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Observation of Long-Lived Phosphorescence in Au(I) Complexes Bearing Chromophoric (N-Heterocyclic Carbene) Ligands

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Keywords: Gold, *N*-heterocyclic carbene, luminescence, triplet state, density-functional theory

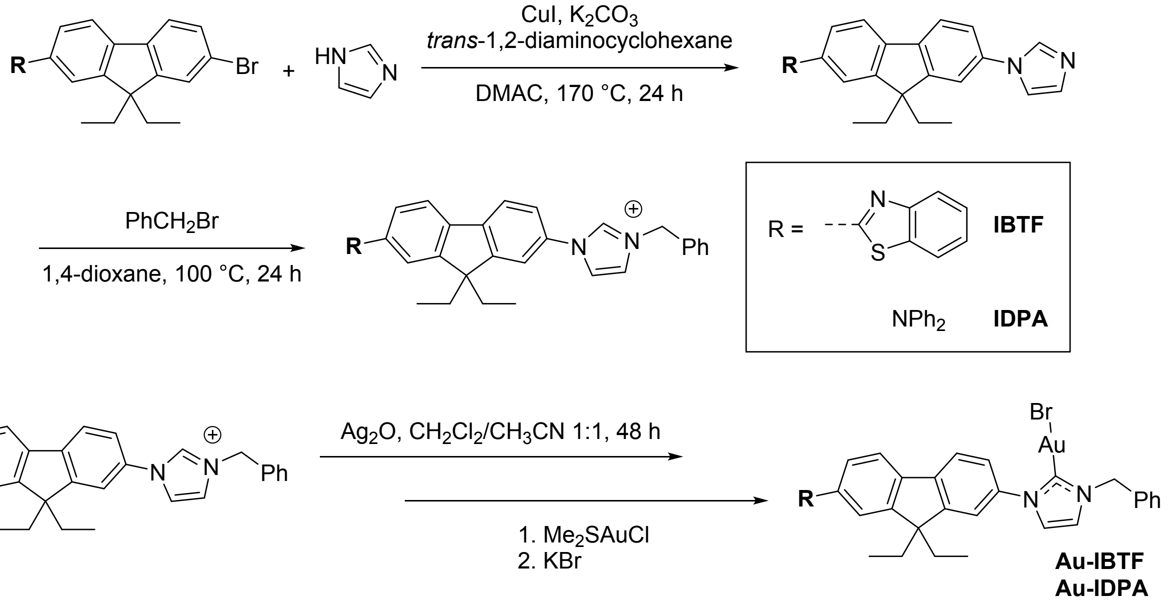
Abstract. Synthesis and optical characterization of two new gold(I) complexes bearing chromophoric *N*-heterocyclic carbene (NHC) ligands are described. Ligands with electron-releasing (diphenylamino) and electron-withdrawing (benzothiazolyl) substituents are described, and metalation with gold(I) bromide is demonstrated. Crystallographic characterization reveals both complexes to have linear, two-coordinate gold and an absence of aurophilic interactions in the solid state. The absorption spectra of both gold(I) complexes are similar to the free ligand absorption spectra indicating ligand localized π-π* absorption. The new gold complexes show moderate fluorescence and observable phosphorescence; binding of a single gold atom suffices to populate triplet excited states. The fluorescence of the benzothiazolyl derivative is π-π* in nature, while the fluorescence of the diphenylamino derivative is charge-transfer in nature. The phosphorescence of both complexes is vibronically structured, indicative of metal-perturbed π-π* character. Phosphorescence at 298 K persists for hundreds of microseconds. Intersystem crossing is the dominant excited state kinetic pathway with quantum yields of intersystem crossing greater than 50% for both gold complexes. Density-functional theory calculations indicate that the lowest excited singlet and triplet states are dominated by the carbene-fluorenyl-substituent conjugate. We believe the incorporation of gold as a heavy atom through a strongly σ-donating and moderately π-accepting NHC-linker provides a general strategy for achieving NHC complexes with phosphorescence.

Introduction. Organometallic chromophores are one type of organic-inorganic hybrid,[1,2] where metal ions, ligands, and ligand substituents are prearranged to act synergistically. A frequent strategy is embedding electron donor and acceptor functionalities alongside π-conjugated moieties to induce intramolecular charge-transfer.[3,4] The spin-orbit coupling of the heavier d-block elements promotes intersystem crossing that populates long-lived triplet excited states.[5,6] These triplet states can sustain electron or energy transfer, or can themselves absorb light. A successful hybrid shows light emission and excited-state dynamics that surpass those of the individual components.

