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An Asymmetric Pt Diimine Acetylide Complex Providing Unique Luminescent Multinuclear Sandwich Complexes with Cu Salts

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Formation and photophysical properties of two types of sandwich complexes supported by asymmetric Pt complex units having two different acetylide moieties are reported. The asymmetric Pt complex unit was obtained via acetylide metathesis reaction between two types of symmetric Pt complexes. The reversible acetylide exchange reaction was effectively suppressed by the incorporation of Cu ion to give unique chiral Pt_4Cu_3 and achiral $Pt_2Cu_4Br_4$ sandwich complexes. The sandwich complexes exhibited moderate photoluminescnece in the solid states, whose photophysical properties were depended on the sandwich structures. These results suggest that asymmetric Pt complex units can give remarkable assembled structures by concerted effect of labile coordination bond and weak noncovalent interactions.

Reversible bond formations and interactions, such as metal–ligand coordination bond, hydrogen bond, charge transfer, π–π interaction, and metal–metal interaction, play crucial roles to construct supramolecular frameworks via self-assembly and self-sorting systems.[1] These techniques can provide not only unique higher dimensional structures but also characteristic features originating from their supramolecular structures. In particular, emissive supramolecular complexes containing Pt ions have been increasingly attracted much attention because self-assembled metallacycles often show tunable photoluminescent properties[2] and strong association of Pt complexes via Pt–Pt interaction and π–π interaction drastically altered their photophysical properties.[3] We have investigated the formation of emissive supramolecular assembly based on the reversible bond formation and noncovalent interactions.[4] In particular, we have recently created luminescent "chiral-at-cluster" complexes by the reaction of square-planar Pt complex unit having a C^C chelating ligand and pyrazolate bridging ligands with Ag ions, showing circularly polarized luminescence (CPL) originated from the chiral sandwich structure.[5]

Pt complexes having bipyridine (bpy) derivatives and two acetylide ligands have focused much attention on unique emissive properties, such as vapochromism, mechanochromism and solid state emission.[6] Numerous photophysical studies of these types of Pt complexes reveal that the emission of these complexes in solution was attributed to the mixed transition of metal-to-ligand charge transfer (MLCT) and ligand-to-ligand charge transfer (LLCT) from the excited state.[6] The acetylide ligands bound to the Pt ions also showed fluxional coordination behavior to coinage metal ions in solution, owing to reversible bond formation between acetylide moieties and additional group 11 metal ions.[7] These features of heteropolynuclear complexes are candidates for a platform of new types of emissive supramolecular assemblies.

Herein, we report intermolecular ligand exchange reactions of Pt complexes to give asymmetric Pt complexes having two different acetylide moieties and unique self-assembly structures of the asymmetric Pt complex unit. It has been reported that asymmetric Pt complexes having two different acetylide ligands were obtained by using an equimolar amount of two different acetylide ligands, resulting in a statistical mixture of the three possible products in a 1:2:1 ratio.[8] Although stepwise synthesis of asymmetric Pt diimine acetylide complexes has also been reported,[9] the acetylide metathesis in the Pt diimine acetylide systems has not been reported so far. Thus, to the best of our knowledge, this is the first example of a formation of asymmetric Pt complexes having two different acetylide ligands through the reversible acetylide exchange reaction. Furthermore, the asymmetric Pt complex units afforded both chiral and achiral luminescent assemblies with copper ions, whose stacking structures were originated from the multiple contributions of reversible bond formation and weak noncovalent interactions through crystallization process.

The asymmetric Pt complex having two different acetylide ligands can be obtained through an intermolecular acetylide exchange reaction between two different Pt complexes. When Pt complex **1aa** and Pt complex **1bb** were mixed with a 1:1 ratio in CH_2Cl_2 at room temperature for 48 h, ligand exchange reaction proceeded to afford asymmetric Pt complex **1ab** in 43% isolated yield (Fig. 1). The ligand exchange is relatively slow process and Pt complex **1ab** was

