Inorg. Chem. **2004**, *43*, 7493–7501

Inorganic Chemistry
Article

Syntheses, Characterization, and Luminescence of Pt^{II}–M^{I} (M = Cu, Ag, Au) Heterometallic Complexes by Incorporating Pt(diimine)(dithiolate) with $[M_2(dppm)_2]^{2+}$ (dppm = Bis(diphenylphosphino)methane)

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Received July 8, 2004

Reaction of Pt(diimine)(edt) (edt = 1,2-ethanedithiolate) with $M_2(dppm)_2(MeCN)_2^{2+}$ (dppm = bis(diphenylphosphino)methane) gave heterotrinuclear complexes $[PtCu_2(edt)(\mu\text{-}SH)(dppm)_3](ClO_4)$ (**11**) and $[PtCu_2(diimine)_2(edt)(dppm)_2](ClO_4)_2$ (diimine = 2,2′-bpyridine (bpy), **12**; 4,4′-dibutyl-2,2′-bipyridine (dbbpy), **13**; phenanthroline (phen), **14**; 5-bromophenanthroline (brphen), **15**) when M = Cu^{I}. The reaction, however, afforded tetra- and trinuclear complexes $[Pt_2Ag_2(edt)_2(dppm)_2](SbF_6)_2$ (**17**) and $[PtAu_2(edt)(dppm)_2](SbF_6)_2$ (**21**) when M = Ag^{I} and Au^{I}, respectively. The complexes were characterized by elemental analyses, electrospray mass spectroscopy, ^{1}H and ^{31}P NMR, IR, and UV–vis spectrometry, and X-ray crystallography for **14**, **17**, and **18**. The $Pt^{II}Cu^{I}_2$ heterotrinuclear complexes **11**–**15** exhibit photoluminescence in the solid states at 298 K and in the frozen acetonitrile glasses at 77 K. It is likely that the emission originates from a ligand-to-metal charge transfer (dithiolate-to-Pt) $^{3}[p(S) \rightarrow d(Pt)]$ transition for **11** and from an admixture of $^{3}[d(Cu)/p(S)\text{–}\pi^{*}(diimine)]$ transitions for **12**–**16**. The $Pt^{II}_2Ag^{I}_2$ heterotetranuclear complexes **17** and **18** are nonemissive in the solid states and in solutions at 298 K but show photoluminescence at 77 K. The $Pt^{II}Au^{I}_2$ heterotrinuclear complexes **19**–**21**, however, are luminescent at room temperature in the solid state and in solution. Compounds **19** and **20** afford negative solvatochromism associated with a charge transfer from an orbital of a mixed metal/dithiolate character to a diimine π^{*} orbital.

Introduction

The chemistry of platinum(II) diimine complexes has attracted much attention over the years owing to their intriguing photophysical properties with manifold emissive origins such as metal cluster-centered (MC), metal-to-ligand charge-transfer (MLCT), metal−metal-to-ligand charge-transfer (MMLCT), ligand-to-ligand charge-transfer (LLCT) transitions, etc.[1−14] The platinum(II) diimine dithiolate complexes are of particular interest because of their long-lived photoluminescence and readily tunable emission energy by introducing electron-donating or -withdrawing substituents to the diimine or dithiolate ligands.[15−25] Furthermore, the S donors of dithiolate exhibit potentially bridging character,[26] making Pt(diimine)(dithiolate) a useful precursor for design-

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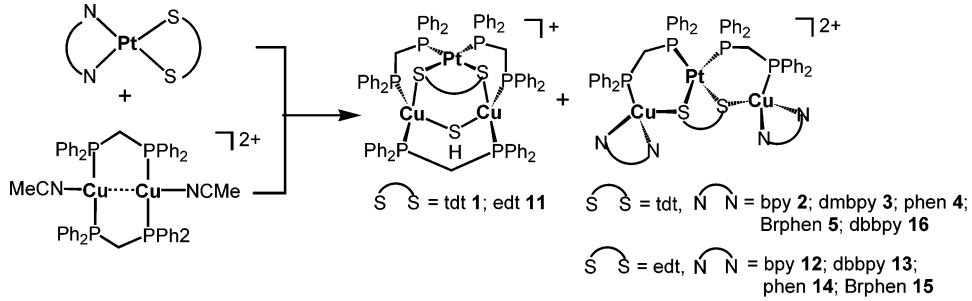
10.1021/ic049104r CCC: $27.50

Scheme 1. Reaction Route of Pt(diimine)(dithiolate) with $[Cu_2(dppm)_2(MeCN)_2]^{2+}$



ing multicomponent or heterometallic complexes that emit more efficient and longer-lived photoluminescence with wider ranges of emissions or colors.

To design luminescent $Pt^{II}-M^{I}$ (M = Cu, Ag, Au) heteronuclear complexes by utilizing Pt(diimine)(dithiolate) as a building block, one of the feasible synthetic strategies is to incorporate $M_2(dppm)_2(MeCN)_2^{2+}$ (dppm = bis(diphenylphosphino)methane).[26] As shown in Schemes 1 and 2, reactions of Pt(diimine)(tdt) (tdt = 3,4-toluenedithiolate) with $Ag_2(dppm)_2(MeCN)_2^{2+}$ not only gave the aimed heterotrinuclear complexes $[PtAg_2(diimine)(tdt)(dppm)_2](SbF_6)_2$[26] but also afforded an unexpected product $[PtAg_2(tdt)(\mu\text{-}SH)(dppm)_3](SbF_6)$ (**6**). Reactions of Pt(diimine)(tdt) with $Cu_2(dppm)_2(MeCN)_2^{2+}$, however, only gave the unexpected $Pt^{II}Cu^{I}_2$ heterotrinuclear compounds $[PtCu_2(tdt)(\mu\text{-}SH)(dppm)_3](ClO_4)$ (**1**) and $[PtCu_2(diimine)_2(tdt)(dppm)_2](ClO_4)_2$. The reaction products with different composition and structural topologies were readily separated by column chromatography. With modification of the electronic effects of the substituents in the diimines, the emission energy of the compounds $[PtAg_2(diimine)(tdt)(dppm)_2](SbF_6)_2$ and $[PtCu_2(diimine)_2(tdt)(dppm)_2](ClO_4)_2$ was finely tunable, and the emissive origins were assigned tentatively.[26] To extend and promote this work, further investigation on the reactions between Pt(diimine)(dithiolate) and $M_2(dppm)_2(MeCN)_2^{2+}$ is necessary by fixing the diimines while altering the substituents in the dithiolate ligands. In this way, the reactivity of Pt(diimine)(edt) (edt = 1,2-ethanedithiolate) was investigated for the purpose of comparison with that of its counterpart Pt(diimine)(tdt). We describe herein the preparation, characterization, and photophysical properties of a series of $Pt^{II}-M^{I}$ (M = Cu, Ag, Au) heterometallic complexes isolated by reactions of Pt(diimine)(edt) (edt = 1,2-ethanedithiolate) with $M_2(dppm)_2(MeCN)_2^{2+}$ (M = Cu, Ag, Au).

