ORGANOMETALLICS

Toward Luminescence Vapochromism of Tetranuclear Au^I–Cu^I Clusters

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Supporting Information

ABSTRACT: A family of triphosphine gold–copper clusters bearing aliphatic and hydroxyaliphatic alkynyl ligands of general formula $[HC(PPh_2)_3Au_3Cu(C_2R)_3]^+$ (R = cyclohexyl (1), cyclopentyl (2), Bu^t (3), cyclohexanolyl (4), cyclopentanolyl (5), 2,6-dimethylheptanolyl (6), 2-methylbutanolyl (7), diphenylmethanolyl (8)) was synthesized via a self-assembly protocol, which involves treatment of the $(AuC_2R)_n$ acetylides with the $(PPh_2)_3CH$ ligand in the presence of Cu⁺ ions and NEt₃. Addition of Cl⁻ or Br⁻ anions to complex 8 results in coordination of the halides to the copper atoms to give neutral $HC(PPh_2)_3Au_3CuHal(C_2COHPh_2)_3$ derivatives (Hal = Cl (9), Br (10)). The title compounds were characterized by NMR and ESI-MS spectroscopy, and the structures of 1, 4, 7, and 8 were



determined by single-crystal X-ray diffraction analysis. The photophysical behavior of all of the complexes has been studied to reveal moderate to weak phosphorescence in solution and intense emission in the solid state with a maximum quantum yield of 80%. Exposure of the solvent-free X-ray amorphous samples 8-10 (R = diphenylmethanolyl) to vapors of the polar solvents (methanol, THF, acetone) switches luminescence with a visible hypsochromic shift of emission of 50–70 nm. The vapochromism observed is tentatively ascribed to the formation of a structurally ordered phase upon absorption of organic molecules by the amorphous solids.

INTRODUCTION

The photophysical properties of coinage-metal compounds have been intensely studied in recent years due to their fascinating versatility as well as the promising potential for technological applications in such areas as e.g. optoelectronics and sensors.¹ The luminescence characteristics of these compounds often depend dramatically on the presence of metal-metal interactions (metallophilicity).² This phenomenon that is usually considered to be an origin of intense photoemission is also responsible for the formation of the families of multimetallic aggregates, which demonstrate exceptional diversity of composition, stereochemistry, and, consequently, physical properties.^{11,3}

The ligand environment of the polymetallic d^{10} complexes usually contains bridging organic groups, which stabilize the cluster core and determine the architecture of the resulting assembly.⁴ The ability of the alkynes to bind late-transitionmetal ions in a bidentate mode through a combination of σ and π bonding has been extensively utilized in the synthetic chemistry of Cu, Ag, and Au. This mode of alkynyl ligand coordination provides additional opportunities for fine tuning of the photophysical characteristics of these types of complexes. For example, modification of the electronic properties of the $-C \equiv CR$ moiety affects the energy of molecular orbitals involved in the emissive electronic transitions.^{1g,5} In addition to the electronic effects, the coordinatively inactive R alkynyl substituents were shown to participate in weak noncovalent interactions (e.g., hydrogen bonding), which can influence both the structural topology and photophysical characteristics of the polynuclear aggregates.⁶ In particular, hydroxyaliphatic alkynyl ligands bearing OH groups were found to form effective O– H⁻⁻O intramolecular interactions, dramatically changing the processes of formation of multimetallic assemblies. This O– H⁻⁻O bonding was shown to lead to molecular entities which could not be accessed using e.g. aromatic $-C \equiv CR$ ligands.^{6b-e}

The subtle effects of the ligand environment on the metalmetal interactions are of particular interest, as they can provide

Received: November 15, 2012 Published: July 23, 2013 access to molecules/materials which exhibit effective luminescence or absorption response to various external stimuli, including the vapors of volatile organic compounds (VOCs).^{6d,7} Coinage-metal complexes showing vapochromic luminescence in the solid state are of great interest due to their potential for highly sensitive and easy to detect sensing of the corresponding analytes.^{7,8}

Recently we have described a family of tetranuclear $Au^{I}-Cu^{I}$ aryl–alkynyl clusters stabilized by the triphosphine ligand tris(diphenylphosphino)methane (Chart 1).⁹

Chart 1. Schematic Representation of Triphosphine Au^I– Cu^I Alkynyl Clusters



Inspired by the reported difference in photophysical properties between the compounds bearing aromatic and aliphatic alkynyl ligands,^{6b,c} we intended to prepare and systematically investigate the luminescence of structurally similar Au^I-Cu^I complexes functionalized with aliphatic and hydroxyaliphatic alkynes having different streric and electronic parameters. In the present paper we report the synthesis, structural characterization, and photophysical studies of a series of heterometallic Au^I-Cu^I complexes, some of which display distinct switching of luminescence upon exposure to the vapors of common organic solvents such as acetone, methanol, and tetrahydrofuran.

EXPERIMENTAL SECTION

General Comments. The $(AuC_2R)_n$ complexes $(R = Bu^t, C_6H_{10}OH, C_5H_8OH, C_9H_{18}OH, C(CH_3)(C_3H_7)OH, C_{13}H_{10}OH)$ were prepared according to the published procedures. ^{6c,e,10} $(AuC_2Cy)_n$ and $(AuC_2Cyp)_n$ acetylides (Cy = cyclohexyl, Cyp = cyclopentyl) were obtained analogously to $(AuC_2Bu^t)_n$.¹⁰ Tris(diphenylphosphino)-methane (tppm; Strem Chemicals) and all solvents were used as received. The solution 1D ¹H and ³¹P NMR and ¹H-¹H COSY spectra were recorded on Bruker Avance 400 and Bruker DPX 300 spectrometers. Mass spectra were measured on a Bruker micrOTOF 10223 instrument in the ESI⁺ mode. Microanalyses were carried out in the analytical laboratories of St. Petersburg State University and the University of Eastern Finland.

Synthesis of Complexes 1–8. $(AuC_2R)_n$ (0.3 mmol) was suspended or dissolved in dichloromethane (15 mL), and a mixture of tris(diphenylphosphino)methane (tppm, 0.1 mmol) and [Cu-(NCMe)₄]PF₆ (0.1 mmol) in the same solvent (5 mL) was added dropwise. The resulting reaction mixture was stirred for 1 h to give a transparent solution, which was then filtered and evaporated. The solid samples obtained were recrystallized as described below.

[$\hat{H}C(PPh_2)_3Au_3Cu(C_2Cy)_3]PF_6$ (1). This complex was recrystallized by slow evaporation of an acetone/heptane/diethyl ether solution to give pale yellow needlelike crystals (154 mg, 91%). Single crystals suitable for X-ray analysis were obtained by slow evaporation of a dichloromethane/hexane solution of 1 at +5 °C. ES MS (m/z): [M]⁺ 1543.25 (calcd 1543.25). ³¹P NMR (CDCl₃, 298 K; δ): 39.7 (s, 3P, tppm), -144.1 (sept, PF₆⁻). ¹H NMR (CDCl₃, 298 K; δ): phosphine, 6.13 (q, H-CP₃, 1H, J_{PH} = 10.0 Hz), AB₂ system 7.10 (dd, H-*meta*, 12H, J_{HH} = ca. 7 Hz), 7.17 (t, H-*para*, 6H, J_{HH} = ca. 7 Hz); 7.85 (unresolved multiplet, H-*ortho*, 12H); alkynyl ligands, 1.43 (m, CH₂, 9H), 1.67 (m, CH₂, 3H), 1.76 (m, CH₂, 6H), 1.92 (m, CH₂, 6H), 2.12 (m, CH₂, 6H), 2.70 (m, CH, 3H). Anal. Calcd for $Au_3C_{61}CuH_{64}F_6P_4$: C, 43.37; H, 3.82. Found: C, 43.27; H, 3.88.