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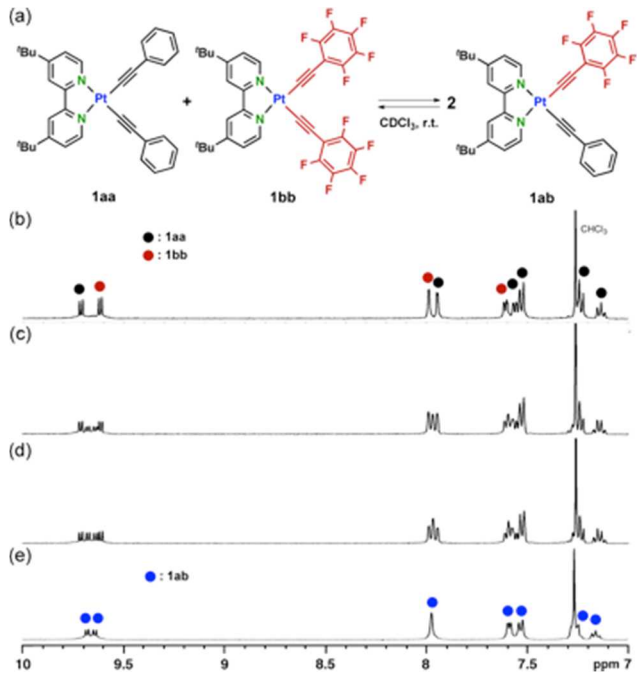

Fig. 1 (a) Schematic representation of the acetylide ligand exchange reaction. (b–e) ^{1}H NMR spectra (400 MHz, $CDCl_3$, r.t.) of (b–d) a mixture of **1aa** and **1bb** in a 1:1 ratio after mixing for (b) 5 min, (c) 24 h, (d) 48 h, and (e) asymmetric Pt complex **1ab**. (black circles: **1aa**, red circles: **1bb**, blue circles: **1ab**).

kinetically stable, resulted in isolation of the product by purification through a silica gel column chromatography technique. The formation of the Pt complexes having two different acetylide units was also confirmed by FAB-MS and elemental analyses. ^{1}H NMR measurement in $CDCl_3$ revealed that the signals corresponding to the **1ab** gradually increased and other new signals assigned to by-products and intermediates were not observed (Fig. 1b–d). The NMR spectra of the mixture did not change over 48 h, indicating that the mixture reached at the thermodynamic equilibrium state. In contrast, NMR signals of **1aa** and **1bb** gradually appeared when pure **1ab** was dissolved into $CDCl_3$ (Fig. S3). These results suggest that the ligand exchange reaction took place in the thermodynamic equilibrium state. Slight shifts of signals were observed in the ^{1}H NMR spectrum of the mixture of **1aa** and **1bb**, suggesting reversible formation of a dimer complex in solution (Fig. S4). Although any reaction intermediates were not observed in ^{1}H NMR measurements, these results suggest that the reversible acetylide ligand exchange reaction might proceed through a pre-organized dimer fashion.

Owing to the equilibrium on intermolecular acetylide exchange reaction as mentioned above, a single crystal of pure **1ab** was not obtained through condensation process from the solution. To avoid disproportionation reaction, coordination of two acetylide moieties toward copper(I) ion in a sandwich fashion is expected to hamper a formation of the dimer structure in solution. When copper salt $[Cu(CH_3CN)_4]BF_4$ was added to the solution of pure **1ab** in 1:1 ratio, ^{1}H NMR spectroscopy showed significant peak shifts, suggesting the formation of copper-adduct $[(\mathbf{1ab})Cu(CH_3CN)]BF_4$ quantitatively (Fig. S5), which was also confirmed by FAB-MS analysis. Copper-adduct $[(\mathbf{1ab})Cu(CH_3CN)]BF_4$ did not give **1aa** and **1bb** over several days. Thus, these features allowed us to obtain a single crystal of the Pt complex having two different acetylide units as a copper adduct.

The asymmetric Pt complex units can construct remarkable multinuclear Pt–Cu sandwich structure through crystallization process. The CH_2Cl_2 solution of **1ab** and $[Cu(CH_3CN)_4]BF_4$ afforded a yellow single crystal of the copper adduct suitable for X-ray crystallographic analysis. Very interestingly, the copper-adduct gave discrete quadruple stacking structure $[(\mathbf{1ab})_4Cu_3](BF_4)_3$ constructed by the four Pt complex molecules and three Cu ions, resulting the Pt–Cu–Pt–Cu–Pt–Cu–Pt alternate helical alignment of the metal ions in the crystal structure (Fig. 2). Although $[(\mathbf{1ab})_4Cu_3](BF_4)_3$ is expected to be formed in solution, the ^{1}H NMR spectrum showed the single set of the signals assigned to $[(\mathbf{1ab})Cu(CH_3CN)]BF_4$, indicating that coordination of CH_3CN to

