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Synthesis and characterization of fluorescent-active triazole-gold complexes

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Fluorescence active fused-triazole was developed as a ligand in gold(I) cation coordination. The coordination ability was evaluated using NMR and fluorescence emission. Our previously reported N-2-aryl-triazoles, though gave good emission, could not form stable complexes with gold cations. A new N-fused-triazole (NFT) derivative was prepared and the ligand indicated good fluorescence emission, and formed strong coordination with gold cations. Both ligand and complex were characterized by X-ray crystallography. Fluorescence properties of various gold complexes (with different primary ligands) were evaluated, which suggested the feasibility of using fluorescence emission as potential tools for future mechanistic investigation.

fluorescence, catalysis, 1,2,3-triazole, gold, conjugation

1 Introduction

Photoactive molecules play an important role in chemistry, biology, and material science [1]. Fluorophores are widely used as novel photoactive materials, molecular sensors and probes, and bio-imaging [2]. The optoelectronic properties of fluorophore can be influenced by its structure and chemical environment [3]. Some particularly interesting systems are transition metal complexes, which feature ligands that directly influence the overall optical property [4]. Fluorescent metal complexes with "closed-core" coordination that promote metal to ligand charge transfer (MLCT) [5]. A classic example is the octahedral $[Ru(bpy)_3]^{2+}$ complex shown in Scheme 1(a) [6]. Metal complexes with simple coordination patterns tend to be less popular in fluorescence studies due to the potential photo quenching in a rather "open" coordination pattern.

It is known that gold(I) complexes adapt two-coordinated linear geometries [7]. The last two decades evidenced the great advancement of gold(I) complex promoted catalysis toward alkyne, alkene and allene activation [8]. However, to the best of our knowledge, there have been no fluorescence active gold complexes reported in literature, which make it difficult to incorporate effective fluorophores into the complexes. In this work, we report the synthesis and characterization of novel fluorescent active gold(I) complexes using a N-fused triazole (NFT) ligand, which achieved strong coordination and exhibited fluorescence emission for the first time (Scheme 1(b)).

In recent years, our group [9] has been interested in investigating the coordination abilities of 1,2,3-triazole toward transition metal cations. To explore this chemistry, effective synthesis of various triazoles is necessary. Thus, we have developed a series of new approaches in triazole functionalization with good to excellent chemo-, regio-, and stereoselectivity [10]. We have found that was the N-2-aryl-1,2,3-triazole (NAT), which displays excellent fluorescence emission in the high energy UV/blue region via a planar intramolecular charge transfer (PICT) [11]. In contrast, the N-1 derivatives, which are the typical regio isomers from click chemistry, do not give any fluorescence emission. We have subsequently explored their binding ability and discovered several new triazole-gold complexes/ catalysts. One

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(A) Fluorescent metal-ligand complex: Metal to ligand charge transfer (MLCT)



(B) This work: Florescent active N-Fused Triazole (NFT) and its gold complexes



Scheme 1 Fluorescence active metal complexes.

particularly interesting system is the triazole-gold catalyst (TA-Au), which promotes alkyne activation [12]. Thus, we explored new fluorescence active gold complexes, which could be developed based on fluorescence active triazoles and might be useful for catalytic mechanism investigation or metal sensing in the future [13].

2 Experimental

2.1 Coordination of N-2-aryl triazole with gold cation

As shown in Figure 1, we first treated fluorescence active NAT-1 with gold cations. The reactions were monitored by ¹H NMR and ³¹P NMR. As discussed previously, the N-1aryl triazole readily coordinates with gold cations (to afford TA-Au), which do not display fluorescence emission. When treating the fluorescence active N-2-aryl triazole, NAT-1, with [PPh₃Au]⁺, a significant change of H-5 proton chemical shift was observed in ¹H NMR (Figure 1(a)). This result suggested that NAT-1 did provide some kind of interaction with gold cation in solution. However, our efforts to isolate complex 2 failed due to the compound decomposition. In fact, NAT-1 failed to provide the "protecting effect" observed with typical triazole ligands toward gold cations. This brought great concern whether NAT-1 could form the desired gold complexes with the desired stability. As indicated by the ³¹P NMR, the mixture of NAT-1 with [PPh₃Au]⁺ gave very similar ³¹P chemical shift as of "naked" [PPh₃Au]⁺, which suggested the weak coordination between NAT-1 and gold. Furthermore, comparing the optical property of the complex and NAT-1 ligand, showed very little difference between their fluorescence emissions. Thus, combining all the information, it is confirmed that NAT-1, though provided good fluorescence emission, could not form a stable complex with gold cation.

As shown in Scheme 2, the coplanar arrangement between the N-2-aryl and the triazole ring blocks the N-1



Figure 1 Coordination of NAT with gold cation.



Scheme 2 N-fused-triazole: coordination and emission.

nitrogen coordination due to the steric hindrance. Although the N-2 aryl group is "free" for rotation to reduce the steric hindrance, breaking co-planar conformation will cause the significant decrease of fluorescence emission, as we reported previously.