[*HC(PPh*₂)₃*Au*₃*Cu*(*C*₂*Cyp*)₃]*PF*₆ (**2**). This complex was recrystallized by slow evaporation of an acetone/heptane/diethyl ether solution to give yellow-orange platelike crystals (130 mg, 79%). ES MS (*m*/*z*): [M]⁺ 1501.20 (calcd 1501.20). ³¹P NMR (CDCl₃, 298 K; δ): 39.7 (s, 3P, tppm), -144.1 (sept, PF₆⁻). ¹H NMR (CDCl₃, 298 K; δ): phosphine, 6.12 (q, *H*-CP₃, 1H, *J*_{PH} = 9.7 Hz), 7.10 (dd, *H-meta*, 12H, *J*_{HH} = 7.4 Hz), 7.17 (t, *H-para*, 6H, *J*_{HH} = 7.4 Hz), 7.85 (unresolved multiplet, *H-ortho*, 12H); alkynyl ligands, 1.72 (m, CH₂, 6H), 1.94 (m, CH₂, 6H), 1.99 (m, CH₂, 6H), 2.17 (m, CH₂, 6H), 2.95 (m, CH, 3H). Anal. Calcd for Au₃C₅₈CuH₅₈F₆P₄: C, 42.29; H, 3.55. Found: C, 42.34; H, 3.58.

 $[HC(PPh_2)_3Au_3Cu(C_2Bu^{\dagger})_3]PF_6$ (3). This complex was prepared using an alternative method. [HC(PPh₂)₃Au₃Cl₃]¹¹ (107 mg, 0.084 mmol) was suspended in dichloromethane (10 mL). HC2But (21 mg, 0.253 mmol) was added to the suspension followed by mixing with a solution of [Cu(NCMe)₄]PF₆ (31 mg, 0.084 mmol) in the same solvent (5 mL). This mixture was treated with neat Et₃N (0.1 mL) to give a yellow solution, which was stirred for 1 h, and then the solvent was evaporated. The yellow-green solid was washed with water (3×5) mL), methanol $(3 \times 5 \text{ mL})$, and diethyl ether $(2 \times 10 \text{ mL})$ and dried under vacuum. Recrystallization by slow evaporation of an acetone/ heptane solution gave pale yellow-green platelike crystals (105 mg, 78%). ES MS (m/z): [M]⁺ 1465.20 (calcd 1465.20). ³¹P{¹H} NMR (CDCl₃, 298 K; δ): 40.1 (s, 3P, tppm), -144.1 (sept, 1P, PF₆). ¹H NMR (CDCl₃, 298 K; δ): phosphine, 6.21 (unresolved multiplet, H– CP_{3} , 1H), 7.07 (dd, H-meta, 12H, $J_{HH} = 7.4$ Hz), 7.17 (t, H-para, 6H, $J_{\rm HH}$ = 7.4 Hz), 7.85 (unresolved multiplet, H-ortho, 12H); alkynyl ligands, 1.55 (s, CH₃, 18H), 1.57 (s, CH₃, 9H). Anal. Calcd for Au₃C₅₅CuH₅₈F₆P₄: C, 41.00; H, 3.63. Found: C, 41.12; H, 3.69.

[*HC*(*PPh*₂)₃*Au*₃*Cu*(*C*₂*C*₆*H*₁₀*OH*)₃]*PF*₆ (4). Single crystals suitable for X-ray analysis were obtained by slow evaporation of an acetone/heptane solution of 4 to give yellow platelike crystals (128 mg, 74%). ES MS (*m*/*z*): [M]⁺ 1591.24 (calcd 1591.23). ³¹P NMR (CDCl₃, 298 K; δ): 40.1 (s, 3P), -144.1 (sept, PF₆⁻). ¹H NMR (acetone-*d*₆, 298 K; δ): phosphine, 6.19 (q, *H*-CP₃, 1H, *J*_{PH} = 9.7 Hz), 7.12 (dd, H-*meta*, 12H, *J*_{HH} = 7.1 Hz), 7.20 (t, H-*para*, 6H, *J*_{HH} = 7.1 Hz), 7.86 (unresolved multiplet, H-*ortho*, 12H); alkynyl ligands, 4.83 (s, OH, 3H), 1.38 (m, CH₂, 3H), 1.68–1.96 (m, CH₂, 21H), 2.29 (m, CH₂, 6H). Anal. Calcd for Au₃C₆₁CuH₆₄F₆O₃P₄: C, 42.17; H, 3.71. Found: C, 42.69; H, 3.86.

[*HC*(*PPh*₂)₃*Au*₃*Cu*(*C*₂*C*₅*H*₈*OH*)₃]*CF*₃*SO*₃ (*5*). [Cu(CF₃SO₃)]₂·C₆*H*₆ was used instead of [Cu(NCMe)₄]PF₆. The solid obtained was recrystallized by slow evaporation of an acetone/heptane solution to give yellow needlelike crystals (110 mg, 65%). ES MS (*m*/*z*): [M]⁺ 1549.17 (calcd 1549.19). ³¹P NMR (CDCl₃, 298 K; δ): 40.0 (s). ¹H NMR (CDCl₃, 298 K; δ): phosphine, 6.18 (q, *H*–CP₃, 1H, *J*_{PH} = 9.8 Hz), 7.11 (dd, H-*meta*, 12H, *J*_{HH} = 7.3 Hz), 7.18 (t, H-*para*, 6H, *J*_{HH} = 7.3 Hz), 7.85 (unresolved multiplet, H-*ortho*, 12H); alkynyl ligands, 1.93 (m, CH₂, 12H), 2.21 (m, CH₂, 6H), 2.32 (m, CH₂, 12H), 4.46 (s, OH, 3H). Anal. Calcd for Au₃C₃₉CuH₅₈F₃O₆P₃S: C, 41.70; H, 3.44. Found: C, 41.77; H, 3.45.

[*HC*(*PPh*₂)₃*Au*₃*Cu*($C_2C_9H_{18}OH$)₃]*PF*₆ (6). This complex was recrystallized by slow evaporation of a CH₂Cl₂/hexanes solution to give fine yellow-green needlelike crystals (134 mg, 72%). ES MS (*m*/*z*): [M]⁺ 1723.42 (calcd 1723.42). ³¹P NMR (acetone- d_6 , 298 K; δ): 40.2 (s, 3P, tppm), -144.8 (sept, PF₆⁻). ¹H NMR (acetone- d_6 , 298 K; δ): phosphine, 6.57 (q, *H*-CP₃, 1H, *J*_{PH} = 10.0 Hz), 7.18 (dd, H-*meta*, 12H, *J*_{HH} = 7.4 Hz), 7.36 (t, H-*para*, 6H, *J*_{HH} = 7.4 Hz), 7.93 (unresolved multiplet, H-*ortho*, 12H); alkynyl ligands, 1.18 (d, CH₃, 18H, *J*_{HH} = 6.7 Hz), 1.24 (d, CH₃, 18H, *J*_{HH} = 6.7 Hz), 1.94 (m, CH/ CH₂, 6H), 2.00 (m, CH/CH₂, 6H), 2.26 (m, CH/CH₂, 6H), 5.24 (s, OH, 3H). Anal. Calcd for Au₃C₇₀CuH₈₈F₆O₃P₄: C, 44.97; H, 4.74. Found: C, 44.99; H, 4.80.

 $[HC(PPh_2)_3Au_3Cu(C_2C(CH_3)(C_3H_7)OH)_3]PF_6$ (7). This complex was recrystallized by slow evaporation of an acetone/heptane solution to give yellow-green platelike crystals (112 mg, 66%). Single crystals suitable for X-ray analysis were obtained by slow evaporation of a chloroform solution of 7 at +5 °C. ES MS (m/z): $[M]^+$ 1555.24 (calcd

1555.24). ³¹P NMR (CDCl₃, 298 K; *δ*): 40.0 (s, 3P, tppm), -144.1 (sept, PF₆⁻). ¹H NMR (CDCl₃, 298 K; *δ*): phosphine, 6.20 (q, *H*-CP₃, 1H, *J*_{PH} = 9.8 Hz), AB₂ system of H-*meta* and H-*para* 7.06-7.25 (unresolved multiplet, 18H), 7.85 (unresolved multiplet, H-*ortho*, 12H); alkynyl ligands, 1.17-1.39 (unresolved multiplet, CH₃, 27H), 2.20 (m, CH, 3H), 4.49 (unresolved multiplet, OH, 3H). Anal. Calcd for Au₃C₅₈CuH₆₄F₆O₃P₄: C, 40.94; H, 3.79. Found: C, 40.99; H, 3.80.