We are investigating modified *N*-heterocyclic carbene (NHC) complexes as triplet-state emitters with prolonged excited-state lifetimes brought about by complexation to gold(I). The chief utility of NHCs in gold chemistry has hitherto been in catalysis, where the carbene ligand stabilizes intermediates against degradation.[7,8] More recent work has demonstrated carbon-gold linkages as passivators of gold surfaces[9,10] and molecular gold clusters.[11,12] *N*-heterocyclic carbenes have been shown to modulate emission chromaticities in high radiative yield lumophores of three-coordinate gold(I).[13] In these complexes, the (NHC)gold(I) moiety accepts electron density in (ligand)metal-to-ligand charge transfer transition that decays radiatively. Chromophoric NHC ligands are less common, although a variety of NHCs with remote fluorescent substituents has been reported.[14,15] Typically, a fluorophore is tethered as an *N*-substituent, and electronic coupling to the carbene heterocycle is weak. There are also numerous examples of polydentate ligands where an NHC is one Lewis base within a cyclometalating ligand.[16,17] In these cases, ligand-to-metal coupling is strong, and metal-to-ligand charge transfer often results. A recent development is the discovery of strong luminescence from carbene-metal amides of group 11.[18,19] In these complexes, a cyclic (alkyl)(amino)carbene (CAAC) ligand serves as electron acceptor from the (amido)metal(I) fragment, leading to conformationally dependent delayed fluorescence. One example is the work of Traskovskis and co-workers[20] who demonstrate that sulfonyl-substituents in the *N*-aryl moieties of (NHC)Cu(I) and -Ag(I) complexes reinforce charge transfer, resulting in thermally activated delayed fluorescence, in another instance of carbene-modulated luminescence. Thompson and co-workers described a di-gold(I)-amide complex where the supporting carbene ligand is a binuclear gold(I) construct. The two gold(I) centers augment electron-accepting character and raise the energy of the emitting excited state. The carbene ligands and gold centers participate jointly in thermally activated delayed fluorescence.[21] A subset of gold(I) complexes displays dual fluorescence/phosphorescence emission; some are white-light emitters.[22–25] Such single-component white lumophores show potential as emitting elements in white-light organic light-emitting diodes (OLEDs).[26,27] However, the rational design of dual lumophores is an ongoing research challenge.

The NHC ligands developed here are 2,7-disubstituted fluorenyls with electron-releasing diphenylamine (IDPA) or electron-withdrawing benzothiazolyl (IBTF) substituents attached at nitrogen, Figure 1. We report synthetic, structural, and optical studies of gold(I) complexes of these ligands to evaluate electronic coupling between gold(I) and fluorenyl across a carbene spacer. Density-functional theory (DFT) calculations indicate ligand-centered emission from states delocalized across the entire NHC ligand. These results illustrate a general strategy for endowing NHC ligands with luminactive triplet excited states. Specifically, gold is embedded as a heavy atom through a strongly σ-donating and moderately π-accepting NHC moiety, which is connected to a fluorenyl carbocycle, itself functionalized with an electron-withdrawing (benzothiazolyl) or electron-releasing (amine) group.[28–31]

Results and Discussion. Syntheses of carbene ligands adopted published protocols for fluorenyl substituents[32] and metalation;[33,34] these are summarized in Scheme 1; full experimental details appear as Supporting Information. Benzothiazolyl and amine-substituted fluorenyl precursors were prepared as described by Tan and co-workers.[32] Attachment of imidazole to the fluorenyl carbocycle proceeded through copper-catalyzed arylation.[35,36] Reaction with benzyl bromide afforded the imidazolium salt, and a standard transmetalation sequence with silver oxide delivered the gold(I) bromide.[34] Both gold(I) complexes were structurally authenticated with thermal ellipsoid depictions and packing diagrams appearing in Figure 1. Two-coordinate, linear gold(I) is evident, and aurophilic interactions are absent in the unit cell. Metric properties of the imidazolyl heterocycle and its substituents are unexceptional. The measured Au–Br bond lengths are statistically distinct,[37] being 2.3983(2) Å (**IDPA-AuBr**) and 2.3911(3) Å (**IBTF-AuBr**). These values indicate that the amine-substituted ligand is a marginally stronger *trans*-influencer than the benzothiazolyl analogue, and that both are stronger *trans*-influencers than the ubiquitous IPr (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene).[38]



Scheme 1. Synthesis of ligands and complexes. DMAC is dimethylacetamide.

