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Communication

A tri-gold triazolide with long-lived luminescence

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ABSTRACT

We report the synthesis and characterization of tri-gold(I) complexes of a phenyltriazolide ligand. This complex luminesces in solution at room temperature and 77 K with emission lifetimes of 4.72 ± 0.8 µs at 298 K and 529 ± 12 µs at 77 K. Density-functional theory calculations on model complexes indicate that the triazolyl ring and aryl substituents approach coplanarity, and that total charge transfer is attenuated in the triplet excited state.

1. Introduction

Ligand-based cycloadditions of gold complexes have a venerable history. (Organophosphine)gold(I) azides react in [3 + 2]-cycloadditions with methylisonitrile to yield a *C*-bound tetrazolide [1], with 1,1,1-trifluoroethanenitrile to afford an *N*-bound tetrazolide [2], and with carbon disulfide to form an azathiaheterocyclic complex, also *N*-bound [2]. These discoveries anticipated the concept of click chemistry, which privileges reactions that combine high yields with operational ease and selectivity [3–6]. Certainly the leading click reaction is the copper-catalyzed [3 + 2]-cycloaddition of organic azides to (mostly) terminal alkynes [7]. In its early days, practitioners of click chemistry concentrated on organic transformations; organometallic reactions that conform substantially to click standards emerged later.

(Phosphine)gold(I) azides were shown in 2007 to combine with terminal alkynes [8]. The resulting triazolides are metalated at carbon, despite a starting material aurated at nitrogen. The same study demonstrated the inverse reaction, where gold(I) alkynyls react with hydrazoic acid equivalents to yield the same triazolide complexes. With this protocol, gold has been attached to acetylinic dendrimers [9] and peptides [10]. Work thereafter revealed a copper-catalyzed reaction between non-hydrolyzable azides and gold(I) alkynyls [11]. This reaction proceeds with the 1,4-regioselectivity of copper-catalyzed organic alkyne-azide cycloadditions. Subsequent research has widened the scope of metalla-click chemistry. Chan, Yam and co-workers [12] have described a luminescent platinum(II) triazolide prepared in a copper-catalyzed cycloaddition of the platinum alkynyl with an aryl azide. Fokin, Lin, Jia, and their co-workers [13] have reported ruthenium(II) alkynyls that react with organic azides to form triazolides. Lastra [14], Lo [15], Meggers [16], and their respective collaborators have shown that (azido)ruthenium complexes add to alkynes and nitriles to afford cycloaddition products; Liu and co-workers have published similar results for molybdenum(II) [17]. Mirica [18], Schatzschneider [19], and co-workers have published reactions of 3d-metal azides with alkynes; the resulting triazolides ligate through nitrogen. Szczepura and co-workers [20] have reacted azide-terminated $[Re_6Se_8]^{2+}$ species with electron-poor alkynes to form triazolides, thus demonstrating metalla-click reactivity of a metal-metal bonded cluster. Gladysz and co-workers [21] report copper-catalyzed reactions of platinum(II) polyynyls with benzyl azide; only terminal $-C{\equiv}CH$ moieties react. A later disclosure from the same group [22] considers click-type assemblies carrying multiple metal centers. Veige and co-workers have published a series of reports on reactions ("iClick") of azidometal reagents and gold(I) alkynyls to yield triazoles metalated at nitrogen and carbon [23,24]. As metalla-click chemistry unfolds [25], metal triazolides with

Abbreviations: DFT, density-functional theory; HOMO, highest occupied Kohn-Sham orbital; LUMO, lowest unoccupied Kohn-Sham orbital.

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remarkable properties are being discovered. For example, we have identified a monogold triazolide that emits triplet phosphorescence with a 19-ms lifetime at 77 K [26].

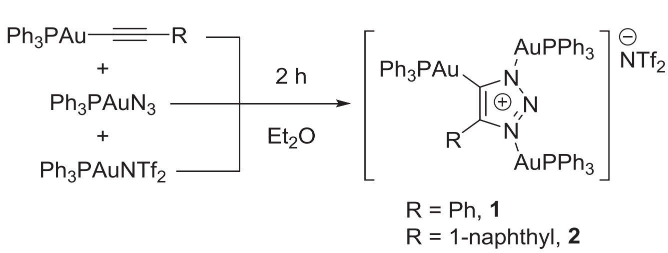
Reported here are triazolides where three gold(I) centers attach through σ-bonds: one to carbon and two to nitrogen. These complexes luminesce with microsecond-length radiative lifetimes at 77 K and 298 K. To our knowledge, they are the first triaurated triazolides. They illustrate an advantage of gold(I): with its propensity for linear two-coordination, gold can bind at multiple sites on organic frameworks with minimal steric hindrance.

2. Results and discussion

Tri-gold triazolide complexes assemble as in Scheme 1. One equivalent each of (triphenylphosphine)gold(I) azide and the corresponding alkynyl and triflimidate are added to diethyl ether in moist air, and stirred at room temperature with exclusion of light. Products are isolated in near-quantitative yields by filtration.

Compound **1** is off-white or yellow as a solid, whereas **2** is red. Solutions of **1** are pale gold; those of **2** are orange. Absorption and emission spectra appear as Fig. 1. Absorption sets in near 400 nm and rises sharply at wavelengths below 300 nm. Ultraviolet-light excitation elicits broad, featureless emission that maximizes at 543 nm in 2-methyltetrahydrofuran solution. This emission quenches on exposure to atmospheric oxygen. The radiative lifetime of **1** is 4.72 ± 0.8 μs at room temperature and 529 ± 12 μs at 77 K. For compound **2**, emission lifetimes are 10.3 ± 1.9 μs at 298 K and 6990 ± 261 μs at 77 K. The long luminescence lifetime and large apparent Stokes shifts (>200 nm for **2**, Fig. 1(b)) suggests phosphorescence from a spin-triplet excited state. The structured emission near 370 nm for **2** is tentatively assigned as a ligand-centered fluorescence. Such dual luminescence has been encountered previously for (triazolyl)- and (aryl)gold(I) species [11].