[*HC*(*PPh*₂)₃*A*u₃*C*u(*C*₂*C*₁₃*H*₁₀*OH*)₃]*PF*₆ (8). A yellow-orange amorphous powder was obtained by slow addition of excess pentane to a dichloromethane solution of 8 (157 mg, 79%). Single crystals suitable for X-ray analysis were obtained by slow evaporation of a dichloromethane/methanol solution of 8 at +5 °C. ES MS (*m*/*z*): [M]⁺ 1843.23 (calcd 1843.24). ³¹P NMR (acetone-*d*₆, 298 K; δ): 40.1 (s, 3P), -144.8 (sept, PF₆⁻). ¹H NMR (acetone-*d*₆, 298 K; δ): phosphine, 6.62 (q, *H*-CP₃, 1H, *J*_{PH} = 9.9 Hz), 7.21 (dd, H-*meta*, 12H, *J*_{HH} = 7.5 Hz), 7.39 (t, H-*para*, 6H, *J*_{HH} = 7.5 Hz), 7.97 (multiplet, H-*ortho*, 12H, *J*_{HH} = 7.1 Hz, *J*_{PH} = 8.2 Hz); alkynyl ligands, 6.18 (s, OH, 3H), 7.25–7.33 (unresolved multiplet, H-*meta* + H-*para*, 18H), 7.65 (d, H-*ortho*, 12H, *J*_{HH} = 7.7 Hz). Anal. Calcd for Au₃C₈₂CuH₆₄F₆O₃P₄: C, 49.45; H, 3.24. Found: C, 49.35; H, 3.35.

[HC(PPh₂)₃Au₃Cu(C₂C₁₃H₁₀OH)₃Cl] (9). *Method A.* CuCl (10 mg, 0.104 mmol) and tris(diphenylphosphino)methane (59 mg, 0.104 mmol) were dissolved in an acetonitrile/dichloromethane mixture (1/ 1 v/v, 10 mL), and a solution of $AuC_2C_{12}H_{10}OH$ (126 mg, 0.312 mmol) in dichloromethane (5 mL) was added to the mixture. The nearly colorless reaction mixture was stirred for ca. 1.5 h. The resulting solution was concentrated to a volume of ca. 5 mL, and slow addition of acetone caused the formation of a white microcrystalline precipitate (138 mg, 71%). The amorphous phase of 9 was obtained in the same way, but the crystallization was provoked by addition of hexane instead of acetone. Single crystals suitable for X-ray analysis were obtained by gas-phase diffusion of acetone into a solution of 9 in chloroform at +5 °C.

Method B. 8 (30 mg, 0.015 mmol) was dissolved in acetone (5 mL), and a solution of NBu₄Cl (4.5 mg, 0.162 mmol) in the same solvent (3 mL) was added. The reaction mixture decolorized immediately, and some white microcrystalline precipitate gradually formed. The reaction mixture was evaporated and washed with acetone (3 × 3 mL), and the white crystalline residue was air-dried (25 mg, 87%). ES MS (m/z): $[M - Cl^{-}]^+$ 1843.24 (calcd 1843.24). ³¹P NMR (CDCl₃, 298 K; δ): 43.1 (s, br). ¹H NMR (CDCl₃, 298 K; δ): phosphine, 7.08 (dd, H-*meta*, 12H, J_{HH} = 7.4 Hz), 7.16 (t, H-*para*, 6H, J_{HH} = 7.4 Hz), 8.29 (unresolved multiplet, H-*ortho*, 12H); alkynyl ligands, 4.91 (s, OH, 3H), AB₂ system centered at 7.24 (H-*meta*, 12H, J_{HH} = ca. 7 Hz) and 7.18 (H-*para*, 12H, J_{HH} = ca. 7 Hz), 7.62 (d, H-*ortho*, 12H, J_{HH} = 7.8 Hz). Anal. Calcd for Au₃C₈₂H₆₄ClCuO₃P₃: C, S2.38; H, 3.43. Found: C, S2.29; H, 3.38.

[HC(PPh₂)₃Au₃Cu(C₂C₁₃H₁₀OH)₃Br] (10). This complex was obtained analogously to 9 (method B) as a white microcrystalline solid (26 mg, 90%). The amorphous phase of **10** was obtained by addition of hexane to a concentrated dichloromethane solution of the complex. Single crystals suitable for X-ray analysis were obtained by gas-phase diffusion of acetone into a solution of **10** in chloroform at +5 °C. ³¹P NMR (CDCl₃, 298 K; δ): 42.7 (s, br). ¹H NMR (CDCl₃, 298 K; δ): phosphine, 7.10 (dd, H-*meta*, 12H, *J*_{HH} = 7.4 Hz), 7.18 (t, H-*para*, 6H, *J*_{HH} = 6.9 Hz), 8.29 (unresolved multiplet, H-*ortho*, 12H); alkynyl ligands, 4.90 (s, OH, 3H), AB₂ system centered at: 7.24 (H-*meta*, 12H, *J*_{HH} = ca. 7 Hz) and 7.18 (H-*para*, 12H, *J*_{HH} = ca. 7 Hz), 7.62 (d, H-*ortho*, 12H, *J*_{HH} = 7.8 Hz). Anal. Calcd for Au₃C₈₂H₆₄BrCuO₃P₃: C, 51.17; H, 3.35. Found: C, 50.84; H, 3.61.

X-ray Structure Determinations. Crystals of 1, 4, and 7–10 were immersed in cryo-oil, mounted in a nylon loop, and measured at a temperature of 100 K except for 10, which was measured at 210 K. The X-ray diffraction data were collected on Bruker Kappa Apex II, Bruker SMART APEX II, and Bruker Kappa APEX II DUO diffractometers using Mo K α radiation ($\lambda = 0.71073$ Å). The APEX2¹² program package was used for cell refinements and data reductions. The structures were solved by direct methods using the SHELXS-97¹³ programs with the WinGX¹⁴ graphical user interface. A semiempirical absorption correction (SADABS)¹⁵ was applied to all

data. Structural refinements were carried out using SHELXL-97.¹³ One of the cyclohexyl rings (C(20)–C(25)) in 1 and the dichloromethane crystallization molecule were disordered. However, no suitable disorder model was found and both geometric and displacement constraints and restraints were applied to these moieties. Also, carbon atoms C(20)–C(25), C(1S), and C(7) were restrained so that their U_{ii} components approximated isotropic behavior.

Some of the solvent molecules in the crystals of 4 and 7 were omitted, as they were disordered and could not be resolved unambiguously. The missing solvent was taken into account by using a SQUEEZE routine of PLATON.¹⁶ The contribution of the solvent to the cell content was not taken into account.

In 9 and 10 both geometric and displacement restraints were applied to the atoms of disordered acetone crystallization molecules. The carbon atom C(4) in 9 was restrained so that its U_{ij} components approximated isotropic behavior. Also, displacement constraints were applied to the atoms C(4) and C(5) in 9. The OH hydrogen atoms in 7 and 10 were positioned according to the electron density map and refined with fixed O-H and H…Br distances; $U_{iso} = 1.5U_{eq}$ (parent oxygen atom). All other hydrogen atoms in 1, 4, and 7–10 were positioned geometrically and were constrained to ride on their parent atoms, with O-H = 0.84 Å, C-H = 0.95–1.00 Å, and $U_{iso} = (1.2-1.5)$ U_{eq} (parent atom). The crystallographic details are summarized in Table S1 (Supporting Information).