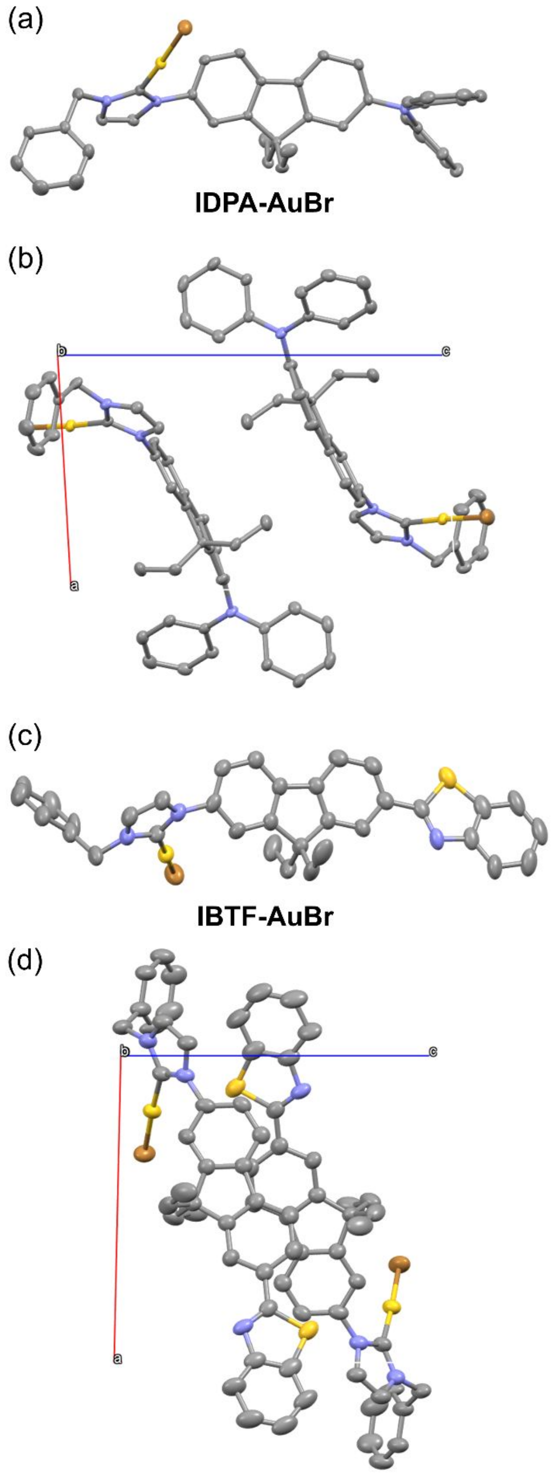


Figure 1. (a) Thermal ellipsoid depiction of **IDPA-AuBr** (50% probability, 100 K). Hydrogen atoms omitted for clarity. (b) Packing diagram of **IDPA-AuBr** shown along *b*. (c) Thermal ellipsoid depiction of **IBTF-AuBr** (50% probability, 100 K). Hydrogen atoms omitted for clarity. (d) Packing diagram of **IBTF-AuBr** shown along *b*. Legend: Gold, Au; blue, N; light yellow, S; brown, Br.

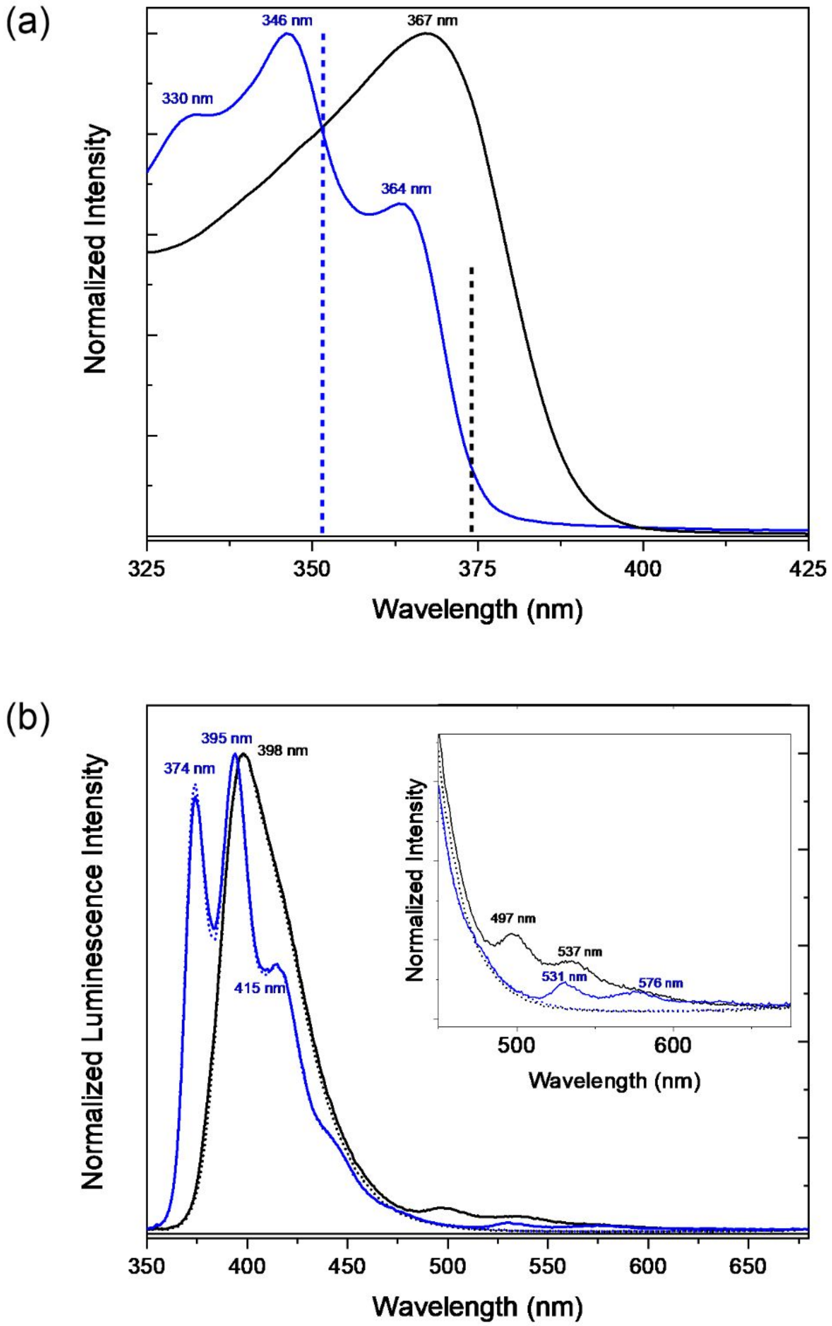


Figure 2. Normalized ground-state absorption (dashed line) and luminescence spectra of **IBTF-AuBr** and **IDPA-AuBr** in toluene at 298 K. The inset compares phosphorescence region of luminescence spectra in oxygenated (dotted line) and deoxygenated (solid line) toluene, showing the sensitivity of long wavelength emission to oxygen. Shown as boldface dotted bars are calculated (TDDFT) energies of singlet-singlet transitions scaled to the calculated oscillator strength (*f*) of each transition. **IDPA-AuBr:** 373 nm, *f* = 0.86; 334 nm, *f* = 0.03. **IBTF-AuBr:** 353 nm, *f* = 1.58.

