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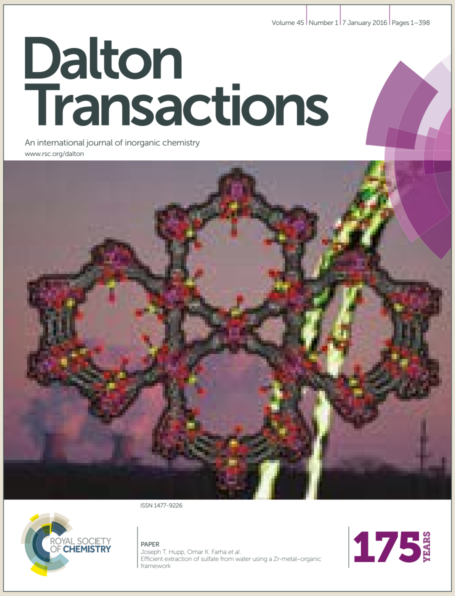

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Journal Name

COMMUNICATION

Luminescent Cyclic Trinuclear Coinage Metal Complexes with Aggregation-Induced Emission (AIE) Performance

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A series of AIE active cyclic trinuclear complexes (Au_3, Ag_3, and Cu_3) have been successfully prepared and elucidated by X-ray crystallography. These complexes showed excellent AIE properties and their quantum yields (QYs) were significantly increased compared to that of the free ligands. The remarkable solution induced AIE activity in atom-precise coinage metal complexes is still scarce, and this work opens a promising avenue for the development of easily prepared metal-based AIE luminogens with high emission efficiency.

Luminogens with aggregation-induced emission (AIE) properties have emerged as a new class of luminescent materials which have shown great possibility to be widely utilized as optoelectronic devices and sensory systems, etc.[1] The AIE effect is considered constructive because the photoemission of the propeller-like molecules could be significantly enhanced after aggregation, which greatly differs from the aggregation-caused quenching (ACQ) observed in many conventional chromophores that possess planar and well-conjugated structures.[2] In general, conventional luminogens only exhibit efficient emission in a molecularly dispersive state and the aggregation of the molecules should be strictly avoided, which could lead to an obstruction of applications.[3] The discovery of the fantastic AIE phenomenon furnishes a high possibility of conquering the ACQ problem.[4] Therefore, various AIE luminescent materials have been designed and synthesized, among which hexaphenylsilole (HPS), tetraphenylethene (TPE) and distyreneanthracene (DSA) moieties are typical representatives.[4a,5]

Nevertheless, a majority of the AIE active molecules are organic and this phenomenon have been rarely explored for metal complexes.[6] Not to mention AIE luminescent materials with precise structures have been synthesized.[7] In addition, compared with the conventional chromophores, luminescent metal complexes do have better photostability, which may result in much better performance in catalytic processes and optoelectronics (e.g., LEDs).[8] Coinage metal complexes have attracted extensive interest in recent years owing to their novel properties and potential applications in various fields.[9,10] Among these physical/chemical properties, luminescence represents one of the most intriguing features of these materials.[11] However, a technical challenge is that the photoluminescence of coinage metal complexes are often weak, and their quantum yields (QYs) rarely exceed 0.1%. Recently, the discovery of AIE phenomenon can be used to design high-luminescence metal complexes to address these obstacles.[12] Xie and co-workers have synthesized $Au_{22}(SG)_{18}$ clusters, which showed red emission with a QY of ~8%. By comparison with those of Au(I)–thiolate complexes, their stronger luminescence intensity was ascribed to AIE. However, the origin of emission in these clusters still remains unaddressed, what makes a major hurdle for the design of excellent AIE materials.[13] Therefore, it remains a further advance to develop a method for the rational design of coinage metal complexes with excellent AIE properties.[4b,14]

Herein, we successfully synthesized a series of prominent AIE active coinage metal complexes, namely $[Au_3(DTBP)_3]\cdot CH_2Cl_2\cdot CHCl_3$, $[Ag_3(DTBP)_3]\cdot 2CHCl_3$ and $[Cu_3(DTBP)_3]\cdot 2CHCl_3$ (denoted as **M_3**, M = Au, Ag or Cu), by reacting 3,5-dimethyl-4-(4-(1,2,2-triphenylvinyl)benzyl)-1H-pyrazole (DTBP) with coinage metal ions in the presence of triethylamine (Figure 1a). All of these complexes have been successfully elucidated by X-ray crystallography. The triangular assemblies of coinage metal atoms and pyrazole groups promoted the formation of ordered layered structure which increased the restriction of intramolecular rotations (RIR) effect of AIE-active units, thus effectively restricted non-radiative decay. Therefore the process promoted highly

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emissive and strongly AIE response, which led to the QYs reach up to 12.01% (**Ag_3**, about 7.5 times to ligand) in the solid state. Our approach using rigid pyrazolyl ligand paves a new way to construct precise structure coinage metal complexes with intense luminescence and prominent AIE performance.