X-ray powder diffraction analysis was carried out using a Rigaku Miniflex II (Cu K α) diffractometer, equipped with a high-speed solidstate Dtex type detector within the 2θ angle range of 5–50° in the Bragg–Brentano geometry. The measurements were done with a scan step 0.02° of 2θ and speed of 2°/min.

Photophysical Measurements. The absolute emission quantum yields of powders were determined according to the Morse procedure¹⁷ using LED pumping and a diffuse reflectance standard. The absorption of powders was estimated by measuring diffusion reflectance and using the Kubelka-Munk theory of light absorption and scattering of powder layers.¹⁸ The vapor-sensitive samples were exposed to saturated solvent vapor in a sealed vessel for 30 min at room temperature prior to the corresponding measurements. All photophysical measurements in solution were carried out in CH₂Cl₂ that was distilled immediately prior to use. All solutions were carefully degassed before lifetime and quantum yield measurements. The absolute emission quantum yield of solution was determined by a comparative method using LED pumping and rhodamine III in ethanol ($\Phi_{\rm em}$ = 0.95 \pm 0.03) as standard with the refraction coefficients of dichloromethane and ethanol equal to 1.42 and 1.36, respectively. An LED (385 nm) was used in the continuous and pulse modes (pulse width, 1–20 μ s; duty of edge, ~90 ns; repetition rate, 100 Hz to 10 kHz). The absolute luminescence quantum yields for solid-state samples were determined as described in the Supporting Information. A Tektronix TDS3014B digital oscilloscope (Tektronix, band width 100 MHz), MUM monochromator (LOMO, interval of wavelengths 10 nm) and Hamamatsu photomultiplier tube were used for lifetime measurements. Emission spectra were recorded using an HR2000 spectrometer (Ocean Optics). A halogen lamp, LS-1-CAL (Ocean Optics), and deuterium lamp, DH2000 (Ocean Optics), were used to calibrate the absolute spectral response of the spectral system in the 200-1100 nm range. Excitation spectra were measured on a Varian Cary Eclipse spectrofluorimeter.

RESULTS AND DISCUSSION

Synthesis and Characterization. The synthesis of the $[HC(PPh_2)_3Au_3Cu(C_2R)_3]^+$ complexes 1–9 is based on depolymerization of the homoleptic gold acetylides $(AuC_2R)_n$ with the triphosphine ligand $HC(PPh_2)_3$ and subsequent treatment of the reaction mixture with Cu^+ ions (Scheme 1, protocol a). In the case of 3 and 9 an alternative method reported earlier for the arylacetylene derivatives^{9a} was found to be more effective (Scheme 1, protocol b).

Scheme 1. Synthesis of the Clusters $1-8^{a}$



^aConditions: CH₂Cl₂, 298 K. Yields: 65-91%.

Clusters 1-6 were characterized using ¹H and ³¹P NMR spectroscopy and ESI-MS. The solid-state structures of 1, 4, 7, and 8 were determined by an X-ray diffraction study (Figure 1 and Figure S1, Supporting Information). However, the poor diffraction of the crystals of 7 did not allow for high-quality refinement and the corresponding data are given only in the Supporting Information. Nevertheless, the structural arrangement of 7 completely fits that revealed for the congeners 1, 4, and 8. The general motif of these compounds is essentially similar to that found for closely related clusters bearing alkynyl ligands with aromatic substituents.⁹ The complexes 1, 4, and 8 contain a tetranuclear {Au₃Cu} metal core stabilized by a tridentate phosphine. The copper ions in these compounds are coordinated to three alkynyl C≡C bonds and additionally bound to the gold atoms, thus forming a trigonal-pyramidal metal framework.

The Au–Au and Au–Cu distances in the pyramidal fragment (see the caption to Figure 1) are generally shorter than the sum of the corresponding of van der Waals radii (3.32 Å for Au–Au and 3.06 Å for Au–Cu), indicating the presence of effective metallophilic interactions. The listed bond lengths are not exceptional and fall in the range found for analogous contacts in the related bimetallic compounds.^{6b,c,9a,19} The copper atoms are bound to the AuC₂R moieties in an asymmetric manner that results in discrimination of the Au–Cu distances. This trend is particularly visible in the clusters with hydroxyaliphatic alkynes, in each of which the elongated Au(1)–Cu(1) separations (3.0850(16) and 3.0606(6) Å in 4 and 8, respectively) point to a considerable weakening of the metal–metal bond network in this direction. The corresponding Cu(1)–C(2) bond lengths are also noticeably affected by this structural feature and were found to be 2.215 and 2.200 Å in 4 and 8, while the Cu(1)–C(4) and Cu(1)–C(6) contacts do not exceed 2.145 Å. The distortions observed in the complexes 4 and 8 are very probably caused by intramolecular O…H–O hydrogen bonding that is clearly evidenced by the short contacts of the O(1)–O(2) and O(1)–O(3) oxygen atoms, which lie in the range 2.760–2.893 Å (for details see Tables S2 and S3 in the Supporting Information).

The ESI-MS of 1-8 display the signals of a singly charged $[HC(PPh_2)_3Au_3Cu(C_2R)_3]^+$ cation, the m/z values and isotopic patterns of which exactly fit the proposed stoichiometry (Figure S2, Supporting Information). The solution NMR data obtained for 1-8 show that these clusters retain the structure found in the solid state, which corresponds to the absence of structural distortions induced by the crystal cell packing and hydrogen bonding. The latter effect may be 'neutralized" by fast intramolecular scrambling of the alkynyl ligands involved in the hydrogen-bond network. The ${}^{31}P{}^{1}H{}$ NMR spectra of 1-8 display singlet resonances of equivalent phosphorus atoms of the triphosphine ligands in a narrow range from 39.7 to 41.2 ppm that matches the idealized C_3 symmetry group of the complexes under study. The ¹H NMR spectra of 1-8 fit well the structural pattern shown in Scheme 1 and the solid-state structures of 1, 4, 7, and 8. In the low-field area (6.1-8.0 ppm) these spectra display a typical set of signals corresponding to the protons of the triphosphine ligands-the quartet around 6.1-6.6 ppm is assigned to the CH group of tppm and the multiplets in the region 7.1-8 ppm are generated by the protons of the phosphine phenyl rings (see the Experimental Section and Figures S3-S10 (Supporting Information)). The high-field group of resonances represents the aliphatic hydrocarbon substituents of the equivalent $\{PAu(C_2R)\}\$ moieties (except for complex 8, which contains only aromatic alkynyl substituents). It is has to be noted that in



Figure 1. Molecular views of the cations of 1, 4, and 8. Counterions and hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) are as follows. For 1: Au(1)-Au(2) = 3.2657(5), Au(1)-Au(3) = 3.1102(6), Au(2)-Au(3) = 3.2413(6), Au(1)-Cu(1) = 2.8557(14), Au(2)-Cu(1) = 2.9697(16), Au(3)-Cu(1) = 2.9818(19), C(2)-Cu(1) = 2.170(10), C(4)-Cu(1) = 2.093(16), C(6)-Cu(1) = 2.153(17). For 4: Au(1)-Au(2) = 3.1319(6), Au(1)-Au(3) = 3.1940(6), Au(2)-Au(3) = 3.2309(6), Au(1)-Cu(1) = 3.0850(16), Au(2)-Cu(1) = 2.9184(15), Au(3)-Cu(1) = 3.0133(17), Cu(1)-C(2) = 2.215(13), Cu(1)-C(4) = 2.122(12), Cu(1)-C(6) = 2.104(12). For 8: Au(1)-Au(2) = 3.2291(3), Au(1)-Au(3) = 3.1973(3), Au(2)-Au(3) = 3.1700(3), Au(1)-Cu(1) = 3.0606(6), Au(2)-Cu(1) = 2.9196(9), Au(3)-Cu(1) = 2.8931(8), Cu(1)-C(2) = 2.200(5), Cu(1)-C(4) = 2.145(6), Cu(1)-C(6) = 2.114(6).

the case of 3 the methyl protons of the $-C(CH_3)_3$ fragments appear as two signals with a 2:1 intensity ratio. This is very probably caused by the restricted rotation of bulky $-C(CH_3)_3$ groups around the $C_2-C(CH_3)_3$ bond, which however does not result in loss of the complex total symmetry.