Experimental Section

Material and Reagents. All manipulations were performed under dry argon atmosphere using Schlenk techniques and a

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vacuum-line system. Solvents were dried by standard methods and distilled prior to use. The reagents potassium tetrachloroplatinum ($K_2[PtCl_4]$), 1,2-ethanedithiol (H_2edt), 1,3-propanedithiol (H_2pdt), 3,4-toluenedithiol (H_2tdt), bis(diphenylphospino)methane (dppm), silver hexafluoroantimonate ($AgSbF_6$), $HAuCl_4$, 2,2′-bipyridine (bpy), 4,4-dibutyl-2,2′-bipyridine (dbbpy), 4,4-dimethyl-2,2′-bipyridine (dmbpy), and 1,10-phenanthroline (phen) were available commercially. 5-Bromophenanthroline (brphen) was prepared by the literature methods.[7d] The compounds Pt(bpy)Cl_2, Pt(dmbpy)Cl_2, Pt(dbbpy)Cl_2, Pt(phen)Cl_2, and Pt(brphen)Cl_2 were synthesized by the described procedures.[27] The compounds $[Cu_2(dppm)_2(MeCN)_2](ClO_4)_2$,[28] $[Ag_2(dppm)_2(MeCN)_2](SbF_6)_2$,[29] $[Au_2(dppm)_2](SbF_6)_2$,[30] and Pt(diimine)(dithiolate) (diimine = bpy, dbbpy, dmbpy, phen, and brphen; dithiolate = edt, pdt, and tdt)[15] were prepared by similar procedures as described in the literature.

CAUTION! Perchlolate salts are potentially explosive and should be handled with care and in small amounts.

$[PtCu_2(edt)(\mu\text{-}SH)(dppm)_3](ClO_4)$ (11) and $[PtCu_2(bpy)_2(edt)(dppm)_2](ClO_4)_2$ (12). To a dichloromethane (20 mL) solution of Pt(bpy)(edt) (44.3 mg, 0.10 mmol), $[Cu_2(dppm)_2(MeCN)_2](ClO_4)_2$ (117.7 mg, 0.10 mmol) was added to give a yellow solution. After being stirred at room temperature for 1 day, the solution was filtered to remove a little of the precipitate. The filtrate was concentrated in vacuo and then chromatographed on a silica gel column. Complex **11** was eluted with dichloromethane/acetone (v/v 15:1) as the second band to give 17 mg of the product. Yield: 10%. Complex **12** was eluted with dichloromethane/acetone (v/v 6:1) as the third band to give 65 mg of the product. Yield: 36%.

11. Anal. Calcd for $C_{77}H_{71}ClCu_2O_4P_6S_3Pt\cdot CH_2Cl_2$: C, 52.49; H, 4.12; S, 5.39. Found: C, 52.71; H, 4.03; S, 5.20. ES-MS (*m/z*): 1601 ($[M - ClO_4]^+$), 1219 ($[PtCu_2(edt)(\mu\text{-}SH)(dppm)_2]^+$), 1119 ($[PtCu(edt)(dppm)_2]^+$), 834 ($[PtCu_2(edt)(\mu\text{-}SH)(dppm)]^+$). IR spectrum (KBr, cm^{-1}): ν 1095 (s, ClO_4). ^1H NMR spectrum (CD_3CN, ppm): δ 7.87−6.65 (m, 60H, C_6H_5), 3.47 (s, 2H, PCH_2P), 3.22 (s, 4H, PCH_2P), 2.60 (s, 4H, SCH_2CH_2S), 0.90 (s, 1H, S*H*). ^{31}P NMR spectrum (CD_3CN, ppm): δ 3.3 (s, $CuPCH_2PPt$, J_{Pt-P} = 1476 Hz), −11.9 (s, $CuPCH_2PPt$), −14.4 (s, $CuPCH_2PCu$).

12. Anal. Calcd for $C_{72}H_{64}Cl_2Cu_2N_4O_8P_4PtS_2\cdot CH_2Cl_2$: C, 49.28; H, 3.74; N, 3.15; S, 3.60. Found: C, 49.75; H, 3.47; N, 2.83; S, 3.95. ES-MS (*m/z*): 1595 ($[M - (ClO_4)]^+$), 1439 ($[PtCu_2(bpy)(edt)(dppm)_2(ClO_4)]^+$), 1217 ($[PtCu(edt)(dppm)_2(ClO_4)]^+$), 747 ($[M - (ClO_4)_2]^{2+}$), 591 ($[PtCu_2(edt)(dppm)_2]^{2+}$). IR spectrum (KBr, cm^{-1}): ν 1093 (s, ClO_4). ^1H NMR spectrum (CD_3CN, ppm): δ 8.32−7.09 (m, 56H, Ph and bpy), 3.56 (s, 4H, PCH_2P), 2.30 (s, 4H, SCH_2CH_2S). ^{31}P NMR spectrum (CD_3CN, ppm): δ 10.0 (d, $CuPCH_2PPt$, J_{Pt-P} = 1487 Hz, $^2J_{P-P}$ = 81 Hz), −17.3 (s, $CuPCH_2PPt$).

$[PtCu_2(dbbpy)_2(edt)(dppm)_2](ClO_4)_2$ (13). This compound was prepared by the same procedure as **12** except for the use of Pt(dbbpy)(edt) instead of Pt(bpy)(edt) to give 73 mg of the product. Yield: 37%. Anal. Calcd for $C_{88}H_{96}Cl_2Cu_2N_4O_8P_4PtS_2\cdot{}^1/_2CH_2Cl_2$: C, 54.20; H, 4.98; N, 2.86; S, 3.27. Found: C, 54.31; H, 5.03; N, 2.71; S, 3.19. ES-MS (*m/z*): 1551 ($[PtCu_2(dbbpy)(edt)(dppm)_2(ClO_4)]^+$), 1219 ($[PtCu(edt)(dppm)_2(ClO_4)]^+$), 1119 ($[PtCu(edt)(dppm)_2]^+$), 860 ($[M - (ClO_4)_2]^{2+}$), 727 ($[PtCu_2(dbbpy)(edt)(dppm)_2]^{2+}$), 591 ($[PtCu_2(edt)(dppm)_2]^{2+}$). IR spectrum (KBr, cm^{-1}): ν 1092 (s, ClO_4). ^1H NMR spectrum (CD_3CN, ppm): δ 8.02−7.07 (m, 52H, Ph and bpy), 3.56 (s, 4H, PCH_2P), 2.35 (s, 4H, SCH_2CH_2S), 1.40−0.89 (m, 36H, Bu^t). ^{31}P NMR spectrum (CD_3CN, ppm): δ 8.6 (d, $CuPCH_2PPt$, J_{Pt-P} = 1477 Hz, $^2J_{P-P}$ = 61 Hz), −17.7 (s, $CuPCH_2PPt$).

$[PtCu_2(phen)_2(edt)(dppm)_2](ClO_4)_2$ (14). This compound was prepared by the same procedure as **12** except that Pt(phen)(edt) was used instead of Pt(bpy)(edt) to afford 60 mg of the product. Yield: 34%. Anal. Calcd for $C_{76}H_{64}Cl_2Cu_2N_4O_8P_4PtS_2\cdot{}^1/_2CH_2Cl_2$: C, 51.48; H, 3.67; N, 3.14; S, 3.59. Found: C, 51.56; H, 3.58; N, 3.08; S, 3.69. ES-MS (*m/z*): 1642 ($[M - (ClO_4)]^+$), 1462 ($[PtCu_2(phen)(edt)(dppm)_2(ClO_4)]^+$), 1119 ($[PtCu(edt)(dppm)_2]^+$), 914 ($[PtCu(phen)(dppm)(edt)]^+$), 772 ($[M - (ClO_4)_2]^{2+}$). IR spectrum (KBr, cm^{-1}): ν 1093 (s, ClO_4). ^1H NMR spectrum (CD_3CN, ppm): δ 8.57−7.16 (m, 56H, Ph and phen), 3.64 (s, 4H, PCH_2P), 2.70 (s, 4H, SCH_2CH_2S). ^{31}P NMR spectrum (CD_3CN, ppm): δ 9.5 (d, $CuPCH_2PPt$, J_{Pt-P} = 1487 Hz, $^2J_{P-P}$ = 61 Hz), −17.5 (s, $CuPCH_2PPt$).

