# **Inorganic Chemistry**

pubs.acs.org/IC

# Synthetically Tunable White-, Green-, and Yellow-Green-Light Emission in Dual-Luminescent Gold(I) Complexes Bearing a Diphenylamino-2,7-fluorenyl Moiety

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complexes, Au-DPA0 and Au-DPA1, are  $\sigma$ -aryls, two, Au-ADPA0 and Au-ADPA1, are  $\sigma$ -alkynyls, and one, Au-TDPA1, is a  $\sigma$ -triazolyl bound through carbon. All complexes show vibronically structured absorption and luminescence bands that are assignable to  $\pi - \pi^*$ transitions localized on the diphenylamine-substituted fluorenyl  $\pi$ system. The excited-state dynamics of all five chromophores are governed by selection of the ancillary ligand and  $\sigma$  attachment of the



diphenylamine-substituted fluorenyl moiety. All of these chromophores are dual luminescent in a toluene solution at 298 K. The luminescence from the aryl derivatives, Au-ADPA0 and Au-DPA1, appears green. The alkynyl derivative containing a phosphine ancillary ligand, Au-ADPA0, is a white-light emitter, while the alkynyl derivative containing an N-heterocyclic carbene ancillary ligand, Au-ADPA1, is a yellow-light emitter. The luminescence from the triazolyl-linked chromophore, Au-TDPA1, appears as yellow-green. Spin-restricted density functional theory calculations support the assignments of ligand-centric optical transitions but with contributions of ligand-to-metal charge transfer involving the vacant Au 6p orbital.

# INTRODUCTION

Gold(I) offers unique advantages as a heavy-atom effector for phosphorescent metal complexes; it has the highest spin-orbit coupling of any stable d-block nuclide.<sup>1</sup> Gold is also the most electronegative metal; hence,  $\sigma$  bonds between carbon and gold are effectively nonpolar.<sup>2-6</sup> The typical gold organometallic is indefinitely stable to air and moisture. Gold-bearing chromophores are now frequently proposed as phosphorescent dopants in organic light-emitting diodes (OLEDs),<sup>7-10</sup> with most efforts focusing on cyclometalates of gold(III).11-15 However, Bochmann, Credgington, and co-workers<sup>16-19</sup> have reported tunable emission from interligand excited states in (N-heterocyclic carbene)gold(I) amide complexes, and prototype OLEDs have been investigated. Recently, Thompson and co-workers<sup>20</sup> have described the photophysical consequences of triplet-state changeover from metal-to-ligand charge transfer (MLCT) to intraligand charge transfer (ICT) and, in so doing, demonstrated the first phosphorescent MLCT excited state of gold(I). Studies of gold(I) naphthyls, pyrenyls, alkynyls, and triazolyls demonstrate that extended  $\pi$  chromophores substituted with a single gold atom can exhibit dual

luminescence.<sup>21-25</sup> Schanze, Veige, and co-workers report white-light emission in di- and tetranuclear (phosphine)gold-(I) complexes<sup>26</sup> and excited-state aurophilic bonding in digold tetrazolides.<sup>27,28</sup> The capping ligand on gold exerts a significant influence on the emission wavelengths and kinetic parameters of excited-state decay.

Recent work from these laboratories<sup>29-31</sup> has demonstrated white-light emission from (organophosphine)gold(I) fluorenyl complexes bearing benzothiazolyl substituents. Dual blue fluorescence and yellow-orange phosphorescence can occur in nearly equal radiative yields to afford white-light emission. The foregoing gold(I) fluorenyls<sup>29–31</sup> are substituted with the electron-withdrawing substituent benzothiazolyl. To the extent that gold(I) is a Lewis acid, these complexes have an acceptor-

Received: August 12, 2021 Published: January 4, 2022





 $\pi$ -acceptor (A- $\pi$ -A) architecture, and luminescence derives from  $\pi$ - $\pi^*$  excited states localized on the benzothiazolefluorenyl ligand. This work describes five gold(I) diphenylaminofluorenyl chromophores with an acceptor- $\pi$ -donor (A- $\pi$ -D) structure. These A- $\pi$ -D chromophores also exhibit dual luminescence in a room temperature toluene solution with one chromophore featuring white-light emission. The influence of  $\sigma$ -linkage (aryl, alkynyl, and triazolyl) between gold(I) and the diphenylaminofluorenyl unit and the ancillary ligand bound to gold(I) on the excited-state dynamics and resultant dualluminescent behavior of the chromophores is explored.

