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Synthesis and Photophysical Properties of Laterally Asymmetric Digold(I) Alkynyls and Triazolyl: Ancillary Ligand and Organic Functionality Dictate Excited-State Dynamics

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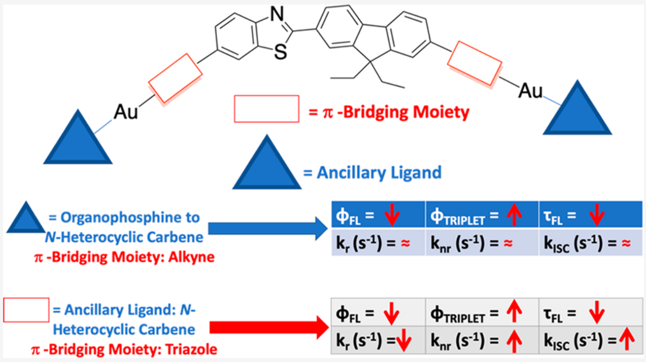

ABSTRACT: Four new laterally asymmetric dinuclear gold(I) complexes made from a new chromophoric ligand (**Au-DiBTF0−3**) have been characterized. Changing the organic ancillary ligand from a phosphine ((**Au-DiBTF0** (PMe_3) and **Au-DiBTF1** (PCy_3)) to an N-heterocyclic carbene (**Au-DiBTF2**) with an alkynyl linking moiety or modifying the alkynyl linkage to a triazolyl moiety with the ancillary ligand being an N-heterocyclic carbene (**Au-DiBTF3**) impacts the ground- and excited-state properties of these systems. All four complexes exhibit structured absorption and emission spectra with weak phosphorescence. A bathochromic shift is observed in both the ground-state absorption and luminescence spectra as the series varies from **Au-DiBTF0** to **Au-DiBTF3**. The dinuclear alkynyl complexes (**Au-DiBTF0−2**) display decreased fluorescence lifetimes and fluorescence quantum yields along with more efficient intersystem crossing when the capping ligand is changed from a trialkylphosphine to an N-heterocyclic carbene. This change results in comparable rates of radiative decay and intersystem crossing and negligible rates of nonradiative decay. Changing the π-bridging moiety (**Au-DiBTF3**) results in a diminished fluorescence quantum yield, shorter fluorescence lifetime, and increased intersystem quantum yield, resulting in faster intersystem crossing accompanied by slower radiative decay and more efficient nonradiative decay relative to the alkynyl-bridged complexes. Density functional theory calculations are in accord with the observed photophysics, with nearly identical S_1-to-T_2 energy gaps for the dinuclear alkynyl complexes (**Au-DiBTF0** and **-2**) and a smaller energy gap for **Au-DiBTF3**. Experimentally, **Au-DiBTF3** has the highest rate constant and quantum yield of intersystem crossing of the new gold(I) organometallics.

Polymetallynes have long been studied as photoactive materials.[1,2,11,12,3−10,13−16] The ease of modifying the alkynyl ligands, coupled with triplet-state photophysics in solution and the solid state, lends them to a variety of applications, including organic light emitting diodes (OLEDS),[17−21] optoelectronics,[18−27] sensors,[13,28,29] and nonlinear optics (NLO),[30−33] among others.[32,33] Much of this work has focused on polymeric and multinuclear Pt(II) complexes. In these d^8 species, the heavy-metal atom facilitates intersystem crossing to the triplet excited state manifold. Gold presents special opportunities in the design of photoactive triplet states. Gold(I), having a d^{10} configuration, is diamagnetic, and its filled d subshell circumvents deactivation by ligand-field excited states. Gold is also the most electronegative metal, with a Pauling electronegativity near that of carbon, rendering the carbon−gold bond effectively nonpolar. Additionally, the spin−orbit coupling constant of gold (5104 cm^{-1}) exceeds that of platinum (4481 cm^{-1}).[34] Finally, gold(I) tends strongly toward linear twofold coordination. Ancillary ligands, such as organophosphines and N-heterocyclic carbenes, solubilize many gold(I) organometallics and allow steric protection of an otherwise open metal site.[35−37,39]