As an extension of the synthetic studies, we modified the reaction shown in Scheme 1 and used the Cu^I halides instead of $[Cu(NCMe)_4]^+$ for the preparation of related bimetallic compounds, as the CuHal salts demonstrate a well-known affinity toward metal- σ -coordinated alkynyl fragments.²⁰ Indeed, in the case of an alkynyl ligand with a diphenylmethanolyl group the halide derivatives of the complex **8** were successfully isolated as white crystalline materials (Scheme 2). The

Scheme 2. Synthesis of the Clusters 9 and 10^{a}



 $^a\mathrm{Conditions:}$ (a) $\mathrm{CH_2Cl_2/acetonitrile,}$ 298 K; (b) acetone; 298 K. Yields: 71–90%.

chloride- and bromide-containing compounds [HC- $(PPh_2)_3Au_3Cu(C_2C_{13}H_{10}OH)_3Cl]$ (9) and [HC- $(PPh_2)_3Au_3Cu(C_2C_{13}H_{10}OH)_3Br]$ (10) were prepared either through a direct self-assembly in the presence of the Cu^I salts or upon treatment of the parent cluster 8 with a stoichiometric amount of the corresponding tetrabutylammonium halide.

The X-ray crystal structures of the neutral complexes 9 and 10 (Figure 2 and Figure S1 (Supporting Information) for ORTEP views) were found to keep unchanged the general structural motif of these tetranuclear clusters. However, it was revealed that the intact CuHal (Hal = Cl, Br) molecules are bound to the π systems of the alkynyl ligands, which results in insertion of the halide ions into the cluster core and



Figure 2. Molecular views of complexes 9 and 10. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å)are as follows. For 9: Au(1)-Au(2) = 3.0266(4), Au(1)-Au(3) = 3.2250(4), Au(2)-Au(3) = 3.1717(4), Cu(1)-Cl(1) = 2.314(2), C(2)-Cu(1) = 2.101(8), C(3)-Cu(1) = 2.075(8), C(4)-Cu(1) = 2.162(8), C(5)-Cu(1) = 2.216(7). For 11: Au(1)-Au(2) = 3.0396(7), Au(1)-Au(3) = 3.2603(7), Au(2)-Au(3) = 3.1950(7), Cu(1)-Br(1) = 2.424(2), C(2)-Cu(1) = 2.151(10), C(3)-Cu(1) = 2.166(12), C(4)-Cu(1) = 2.187(10), C(5)-Cu(1) = 2.307(11).

considerable distortion of its architecture in comparison to the cationic congeners 1-8. In these structures only two alkynyl units are involved in Cu- π -C=C bonding with the values of Cu-C distances falling in the same range as those for 1, 4, and 8. However, in 9 and 10 the shortest distance between the third Au-C \equiv C- moiety and the copper atom (Cu(1)-C(6)) exceeds 3.45 Å, indicating the absence of an appreciable interaction. In line with this observation no Au-Cu metallophilic bonds were found in both 9 and 10, as the corresponding distances are longer than 3.45 Å. The aurophilic interactions are still retained within the Au₃ triangles, as the Au-Au bond lengths range from 3.0266(4) to 3.2603(7) Å. These significant structural changes evidently arise from insertion of the halide ion into the cavity formed by the alkynyl ligands that also results in substitution of the O…H-O hydrogen-bonding network for a Hal…H-O network. This is clearly demonstrated by the values of the Hal···H distances, which fall in the range 2.4-2.5 Å (for details see Tables S4 and S5 in the Supporting Information).

The ESI-MS of 9 and 10 are identical with that of 8 and show the dominating signal of a singly charged [HC- $(PPh_2)_3Au_3Cu(C_2C_{13}H_{10}OH)_3]^+$ molecular cation formed under the conditions of the ESI experiment. The roomtemperature ${}^{31}P{}^{1}H$ NMR spectra of 9 and 10 demonstrate a broadened singlet resonance that is indicative of the equivalence of all phosphorus atoms. The symmetrization of the structures found for 10 and 11 in solid state is probably a result of the fast dynamic process, which involves coordination-decoordination of the CuHal fragment and its inramolecular "merry-go-round" movement inside the tris-(alkynylgold) cluster core. The ¹H NMR spectra also match well this hypothesis and consist of two groups of signals corresponding to the aromatic and OH protons of the equivalent alkynyl ligands and those of the triphosphine phenyl rings (Figures S11 and S12 in the Supporting Information). In general the NMR spectral patterns observed for 9 and 10 resemble closely that of the parent cluster 8, which also indicates higher symmetry of the halide derivatives in solution in comparison to the solid state.

Photophysical Properties. Solution. All complexes studied display weak to moderate emission in solution at room temperature. The spectroscopic and luminescence characteristics of 1-10 in solution are given in Table 1 and Figure S13 (Supporting Information). These properties of 1-10 are similar to those demonstrated by their relatives containing alkynyl ligands with aromatic substituents.^{9a} The absorption spectra are determined by the low-energy electronic transitions (350-450 nm) centered in the cluster core and the high-energy IL transitions (λ < 350 nm) localized at the alkynyl and phosphine ligands.^{9a} The complexes show yellow-orange emission (λ_{em} 580–671 nm) with quantum yields in the 0.003-0.046 range. In comparison to 1-10 their Au-Cu close congeners bearing aromatic alkynes demonstrate systematically a blue shift of luminescence maxima (560-580 nm) but very similar quantum efficiencies (0.007-0.034) and lifetimes as well $(1.0-2.8 \ \mu s)$.^{9b} Moreover, the trinuclear Au(I) complexes [Au₃(tppm)Hal₃] exhibit similar photophysical characteristics.^{19a} The excited-state lifetimes in the microsecond domain together with substantial Stokes shifts point to the phosphorescent nature of the emission.

Solid State. Much more interesting behavior is observed in the solid phase, where the luminescence quantum yield is substantially higher (approaching 60%) and the complexes

Table 1. Photophysical Properties of 1-10 in Solution^a

	$\lambda_{abs}, nm (10^{-3}\varepsilon, cm^{-1} M^{-1})$	$\lambda_{\rm ex}$ nm	λ _{em} , nm	$ au_{ m obs},\ \mu { m s}^{b}$	$ au_{ m obs}, \ \mu { m s}^c$	Φ , % ^b	Φ, %'
1	296 (21) sh; 319 (14); 388 (1)	332; 397	656	2.3	0.9	2.1	0.6
2	295 (16) sh; 320 (10); 389 (1)	333; 398	655	8.2	0.9	2.7	0.7
3	314 sh (23); 372 (2)	302; 339; 389	631	1.9	1.1	1.6	0.8
4	297 (22.1) sh; 318 (16.8) sh; 377 (0.8)	305; 335; 393	579	4.0	2.5	3.5	2.0
5	296 (31.5) sh; 318 (23) sh; 380 (2)	307; 335 sh; 394	618	4.1	2.5	0.3	0.2
6	297 (174) sh; 318 (12); 385 (1)	300; 330 sh; 394	580	3.5	2.5	3.7	1.8
7	296 (15)sh; 317 (12) ; 378 (1)	302; 333 sh; 387	587	2.4	1.5	1.9	0.9
8	296 (19) sh; 317 (14); 382 (1)	334 sh; 389	644	5.9	2.9	4.6	2.1
9	296sh (19); 317 (14) ; 382 (1)	334 sh; 389	644	1.9	1.7	1.1	0.9
10	296 sh (19); 317 (14); 382 (1)	334 sh; 389	644	1.8	1.5	1.0	0.7

^{*a*}Conditions: CH₂Cl₂, 298 K, λ_{ex} 385 nm. ^{*b*}Degassed solution (average error ca. 5%). ^{*c*}Aerated solution (average error ca. 5%).

