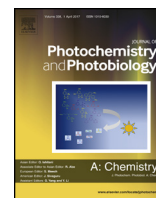




Contents lists available at ScienceDirect

# Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: [www.elsevier.com/locate/jphotochem](http://www.elsevier.com/locate/jphotochem)

Invited paper

## Photophysical and ion-binding studies of a tetranuclear alkynylgold(I) isonitrile complex



Frankie Chi-Ming Leung, Vivian Wing-Wah Yam\*

*Institute of Molecular Functional Materials (Areas of Excellence Scheme, University Grants Committee (Hong Kong)) and Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, China*

### ARTICLE INFO

#### Article history:

Received 8 August 2017

Received in revised form 1 September 2017

Accepted 11 September 2017

Available online 15 September 2017

**Dedicated to Prof. Chen-Ho Tung on the occasion of his 80<sup>th</sup> birthday.**

#### Keywords:

Gold(I)

Gold interactions

Auophilicity

Cadmium

Amide binding

### ABSTRACT

A number of polyamide-containing multinuclear alkynylgold(I) isonitrile complexes have been designed, synthesized and characterized. The tetranuclear gold(I) complex is found to show spectroscopic responses in the presence of cadmium ions. The photophysical properties of the complex can be modulated via the suppression of photo-induced electron transfer (PET) and intramolecular Au··Au interactions. The binding mode of the complex has also been investigated by <sup>1</sup>H NMR spectroscopy. The complex is found to be highly selective towards cadmium ions as well as zinc ions.

© 2017 Elsevier B.V. All rights reserved.

## 1. Introduction

There is a growing interest in the development of fluorescent probes due to their high sensitivity and fast response time [1,2]. In the majority of the fluorescent chemosensors reported so far, the signaling of the binding event is achieved by the modulation of photo-induced electron transfer (PET) [3–5], formation of chromophore (excimer) [6,7] and Forster resonance energy transfer (FRET) processes [8–10]. When compared to the traditional organic chemosensors, the long-lived triplet emission of transition metal complexes as the spectroscopic reporter can offer some advantages, such as larger Stokes shift, longer-lived luminescence and less destructive lower excitation energy.

Recently, there has been a growing interest in the study of polynuclear gold(I) complexes, in particular with regard to the phenomenon of aurophilicity associated with these complexes, which results from weak Au··Au interactions [10–22]. A series of multinuclear gold(I) complexes which can act as luminescence ion probes for different metal ions has been reported by us previously [23–32]. These complexes have exploited the utilization of the on/off switching of Au··Au interactions for metal ion sensing. The metal ions with appropriate size are encapsulated in the complex

in a sandwiched fashion, resulting in the bringing of the gold atoms into close proximity and the formation of emission band of ligand-to-metal-metal charge transfer (LMMCT) origin [29–32].

As an extension of our previous efforts in this interesting area, we aimed at increasing the extent of Au··Au interactions upon the binding of heavy metal ions using multi-nuclear gold(I) complexes with multiple binding sites. In this regard, cadmium ions are selected as the ion of interest as the toxicity and environmental hazard of cadmium ions are well known [33]. The absorption of cadmium ions by human beings can cause a serious softening of the bone [33,34]. As a consequence, cadmium-indicating methodologies, which are developed to provide critical information for cadmium hazard assessment and pollution management, are in high demand [35].

Herein we report the design and synthesis of a polyamide-containing tetranuclear alkynylgold(I) complex with four isonitrile pendants for the binding of cadmium ion. With such a design, it is believed that once the cadmium ion is encapsulated in between the polyamide pendant units in the gold(I) complex on binding [36,37], such that the four rigid and linear arylalkynylgold(I) units (which were initially free to rotate) would be forced further apart from each other, and as a result would lead to the decrease in the signal due to Au··Au interactions in the emission spectroscopy. In this work, less steric demanding alkynyls and isonitrile ligands would serve as good candidates for the design of chemosensing systems due to their simple linear geometry and rigidity, in

\* Corresponding author.