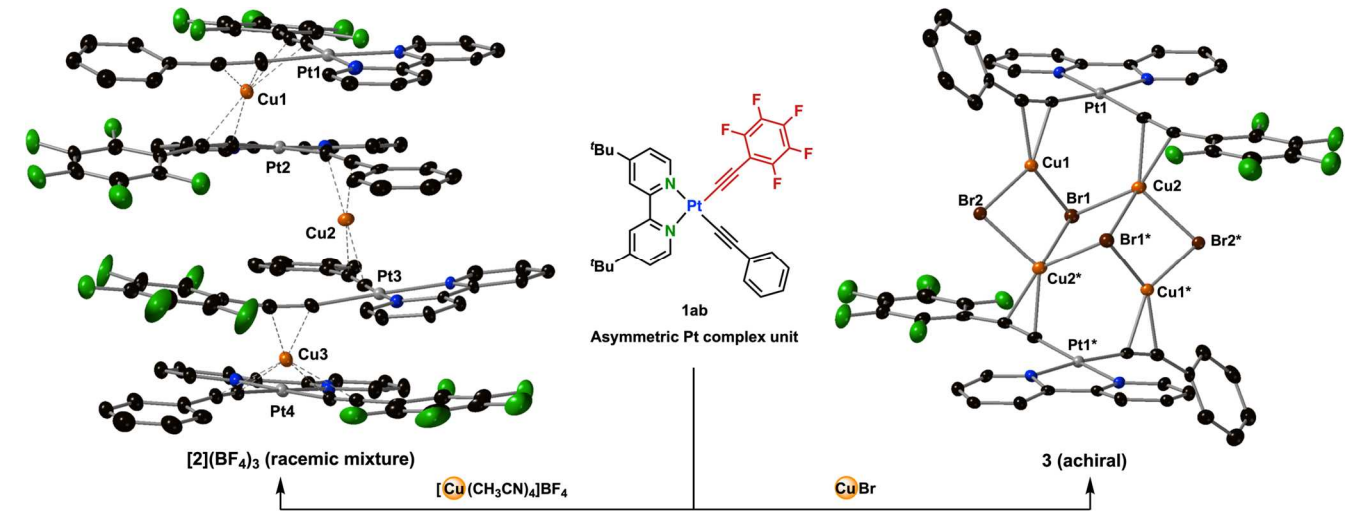

Fig. 2 ORTEP drawing of chiral Pt_4Cu_3 and achiral $Pt_2Cu_4Br_4$ complexes sandwiched by asymmetric Pt complex unit **1ab** with the atom numbering scheme (50% probability ellipsoids). Tertiary butyl groups, hydrogen atoms, anions and solvent molecules are omitted for clarity. Selected atomic distances [Å] for the Pt_4Cu_3 complex ($[\mathbf{2}](BF_4)_3$): Pt1···Cu1, 2.994(2); Cu1···Pt2, 3.394(2); Pt2···Cu2, 2.817(1); Cu2···Pt3, 2.987(1); Pt3···Cu3, 3.372(1); Cu3···Pt4, 2.963(2). The $Pt_2Cu_4Br_4$ complex (**3**): Pt1···Cu1, 3.406(1); Pt1···Cu2, 3.271(1); Cu1···Cu2, 3.307(1); Cu1–Br1, 2.4318(12); Cu1–Br2, 2.3848(11); Cu2–Br1*, 2.4170(12); Cu2–Br2*, 2.4363(12).

Cu ion effectively suppressed the self-assembled process of Pt–Cu units in solution state (Fig. S5). It has been reported that Pt diimine complexes having two acetylide units with Cu ions afforded several structural isomers owing to the fluxional nature of Pt–Cu dative bonds and π-coordination of acetylide units.[7] In addition, C_6H_5 arene unit and C_6F_5 perfluoroarene unit are known to show the van der Waals and quadrupole–quadrupole interactions.[10] The X-ray structure of Pt_4Cu_3 complex showed different coordination modes of Cu ions toward acetylide moieties, weak dative bonding of Pt ions to Cu ions (< 3.0 Å), and effective π–π stacking (< 3.5 Å) between C_6H_5 and C_6F_5 moieties. Large steric hindrance from ^{t}Bu groups on the bipyridine ligands also contributed to the twisted stacking structure and hampered the dimer formation of Pt complex moieties, affording the remarkable stacking structure. Thus, this unique stacking formation may originate from the concerted effects of labile coordination bond and weak noncovalent interactions through the crystalline process.

