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Different structural preference of Ag(I) and Au(I) in neutral and cationic luminescent heteropolynuclear platinum(II) complexes: Z (U)-shaped Pt_2M_2 type vs. trinuclear PtM_2 type†

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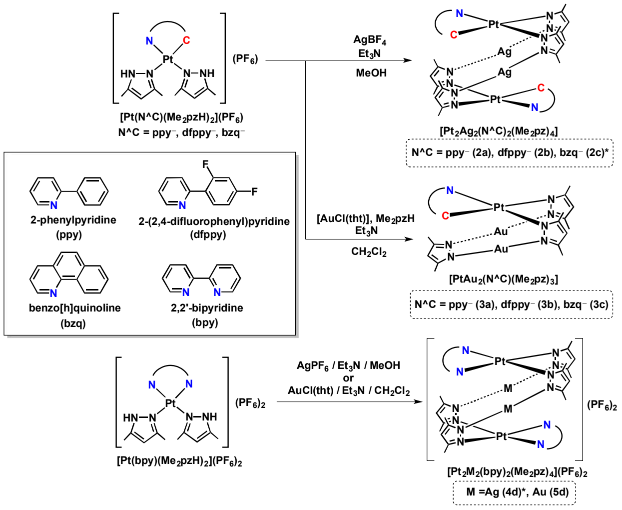
The reactions of monocationic Pt(II) complexes bearing N^C chelate ligands and Me_2pzH, $[Pt(N^{\wedge}C)(Me_2pzH)_2]PF_6$ (N^C = 2-phenylpyridinate (ppy^-), 2-(2,4-difluorophenyl)pyridinate ($dfppy^-$), benzo[*h*]quinolinate (bzq^-); Me_2pzH = 3,5-dimethylpyrazole), with Ag(I) ions gave Z (or U)-shaped neutral tetranuclear Pt_2Ag_2 complexes $[Pt_2Ag_2(N^{\wedge}C)_2(Me_2pz)_4]$, while those with Au(I) ions gave neutral trinuclear $PtAu_2$ complexes $[PtAu_2(N^{\wedge}C)(Me_2pz)_3]$. On the contrary, the reactions of dicationic Pt(II) complex bearing N^N chelate ligand and Me_2pzH, $[Pt(bpy)(Me_2pzH)_2](PF_6)_2$ (bpy = 2,2'-bipyridine), with Ag(I) and Au(I) ions both gave Z (or U)-shaped dicationic tetranuclear Pt_2M_2 complexes, $[Pt_2M_2(bpy)_2(Me_2pz)_4](PF_6)_2$ (M = Ag, Au). The structures of heteropolynuclear Pt(II) complexes were dominated by the nature of incorporated group 11 metal ions and the charge of complexes.



Scheme 1 Synthesis of $[Pt_2Ag_2(N^{\wedge}C)_2(Me_2pz)_4]$ and $[PtAu_2(N^{\wedge}C)(Me_2pz)_3]$ (N^C = ppy^-, $dfppy^-$, bzq^-) as well as $[Pt_2M_2(bpy)_2(Me_2pz)_4](PF_6)_2$ (M = Ag, Au). Asterisk denotes twisted U-shape structure.

Platinum(II) complexes containing polypyridyl ligands such as α-diimines and terpyridines are known to exhibit luminescence from various excited states depending on the nature of aromatic chelate ligands and the extent of metal-metal interactions with neighboring Pt(II) ions intermolecularly or intramolecularly.[1] The emissive state of Pt(II) complexes are very sensitive to the slight structural changes, leading to the interesting phenomena such as vapochromism, mechanochromism and thermochromism.[2] It is also known that heteropolynuclear complexes consisting of Pt(II) ions, monovalent group 11 metal ions and alkynyl or pyrazolate ligands exhibit colorful luminescence corresponding to the nature of incorporated group 11 metal ions.[3] Large difference of emission energy may be attributed to the increase of HOMO energy level in the order of Ag < Au < Cu and the large contribution of p and s orbitals of group 11 metal ions to the LUMO, which mainly consists of an in-phase combination of 6p of Pt(II) ions and *n*s and *n*p of group 11 metal ions (6p and 6s for Au(I), 5p and 5s for Ag(I), 4s and 4p for Cu(I)).[3e,3f] It is thus desired that the heteropolynuclear Pt(II) complexes bearing aromatic chelate ligands show interesting photophysical properties based on the superposition of the following characters: the characters of Pt(II) complexes bearing aromatic chelate ligands and those of heteropolynuclear Pt(II) complexes possessing tunable emission energy. Although a number of heteropolynuclear Pt(II) complexes possessing different structures have been reported so far, the examples of heteropolynuclear Pt(II) complexes bearing aromatic N^N chelate ligands or aromatic N^C chelate ligands are still limited.[3a-c] In such heteropolynuclear Pt(II) complexes, the intramolecular Pt···M and intermolecular Pt···Pt interactions and/or π-π stacking interactions of aromatic chelate ligands are expected.