#### X-RAY CRYSTALLOGRAPHY AND GROUND-STATE ABSORPTION

Five new gold(I) diphenylaminofluorenyl (DPA) complexes have been synthesized with full chemical characterization. The molecular naming convention follows an Au-xDPAn nomenclature. x is used to designate the  $\sigma$  attachment of the diphenylamine-substituted fluorenyl moiety to gold(I), with DPA representing a  $\sigma$ -aryl linkage, ADPA representing a  $\sigma$ alkynyl linkage, and TDPA representing a  $\sigma$ -triazolyl linkage. *n* signifies the ancillary ligand attached to gold(I), with 0 representing a triphenylphosphine ligand and 1 representing an N-heterocylic carbene ligand. Note that the 2,6-diisopropylphenyl-substituted carbene was used in Au-DPA1 and the mesityl-substituted carbene was used in both Au-ADPA1 and Au-TDPA1. The syntheses, <sup>1</sup>H NMR, high-resolution mass spectrometry, and elemental analysis are given in the Supporting Information (SI). The structures of the Au<sup>1</sup>-DPA compounds are depicted in Figure 1.



Figure 1. Structures of diphenylamine-substituted chromophores presented in this study.

Four of these new compounds, Au-ADPA0, Au-ADPA1, Au-TDPA1, and Au-DPA0, were characterized crystallographically. The crystal structures and metric details are given in the SI. All gold centers are approximately linear. None of the complexes exhibit Au–Au or  $\pi$ -stacking interactions. The Au–C<sub>aryl</sub> bond length in Au-DPA0 is 2.052(7) Å, which is significantly longer<sup>32</sup> than the 2.008(3) Å Au–C<sub>alkynyl</sub> bond in Au-ADPA0. The Au–P bond length of 2.203(2) Å in Au-DPA0 is significantly shorter than that of Au-ADPA0, 2.28(1) Å, implying that the alkynyl carbon is the stronger trans influencer.<sup>33</sup> For the N-heterocyclic carbene complex Au-ADPA1, the Au–C<sub>carbene</sub> bond length is 2.009(2) Å, and the Au– $C_{alkynyl}$  bond length is 1.975(2) Å. The latter is significantly shorter than the corresponding distance in the phosphine analogue Au-ADPA0. For triazolyl Au-TDPA1, the Au– $C_{carbene}$  bond length is 2.039(3) Å, which is significantly longer than the Au– $C_{carbene}$  bond in Au-ADPA1, indicating that the triazolyl carbon is a stronger trans influencer than the alkynyl carbon. The Au– $C_{triazolyl}$  bond length is 2.041(3) Å, which is significantly longer than the Au– $C_{alkynyl}$  bond length [1.975(2) Å] in Au-ADPA1. These bond metrics are similar to those that we previously encountered in the gold(I) complexes of benzothiazoyl-substituted fluorenyls.<sup>29,30</sup>

