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### Aggregation-induced emission (AIE) behavior and thermochromic luminescence properties of a new gold(I) complex<sup>†</sup>

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A new gold complex that shows the AIE effect as well as the thermochromic fluorescence switch is reported. This interesting phenomenon is attributed to changes in the intermolecular  $Au \cdots Au$  interactions and the formation of nano-aggregates.

Recently, luminescent organic molecules have attracted great interest because of their potential applications in fields such as sensors, storages and optical devices.<sup>1</sup> Of particular interest are those luminescent materials with tunable and reversible emission in the solid state, which are brought about by exerting different external stimuli. The properties of stimuli-responsive fluorescent materials include photochromism, electrochromism, thermochromism, solvatochromism, mechanochromism, vapochromism and biochromism.<sup>2</sup> However, studies on stimuliresponsive fluorescent materials remain inadequate owing to the absence of effective guidelines for the design of molecular structures possessing simultaneously the multiple features of different smart materials.

Meanwhile, most organic luminescent materials exhibit very strong luminescence in their dilute solutions, but this tends to be weakened or quenched at high concentrations, a phenomenon widely known as aggregation-caused quenching (ACQ).<sup>3</sup> In 2001, Tang *et al.* found that some propeller-shaped molecules exhibit the phenomenon of aggregation-induced emission (AIE), which is exactly the opposite to the ACQ effect.<sup>4</sup> In 2002, Park *et al.* reported that a new class of organic CN-MBE nanoparticles exhibit strongly enhanced fluorescence emission, and so these were called aggregation-induced emission enhancement (AIEE) materials.<sup>5</sup> Since then, a variety of AIE and AIEE materials have been prepared and utilized in various applications. However, most of these have been organic compounds. A number of possible mechanistic pathways, including conformational planarization, J-aggregate formation, twisted intramolecular charge transfer (TICT), and restriction of intramolecular rotation (RIR), have been proposed.<sup>6</sup> AIE luminogens based on transition metal complexes have also been detected occasionally. To date, however, limited studies have been conducted on the AIE of cationic iridium(m) complexes,<sup>7</sup> zinc( $\pi$ ) ion complexes *etc.*<sup>8</sup> The changes are also realized by tuning the molecular packing in the solid state. However, it may be that the metal-metal interaction is already present in the form of adjacent intermolecular interactions, which can therefore be used to adjust their optoelectronic properties. This observation may enable us to design additional types of metal materials with the AIE property. Independently, the exploration and development of gold(I) chemistry represents a fascinating and challenging area, and has attracted growing interest over the last two decades.<sup>9</sup> Aurophilic Au-Au interactions have been one of the most intriguing topics in gold chemistry, and have been one of the reasons for driving the rapid development of both physical and chemical studies of gold chemistry.

In this work, we report a novel gold(1) compound with a 1-(decyloxy)-4-isocyanobenzene bridge (Scheme 1). Compound 1 has attracted great interest because it exhibits AIE characteristics and thermochromic behavior, and its fluorescent properties show reversible changes from blue to yellow-green in response to temperature stimuli. This interesting phenomenon may be attributed to the intermolecular packing.



Scheme 1 The structure of complex 1 and its single crystal structure.

Key Laboratory of Pesticide and Chemical Biology, Ministry of Education, College of Chemistry, Central China Normal University, Wuhan 430079, P. R. China. E-mail: chshliu@mail.ccnu.edu.cn; Fax: +86-27-67867725; Tel: +86-27-67867725 † Electronic supplementary information (ESI) available: Synthesis, PL and UV spectra, details of the data collection, and selected bond distance and angles. CCDC 918147. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3cc00157a



**Fig. 1** (a) PL spectra of the dilute solutions of **1** ( $2.0 \times 10^{-5} \text{ mol L}^{-1}$ ) in EtOH–H<sub>2</sub>O mixtures with different volume fractions of water (excitation wavelength = 310 nm). The inset shows the emission images of **1** ( $2.0 \times 10^{-5} \text{ mol L}^{-1}$ ) in pure EtOH as well as 40%, and 60% water fraction. (b) PL spectra of compound **1** ( $2.0 \times 10^{-5} \text{ mol L}^{-1}$ ) in water–EtOH mixtures with different volume fractions of water (40%–50%). Excitation wavelength = 310 nm.