We have previously reported that the reaction of $[Pt(bpym)Cl_2]$ (bpym = 2,2'-bipyrimidine) with 3,5-dimethylpyrazole (Me_2pzH) afforded a unique mononuclear Pt(II) complex, $[Pt(bpym)(Me_2pz)(Me_2pzH)]Cl$, which potentially acts as a bidentate

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† Electronic Supplementary Information (ESI) available: Experimental details of the preparation of the new compounds, crystallographic information, molecular and crystal structures, photophysical data and results of theoretical calculations. CCDC 1438721-1438727. For ESI and crystallographic data in CIF or other electronic format, see DOI: 10.1039/x0xx00000x

ligand through uncoordinated N atoms on the $Me_2pz(H)$ ligands.[4] Further development of similar Pt(II) complexes bearing N^C chelate ligands (ppy^- (2-phenylpyridinate), $dfppy^-$ (2-(2,4-difluorophenyl)pyridinate), bzq^- (benzo[*h*]quinolinate)) afforded a new class of heteropolynuclear Pt(II) complexes. Very interestingly, the reactions of $[Pt(N^{\wedge}C)(Me_2pzH)_2]PF_6$ (N^C = ppy^-, $dfppy^-$, bzq^-) with Ag(I) ions gave Z (or U)-shaped tetranuclear Pt_2Ag_2 complexes $[Pt_2Ag_2(N^{\wedge}C)_2(Me_2pz)_4]$, while those with Au(I) ions gave trinuclear $PtAu_2$ complexes $[PtAu_2(N^{\wedge}C)(Me_2pz)_3]$. This is in contrast to the general tendency that the heteropolynuclear Pt(II) complexes containing group 11 metal ions possess essentially the same structure, except for the case that the group 11 metal ion has coordination bond with halide ions.[3a, 3b, 3e-g] To elucidate the main factor of structural preference, similar reactions were performed by using Pt(II) complex bearing N^N chelate ligand, $[Pt(bpy)(Me_2pzH)_2](PF_6)_2$. Surprisingly, the reaction of $[Pt(bpy)(Me_2pzH)_2](PF_6)_2$ with Ag(I) and Au(I) ions both afforded Z (or U)-shaped tetranuclear complexes $[Pt_2M_2(bpy)_2(Me_2pz)_4](PF_6)_2$ (M = Ag, Au). We report here the syntheses, structures, and photophysical properties of a series of neutral and cationic heteropolynuclear Pt(II) complexes.

The reactions of mononuclear Pt(II) complexes bearing N^C chelate ligands $[Pt(N^{\wedge}C)(Me_2pzH)_2]PF_6$ with $AgBF_4$ in a 1:1 ratio in the presence of Et_3N in MeOH afforded neutral Z-shaped Pt_2Ag_2 complexes $[Pt_2Ag_2(N^{\wedge}C)_2(Me_2pz)_4]$ (N^C = ppy^- (**2a**), $dfppy^-$ (**2b**)) as well as U-shaped $[Pt_2Ag_2(bzq)_2(Me_2pz)_4]$ (**2c**) (Scheme 1). On the contrary, similar reactions of $[Pt(N^{\wedge}C)(Me_2pzH)_2]PF_6$ with [AuCl(tht)] in a 1:1 ratio in the presence of Et_3N in CH_2Cl_2 did not afford expected Z-shaped Pt_2Au_2 complexes, but gave the trinuclear $PtAu_2$ complexes $[PtAu_2(N^{\wedge}C)(Me_2pz)_3]$ (N^C = ppy^- (**3a**), $dfppy^-$ (**3b**), bzq^- (**3c**)) bearing Me_2pz bridge between two Au atoms. Thus the synthetic procedure was optimized by changing the Pt(II)/Au(I) ratio to 1:2 as well as further addition of Me_2pzH into the reaction mixture. The structures of Pt_2Ag_2 and $PtAu_2$ complexes were confirmed by single-crystal X-ray structural analyses (Table S1†).

