### Journal Pre-proofs

New gold (I) complexes with 5-aromatic ring-1, 3, 4-oxadiazole-2-thione and triphenylphosphine as potential multifunctional materials

Yu Qiang Zhao, Jie Zhou, Renze He, Guang Ke Wang, Lan Xi Miao, Xiao Guang Xie, Ying Zhou

PII:	S0040-4039(20)31179-5
DOI:	https://doi.org/10.1016/j.tetlet.2020.152668
Reference:	TETL 152668
To appear in:	Tetrahedron Letters
Received Date:	7 August 2020
Revised Date:	5 November 2020
Accepted Date:	9 November 2020



Please cite this article as: Qiang Zhao, Y., Zhou, J., He, R., Ke Wang, G., Xi Miao, L., Guang Xie, X., Zhou, Y., New gold (I) complexes with 5-aromatic ring-1, 3, 4-oxadiazole-2-thione and triphenylphosphine as potential multifunctional materials, *Tetrahedron Letters* (2020), doi: https://doi.org/10.1016/j.tetlet.2020.152668

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2020 Published by Elsevier Ltd.



Tetrahedron Letters journal homepage: www.elsevier.com

# New gold (I) complexes with 5-aromatic ring-1, 3, 4-oxadiazole-2-thione and triphenylphosphine as potential multifunctional materials

Yu Qiang Zhao <sup>a</sup>, Jie Zhou <sup>a</sup>, Renze He <sup>a</sup>, Guang Ke Wang <sup>a</sup>, Lan Xi Miao <sup>a</sup>, Xiao Guang Xie <sup>a</sup> and Ying Zhou <sup>a</sup>, \*

<sup>a</sup> College of Chemical Science and Technology, Yunnan University, Kunming, 650091, China

#### ARTICLE INFO \* Corresponding author. Tel.: +86-871-65033715; fax: +86-871-65033715; e-mail: yingzhou@ynu.edu.cn

Article history: Received Received in revised form Accepted Available online

Keywords: Gold (I) complexes Triphenylphosphine Photoluminescence Multifuctional material Three new gold (I) complexes (4a, 4b, 4c) with 5-aromatic ring-1, 3, 4-oxadiazole-2-thione and triphenylphosphine as ligands were synthesized. Structures of 4a and 4b were determined through X-ray single-crystal diffraction, and it displayed that 4a and 4b had the same metal coordination pattern, wherein the ligand was coordinated by the sulfur atom to the central metal ion of gold (I). The optical properties of these gold (I) complexes were studied both in solution and in solid-state. In DMSO, 4a and 4b peaked at 415 nm and 443 nm, respectively, and the CIE coordinates of 4a and 4b in the solid-state were in the green area namely, (0.26, 0.46) and (0.24, 0.41). HOMO/LUMO levels and bandgaps of 4a, 4b and 4c were assessed by UV spectrum estimation, electrochemical method, and theoretical calculations. The observation hinted that the photophysical properties and energy levels of these gold (I) complexes can be adjusted by the introduction of different substituent aromatic rings at the 5-position of the 1, 3, 4-oxadiazole-2-thiol moiety. The findings of good optical, electrochemical and thermal properties of these new gold (I) complexes demonstrated their potential in the future studies as multifunctional materials.

2009 Elsevier Ltd. All rights reserved.

#### 1. Introduction

In recent decades, gold complexes have been extensively studied owing to their outstanding performance in many fields.<sup>[1-4]</sup> Their unique physiological activity has promoted numerous researches on gold metal-organic complexes in anticancer, antibacterial and antiparasitic drugs.<sup>[5-6]</sup> In 2020, Chi-Ming Che *et al.* reported various gold (III) mesoporphyrin IX dimethyl esters (AuMesoIX) with thiol targeting ability, which showed effective antitumor activity in ovarian cancer mouse models.<sup>[7]</sup> In the same year, Sylvie Garneau-Tsodikova and Samuel G. Awuah reported a series of gold (I)-phosphine complexes with potent inhibitory activity for *Candida Auris*.<sup>[8]</sup> Additionally, Au complexes often utilized in the field of chemical catalysts. Recently, Hashmi *et al.* reported gold metal-organic complexes for the purpose of C-H activation, <sup>[9]</sup> and Nakada *et al.* examined gold (I) as a catalyst for catalytic ring isomerization reaction.<sup>[10]</sup>

In particular, the strong gold coordination bond and high spin coupling constant endows gold metal-organic complex with high stability and efficiency for triplet excitation capture.<sup>[11]</sup> Reports have shown that certain luminescent gold (III) complexes possess good photoelectric properties, and have been successfully applied as emitting <sup>[12-13]</sup> and photovoltaics (PV) materials. <sup>[14]</sup> Vivian Wing-Wah Yam *et al.* explored sky-blue-emitting gold (III)

complexes as solution-processable and vacuum-deposited organic light-emitting diodes (OLEDs), <sup>[15]</sup> as well as specific horizontally oriented gold (III) complexes that exhibit high photoluminescence quantum yields of 70% and high horizontal dipole ratio of 0.87, which were employed as green-emitting OLEDs. <sup>[16]</sup>