Ground-state absorption spectra for the gold(I) diphenylaminofluorenyl compounds collected in toluene are shown in Figure 2. The two alkynyl complexes and the triazolyl complex have comparable ground-state absorption spectra characterized by two distinct absorption transitions. A low-energy absorption transition is observed around 370 nm and displays vibronic structure. The molar absorptivity of this absorption transition is on the order of  $4 \times 10^4$  M<sup>-1</sup> cm<sup>-1</sup> for Au-ADPA0 and Au-TDPA1. The molar absorptivity of the low-energy absorption transition is higher for Au-ADPA1 with a value close to 8  $\times$  $10^4 \text{ M}^{-1} \text{ cm}^{-1}$ . A second, higher-energy absorption transition is found at approximately 310 nm. It is broad and has a molar absorptivity value that is roughly half of the low-energy absorption transition. The ground-state absorption spectra of the Au-ADPA complexes and Au-TDPA1 are nearly identical in energy, band shape, and molar absorptivity values to the free alkynyl DPA ligand.<sup>34</sup> This leads us to conclude that these ground-state absorption transitions are  $\pi - \pi^*$  in character. The low-energy ground-state absorption maximum experiences a slight hypsochromic shift as the ancillary ligand is changed from a phosphine in Au-ADPA0 (376 nm) to an Nheterocyclic carbene in Au-ADPA1 (373 nm). A further hypsochromic shift is observed when the bridging moiety is converted to a triazole in Au-TDPA1 (369 nm). The lowenergy ground-state absorption maximum of Au-DPA0 occurs at 357 nm, while Au-DPA1 possesses a low-energy groundstate absorption maximum at 340 nm with a shoulder at 354 nm. These wavelengths represent a significant hypsochromic shift compared to their alkynyl and triazolyl counterparts. The ground-state absorption maxima of the Au-DPA complexes also experience a hypsochromic shift when the ancillary ligand is varied from a phosphine to an N-heterocyclic carbene in the Au-DPA complexes. Both complexes have molar absorptivity values on the order of  $3.5 \times 10^3$  M<sup>-1</sup> cm<sup>-1</sup>. The ground-state absorption spectra of the Au-DPA complexes are similar in energy, band shape, and molar absorptivity relative to the unsubstituted fluorene-DPA ligand.35 We also conclude that these ground-state absorption transitions are  $\pi - \pi^*$  in character.

#### STEADY-STATE LUMINESCENCE AND LUMINESCENCE QUANTUM YIELDS

All luminescence spectra were collected in toluene following three freeze-pump-thaw degas cycles. Pertinent photophysical properties are summarized in Table 1. Representative fluorescence quantum yield data and the data used in calculation of the phosphorescence quantum yields are given in the SI. Normalized steady-state luminescence spectra of the gold complexes and a CIE 1931 color coordinate plot appear in Figure 3. All five complexes display dual luminescence in freeze-pump-thaw degassed toluene. The fluorescence and phosphorescence spectra of these complexes are both highly



Figure 2. (Left) Ground-state absorption spectra of Au-ADPA0 (black), Au-ADPA1 (red), and Au-TDPA1 (blue) collected in toluene. (Right) Ground-state absorption spectra of Au-DPA0 (olive) and Au-DPA1 (purple) collected in toluene.