Normalized ground-state absorption and luminescence spectra of **IDPA-AuBr** and **IBTF-AuBr** in toluene solution appear in Figure 2. The ground-state absorption spectra of **IDPA-AuBr** and **IBTF-AuBr** in units of molar absorptivity versus wavelength appear in Figure S1. The new complexes are ultraviolet chromophores. Absorption of **IDPA-AuBr** sets in at 400 nm and peaks at 367 nm. The **IDPA-AuBr** absorption spectrum is similar in band shape and energy to 9,9-diethyl-2-diphenylaminofluorene,[39,40] indicating that the absorption transition is an IDPA-localized π-π* transition. Absorption of **IBTF-AuBr** begins near 375 nm, maximizes at 346 nm, and displays vibronic structure. The absorption spectrum of **IBTF-AuBr** is also similar in band shape and energy to that of 2-(9,9-diethyl-9H-fluoren-2-yl)-benzothiazole.[41,42] Both gold complexes are dual luminescent in deoxygenated toluene. Fluorescence of **IDPA-AuBr** peaks at 398 nm with a shoulder near 420 nm. The fluorescence is broad and featureless, indicating charge-transfer character in the singlet excited-state of **IDPA-AuBr**. Phosphorescence of **IDPA-AuBr** extends from 475–600 nm with a peak at 497 nm. The phosphorescence displays vibronic structure, indicating metal-perturbed π-π* character in the triplet excited state of **IDPA-AuBr**. Fluorescence of **IBTF-AuBr** maximizes at 395 nm with sharply resolved vibronic structure, suggesting π-π* character in the singlet excited-state of **IBTF-AuBr**. Phosphorescence of **IBTF-AuBr** extends from 500–600 nm with a maximum at 531 nm. The phosphorescence of **IBTF-AuBr** is also vibronically structured, indicative of metal-perturbed π-π* character in the triplet excited-state of **IBTF-AuBr**.

Table 1. Photophysical properties of **IDPA-AuBr** and **IBTF-AuBr** collected in toluene solution at 298 K.

Experimental Results	**IDPA-AuBr**	**IBTF-AuBr**
λ_{ABS}/nm (10^4 $M^{-1}cm^{-1}$)	367 (8.7)	330, 346 (4.8), 364
λ_{FL}/nm	398	374, 395, 415
$E_S{}^A$ /eV	3.12	3.32
$\lambda_{PHOS}{}^B$ /nm	497, 537	531, 576
$E_T{}^A$ /eV	2.49	2.33
ΔE_{ST} /eV	0.63	0.99
$\Phi_F{}^C$	0.15 ± 0.02	0.17 ± 0.01
$\Phi_{ISC}{}^D$	0.53 ± 0.03	0.56 ± 0.04

τ_F /ns	1.19 ± 0.04	0.77 ± 0.13
$k_{r,F}$ /s^{-1}	1.26×10^8	2.21×10^8
$k_{nr,F}$ /s^{-1}	2.69×10^8	3.51×10^8
k_{ISC} /s^{-1}	4.45×10^8	7.27×10^8
$\Phi_P^{B,E}$	0.01	0.004
τ_P^B /µs	320 ± 20	1010 ± 40
$k_{r,P}$ /s^{-1}	31	4
$k_{nr,P}$ /s^{-1}	3,094	986

[A] Estimated from the maximum of the emission band due to low phosphorescence signals.
[B] Measured in deoxygenated toluene. Oxygen was removed using three freeze-pump-thaw degas cycles.
[C] Absolute fluorescence quantum yield measured using an integrating sphere.
[D] Intersystem crossing quantum yields were determined using photosensitized singlet oxygen phosphorescence measurements with phenazine as the reference. See SI for methods.
[E] Relative phosphorescence quantum yields were calculated based on fluorescence quantum yields.[25]

The dual luminescent character of the chromophores enables the calculation of the singlet-triplet energy gap (ΔE_{ST})**.** The ΔE_{ST} of **IBTF-AuBr** (0.99 eV) is significantly larger than the ΔE_{ST} of **IDPA-AuBr** (0.63 eV). These values of ΔE_{ST} follow the same trend as those determined for complexes with direct Au(I) σ-attachment to the fluorenyl carbocycle in 9,9-diethyl-2-diphenylaminofluorene (Au-DPA) or 2-(9,9-diethyl-9H-fluoren-2-yl)-benzothiazole (Au-BTF), where the ΔE_{ST} of Au-DPA was found to be 0.77 eV[40] and the ΔE_{ST} of Au-BTF was found to be 0.90 eV.[43] The introduction of the N-heterocyclic carbene moiety decreases the ΔE_{ST} in **IDPA-AuBr** (0.66 eV) relative to Au-DPA (0.77 eV)[40] and increases the ΔE_{ST} in **IBTF-AuBr** (0.99 eV) relative to Au-BTF (0.90 eV).[43]