E-mail address: [wvyam@hku.hk](mailto:wvyam@hku.hk) (V.W.-W. Yam).

addition to the presence of a  $\pi$ -conjugated system which is usually involved in the origin of luminescence [38]. It is envisaged that this work can open up new design strategies for the molecular recognition of heavy metal ions by gold(I) complexes of higher nuclearity and their potential applications in heavy and toxic metal cation-sensing.

## 2. Experimental

### 2.1. Materials and reagents

Chlorotetrahydrothiophene gold(I) ([Au(tht)Cl]) are synthesized according to the literature methods [39]. Ethyl bromoacetate, *o*-phenylenediamine, aniline and 2,6-dimethylisocyanide are purchased from Sigma-Aldrich. 4-(Dimethylamino)pyridine (DMAP) is purchased from Matrix Scientific. 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC-HCl) is purchased from GL Biochem (Shanghai) Ltd. The commercially available chemicals are used as received without further purification. All reactions are carried out under an inert atmosphere of nitrogen using standard Schlenk techniques.

### 2.2. Synthesis of *o*-phenylenediamine-(CH<sub>2</sub>CONHC≡CH)<sub>4</sub>

*o*-Phenylenediamine (5.0 g, 46 mmol) was reacted with ethyl bromoacetate (31 g, 185 mmol) in the presence of sodium carbonate (63.5 g, 460 mmol) in acetonitrile (1000 mL) at 80 °C for overnight. A white precipitate was formed when deionized water (2000 mL) was poured into the reaction mixture. The solid (5.0 g, 12.6 mmol) was collected by filtration and then reacted with sodium hydroxide (NaOH) (0.5 g, 13.0 mmol) in THF (50 mL) at room temperature for 4 h. The solvent was removed in vacuo and the residue was washed with water. The initial product was then mixed with propargylamine (2.8 g, 55.5 mmol), EDC-HCl (9.6 g, 50.4 mmol) and DMAP (6.1 g, 50.4 mmol) and the mixture was dissolved in distilled DMF (50 mL). The mixture was stirred at room temperature for overnight under an inert atmosphere of nitrogen. The solvent was removed in vacuo, and then the residue was washed with water to give the desired ligand as a white solid. Yield: 1.90 g (31%). Positive EI-MS: ion clusters at *m/z* 488 [M]<sup>+</sup>. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, 298 K, relative to Me<sub>4</sub>Si,  $\delta$ /ppm):  $\delta$  = 3.01 (s, 4H, —C≡CH), 3.97 (s, 8H, —NCH<sub>2</sub>CON—), 4.04 (d, *J* = 5.2 Hz, 8H, —NCH<sub>2</sub>C≡C—), 6.53 (d, *J* = 4.2 Hz, 2H, —NC<sub>6</sub>H<sub>4</sub>N—), 6.84 (t, *J* = 4.2 Hz, 2H, —NC<sub>6</sub>H<sub>4</sub>N—), 7.49 (s, 4H, —CONH—). IR (KBr)  $\nu$ /cm<sup>-1</sup>: 3322 (s, b,  $\nu$ (N—H)), 2219 (w, sh,  $\nu$ (C≡C)), 1680 (s, sh,  $\nu$ (C=O)), 1555 (m, sh,  $\nu$ (CON—H bending)).

