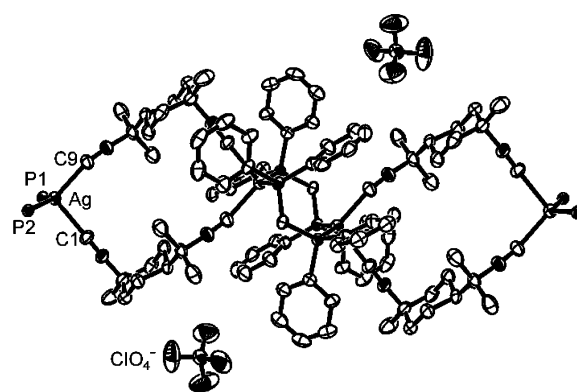
When **4** is dissolved in acetonitrile and *tert*-butyl methyl ether is slowly diffused into the solution, irregular-shaped crystals are obtained which exhibit a different ^{1}H NMR integration for the dppb and *t*-BuNC ligands in comparison with the starting material. The X-ray analysis reveals the presence of a new polymer, where a 2-D structure is observed (Figures 4 and 5). This structure can be described as a "honeycomb" or "chicken wire" pattern consisting of large {Ag(dppb)$^+$}$_6$ macrocycles. These macrocycles exhibit three different conformations of the dppb ligands. The Ag atoms are tetracoordinated by three P and one C atoms. This structure shares similar properties with the {Ag$_2$(dpph)$_3$(O$_2$-CCF$_3$)$_3$}$_n$ and {[Au$_2$(dppb)$_3$](Au(CN)$_2$)}$_n$ 2-D polymers recently reported by Brandys and Puddephatt.[23,24] The distorted hexagonal {Ag(dppb)$^+$}$_6$ macrocycles in **5** exhibit three sets of closest-neighbor Ag···Ag distances (8.95, 9.90, and 10.00 Å). The interior of this 42-membered ring exhibits long Ag···Ag diagonal distances varying from 16 to 20 Å and contains two MeCN molecules of crystallization (Figure 5) and two BF$_4^-$ counterions.
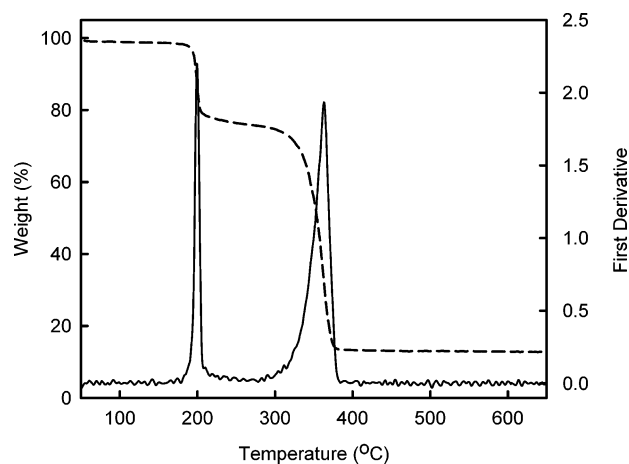
(20) Aurivillius, K.; Wendel, K. *Acta Crystallogr., Sect. B.: Struct. Crystallogr. Cryst. Chem.* **1976**, *32*, 2941.
(21) The crystals for **7** and **8** appear identical under the microscope.
(22) Brandys, M.-C.; Puddephatt, R. J. *Chem. Commun.* **2001**, 1508.
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Figure 4. Ball and stick diagram of a segment of **5** showing the 2-D "Ag$_2$(dppb)$_3$$^{2+}$" repetitive unit. The H atoms, MeCN crystallization molecules, counterion, and *t*-BuNC ligand are omitted for clarity.

Figure 5. Ball and stick diagram of a large segment of **5** showing the 2-D structure. The H atoms and counterion are not shown for clarity. Two of the MeCN molecules of crystallization are shown. These are related by symmetry.

Figure 6.

dmb-Containing Materials. 11−18 were prepared in the same manner as the *t*-BuNC-containing polymers. Crystals suitable for X-ray analysis were obtained for **12b** (Figure 6). The data reveal an unprecedented 1-D structure of a mixed-ligand chain (Chart 4), best described as a polymer of Ag$_2$(dppm)$_2$$^{2+}$ dimers that are doubly bridged by dmb ligands. *d*(Ag···Ag) values between the tetrahedral Ag atoms are 4.028(1) and 9.609(1) Å for the dppm and dmb bridged

Figure 7. TGA trace for the polymer {[Ag(dpph)(dmb)]BF$_4$}$_n$ (**18**).