Importantly, compared with extensive gold (III) complex research, exploration of multi-functional gold (I) metal-organic complexes in photoluminescence is scarce.<sup>[17-18]</sup> Recently, gold (I) complexes containing 1, 3, 4-oxadiazolines and phosphine ligands have been reported as potential anticancer and antileishmanial agents.<sup>[19-20]</sup> Furthermore, the emission and electronic transmission properties of gold (I) complexes are rarely examined. Inspired by the novel structures and promising properties of gold (I)-based 1, 3, 4-oxadiazole derivatives, we studied the preparation of new gold (I) metal-organic complexes with good photoluminescent and potential electron-transporting properties that are applicable in the field of photoluminescence and photoelectric.

In this work, we designed and synthesized three new gold (I) complexes (4a, 4b, and 4c) with 5-aromatic ring-1,3,4-oxadiazole-2-thiol and triphenylphosphine ligands (Scheme 1). The structures of complexes 4a and 4b were determined through X-ray single-crystal diffraction, in which they displayed comparable metal coordination patterns. Additionally, complexes

4a

urnal Pre-proofs

solid-state. The observed increase of electron donor capability of the aromatic nucleus at 5 position of 1,3,4-oxadiazole-2-thiol, promoted an obvious redshift in the UV-vis spectra of complexes 4a, 4b to 4c. In the solid phase, complexes 4a and 4b exhibited strong green emission, while complex 4c showed no fluorescence because of the obvious aggregation causing fluorescence quenching. The HOMO/LUMO and band gaps (Eg) the prepared complexes were determined by optical tests, electrochemical measurements and theoretical calculations. Semiconductor-like band gaps with low LUMO energy level were found for complex 4c, making it a potential candidate as electronic transport material. Comparison of the complex's properties showed that their photophysical properties and energy levels could be adjusted via the introduction of substitutes at the 5-position of 1,3,4-oxadiazole-2-thiol ligand. Therefore, according to the obtained results, with further rational design, some multifunctional gold (I) complexes will have enormous potential and prospects in the application of optoelectronic devices.

#### 2. Results and Discussion

#### 2.1. synthesis and structure

The synthetic route to the compounds is shown in Scheme 1. 6-membered aromatic acid or naphthoic acid was used as the starting material for reaction with ethanol to form esters, wherein DMAP and EDC were used as catalysts. Then the corresponding esters reacted with hydrazine hydrate (N2H4·H2O) and CS2 to form 1, 3, 4-oxadiazole-2-thiol ligands, 3a-3c in two steps. A previously reported work has demonstrated that two tautomeric forms of 1, 3, 4-oxadiazole-2-thione/thiol can coexist (Fig S37),<sup>[20]</sup> while the X-ray diffraction data for 4a and 4b (Table 2) in this work indicate that the ligands 3a-3c presented a thiolate form in the complexes. Triphenylphosphine gold chloride (AuCl(PPh<sub>3</sub>)) was dissolved along with the corresponding ligands in a mixed solvent system of acetone/dichloromethane (1:1) to form the target complexes. Structures of the intermediates and final products have been verified by <sup>1</sup>H NMR, <sup>13</sup>C NMR, and HR-MS. (Fig S3-S39)



Scheme 1.Synthetic processes and methods for compounds 1a-1c, 2a-2c, 3 a-3c, 4a-4c

Fortunately, the crystals of **4a** and **4b** were obtained by the solvent dispersion method (dichloromethane/diethyl ether), and their structures were determined by single-crystal X-ray diffraction. The crystal data and structure refinement details for the complexes **4a** and **4b** are summarized in Table 1. From the data, it is evident that **4a** and **4b** have the same metal-coordination pattern, in which the ligand is coordinated to the central metal ion of gold(I) via the sulfur atom, which is consistent with the previously reported two-coordinated gold(I) compounds. <sup>[20-23]</sup>The bond angles of P(1)-Au(1)-S(1) = 178.87° (for **4a**) and P(1)-Au(1)-S(1) = 177.83° (for **4b**) revealed that the coordinated sphere deviated slightly from the linear geometry in these complexes, which may be related to the steric effect of the

effect of the groups at 5-positon in **3a** and **3b**. (Table 2) The closest Au···Au bond distances were found to be 3.536 Å (for **4a**) and 4.773 Å (for **4b**), larger than the sum of the van der Waals radii (3.40 Å), and it, therefore, indicates there is no significant gold–gold interaction in the two compounds. In the complex **4b**, intramolecular hydrogen bonds were formed by O2–H2···N2 interactions, and weak non-classical intramolecular hydrogen bonds formed by C8–H8···O1 interactions were observed, with the Donor–Acceptor (D···A) distances being 2.673(5) and 2.872(5) Å, respectively. (Fig S40, Table S1)