bearing the alkyne ligand with R = diphenylmethanolyl (8–10) show distinct vapochromic behavior upon exposure to polar solvent vapors. The photophysical data for compounds 1–10 in the solid state are given in Table 2, and the absorption and emission spectra of complexes 8–10 are given in Figures 3 and 4 and Figure S14 (Supporting Information). The samples of 1–7 give strong absorption bands at ca. 300 nm and relatively weak bands in the 350–450 nm range, which may be assigned

Table 2. Photophysical Properties of 1-10 in the Solid State^{*a*}

	$\lambda_{\rm em}$, nm				
	$\lambda_{\rm abs}$, nm	298 K	77 K	$\tau_{\rm obs}(298~{\rm K}),~\mu{\rm s}^b$	Ф(298 К), %
1	323, 383	560	560	3.0 (1); 8.4 (0.6)	2.8
2	335, 430 sh	590	580	3.0 (1); 8.4 (0.9)	2.6
3	313, 373 sh	597	546	2.7 (1); 10.2 (0.56)	2.5
4	314, 379	543	548	9 (0.6); 23 (1.0)	44
5	316, 390 sh	583	588	20	13
6	320, 384	546	540	20 (0.83); 9 (1.0)	48
7	315, 384	567	569	41 (1); 21 (0.63)	22
8 ^c	317, 374 sh	557	566	22.3 (1); 9.6 (0.55)	20
8^d	290, 378	501	476	21	60
8 ^e	290, 378	501		22	80
9 ^c	320	550	561	24 (1); 9 (0.45)	13
9 ^f	300	480		1.4 (1); 8.5 (0.15)	5
9 ^g	300	478		1.4 (1); 8.5 (0.05)	18
9^h	300	490		1.9 (1); 12 (0.2)	12
10 ^c		550	561	20 (1); 6 (0.45)	
10^e		480	479	1.7 (1); 10 (0.1)	
10 ^g	293	480		1.6 (1); 10 (0.07)	22
10^{h}		491		1.8 (1); 12 (0.25)	

^{*a*}Conditions: 25 °C, λ_{ex} 385 nm. Relative intensities of exponents for the double-exponential decays are given in parentheses. ^{*b*}Average error ca. 10%. ^{*c*}Amorphous powder, solvent free. ^{*d*}Amorphous powder, exposed to MeOH. ^{*e*}Crystalline solvates with MeOH. ^{*f*}Amorphous powder, exposed to acetone. ^{*g*}Crystalline solvates with acetone. ^{*h*}Amorphous powder, exposed to THF.



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Figure 3. (left) Solid-state absorption and emission spectra of 8 (λ_{ex} 385 nm; 298 and 77 K). (right) Appearance of 8 under UV excitation (λ_{ex} 254 nm).



Figure 4. (left) Solid-state absorption and emission spectra of 9 (λ_{ex} 385 nm). (right) Appearance of 9 under UV excitation (λ_{ex} 254 nm). The asymmetry of the emission band of THF-treated complex 9 is a result of incomplete solvation.

to IL and intracore electron transitions analogously to interpretation of the UV-vis spectra in solution. Similar to the properties of solution the solid-state samples display a Stokes shift of ca. 200 nm and excited-state lifetimes in the microsecond domain. However, the solid-state emission shows double-exponential decay with substantially higher values of the lifetimes, which are up to 41 μ s in the case of 7. The quantum yields for unsolvated solids display substantial variations for different compounds ranging from 0.0265 (complex 3) to 0.48 (complex 6). It is interesting that the complexes bearing alkynyl ligands without hydroxyl groups as substituents show the lowest values of quantum yields. A substantial increase in the emission efficiency for the complexes containing hydroxyalkynyl ligands is very probably related to intra- and intermolecular hydrogen bonding interactions in the solid state that blocks vibrational nonradiative relaxation of the excited states

The emission spectra for complexes 1-11 were also measured at 77 K (see Table 2 and Figure S14 (Supporting Information)). All compounds studied display narrowing of the emission band at 77 K and a relatively small shift of the emission maxima, which does not exceed 11 nm for the most complexes, except for 3 and 8c. It is worth noting that in all cases the low-temperature emission bands are well under the contour of the room-temperature spectra. This type of behavior is compatible with the changes in population of vibrational levels of the ground state and relaxed excited states upon cooling the systems without variations in the nature of emitting chromophoric centers.

Compounds 8-10 display substantial variation of their photophysical characteristics upon absorption of polar organic

solvents. For example, treatment of 8 with methanol vapors for 30 min results in a ca. 50 nm hypsochromic shift of absorption and emission bands and is accompanied by a 3-fold increase of the luminescence intensity, reaching a value of 60%. The effect is clearly visible by the naked eve upon irradiation of the samples with UV light (see Figure 3). It is worth noting that the short exponent of the emission ($\tau = 9.6 \ \mu s$) observed in the starting sample disappear to leave only a long-lived exponent (τ = 21 μ s). In turn, interaction of the solvent-free samples of 9 and 10 with acetone and THF vapors also gives a hypsochromic shift of the corresponding emission bands for 60-80 nm (see Figure 4 and Figure S15 (Supporting Information)) and leads to a substantial drop in the values of the both short and long exponents of emission decay. It has to be also noted that crystalline samples obtained from the solvent mixtures containing methanol, acetone, and THF, respectively, display nearly identical photophysical characteristics in comparison to the samples obtained by saturation of the solvent-free solids with the solvent vapor (see Table 2 and Figure S14 (Supporting Information)). Unfortunately, the very high solubility of 8 in acetone and THF prevents observation of solid-state vapochromism in these particular cases.

Vapochromic behavior was observed for a range of transitionmetal complexes and has been recently reviewed.²¹ Changes in the nature and energy of the orbitals responsible for the emission of the solid-state samples exposed to solvent vapors (or volatile organic compounds, VOC) stem from very different reasons, among which the most typical are metal-VOC bonding, ^{8c,h,22} breaking/formation of metallophilic bonds, ^{7,86,23} $\pi-\pi$ stacking and donor-acceptor bonding²⁴ between VOC and emitter molecules, hydrogen bonding,²⁵ and, rarely, reversible isomerization^{6d,8a,26} induced by the insertion of a VOC in the crystal lattice. The vapochromic d¹⁰ complexes of the copper subgroup as well as d⁸ platinum complexes are VOC responsive mostly due to the variations in intra- or intermolecular metal-metal distances upon VOC absorption. In 8 the chromophore center $\{Cu(AuC_2R)_3\}$ cluster core seems to be rather stable and does not demonstrate appreciable variations in metallophilic bonding in comparison to its congeners (4-7), which do not display vapochromism and do not contain polar solvent molecules in the crystal lattices. However, a clearly visible hydrogen-bonding interaction between methanol and hydroxyl groups of the alkynyl substituents was found in the solid state structure (see Figure S16 in the Supporting Information). This hydrogen bonding is evidently an electron-withdrawing interaction relative to the chromophoric center, which lowers the energy of the corresponding ground-state orbitals and eventually results in a blue shift of emission in these types of compounds.9a,27 Another particular feature of the vapochromic phases is also worth noting. The solid phases formed from the solution in the absence of methanol are X-ray amorphous in contrast to the crystalline phase obtained from the methanol-containing solutions. The crystallographic properties of 8 in the solid state were monitored upon treating the powder with methanol vapor. Figure 5 shows variations in the X-ray powder diffraction patterns of cluster 8 before and after exposure to methanol vapors. The powder obtained from dichloromethane solution and thoroughly dried in vacuo is X-ray amorphous and displays weak luminescence with the spectroscopic parameters given in Table 2 and the spectra shown in Figure 3. This sample was then subjected to vapors of methanol for 1 h at room temperature, which results in a slight change of the sample



Figure 5. Powder X-ray diffraction patterns of cluster 8: the solvent-free powder, the powder treated with MeOH vapors for 1 h, and the pattern calculated from the single-crystal data.