Chart 4

{M$_2$(dppm)$_2$(dmb)$_2$$^{2+}$}$_n$; M = Cu, Ag

Table 4. TGA Data for the Polymers **3**, **4**, **6**, **7**, **9**−**11**, **12a**, and **13**−**18**[a]

	wt loss 1 (loss of isocyanides)[b]			wt loss 2 (loss of diphos)[b]			residue (metal alone)	
	temp (°C)	expt (%)	theor (%)	temp (°C)	expt (%)	theor (%)	expt (%)	theor (%)
3	171−229	22	23	305−445	68	68	10	9
4	144−176	21	21	300−420	65	65	14	14
6	180−220	23	22	310−420	66	69	11	9
7	150−200	20	21	290−385	67	65	13	14
9	162−224	21	21	297−458	70	70	9	8
10	150−190	21	21	288−424	66	66	13	13
11	150−330	36	38	330−400	55	53	9	9
12a	170−220	22	25	280−400	63	61	15	14
13	178−340	36	36	340−442	54	56	10	8
14	176−231	23	23	300−415	64	63	13	14
15	195−340	34	35	350−420	58	57	8	8
16	190−210	26	23	270−410	61	64	13	13
17	180−249	36	35	333−455	56	57	8	8
18	173−226	24	23	300−395	64	64	12	13

[a] The uncertainty is estimated to be ∼2−3% because of a small drift in the baseline. No data were acquired for **1**, **2a**, **2b**, **5**, **7**, **8**, and **12b**. [b] For the {M(diphos)(CN-t-Bu)$_2$$^+$}$_n$ (M = Cu, Ag) and {Ag(diphos)(dmb)$^+$}$_n$ polymers (**3**, **4**, **6**, **7**, **9**, **10**, **12a**, **14**, **16**, and **18**), the weight loss events associated with the loss of BF$_4$$^−$ overlaps with the weight loss associated with the diphosphine ligands (weight loss 2). For the {Cu(diphos)(dmb)$_2$$^+$}$_n$ polymers (**11**, **13**, **15**, **17**), the weight loss event associated with the loss of BF$_4$$^−$ overlaps with the weight loss associated with the dmb ligands (weight loss 1). The data are presented as such.

units, respectively. The dmb ligand adopts the rarely encountered "Z-shape" (*gauche* conformation)[25] to avoid the inter-Ag$_2$(dppm)$_2$$^{2+}$ unit Ph⋯Ph steric interactions that would otherwise be obtained in the *anti* conformation. Ring stress is observed, as the ∠PAgP (136.5), ∠PAgC (103.5 (average)), and ∠CAgC (99.0°) angles deviate from the ideal tetrahedral angle, and the AgC bond lengths differ (2.25 and 2.33 Å; Table 3). The Ag$_2$C$_4$P$_2$ ring does not exhibit the typical S$_8$ crown structure, but rather the 4 P atoms describe a plane where one Ag and one C atom lie above and below the plane, describing a local C_i symmetry.
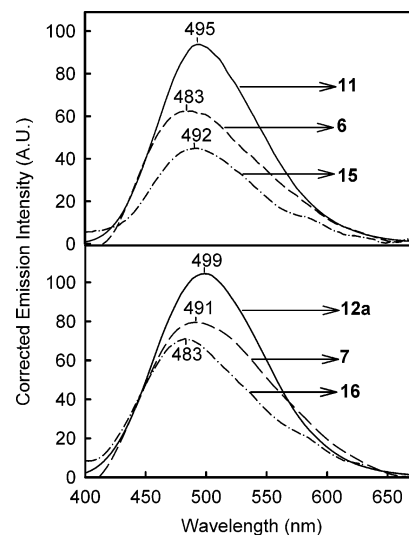
Physical Properties. The colorless polymers are soluble or weakly soluble in common organic solvents (such as acetonitrile, methanol, dichloromethane, and chloroform). The materials prove to be thermally stable to at least 150 °C (TGA) and photochemically stable to sun light (over several months as no change in color or spectroscopic profile was observed). The TGA traces exhibit two thermal events. They occur between 150 and 340 °C (see Figure 7, as an example, and Table 4), the lower of the two being the loss of the isocyanide and the higher being the loss of the diphosphine ligands. The loss of the counterion is spread over a greater temperature range and overlaps with the ligand losses (see foonote of Table 4). The loss of the isocyanide occurs in a narrower temperature window as observed by the first derivative of the TGA traces. In general, the loss of the t-BuNC group occurs at a slightly lower temperature than in the corresponding dmb polymer.