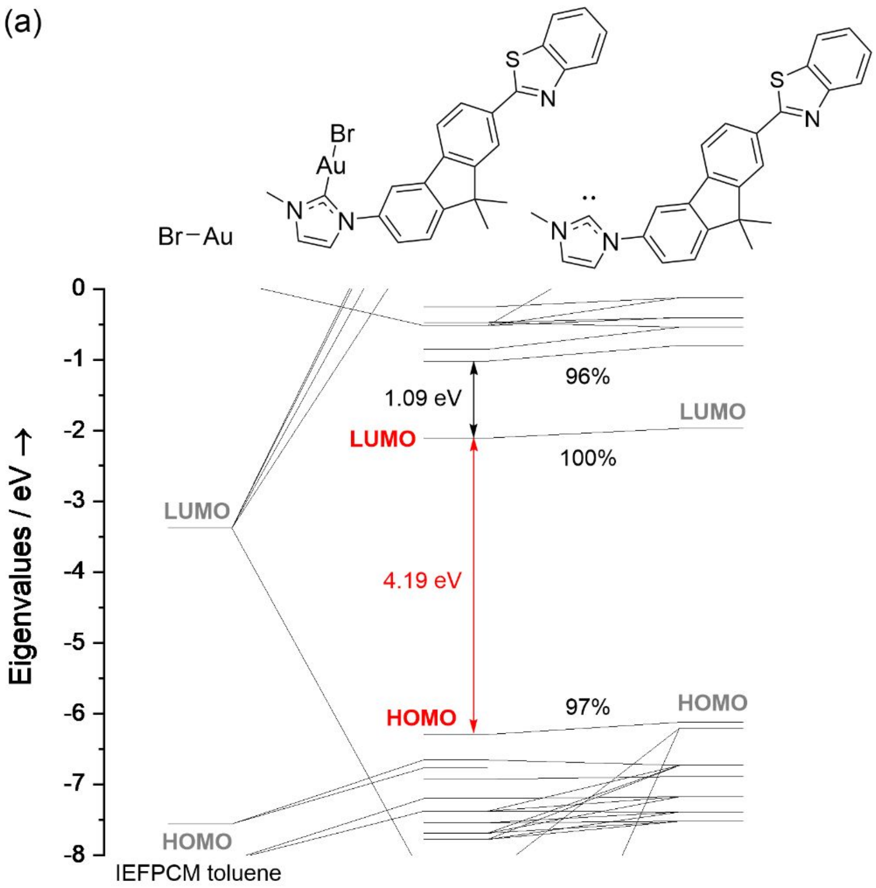
Fluorescence quantum yield, phosphorescence quantum yield, singlet oxygen phosphorescence quantum yield, fluorescence lifetime, and phosphorescence lifetime data collected in toluene are depicted in Figures S2-S6. Table 1 summarizes fluorescence (Φ_F), phosphorescence (Φ_P), and intersystem crossing (Φ_{ISC}) quantum yields, fluorescence (τ_F) and phosphorescence (τ_P) lifetimes, and rate constants of radiative and non-radiative decay from the singlet excited state ($k_{r,F}$ and $k_{nr,F}$, respectively), radiative and non-radiative decay from the triplet excited state ($k_{r,P}$ and $k_{nr,P}$, respectively), and of intersystem crossing (k_{ISC}) of the chromophores in toluene solution. Φ_F values of both chromophores are similar. The Φ_F of **IDPA-AuBr** was determined to be 0.15 ± 0.02 and the Φ_F of **IBTF-AuBr** was determined to be 0.17 ± 0.01.

