



Carbazole-based aggregation-induced emission (AIE)-active gold(I) complex: Persistent room-temperature phosphorescence, reversible mechanochromism and vapochromism characteristics



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ARTICLE INFO

Article history:

Received 26 January 2017

Received in revised form

30 April 2017

Accepted 2 May 2017

Available online 4 May 2017

Keywords:

Gold(I) complex

Carbazole

Aggregation-induced emission

Persistent room-temperature

phosphorescence

Mechanochromism

Vapochromism

ABSTRACT

A carbazole-based gold(I) complex **1** has been successfully synthesized. Its structure was characterized by nuclear magnetic resonance spectroscopy, elemental analysis and single crystal X-ray diffractometry. Its aggregation-induced emission behavior was studied by ultraviolet/visible, photoluminescence spectroscopy and scanning electron microscope. Its solid-state mechanochromic and thin-film vapochromic luminescence behaviors were also investigated by photoluminescence spectroscopy. The results demonstrated that luminogen **1** showed obvious aggregation-induced emission property. Furthermore, **1** also exhibited reversible high-contrast mechanochromic and vapochromic luminescence behaviors. More interestingly, **1** can emit persistent room-temperature phosphorescence with a solid-state emission lifetime up to 86.84 ms, which is the highest lifetime value among all the reported gold(I) complexes so far. To the best of our knowledge, the gold(I) complex is the first example of an AIE-active luminogen with persistent room-temperature phosphorescence, reversible mechanochromism and vapochromism characteristics.

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1. Introduction

The development of efficient luminescent materials has received a great deal of attention both in fundamental science and practical applications [1–3]. Especially, smart luminescent materials responding to external stimuli have attracted increasing interest due to their potential applications in the fields of sensors, security inks and optoelectronic devices [4–8]. Mechanochromic emissive materials, as a class of smart luminescent materials, have aroused widespread concern [9–12]. Vapochromic materials, which involve luminescent changes upon exposure to volatile organic vapors, are also one promising type of smart luminescent materials [13–19]. High aggregative-state emission and obvious color contrast before and after stimulating are two extremely important factors for the highly efficient application of stimuli-responsive smart materials [20]. However, most conventional

luminogens commonly show poor aggregate state emission efficiency because of the presence of notorious aggregation caused quenching (ACQ) phenomenon [21], which blocks the effective development of stimuli-responsive materials. Fortunately, a new photophysical process of aggregation-induced emission (AIE) was discovered by Tang et al. in 2001 [22]. The luminogens possessing AIE effect can achieve bright luminescence by the aggregate formation. Therefore, it is very significant to synthesize multistimuli-responsive AIE materials with mechanochromism and vapochromism characteristics. Over the past two decades, gold(I) chemistry has aroused the interest of many researchers owing to the occurrence of fascinating aurophilic interactions between gold centers [23–32]. To date, nevertheless, AIE-active gold(I) complexes with mechanochromic and vapochromic behaviors are rather rare [28,30,33–35].

Carbazole-based luminescent materials are valuable candidates in the domain of photoelectronic devices [36–39]. Unfortunately, the ACQ effect hinders the high-efficiency application of these luminescent materials containing carbazole unit. Thus, it is a meaningful research topic to design and synthesize carbazole-based derivatives with AIE property. On the other hand, most phosphorescence-emitting metal complexes with

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mechanochromism behavior exhibit short phosphorescence lifetimes (<1 ms) [40–42], and metal complex simultaneously possessing persistent room-temperature phosphorescence and reversible mechanochromism characteristics has yet to be reported, not to mention AIE-active vapochromic gold(I) complex with these intriguing properties. In this work, we described a carbazole-based mononuclear gold(I) complex **1** (Chart 1). AIE, mechanochromism and vapochromism characteristics of the luminogen were systematically investigated. **1** exhibited obvious AIE behavior, Furthermore, **1** also showed reversible high-contrast mechanochromic and vapochromic luminescence. More importantly, **1** can emit persistent solid-state room-temperature phosphorescence with luminescence lifetime up to 86.84 ms.

2. Materials and methods

2.1. Experimental

General: All manipulations were carried out under an argon atmosphere by using standard Schlenk techniques, unless otherwise stated. The starting material carbazole purchased from Alfa Aesar was used as received. CH₂Cl₂ was dried with CaH₂ then distilled. All other starting materials and reagents were obtained as analytical-grade from commercial suppliers and used without further purification. Compound **1-b** [43] and C₆F₅Au(tht) (tht = thiophane) [44] were prepared by procedures described in the corresponding literature. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were collected on American Varian Mercury Plus 400 spectrometer (400 MHz). ¹H NMR spectra are reported as followed: chemical shift in ppm (δ) relative to the chemical shift of TMS at 0.00 ppm, integration, multiplicities (*s* = singlet, *d* = doublet, *t* = triplet, *m* = multiplet), and coupling constant (Hz). ¹³C NMR chemical shifts reported in ppm (δ) relative to the central line of triplet for CDCl₃ at 77 ppm. ¹⁹F NMR chemical shifts are relative to C₆F₆ (δ = -163.00). EI-MS was obtained using Thermo scientific DSQ II. Elemental analyses (C, H, N) were carried out with a PE CHN 2400 analyzer. Ultraviolet/Visible spectra were obtained on U-3310 UV Spectrophotometer. Fluorescence spectra were recorded on a Hitachi-F-4500 fluorescence spectrophotometer and Fluoromax-P luminescence spectrometer (HORIBA JOBIN YVON INC.). Luminescent decay experiment was measured by Edinburgh FLS980 spectrometer. XRD studies were recorded on a Shimadzu XRD-6000 diffractometer using Ni-filtered and graphite-monochromated Cu K α radiation (λ = 1.54 Å, 40 kV, 30 mA). The N, N-dimethyl formamide (DMF)/water mixtures with various water fractions were prepared by slowly adding ultra-pure water into the DMF solution of samples. Absolute luminescence quantum yields were measured by HAMAMATSU ABSOLUTE PL QUANTUM YIELD SPECTROMETER C11347. Dynamic light scattering (DLS) measurements were performed on the Zetasizer instrument ZEN3600 (Malvern, UK) with a 173° back scattering angle and He–Ne laser (λ = 633 nm). The X-ray crystal-structure determination of complex **1** was obtained on a Bruker APEX DUO CCD system. The aggregate behavior and the solid-state surface morphology of **1** were investigated by scanning electron microscopy (SEM, Zeiss, Sigma). Column chromatographic separations were carried out on silica gel (200–300 mesh). TLC was performed by using commercially prepared 100–400 mesh silica gel plates (GF254) and visualization was effected at 254 nm.