15 and **17** exhibit T_g (glass transition; DSC) at 47 (ΔC_p = 0.55) and 39 °C (ΔC_p = 0.45 J/(g·deg)), respectively. No T_g was observed from −20 to 150 °C for any of the other materials. The Ag-containing materials are generally more

Figure 8. Comparison of the solid-state emission spectra of **6**, **11**, **15**, **7**, **12a**, and **16** at room temperature. The intensity has not been normalized so that the bands could be distinguished.

soluble in common solvents (as listed above) and form brittle films when the solvent is evaporated. Conversely, the Cu polymers are somewhat less soluble but can form stand-alone films from spin-coating or simple solution evaporation. Polymers **15**−**17** swell in most solvents during attempts to dissolve them (which prevented us from obtaining reliable solution ^{1}H NMR spectra) or are simply insoluble. In DMF, {Cu(diphos)(dmb)BF$_4$}$_n$ polymers produce either highly viscous solutions or a polymer film on the solution surface (Supporting Information). The XRD patterns indicate that the Ag materials are more crystalline than those of Cu. This property is well-known for the {M(dmb)$_2$$^+$}$_n$ polymers,[4b,d] where for M = Ag and Cu shorter (n ∼ 8)[2c] and longer chains (n ∼ 300) are observed.[4e] In addition, the {[Ag(diphos)-

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Table 5. Solid-State Spectroscopic and Emission Lifetimes for **3**, **4**, **6**, **7**, **9−11**, **12a**, and **13−18**[a]

{[Cu(diphos)(CN-*t*-Bu)₂]BF₄}ₙ				{[Ag(diphos)(CN-*t*-Bu)₂]BF₄}ₙ			
polymer	morphology	λ_{max} (nm)	τ_e (μs)	polymer	morphology	λ_{max} (nm)	τ_e (μs)
3	SC	475	22 ± 5	4	C	481	14 ± 3
6	SC	483	31 ± 5	7	C	491	55 ± 4
9	SC	485	12 ± 3	10	C	486	56 ± 4
{[Cu(diphos)(dmb)]BF₄}ₙ				{[Ag(diphos)(dmb)]BF₄}ₙ			
11	A	495	42 ± 7	12a	C	499	27 ± 3
13	A	490	15 ± 5	14	C	487	26 ± 5
15	A	492	24 ± 5	16	C	483	48 ± 4
17	A	485	18 ± 3	18	C	487	6 ± 1

[a] C = crystalline, SC = semicrystalline, A = amorphous, at 293 K.

(dmb)]BF₄}ₙ (**10**, **14**, **16**, and **18**) polymers exhibit weak ν(NC) IR peaks at ∼2130 cm⁻¹ (in the solid state) consistent with uncoordinated RNC groups (i.e. end-of-chain), suggesting that these materials may be oligomers. This feature is consistent with the highly crystalline morphology.

Luminescence. The luminescence properties of **3**, **4**, **6**, **7**, **9−11**, **12a**, and **13−18** in the solid state were investigated at 293 K (Figure 8 and Table 5). The solids emit with λ_{max} in the 491 ± 8 nm window and with emission lifetimes of 6 < τ_e < 56 μs, which is indicative of phosphorescence. These λ_{max}'s and τ_e's are typical of Cu−P- and Ag−P-containing chromophores.[26] On the basis of recent spectroscopic findings and theorical DFT calculations on the related compounds M(CN-*t*-Bu)₄⁺ (M=Cu, Ag)[4b] and [Cu₂(dppm)₂(O₂-CMe)]⁺,[27] the excited-state responsible for the luminescence is assigned to a metal-to-ligand charge transfer (MLCT), where the ligand manifold is both the π-system of the CNR

and PPh₂ groups. The similarity in photophysical properties between the Cu- and Ag-containing materials is not surprising or, at least, is not unprecedented.[4b,28] The interpretation of this result is not simple since the structures of many of the investigated materials are not known.[29]

Supporting Information Available: XRD patterns for **3**, **4**, **6**, **7**, **9**, **10**, **12a**, **13**, **14**, and **16−18**, a picture showing vials of **15** and **17** in DMF, and X-ray crystallographic files for **1**, **2b**, **5**, **7**, **8**, and **12b** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC034806M

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(28) The presence of an exciton phenomenon is possible. Previous works[4b] showed that the λ_{max}'s of emission for the polymer salts {[Ag-(dmb)₂]Y}ₙ (Y = BF₄⁻, PF₆⁻, NO₃⁻, CH₃CO₂⁻) and {[Cu(dmb)₂]-BF₄}ₙ were counterion dependent, despite the fact that no interaction with the chromophore was apparent (but small structural perturbations were observed), and changed with experimental conditions (i.e. temperature and physical state). As a consequence the λ_{max}'s of emission become unpredictable.

(29) The photophysical properties for the polymers in solution are not investigated as strong RNC ligand dissociation occurs for the Ag materials.