To date, investigations of dinuclear gold(I) complexes have emphasized chromophoric bridging alkynyls attached to (phosphine)gold(I) centers.[38−40] Wu and co-workers reported the synthesis and photophysics (including fluorescence lifetimes and excited-state quantum yields) of laterally symmetric dinuclear gold(I) phosphines with variations in the bridging alkynyl chromophore.[41] Schanze and co-workers conducted two separate photophysical studies comparing laterally symmetric dinuclear gold(I) and platinum(II) alkynyls.[42,43] In those reports, variations in the bridging chromophore or ancillary ligand were not explored. Lastly, Patra and co-workers described dinuclear gold(I) alkynyls with

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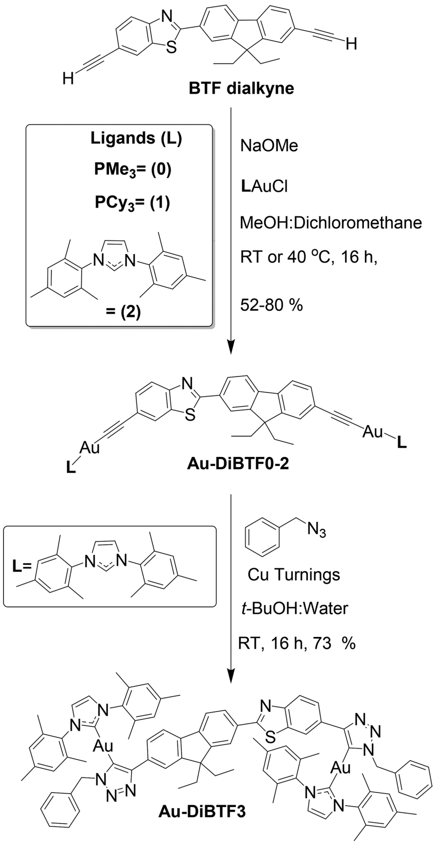
fluorenyl-based organic frameworks whose photophysical properties could be tuned by introducing donor/acceptor moieties on the alkynyl backbone.[44]

Understanding of the fundamental relationship between structure and photophysical properties in dinuclear gold(I) alkynyls remains limited. Of primary importance are excited-state lifetimes and quantum yields of emission and intersystem crossing. We have therefore investigated the excited-state properties of laterally asymmetric dinuclear gold(I) complexes with attention to the effects of the capping ligand and the bridging chromophore.

The new benzothiazole-2,7-fluorenyl dialkyne (BTF dialkyne) ligand precursor was prepared by a modification of a previously reported literature procedure (Scheme S1).[31] Experimental details appear in the Supporting Information. Metalation with gold(I) was achieved by in situ deprotonation of the BTF dialkyne ligand and addition of this solution to a suspension of the chlorogold(I) precursor. This procedure yielded the new compounds **Au-DiBTF0−2** after 16 h (Scheme 1).[43] **Au-DiBTF2** was further functionalized through a previously published copper-catalyzed click reaction to yield **Au-DiBTF3** (Scheme 1).[45] An X-ray diffraction crystal structure of **Au-DiBTF3** as well as experimental procedures for the synthesis of all four compounds are given in the Supporting Information.

Scheme 1. Synthesis of Au-DiBTF0−3



The new gold(I) organometallics were subjected to thermogravimetric analysis (TGA). The mass loss as a function of temperature was dependent on the chemical identity of the ligands. Mass loss began at 230 °C in **Au-DiBTF0**, 260 °C in **Au-DiBTF1**, 350 °C in **Au-DiBTF2**, and 310 °C in **Au-DiBTF3**. The results of the TGA experiments appear in Figure S11.

