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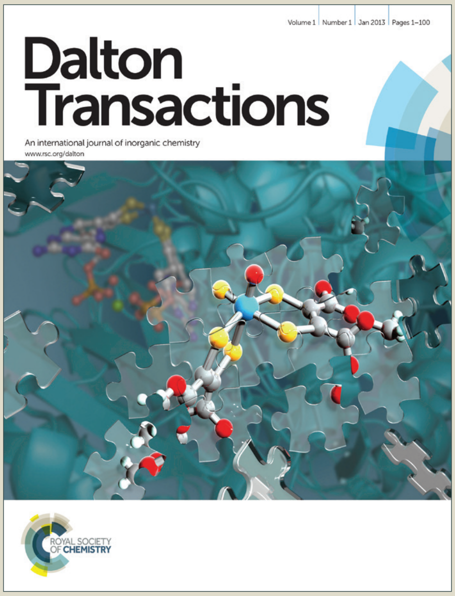

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A novel carbazole-based gold(I) complex with interesting solid-state multi-stimuli-responsive characteristics†

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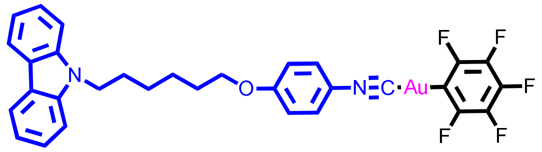
A new carbazole-based mononuclear gold(I) complex was designed and synthesized. The novel luminogen shows significative solid-state reversible mechanochromism, dual-responsive thermochromism and sensitive thin-film vapochromism properties. In addition, we obtained two kinds of crystals of the luminogen, which are conducive to the reasonable explanation of these interesting characteristics.

Luminescent organic materials, especially smart fluorescent materials as a response to environmental stimuli, have attracted extensive interest due to their potential for applications in some areas such as fluorescent switches, sensors, data storage, and optical devices.[1-4] For more than a decade, gold(I) chemistry has received considerable attention due to the occurrence of intriguing aurophilic Au-Au interactions.[5-8] Mechanochromic materials, as one rather important type of smart luminescent materials, have also aroused a great deal of attention.[9-12] To date, the majority of gold(I) complexes which exhibit mechanochromic behaviors have been shown to be dinuclear gold(I) complexes. The mononuclear gold(I) complexes with mechanochromic properties are insufficient[13] and preparing such complexes based on a mononuclear gold(I) scaffold structure is urgent and challenging. On the other hand, temperature is one of the most common environmental stimuli, and therefore thermochromic materials, which are capable of changing colour with temperature, can be applied to temperature-sensing systems.[14] In the last few decades, significant breakthroughs have been made in the field of thermochromism. Dual-responsive thermochromic material, which exhibits two invertible colour changes over a range of temperatures, is more conducive to practical application.[15] Luminescence vapochromism, which involves changes in the photoluminescence properties upon exposure to vapors of volatile organic compounds, is a promising phenomenon.[16-19] Finding appropriate sensors for detrimental chemical substances that are likely to exist in the environment or at our workplaces is very important. Meanwhile, the vapochromic molecules are practically applied in solid state commonly as thin films. Thus, the discovery of thin-film vapochromic materials suitable for sensing volatile organic compounds is an attractive research topic and deserves great attention. Until now, examples on multi-stimuli-responsive smart fluorescent materials of one chromophore are still inadequate, which is due to the absence of effective guidelines for the design of switchable fluorescent molecules possessing synchronously all the features of various smart materials. Furthermore, luminogen possessing simultaneously reversible mechanochromism, dual-responsive thermochromism, and sensitive thin-film vapochromism characteristics has yet to be discovered, not to mention metal-bearing luminescent molecule with these alluring properties. Herein, we describe a novel monoisocyano-based mononuclear gold(I) complex with a carbazole-based skeleton (Scheme 1). The existence of carbazole unit provides the possibility for generation of weak intermolecular C-H···F interaction. Complex **1** is a preeminent luminescent molecule which merits significant attention due to its significative reversible mechanochromism, dual-responsive thermochromism, and sensitive thin-film vapochromism properties. In addition, we obtained two types of crystals of **1**, which are helpful to the reasonable explanation of these interesting characteristics.



Scheme 1 The molecular structure of complex **1**.

Compound **1** was obtained in 92% yield by the coordination reaction of intermediate product **1c** and $C_6F_5Au(tht)$ (tht = tetrahydrothiophene). Specific procedures of the reasonable synthetic strategy are shown in Scheme S1 (ESI†).