### 2.3. Synthesis of aniline-(CH<sub>2</sub>CONHC≡CH)<sub>2</sub>

The procedure was similar to the synthesis of *o*-phenylenediamine-(CH<sub>2</sub>CONHC≡CH)<sub>4</sub>, except aniline (4.0 g, 43 mmol) was used instead of *o*-phenylenediamine to give the desired ligand as a white solid. Yield: 0.57 g (40%). Positive EI-MS: ion clusters at *m/z* 283 [M]<sup>+</sup>. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, 298 K, relative to Me<sub>4</sub>Si,  $\delta$ /ppm):  $\delta$  = 3.04 (s, 2H, —C≡CH), 4.02 (s, 4H, —NCH<sub>2</sub>CON—), 4.08 (d, *J* = 5.2 Hz, 4H, —NCH<sub>2</sub>C≡C—), 6.38 (d, *J* = 4.2 Hz, 2H, —NC<sub>6</sub>H<sub>5</sub>), 6.67 (t, *J* = 4.2 Hz, 1H, —NC<sub>6</sub>H<sub>5</sub>), 7.16 (t, *J* = 4.2 Hz, 2H, —NC<sub>6</sub>H<sub>5</sub>), 7.52 (s, 2H, —CONH—). IR (KBr)  $\nu$ /cm<sup>-1</sup>: 3316 (s, b,  $\nu$ (N—H)), 2218 (w, sh,  $\nu$ (C≡C)), 1682 (s, sh,  $\nu$ (C=O)), 1555 (m, sh,  $\nu$ (CON—H bending)).

### 2.4. Synthesis of complex 1

*o*-Phenylenediamine-(CH<sub>2</sub>CONHC≡CH)<sub>4</sub> (100 mg, 0.20 mmol) and [Au(tht)Cl] (272 mg, 0.85 mmol) were dissolved in dichloromethane (30 mL). Then triethylamine (323  $\mu$ L, 3.2 mmol) was

added to the solution. The reaction was stirred at 0 °C in an ice bath for 30 min under an inert atmosphere of nitrogen. Then, 2,6-dimethylisocyanide (118 mg, 0.90 mmol) is added into the reaction mixture and the reaction mixture was allowed to stir at room temperature for 1.5 h under inert atmosphere. The solvent was removed in vacuo and the residue was washed with methanol. The solid was further purified by recrystallization via the diffusion of diethyl ether vapor into a dichloromethane solution of the complex to give the desired product as a pale yellow solid. Yield: 190 mg (53%). Positive ESI-MS: ion clusters at *m/z* 1861 [M+2MeOH]<sup>+</sup>, 1796 [M]<sup>+</sup>, 1731 [M+2MeOH—C≡NC<sub>6</sub>H<sub>10</sub>]<sup>+</sup>. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>, 298 K, relative to Me<sub>4</sub>Si,  $\delta$ /ppm):  $\delta$  = 2.39 (s, 24H, —Me), 3.99 (s, 8H, —NCH<sub>2</sub>CON—), 4.03 (d, *J* = 4.8 Hz, 8H, —NCH<sub>2</sub>C≡C—), 6.94 (m, 2H, —NC<sub>6</sub>H<sub>4</sub>N—), 7.07 (m, 2H, —NC<sub>6</sub>H<sub>4</sub>N—), 7.14 (d, *J* = 4.8, 8H, —C≡NC<sub>6</sub>H<sub>3</sub>—), 7.29 (t, *J* = 4.8 Hz, 4H, —C≡NC<sub>6</sub>H<sub>3</sub>—), 7.61 (t, *J* = 4.0 Hz, 4H, —CONH—). IR (KBr)  $\nu$ /cm<sup>-1</sup>: 3316 (s, b,  $\nu$ (N—H)), 2232 (s, sh,  $\nu$ (C≡N)), 2133 (w, sh,  $\nu$ (C≡C)), 1679 (s, sh,  $\nu$ (C=O)), 1550 (m, sh,  $\nu$ (CON—H bending)). Elemental analyses calcd (%) for C<sub>62</sub>H<sub>60</sub>Au<sub>4</sub>N<sub>10</sub>O<sub>4</sub>·2MeOH: C, 41.30; H, 3.68; N, 7.53. Found: C, 41.15; H, 3.63; N, 7.48.