Ground-state absorption and emission spectra for **Au-DiBTF0−3** in toluene appear in Figure 1. All of the absorption spectra show similarly structured band shapes. The spectra display two distinct lower-energy maxima with a higher-energy shoulder. Altering the linking moiety (alkyne vs triazole) or the capping ligand (phosphine vs N-heterocyclic carbene) shifts the ground-state absorption spectra of the complexes. **Au-DiBTF0** and **Au-DiBTF1**, which contain a trialkylphosphine ancillary ligand, possess the highest-energy absorption maxima (λ_{abs}) with values of 383 and 384 nm, respectively. Changing the ancillary ligand from a phosphine to a carbene in **Au-DiBTF2** red-shifts the absorption maximum to 387 nm. Lastly, altering the organic alkynyl to a triazole functionality further red-shifts the absorption maxima of **Au-DiBTF3** to 390 nm. All of the complexes exhibit similar extinction coefficients (ε) of $(5-7) \times 10^4$ M^{-1} cm^{-1} in dichloromethane.

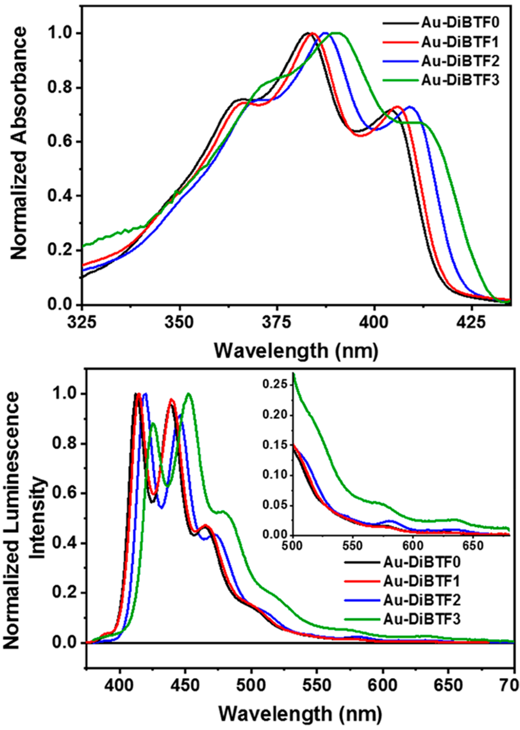


Figure 1. Ground-state absorption and emission spectra of **Au-DiBTF0** (black), **Au-DiBTF1** (red), **Au-DiBTF2** (blue), and **Au-DiBTF3** (green) in toluene. Emission measurements were collected following three freeze−pump−thaw cycles. Inset: detail of the emission spectra from 500 to 700 nm.

The emission spectra of these complexes show structured fluorescence at 400−550 nm and weak phosphorescence at 550−700 nm (Figure 1). The fluorescence maxima (λ_{fl}) follow the same energy trends as the absorption spectra, with a bathochromic shift observed in going from **Au-DiBTF0** to **Au-DiBTF3**. Because of the weak phosphorescence in these systems, it is difficult to assign the emission maxima (Figure 1 inset). The structured absorption and emission profiles indicate that the transitions are mainly of $\pi-\pi^*$ character in all four complexes.[46]

Fluorescence lifetimes (τ_{fl}), fluorescence quantum yields (φ_{fl}), and intersystem crossing quantum yields ($\varphi_{triplet}$) were obtained for the new gold(I) complexes (Table 1). Data from