The molecular structures of **2a** and **3b** are shown in Fig. 1. The Z-shaped complex **2a** has a crystallographically imposed center of symmetry at the midpoint of Ag1···Ag1*, and half of the atoms in the molecule are independent. The Pt···Pt, Pt···Ag and Ag···Ag distances in **2a** are 5.9137(15), 3.2815(7)~3.4301(8) and 3.1772(7) Å, respectively (Table S2†). It is worthwhile to compare these metal-metal distances with those of 3,5-dimethylpyrazolato-bridged heteropolynuclear Pt(II) complex $[Pt_2Ag_4(Me_2pz)_8]$ (Pt···Pt, 5.1578(8) Å; Pt···Ag, 3.4514(7)~3.5147(8) Å; Ag···Ag, 3.272(1)~4.711(1) Å).[3e] Interestingly, the Pt···Pt distance in **2a** is longer than that in $[Pt_2Ag_4(Me_2pz)_8]$, while the Pt···Ag and Ag···Ag distances in **2a** are shorter than those in $[Pt_2Ag_4(Me_2pz)_8]$. The N and C atoms bound to Pt atom in a ppy ligand are disordered to each other in the crystal structure. In principle, Z-shaped Pt_2Ag_2 complex has two geometrical isomers possessing C_2 and C_i symmetry (Fig. S22†). The ^1H NMR spectrum of the microcrystalline sample of **2a** showing eight methyl signals with almost the same integral indicates the existence of two isomers in a 1:1 ratio in each crystal. An attempt to separate the two geometrical isomers by gel permeation chromatography (GPC) was unsuccessful. The dfppy analogue **2b** also takes Z-shaped structure and was obtained as a mixture of two geometrical isomers in a 1:1 ratio (Fig. S1†). The bzq analogue **2c**, however, takes twisted U-shape structure (Fig. S2†). Single-crystal X-ray structural analysis of **2c** revealed that the N and C atoms bound to Pt atom in the bzq ligand are also disordered to each other. Although **2c** potentially consists of three geometrical isomers (Fig. S22†), the ^1H NMR spectrum of the microcrystalline sample of **2c** suggests that **2c** also involves two isomers in a 1:1 ratio.

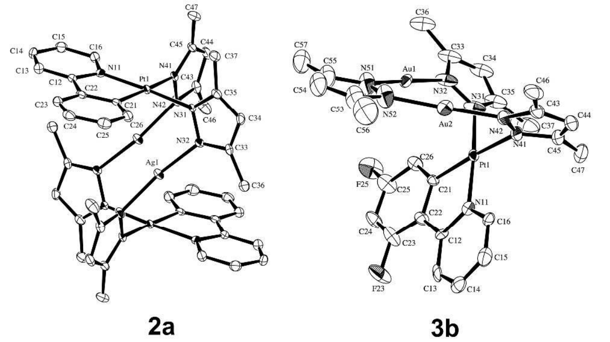


Fig. 1 Molecular structures of $[Pt_2Ag_2(ppy)_2(Me_2pz)_4]$ (**2a**) and $[PtAu_2(dfppy)(Me_2pz)_3]$ (**3b**) with the atom numbering scheme (50% probability ellipsoids). Selected bond lengths (Å) and angles (°) for **2a**: Pt1···Pt1', 5.9137(15); Pt1···Ag1, 3.2815(7); Pt1···Ag1', 3.4301(8); Ag1···Ag1', 3.1772(7); N32-Ag1-N42', 161.89(11). **3b**: Pt1···Au1, 3.4026(7); Pt1···Au2, 3.3979(9); Au1···Au2, 3.0070(9); N32-Au1-N51, 175.7(4); N42-Au2-N52, 176.3(5).

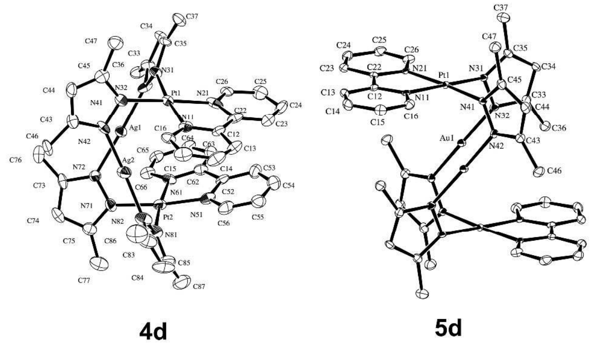
On the contrary, the $PtAu_2$ complex **3b**, in which Pt(dfppy) unit and $Au_2(Me_2pz)$ unit are bridged by two Me_2pz ligands, takes asymmetric butterfly-like structure (Figure 1). The Pt···Au and Au···Au distances in **3b** are 3.3979(9)~3.4026(7) Å and 3.0070(9) Å, respectively. Since **3b** was obtained as a racemate, **3b** crystallized in a centric space group $P2_1/c$. The disorder of dfppy ligand was not observed for the crystal structure of **3b**. The molecular structure of **3c** resembles that of **3b** (Fig. S3†). The racemate **3c** also crystallized in a centric space group $P-1$, though the disorder of N and C atoms bound to Pt atom in the bzq ligand was observed for **3c**.