Molecule 1 was synthesized as a white solid in 65% yield according to the synthetic route shown in Scheme S1 (ESI<sup> $\dagger$ </sup>). Detailed procedures for its synthesis and characterization can be found in the ESI.<sup> $\dagger$ </sup>

To survey the AIE property of complex **1**, the photoluminescence (PL) spectra and UV spectra (Fig. S1, ESI<sup>†</sup>) were studied in EtOH–H<sub>2</sub>O mixtures with various water contents. Interestingly, the PL intensity was not only significantly enhanced with the addition of water, but the emission color also changed from blue (402 nm and 425 nm) to yellow-green (559 nm), as shown in Fig. 1a. This is very unusual.

Complex 1 in pure EtOH  $(2.0 \times 10^{-5} \text{ mol L}^{-1})$  exhibited very weak photoluminescence (PL) intensity, as shown in Fig. S2 (ESI<sup>†</sup>). However, when the water fraction in the EtOH solution exceeded 30%, an emission band was observed with  $\lambda_{max}$  at 402 nm and 425 nm. The intensity in pure EtOH was 0.88 a.u., which increased to ~70.59 a.u. in the 40% EtOH-H<sub>2</sub>O mixture, showing an approximately 80-fold enhancement, due to the formation of nano-aggregates. As the compound is insoluble in water, increasing the water fraction in the mixed solvent might change the form of the compound from a dissolved or welldispersed state in pure EtOH to aggregated particles in the mixtures with high water content. The emission of 1 is thus caused by aggregation, which is typically AIE active.

As shown in Fig. 1b, when the water fraction exceeded 40%, the addition of water to the EtOH solution resulted in a decrease in the intensities of the two emission bands at 402 nm and 425 nm, and an increase in the intensity of the new emission bands at 559 nm. When the water fraction reached 54%, the blue emission completely disappeared, and the yellow-green emission became very obvious. The intensity at 402 nm in pure EtOH was 0.88 a.u., while the intensity at 559 nm increased to  $\sim$  33.59 a.u. in the 52% EtOH-H<sub>2</sub>O mixture, showing an approximately 38-fold enhancement. We speculate that two kinds of nano-aggregates might be formed, causing the difference in molecular packing and the change in the intermolecular gold-gold interactions. However, the PL intensities of the yellow-green emission bands are weakened if the water fraction is further increased (Fig. S3, ESI<sup>†</sup>). The changes in the PL intensity of compound 1 with the different water fractions (0%-90%) are shown in Fig. S4 (ESI<sup>+</sup>). This phenomenon is often observed in compounds with AIE

properties and two possible explanations have been proposed. First, after the aggregation, only the molecules on the surface of the nanoparticles emit light and contribute to the fluorescence intensity upon excitation, and this leads to a decrease in the fluorescence intensity.<sup>10</sup> However, the enhancement of the intermolecular gold-gold interactions could enhance light emission. The net outcome of these antagonistic processes depends on which process plays the dominant role in affecting the fluorescent behavior of the aggregated molecules. Second, the solute molecules can aggregate into nanoparticle suspensions upon addition of water. However, the amorphous particles formed in this way are not stable enough, which then leads to a reduction in PL intensity. The two kinds of nano-aggregates obtained were characterized by DLS (dynamic light scattering). The results revealed the presence of real nano-aggregates as a major component (Fig. S5, ESI<sup>†</sup>). The size of nano-aggregates became smaller with an increase in the volume fractions of water. It largely resulted in a change in the molecular packing and changes in the intermolecular gold-gold interactions. Furthermore, we have also investigated the PL intensity of 1 in the 40% and 60% EtOH-H<sub>2</sub>O mixture at the concentration of  $0.5 \times 10^{-5}$  M and  $1 \times 10^{-5}$  M. As shown in Fig. S6 (ESI<sup>+</sup>), the PL intensity is weakened with the decrease in the concentration of 1. However, PL intensity is not linear with the concentration of 1, which may be due to the inner-filter effect.