Table 1. Photophysical Properties of Digold Alkynyl and Triazolyl Complexes at 298 K in Toluene[a]

complex	Au-DiBTF0	Au-DiBTF1	Au-DiBTF2	Au-DiBTF3
λ_{abs} (nm)	383	384	387	390
ε (10^4 M^{-1} cm^{-1})[a]	6.00	5.10	6.76	6.99
λ_{fl} (nm)	413	413	418	427
φ_{fl}	0.55 ± 0.02	0.55 ± 0.02	0.44 ± 0.01	0.28 ± 0.02
$\varphi_{triplet}$	0.51 ± 0.01	0.43 ± 0.02	0.57 ± 0.02	0.68 ± 0.01
τ_{fl} (ps)	438 ± 5	442 ± 1	380 ± 1	369 ± 1
k_r (s^{-1})	1.3×10^9	1.2×10^9	1.2×10^9	7.6×10^8
k_{nr} (s^{-1})	$\leq 2.3 \times 10^7$	$\leq 4.5 \times 10^7$	$\leq 2.6 \times 10^7$	1.08×10^8
k_{ISC} (s^{-1})	1.2×10^9	9.7×10^8	1.5×10^9	2.4×10^9

[a] All of the reported molar extinction coefficients were measured in dichloromethane because of the minimal solubility of **Au-DiBTF3** in toluene. The estimated error is ±5%. Details are given in the Supporting Information.

these experiments are shown in Figures S12–S15. **Au-DiBTF0** and **Au-DiBTF1** display similar fluorescence quantum yields, fluorescence lifetimes, and intersystem crossing quantum yields. Comparatively, **Au-DiBTF2** shows a lower fluorescence quantum yield, shorter fluorescence lifetime, and increased intersystem crossing quantum yield. This trend continues for **Au-DiBTF3**, which has the lowest fluorescence quantum yield, shortest fluorescence lifetime, and highest intersystem crossing quantum yield. The combination of the fluorescence lifetime, fluorescence quantum yield, and intersystem crossing quantum yield allows for the calculation of the rate constants for radiative decay (k_r), nonradiative decay (k_{nr}), and intersystem crossing (k_{ISC}). For the the alkynyl complexes (**Au-DiBTF0–2**), the rate constants for radiative decay and intersystem crossing have magnitudes on the order of 1×10^9 s^{-1}. The rate of nonradiative decay for these compounds is roughly 2 orders of magnitude lower. In **Au-DiBTF3**, the intersystem crossing rate constant is a factor of 2 larger than those in **Au-DiBTF0–2**, the radiative decay rate constant is a factor of 2 smaller than those of **Au-DiBTF0–2**, and the nonradiative decay rate constant is appreciably larger than those of **Au-DiBTF(0–2)**. Despite subtle changes in their fluorescence lifetimes, fluorescence quantum yields, and intersystem crossing quantum yields, the decay pathways of the excited-singlet states in **Au-DiBTF0–2** are essentially identical. Conversion of the alkynyl linker to a triazolyl linker in **Au-DiBTF3** results in entirely different excited-state dynamics relative to **Au-DiBTF0–2.**

Density functional theory (DFT) calculations were performed on models of **Au-DiBTF0, Au-DiBTF2,** and **Au-DiBTF3**. The trimethylphosphine ligand of **Au-DiBTF0** was retained, but methyl groups were substituted for the mesityl groups on the N-heterocyclic carbene, methyl groups for the ethyl groups on the fluorenyl moiety, and methyl groups for the benzyl groups on the triazolyls in **Au-DiBTF3**. The computational results obtained for the (trimethylphosphine)-gold(I) alkynyl complex are taken as representative of both phosphine-containing complexes on the basis of their structural similarity. Frontier Kohn–Sham orbital diagrams of model complexes appear in Figures S16–S18. The calculations show that both the highest occupied Kohn–Sham molecular orbital (HOMO) and the lowest unoccupied Kohn–Sham molecular orbital (LUMO) are localized almost entirely on the BTF dialkynyl ligand. Kohn–Sham orbital energy level diagrams are also shown in Figures S16–S18. In all three complexes, the HOMO is composed of greater than 96% alkynyl ligand electron density, with the remaining electron density largely Au(I) in character. These results are in accord with the ligand-centered emission observed for all of the complexes.