It is now obvious that the reactions of monocationic Pt(II) complexes bearing N^C chelate ligands and Me_2pzH, $[Pt(N^{\wedge}C)(Me_2pzH)_2]PF_6$, with Ag(I) ions afford Z (or U)-shaped neutral tetranuclear Pt_2Ag_2 complexes $[Pt_2Ag_2(N^{\wedge}C)_2(Me_2pz)_4]$, while those with Au(I) ions afford neutral trinuclear $PtAu_2$ complexes $[PtAu_2(N^{\wedge}C)(Me_2pz)_3]$. To elucidate the main factor of structural preference of heteropolynuclear Pt(II) complexes, similar reactions were performed by using dicationic Pt(II) complex bearing N^N chelate ligand, $[Pt(bpy)(Me_2pzH)_2](PF_6)_2$. Since Z (or U)-shaped cationic tetranuclear Pt_2M_2 complexes $[Pt_2M_2(bpy)_2(Me_2pz)_4](PF_6)_2$ (M = Ag (**4d**), Au (**5d**)) were obtained irrespective of the incorporated metal ions, it was concluded that the structure of cationic heteropolynuclear Pt(II) complex was dominated by its charge.

The structures of complex cations in **4d** and **5d** are shown in Fig. 2. The complex cation in **4d** takes U-shaped structure with twisting about Pt···Pt axis at 68.0° (av.). The coordination planes of Pt atoms incline about 18.6° so as to maximize the π-π interactions between two bpy ligands. The Pt···Pt, Pt···Ag and Ag···Ag distances in **4d** are 5.0943(7), 3.4232(6)~3.5202(6) and 3.1490(7) Å, respectively (Table S7†). On the other hand, the complex cation in **5d** takes Z-shaped structure similarly to **2a** and **2b**. The complex cation in **5d** has a crystallographically imposed center of symmetry at the midpoint of Au1···Au1*, and half of the atoms in the complex cation are independent. The Pt···Pt, Pt···Au and Au···Au distances in **5d** are 6.1628(9), 3.3449(5)~3.5534(5) and 3.1064(7) Å, respectively (Table S8†).

The remarkable features of these neutral heteropolynuclear Pt(II) complexes $[Pt_2Ag_2(N\^{}C)_2(Me_2pz)_4]$ and $[PtAu_2(N\^{}C)(Me_2pz)_3]$ are that they exhibit very intense blue-green to yellow luminescence in the solid state (Φ = 0.34 (**2a**), 0.69 (**2b**), 0.51 (**3a**), 0.55 (**3b**), 0.52 (**3c**)) except for **2c** (Φ = 0.04) (Fig. 3, Table S9†). They also exhibit luminescence in solution moderately (Φ = 0.01 ~ 0.04). The emission spectra of these complexes are all structured both in the solid state and in CH_2Cl_2 with the lifetimes of microsecond regime. The solution state emission energies of neutral Pt_2Ag_2 complexes are almost comparable with those of corresponding $PtAu_2$ complexes irrespective of N^C chelate ligand (Table S9†).

The cationic heteropolynuclear Pt(II) complexes $[Pt_2M_2(bpy)_2(Me_2pz)_4](PF_6)_2$ show relatively intense blue luminescence in the solid state (Φ = 0.11 (**4d**), 0.17 (**5d**)) with the lifetimes of microsecond regime (Fig. 4). They exhibit broad emission spectra in solution, which are in sharp contrast with the structured emission spectra of them in the solid state as well as those of neutral Pt_2Ag_2 and $PtAu_2$ complexes both in the solid state and in solution (Fig. S19†). The solution state emission energy of **4d** is higher than that of **5d**, while that of **4d** is lower than those of neutral Pt_2Ag_2 and $PtAu_2$ complexes. Very interestingly **5d** displays drastic emission color change (mechanochromic behavior) from blue (λ_{max} = 460, 493, 524 nm) to yellow-green (λ_{max} = 555 nm) accompanied by broadening of structured emission spectrum upon grinding. The original blue emission can be recovered by the addition of a drop of CH_2Cl_2 to the ground sample. The emission spectrum of the ground sample with a drop of CH_2Cl_2 added almost coincides with that of unground sample (Fig. 4). The recovering of the crystal structure was also confirmed by the measurement of XRD patterns (Fig. S21†).