$[PtCu_2(brphen)_2(edt)(dppm)_2](ClO_4)_2$ (15). The same synthetic procedure as **12** was applied except that Pt(brphen)(edt) was used instead of Pt(bpy)(edt) to afford 60 mg of the product. Yield: 31%. Anal. Calcd for $C_{76}H_{62}Br_2Cl_2Cu_2N_4O_8P_4PtS_2\cdot{}^1/_2CH_2Cl_2$: C, 47.30; H, 3.27; N, 2.88; S, 3.30. Found: C, 47.67; H, 3.03; N, 2.76; S, 3.64. ES-MS (*m/z*): 1642 ($[M - (ClO_4)]^+$), 1540 ($[PtCu_2(brphen)(edt)(dppm)_2(ClO_4)]^+$), 1219 ($[PtCu(edt)(dppm)_2(ClO_4)]^+$), 1119 ($[PtCu(edt)(dppm)_2]^+$), 995 ($[PtCu(brphen)(dppm)(edt)]^+$), 851 ($[M - (ClO_4)_2]^{2+}$), 736 ($[Cu_2(brphen)_2(edt)]^+$). IR spectrum (KBr, cm^{-1}): ν 1094 (s, ClO_4). ^1H NMR spectrum (CD_3CN, ppm): δ 8.83−7.16 (m, 54H, Ph and phen), 3.64 (s, 4H, PCH_2P), 2.48 (s, 4H, SCH_2CH_2S). ^{31}P NMR spectrum (CD_3CN, ppm): δ 8.0 (d, $CuPCH_2PPt$, J_{Pt-P} = 1477 Hz, $^2J_{P-P}$ = 61 Hz), −17.0 (s, $CuPCH_2PPt$).

$[PtCu_2(dbbpy)_2(tdt)(dppm)_2](ClO_4)_2$ (16). The synthetic procedure is the same as **12** except that Pt(dbbpy)(tdt) was used instead of Pt(bpy)(edt) to give 63 mg of the product. Yield: 30%. Anal. Calcd for $C_{93}H_{98}Cl_2Cu_2N_4O_8P_4PtS_2\cdot CH_2Cl_2$: C, 54.65; H, 4.88; N, 2.71; S, 3.10. Found: C, 54.87; H, 5.10; N, 2.58; S, 2.97. ES-MS (*m/z*): 1880 ($[PtCu_2(dbbpy)_2(tdt)(dppm)_2(ClO_4)]^+$), 1612 ($[PtCu_2(dbbpy)(tdt)(dppm)_2(ClO_4)]^+$), 1181 ($[PtCu(tdt)(dppm)_2]^+$), 1065 ($[PtCu(tdt)(dppm)_2]^+$), 891 ($[M - (ClO_4)_2]^{2+}$), 622 ($[PtCu(dbbpy)(tdt)(dppm)]^+$). IR spectrum (KBr, cm^{-1}): ν 1095 (s, ClO_4). ^1H NMR spectrum (CD_3CN, ppm): δ 8.08−7.24 (m, 55H, Ph and bpy), 3.81 (s, 4H, PCH_2P), 1.59 (s, 3H, CH_3), 1.35 (m, 36H, Bu^t). ^{31}P NMR spectrum (CD_3CN, ppm): δ 7.7 (s, $CuPCH_2PPt$, J_{Pt-P} = 1456 Hz), −16.8 (s, $CuPCH_2PPt$).

$[Pt_2Ag_2(edt)_2(dppm)_2](SbF_6)_2$ (17). To a dichloromethane (20 mL) solution of Pt(bpy)(edt) (44.3 mg, 0.10 mmol), $[Ag_2(dppm)_2(MeCN)_2](SbF_6)_2$ (153.8 mg, 0.10 mmol) was added to give a bright yellow solution. After being stirred at room temperature for 1 day, the solution turned almost colorless. The solvent was then removed in vacuo, and the residue was redissolved in 3 mL of acetonitrile. Layered diethyl ether onto the acetonitrile solution affords colorless

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Table 1. Crystallographic Data of **14**·$^1/_2$Et$_2$O·$^1/_2$CH$_3$OH, **17**·Et$_2$O·$^1/_2$H$_2$O, and **18**·Et$_2$O·$^1/_2$H$_2$O

	14·$^1/_2$Et$_2$O·$^1/_2$CH$_3$OH	**17**·Et$_2$O·$^1/_2$H$_2$O	**18**·Et$_2$O·$^1/_2$H$_2$O
empirical formula	$C_{78.5}H_{72}Cl_2Cu_2N_4O_9P_4PtS_2$	$C_{58}H_{63}Ag_2F_{12}O_{1.5}P_4Pt_2S_4Sb_2$	$C_{60}H_{67}Ag_2F_{12}O_{1.5}P_4Pt_2S_4Sb_2$
fw	1795.54	2113.65	2141.70
space group	*C*2/*c*	*P*2$_1$/*n*	*P*2$_1$/*n*
a, Å	19.0913(4)	12.7116(5)	12.6868(8)
b, Å	16.3501(4)	18.9579(7)	19.1881(12)
c, Å	27.994	16.2170(7)	16.2437(10)
β, deg	91.4210(10)	94.2270(10)	91.151(2)
V, Å^3	8735.5(2)	3897.4(3)	3953.5(4)
Z	8	4	4
ρ_{calcd}, g/cm^3	1.433	1.872	1.869
μ, mm^{-1}	2.319	5.009	4.939
radiation (λ, Å)	0.71073	0.71073	0.71073
temp, K	293(2)	293(2)	293(2)
R1(F_o)^a	0.0887	0.0721	0.0803
wR2(F_o^2)^b	0.2129	0.1585	0.1288
GOF	1.194	1.207	1.172

^{a} $R1 = \sum|F_o - F_c|/\sum F_o$. ^{b} $wR2 = \sum[w(F_o^2 - F_c^2)_2]/\sum[w(F_o^2)]^{1/2}$.

crystals in a few days. Yield: 45% (90 mg). Anal. Calcd for $C_{54}H_{52}Sb_2F_{12}P_4S_4Ag_2Pt_2$: C, 31.94; H, 2.58. Found: C, 32.04; H, 2.28. ES-MS (*m*/*z*): 1794 ([M − (SbF$_6$)]$^+$), 779 ([M − (SbF$_6$)$_2$]$^{2+}$), 635 ([Ag$_2$(edt)$_2$(SbF$_6$)]$^+$). IR spectrum (KBr,cm^{-1}): ν 659 (s, SbF$_6$). ^{1}H NMR spectrum (CD$_3$CN, ppm): δ 7.70−7.63 (m, 40H, C$_6$H$_5$), 3.38 (s, 4H, PC*H*$_2$P), 2.50 (m, 8H, SC*H*$_2$CH$_2$S). ^{31}P NMR spectrum (CD$_3$CN, ppm): δ −44.6 (s, J_{Pt-P} = 1179 Hz).

[Pt$_2$Ag$_2$(pdt)$_2$(dppm)$_2$](SbF$_6$)$_2$ (18). The same procedure as **17** was applied except that Pt(bpy)(pdt) was employed instead of Pt(bpy)(edt) to afford 85 mg of the product. Yield: 42%. Anal. Calcd for $C_{56}H_{56}Sb_2F_{12}P_4S_4Ag_2Pt_2$: C, 32.67; H, 2.74; S, 6.23. Found: C, 32.50; H, 2.30; S, 5.94. ES-MS (*m*/*z*): 793 ([M − (SbF$_6$)$_2$]$^{2+}$) IR spectrum (KBr,cm^{-1}): ν 659 (s, SbF$_6$). ^{1}H NMR spectrum (CD$_3$CN, ppm): δ 7.98−7.47 (m, 40H, C$_6$H$_5$), 2.77 (m, 8H, SC*H*$_2$CH$_2$CH$_2$S), 2.58 (s, 4H, PC*H*$_2$P), 1.85 (m, 4H, SCH$_2$C*H*$_2$CH$_2$S). ^{31}P NMR spectrum (CD$_3$CN, ppm): δ −52.3 (s, J_{Pt-P} = 1194 Hz).