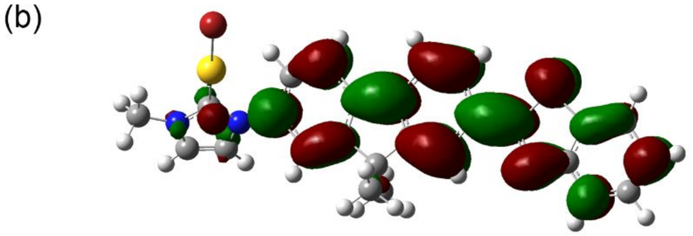
Φ_{ISC} values of both chromophores are also similar: 0.53 ± 0.03 for **IDPA-AuBr** and 0.56 ± 0.04 for **IBTF-AuBr**. The fluorescence lifetimes τ_F of the chromophores were found to be quantitatively different. The τ_F of **IDPA-AuBr** (1.19 ± 0.04 ns) is longer than the τ_F of **IBTF-AuBr** (0.77 ± 0.13 ns). The collection of Φ_F, Φ_{ISC}, and τ_F allowed the calculation of $k_{r,F}$, $k_{nr,F}$, and k_{ISC} for both chromophores. The singlet excited-state dynamics in **IDPA-AuBr** and **IBTF-AuBr** are similar. Singlet excited-state decay occurs predominately through intersystem crossing as Φ_{ISC} is greater than 0.50 for both complexes. Non-radiative decay is the second largest contributor to singlet excited-state decay as the Φ_F of both chromophores are only on the order of 0.15. The magnitudes of $k_{r,F}$ (1.26×10^8 s^{-1}), $k_{nr,F}$ (2.69×10^8 s^{-1}), and k_{ISC} (4.45×10^8 s^{-1}) are smaller for **IDPA-AuBr** than the magnitudes of $k_{r,F}$ (2.21×10^8 s^{-1}), $k_{nr,F}$ (3.51×10^8 s^{-1}), and k_{ISC} (7.27×10^8 s^{-1}) for **IBTF-AuBr**, giving rise to the longer fluorescence lifetime of **IDPA-AuBr** relative to **IBTF-AuBr**. The inclusion of the *N*-heterocyclic carbene linkage influences the singlet excited-state dynamics in **IDPA-AuBr** and **IBTF-AuBr** relative to direct Au(I) σ-attachment in Au-DPA[40] and Au-BTF[42]**.** For example, τ_F is an order of magnitude longer in **IDPA-AuBr** relative to Au-DPA, due to slower rates of radiative decay, non-radiative decay, and intersystem crossing in **IDPA-AuBr**; τ_F is approximately three times longer in **IBTF-AuBr** relative to Au-BTF. Likewise, the magnitudes of the radiative, non-radiative, and intersystem crossing rate constants are smaller in **IBTF-AuBr**. The inclusion of the *N*-heterocyclic carbene linkage also alters the phosphorescent properties in **IDPA-AuBr** and **IBTF-AuBr** relative to the Au-DPA[40] and Au-BTF[42] complexes. The Φ_P of **IDPA-AuBr** (0.01) and **IBTF-AuBr** (0.004) are both an order of magnitude smaller than the Φ_P of Au-DPA (0.21) and Au-BTF (0.11), while the τ_P of **IDPA-AuBr** (320 ± 20 μs) and **IBTF-AuBr** (1010 ± 40 μs) are similar to the τ_P of Au-DPA (405 ± 23 μs) and Au-BTF (872 ± 59 μs). The determination of Φ_P and τ_P also allow for the calculation of the rate constant for radiative decay from the triplet excited-state. The value of $k_{r,P}$ for **IDPA-AuBr** is 31 s^{-1} and the value of $k_{r,P}$ for **IBTF-AuBr** is 4 s^{-1}. Both values are more than an order of magnitude slower than the values of $k_{r,P}$ determined for Au-DPA[40] (353 s^{-1}) and Au-BTF[42] (98 s^{-1}). A significant question amongst the authors during the course of this research was whether or not the inclusion of the NHC-linkage would prohibit phosphorescence from the fluorenyl benzothiazole or fluorenyl diphenyl amine units. The two most important considerations for phosphorescence in these materials are the magnitudes of k_{ISC} and $k_{r,P.}$ The inclusion of the NHC-linkage results in lowered values of both k_{ISC} and $k_{r,P}$ relative to the analogs with direct Au(I) attachment to the fluorenyl carbocycle.[40,42] This results in diminished phosphorescence in the NHC analogs but does not exclude phosphorescence. This group of authors has seen similar behavior when Au(I) is linked to fluorenyl benzothiazole[44] or fluorenyl diphenyl amine[40] units through a triazolyl linkage; the magnitude of k_{ISC} and $k_{r,P}$ are diminished relative to the analogs with direct Au(I) attachment and the triazolyl bridged compounds remain phosphorescent. We believe this design strategy where a gold is embedded as a heavy atom through a strongly σ-donating and moderately π-accepting NHC moiety provides a foundation for achieving NHC complexes with phosphorescence. Future work will focus on the influence of structural changes to the chromophoric NHC ligand and the coordinated metal atom on the magnitudes of k_{ISC} and $k_{r,P.}$ A more thorough understanding of how molecular structure effects the excited state dynamics in organometallic complexes containing chromophoric NHC ligands will allow the design of complexes with tunable dual luminescent properties.

Static and time-dependent density-functional theory (DFT) calculations were performed on **IDPA-AuBr′** and **IBTF-AuBr′**, which are truncated models of **IDPA-AuBr** and **IBTF-AuBr**, respectively, where *N*-benzyl and fluorenyl ethyl groups are replaced with methyls for computational tractability. Calculations employ continuum toluene solvation. Geometries were optimized without restraint, and harmonic vibrational frequency calculations found the converged structures to be potential energy minima. Optimized Au–Br bond lengths are 2.4228 Å (**IDPA-AuBr′**) and 2.4218 Å (**IBTF-AuBr′**), consistent with crystallography data and further suggesting that the amine-functionalized ligand is the stronger *trans*-influencer by a small margin. Mayer bond orders[45,46] between gold and bromide echo this result, with Au–Br bond orders of 0.858 (**IDPA-AuBr′**) and 0.861 (**IBTF-AuBr′**); the stronger *trans* influence of the amine-bearing ligand leads to the longer, and presumably weaker, Au–Br linkage.

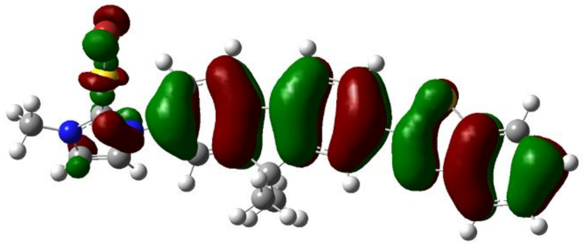
Bond dissociation enthalpies of the Au–C and Au–Br linkages were calculated for **IDPA-AuBr′** and **IBTF-AuBr′**. Results appear in Table S3, Supporting Information. **IDPA** forms a stronger C–Au bond than **IBTF**, by 0.66 kcal mol^{-1}. Correspondingly, **IDPA-AuBr′** shows a lesser heterolytic Au–Br bond dissociation energy than **IBTF-AuBr′**, by 2.23 kcal mol^{-1}. Homolytic Au–Br bond dissociation energies of the two compounds are virtually equal. These calculations accord with the stronger *trans*-influence of **IDPA-AuBr** found crystallographically and indicated in the optimized geometry of model compound **IDPA-AuBr′**.