Table 1. Pertinent Photophysical Properties<sup>a</sup>

	gold complex					
	alkynyl			aryl		
experimental results	Au-ADPA0	Au-ADPA1	Au-TDPA1	Au-DPA0	Au-DPA1	
$\lambda_{\rm ABS}/{ m nm}~(\epsilon,~ imes 10^4~{ m M}^{-1}~{ m cm}^{-1})$	376 (5.4)	373 (8.3)	369 (4.4)	357 (3.5)	340 (3.6), sh -354 (3.4)	
$\lambda_{\rm FL}^{\ b}/\rm nm$	381	378	376	364	364	
$E_{\rm S}^{\ b}/{\rm eV}$	3.25	3.28	3.30	3.41	3.41	
$\lambda_{\rm PHOS}^{b}/\rm nm$	506	506	494	469	469	
$E_{\rm T}^{\ b}/{\rm eV}$	2.45	2.45	2.50	2.64	2.64	
$\Delta E_{ m ST}/ m eV$	0.80	0.83	0.80	0.77	0.77	
$\Phi_{ m F}$	$0.20 \pm 0.02$	$0.13 \pm 0.01$	≤0.01 <sup>c</sup>	$0.06 \pm 0.01$	$0.07 \pm 0.01$	
${\Phi_{\mathrm{p}}}^d$	0.09	0.13	≤0.05	0.17	0.21	
$\Phi_{\rm ISC}{}^e$	$0.54 \pm 0.01$	$0.62 \pm 0.03$	$0.70 \pm 0.01$	$0.59 \pm 0.03$	$0.54 \pm 0.09$	
$ au_{ m F}/ m ps$	$168 \pm 8$	$124 \pm 3$	$21 \pm 10$	$36 \pm 5$	$92 \pm 3$	
$ au_{ m P}/\mu{ m s}$	$178 \pm 30$	499 ± 15	$364 \pm 66$	$482 \pm 73$	$405 \pm 23$	
$k_{\rm r}/{ m s}^{-1}$	$1.19 \times 10^{9}$	$1.05 \times 10^{9}$	$3.33 \times 10^{8}$	$1.67 \times 10^{9}$	$7.60 \times 10^{8}$	
$k_{\rm nr}/{ m s}^{-1}$	$1.55 \times 10^{9}$	$2.02 \times 10^{9}$	$9.67 \times 10^{9}$	$9.72 \times 10^{9}$	$4.24 \times 10^{9}$	
$k_{\rm ISC}/{ m s}^{-1}$	$3.21 \times 10^{9}$	$5.00 \times 10^{9}$	$2.33 \times 10^{10}$	$1.64 \times 10^{10}$	$5.87 \times 10^{9}$	

<sup>*a*</sup>Data collected in toluene. <sup>*b*</sup>Estimated from the onset of the emission band. The values listed in the table represent the wavelength and energy at  $1/_{10}$ th the emission peak maximum. <sup>*c*</sup>Under these experimental conditions, the integrating sphere is accurate for quantum yield values greater than 0.05 (Edinburgh Instruments FLS980 Series Reference Guide).  $\Phi_F$  was deemed to be between 0.005 and 0.01 for Au-TDPA1 after two trials. We believe that a  $\Phi_F$  value of 0.01 represents an appropriate upper limit for this chromophore. <sup>*d*</sup>Phosphorescence quantum yields were determined using a relative method. See the SI. <sup>*e*</sup>Intersystem-crossing quantum yields were determined using photosensitized singlet oxygen phosphorescence measurements with phenazine as a standard. See the SI.



**Figure 3.** (Left) Normalized steady-state luminescence intensity of the Au-ADPA ( $\lambda_{ex} = 355 \text{ nm}$ ), Au-TDPA ( $\lambda_{ex} = 355 \text{ nm}$ ), and Au-DPA ( $\lambda_{ex} = 345 \text{ nm}$ ) analogues. (Right) Corresponding CIE 1931 plots for the individual complexes.