[PtAu$_2$(bpy)(tdt)(dppm)$_2$](PF$_6$)$_2$ (19). A mixture of Pt(bpy)(tdt) (50.5 mg, 0.10 mmol) and [Au$_2$(dppm)$_2$](PF$_6$)$_2$ (145.3 mg, 0.10 mmol) in dichloromethane (20 mL) was stirred for 1 day to yield a purple red suspension. The solvent was then removed in vacuo, and the residue was dissolved in 4 mL of acetonitrile. After filtration, the filtrate was layered with diethyl ether to give red crystals. Yield: 54% (105 mg). Anal. Calcd for $C_{67}H_{58}N_2F_{12}P_6S_2Au_2Pt$: C, 41.10; H, 2.99; N, 1.43; S, 3.27. Found: C, 41.19; H, 2.90; N, 1.67; S, 3.36. ES-MS (*m*/*z*): 1813 ([M − (PF$_6$)]$^+$), 1307 ([Au$_2$(dppm)$_2$(PF$_6$)]$^+$), 1087 ([PtAu(bpy)(tdt)(dppm)]$^+$), 835 ([M − (PF$_6$)$_2$]$^{2+}$), 582 ([Au$_2$(dppm)$_2$]$^{2+}$). IR spectrum (KBr, cm^{-1}): ν 840 (s, PF$_6$). ^{1}H NMR spectrum (CD$_3$CN, ppm): δ 7.74−7.44 (m, 51H, Ph and bpy), 4.44 (s, 4H, PC*H*$_2$P), 1.95 (s, 3H, C*H*$_3$). ^{31}P NMR spectrum (CD$_3$CN, ppm): δ 36.8 (s).

[PtAu$_2$(dmbpy)(tdt)(dppm)$_2$](SbF$_6$)$_2$ (20). The compound was prepared by a similar procedure to **19** utilizing Pt(dmbpy)(tdt) and [Au$_2$(dppm)$_2$](SbF$_6$)$_2$ to give 125 mg of reddish orange crystals. Yield: 58%. Anal. Calcd for $C_{69}H_{62}N_2F_{12}P_4S_2Sb_2Au_2Pt$: C, 38.23; H, 2.88; N, 1.29; S, 2.96. Found: C, 38.10; H, 2.62; N, 1.41; S, 3.08. ES-MS (*m*/*z*): 1932 ([M − (SbF$_6$)]$^+$), 1397 ([Au$_2$(dppm)$_2$(SbF$_6$)]$^+$), 1116 ([PtAu(dmbpy)(tdt)(dppm)]$^+$), 1163 ([PtAu$_2$(dmbpy)(tdt)(SbF$_6$)]$^+$), 849 ([M-(SbF$_6$)$_2$]$^{2+}$), 582 ([Au$_2$(dppm)$_2$]$^{2+}$). IR spectrum (KBr, cm^{-1}): ν 660 (s, SbF$_6$). ^{1}H NMR spectrum (CD$_3$CN, ppm): δ 7.75−7.44 (m, 49H, Ph and bpy), 4.43 (s, 4H, PC*H*$_2$P), 1.95 (s, 3H, C*H*$_3$), 1.29 (s, 6H, C*H*$_3$). ^{31}P NMR spectrum (CD$_3$CN, ppm): δ 35.9 (s).

[PtAu$_2$(edt)(dppm)$_2$](SbF$_6$)$_2$ (21). A mixture of Pt(bpy)(edt) (44.3 mg, 0.10 mmol) and [Au$_2$(dppm)$_2$](SbF$_6$)$_2$ (163.4 mg, 0.10 mmol) in dichloromethane (20 mL) was stirred for 1 day to yield a pale yellow solution. The solvent was then removed in vacuo, and the residue was dissolved in 4 mL of acetonitrile. The product was crystallized as colorless crystals by diffusion of diethyl ether into the acetonitrile solution. Yield: 65% (125 mg). Anal. Calcd for $C_{52}H_{48}F_{12}P_4S_2Sb_2Au_2Pt$: C, 32.51; H, 2.52; S, 3.34. Found: C, 32.62; H, 2.57; S, 3.49. ES-MS (*m*/*z*): 1685 ([M − (SbF$_6$)]$^+$), 727 ([M − (SbF$_6$)$_2$]$^{2+}$). IR spectrum (KBr, cm^{-1}): ν 660 (s, SbF$_6$). ^{1}H NMR spectrum (CD$_3$CN, ppm): δ 7.84−7.07 (m, 40H, C$_6$H$_5$), 3.72 (s, 2H, PC*H*$_2$P), 3.63 (s, 2H, PC*H*$_2$P). 3.51 (s, 4H, SC*H*$_2$CH$_2$S). ^{31}P NMR spectrum (CD$_3$CN, ppm): δ 33.2 (s, PtPCH$_2$*P*Au), −49.4 (s, J_{Pt-P} = 1264 Hz, Pt*P*CH$_2$PAu).

Crystal Structural Determination. Crystals coated with epoxy resin or sealed in capillaries with mother liquors were measured on a Siemens SMART CCD diffractometer by an ω scan technique at room temperature using graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation. An absorption correction by SADABS was applied to the intensity data. The structures were solved by direct method, and the heavy atoms were located from E-map. The remaining non-hydrogen atoms were determined from the successive difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically except those mentioned otherwise. The hydrogen atoms were generated geometrically and refined with isotropic thermal parameters. The structures were refined on F^2 by full-matrix least-squares methods using the SHELXTL-97 program package.[31] The crystallographic data of **14**, **17**, and **18** are summarized in Table 1.

Physical Measurements. Elemental analyses (C, H, N, and S) were performed on a Perkin-Elmer model 240C automatic instrument. Electrospray mass spectra (ES-MS) were recorded on a Finnigan LCQ mass spectrometer using dichloromethane/methanol or acetonitrile/methanol as mobile phase. UV−vis absorption spectra in acetonitrile solutions were measured on a Perkin-Elmer Lambda 25 UV−vis spectrometer. Infrared spectra were recorded on a Magna750 FT-IR spectrophotometer with a KBr pellet. ^{1}H and ^{31}P NMR spectra were measured on a Varian UNITY-500 spectrometer with SiMe$_4$ as the internal reference and 85% H$_3$PO$_4$ as external standard, respectively. Emission and excitation spectra were recorded on a Perkin-Elmer LS 55 luminescence spectrometer with a red-sensitive photomultiplier type R928. Emission lifetimes were determined on an Edinburgh Analytical Instrument (F900 fluorescence spectrometer) using an LED laser at 397 nm excitation, and the resulting emission was detected by a thermoelectrically cooled Hamamatsu R3809 photomultiplier tube. The instrument