Figure 1 (a) Schematic diagram of the smallest asymmetric unit structure of 4a; (b) Packing diagram for 4a, viewed along the *b* axis; (c) Schematic diagram of the smallest asymmetric unit structure of 4b; (d) Packing diagram for 4b, viewed along the *a* axis

 Table 1. Crystal data and structure refinement parameters for compounds 4a and 4b.

	<b>4a</b>	4b
Formula	C27H22AuN2OPS	$C_{26}H_{20}AuN_2O_2PS$
Formula weight/g mol-1	650.46	652.44
Temperature/K	293(2)	293(2)
Crystal system	Monoclinic	Triclinic
Space group	C2/c	$P\bar{\iota}$
a / Å	28.860(6)	9.4161 (15)
b / Å	8.8714(19)	10.8851(18)
c / Å	20.482(5)	11.888(2)
α/°	90	88.152(2)
β / °	111.494(2)	86.769(2)
γ/°	90	82.293(2)
V/ Å <sup>3</sup>	4879.2(18)	1205.2(3)
Z	8	2
Crystal size / mm <sup>3</sup>	0.330 x 0.210 x 0.210	$0.48 \times 0.25 \times 0.230$
$D_{calc} / g \cdot cm^{-3}$	1.771	1.798
µ/ mm <sup>-1</sup>	6.204	6.283
F(000)	2528	632
$R_{ m int}$	0.0312]	0.0224]
	$-34 \le h \le 34$	$-11 \le h \le 11$
Limiting indices	$-10 \le k \le 6$	$-12 \le k \le 12$
	$-24 \le l \le 24$	$-14 \le l \le 14$
Goodness-of-fit on F <sup>2</sup>	1.10/ R = 0.0281	1.039
Final R indices [I>2sigma(I)]	$\begin{bmatrix} R_1 - 0.0281 \\ wR_2 = 0.0741 \end{bmatrix}$	$R_1 = 0.0230$ $wR_2 = 0.0613$
$\mathbf{D}$ 1 (11.1.4.)	$R_1 = 0.0414$	$R_1 = 0.0286$
R indices (all data)	$wR_2 = 0.0947$	$wR_2 = 0.0636$
Largest diff. peak and hole/(	e·Ă· 0.568/ -1.068	0.49/-0.664
an $\Sigma \  \mathbf{\Gamma} \  = \  \mathbf{\Gamma} \  / \nabla \  \mathbf{\Gamma} \  h$	<b>D</b> $(\mathbf{r}^2, \mathbf{r}^2)^2$	$\nabla (\Gamma 2) 211/2$

 ${}^{a}R_{1} = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|; \quad {}^{b}wR_{2} = [\Sigma w(F_{o}^{2} - F_{c}^{2})^{2} / \Sigma w(F_{o}^{2})^{2}]^{1/2}$ 

Table 2. Selection of the main geometric parameters, bond lengths and bond angles to the 4a and 4b

4a						
Bond lengths	[Å]	Bond angles	[Å]			
Au(1)-P(1)	2.2628(14)	P(1)-Au(1)-S(1)	178.48(5)			
Au(1)-S(1)	2.3030(16)	C(9)-S(1)-Au(1)	103.75(19)			
N(1)-N(2)	1.428(7)	C(10)-P(1)-Au(1)	112.66(18)			
S(1)-C(9)	1.719(6)	C(16)-P(1)-Au(1)	113.58(17)			
		C(22)-P(1)-Au(1)	114.35(19)			
		N(2)-C(9)-S(1)	126.1(4)			
		O(1)-C(9)-S(1)	122.0(4)			

4b								
Bo Journal								
Au(1)-P(1)	2.2565(11)	P(1)-Au(1)-S(1)	177.83(4)					
Au(1)-S(1)	2.3048(12)	C(1)-S(1)-Au(1)	102.50(14)					
N(1)-N(2)	1.407(5)	C(9)-P(1)-Au(1)	114.54(14)					
S(1)-C(1)	1.731(5)	C(15)-P(1)-Au(1)	112.38(14)					
		C(21)-P(1)-Au(1)	111.61(13)					
		N(1)-C(1)-S(1)	127.4(3)					
		O(1)-C(1)-S(1)	120.2(3)					