structured. The observed vibronic structure in the fluorescence and phosphorescence spectra suggests that the luminescence is  $\pi - \pi^*$  in character.<sup>36</sup> Au-ADPA1 and Au-TDPA1 have similar fluorescence maxima [378 nm (3.28 eV) and 376 nm (3.30 eV), respectively], while the fluorescence maximum of Au-ADPA0 occurs at slightly longer wavelength and lower energy (381 nm and 3.25 eV, respectively). The phosphorescence maxima of Au-ADPA0 and Au-ADPA1 appear at the same wavelength and energy (506 nm and 2.45 eV, respectively). The phosphorescence maximum of Au-TDPA1 occurs at a slightly shorter wavelength and higher energy (494 nm and 2.50 eV, respectively). The fluorescence and phosphorescence maxima and energies of Au-DPA0 and Au-DPA1 are identical, with the fluorescence maxima observed at 364 nm (3.41 eV) and the phosphorescence maxima observed at 469 nm (2.64 eV). The observation of dual luminescence in these samples allowed for calculation of the energy gap between the singlet and triplet excited states (singlet-triplet gap,  $\Delta E_{ST}$ ). The calculated singlet-triplet gap for the N-heterocyclic carbenecontaining alkynyl compound, Au-ADPA1 (0.83 eV), is slightly larger than that for Au-ADPA0 and Au-TDPA1 (0.80 eV). The singlet-triplet gaps for the aryl chromophores, Au-DPA0 and Au-DPA1, are identical with a value of 0.77 eV. Determination of the fluorescence and phosphorescence quantum yields allows for a quantitative comparison of the dual luminescence in these chromophores. The alkynylbridged chromophores, Au-ADPA0 and Au-ADPA1, both have fluorescence quantum yields >0.10, with the value obtained for Au-APDA0 being higher (0.20) than the value obtained for Au-ADPA1 (0.13). Conversely, the phosphorescence quantum yield of Au-APDA1 (0.13) is higher than the phosphorescence quantum yield of Au-ADPA0 (0.09). Both the fluorescence and phosphorescence quantum yields of the triazole-bridged chromophore, Au-TDPA1, are lower than those of the alkynyl-bridged chromophores, Au-ADPA0 and Au-ADPA1. The phosphorescence quantum yield ( $\leq 0.05$ ) of Au-TDPA1 is significantly larger than the fluorescence quantum yield ( $\leq 0.01$ ) of Au-TDPA1. The aryl derivatives, Au-DPA0 and Au-DPA1, display similar fluorescence quantum yields (0.06 and 0.07, respectively) with quantitatively higher phosphorescence quantum yields (0.17 and 0.21, respectively). The observation of highly variable fluorescence and phosphorescence quantum yields as well as the differences in the fluorescence and phosphorescence energies across the series of molecules results in differences in the chromaticity of the individual chromophores. Four separate chromaticity coordinates are observed in this series of chromophores. The phosphorescence quantum yields of Au-DPA0 and Au-DPA1 are large relative to their fluorescence quantum yields, with broad phosphorescence spanning from 475 to 655 nm and a maximum at 490 nm, resulting in green-light emission from these chromophores. The phosphorescence quantum yield in Au-TDPA1 is significantly larger than its fluorescence quantum yield, with broad phosphorescence spanning from 475 ato 700 nm and a maximum at 516 nm. Yellow-green emission is observed in Au-TDPA1. The fluorescence and phosphorescence quantum yield values as well as the relative fluorescence and phosphorescence energies are balanced in a manner that enables white-light emission from Au-ADPAO. The relative fluorescence and phosphorescence energies of Au-ADPA1 are similar to those in Au-ADPA0; however, the phosphorescence quantum yield is enhanced in Au-ADPA1. This produces yellow-light emission from Au-ADPA1.