4d **5d**

Fig. 2 ORTEP drawing of the complex cations of $[Pt_2Ag_2(bpy)_2(Me_2pz)_4](PF_6)_2$ (**4d**) and $[Pt_2Au_2(bpy)_2(Me_2pz)_4](PF_6)_2$ (**5d**) with the atom numbering scheme (50% probability ellipsoids). Selected bond lengths (Å) and angles (°) for **4d**: Pt1···Pt2, 5.0943(7); Pt1···Ag1, 3.4323(6); Pt1···Ag2, 3.5202(8); Pt2···Ag1, 3.5124(5); Pt2···Ag2, 3.4232(6); Ag1···Ag2, 3.1490(7); N32-Ag1-N72, 166.00(18); N42-Ag2-N82, 173.70(18). **5d**: Pt1···Pt1′, 6.1628(9); Pt1···Au1, 3.5534(5); Pt1···Au1′, 3.3449(5); Au1···Au1′, 3.1064(4); N32-Au1-N42′, 171.50(11).

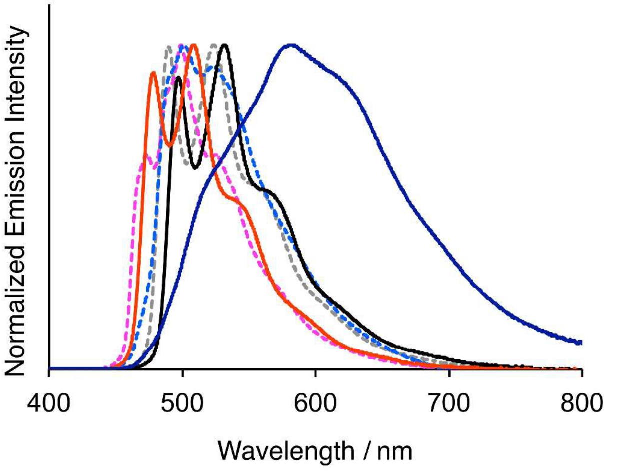


Fig. 3 Normalized emission spectra of **2a** (━━), **2b** (━━), **2c** (━━), **3a** (- - -), **3b** (- - -) and **3c** (- - -) in the solid state at 295 K (λ_{ex} = 350 nm).

To shed light on the photophysical properties of a series of heteropolynuclear Pt(II) complexes, the absorption bands of these complexes were theoretically investigated with the time-dependent density functional theory (TD-DFT) method. Since there exists two geometrical isomers possessing C_2 and C_i symmetry for **2a** and **2b** and three possible isomers for **2c**, DFT calculations were performed for all isomers. The notation of geometrical isomers of Pt_2Ag_2 complexes is summarized in Fig. S22.† Although the molar absorptivity of each complex is slightly different, the features of the absorption spectra are very similar to each other between neutral Pt_2Ag_2 and $PtAu_2$ complexes bearing the same N^C chelate ligand (Figs. S13-S15†). The cationic Pt_2Ag_2 and Pt_2Au_2 complexes with N^N chelate ligand (bpy) also have similar tendency (Fig. S16†).

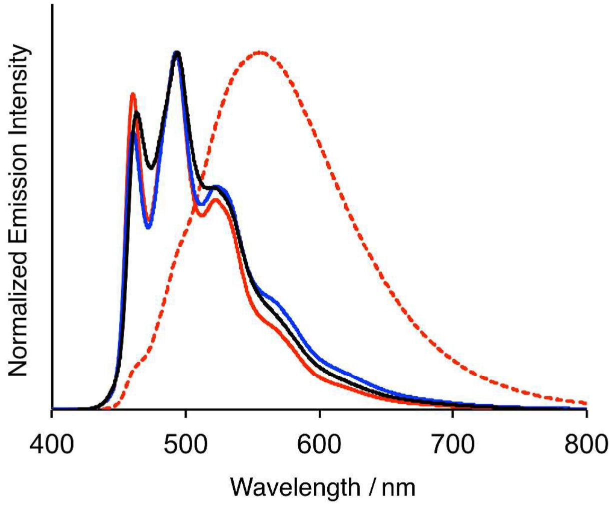


Fig. 4 Normalized emission spectra of **4d** (━━) and **5d** (━━) in the solid state (unground) at 295 K (λ_{ex} = 350 nm). The red broken and blue solid lines also show the emission spectra of **5d**: completely ground sample (- - -) and ground sample with a drop of CH_2Cl_2 added (━━).