#### 2.2. Photophysical properties

The UV-vis absorption spectroscopy of 4a, 4b and 4c were assessed in both DMSO solution (10 µM) and powder state. As shown in Figure 2 and Table 3, the maximum absorption wavelengths  $(\lambda_{max})$  of these complexes in DMSO solution were 298 nm (4a), 315 nm (4b), and 336 nm (4c), and in the powder state, were 330 nm (4a), 335 nm (4b), and 348 nm (4c), respectively. According to the previous literature reports<sup>[17]</sup>, the UV-vis absorption of these three compounds had been assigned as follows: for 4a, the acromion at 276 nm was attributed to the  $\pi$ - $\pi$ \* transition of PPh<sub>3</sub> and the absorption peak at 298 nm was attributed to intraligand (IL) transitions (oxadiazole derivatives) and LMCT (S  $\rightarrow$  Au); for 4b, the peaks of 270 nm and 277 nm were attributed to the n- $\pi^*$  transition and the  $\pi$ - $\pi^*$  transition of PPh<sub>3</sub>, respectively. Meanwhile, the absorption at 291 nm of 4b was attributed to IL (oxadiazole derivatives) and the one at 315 nm was assigned to LMCT (S  $\rightarrow$  Au). The wide peak of 4c around 336 nm belonged to LMCT (S  $\rightarrow$ Au). The differences in the positions of the UV absorption bands in the solution of these three complexes came from the structural characteristics of the aromatic nucleus present at the 5-position of 1, 3, 4-oxadiazole-2thiol and the related intramolecular charge-transfer between the acceptor and the donor sites within the molecules. <sup>[24]</sup> With the increase of electron donor capability of the aromatic nucleus, the positions of maximum absorption peaks in 4a-4c appear obvious redshift. (Figure 2a) Compared to the ones in solution, the maximum absorption wavelengths ( $\lambda_{max}$ ) in the solid phases of 4a and 4b were found red-shifted due to the molecular aggregation, which therefore weakened the differences in the maximum position of 4a-4b in the solid phase. <sup>[25]</sup> Band gaps (Eg) of the three complexes (solution/powder) were calculated to be 4a: 3.65 eV/3.25 eV, 4b: 3.72 eV/3.16 eV and 4c: 3.36 eV/3.09 eV, at the onset ( $\lambda_{onset}$ ) of the UV-Vis absorption spectrum. <sup>[26]</sup> (Table 3)



Figure 2 . UV-Vis absorption spectra of gold (I) phosphine complexes in DMSO solution (10  $\mu M$ ) (a) and powder state (b). All spectrum data was collected at room temperature.

The fluorescence behaviors of all the three complexes were also investigated at the concentration of 10  $\mu$ M in DMSO. (Fig S41-S44) In solutions, the photoluminescence quantum yields (PLQY) of 4a (7.9 %), 4b (12.4 %) and 4c (18.3 %) increased regularly with the increasing of structure rigidity: the hydrogen bonding made 4b more rigid than 4a, and 4c with naphthyl showed more rigid than 4b. The fluorescence emission of 4a and

nm and 95 nm/ 159 nm, respectively. The greater stokes shift in solid state showed that the intermolecular interaction increases the non-radiative relaxation of the excited state energy in solid. In these three complexes, the strongest  $\pi$ - $\pi$  accumulation effects of **4c** resulted in the largest Stokes shift with 113 nm in DMSO.

Compared with the difference of 66 nm in the maximum fluorescence emission wavelength between the two states of **4b**, **4a** showed an even larger red-shift of 85 nm in solution and in solid, which can be accredited to an increased non-radiative decay due to increased intermolecular interactions caused by aggregation.<sup>[27-28]</sup> We think, compared with the *p*-methyl substituted benzene moiety in **4a**, the *o*-hydroxy substituted benzene moiety in **4b** is probably more successful in reducing the intermolecular interaction in the aggregated state. <sup>[29]</sup> The fluorescence lifetime of **4a** and **4b** in solid were shorter than that in solutions, with one possible reason of the enhancement of molecular interaction in the solid state, which shortened the lifetime of excited state. (Table3)

We found the solid fluorescence peak of **4b** redshifted 9 nm, compared with that in **4a**, because of the enhancement of the electron donor ability of the ligand substituents. The commission international de l'eclairage (CIE) coordinates of **4a** and **4b** in the powder state were proven to be in the green area with the values being (0.26, 0.46) and (0.24, 0.41), respectively. Interestingly, **4c** has almost no fluorescence in the solid state. The possible reason for that was the naphthalene ring in **4c** showed strong  $\pi$ - $\pi$ accumulation effects, which lead to an obvious fluorescence aggregation-caused quenching (ACQ) in solid state.

