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Homo- and hetero-metallophilicity-driven synthesis of highly emissive and stimuli-responsive Au(I)-Cu(I) double salts

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Complex salts composed of cationic Au(I) and anionic Cu(I) species were synthesized by utilizing bis(diphenylarsino)methane (dpam) and bis(diphenylphosphino)methane (dppm) ligands. The discrete tetranuclear complexes were obtained as crystals, and the fourmetal chain, Cu---Au---Cu, was linked through homo- and hetero-metallophilic interactions. Three crystal polymorphs were obtained for the dpam- and dppm-complexes, depending on the recrystallization solvent. All the crystals exhibited intense phosphorescence (quantum yields up to 0.97) at room temperature, and the emission color of each crystal was significantly different. The crystals could be interconverted by exposure to solvent vapor, and this was accompanied by a drastic change in the emission color.

Non-covalent metal-metal interaction, also known as metallophilicity, can be utilized to generate unique structures and/or advanced functionalities.¹⁻⁴ Homo-metallophilicity, such as aurophilicity (Au···Au),² argentophilicity (Ag···Ag),³ and cuprophilicity (Cu···Cu),⁴ has been traditionally utilized for the construction of metal clusters. On the other hand, heterometallophilicity allows the generation of diverse structures and functionalities, particularly in the d¹⁰-d¹⁰ heterometallic complexes.⁵ Among them, supramolecular architectures through Au…Cu interactions have been developed for luminescent materials to utilize their phosphorescence properties. Metallophilic interactions are susceptible to external stimuli, and Au-Cu complexes exhibiting luminescent vapochromism and thermochromism have been reported so far.^{5b,d,6} On the other hand, Au-Au homo-metallophilicity and Au…Cu hetero-metallophilicity often co-exist in a complex manner,⁷ and thus the resultant structures resemble a roll of the dice.

Goshokaido-cho, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan. ^{C.} Materials Innovation Lab, Kyoto Institute of Technology, Goshokaido-cho, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan. Synthesis of complex salts in which a cationic and an anionic metal complex form an ion pair are an effective strategy for realizing hetero- and homo-metallophilic interactions. Chen and coworkers reported the self-assembly of cationic Au(I) complex and anionic Cu complex through Au…Cu interactions (Figure 1a).^{5c,d} The cationic Au(I) complex is supported by neutral *N*-heterocyclic carbene (NHC) ligands, and the Cu(I) dihalide, cyanide, or acetylide is used as the counter anion. The cation-anion metathesis reaction between the $[Au(NHC)_2]^+$ and $[CuX_2]^-$ precursors produces the complex salt, and the electrostatic attractions assist the formation of Au…Cu interactions. For further structural diversity, the co-existence of homo- and hetero-metallophilicity is desirable. However, no molecular design for such a complex using complex salts has been established yet.



Fig. 1 (a) Example of a complex salt containing heterometallophilic interactions. (b) Discrete tetranuclear complex containing mixed homo- and hetero-metallophilic interactions.

Recently, we found that diarsine ligands are effective in the precise design of inter- and intramolecular metallophilic interactions for AuCl or Cul complexes.⁸ The length and flexibility of the linker between the arsenic atoms determine the form of the metallophilic interactions. Importantly, arsenic ligands can form less directional coordinated bonds than the corresponding phosphine ligands because the lone pair of an arsenic ligand has a higher s-character than that of a phosphorus ligand.⁹ As a result, the coordination direction of arsenic ligands can be effectively adjusted to realize metallophilic interactions.

In this work, it has been shown that bis(diphenylarsino)methane (dpam)¹⁰ can support intramolecular Au…Au interaction and that the covalently bonded chlorides of the Au(I) cations can be captured by CuCl

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Electronic Supplementary Information (ESI) available: experimental details, X-ray crystallography, and results of computational calculations. Supplementary crystallographic data: no. 2064781 (α -1), 2064785 (β -1), 2064782 (γ -1), 2064786 (α -2), 2064784 (β -2), and 2064783 (γ -2). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. For ESI and crystallographic data in CIF see DOI: 10.1039/c000000x/