Mechanochromic property of complex **1** was investigated via photoluminescence (PL) spectroscopy. As Figure 1 shows, the fluorescence spectrum of solid sample **1** exhibited very broad emission covering the total visible spectrum, which corresponds to white emission under 365 nm UV irradiation. Interestingly, a new broad emission band with a λ_{max} at 513 nm appeared upon gentle

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grinding of sample **1**, and the corresponding luminescence was converted from white to green. This green luminescence possibly involves charge transfer from ligand to metal-metal (LMMCT).[20] Moreover, the green fluorescence reverted to its original white colour after a 30 s treatment of the ground sample with fuming dichloromethane solvent vapor. It is noteworthy that the repeatability of this white-to-green mechanofluorochromic conversion is superior (Fig. S1, ESI†). It was believed that the mechanical external stimulation possibly caused a change in the molecular morphology. In order to gain more insight into this proposed mechanism of mechanochromism, the structural transition of the solid sample of **1** was studied via X-ray diffraction (XRD). As Figure 2 shows, the grinding led to weakening and broadening of all the reflection peaks, indicating that the use of mechanical force resulted in a crystal-to-amorphous morphology transformation. Furthermore, the initial intense and sharp diffraction peaks were restored via molecular repacking upon treatment of dichloromethane solvent vapor. Thus, the XRD test results proved that the mechanochromism behavior of **1** can be attributed to the morphology transformation between the crystalline and amorphous states.

Moreover, we obtained one type of single crystal of **1** that was both appropriate for X-ray structure analysis and very rare white-emitting, which is consistent with the solid fluorescence of **1**. Details of the crystal information and data collection are summarized in Table S1 (ESI†).

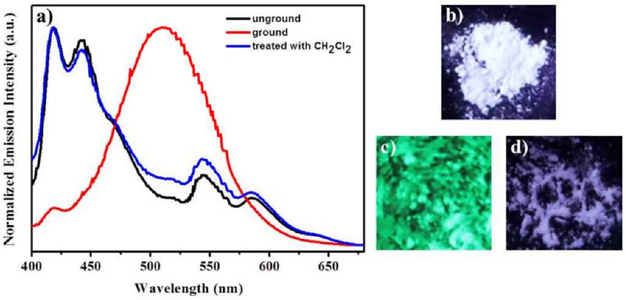

Fig. 1 (a) Luminescence spectra of unground solid sample **1**, after being ground and fumed with dichloromethane solvent vapor. The excitation wavelength is 365 nm. Fluorescence imaging of **1** taken under irradiation of a 365 nm UV light: (b) as-synthesized solid sample; (c) ground sample; (d) sample after treatment with dichloromethane vapor.

The bond angles and distances are listed in Table S2 (ESI†). Figure 3 reveals that the shortest intermolecular Au-Au distance of the white light-emitting complex **1** is 4.938 Å, indicating the absence of strong significant aurophilic interactions.[21] Nevertheless, the presence of weak C-H···F interactions ($d_{H\cdots F}$ = 2.504 Å, 2.494 Å, 2.668 Å, 2.643 Å, 2.522 Å, 2.646 Å, Fig. S2, ESI†) and π-π interactions (d = 3.442 Å, Fig. S3, ESI†) contributes to molecular packing, and facilitates slipping with the application of external mechanical stimuli. When the solid powder sample is ground, a metastable state is formed, and generation of intermolecular aurophilic interactions is responsible for the green emission.[20]

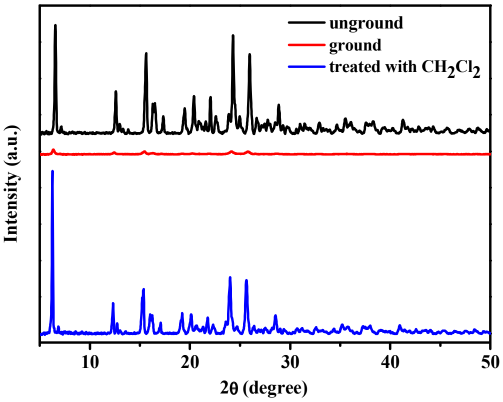

Fig. 2 XRD patterns of solid sample **1**: unground, ground and after treatment with dichloromethane vapor.