The results suggested that the fluorescence emission of these gold (I) complexes can be adjusted by the introduction of different substituent groups in 5-position in 1, 3, 4-oxadiazole-2thiol. The introduction of large heterocyclic structures with strong electron donor capability will help to improve the quantum yields. By reducing the size of the of the heterocyclic structures, it may get new pure blue gold (I) complexes-based luminescent materials. Therefore, this is of great significance for the design of gold (I) complexes, that is, different optical properties can be realized by introduction of various ligands to suit for the future applications.



**Figure 3.** (a) Fluorescence emission spectra of **4a** in different states; (b) Fluorescence emission spectra of **4b** in different states; (c) Fluorescence emission and excitation spectra of **4c** in DMSO; (d) CIE coordinates of compounds in different states. The test concentration of all compounds is 10  $\mu$ M in DMSO. All spectrum data was collected at room temperature.

Table 3. The photophysical and electrochemical properties of the 4a, 4b and 4c

						,			
States	$\lambda_{ex}(nm)$	$\lambda_{em} \ (nm)$	Stokes	PLQY	T (ns)	HOMO <sup>a/b</sup> (eV)	LUMO <sup>a/b</sup> (eV)	$E_{g}^{a/b}(eV)$	E <sub>g</sub> <sup>c</sup> (eV)

4	Tetrahedron									
	Journal Pre-proofs									
40	Solutions	242	415	73	7.9	5.70	6 70/ 5 16	2 78/ 1 21	2 01/2 05	3.65
<del>4</del> a	Powders	542	500	158	15.6 3.70	-0./9/-5.10	-5./0/-1.21	5.01/5.95	3.25	
4b	Solutions	350	443	93	12.4	6.35	-6.67/-5.09	-3.79/-1.77	2.88/3.32	3.72
40	Powders		509	159	11.3	3.16				3.16
4c	Solutions 380	Sutions 280 402 112	18.3	3 63	6 24/ 5 17	-3 62/-1 20	2 62/2 88	3.36		
		-75	115	10.5	5.05	-0.24/-3.17	-3.02/-1.2)	2.02/5.88	3.09	

<sup>a</sup>Calculated from cyclic voltammograms by formula HOMO = - ( $4.71 + E_{ox}$ ) (eV), LUMO = - ( $4.71 + E_{red}$ )

<sup>b</sup>Calculated by Gaussian 09 software at the B3LYP/6-31G (d, p) level

 $^{c}E_{g}$  = 1240 /  $\lambda_{onset}$  (  $\lambda_{onset}$  is the wavelength of the on-set of the UV-vis absorption spectrum)

 $\lambda_{ex}: Maximum \ excitation \ wavelength; \ \lambda_{em}: Maximum \ emission \ wavelength; \ PLQY: Photoluminescence \ quantum \ yield; \ T: Fluorescence \ lifetime; \ Eg: \ Band \ gap \ and \ gap \ ga$ 

#### 2.3. Electrochemical and Thermal Properties

Cyclic voltammetry (CV) was performed with a traditional three-electrode system to estimate the HOMO and LUMO energy levels of the Au complexes 4a, 4b, and 4c. The oxidation peak potentials of 4a, 4b, and 4c were found to be 2.08 V, 1.96 V, and 1.53 V, respectively. The reduction peak potentials of 4a, 4b, and 4c were found to be -0.93 V, -0.92 V, and -1.09 V, respectively (Figure 4). The HOMO and LUMO energy levels were calculated according to the methods reported in the literature, <sup>[30]</sup> and the data (HOMO /LUMO) obtained for these complexes were -6.79 eV / -3.78 eV (4a), -6.67 eV / -3.79 eV (4b), -6.24 eV / -3.62 eV (4c). (Table 3) The band gaps (Eg) of Au complexes determined from electrochemical method (CV) and UV spectrum estimation (DMSO/solid) were 3.01 eV, 3.65 eV and 3.25 eV for 4a, 2.88 eV, 3.72 eV and 3.16 eV for 4b, and 2.62 eV, 3.36 eV and 3.09 eV for 4c, respectively. Compared with the LUMO level of the common electron-transport materials like BODIPY (-3.05 eV)<sup>[31]</sup> and Alq<sub>3</sub> (-3.0 eV) <sup>[32]</sup>, 4c seems to be suitable for electron transport because of its similar low LUMO level and band gap to Alq<sub>3</sub>. The most valuable output from this study, however, is that the complexes 4a, 4b, and 4c have excellent thermal stability, and their decomposition temperatures under nitrogen atmosphere are 328.6 °C, 329.9 °C, and 318.9 °C, respectively. (Figure 5) Due to the good thermal stability and LUMO level, we think 4c has the potential to be used as electron-transport materials in OLEDs.