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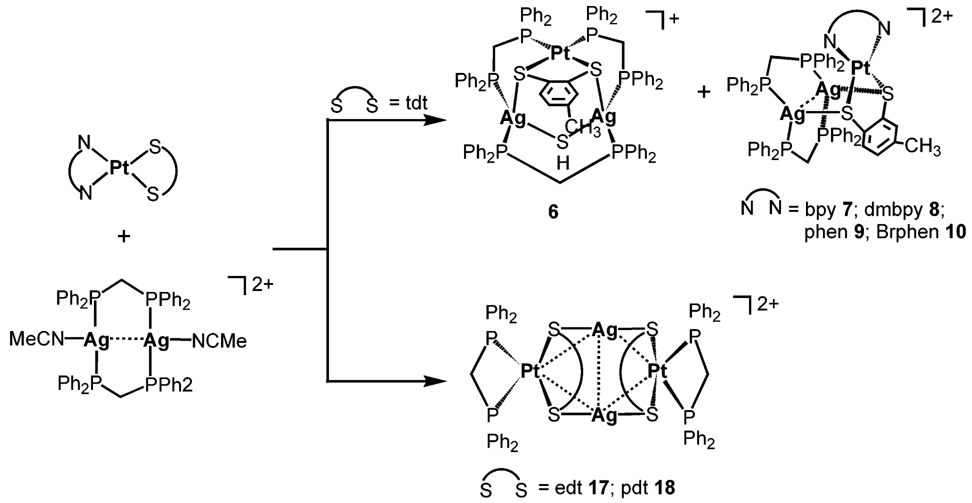
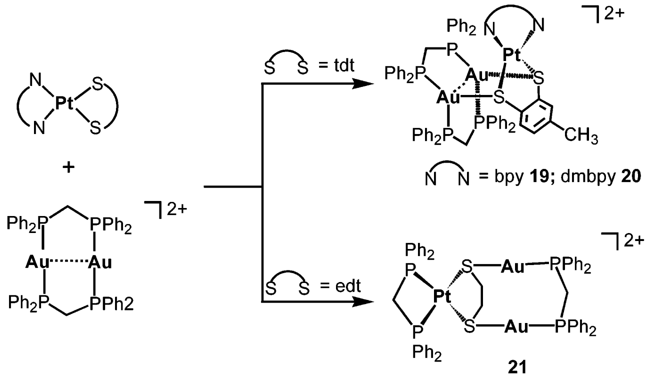
Scheme 2. Reaction Route of Pt(diimine)(dithiolate) with $[Ag_2(dppm)_2(MeCN)_2]^{2+}$



Scheme 3. Reaction Route of Pt(diimine)(dithiolate) with $[Au_2(dppm)_2]^{2+}$



response function at the excitation wavelength was deconvoluted from the luminescence decay, and the decay was fitted to exponential functions using a least-squares method.

Results and Discussion

Syntheses and Characterization. The synthetic routes are summarized in Schemes 1−3 for Pt−Cu, Pt−Ag, and Pt−Au complexes, respectively. As shown in Scheme 1, heterotrinuclear complexes $[PtCu_2(edt)(\mu\text{-}SH)(dppm)_3](ClO_4)$ (**11**) and $[PtCu_2(diimine)_2(edt)(dppm)_2](ClO_4)_2$ (diimine = bpy, **12**; dbbpy, **13**; phen, **14**; brphen, **15**) were isolated by reactions of Pt(diimine)(edt) with $[Cu_2(dppm)_2(MeCN)_2]^{2+}$ in equimolar ratios. The two types of heterotrinuclear complexes were separated readily by column chromatography. Scheme 2 depicts the reaction route between Pt(diimine)(dithiolate) and binuclear Ag^{I} component $[Ag_2(dppm)_2(MeCN)_2]^{2+}$. Although $Pt^{II}_2Ag^{I}$ heterotrinuclear complexes $[PtAg_2(tdt)(\mu\text{-}SH)(dppm)_3](ClO_4)$ (**6**) and $[PtAg_2(diimine)(tdt)(dppm)_2](ClO_4)_2$ were afforded when dithiolate = tdt, only a colorless $Pt^{II}_2Ag^{I}_2$ heterotetranuclear compound $[Pt_2Ag_2(dithiolate)_2(dppm)_2](SbF_6)_2$ (dithiolate = edt, **17**; pdt, **18**) was isolated when dithiolate = edt or pdt. In Scheme 3, incorporating Pt(diimine)(dithiolate) with the binuclear Au^{I} component $[Au_2(dppm)_2]^{2+}$ gave the desired products $[PtAu_2(diimine)(tdt)(dppm)_2](SbF_6)_2$ (diimine = bpy, **19**; dmbpy, **20**) when dithiolate = tdt, but an unexpected compound $[PtAu_2(edt)(dppm)_2](SbF_6)_2$ (**21**) was only isolated when dithiolate = edt. Noteworthily, reaction of Pt(diimine)(dithiolate) with $[M_2(dppm)_2(MeCN)_2]^{2+}$ gave both the desired and unexpected $Pt^{II}M^{I}_2$ heterotrinuclear compounds when dithiolate = tdt but only afforded the unexpected $Pt^{II}-M^{I}$ tri- or tetranuclear compounds when dithiolate = edt or pdt. This difference is likely due to the higher stability of the Pt(diimine)(tdt) compared with that of Pt(diimine)(edt)/Pt(diimine)(pdt). As mentioned in the previous study,[26] formation of the unexpected instead of the desired $Pt^{II}-M^{I}$ (M = Cu, Ag, Au) compounds may be attributed to factors such as a better affinity of the Pt^{II} ion for P than for N donors, steric requirements, and thermodynamic stability.

The complexes were characterized by elemental analyses (C, H, N, and S), ES-MS, and ^{1}H and ^{31}P NMR spectrometry. The structures of compounds **14**, **17**, and **18** were also determined by X-ray crystallography. In the ES-MS spectrum of compound **11** (Supporting Information, Figure S1), the principle positive fragments $[M - ClO_4]^{+}$, $[PtCu_2(edt)(\mu\text{-}SH)(dppm)_2]^{+}$, $[PtCu(edt)(dppm)_2]^{+}$, and $[PtCu_2(edt)(\mu\text{-}SH)(dppm)]^{+}$ were observed. For compounds **12**−**21**, the ES-MS spectra (Supporting Information, Figure S2−S5) show the molecular monocation $[M - (ClO_4/SbF_6/PF_6)]^{+}$ and dication $[M - (ClO_4/SbF_6/PF_6)_2]^{2+}$ as the principal peaks.

The ^{31}P NMR signals (Supporting Information, Figure S6−S10) of the $Pt^{II}-M^{I}$ tri- and tetranuclear complexes are characteristic of their structures. Typical satellite peaks due to remarkable Pt−P coupling with $J_{Pt-P} = 1180-1490$ Hz were observed in **11**−**18** and **21**. Compound **11** shows the Pt^{II} satellite signals centered at 3.3 ppm with $J_{Pt-P} = 1476$ Hz and two singlets at −11.9 and −14.4 ppm, respectively, because of two types of P donors bonded to the Cu^{I} centers. For $Pt^{II}Cu^{I}_2$ compounds **12**−**16**, although the P donors bound to Pt^{II} centers show a set of satellite signals centered at ca. 7.7−10.0 ppm with J_{Pt-P} in the range 1456−1487 Hz, those bound to Cu^{I} centers display one singlet at ca. −17.0 ppm. The $Pt^{II}_2Ag^{I}_2$ complexes **17** and **18**, however, show the P satellite signals centered at −44.6 and −52.3 ppm with J_{Pt-P} = 1179 and 1194 Hz, respectively, coinciding to a chelating coordination of the P donors to Pt^{II} center. Only one singlet

Table 2. Selected Bond Distances (Å) and Angles (deg) of Compounds **14**, **17**, and **18**