It should be noted that the asymmetric Pt complex units **1ab** in Pt_4Cu_3 complex [**2**](BF$_4$)$_3$ generated planar chirality, leading to the formation of chiral cluster compounds, which is classified into "chiral-at-cluster".[5] The single crystals of [**2**](BF$_4$)$_3$ contained the racemic mixture of the enantiomers and the optical resolution could not be achieved owing to less stability of the stacking structure in solution originated from fluxional nature of π-coordination of acetylide moieties toward Cu ion. Nevertheless, these results clearly demonstrated that asymmetric Pt acetylide units together with coinage metal ions could provide new synthetic route giving "chiral-at-cluster" complexes.

In addition to the "chiral-at-cluster" stacking assembly in [**2**](BF$_4$)$_3$, the asymmetric Pt complex unit also provided a sandwich-shaped Cu_4Br_4 cluster. When Pt complex **1ab** reacted with CuBr in CH_2Cl_2, the reaction mixture afforded $Pt_2Cu_4Br_4$ complex **3** as orange crystals. The X-ray structure of **3** clearly showed ladder-shaped Cu_4Br_4 cluster sandwiched by the Pt complex units, where Cu ions supported by halide bridge (Cu–Br distances: 2.3848(12)–2.4363(12) Å) and π-coordination from acetylide moieties in **1ab** (Fig. 3). Since the Pt···Cu distances in **3** are slightly longer than those in [**2**](BF$_4$)$_3$, the Mayer bond indices for **3** suggested absence of the dative bond (Table S8). Symmetric Pt acetylide complexes with Cu salts typically give 1:1 Pt–Cu complexes, where the Cu ion forms a trigonal planar geometry supported by π-coordination from two acetylide units.[7] Thus, slight difference of coordination ability between the two different acetylide units in **1ab** effectively perturbed the product structure to build up the ladder-shaped Cu_4Br_4 cluster between two Pt complex units.[11]

Numerous studies on the photophysical properties of Pt diimine acetylide complexes have been reported.[3] Therefore, we next investigated the emission properties of the asymmetric Pt acetylide complex and their Cu sandwich complexes. The reversible acetylide ligand exchange reaction leads to fine tuning of the photophysical properties of Pt complexes having two acetylide units (Fig. S8). The absorption spectra of **1aa**, **1bb** and **1ab** in $CHCl_3$ at room temperature showed intense absorption bands at ca. 250–300 nm and moderately intense bonds at ca. 350–450 nm. In particular, the absorption maximum of low-energy bands is dependent on the electronic features of the acetylide units. The Pt complex **1bb**, bearing two-electron deficient perfluoroarene units, displays an

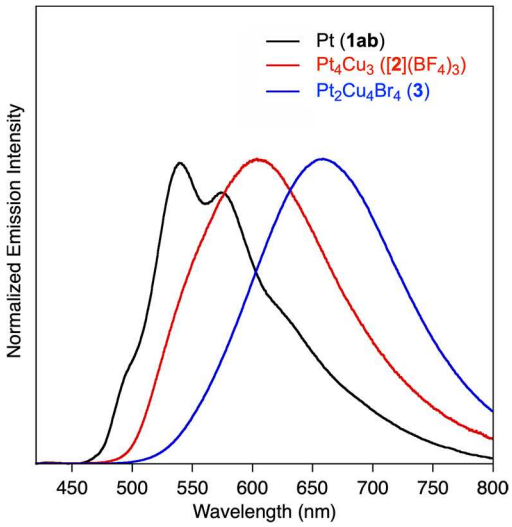

Fig. 3 Normalized emission spectra of the complexes in the solid states (λ_{ex} = 355 nm).