Figure 4. Cyclic voltammetry curves for 4a, 4b and 4c

#### 2.4. Theoretical calculations

Density functional calculations reveal that the band gaps of 4a, 4b, and 4c are 3.95 eV, 3.32 eV, and 3.88 eV, respectively. (Fig S46, Table 3) 4a showed the biggest  $E_g$  value, because of the weak electron-donating group (-CH<sub>3</sub>), and the substituent effects of 5-position in 1, 3, 4-oxadiazole-2-thiol were proven again in the calculation results. It should be pointed out that the deviations between the values obtained from theoretical calculation and the experimental measurement results in solution may be attributed to the limit of DFT calculation based on single-molecule in gas state.



Figure 5. TG and DGT curve of 4a,4b and 4c

#### 3. Conclusions

We successfully synthesized three bidentate gold (I) metalorganic complexes (4a, 4b, 4c) with 5-aromatic ring-1, 3, 4oxadiazole-2-thione and triphenylphosphine as ligands. The structures of 4a and 4b were studied by single-crystal X-ray diffraction. In solid-state, the CIE coordinates of 4a and 4b were (0.26, 0.46) and (0.24, 0.41) which belonged to the green area. 4a showed the biggest  $E_g$  value according to the theoretical calculations and 4c seems to be suitable for electron transport because of its similar low LUMO level and band gap to Alq<sub>3</sub> and the good thermal stability. These results showed that the optical properties and energy levels of these gold (I) complexes were affected by the substituents at 5-position in 1, 3, 4-oxadiazole-2thiol ligands. It indicated these complexes had the potential as multifunctional materials to be used in emission or electron transporting layers in OLEDs, which have important guiding significance for future design of gold (I) complexes.

Acknowledgments

Foundation of China (No. 21672185, 22067019).

#### **Supplementary Material**

The CCDC for **4a** and **4b** are 1885642 and 1891214, respectively. The supporting information for this article, including checkcif files, is available on the WWW under https://doi.org/10.1016/j.tetlet.2020.xxxxx.

#### References

T

- Mora, M.; Gimeno, M. C.; Visbal, R. Recent advances in gold-NHC complexes with biological properties. Chem. Soc. Rev. 2019, 48, 447-462.
- [2] Wang, T.; Song, Y.; Jin, L.; Li, J.; Gao, Y.; Shi, S. Assembly of Preformed Gold Nanoparticles onto Thermoresponsive Poly(Nisopropylacrylamide)-Based Microgels on the Basis of Au-thiol Chemistry. Chin. J. Chem. 2017, 35, 1755-1760.
- [3] Zhang, M.; Di, X.; Zhang, M.; Zhang, J. Gold(I)-Catalyzed Diastereo- and Enantioselective Synthesis of Polysubstituted Pyrrolo[3,4-d][1,2]oxazines. Chin. J. Chem. 2018, 36, 519-525.
- [4] Kumar, R.; Nevado, C. Cyclometalated Gold(III) Complexes: Synthesis, Reactivity, and Physicochemical Properties. Angew. Chem. Int. Ed. 2017, 56, 1994-2015.
- [5] Schmidt, C.; Karge, B.; Misgeld, R.; Prokop, A.; Franke, R.; Brçnstrup, M.; Ott, I. Gold(I) NHC Complexes: Antiproliferative Activity, Cellular Uptake, Inhibition of Mammalian and Bacterial Thioredoxin Reductases, and Gram-Positive Directed Antibacterial Effects. Chem. Eur. J. 2017, 23, 1869 – 1880.
- [6] Zhang, J.; Zhang, B.; Li, X.; Han, X.; Liu, R.; Fang, J. Small molecule inhibitors of mammalian thioredoxin reductase as potential anticancer agents: An update. Med. Res. Rev. 2019, 39, 5-39.
- [7] Tong, K.-C.; Lok, C.-N.; Wan, P.-K.; Hu, D.; Fung, Y. M. E.; Chang, X.-Y.; Huang, S.; Jiang, H.; Che, C.-M. An anticancer gold(III)-activated porphyrin scaffold that covalently modifies protein cysteine thiols. P. Natl. Acad. Sci. USA. 2020, 117, 1321-1329.
- [8] Dennis, E. K.; Kim, J. H.; Parkin, S.; Awuah, S. G.; Garneau-Tsodikova, S. Distorted Gold(I)–Phosphine Complexes as Antifungal Agents. J. Med. Chem. 2020, 63, 2455-2469.
- [9] Yang, Y.; Antoni, P.; Zimmer, M.; Sekine, K.; Mulks, F. F.; Hu, L.; Zhang, L.; Rudolph, M.; Rominger, F.; Hashmi, A. S. K. Dual Gold/Silver Catalysis Involving Alkynylgold(III) Intermediates Formed by Oxidative Addition and Silver-Catalyzed C-H Activation for the Direct Alkynylation of Cyclopropenes. Angew. Chem. Int. Ed. 2019, 58, 5129-5133.
- [10] Oki, Y.; Nakada, M. Research on Au (I)-catalyzed ene-yne cycloisomerization for construction of quassinoid scaffold. Tetrahedron Lett. 2018, 59, 926-929.
- [11] Zhou, D.; To, W. P.; Tong, G. S. M.; Cheng, G.; Du, L.; Phillips, D. L.; Che, C. M. Tetradentate Gold (III) Complexes as Thermally Activated Delayed Fluorescence (TADF) Emitters: Microwave-Assisted Synthesis and High-Performance OLEDs with Long Operational Lifetime. Angew. Chem. Int. Ed. 2020, 59, 6375-6382.
- [12] Leung, M. Y.; Tang, M. C.; Cheung, W. L.; Lai, S. L.; Ng, M.; Chan, M. Y.; Wing-Wah Yam, V. Thermally Stimulated Delayed Phosphorescence (TSDP)-Based Gold(III) Complexes of Tridentate Pyrazine-Containing Pincer Ligand with Wide Emission Color Tunability and Their Application in Organic Light-Emitting Devices. J. Am. Chem. Soc. 2020, 142, 2448-2459.