Density-functional theory calculations were carried out on **1**′ and **2**′ where methyl groups on phosphorus replace phenyls for computational tractability. Computations employed the parameter free PBE0 hybrid functional, which we have used earlier in studies of the ultrafast spectroscopy of gold(I) aryls [27,28]. Calculations of the ground-state singlets are spin-restricted; those of triplets, unrestricted. Harmonic vibrational calculations indicate the converged singlet and triplet structures to be minima of their respective potential energy hypersurfaces. Optimized metrics for both spin states are closely similar *except* for the dihedral angle between the triazolyl and the adjacent phenyl ring. The converged structures of triplet-state **1**′ and **2**′ appear as Fig. 2, along with calculated metrics. For comparison, optimized ground-state structures are depicted in Fig. S1, Supporting Information. In the triplet structure of **1**′, the triazolyl and phenyl rings are almost perfectly coplanar. In the ground state, the dihedral angle between best-fit planes is 1.7°. That is, conjugation between aromatic rings increases in the excited state. The calculated $C_{triazolyl}–C_{phenyl}$ bond distance shrinks 0.086 Å on exciting from the ground to the triplet state. Moreover, the triplet structure shows bond length alternation



Scheme 1. Synthesis of tri-gold(I) products.

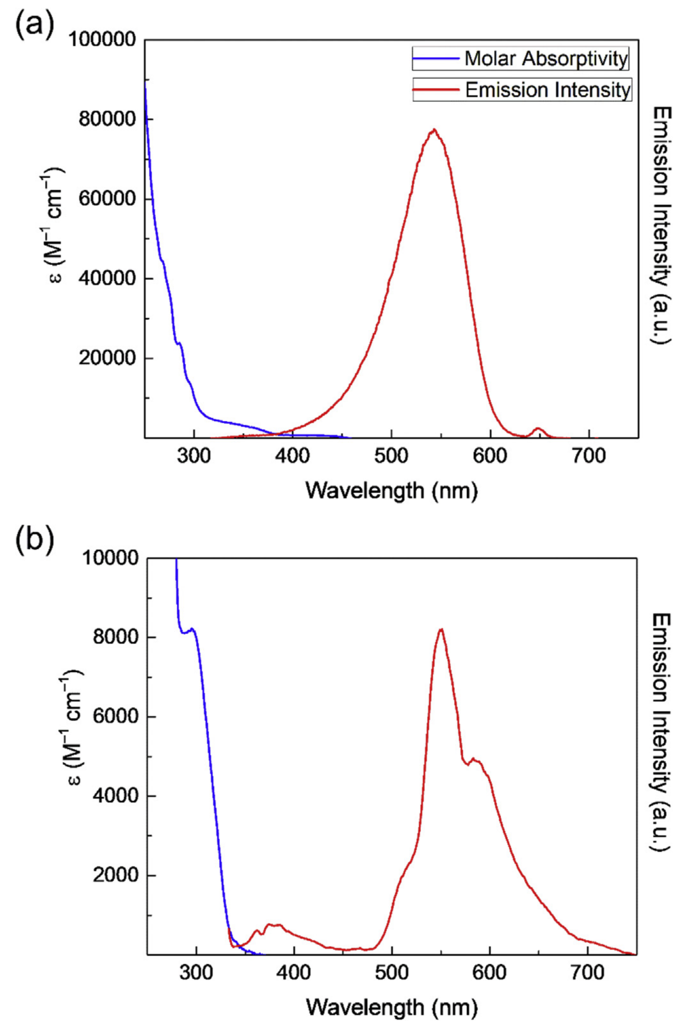


Fig. 1. Absorption (blue) and emission (red) spectra (298 K) in 2-methyltetrahydrofuran solution: (a) **1**, and (b) **2**. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

suggesting quinoidal character, consistent with increased conjugation within the aromatic system, *vide supra*. The calculated structure of triplet **2**′ is also planarized compared to the ground-state structure. Ring dihedral angles are calculated to be 63.8° in the ground state and 40.2° in the triplet.

Fig. 3(a) depicts a fragment orbital energy level diagram derived from a spin-unrestricted calculation of ^{3}**1**′. In this diagram, energy levels of ^{3}**1**′ are correlated with those of the triplet ligand fragment and the singlet (trimethylphosphine)gold(I) cations. The singly occupied HOMOs reside almost wholly on the conjugated ligand (where HOMO is highest occupied Kohn-Sham orbital). Spin-α orbitals are plotted as Fig. 3(b). The orbital energy level diagram of ^{3}**2**′, which is similar, appears as Fig. S3, Supporting Information. A time-dependent DFT calculation on the optimized structure of ^{3}**1**′ finds that the first triplet state consists (>97%) of a one-particle transition between the HOMO and LUMO of the electronic ground state. This triplet state can be considered as the union of three singlet (trimethylphosphine)gold(I) cations with a triplet phenyltriazolide dianion. The first triplet of **2**′ is similar, consisting (97%) of a LUMO ← HOMO transition from the ground state (in the calculated geometry of the triplet).

A Dapprich-Frenking charge decomposition analysis [29] finds that 0.75 electrons are transferred from the triazolide to the three (phosphine)gold(I) fragments in ground-state **1**′, whereas the net