color and drastic variation in the sample luminescence parameters (see above). An X-ray powder diffraction study of the solvated sample shows that reorganization of the solid occurred to give the crystalline phase, which displays a diffraction pattern closely analogous to that calculated for the single-crystal analysis of 8 (Figure 5). The data obtained clearly indicate that the observed effect of the solvent absorption on the emission characteristics of the solid phases may be dictated not only by the intermolecular interaction between isolated solvent and emitter molecules but also by the far-order cooperative effects, which distinguish the crystalline and amorphous solids. This can be of particular importance for the vapochromism of 9, where an X-ray crystallographic study did not reveal any significant interaction of the solvent molecule (acetone) with the chromophoric center (see Figure S16 in the Supporting Information), which could change the energy of molecular orbitals responsible for the phosphorescence observed. It is also worth noting that an X-ray powder diffraction study of the acetone absorption by the amorphous samples of 9 and 10, respectively, display essentially similar structural transformations (amorphous to crystalline), as indicated by the diffraction patterns shown in Figure S17 (Supporting Information). Interestingly, complex 8 demonstrates selectivity to methanol, as ethanol vapors have no effect on the solid-state emission of the solvent-free sample, pointing to the inability of ethanol to promote formation of the solvated crystalline phase due to its different molecular size. This discrimination between two close homologues is an additional indication of the solid-state phase transformation, responsible for the changes in luminescence.

Solvation of the complex 8 is virtually irreversible, as a prolonged vacuum does not have any appreciable effect on the properties of the sample treated with MeOH vapors. The clusters 9 and 10 tend to lose slowly absorbed solvent molecules. However, complete reversibility could not be achieved even upon exposure of these compounds to high vacuum and pure solvent-free systems were not observed.

CONCLUSION

A series of heterometallic gold–copper complexes based on tridentate phosphine and alkynyl ligands with aliphatic and hydroxyaliphatic substituents was synthesized and structurally characterized. It was shown that weak interactions—intramolecular hydrogen bonding of the hydroxyaliphatic substituents as well as insertion of halide anions—may result in considerable structural distortions of the central heterometallic

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cluster core. The compounds obtained display moderate to weak phosphorescence in solution and considerably higher triplet emission in the solid state. It was found that the complexes 8-10 containing an alkyne ligand with R = diphenylmethanolyl display vapochromic behavior upon exposure of the solvent-free X-ray amorphous solid samples to polar VOCs (methanol, THF, acetone). The VOC absorption results in a visible hypsochromic shift of emission of 50–70 nm that opens the possibility for the use of these compounds in VOC sensing devices. The vapochromism observed may be tentatively ascribed to the formation of a structurally ordered phase upon absorption of acetone and THF by an X-ray amorphous solid.

ASSOCIATED CONTENT

Supporting Information

Tables, text, figures, and CIF files giving X-ray crystallographic for 1, 4, and 7–10, ESI-MS spectra of 1–9, and additional NMR, absorption and emission spectroscopic data. This material is available free of charge via the Internet at http:// pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) (a) Zhang, Q.; Zhou, Q.; Cheng, Y.; Wang, L.; Ma, D.; Jing, X.; Wang, F. Adv. Mater. 2004, 16, 432-436. (b) Che, C.-M.; Lai, S.-W. Luminescence and Photophysics of Gold Complexes. In Gold Chemistry; Mohr, F., Ed. Wiley-VCH: Weinheim, Germany, 2009; pp 249-282. (c) Czerwieniec, R.; Hofbeck, T.; Crespo, O.; Laguna, A.; Gimeno, M. C.; Yersin, H. Inorg. Chem. 2010, 49, 3764-3767. (d) Au, V. K.-M.; Wong, K. M.-C.; Tsang, D. P.-K.; Chan, M.-Y.; Zhu, N.; Yam, V. W.-W. J. Am. Chem. Soc. 2010, 132, 14273-14278. (e) Czerwieniec, R.; Yu, J.; Yersin, H. Inorg. Chem. 2011, 50, 8293-8301. (f) Hashimoto, M.; Igawa, S.; Yashima, M.; Kawata, I.; Hoshino, M.; Osawa, M. J. Am. Chem. Soc. 2011, 133, 10348-10351. (g) He, X.; Yam, V. W.-W. Coord. Chem. Rev. 2011, 255, 2111-2123. (h) Lu, W.; Kwok, W.-M.; Ma, C.; Chan, C. T.-L.; Zhu, M.-X.; Che, C.-M. J. Am. Chem. Soc. 2011, 133, 14120-14135. (i) Hsu, C.-W.; Lin, C.-C.; Chung, M.-W.; Chi, Y.; Lee, G.-H.; Chou, P.-T.; Chang, C.-H.; Chen, P.-Y. J. Am. Chem. Soc. 2011, 133, 12085-12099.

(2) (a) Fernandez, E. J.; Laguna, A.; Lopez-de-Luzuriaga, J. M. Dalton Trans. 2007, 1969–1981. (b) López-de-Luzuriaga, J. M. Luminescence of Supramolecular Gold-Containing Materials. In *Modern Supra*- molecular Gold Chemistry; Laguna, A., Ed.; Wiley-VCH: Weinheim, Germany, 2008; pp 347-402.

(3) (a) Wei, Q.-H.; Zhang, L.-Y.; Yin, G.-Q.; Shi, L.-X.; Chen, Z.-N. J. Am. Chem. Soc. 2004, 126, 9940–9941. (b) Crespo, O.; Gimeno, M. C.; Laguna, A.; Larraz, C.; Villacampa, M. D. Chem. Eur. J. 2007, 13, 235–246. (c) Yu, S.-Y.; Sun, Q.-F.; Lee, T. K.-M.; Cheng, E. C.-C.; Li, Y.-Z.; Yam, V. W.-W. Angew. Chem., Int. Ed. 2008, 47, 4551–4554. (d) Qiao, J.; Shi, K.; Wang, Q.-M. Angew. Chem., Int. Ed. 2010, 49, 1765–1767.

(4) Silvestru, C. Gold-Heterometal Interactions and Bonds. In *Modern Supramolecular Gold Chemistry*; Laguna, A., Ed.; Wiley-VCH: Weinheim, Germany, 2008; pp 181–295.

(5) (a) Yip, S.-K.; Chan, C.-L.; Lam, W. H.; Cheung, K.-K.; Yam, V. W.-W. *Photochem. Photobiol. Sci.* **2007**, *6*, 365–371. (b) Koshevoy, I. O.; Karttunen, A. J.; Tunik, S. P.; Jänis, J.; Haukka, M.; Melnikov, A. S.; Serdobintsev, P. Y.; Pakkanen, T. A. *Dalton Trans.* **2010**, *39*, 2676–2683.

(6) (a) Xie, Z.-L.; Wei, Q.-H.; Zhang, L.-Y.; Chen, Z.-N. Inorg. Chem. Commun. 2007, 10, 1206–1209. (b) Manbeck, G. F.; Brennessel, W. W.; Stockland, J.; Robert, A.; Eisenberg, R. J. Am. Chem. Soc. 2010, 132, 12307–12318. (c) Koshevoy, I. O.; Lin, C.-L.; Karttunen, A. J.; Jänis, J.; Haukka, M.; Tunik, S. P.; Chou, P.-T.; Pakkanen, T. A. Chem. Eur. J. 2011, 17, 11456–11466. (d) Koshevoy, I. O.; Chang, Y.-C.; Karttunen, A. J.; Haukka, M.; Pakkanen, T.; Chou, P.-T. J. Am. Chem. Soc. 2012, 134, 6564–6567. (e) Koshevoy, I. O.; Chang, Y.-C.; Karttunen, A. J.; Selivanov, S. I.; Jänis, J.; Haukka, M.; Pakkanen, T. A.; Tunik, S. P.; Chou, P.-T. Inorg. Chem. 2012, 51, 7392–7403.

(7) Lasanta, T.; Olmos, M. E.; Laguna, A.; Lopez-de-Luzuriaga, J. M.; Naumov, P. J. Am. Chem. Soc. **2011**, 133, 16358–16361.