Results and discussion

A number of TPE-based discrete organic molecular structures have been determined by experimental characterization.[15] However, coinage metal complexes with precise structure are still rare. **Au_3**, **Ag_3** and **Cu_3** were facilely synthesized via one-pot method by reacting stoichiometric coinage metal salts or precursors with pyrazole ligands in the presence of trimethylamine.[16] Needle single crystals suitable for X-ray structural analysis were obtained by recrystallizing the samples via vapor diffusion of *n*-hexane into their chloroform solutions (Supporting Information for details). DTBP was first synthesized and its purity was confirmed by ^{1}H NMR and ^{13}C NMR (Figures S1−4). The phase purity and chemical formula of **Au_3**, **Ag_3** and **Cu_3** were further verified by *in situ* power X-ray diffraction (PXRD) patterns, thermogravimetric analysis (TGA) and elemental analysis (Figures S5−9).

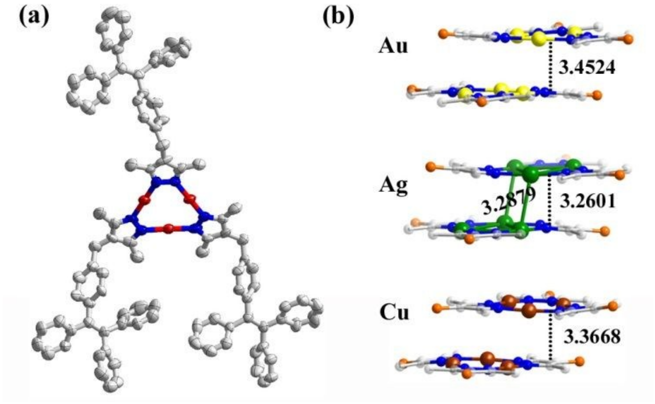

Figure 1. (a) Schematic represented the crystal structures of **M_3**. Thermal ellipsoids set at 50% thermal probability. (b) Interlayer stacking structure of **Au_3**, **Ag_3** and **Cu_3**. Color codes: yellow, Au; green, Ag; brown, Cu; blue, N; gray C (red, M; orange, R = –CH_2TPE). All hydrogen atoms are omitted for clarity.

Single crystal X-ray structure analyses revealed that **Au_3** and **Ag_3** crystallize in triclinic space group *P*-1, while **Cu_3** crystallizes in monoclinic space group $P2_1/c$ (Table S1). Their asymmetric units exhibit cyclic trinuclear isostructures (Figure 1a). Three pyrazole groups uniformly adopt the μ_2-η_1, η_1 ligation mode to link two metal ions to build a stable triangular plane. Notably, the Ag(I)···Ag(I) distances between adjacent molecules are about 3.2879 Å in **Ag_3**, indicating the existence of argentophilic interactions. However, due to the steric hindrance of TPE molecules, intermolecular metallophilic interactions are not formed in the stacked structures of **Au_3** and **Cu_3** (Figure 1b).[17] Interestingly, in the dispersed state, the stable **M_3** structures do not restrict the incorporated TPE molecules (free to rotate) due to the presence of methylene.

The luminescent properties of **M_3** were further investigated. **M_3** crystals emitted intense blue-green luminescence (λ_{max} = 490 nm) under UV light (Figure 2), while DTBP ligand showed blue-green emission (λ_{max} = 494 nm) (Figure S10). The similar profiles indicated that the emissions of complexes are ligand-centered. Furthermore, the nanosecond-scale emissive lifetime of **M_3** emission bands (e.g., τ Ag_3 = 6.42 ns) (Figures S11−13) and DTBP emission bands (τ_{DTBP} = 2.60 ns) (Figure S14) indicated the characteristics of fluorescence, originating from ligand emission.[7,18]

As a well-known AIE luminogen, TPE has unique structural characteristics with phenyl rotor, of which the RIR process leads to AIE effect.[1] Irradiation of a dilute tetrahydrofuran solution (a good solvent of DTBP (<10^{-3} M)) at 365 nm showed almost no fluorescence at 474 nm. However, the increasing amount of water (a poor solvent for DTBP) to the mixed solution greatly enhanced the blue-green emission intensity (3.2×10^4 times), and the QY was measured using an integrating sphere to be 1.59% in the solid state, indicating its strong AIE behavior (Figures S15−17).