absorption maximum at 380 nm, while this band is red-shifted to λ_{max} = 387 nm and 396 nm for **1ab** and **1aa**, respectively. Photoluminescent properties recorded in $CHCl_3$ at room temperature also showed the same trend as those determined in the photoabsorption properties. As increasing the number of electron deficient perfluoroarene units in the Pt complex unit, the emission peaks gradually blue-shifted and the emission intensity became weaker (λ_{max} = 570 nm, Φ = 42%, and τ = 1.24 μs for **1aa**; λ_{max} = 565 nm, Φ = 20%, and τ = 0.96 μs for **1ab**; λ_{max} = 520 nm, Φ = 11%, and τ = 0.17 μs for **1bb**). In contrast to the broad emission spectrum of **1ab** in solution (Fig. S8), structured emission spectrum was observed in the solid state (λ_{max} = 539 nm, Φ = 7%, and τ = 0.28 μs (Fig. 3)). Time-dependent density functional theory (TD-DFT) calculations using CAM-B3LYP functional was performed to evaluate the nature of the major electronic transitions for the Pt complex **1ab** (Fig. S12 and Table S4). The results of calculations indicate that the low-energy bands arose mainly from the combination of ^{1}LLCT (from C_6H_5 acetylide units to π*(bpy)) and ^{1}MLCT transitions, which reasonably explains the trends of photophysical properties of the Pt complexes (**1aa**, **1ab** and **1bb**). These features are good agreements with other Pt acetylide systems.[3]

Chiral-at-cluster Cu sandwich complex [**2**](BF$_4$)$_3$ and achiral cluster **3** also showed photoluminescence in the crystalline states, whose photophysical properties were dependent on the unique structures. Incorporation of Cu ions into the asymmetric Pt complex units induced bathochromic shifts of their emission spectra (Fig. 3). The quadruple sandwich Pt_4Cu_3 complex [**2**](BF$_4$)$_3$ and $Pt_2Cu_4Br_4$ complex **3** showed orange and red emission (λ_{max} = 604 nm, Φ = 13%, and τ = 0.72 μs for [**2**](BF$_4$)$_3$; λ_{max} = 659 nm, Φ = 49%, and τ = 0.70 μs for **3**), respectively. The TD-DFT calculations of the cluster units clearly suggested that the phosphorescence of Pt_4Cu_3 complex [**2**]$^{3+}$ and $Pt_2Cu_4Br_4$ complex **3** mainly originated from ^{3}LLCT (from C_6H_5 acetylide units to π*(bpy) in the outer Pt complex unit) and a mixed state of ^{3}MLCT/^{3}XLCT (from Cu and Br

ions to π*(bpy) in the Pt complex units) excited states, respectively (Figs. S13–S14).

It was reported that some polynuclear Cu(I) assemblies show thermally activated delayed fluorescence (TADF) behavior, which includes a characteristic luminescence from thermally activated population of the lowest energy excited singlet state (S_1) via reverse intersystem crossing from the lowest energy triplet state (T_1).[12] To check this possibility from the Pt–Cu complexes, we carried out temperature-dependent photophysical studies of the complexes [**2**]$(BF_4)_3$ and **3** (Figure S10). The emission spectra measured at low temperature did not change significantly and longer emission lifetimes were observed at low temperatures owing to the effective inhibition of thermal deactivation in the excited species. Thus, these results suggest that the Pt_4Cu_3 complex [**2**]$(BF_4)_3$ and $Pt_2Cu_4Br_4$ complex **3** do not have TADF character in the photoluminescence. The interpretation was also consistent with the results of TD-DFT calculation, showing that the Pt complex units mainly contributed to the excited states.

In summary, we have revealed reversible acetylide ligand exchange reaction on a mononuclear Pt complex that can provide asymmetric Pt complexes having two different acetylide units. The asymmetric Pt complex afforded the Pt_4Cu_3 discrete quadruple stacking structure and the $Pt_2Cu_4Br_4$ sandwich complex through crystallization processes in the presence of Cu ions. This result demonstrated that self-assembly of asymmetric units can give unique supramolecular structure. A key to obtain the unique structure is thanks to the concerted weak noncovalent interactions and fluxional coordination bonds. In addition, photophysical properties of the complexes derived from the asymmetric Pt complex units can also be controlled by the incorporation of Cu ions. Therefore, self-assembly of asymmetric Pt complex units with Cu ions assisted by labile coordination bond and weak noncovalent interactions will offer a new strategy to build up unique sandwich structures showing luminescent properties, whose structures are unobtainable from symmetric components,.

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Conflicts of interest

There are no conflicts to declare.

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