Calculated transition energies agree well with the experimental results (Tables S11 and S12†). The molecular orbitals, which contribute to the excitations in Tables S11 and S12,† are depicted in Figs. S23-S25.† Orbital composition percentages of these orbitals are listed in Table S13.† These data imply that the lowest energy absorption bands of Pt_2M_2 (M = Ag, Au) and $PtAu_2$ complexes bearing ppy^- (**2a**), $dfppy^-$ (**2b**, **3b**) and bpy ligands (**4d**, **5d**) are assigned mainly to the combination of the metal-to-ligand charge-transfer (MLCT) and ligand-to-ligand charge-transfer (LLCT) transitions, mixed with ligand-centered (LC) in character, regardless of the charge of complexes. On the contrary, the character of LC transition increases in the neutral Pt_2Ag_2 and $PtAu_2$ complexes bearing bzq^- ligand (**2c**, **3c**); in these cases, the lowest energy absorption bands are assigned mainly to the combination of MLCT and LC transitions, mixed with LLCT in character. Optimization of the geometries of triplet excited states revealed that the emissions of neutral Pt_2Ag_2 and $PtAu_2$ complexes are attributed to phosphorescence mainly from ^{3}LC excited state. On the other hand, the emissions of cationic Pt_2Ag_2 and Pt_2Au_2 complexes (**4d**, **5d**) are attributed to phosphorescence mainly from ^{3}LLCT excited state. These assignments are fully consistent with the observations in CH_2Cl_2 solution that the neutral complexes exhibit structured emission spectra, while the cationic complexes exhibit broad ones. Consequently, in contrast to the Pt_2M_4 type heteropolynuclear complexes bearing alkynyl or pyrazolate ligands, the effect of the incorporated group 11 metal ions toward emission energy is small in the heteropolynuclear Pt(II) complexes bearing N^C and N^N chelate ligands. Furthermore, it is noteworthy that little difference in the calculated emission energy was obtained among geometrical isomers.[5] The calculated emission energies agree well with experimental values, though that for **5d** is slightly higher than the observed energy (Table S10†).

In conclusion, the development of mononuclear Pt(II) complexes bearing N^C chelate ligands (ppy^-, $dfppy^-$, bzq^-) and N^N chelate ligand (bpy) with Me_2pzH opened the route for the synthesis of a series of neutral heteropolynuclear Pt(II) complexes, $[Pt_2Ag_2(N^\wedge C)_2(Me_2pz)_4]$ and $[PtAu_2(N^\wedge C)(Me_2pz)_3]$ and cationic complexes $[Pt_2M_2(bpy)_2(Me_2pz)_4](PF_6)_2$ (M = Ag, Au). Structures of the neutral heteropolynuclear Pt(II) complexes are apparently dominated by the nature of incorporated group 11 metal ions, while the cationic heteropolynuclear Pt(II) complexes favors Z (or U)-shaped tetranuclear Pt_2M_2 complexes regardless of the incorporated group 11 metal ions. Although the single-crystals of neutral Z (or U)-shaped tetranuclear Pt_2M_2 complexes consist of two geometrical isomers arising from the asymmetry of N^C chelate ligands, the difference in photophysical properties of geometrical isomers is not distinguishable. Consequently, in contrast to the Pt_2M_4 type heteropolynuclear complexes bearing alkynyl or pyrazolate ligands, the effect of the incorporated group 11 metal ions toward emission energy is small in the heteropolynuclear Pt(II) complexes bearing N^C and N^N chelate ligands.

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Graphical Abstract

Different structural preference of Ag(I) and Au(I) in neutral and cationic luminescent heteropolynuclear platinum(II) complexes: Z (U)-shaped Pt_2M_2 type vs. trinuclear PtM_2 type

Kazuki Nishihara, Misa Ueda, Ami Higashitani, Yoshihide Nakao, Yasuhiro Arikawa,

Shinnosuke Horiuchi, Eri Sakuda, and Keisuke Umakoshi

The structures of neutral and cationic luminescent heteropolynuclear Pt(II) complexes are dominated by the incorporated group 11 metal ions and the charge of complexes.