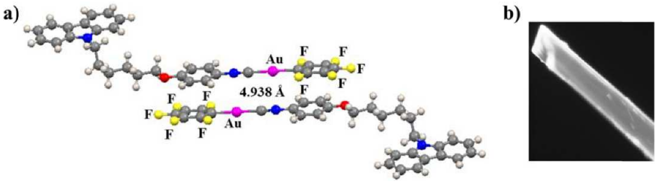

Fig. 3 (a) The structural organization of white light-emitting complex **1**; (b) The fluorescence image of white light-emitting crystal of **1** under 365 nm UV irradiation.

Next, the thermochromic property of **1** was also determined by luminescence spectroscopy. As Figure 4 shows, the white fluorescence of luminogen **1** decreased gradually with increasing temperature. Intriguingly, the strong white-emitting ability of **1** recovered with a decrease in temperature to the initial value. Repeated experiments proved that opening and closing of the white emission was reversible for multiple times (Fig. S4, ESI†). To our surprise, a new emission band with a λ_{max} at 550 nm appeared at a temperature of 132 ℃, namely the melting point of complex **1**, and the emission colour changed to yellow. The yellow-emitting luminogen **1** was subsequently converted to green with a decrease of temperature to room temperature. The yellow-to-green emission change was reversible during consecutive heating and cooling cycles over a temperature range of 20-132 ℃ (Fig. S5, ESI†). The powder XRD test data indicate that the green-emitting solid sample is amorphous state (Fig. S6, ESI†). Furthermore, the green-emitting luminogen **1** could be restored to the white emission upon exposure to dichloromethane solvent vapor thereby resulting in interesting dual-responsive thermochromism behavior of the novel luminogen

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1. This heating-induced fluorescence variations of solid sample **1** were possibly associated with the changes in the molecular packing.[22]

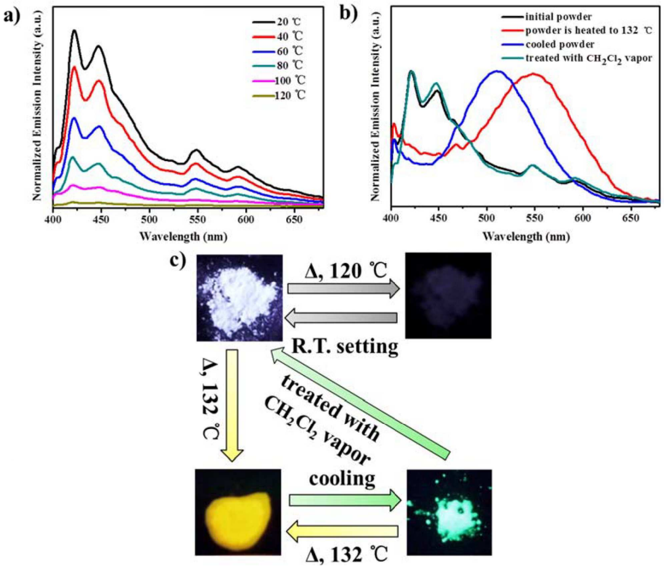

Fig. 4 a) PL spectra of luminogen **1** over a temperature range of 20-120 ℃. Excitation wavelength: 365 nm. b) PL spectra of **1** initial powder, heated powder (132 ℃), cooled powder and treated with CH_2Cl_2 vapor. Excitation wavelength: 365 nm. c) The diagram of dual-responsive thermochromism behavior of **1**.

Subsequently, the thin-film vapochromic effect of luminogen **1** was investigated via PL spectroscopy. Complex **1** exhibited high solubility in most of the common solvents, which allowed the formation of corresponding thin film. Consistent with the fluorescence of **1** in DMF-H_2O mixtures with high water content (Fig. S7, ESI†), the thin-film of **1** emitted strong green luminescence. The vapo-triggered emission spectral changes of **1** are shown in Figure 5. When the thin film of **1** was exposed to vapors of volatile organic compounds (VOCs), including benzene, pyridine, acetone, dichloromethane, toluene, trichloromethane, tetrahydrofuran, acetonitrile, diethyl ether, ethyl acetate, etc., the emission band centred at 512 nm red-shifted to the yellow-emitting region with λ_{max} at 556 nm, and the bright green luminescence was converted to yellow emission. Moreover, the yellow emission reverted to the initial green emission when the thin film of **1** was removed from the VOC vapors. More importantly, luminogen **1** exhibited an sensitive vapor response (For a selected example: see Movie S1, ESI†), which is very favorable for **1** to sense volatile organic compounds. Single crystals, with dichloromethane molecules of **1**, appropriate for single-crystal X-ray structure analysis were obtained by the recrystallization method involving tardy diffusion of n-hexane into solutions of **1** in dichloromethane. Detailed information of the corresponding crystal is provided in the ESI.†