Yam, V. W. Highly Emissive Fused Heterocyclic Alkynylgold(III) Complexes for Multiple Color Emission Spanning from Green to Red for Solution-Processable Organic Light-Emitting Devices. Angew. Chem. Int. Ed. 2018, 57, 5463-5466.

- [14] Ghosh, B.; Febriansyah, B.; Harikesh, P. C.; Koh, T. M.; Hadke, S.; Wong, L. H.; England, J.; Mhaisalkar, S. G.; Mathews, N. Direct Band Gap Mixed-Valence Organicinorganic Gold Perovskite as Visible Light Absorbers. Chem. Mater. 2020, 32, 6318-6325.
- [15] Tang, M.-C.; Kwok, W.-K.; Lai, S.-L.; Cheung, W.-L.; Chan, M.-Y.; Wing-Wah Yam, V. Rational molecular design for realizing high performance sky-blue-emitting gold(iii) complexes with monoaryl auxiliary ligands and their applications for both solution-processable and vacuumdeposited organic light-emitting devices. Chemical Science 2019, 10, 594-605.
- [16] Tang, M.-C.; Li, L.-K.; Lai, S.-L.; Cheung, W.-L.; Ng, M.; Wong, C.-Y.; Chan, M.-Y.; Yam, V. W.-W. ; Design Strategy Towards Horizontally Oriented Luminescent Tetradentate-Ligand-Containing Gold(III) Systems.Angew Chem Int Ed 2020, 59, 2-11.
- [17] Forward, J. M.; Bohmann D.; Fackler, J. P.; Staples, R. J. Luminescence Studies of Gold(I) Thiolate Complexes. Inorg. Chem. 1995, 34, 6330–6336.
- [18] Narayanaswamy, R.; Young, M. A.; Parkhurst, E.; Ouellette, M.; Kerr, M. E.; Ho, D. M.; Elder, R. C.; Bruce, A. E.; Bruce, M. R. M. Synthesis, Structure, and Electronic Spectroscopy of Neutral, Dinuclear Gold(I) Complexes. Gold(I)-Gold(I) Interactions in Solution and in the Solid State. Inorg. Chem. 1993, 32, 2506-2517.
- [19] Garcia, A.; Machado, R. C.; Grazul, R. M.; Lopes, M. T. P.;
  Corrêa, C. C.; Dos Santos, H. F.; de Almeida, M. V.; Silva, H. ; Novel antitumor adamantane–azole gold(I) complexes as potential inhibitors of thioredoxin reductase. J. Biol. Inorg. Chem. 2016, 21, 275-292.
- [20] Chaves, J. D. S.; Tunes, L. G.; de, J. F. C. H.; Francisco, T. M.; Correa, C. C.; Murta, S. M. F.; Monte-Neto, R. L.; Silva, H.; Fontes, A. P. S.; de Almeida, M. V. Novel gold(I) complexes with 5-phenyl-1,3,4-oxadiazole-2-thione and phosphine as potential anticancer and antileishmanial agents. Eur. J. Med. Chem. 2017, 127, 727-739
- [21] Hunks, W. J.; Jennings, M. C.; Puddephatt, R. J. Coordination polymers of gold (I) with dithiolate and diphosphine ligands. Chem. Commun. 2002, 1834-1835.
- [22] Ma, C.; Chan, C. T.; To, W. P.; Kwok, W. M.; Che, C. M. Deciphering Photoluminescence Dynamics and Reactivity of the Luminescent Metal-Metal-Bonded Excited State of a Binuclear Gold (I) Phosphine Complex Containing Open Coordination Sites. Chemistry 2015, 21, 13888-13893.
- [23] Tzeng, B.-C.; Chan, C.-K.; Cheung, K.-K.; Che, C.-M.; Peng, S.-M. Dramatic solvent effect on the luminescence of a dinuclear gold(I) complex of quinoline-8-thiolate. Chem Commun. 1997, 135-136.
- [24] Cao, L.; Zhang, L.; Wei, Q.; Zhang, J.; Chen, D.; Wang, S.; Su, S.-j.; Wang, T.; Ge, Z. Bipolar fluorophores based on intramolecular charge-transfer moieties of sulfone for nondoped deep blue solution-processed organic light-emitting diodes. Dyes Pigments 2020, 176, 108242. https: // doi.org/ 10.1016/ j.dyepig.2020.108242
- [25] Noginov, M. A.; Vondrova, M.; Williams, S. M.; Bahoura, M.; Gavrilenko, V. I.; Black, S. M.; Drachev, V. P.; Shalaev, V. M.; Sykes, A. Spectroscopic studies of liquid solutions of R6G laser dye and Ag nanoparticle aggregates. J. Opt. A-Pure Appl. Op. 2005, 7, S219-S229.