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to form intermolecular Au…Cu interactions (Figure 1b). Thus, the co-existence of homo-metallophilic Au…Au and heterometallophilic Au…Cu interactions was achieved in the obtained complex salt [Au₂(dpam)₂]-[CuCl₂]₂. This molecular design was expanded to the phosphorus ligand. bis(diphenylphosphino)methane (dppm). As expected, $[Au_2(dppm)_2]$ - $[CuCl_2]_2$ was readily synthesized from Au₂Cl₂(dppm)₂ and CuCl, and Au…Au and Au…Cu interactions were formed as well. Both $[Au_2(dpam)_2]$ - $[CuCl_2]_2$ and [Au₂(dppm)₂]-[CuCl₂]₂ exhibited strong luminescence with diverse colors and stimuli-responsiveness. Particularly, highly efficient near infrared (NIR) emission was observed for one of the polymorphs of [Au₂(dpam)₂]-[CuCl₂]₂, whose molecular packing was probably supported by the less directional coordination of the arsenic ligand, dpam.

Complex salts $[Au_2(dpam)_2]$ - $[CuCl_2]_2$ (1) and $[Au_2(dppm)_2]$ - $[CuCl_2]_2$ (2) were synthesized according to Scheme 1. AuCl(dms) (dms = dimethyl sulfide) was mixed with bidentate ligand dpam or dppm in dichloromethane (CH₂Cl₂) at room temperature for 1 h to afford Au₂Cl₂(L) (L = dpam or dppm). A CH₂Cl₂ solution of Au₂Cl₂(L) and additional ligand was mixed with an acetonitrile (MeCN) solution of CuCl at room temperature for 1 h to produce $[Au_2(dpam)_2]$ - $[CuCl_2]_2$ (1) and $[Au_2(dppm)_2]$ - $[CuCl_2]_2$ (2). Notably, the isolated yields were high; the total yields were 80% (1) and 89% (2).



Scheme 1. Synthesis of complex salts 1 and 2.

Single crystals suitable for X-ray diffraction (XRD) analysis were grown by the slow mixing of CH₂Cl₂ solution with poor solvents (Figure 2). Depending on the poor solvents for recrystallization, different crystals were obtained for both 1 and 2 under the same conditions. Hexane, acetonitrile (MeCN)/diethyl ether (Et₂O), and methanol (MeOH) gave the α -, β -, and γ -forms, respectively; the space groups were P-1 (α -**1**, α -**2**, and γ -**2**) and C2/c (β -**1**, γ -**1**, and β -**2**). The observed conformations were similar, except for y-2. The Au…Au (α -1: 3.1408(4) Å, β-1: 3.1636(7) Å, γ-1: 3.1192(7) Å, α-2: 3.0656(4) Å, β -**2**: 3.0835(7) Å) and Au···Cu (α -**1**: 2.7491(9) Å, β -**1**: 2.7868(7) Å, γ-1: 2.861(1) Å, α-2: 2.7705(6) Å, β-2: 2.8117(7) Å) distances were within the sum of the van der Waals radii of the atoms (Au: 2.10 Å, Cu: 1.92 Å),¹¹ indicating the coexistence of homo- and hetero-metallophilic interactions. The Au---Au interactions were supported by the ligand backbones, while the Au…Cu interactions were supported by the electrostatic interactions. These results demonstrate that the combination of methylene-linked bidentate ligands and complex salt formation is effective for realizing the co-existence of homoand hetero-metallophilic interactions. The XRD pattern of γ -2 indicated the presence of two conformations, γ -**2-1** and γ -**2-2**, as shown in Figure 2f. The structure of the y-2-1 conformer was similar to those of the α - and β -type crystals, and the Au…Au and Au…Cu distances were 2.9785(5) Å and 2.8465(6)

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Å, respectively. In contrast, the Au…Cu interaction was absent from the other conformer (γ -**2**-**2**) probably because of the 10 kg distance (4.7413(7) Å), while the Au…Au interactions (2.9594(4) Å) were present in it. We then focused on the Cu…Au…Au angles in the complexes. In the α - and β -type crystals, the angles were similar to each other: 134.50(2)° (α -**1**), 133.14(2)° (α -**2**), 140.70(2)° (β -**1**), 140.22(2)° (β -**2**). The Cu…Au…Au…Cu chain of γ -**1** was highly distorted, considering the small angle (114.99(3)°). It is probable that this distortion originated because of the less directional coordination of the arsenic atoms, as reported for some transition metal complexes.¹² In the case of the diphosphine ligand, the Cu…Au…Au…Cu chain of γ -**2** was cleaved in one conformer, while a non-distorted chain (Cu…Au…Au angle = 130.21(2)°) was present in the other.