14		**17**		**18**	
		Bond Distances			
Pt−P1	2.295(3)	Pt−P2	2.264(4)	Pt−P1	2.263(4)
Pt−S	2.322(3)	Pt−P1	2.267(3)	Pt−P2	2.263(4)
Cu−N2	2.055(12)	Pt−S1	2.341(4)	Pt−S2	2.335(4)
Cu−N1	2.078(12)	Pt−S2	2.342(4)	Pt−S1	2.340(4)
Cu−P3	2.196(4)	Pt−AgA	3.0624(13)	Pt−Ag	3.1276(14)
Cu−S	2.324(4)	Pt−Ag	3.1418(13)	Pt−AgA	3.1504(14)
		Ag−S2	2.416(4)	Ag−S1A	2.390(4)
		Ag−S1A	2.424(4)	Ag−S2	2.397(5)
		Ag−AgA	3.271(2)	Ag−AgA	3.273(3)
		Bond Angles			
P1−Pt−P1A	96.67(18)	P2−Pt−P1	73.21(13)	P1−Pt−P2	73.27(15)
P1−Pt−S0A	175.00(12)	P2−Pt−S1	98.44(15)	P1−Pt−S2	93.38(16)
P1−Pt−S	88.29(12)	P1−Pt−S1	171.64(15)	P2−Pt−S2	166.57(16)
P1A-Pt−S	175.00(12)	P2−Pt−S2	172.51(15)	P1−Pt−S1	167.42(16))
S0A-Pt−S	86.75(16)	P1−Pt−S2	99.30(15)	P2−Pt−S1	94.29(16)
N2−Cu−N1	82.1(5)	S1−Pt−S2	89.05(16)	S2−Pt−S1	99.10(16)
N2−Cu−P3	130.8(4)	S2−Ag−S1A	174.21(15)	S1A-Ag−S2	173.17(17)
N1−Cu−P3	122.8(4)	C2−S1−Pt	102.1(7)	C2−S1−Pt	112.6(7)
N2−Cu−S	102.6(3)	C2−S1−AgA	108.6(8)	C2−S1−AgA	108.4(7)
S3−Cu1−P2	107.4(4)	Pt−S1−AgA	79.95(12)	Pt−S1−AgA	83.52(14)
P3−Cu−S	107.50(13)	C3−S2−Pt	102.1(8)	C4−S2−Pt	113.9(7)
Pt−S−Cu	103.2(5)	C3−S2−Ag	101.9(9)	C4−S2−Ag	107.4(7)
C2−S−Cu	107.2(5)	Pt−S2−Ag	82.64(13)	Pt−S2−Ag	82.72(14)
C2−S−Pt	112.97(15)				

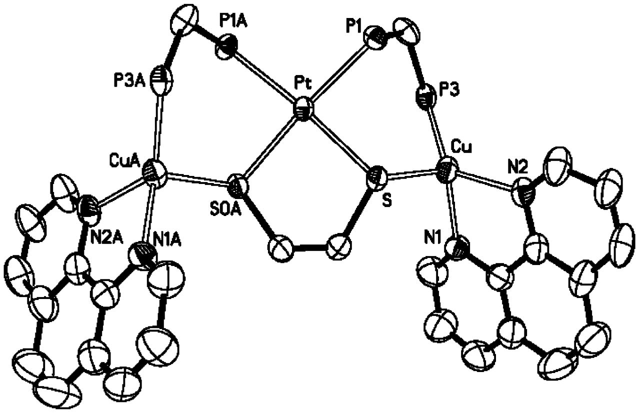
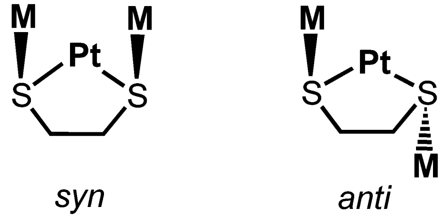


Figure 1. ORTEP drawing of the complex cation of **14** with atom labeling scheme showing 30% thermal ellipsoids. Phenyl rings on the phosphorus atoms are omitted for clarity.

was observed in the ^{31}P NMR spectra of compounds **19** (36.8 ppm) and **20** (35.9 ppm), revealing that the P donors are only bonded to Au^{I} atoms as shown in Scheme 3. For compound **21** (Supporting Information, Figure S10), in addition to typical satellite peaks centered at −49.4 ppm because of Pt−P coupling with J_{Pt-P} = 1264 Hz, it exhibits one singlet at 33.2 ppm ascribed to the P donors bonded to Au^{I} centers. Lack of a P−P coupling suggests that dppm adopts two symmetric coordination modes chelating and bridging the Pt^{II} and Au^{I} centers, respectively, resulting in two equivalent P donors in each dppm as shown in Scheme 3.

Chart 1. Chelating and Bridging Mode of Edt in Syn and Anti Conformations



Crystal Structures. Selected atomic distances and angles for compounds **14**, **17**, and **18** are presented in Table 2. An ORTEP drawing of the coordination dication [PtCu$_2$(phen)$_2$(edt)(dppm)$_2$]$^{2+}$ of **14** is depicted in Figure 1. The Pt^{II} and Cu^{I} centers are bridged by dppm and edt to afford a V-type PtCu$_2$ (Cu−Pt−CuA = 136.1°) heterotrinuclear structure. The Pt^{II} center is located at an approximate square-planar environment with a P$_2$S$_2$ chromophore, and the Cu^{I} center affords a distorted tetrahedral geometry composed of N$_2$PS donors. The edt ligand chelates a Pt^{II} center and bridges two Cu^{I} centers in an anti conformation as shown in Chart 1.[26] The plane defined by the Cu$_2$S$_2$ atoms is perpendicular to the coordination plane of the Pt atom built by the P$_2$S$_2$ donors. The atoms Cu and CuA are located above and below the Pt coordination plane at 1.66 and −1.66 Å, respectively. The Pt···Cu and Cu···Cu separations are 3.874 and 7.187 Å, respectively.

As compounds **17** and **18** exhibit the same structures, only the complex dication [Pt$_2$Ag$_2$(edt)$_2$(dppm)$_2$]$^{2+}$ of **17** is shown in Figure 2. It consists of two Ag^{I} and two Pt(dppm)(dithiolate) (dithiolate = edt, **17**; pdt, **18**) components incorporating with one another by the bridging dithiolate S donors. The Pt$_2$Ag$_2$ atoms afford an approximately rhombic cluster core. The Ag−Pt distances are in the ranges of 3.06−3.15 Å, shorter than those (3.24−3.43 Å) observed in 1,1-ethylenedithiolato Pt$^{II}_2$Ag$^{I}_2$ heterotetranuclear complexes [Pt$_2$Ag$_2$(PPh$_3$)$_2${S$_2$C═C{C(O)Me}$_2$}$_2$](ClO$_4$)$_2$ containing monodentate PPh$_3$.[32] The Ag−Ag distances (ca. 3.27 Å), however, are longer than those (3.14 Å) found in the 1,1-ethylenedithiolato Pt$^{II}_2$Ag$^{I}_2$ heterotetranuclear complexes.[32] The Pt···Pt separations (5.27 and 5.34 Å for **17** and **18**,

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(32) (a) Vicente, J.; Chicote, M. T.; Huertas, S.; Bautista, D.; Jones, P. G.; Fischer, A. K. *Inorg. Chem.* **2001**, *40*, 2051. (b) Vicente, J.; Chicote, M. T.; Huertas, S.; Jones, P. G.; Fischer, A. K. *Inorg. Chem.* **2001**, *40*, 6193.

Table 3. Absorption and Emission Data of Compounds **11**−**21**

compound	medium	λ_{abs}/nm (ϵ/dm^3 mol^{-1} cm^{-1})	λ_{em}/nm (τ_{em}/μs) at 298 K	λ_{em}/nm at 77 K
11	solid		616 (1.67)	614
	MeCN	268 (41760), 290 (27640), 330 (8380)		588
12	solid		618 (0.078)	637
	MeCN	225 (76220), 275 (45690), 370 (3253)		606
13	solid		600 (0.21)	614
	MeCN	223 (64400), 273 (38780), 375 (4080)		600
14	solid		601 (0.10)	619
	MeCN	238 (62660), 268 (61430),383 (9760)		624
15	solid		626 (0.26)	639
	MeCN	245 (57050), 263 (54650), 402 (8300)		635
16	solid		585 (0.36)	597
	MeCN	220 (64430), 283 (28310), 350 (4630)		570
17	solid			648
	MeCN	222 (63800), 245 (64980), 320 (5042)		605
18	solid			664
	MeCN	229 (52590), 246 (54340), 330 (5130)		614
19	solid		642 (1.44)	631
	MeCN	242 (67200), 293 (55900), 549 (7015)	606 (0.035)	660
20	solid		609 (1.17)	605
	MeCN	226 (61780), 294 (43000), 533 (4322)	576 (0.021)	629
21	solid		563 (0.66)	625
	MeCN	221 (68500), 240 (70180), 320 (5570)	556 (0.015)	598