#### INTERSYSTEM-CROSSING EFFICIENCY, LUMINESCENCE LIFETIMES, AND RATE CONSTANT DETERMINATION

Photosensitized singlet oxygen phosphorescence spectra, fluorescence lifetime decays, and phosphorescence lifetime decays obtained for Au-ADPA0, Au-ADPA1, Au-TDPA1, Au-DPA0, and Au-DPA1 are shown in the SI. The values obtained from fits of the data are collected in Table 1. The photosensitized singlet oxygen quantum yield  $(\Phi_{\Delta})$  obtained from aerated solutions of each chromophore can be used to approximate the lower limit of the intersystem-crossing quantum yield ( $\Phi_{ISC}$ ). In Au-ADPA0, Au-ADPA1, and Au-**TDPA1**, the value of  $\Phi_{\rm ISC}$  is strongly dependent on the nature of the ancillary ligand and the bridging moiety.  $\Phi_{ISC}$  increases from 0.54 in Au-ADPA0 to 0.62 in Au-ADPA1 as the ancillary ligand is changed from a phosphine to an N-heterocyclic carbene.  $\Phi_{ISC}$  is further increased to 0.70 in Au-TDPA1 when the bridging moiety is changed from an alkynyl linker to a triazolyl linker. The  $\Phi_{\rm ISC}$  values obtained for Au-DPA0 and Au-DPA1 are similar to the values of 0.59 and 0.54, respectively. The fluorescence lifetimes of all five Au-DPA complexes are shorter than 200 ps. The fluorescence lifetimes of Au-ADPA0, Au-ADPA1, and Au-TDPA1 are also strongly dependent on the nature of the ancillary ligand and the bridging moiety. Au-ADPA0 possesses the longest lifetime in the group, with a fluorescence lifetime of  $168 \pm 8$  ps. The fluorescence lifetime decreases to  $124 \pm 3$  ps in Au-ADPA1 as the ancillary ligand is changed from triphenylphosphine to an N-heterocyclic carbene. The fluorescence lifetime is further diminished to  $\leq$ 30 ps when the bridging moiety is changed from an alkynyl to a triazolyl in Au-TDPA1. The fluorescence lifetimes of Au-DPA0 and Au-DPA1 are shorter than those of their alkynyl analogues; the fluorescence lifetime of Au-DPAO is  $36 \pm 5$  ps, while the fluorescence lifetime of Au-DPA1 is 92 ± 3 ps. The change in lifetime between Au-DPA0 and Au-DPA1 represents an increase in the fluorescence lifetime when the ancillary ligand is changed from a phosphine to an Nheterocyclic carbene. All five complexes possess phosphorescence lifetimes exceeding 150  $\mu$ s at ambient temperature. Au-ADPA0 has the shortest phosphorescence lifetime of 178  $\mu$ s, while Au-ADPA1 possesses the longest phosphorescence lifetime of 499  $\mu$ s. Determination of the fluorescence quantum yield ( $\Phi_{FL}$ ), intersystem-crossing quantum yield ( $\Phi_{ISC}$ ), and fluorescence lifetime  $(\tau_{\rm FL})$  allows for calculation of the radiative  $(k_r)$ , nonradiative  $(k_{nr})$ , and intersystem-crossing  $(k_{\rm ISC})$  rates that govern deactivation of the singlet excited states in these chromophores. The radiative decay rates of Au-**ADPA0**  $(1.19 \times 10^9 \text{ s}^{-1})$  and **Au-ADPA1**  $(1.05 \times 10^9 \text{ s}^{-1})$  as well as the nonradiative decay rates of Au-ADPA0 ( $1.55 \times 10^9$ s<sup>-1</sup>) and Au-ADPA1 ( $2.02 \times 10^9 \text{ s}^{-1}$ ) are similar, whereas the rate of intersystem crossing in Au-ADPA1 ( $5.00 \times 10^9 \text{ s}^{-1}$ ) is quantitatively larger than that in Au-ADPA0  $(3.21 \times 10^9 \text{ s}^{-1})$ . Deactivation of the singlet excited state of Au-TDPA1 is remarkably different from deactivation of the singlet excited states of Au-ADPA0 and Au-ADPA1. The radiative decay rate  $(3.33 \times 10^8 \text{ s}^{-1})$  of **Au-TDPA1** is nearly an order of magnitude slower than those of Au-ADPA0 and Au-ADPA1, while both the rates of nonradiative decay (9.67  $\times$  10<sup>9</sup> s<sup>-1</sup>) and intersystem crossing  $(2.33 \times 10^{10} \text{ s}^{-1})$  are nearly an order of magnitude faster in Au-TDPA1 compared to Au-ADPA0 and Au-ADPA1. The radiative, nonradiative, and intersystemcrossing rates are all notably different in Au-DPA0 and Au-



Figure 4. Partial Kohn–Sham orbital energy level diagram of the model complex Au-DPA1' showing the selected orbitals. The percentages are of the orbital density.





**DPA1** compared to their alkynyl and triazolyl counterparts. The calculated values for the radiative  $(1.67 \times 10^9 \text{ s}^{-1})$ , nonradiative  $(9.72 \times 10^9 \text{ s}^{-1})$ , and intersystem-crossing  $(1.64 \times 10^{10} \text{ s}^{-1})$  rates of **Au-DPA0** are all approximately 2 times greater than the calculated values for the radiative  $(7.60 \times 10^8 \text{ s}^{-1})$ , nonradiative  $(4.24 \times 10^9 \text{ s}^{-1})$ , and intersystem-crossing  $(5.87 \times 10^9 \text{ s}^{-1})$  rates of **Au-DPA1**.