Figure 3 depicts a partial Kohn-Sham orbital energy level diagram of **IBTF-AuBr′** along with depictions of frontier orbitals. The highest occupied Kohn-Sham orbital (HOMO) and the lowest unoccupied Kohn-Sham orbital (LUMO) are tightly localized on the NHC. The majority (60%) of electron density in the HOMO resides on the fluorenyl carbocycle, and a similar proportion recurs in the LUMO. The benzothiazolyl heterocycle accounts for 34% of density in the HOMO and 38% in the LUMO. In neither orbital does gold contribute more than 2% of density. An orbital energy level diagram of **IDPA-AuBr′** appears as Figure S11, Supporting Information. Frontier orbitals are localized on the carbene ligand. Majority density of the HOMO resides on the amine; this arrangement is consistent with the electron-releasing character of amine nitrogen.[47,48] The LUMO has greater involvement of the fluorenyl and gold. This finding concurs with the experimental observation of unstructured absorption and fluorescence in **IDPA-AuBr**, which suggests charge-transfer character of the lowest singlet excited state. Calculated HOMO-LUMO gaps in both complexes are sizable and reflect the ligand-centeredness of the frontier orbitals.





LUMO: 3% carbene, 59% fluorenyl, 38% benzothiazolyl



HOMO: 2% Au, 5% Br, 3% carbene, 60% fluorenyl, 34% benzothiazolyl

Figure 3. (a) Partial Kohn-Sham orbital energy level diagram of **IBTF-AuBr’** in continuum toluene. Percentages are of electron density. (b) Plots of selected orbitals. Contour level 0.02 a.u.

Figure 4 reproduces density-of-states (DOS) plots of both complexes. For **IBTF-AuBr′**, occupied orbitals are dominated jointly by the fluorenyl and benzothiazolyl substituents. Bromine-centered states lie lower in energy, at *ca.* –6.75 eV. Occupied orbitals on gold lie lower still. Low-lying virtual orbitals have strong contributions from benzothiazolyl and fluorenyl. Orbitals centered on gold occur at much higher energies, setting in near –1 eV. There is little density on bromine in any vacant orbital up to 0 eV. For amine-substituted **IDPA-AuBr′**, high-energy occupied orbitals lie primarily on the diphenylamine and fluorenyl moieties. Density on gold and bromine is only prominent below –6 eV. The low-energy unoccupied orbitals consist mainly of fluorenyl π-density. Contributions from diphenylamine, imidazolyl, and gold appear at progressively higher energies. Taken together, the DOS plots suggest that the lowest excited states of both gold(I) chromophores center on the substituted fluorenyl, with gold and bromine acting as spectators. Specifically, the d^{10} electron count of gold(I) forecloses the possibility of ligand-field quenching or low-energy metal-to-ligand or ligand-to-metal charge transfer states.