2.2. Synthesis

2.2.1. Synthesis of monoisocyno ligand **1-d**

Synthesis of **1-c**: A mixture of compound **1-b** (3.0 g, 11.6 mmol), formic acid (30 ml) were stirred for overnight at 110 °C. After

completion of present reaction, formic acid was removed from reaction system by distillation, the residual mixture was extracted with dichloromethane (3 × 30 ml), the combined organic layers were washed with brine, dried (Na₂SO₄), and concentrated in vacuo. The residues were purified by column chromatography, affording the expected pale solid product in a yield of 83%. ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.83–8.46 (m, 1H), 8.16–8.13 (m, 2H), 7.77 (d, *J* = 8 Hz, 1H), 7.58–7.52 (m, 2H), 7.44–7.27 (m, 8H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 162.5, 159.1, 140.8, 140.8, 135.9, 135.8, 134.8, 134.0, 128.5, 127.8, 126.0, 126.0, 123.3, 123.3, 121.2, 120.4, 120.3, 120.1, 120.0, 109.6, 109.5. EI-MS: *m/z* = 286.16[M]⁺. Anal. Calcd. for C₁₉H₁₄N₂O: C, 79.70; H, 4.93; N, 9.78. Found: C, 79.74; H, 4.95; N, 9.75.

Synthesis of **1-d**: A CH₂Cl₂ suspension (15 ml) of **1-c** (1.0 g, 3.5 mmol) and triethylamine (5 ml) was cooled to 0 °C. To the mixture was added dropwise a CH₂Cl₂ solution (10 ml) of triphosgene (1.16 g, 3.9 mmol). The mixture was refluxed under an argon atmosphere for 3 h, then 10% aq. Na₂CO₃ (50 ml) was added dropwise at room temperature. the mixture was extracted with dichloromethane (3 × 30 mL). The combined organic layers were washed with brine, dried (Na₂SO₄), and concentrated in vacuo. The residues were purified by column chromatography, affording the expected grey solid product in a yield of 77%. ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.14 (d, *J* = 8 Hz, 2H), 7.63 (s, 4H), 7.45–7.30 (m, 6H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 165.3, 140.2, 138.7, 128.0, 127.7, 126.2, 123.7, 120.6, 120.4, 109.4. EI-MS: *m/z* = 268.14[M]⁺. Anal. Calcd. for C₁₉H₁₂N₂: C, 85.05; H, 4.51; N, 10.44. Found: C, 85.02; H, 4.55; N, 10.41.

2.2.2. Synthesis of complex **1** containing mononuclear gold(I) unit

Synthesis of **1**: A mixture of C₆F₅Au(tht) (0.26 g, 0.57 mmol) and **1-d** (0.15 g, 0.56 mmol) was stirred in CH₂Cl₂ (20 ml) over night under an argon atmosphere at room temperature. After completion of present reaction, the solvent was evaporated. A small amount of CH₂Cl₂ was added, and then a lot of *n*-hexane was added. Collecting the white solid product by suction filtration. Yield = 93%. ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.15 (d, *J* = 8 Hz, 2H), 7.80 (s, 4H), 7.46–7.34 (m, 6H). ¹⁹F NMR (CDCl₃): δ (ppm) = -116.60, -157.80, -162.87. Anal. Calcd. for C₂₅H₁₂AuF₅N₂: C, 47.49; H, 1.91; N, 4.43. Found: C, 47.56; H, 1.95; N, 4.38.

3. Results and discussion

3.1. Synthesis

The carbazole-based mononuclear gold(I) complex **1** was prepared according to the corresponding synthetic strategy presented in Scheme 1. The intermediate product **1-d** as starting material reacted with C₆F₅Au(tht) (tht = thiophane) to afford the target gold(I) complex **1** in 93% yield.

3.2. Crystallographic details

Single crystals of complex **1** suitable for X-ray analysis were obtained by slow diffusion of *n*-hexane into its dilute solution of dichloromethane. A crystal of **1** with approximate dimensions of 0.30 × 0.05 × 0.02 mm³ for **1** was mounted on a glass fiber for diffraction experiment. Intensity data were collected on a Nonius Kappa CCD diffractometer with Mo K α radiation (0.71073 Å) at room temperature. The structures were solved by a combination of direct methods (SHELXS-97) [45] and Fourier difference techniques and refined by full-matrix least-squares (SHELXL-97) [46]. All non-H atoms were refined anisotropically. The hydrogen atoms were placed in the ideal positions and refined as riding atoms. Further crystal data are provided in Table S1 (Supporting Information). The

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