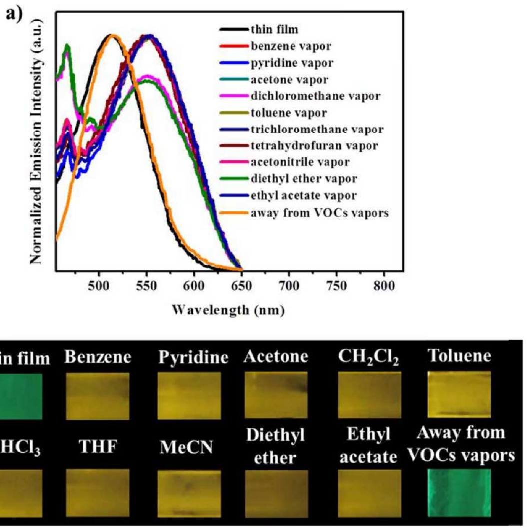

Fig. 5 a) Emission spectra changes of **1** thin film, exposing to VOCs vapors and away from VOCs vapors. Excitation wavelength: 365 nm; b) Photographic images of **1** thin film, upon exposure to vapors of VOCs and away from VOCs vapors under 365 nm UV light.

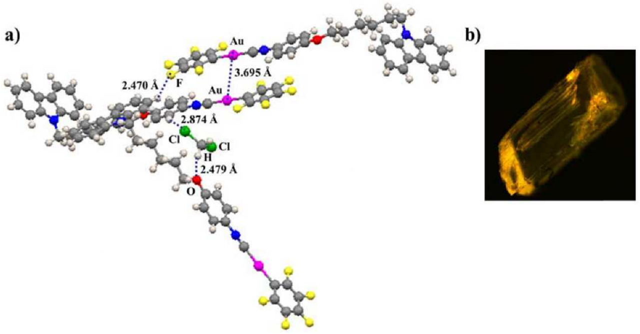

Fig. 6 a) The structural organization of single crystal with dichloromethane molecules of complex **1**; b) Photographic image of yellow light-emitting crystal of **1** under 365 nm UV irradiation.

As Figure 6 reveals, the existence of dichloromethane molecules results in the formation of intermolecular C-H···Cl interactions ($d_{H\cdots Cl}$ = 2.874 Å) and intermolecular C-H···O interactions ($d_{H\cdots O}$ = 2.479 Å), which alter the molecular stacking and shorten the intermolecular distance between the shortest Au atoms. These single crystals with dichloromethane molecules emitted yellow fluorescence under 365 nm UV irradiation, which is consistent with the luminescence of luminogen **1** exposed to vapors of VOCs. The acquisition of the yellow-emitting single crystals is very important in explaining the sensitive thin-film vapochromism mechanism of **1**.

Conclusions

In summary, we have discovered an carbazole-based mononuclear gold(I) complex, which exhibits reversible mechanochromic

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behavior, noteworthy dual-responsive thermochromism, and sensitive thin-film vapochromism characteristics. Furthermore, two kinds of crystals of complex **1** were fortunately obtained. On the basis of single-crystal structural organizations of the two types of crystals, it is speculated that the changes of luminogen **1** in the molecular arrangement and the formation of intermolecular aurophilic interactions are possibly responsible for its valuable and remarkable properties. To the best of our knowledge, this novel gold(I) complex is the first example of fluorescent molecule, which exhibits reversible mechanochromism, dual-responsive thermochromism and sensitive thin-film vapochromism characteristics. The intriguing multi-stimuli-responsive feature of complex **1** may have the potential for applications in pressure-, temperature-, and vapor-sensing materials. In addition, the results of this study will be beneficial for the design of new multi-stimuli-responsive luminescent materials. Further investigation and exploration of mononuclear gold(I) complex with other fascinating properties are currently underway at our laboratory.

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†Electronic Supplementary Information (ESI) available: Detailed experimental sections, NMR spectra, mass spectra, details of the crystal data collection, bond distance and angles. CCDC 1044227 and 1044242 (compound **1**), and characterization datas mentioned in the paper. See DOI: 10.1039/b000000x/

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