Thermochromic materials,<sup>11</sup> typically dyes and pigments that are able to change color reversibly with changes in temperature, have been the subject of curiosity-driven research and commercial exploitation for decades, mainly because of their appealing color-changing visual effect in specialty inks, paints, plastics and textiles. The emission spectra of the crystals of 1 show two emission bands, at 407 nm and 428 nm, which can be attributed to the fluorescence from the intra-ligand localized  $\pi$ - $\pi$ \* excited state.<sup>11</sup> Intriguingly, after gentle heating (>55 °C) of the sample in a slender piece of glass, a broad emission band, with a maximum wavelength of 530 nm, was observed, in which aurophilic interactions may be responsible for the new ligand-to-metal-metal charge transfer (LMMCT) excited state  $[C_6F_5 \rightarrow Au \cdots Au]$ <sup>12</sup> Evidently, complex **1** exhibits temperatureinduced luminescence changes. That is, complex 1 is a thermochromic material. When the temperature falls to 25 °C, the solid exhibits an emission band similar to that of the initial sample. An attempt to repeat this blue-to-yellow-green emission cycle was successful. The PL intensity of complex 1 was reversible during consecutive heating and cooling cycles over the temperature range 25 °C–59 °C (Fig. S7, ESI<sup>†</sup>). Photographic images of



Fig. 2 (a) Normalized PL spectra of 1 initial, heated and cooled powder, (b) images of the compound before heating and after heating under 365 nm UV illumination.



Fig. 3 The structural organization of complex 1.

the color and luminescence changes for **1** are presented in Fig. 2. It is possible that the heating resulted in a change in the molecular packing and in the intermolecular gold–gold interactions. Cooling then made the amorphous phase rearrange into the more stable crystalline phase.

Fortunately, it is possible to obtain single crystals of complex 1 suitable for X-ray analysis by slow diffusion of *n*-hexane into a dichloromethane solution containing 1, as shown in Scheme 1b. Further crystal data and details of the data collection are summarized in Table S1 (ESI<sup>+</sup>). Selected bond distances and angles are given in Table S2 (ESI<sup>+</sup>). In complex 1, the Au-C(6) and C(7)-Au distances are 2.024(6) and 1.977(7) Å while the C(6)–Au–C(7) angle is  $177.8(3)^{\circ}$ . These distances are consistent with those in (CyNC)Au<sup>I</sup>Br, where the Au-Br and C-Au distances are 2.372(8) and 1.972(7) Å, respectively, and the C-Au-Br angle is 178.05(17)°.13 According to previous literature, it has been accepted that intermolecular Au...Au interactions occur when the intermolecular distance between the gold atoms is within the range 2.7-3.3 Å.<sup>14</sup> As shown in Fig. 3, molecules of 1 are weakly self-associated, with an Au ··· Au distance of 3.782 Å. These self-associated molecules are situated in such a way that they form extended loose chains with neighboring Au ··· Au distances of 4.83 Å. In this case, no obvious intermolecular gold-gold interaction is indicated.

However, the existence of weak  $\pi$ - $\pi$  interactions (d = 3.700 Å) and intermolecular C-H···F ( $d_{H...F} = 2.459$  Å, 2.646 Å) and C···F ( $d_{C...F} = 3.111$  Å) promote molecular packing, as indicated in Fig. S8 (ESI†). When water is added to the EtOH solution or the blue luminescent powder is heated, nano-aggregates or an amorphous phase are formed, with aurophilic interactions that are responsible for the lower energy yellow-green emission, as shown in Scheme 2.

In summary, a novel gold(1) compound with a 1-(decyloxy)-4-isocyanobenzene unit has been successfully synthesized.



Scheme 2 An illustration of the luminescence changes of complex 1.

It is AIE-active and thermochromic since: (1) the addition of water to solutions of **1** in common organic solvents (EtOH) formed two kinds of nano-aggregates, showing blue and yellow-green emission; (2) the emission of **1** can be switched between "blue" and "yellowgreen" repeatedly using simple heating–cooling cycles. The change in the intermolecular gold–gold interactions, weak  $\pi$ – $\pi$  interactions and intermolecular interactions (such as the C–H···F and C···F interactions) were found to play an important role in determining these desirable properties. Further studies will focus on the functionalization of structures in order to find other AIE and stimuliresponsive fluorescent materials with desirable properties.

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