Interestingly, **M_3** complexes suggested a similar emission pattern with higher fluorescence intensity and QYs compared to those of the free ligand. The QYs of **Au_3**, **Ag_3** and **Cu_3** determined was found to be 6.92%, 12.01% and 9.82% at room temperature in the solid state, respectively (**Ag_3**, about 7.5 times to ligand), which should be ascribed to the structural rigidity resulted by the stack between planes, which could effectively restrict non-radiative decay. Furthermore, the ordered stack of interlayer can form more stable internal complexes architecture. Especially, argentophilic interactions within **Ag_3** shortened the overall intermolecular Ag(I)···Ag(I) distances, resulting in the QY higher than that of **Au_3** and **Cu_3** (Figure 1b).[19]

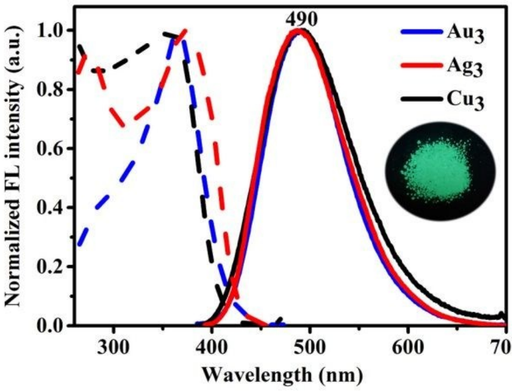

Figure 2. Fluorescence spectra of **Au_3** (blue curve), **Ag_3** (red curve), and **Cu_3** (black curve) excited (dotted line) at 366 nm in the solid state at room temperature. Inset is the fluorescence images of **Ag_3** under 365 nm UV light.

The intense blue-green emission of **Ag_3** as an example encouraged us to study its AIE property. The dependence between the aggregates and luminescence intensity of **Ag_3** was detected for the aggregates from solvent-induced aggregation. As illustrated in Figure 3a, the aggregation degree was controlled by the polarity of the mixed solvent, which could be varied by the volume fraction of isopropanol in the solvent f_e (f_e = $vol_{isopropanol}/vol_{tetrahydrofuran+isopropanol}$, isopropanol is the poor solvent). The **Ag_3** solution turned cloudy with weak blue

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emission when f_e reached 40% due to the initial aggregation. When f_e increased to 70%, the solution showed stronger blue-green luminescence emission, suggesting the presence of well-dispersed colloids of denser aggregates (Figure 3b). The solvent-induced AIE of **Ag_3** was reversible since decreasing f_e could re-dissolve the aggregates, thereby annulling the AIE mechanism and subsequently quenching the luminescence.

Photoemission spectra were recorded to interpret the emission changes due to variations in aggregation degree (Figure 3c). Before f_e reached 60%, the luminescence intensity increased monotonically with the increase in aggregation degree. When f_e reached 70%, the main peak in the emission spectrum shifted from 454 (blue emitting) to 473 nm (blue-green emitting), which was similar to the photoemission spectra of DTBP shown in Figure S16, and it could be attributed to the solvent effect.[20] Moreover, the QYs of **Au_3**, **Ag_3** and **Cu_3** were found to be 5.48%, 7.94% and 3.98%, respectively, with f_e = 80% and concentration of 1.57×10^{-4} M, which are lower than the corresponding QYs in solid state. These results further support the AIE behaviours of these complexes. To keep the concentration of DTBP same, the QY of DTBP ligand was found to be 0.84% with a concentration of 4.71×10^{-4} M.

The UV–vis spectroscopy was also used to follow the aggregate degree of **Ag_3** with increasing f_e, while it showed a main peak at 314 nm (Figure 3d). When f_e increased further from 50% to 95%, the formation of smaller and denser aggregates was indicated by bathochromic shifts of the spectra (Figure 3d, solid black arrow). In the process, the high polarity of the solvent gave impetus of red shift. In addition, hyperchromic shift of the UV–vis absorption spectra appeared due to the large increase in background scattering (dotted black arrow).[6a]