Fig. 2 ORTEP (at 50% probability) and lengths and angles of the metallophilic interactions of **1** and **2**. Phenyl groups are shown by wireframe, and hydrogen atoms are omitted for clarity.

The photoluminescence (PL) spectra of **1** and **2** were recorded in the solid states (Table 1 and Figure 3). The α - and β -type crystals showed green and greenish-yellow emissions, respectively, and the emission colors of γ -**1** and γ -**2** were nearinfrared and white, respectively. This difference in emission wavelength (λ_{em}) can be attributed to the distance and angles of the metallophilic interactions. λ_{em} of γ -**1** was remarkably long; the emission peak was above 1100 nm. The white emission of γ -**2** was composed of two peaks that are derived from the two conformers indicated in the XRD pattern. Notably, the quantum yields (Φ) of the complexes were

Table 1. PL properties of 1 and 2.				
	$\lambda_{ m ex}^{~[a]}$ [nm]	$\lambda_{ m em}{}^{ m [b]}$ [nm]	$\pmb{\Phi}^{[c]}$	τ ^[d] [μs]
α-1	397	533	0.96	8.8
<i>B</i> -1	341	551	0.97	12.0
γ- 1	348	814	0.11	8.6
α- 2	397	522	0.91	8.8
<i>в</i> - 2	327	533	0.95	9.9
γ- 2	400	527, 624	0.82	11.8

[a] Excitation maxima corresponding to the emission maxima. [b] Emission maxima corresponding to the excitation maxima. [c] Absolute quantum yield.[d] Emission lifetimes monitored at the emission maxima.

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remarkably high even at room temperature in the solid states; $\Phi = 0.82-0.97$ (visible region) and 0.11 (near-infrared region). The µs-order emission lifetimes implied that the emissions were attributed to phosphorescence. Since phosphorescent dyes exhibiting highly efficient solid-state emission at room temperature are desired for luminescent materials, this series of complexes are promising. In particular, γ -1, which exhibits intense emission in the near-infrared region,¹³ is beneficial for bio-imaging¹⁴ because its PL spectrum reaches the second window.



Fig. 3 PL spectra of **1** and **2** in the crystalline states at room temperature. The minor peak around 500 nm of γ -**1** is derived from the crashed samples generated during the measurement.

We next examined luminescent vapochromism (Figure 4). The crystalline samples were exposed to CH₂Cl₂ or MeOH vapor for sufficient time (around one day). The powder XRD (PXRD) pattern showed that the β - and γ -crystals of **1** and **2** were converted to the α -crystals by CH₂Cl₂ vapor (Figures S1 and S2), being a good solvent. The α -forms might be more stable than the heta- and γ -forms, and thus the crystalline samples were converted to the α -forms by CH₂Cl₂ vapor regardless of the starting crystalline polymorph. Additionally, MeOH vapor converted the α -crystals of **1** and **2** to the γ crystals, while exposure to the β -crystals gave a complex mixture. MeOH was employed as a poor solvent to grow the ycrystals through recrystallization, and thus it is rational that MeOH vapor produced the γ -crystals. According to the crystalto-crystal transitions, the emission colors were green (α -1 and α -**2**), near-infrared (γ -**1**), or white (γ -**2**). The PL spectra (Figures S5 and S6) as well as the PXRD patterns were almost completely altered upon exposure to the solvent vapors, indicating that the crystal-to-crystal transitions progressed efficiently. This sharp response implies that the synthesized complexes are susceptible to a particular change in the surrounding, reflecting the characteristics of the structures in which unsupported metallophilic interactions coexists.



Fig. 4 Emission behavior of (a) **1** and (b) **2** in response to external stimuli such as solvent vapor and grinding (irradiation at 365 nm for obtaining the photographs).

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No emission ($\phi < 0.01$) was observed from **1** and **2** for all the polymorphs (α -, β -, and γ -forms) Dupoh 1granding 1716 mortar. The PXRD pattern showed significantly weakened signals after grinding, suggesting the occurrence of crystal-toamorphous transition. In the amorphous phases, the metallophilic chains responsible for the emission could be cleaved, thus turning off the emission. It is also possible that the amorphous phases gave sufficient space for molecular motions to quench the energies of the excitons. Then, exposure to CH₂Cl₂ and MeOH vapor for 1 h induced crystallization of the amorphous samples, forming the α - and y-forms, respectively, as determined from the PL spectra and PXRD patterns. After exposure to the vapors, the emission of 1 and **2** were turned on, and the emission colors were green (α -**1** and α -2), near-infrared (γ -1), or white (γ -2). This was wellconsistent with the aforementioned vapor-induced crystal-tocrystal transitions. Turn-on sensing is an important strategy to develop visually recognizable systems, and thus, the amorphous samples of 1 and 2 are promising for vapor detection.