## DFT CALCULATIONS

The electronic structures of new gold(I) complexes were evaluated computationally with static and time-dependent

density functional theory (DFT) calculations. The geometries were optimized without restraint, and harmonic frequency calculations found the converged structures to be potentialenergy minima. All calculations included continuum solvation in toluene (see the SI).

Figure 4 depicts a frontier Kohn–Sham orbital energy level diagram of the model complex Au-DPA1', where aryl substituents on the carbene are truncated with 2,6-xylyl groups. Also shown are depictions of the highest occupied Kohn–Sham orbital (HOMO) and lowest unoccupied Kohn–Sham orbital (LUMO). The HOMO is delocalized across the

aryl carbanionic ligand with similar proportions of fluorenyl and diphenylamine density. The LUMO is distributed across the chromophore with sizable electron density located on the carbene ancillary ligand (25%) and the gold(I) atom (14%). A sizable energy gap (4.17 eV) separates the HOMO and LUMO.

The electronic structure of alkynyl **Au-ADPA1'** parallels that of the aryl. Again, the HOMO spreads across the  $\sigma$ -alkynyl ligand, with preponderant density on the fluorenyl fragment. The LUMO is essentially an alkynylfluorenyl  $\pi$  function that overlaps the vacant 6p orbital of gold (Figure S8). The HOMO–LUMO gap is slightly narrower than that of **Au-DPA1'**, consistent with the more extensive conjugation of the alkynyl moiety and in agreement with our experimental data.

Time-dependent DFT (TD-DFT) calculations indicate that excitation from any or alkynyl  $\pi$  functions accounts for the lowest-lying excited states. For carbene-ligated Au-DPA1', the first (Franck-Condon) singlet excited state consists 91% of a LUMO  $\leftarrow$  HOMO one-particle transition. For alkynyl Au-ADPA1', this figure is 95%. Plots of these frontier orbitals (Figure S7) indicate that this transition has combined ICT/ LMCT character, where the vacant Au 6p orbital accepts  $\pi$ electron density from the carbanionic ligand. The orbital compositions of the first (Franck-Condon) singlet excited states of the phosphine complexes Au-DPA0 and Au-ADPA0 are more complicated. For these complexes, the first Franck-Condon singlet state consists of two one-particle transitions involving the HOMO that engage in configuration interaction. For Au-DPA0, LUMO  $\leftarrow$  HOMO (52%) and LUMO+3  $\leftarrow$ HOMO (41%) excitations account for the first singlet, whereas for Au-ADPA0, the corresponding transitions are LUMO  $\leftarrow$ HOMO (63%) and LUMO+2  $\leftarrow$  HOMO (33%). For both complexes, the intermingling transitions involve charge transfer from the fluorenyl to PPh<sub>3</sub> and gold (LUMO) and to the PPh<sub>3</sub> ligand (LUMO+2 or +3). The compositions of Franck-Condon excited states appear in the SI.

Figure 5 plots the energies of Franck–Condon singlet and triplet excited states relative to the ground state ( $S_0$ ). A recurring pattern across all gold complexes is that four triplet excited states lie below the first singlet for the aryl complexes and three triplet excited states lie lower for alkynyls and two for the triazolyl compound. The calculations suggest that, for the aryl and triazolyl complexes,  $T_4$  and  $T_2$ , respectively, act as gateway states for intersystem crossing because of their slight energetic separation from  $S_1$  (<0.1 eV in all cases). For alkynyl complexes, the splitting between  $S_1$  and  $T_3$  is slightly larger. The two alkynyls and the triazolyl complex have larger  $T_2-T_1$  energy gaps than either of the aryl complexes, which may impede internal conversion to  $T_1$ . The aryls **Au-DPA0** and **Au-DPA1'** were calculated to have  $T_2-T_1$  energy gaps that are smaller (~0.3 eV) and nearly equal.