Y.;

strategy for tuning the energy level of naphthalenediimide: Promoted formation of radical anions with extraordinary stability. Chem. Sci. 2015, 6, 3342-3346.

- [27] Ouyang, X.; Wang, G.; Zeng, H.; Zhang, W.; Li, J. Design and synthesis of 2-substituted-8-hydroxyquinline zinc complexes with hole-transporting ability for highly effective yellow-light emitters. J. Organomet. Chem. 2009, 694, 3511-3517.
- [28] Yam, V. W.-W.; Cheng, E. C.-C. Design of luminescent sulfurcontaining polynuclear gold (I) complexes for advanced nanomaterials and chemosensors.Gold Bulletin 2001, 34, 20-23.
- [29] Forward, J. M.; Bohmann, D.; Fackler, J. P.; Staples, R. J. Luminescence Studies of Gold(I) Thiolate Complexes. Inorg. Chem. 1995, 34, 6330-6336.
- [30] Dong, Y.-B.; Chen, Z.; Yang, L.; Hu, Y.-X.; Wang, X.-Y.; Yin, J.; Liu, S. H. Effect of alkyl chain length on the luminescence on-off mechanochromic behavior of solid-state Gold(I) isocyanide complexes. Dyes Pigments. 2018, 150, 315-322.
- [31] Zhou, Y.; Xiao, Y.; Li, D.; Fu, M.; Qian, X. Novel Fluorescent Fluorine–Boron Complexes: Synthesis, Crystal Structure,



[32] Burrows, P. E.; Shen, Z.; Bulovic, V.; McCarty, D. M.; Forrest, S. R.; Cronin, J. A.; Thompson, M. E. Relationship between electroluminescence and current transport in organic heterojunction light-emitting devices. J. Appl. Phys. 1996, 79, 7991-8006.

#### **Graphical Abstract**

Leave this area blank for abstract info.

## New gold (I) complexes with 5-aromatic ring-1, 3, 4-oxadiazole-2-thione and triphenylphosphine as potential multifunctional materials

Yu Qiang Zhao, Jie Zhou, Renze He, Guang Ke Wang, Lan Xi Miao, Xiao Guang Xie and Ying Zhou\*



Three new gold (I) complexes (4a, 4b, 4c) with 5-aromatic ring-1, 3, 4-oxadiazole-2-thione and triphenylphosphine as ligands were synthesized. Structures of 4a and 4b were determined through X-ray singlecrystal diffraction, and it displayed that 4a and 4b had the same metal coordination pattern, wherein the ligand was coordinated by the sulfur atom to the central metal ion of gold (I). The optical properties of these gold (I) complexes were studied both in solution and in solid-state. In DMSO, 4a and 4b peaked at 415 nm and 443 nm, respectively, and the CIE coordinates of 4a and 4b in the solid-state were in the green area namely, (0.26, 0.46) and (0.24, 0.41). HOMO/LUMO levels and bandgaps of 4a, 4b and 4c were assessed by UV spectrum estimation, electrochemical method, and theoretical calculations. The observation hinted that the photophysical properties and energy levels of these gold (I) complexes can be adjusted by the introduction of different substituent aromatic rings at the 5-position of the 1, 3, 4-oxadiazole-2-thiol moiety. The findings of good optical, electrochemical and thermal properties of these new gold (I) complexes demonstrated their potential in the future studies as multifunctional materials.

6

[2(

oxadiazole-2-thione were synthesized. •Structures of 4a and 4b were determined through X-ray single-crystal diffraction. •These new gold (I) complexes showed good optical, electrochemical and thermal properties. • These new gold (I) complexes demonstrated their potential in the future studies as multifunctional materials.