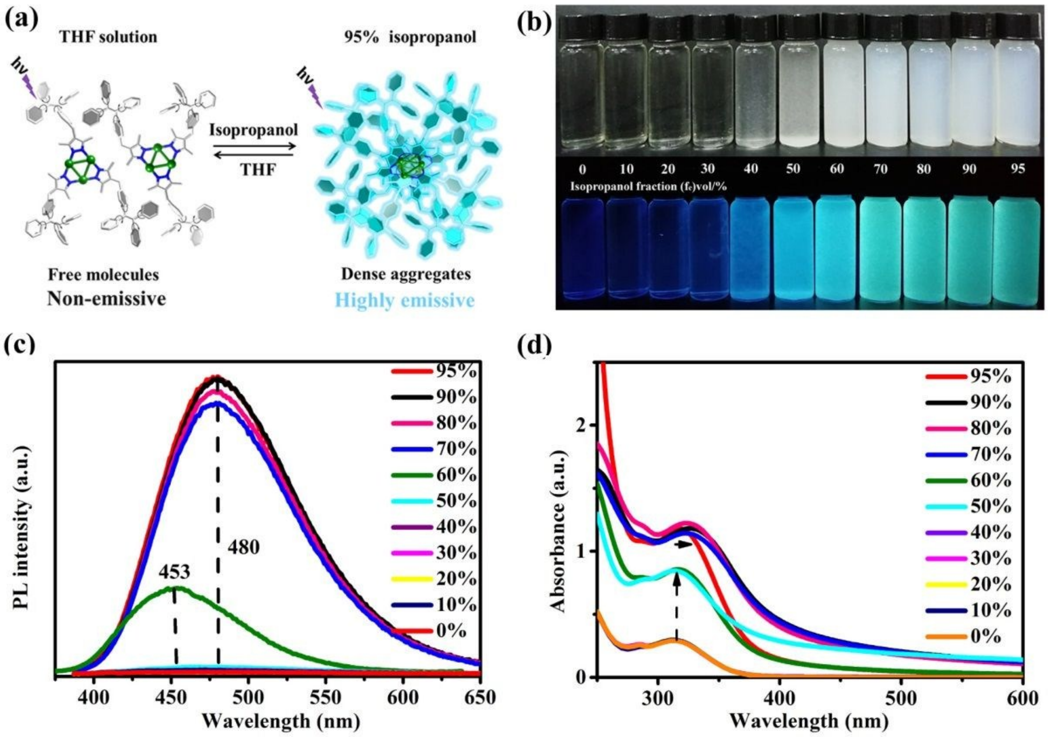

Figure 3. (a) Schematic illustration of solvent-induced AIE properties of **Ag_3** complex. (b) Digital photo of **Ag_3** complex (concentration: 2×10^{-4} M) in mixed solvents with different f_e under visible (top row) and UV (bottom row) light. (c) Photoemission spectra and (d) UV–vis absorption spectra of **Ag_3** in mixed solvents with different f_e.

Au_3 and **Cu_3** also showed similar AIE properties. Unlike **Au_3** and **Ag_3**, dichloromethane was used as good solvent for **Cu_3**, as **Cu_3** could be oxidized more easily in THF. Figures S18–20 showed that the **Au_3** solution was non-luminescent until f_e reached 70%, afterwards the solution turned intense blue-green emission. The spectra showed that their fluorescence intensity gradually increased (λ_{max} = 469 nm). Correspondingly, the AIE images of **Cu_3** had the same pattern with **Ag_3**, as the λ_{max} = 470 nm until f_e reached 70% or higher (Figures S21–23). Therefore, the visible eyesight of these complexes expressed excellent AIE performance in solution-induced system, and such AIE luminescent materials could find their applications as biosensing, bioimaging, and dual-functional utilities.

Conclusions

In summary, we have developed a series of TPE-incorporated coinage metal complexes **Au_3**, **Ag_3** and **Cu_3**, which exhibit excellent AIE performance. Crystal structures of these cyclic trinuclear complexes were successfully elucidated by X-ray crystallography. These complexes showed intense ligand-centered blue-green emission at 490 nm. The coordination induced intermolecular stacking interactions in these complexes highly promoted structural rigidity and their QYs were significantly enhanced (12.01% for **Ag_3**, about 7.5 times to that of ligand in the solid state). Meanwhile, the aggregation degree positively correlated with the fluorescence

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intensity, indicating that the solution-induced AIE activity was significantly affected by the RIR and emissive efficiency improved in aggregation process. As a new strategy to expand the field of AIE molecules, the coinage metal complexes produced precise structure nanomaterials with strong fluorescence which may be applied to diversified fields. Moreover, the self-assembly provided a promising method for enhancing luminescence of AIE molecules in nanoscale complexes.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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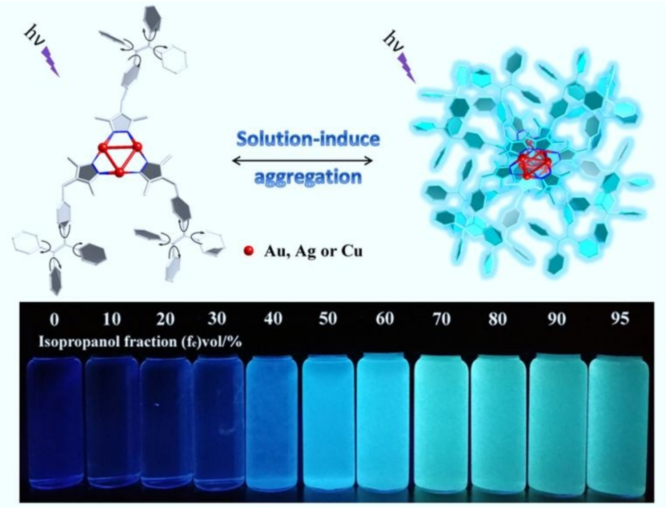
Graphical abstract



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