### 2.5. Synthesis of complex 2

The procedure was similar to the synthesis of complex 1, except aniline-(CH<sub>2</sub>CONHC≡CH)<sub>2</sub> (100 mg, 0.35 mmol) was used instead of *o*-phenylenediamine-(CH<sub>2</sub>CONHC≡CH)<sub>4</sub> to give the desired complex as a white solid. Yield: 211 mg (64%). Positive ESI-MS: ion clusters at *m/z* 978 [M+MeOH]<sup>+</sup>, 937 [M]<sup>+</sup>. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, 298 K, relative to Me<sub>4</sub>Si,  $\delta$ /ppm):  $\delta$  = 2.38 (s, 12H, —Me), 3.94 (d, *J* = 5.6 Hz, 4H, —NCH<sub>2</sub>CON—), 4.04 (s, 4H, —NCH<sub>2</sub>C≡C—), 6.67 (d, *J* = 5.2 Hz, 1H, —NC<sub>6</sub>H<sub>5</sub>), 7.07 (m, 2H, —NC<sub>6</sub>H<sub>5</sub>), 7.17 (t, *J* = 5.2 Hz, 2H, —NC<sub>6</sub>H<sub>5</sub>), 7.28 (d, *J* = 5.2 Hz, 4H, —C≡NC<sub>6</sub>H<sub>3</sub>—), 7.42 (d, *J* = 5.2 Hz, 2H, —C≡NC<sub>6</sub>H<sub>3</sub>—), 9.07 (d, *J* = 4.4 Hz, 2H, —CONH—). IR (KBr)  $\nu$ /cm<sup>-1</sup>: 3304 (s, b,  $\nu$ (N—H)), 2228 (s, sh,  $\nu$ (C≡N)), 2139 (s, sh,  $\nu$ (C≡C)), 1671 (w, sh,  $\nu$ (C=O)), 1564 (m, sh,  $\nu$ (CON—H bending)). Elemental analyses calcd (%) for C<sub>34</sub>H<sub>33</sub>Au<sub>2</sub>N<sub>5</sub>O<sub>2</sub>·MeOH: C, 43.35; H, 3.85; N, 4.95. Found: C, 43.23; H, 3.80; N, 4.87.

### 2.6. Physical measurements and instrumentation

<sup>1</sup>H NMR and 2D <sup>1</sup>H NMR spectra were recorded on a Bruker DPX-400 or Bruker DPX-500 Fourier Transform NMR spectrometer with chemical shifts reported relative to tetramethylsilane, (CH<sub>3</sub>)<sub>4</sub>Si. Positive-ion ESI mass spectra were recorded on a Finnigan LCQ mass spectrometer. FTIR spectra of the complexes were obtained as KBr disk on a Bio-Rad FTS-7 Fourier transform infrared spectrophotometer (4000–400 cm<sup>-1</sup>). Elemental analysis of the complexes were performed on a Carlo Erba 1106 elemental analyzer at the Institute of Chemistry of the Chinese Academy of Sciences in Beijing. Electronic absorption spectra were recorded on a Varian Cary 50 UV-vis spectrophotometer. Steady-state excitation and emission spectra were recorded on a Spex Fluorolog-3 Model FL3-211 fluorescence spectrofluorometer equipped with a R2658P PMT detector. Photophysical measurements in low-temperature transparent glass were carried out with the sample solution loaded in a quartz tube inside a quartz-walled Dewar flask. Liquid nitrogen was placed into the Dewar flask for low temperature (77 K) photophysical measurements. Excited-state lifetimes of solution and glass samples were measured using a conventional pulsed laser system. The excitation source used was the 355-nm output (third harmonic, 8 ns) of a Spectra-Physics Quanta-Ray Q-switched GCR-150 pulsed Nd:YAG laser (10 Hz). Luminescence decay signals were detected by a Hamamatsu R928 photomultiplier tube and recorded on a Tektronix model TDS-620A (500 MHz, 2GS/s) digital oscilloscope, and analyzed using a

Download English Version:

<https://daneshyari.com/en/article/6492741>

Download Persian Version:

<https://daneshyari.com/article/6492741>

[Daneshyari.com](https://daneshyari.com)