(8) (a) Cariati, E.; Bu, X.; Ford, P. C. Chem. Mater. 2000, 12, 3385–3391. (b) Fernandez, E. J.; Lopez-de-Luzuriaga, J. M.; Monge, M.; Montiel, M.; Olmos, M. E.; Perez, J.; Laguna, A.; Mendizabal, F.; Mohamed, A. A.; Fackler, J. P. J. Inorg. Chem. 2004, 43, 3573–3581. (c) Katz, M. J.; Ramnial, T.; Yu, H.-Z.; Leznoff, Daniel B. J. Am. Chem. Soc. 2008, 130, 10662–10673. (d) Strasser, C. E.; Catalano, V. J. J. Am. Chem. Soc. 2010, 132, 10009–10011. (e) Laguna, A.; Lasanta, T.; Lopez-de-Luzuriaga, J. M.; Monge, M.; Naumov, P.; Olmos, M. E. J. Am. Chem. Soc. 2010, 132, 456–457. (f) Lim, S. H.; Olmstead, M. M.; Balch, A. L. J. Am. Chem. Soc. 2011, 133, 10229–10238. (g) Rawashdeh-Omary, M. A.; Rashdan, M. D.; Dharanipathi, S.; Elbjeirami, O.; Ramesh, P.; Dias, H. V. R. Chem. Commun. 2011, 47, 1160–1162. (h) Lefebvre, J.; Korčok, J. L.; Katz, M. J.; Leznoff, D. B. Sensors 2012, 12, 3669–3692.

(9) (a) Shakirova, J. R.; Grachova, E. V.; Gurzhiy, V. V.; Koshevoy, I. O.; Melnikov, A. S.; Sizova, O. V.; Tunik, S. P.; Laguna, A. *Dalton Trans.* **2012**, *41*, 2941–2949. (b) Shakirova, J. R.; Grachova, E. V.; Melekhova, A. A.; Krupenya, D. V.; Gurzhiy, V. V.; Karttunen, A. J.; Koshevoy, I. O.; Melnikov, A. S.; Tunik, S. P. *Eur. J. Inorg. Chem.* **2012**, 4048–4056.

(10) Coates, G. E.; Parkin, C. J. Chem. Soc. 1962, 3220-3226.

(11) Stützer, A.; Bissinger, P.; Schmidbaur, H. Chem. Ber. 1992, 125, 367–372.

(12) APEX2 - Software Suite for Crystallographic Programs; Bruker AXS, Madison, WI, 2009.

(13) Sheldrick, G. M. Acta Crystallogr., Sect. A 2008, A64, 112-122.

(14) Farrugia, L. J. J. Appl. Crystallogr. 1999, 32, 837–838.

(15) Sheldrick, G. M. SADABS-2008/1 - Bruker AXS area detector scaling and absorption correction; Bruker AXS, Madison, WI, 2008.

(16) Spek, A. L. PLATON, A Multipurpose Crystallographic Tool; Utrecht University, Utrecht, The Netherlands, 2005.

(17) Wrighton, M. S.; Ginley, D. S.; Morse, D. L. J. Phys. Chem. 1974, 78, 2229-2233.

(18) Kubelka, P.; Munk, F. Z. Tech. Phys. 1931, 12, 593-601.

(19) (a) Xiao, H.; Weng, Y.-X.; Wong, W.-T.; Mak, T. C. W.; Che, C.-M. J. Chem. Soc, Dalton Trans. **1997**, 221–226. (b) Bardaji, M.; Laguna, A.; Jones, P. G.; Fischer, A. K. Inorg. Chem. **2000**, 39, 3560– 3566. (c) He, X.; Cheng, E. C.-C.; Zhu, N.; Yam, V. W.-W. Chem. Commun. **2009**, 4016–4018. (d) Tong, G. S. M.; Kui, S. C. F.; Chao, H.-Y.; Zhu, N.; Che, C.-M. Chem. Eur. J. **2009**, 15, 10777–10789.

Organometallics

(e) Lee, T. K.-M.; Zhu, N.; Yam, V. W.-W. J. Am. Chem. Soc. 2010, 132, 17646-17648.

(20) (a) Abu-Salah, O. M.; Al-Ohaly, A. R. A. J. Chem. Soc., Dalton Trans. 1988, 2297–2300. (b) Lang, H.; del Villar, A.; Rheinwald, G. J. Organomet. Chem. 1999, 587, 284–289. (c) Lang, H.; Kocher, S.; Back, S.; Rheinwald, G.; van Koten, G. Organometallics 2001, 20, 1968– 1972. (d) Fornies, J.; Gomez, J.; Lalinde, E.; Moreno, M. T. Inorg. Chim. Acta 2008, 347, 145–154. (e) Dietrich, S.; Mansilla, N.; Hildebrandt, A.; Wetzold, N.; Rheinwald, G.; Rüffer, T.; Lang, H. J. Organomet. Chem. 2011, 696, 2491–2498.

(21) Zhang, X.; Li, B.; Chen, Z.-H.; Chen, Z.-N. J. Mater. Chem. 2012, 22, 11427-11441.

(22) (a) Albrecht, M.; Lutz, M.; Spek, A. L.; Koten, G. v. *Nature* **2000**, 406, 970–974. (b) Ley, A. N.; Dunaway, L. E.; Brewster, T. P.; Dembo, M. D.; Harris, T. D.; Baril-Robert, F.; Li, X.; Patterson, H. H.; Pike, R. D. *Chem. Commun.* **2010**, 4565–4567.

(23) (a) Mansour, M. A.; Connick, W. B.; Lachicotte, R. J.; Gysling, H. J.; Eisenberg, R. J. Am. Chem. Soc. **1998**, 120, 1329–1330. (b) Buss, C. E.; Mann, K. R. J. Am. Chem. Soc. **2002**, 124, 1031–1039. (c) Kato, M.; Omura, A.; Toshikawa, A.; Kishi, S.; Sugimoto, Y. Angew. Chem., Int. Ed. **2002**, 41, 3183–3185. (d) Drew, S. M.; Smith, L. I.; McGee, K. A.; Mann, K. R. Chem. Mater. **2009**, 21, 3117–3124. (e) Mo, L.-Q.; Jia, J.-H.; Sun, L.-j.; Wang, Q.-M. Chem. Commun. **2012**, 48, 8691–8693.

(24) (a) Abe, T.; Shinozaki, K. Inorg. Chem. 2005, 44, 849–851.
(b) Abe, T.; Suzuki, T.; Shinozaki, K. Inorg. Chem. 2010, 49, 1794– 1800. (c) Lee, C.-S.; Sabiah, S.; Wang, J.-C.; Hwang, W.-S.; Lin, I. J. B. Organometallics 2010, 29, 286–289. (d) Lee, C.-S.; Zhuang, R. R.; Sabiah, S.; Wang, J.-C.; Hwang, W.-S.; Lin, I. J. B. Organometallics 2011, 30, 3897–3900.

(25) (a) Liu, Z.; Bian, Z.; Bian, J.; Li, Z.; Nie, D.; Huang, C. Inorg. Chem. 2008, 47, 8025–8030. (b) Lu, W.; Chan, M. C. W.; Zhu, N.; Che, C.-M.; He, Z.; Wong, K.-Y. Chem. Eur. J. 2003, 9, 6155–6166. (c) Pattacini, R.; Giansante, C.; Ceroni, P.; Maestri, M.; Braunstein, P. Chem. Eur. J. 2007, 13, 10117–10128.

(26) Li, Y.-J.; Deng, Z.-Y.; Xu, X.-F.; Wu, H.-B.; Cao, Z.-X.; Wang, Q.-M. Chem. Commun. 2011, 47, 9179–9181.

(27) Koshevoy, I. O.; Lin, Y.-C.; Karttunen, A. J.; Chou, P.-T.; Vainiotalo, P.; Tunik, S. P.; Haukka, M.; Pakkanen, T. A. *Inorg. Chem.* **2009**, *48*, 2094–2102.