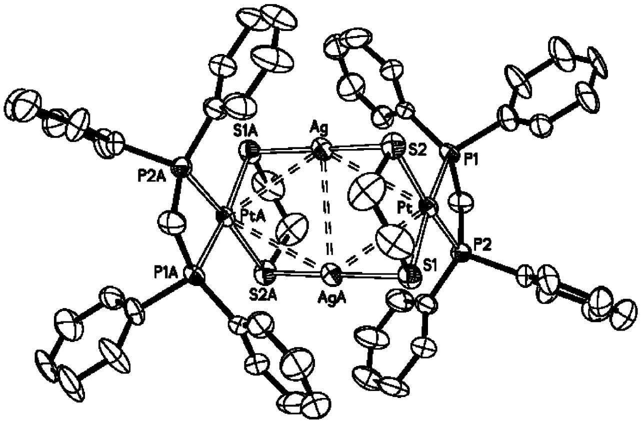

Figure 2. ORTEP drawing of the complex cation of **17** with atom labeling scheme showing 30% thermal ellipsoids.

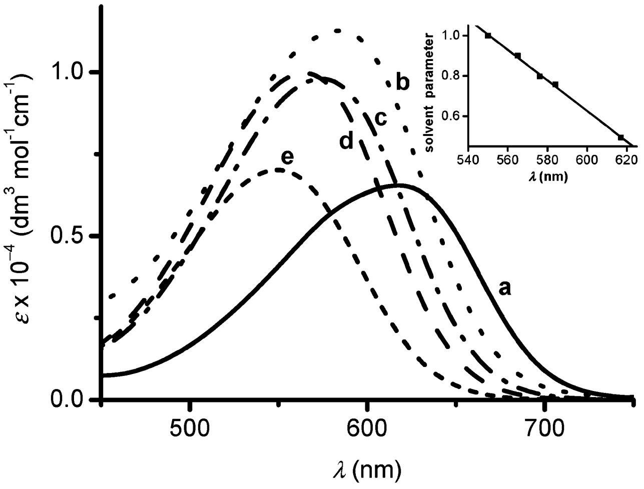

Figure 3. Charge-transfer-to-diimine absorption band of **19** in (a) THF, (b) CH_2Cl_2, (c) acetone, (d) dimethylformamide, and (e) CH_3CN.

respectively) are far beyond the distances for Pt−Pt contacts. The Pt−P, Pt−S, and Ag−S lengths are in the ranges 2.263(4)−2.267(3), 2.335(4)−2.342(4), and 2.390(4)−2.424(4) Å, respectively, shorter slightly compared with those observed in the 1,1-ethylenedithiolato heterotetranuclear complexes $[Pt_2Ag_2(PPh_3)_2\{S_2C{=}C\{C(O)Me\}_2\}_2](ClO_4)_2$.[32] Although the Pt center is located in an approximate square plane surrounded by P_2S_2 donors, the Ag center adopts quasi-linear coordination with the S2−Ag−S1A angle being 174.2 and 173.1° for **17** and **18**, respectively. The edt/pdt chelates the Pt^{II} center and bridges two Ag^{I} centers in a syn orientation as shown in Chart 1. The S−Pt−S bite angles of chelating dithiolates are 89.05(16) and 99.10(16)° for **17** and **18**, respectively. The P−Pt−P bite angles (73.21(13)° for **17** and 73.27(15)° for **18**) of the chelating dppm deviate significantly from 90°. The Ag atoms are situated above the Pt coordination planes at 2.33 and 2.40 Å for **17** and **18**, respectively. The dppm acts as a chelating ligand bound to the Pt center instead of bridging $Pt^{II}-Cu^{I}$ centers as observed in compound **14**.

Photophysical Properties. Absorption and emission data of compounds **11**−**21** are summarized in Table 3. The electronic absorption spectrum of **11** in acetonitrile solution displays two high-energy absorption bands at ca. 220 and 270 nm together with a shoulder band at ca. 330 nm. The compounds **12**−**16** in acetonitrile solutions exhibit intense high-energy absorption peaks at ca. 220−240 nm and 260−280 nm and a low-energy shoulder band at 350−400 nm. For compounds **17**, **18**, and **21**, a low-energy band appears at ca. 320−350 nm besides strong absorption bands at ca. 220−250 nm ascribed to the ligand-centered transitions.

In the UV−vis spectra of compounds **19** and **20**, in addition to two intense high-energy absorption bands at ca. 230−240 and 290 nm because of the ligand-centered transitions, a broad and solvent-dependent absorption band with low energy is observed. With a decrease of the solvent polarity, the low-energy absorption maxima are significantly red-shifted. As indicated in Figure 3, plots of the energy of charge-transfer band maxima versus solvent polarity parameters give excellent linear correlations with a linear regression agreement of $R^2 > 0.98$. Obviously, the trend of the observed shift with solvent polarity demonstrates a negative solvato-

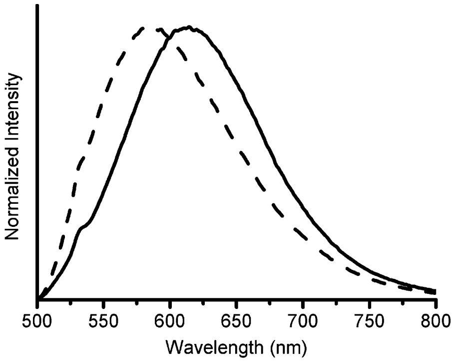

Figure 4. Emission spectra of **11** (solid line) and [PtCu$_2$(tdt)(dppm)$_2$(μ-SH)](ClO$_4$)$_2$ (**1**) (dashed line) in the solid states at 77 K.

chromic effect, suggesting an assignment of this transition as a charge transfer from an orbital of a mixed metal/dithiolate character to a diimine π* orbital.[15a,d,g,33] Similar negative solvatochromic properties have also been observed in the precursor compounds Pt(diimine)(dithiolate).[15a]

With excitation at $\lambda_{ex} > 340$ nm, the compound [PtCu$_2$(edt)(μ-SH)(dppm)$_3$](ClO$_4$) (**11**) shows photoluminescence in the solid state and in frozen acetonitrile glass at 77 K. A microsecond range of lifetime in the solid state at 298 K is indicative of phosphorescence character. By comparison of the emission spectra of the compounds [PtM$_2$(tdt)(μ-SH)(dppm)$_3$](ClO$_4$) (M = Cu, **1**; Ag, **6**) in the previous study,[26] it has been demonstrated that the emission energy shows inappreciable difference on going from **1** (M = Cu) to **6** (M = Ag). Thus, a possible assignment of the emitting state to a SH/dithiolate → M ligand-to-metal charge-transfer (LMCT) transition can be excluded.[34,35] As indicated in Figure 4, emission energy of the edt compound [PtCu$_2$(edt)(μ-SH)(dppm)$_3$](ClO$_4$) (**11**) exhibits an obvious red shift relative to that of the tdt compound [PtCu$_2$(tdt)(μ-SH)(dppm)$_3$](ClO$_4$) (**1**).[26] This is in accord with the electron-donating ability and the energy level of the dithiolate ligand in the order edt > tdt. Therefore, it is likely that the emission arises from a spin-forbidden dithiolate-to-platinum charge transfer (^{3}LMCT) transition.[34,35]