The results of time-dependent DFT (TDDFT) calculations on Franck–Condon singlet and triplet states are consistent with the similar excited-state decay pathways for the dialkynyl complexes, with nearly identical energy gaps between the S_1 and T_2 states for the model complexes **Au-DiBTF0′** and **Au-DiBTF2′** (Figure 2). However, **Au-DiBTF3′** has a much smaller S_1-to-T_2 energy gap, in accordance with the k_{ISC} value that is 2 times larger than those for **Au-DiBTF0–2**, along with the highest intersystem crossing quantum yield, lowest fluorescence quantum yield, and shortest fluorescence lifetime among all of the complexes (Figure 2).

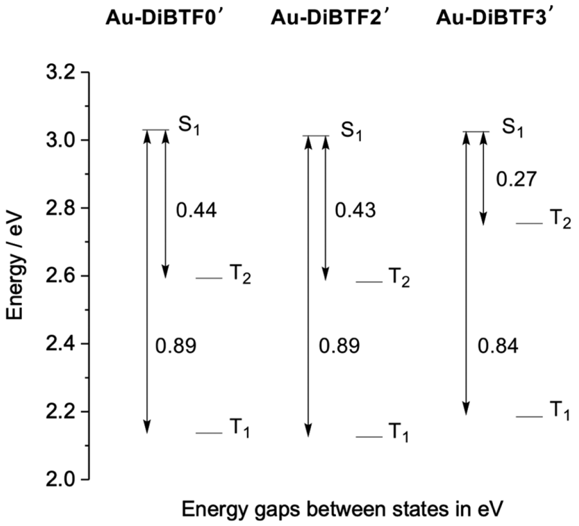


Figure 2. Energies of low-lying Franck–Condon singlet and triplet states calculated for model complexes with TDDFT.

Four new laterally asymmetric dinuclear gold(I) complexes originating from a benzothiazole fluorenyl dialkynyl ligand have been synthesized and photophysically characterized. Our results demonstrate that modification of the ancillary ligand (phosphine to carbene) or the linkage (alkynyl to triazole) changes the ground- and excited-state properties. Slight structural modifications in the phosphine capping ligands exert muted effects on the ground-state absorption spectra, luminescence spectra, fluorescence quantum yield, intersystem crossing quantum yield, and fluorescence lifetime. Slight decreases in the fluorescence quantum yield and fluorescence lifetime coinciding with a slight enhancement of the intersystem crossing quantum yield were observed when the ancillary ligand was changed from a phosphine to an N-heterocyclic carbene. This results in nearly identical singlet-state dynamics for **Au-DiBTF0−2**. Changing the bridging moiety results in the largest impact on the excited-state dynamics, as observed in the photophysical behavior of the triazolyl complex (**Au-DiBTF3**). The ground-state absorption and luminescence spectra of this complex show the largest bathochromic shifts in the series. These are accompanied by greater variation in the fluorescence quantum yield, intersystem crossing quantum yield, and fluorescence lifetime. The kinetic evolution of the singlet excited state of **Au-DiBTF3** differs from that of the alkynyl-bridged counterparts. Computational results echo the observed excited-state behavior, as **Au-DiBTF0** has an S_1-to-T_2 energy gap almost identical to that of **Au-DiBTF2**, whereas **Au-DiBTF3** has the smallest S_1-to-T_2 energy gap of the complexes, suggesting a higher intersystem crossing rate constant and quantum yield compared with **Au-DiBTF0−2**. To conclude, this study demonstrates how changes in both the ancillary ligands and the linkages to the gold atoms alter the excited-state dynamics in a series of dinuclear gold complexes. Research is currently underway in this laboratory to further investigate the effects of both the ancillary ligand and the linkage to the gold atom on the excited-state dynamics in a variety of systems containing gold.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.9b00768.

Experimental details, synthetic procedures, and computational and crystallographic data (PDF)

Cartesian coordinates (XYZ)

Accession Codes

CCDC 1953525 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: +44 1223 336033.

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Notes

The authors declare the following competing financial interest(s): Case Western Reserve University has filed for patent protection of the gold(I) organometallics described herein.

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