Finally, we conducted dispersion-corrected densitv functional theory (DFT) calculations (B3LYP-D3 functional) to reveal the importance of the co-existence of homometallophilic Au…Au and hetero-metallophilic Au…Cu interactions in the electronic properties of 1 and 2. For this, we used the atomic coordination of 1 and 2 obtained from the Xray analyses. Average interaction energies between the $[Au_2(L)_2]$ and $[CuCl_2]$ moieties were obtained (Table S10). Negative E_{interact} values were observed for all the structures, indicating the presence of attractive interactions between the $[Au_2(L)_2]$ and $[CuCl_2]_2$ moieties to stabilize their structures. All the structures, except that of y-2-2, have Au…Cu coupling around 2.8 Å; at the same time, they are stabilized by attractive interactions between the $[Au_2(L)_2]$ and $[CuCl_2]$ moieties. Therefore, they exhibit hetero-metallophilicity. Although the stabilization of γ -**2-2** is comparable to that of the other conformers, it does not exhibit hetero-metallophilicity due to the lack of Au…Cu coupling around 2.8 Å.

The presence or absence of hetero-metallophilicity plays an essential role in determining the electronic properties of the frontier orbitals of 1 and 2, as shown in Figure S7. The amplitude of the frontier occupied and unoccupied orbitals appears on the $[Au_2(L)_2]$ moiety in the conformers with heterometallophilicity (*i.e.*, **1** and **2**, except γ -**2-2**). Figure S8 shows the HOMO and LUMO in α -1. In the frontier orbitals, the Aubased orbitals can overlap due to the Au…Au coupling around 3.0 Å, which can be induced by binding methylene-linked bidentate ligands to the Au cations. On the other hand, γ -2-2, with no hetero-metallophilicity, has frontier occupied orbital appearing on [CuCl₂]₂, although the LUMO has amplitude on the $[Au_2(L)_2]$ moiety. Thus, we confirmed that the heterometallophilicity in 1 and 2, except y-2-2, is responsible for their homo-metallophilicity; detailed discussion has been included in the supporting information. As listed in Table S11, timedependent DFT calculations revealed that the combination between Au-based frontier occupied and unoccupied orbitals, which can be seen in 1 and 2, except y-2-2, is responsible for

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the electronic transition, which is the first step for photoemission. On the other hand, no electronic transition with substantial oscillator strength was observed for γ -**2-2** due to the absence of the Au-based frontier occupied orbitals. Furthermore, Figure S7 shows that γ -**1** has energetically close occupied orbitals as well as energetically close unoccupied orbitals in the frontier orbital region; the orbitals are shown in Figure S9. The energetically close frontier orbitals in γ -**1**, with the smallest Cu···Au···Au angles that are unique from the other conformers with larger Cu···Au···Au angles, can contribute to the electronic transition, as seen in Table S11. This can differentiate it from the other structures in terms of the emission properties.

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In conclusion, we have synthesized Au(I)…Cu(I) double salts containing homo- and hetero-metallophilic interactions based on bidentate ligands, dpam and dppm. X-ray crystallography revealed the structures of the discrete tetranuclear complexes 1 and 2. They formed three types of crystalline polymorphs, *i.e.*, α -, β -, and γ -forms, depending on the recrystallization solvents. All the crystals exhibited remarkably strong phosphorescence at room temperature (quantum yields up to 0.97), and various emission colors were observed including near-infrared and white. Vapor-induced crystal-to-crystal transitions resulted in diverse interconversion of emission colors. Grinding the crystals in a mortar gave amorphous samples that did not exhibit emission, while CH₂Cl₂ and MeOH vapors converted the amorphous samples to the α - and γ forms crystals, respectively, turning on the emission with the corresponding colors. DFT calculations indicated that the coexistence of homo- and hetero-metallophilicity plays pivotal roles in the electronic structures responsible for the luminescence. The present work proposes a novel molecular design for highly emissive and stimuli responsive heteromultinuclear d¹⁰ complexes. We are currently investigating the detailed mechanism for the efficient emissions, phase transition behaviors, and different effects of diarsine and diphosphine ligands on the properties of this kind of complexes.

Conflicts of interest

There are no conflicts to declare.

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