The Pt^{II}Cu$^{I}_2$ heterotrinuclear complexes **12**−**16** are non-emissive in solutions but show emission in the solid state at 298 K and in frozen glasses at 77 K. The lifetime in the solid state at 298 K is in the range of microseconds, suggestive of spin-forbidden character in the emissive states. As demonstrated in the tdt compounds [PtCu$_2$(diimine)$_2$(tdt)(dppm)$_2$](ClO$_4$)$_2$, the emission energy of the edt compounds [PtCu$_2$(diimine)$_2$(edt)(dppm)$_2$](ClO$_4$)$_2$ is also dependent on the electronic properties of the substituents in the diimine ligands. Although a blue shift of the emission energy is observed on going from the bpy compound **12** to the dbbpy counterpart **13**, the brphen compound **15** shows a red shift relative to the phen counterpart **14**. This accords with the electron-donating ability in the diimine ligands with the π* energy in the order bpy < dbbpy and phen > brphen. Therefore, the emissive state of **12**−**15** is likely associated with a ^{3}[d(Cu)−π*(diimine)] MLCT transition.[26] Moreover, by comparison of the compounds [PtCu$_2$(dbbpy)$_2$(dithiolate)(dppm)$_2$](ClO$_4$)$_2$ (dithiolate = edt, **13**; tdt, **16**) containing the same diimine but different dithiolate ligands, it is indicated that the emission energy of the edt compound **13** shows a notable red shift relative to that of the tdt compound **16** as depicted in Figure 5. The same trend is also observed for other groups of compounds [PtCu$_2$(diimine)$_2$(edt)(dppm)$_2$](ClO$_4$)$_2$ and [PtCu$_2$(diimine)$_2$(tdt)(dppm)$_2$](ClO$_4$)$_2$ [26] containing the same diimine but different dithiolate ligands. Thus, an emission contribution from a dithiolate-to-diimine [p(S) → π*(diimine)] ligand-to-ligand charge-transfer (LLCT) transition is also likely. In this way, the emission origin of the Pt^{II}Cu$^{I}_2$ heterotrinuclear complexes is better assigned as admixture of ^{3}[d(Cu)/p(S) → π*(diimine)] transitions.

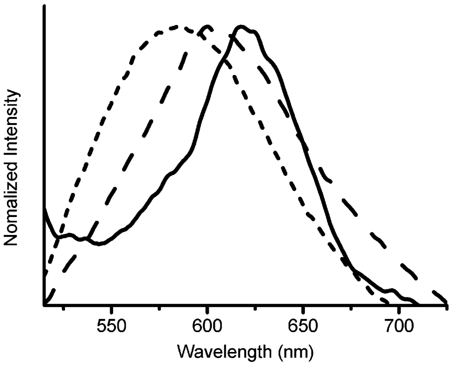

Figure 5. Emission spectra of **12** (solid line), **13** (dashed line), and **16** (dotted line) in the solid states at 298 K.

The Pt$_2$Ag$_2$ heterotetranuclear compounds **17** and **18** are only emissive at 77 K. With $\lambda_{ex} > 330$ nm, the emission energy shows an appreciable red shift from the edt complex **17** to the pdt complex **18** whether in the solid state or in acetonitrile glasses at 77 K (Table 1). This is consistent with the appreciably better electron-donating ability of pdt than that of edt. Therefore, the excited state is ascribed tentatively as a [dithiolate → Pt$_2$Ag$_2$] LMCT transition.[34,35]

Compounds **19** and **20** show intense emission in the solid states and in acetonitrile solutions at room temperature. The emissive lifetime in the microsecond ranges is suggestive of a triplet state parentage. Excitation spectra of **19** and **20** in fluid acetonitrile solutions are similar to their low-energy absorption bands, indicative of their similar origin. Furthermore, introducing electron-donating methyl to bpy gives rise to an obvious blue shift of the emission in view of the emission energy in the order **19** < **20**. As a consequence, it is likely that the emission originates from a triplet state of ^{3}[d(Pt)/p(S) → π*(diimine)] MLCT character.[26] Unlike the corresponding solvent-dependent low-energy absorption bands that show a noteworthy solvatochromism, the emission spectra are less sensitive to the solvent polarity (Supporting Information, Figure S11). In addition, the emission energy of the compounds [PtAu$_2$(diimine)(tdt)(dppm)$_2$]$^{2+}$ shows a notable blue shift ($\Delta E_{em} = 0.17-0.35$ eV) relative to that of the corresponding precursor compounds Pt(diimine)(tdt) (Supporting Information, Figure S12). A similar phenomenon

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also has been observed in the $Pt^{II}Ag^{I}_2$ complexes $[PtAg_2(diimine)(tdt)(dppm)_2]^{2+}$ of tdt.[26] This can readily be elucidated by the lowered energy of the d(Pt)/p(S) orbitals because of introducing a $M_2(dppm)_2$ (M = Ag, Au) unit, thus raising the energy gap between d(Pt)/p(S) (HOMO) and diimine π^* orbitals (LUMO). Hence, the emissive energy of the square planar Pt^{II} diimine chromophores is finely tunable by incorporating the metal components $[M_2(dppm)_2]^{2+}$ owing to altering the energy gap between the HOMO and LUMO.

With excitation at $\lambda_{ex} > 300$ nm, compound **21** shows emission in the solid state and in aectonitrile solution at room temperature. The lifetime is in the range of sub-microsecond (Table 3) at 298 K. It is likely that the emission is related to a dithiolate-to-metal cluster [dithiolate → $PtAu_2$] LMCT transition as described for Pt_2Ag_2 compounds **17** and **18**. However, an alternative assignment of the emission origin as a S → Au LMCT transition[36] or a $^3[d(Pt) \rightarrow \pi^*_{dithiolate}]$ MLCT (platinum-to-dithiolate charge transfer) transition[37] cannot be excluded at present.

Conclusions

A series of $Pt^{II}-M^{I}$ (M = Cu, Ag, Au) tri- and tetranuclear complexes with diverse structural topologies were prepared by reaction of Pt(diimine)(dithiolate) with $M_2(dppm)_2(MeCN)_2^{2+}$. Compounds $[PtAu_2(diimine)(tdt)(dppm)_2](SbF_6)_2$ result from the designed incorporation of Pt(diimine)(dithiolate) with $Au_2(dppm)_2^{2+}$. Other types of $Pt^{II}-M^{I}$ complexes are derived from rupturing of metal−ligand bonds in the original metal components and recombination between the ligands and the metal ions. Formation of $[PtCu_2(edt)(\mu\text{-}SH)(dppm)_3](ClO_4)$ (**11**) is involved in disruption of the C−S bonds in the edt ligand. The $Pt^{II}-M^{I}$ heterometallic complexes show rich emission properties with manifold emissive parentages. It is demonstrated that incorporating Pt(diimine)(dithiolate) with $[M_2(dppm)_2]^{2+}$ affords a feasible synthetic approach to attain heterometallic and multicomponent materials that emit long-lived photoluminescence with tunable wavelengths and emission energy. Further study is being pursued by reaction Pt(diimine)(dithiolate) with other emissive metal components with substitutable coordination sites.

Acknowledgment. This work was supported by NSFC (20171044, 20273074, and 20490210), NSF of Fujian Province (E0420002 and E0310029), the fund from the Chinese Academy of Sciences, and the national basic research program (001CB108906) from the ministry of sciences and technology of China.

Supporting Information Available: ES-MS and ^{31}P NMR spectra of compounds **11**, **12 17**, **19**, and **21** with different structural topologies, emission spectra of **19** in various solvents with different polarity, emission spectra of **19**, **20**, and the precursor compounds in acetonitrile at 298 K, X-ray crystallographic files in CIF format for the structure determination of compounds **14**$\cdot{}^1/_2Et_2O\cdot{}^1/_2CH_3OH$, **17**$\cdot Et_2O\cdot{}^1/_2H_2O$, and **18**$\cdot Et_2O\cdot{}^1/_2H_2O$. This material is available free of charge via the Internet at http://pubs.acs.org.

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