#### CONCLUSIONS

This work further establishes the gold(I) fluorenyl fragment as a building block for functional, dual-luminescent chromophores. Five new gold(I) fluorenyls are reported, where a diphenylamine moiety is attached to the fluorenyl opposite gold. This work complements our earlier studies on fluorenyls substituted with the electron-withdrawing benzothiazolyl heterocycle.

Structural characterization of four gold(I) complexes shows the expected propensity of Au(I) (d<sup>10</sup>) to bind in a linear, twocoordinate geometry. The structures of **Au-DPA0** and **Au**- **ADPA0** establish that the alkynyl linker is a stronger trans influencer than aryl carbon.

The new complexes all exhibit dual fluorescence and phosphorescence emission, demonstrating that the spinorbit coupling of gold suffices to populate triplet excited states of conjugated, carbocyclic moieties such as fluorenyl. Absorption, fluorescence, and phosphorescence profiles show vibronic structure, all suggesting intraligand  $\pi - \pi^*$  excited states. Extending the conjugation of the fluorenyl core with either an alkynyl or a triazolyl linker shows the expected red shift in the absorption maxima, but the alkynyl  $\rightarrow$  triazolyl ("gold click") transformation leaves the fluorescence maximum unchanged and slightly blue-shifts the phosphorescence peak. The combination of fluorescence and phosphorescence emission controls the chromaticity of these lumophores, leading to emission that is green (aryl complexes Au-ADPA0 and Au-DPA1), white (Au-ADPA0), yellow (Au-ADPA1), or yellow-green (Au-TDPA1). Singlet-state emission persists for picoseconds, whereas triplet emission is long-lived, ranging from ca. 180 to 500  $\mu$ s at 298 K in deoxygenated solvents. Intersystem crossing is the dominant kinetic pathway in the S<sub>1</sub> state of all derivatives, and for all complexes,  $k_{nr}$  exceeds  $k_r$ . TD-DFT calculations indicate four (Au-DPA0 and Au-DPA1) or two (Au-ADPA0, Au-ADPA1, and Au-TDPA1) Franck-Condon triplet states below the first Franck-Condon singlet excited state. The small  $S_1-T_2$  energy gap calculated for the triazolyl complex Au-TDPA1 accounts for its notably rapid intersystem-crossing rate, although its  $\Phi_{ISC}$  value is similar to those of the other four compounds. The work indicates that the chromaticities of gold(I) fluorenyls are controllable through the choice of the capping ligand and through the linking moiety: direct C-Au  $\sigma$  bond, alkynyl, or triazolyl. Additional work on the structure-property relationships of triplet-active organogold(I) species is ongoing.

### ASSOCIATED CONTENT

#### **1** Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c02405.

Materials and experimental methods, synthetic details for new compounds, <sup>1</sup>H NMR, high-resolution mass spectrometry, elemental analysis, fluorescence lifetime decays, fluorescence quantum yield data, data used in the calculation of phosphorescence quantum yields, photosensitized singlet oxygen phosphorescence data, phosphorescence lifetime decays, orbital energy-level diagrams, and a summary of the calculated electronic transitions obtained from TD-DFT calculations (PDF)

#### Accession Codes

CCDC 2069839–2069842 contain 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, UK; fax: +44 1223 336033.

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#### Notes

The authors declare no competing financial interest.

#### ACKNOWLEDGMENTS

This work is supported by the Air Force Office of Scientific Research (AFOSR; Contract FA9550-18-1-0247 to T.G.G.). All AFRL-affiliated authors recognize the AFOSR under Award 9550-19-1-18RX056 and the AFRL/RXAP under Contract FA8650-16-D-5402-0001. The National Science Foundation is acknowledged through the Major Research Instrumentation Program under Grant CHE 1625543 to M.Z. (funding for the single-crystal X-ray diffractometer).

#### DEDICATION

Dedicated to the memory of R. H. Holm.

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