To achieve our desired fluorescence active stable gold complexes, we designed the N-fused triazole **3**. Our rationale was that NFT **3** has a nitrogen coordination site with significantly reduced steric hindrance. Thus, it will form strong coordination as a regular triazole toward gold cation. In addition, the extended conjugating system will likely provide fluorescence activity, which may or may not be influenced by the metal coordination. To explore this hypothesis, both ligand **3** and complexes need to be prepared.

2.2 Synthesis and characterization of NFT **3** and Complex **4** NFT **3** was prepared as described in Figure 2. The carboxylic acid **5** was reduced to alcohol **6** in 97% yield. Benzyl alcohol **6** was then treated with PBr₃ followed by $S_N 2$ azidation, giving 2-iodo benzyl azide **7** in 82% yield. Sonogashira coupling followed by azide-alkyne Huisgen cycloaddition gave the desired NFT ligand **3** in 53% yield. Treating **3** with [PPh₃-Au]⁺ under previously reported condition gave the desired complex **4** in >90 % yield. The molecular structures of both ligand **3** and complex **4** are



a) BH₃ in THF (2.0 equiv.), THF (0.50 mol/L), 0 °C; b) PBr₃ (1.8 equiv.), DCM (0.40 mol/L), 25 °C, then NaN₃, (2.0 equiv.), DMSO (0.20 mol/L), 60 °C; c) phenylacetylene (1.5 equiv.), Et₃N (6.0 equiv.), CuI (7.0 mol%), Pd(PPh₃)₂Cl₂ (3.5 mol%), DMF (0.14 mol/L), 25 °C, then 120 °C; d) PPh₃AuCl (1.0 equiv.), AgOTf (1.0 equiv.), DCM (0.10 mol/L), 25 °C.

Figure 2 Synthesis of NFT 3 and its gold complex 4a.

confirmed by X-ray crystallography [14].

Based on the crystal structures, the dihedral angles of the 4-phenyl ring and the triazole ring are 36.4° and 37.0° in ligand **3** and complex **4a** respectively. The length of Au–N bond is 2.065 Å, very similar to the distance of the Au–N bond of TA–Au (2.063 Å). In addition, the ³¹P NMR resonance of **4a** was shifted downfield to δ 29.6 ppm. All these results are consistent with the formation of strong coordination between ligand **3** and [L-Au]⁺ as proposed.

The characterization of compounds was shown in the Supporting Information online.

3 Results and discussion

To evaluate the fluorescence properties of this new class of complexes, a series of $[L-Au]^+$ cations were prepared. The fluorescence properties of ligand **3** and all of these complexes were summarized in Table 1 (see detailed optical

 Table 1
 Optical properties of ligand 3 and complexes 4 ^{a, b)}



	Ex λ_{max} (nm)	Em λ_{max} (nm)	$\Phi^{b}(x10^{-3})$	Intensity $(\times 10^{-3})$	Stokes shift
3	285	368	0.69	4.45	83
4a	285	342	1.1	8.31	57
4b	285	362	0.96	8.16	77
4c	263	342	0.75 ^{c)}	5.96	79
4d	285	368	0.75	5.28	83
4e	293	356	0.87	6.74	63
4f	293	368	0.95	5.79	75

a) Sample information: 1.0×10^{-5} mol/L in acetonitrile; b) quantum yields (*F*) were determined based on 1.0×10^{-5} mol/L 9,10-diphenylanthracene in cyclohexane (*F*=0.90) except **4c**; c) quantum yields (*F*) were determined based on 1.0×10^{-5} mol/L naphthalene in cyclohexane (*F*=0.23); d) calculated photo emission integration from the original spectra. All fluorescence measured under identical conditions (see the Supporting Information online).

data in Supporting Information online).

The emission data show that ligand **3** gave good fluorescence emission as expected. Complexes **4a–4f** are generally stable, and they are all fluorescence active, which made them an interesting new class of fluorescence active gold catalysts. When compared to ligand **3**, all of these goldtriazole complexes show higher fluorescence emission and improved quantum efficiency. These results strongly suggested that the gold cation coordination facilitated fluorescent decay pathway to the excited state [6,15]. The small changes in excitation λ_{max} and emission λ_{max} implied that little metal to ligand charge transfer occurred in this new class of gold complexes. With this new class of fluorescence active gold complexes, ON-OFF chemodosimeter to monitor the gold catalysis system are plausible, and are currently under investigation in our group.

4 Conclusions

In summary, investigations of fluorescence active triazole gold complexes have been conducted. While the fluorescence active N-2-aryl-triazoles (NATs) failed to produce stable complexes with gold(I) cations, the fluorescence active N-fused-triazole (NFT) was prepared and successfully used as a ligand to form a new class of gold complexes. These efforts led to the development of the first fluorescence active gold(I) catalysts, which enable a new approach for mechanistic investigations and the potential sensing device development. Both areas are currently ongoing in our group.

Supporting information

The supporting information is available online at chem.scichina.com and link.springer.com/journal/11426. The supporting materials are published as submitted, without typesetting or editing. The responsibility for scientific accuracy and content remains entirely with the authors.

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