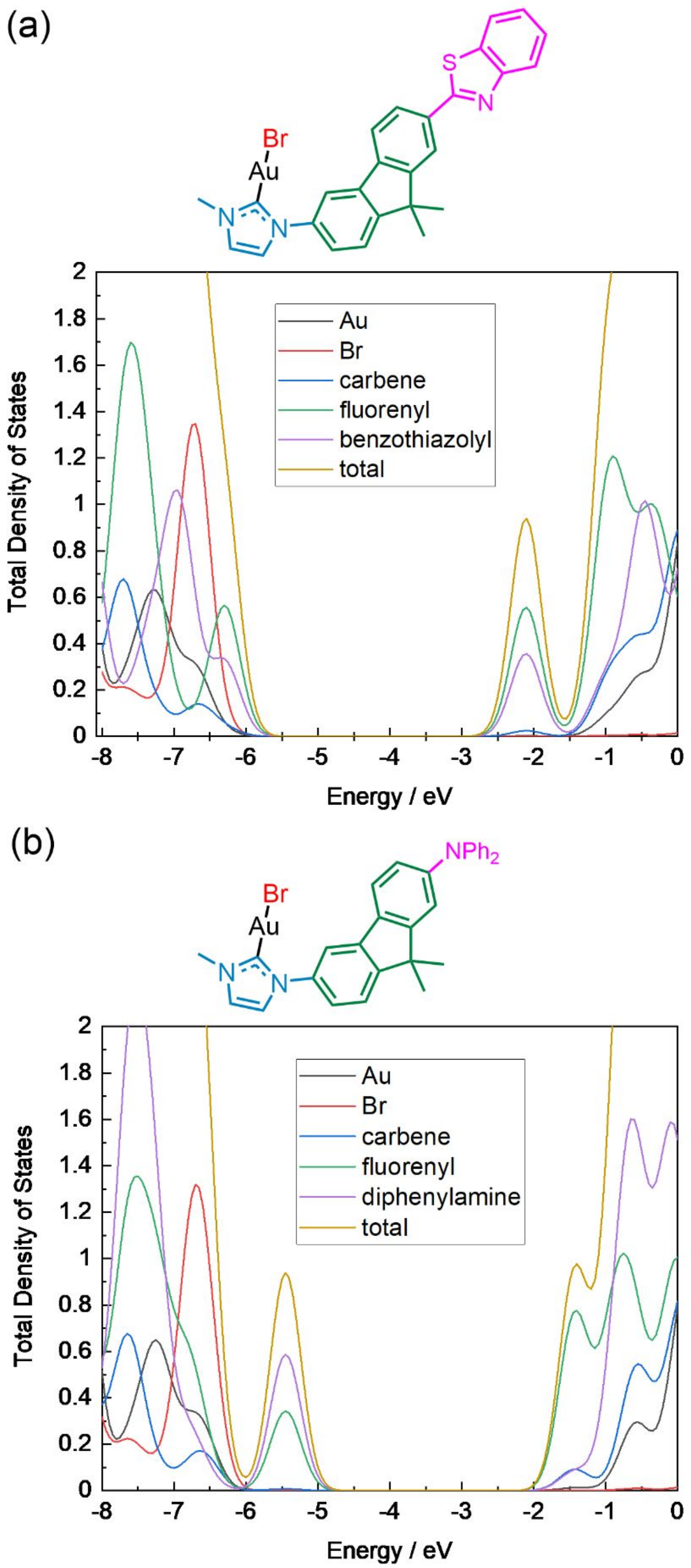


Figure 4. Total density-of-states plots of (a) **IBTF-AuBr**, and (b) **IDPA-AuBr**.

Time-dependent DFT (TDDFT) calculations were performed to discern the character of the lowest-lying excited states. Calculated Franck-Condon S_1 states are clear LUMO←HOMO one-particle transitions (>96%) for **IDPA-AuBr′** and **IBTF-AuBr′**. Calculated T_1 states are more complex. Multiple single-particle transitions undergo configuration interaction, with the LUMO←HOMO transition dominating (>72%). Natural transition orbitals (NTOs)[49,50] were calculated for the Franck-Condon T_1 state. Results are diagrammed in Figure 5. For both complexes, the Franck-Condon T_1 state is delocalized across the fluorenyl and its substituent, with little involvement of bromine or gold.

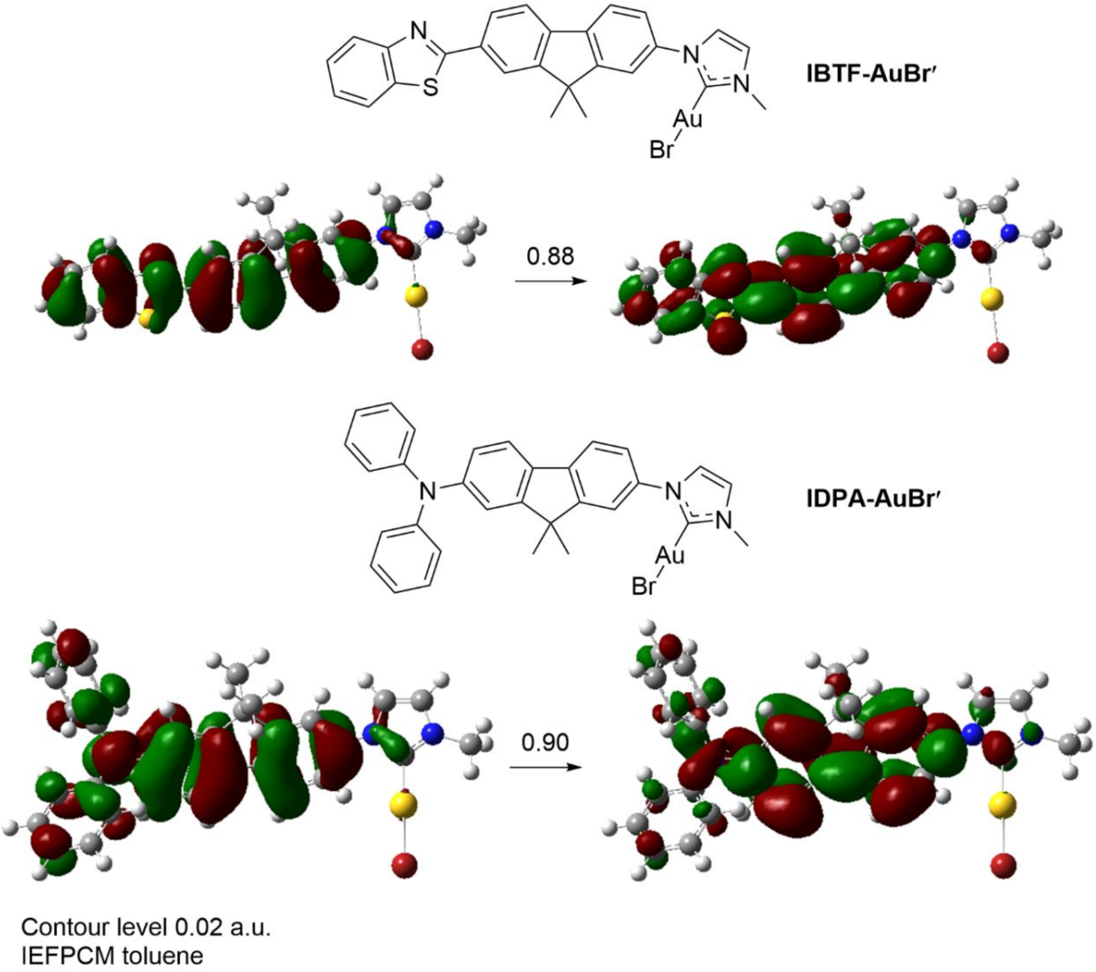


Figure 5. Natural transition orbitals, including weighting factors, for Franck-Condon T_1 states of **IBTF-AuBr′** and **IDPA-AuBr′** in continuum (IEFPCM) toluene. Contour levels 0.02 a.u.

Conclusions. Two new chromophoric N-heterocyclic carbene ligands have been devised based on 2,7-disubstitued fluorenyls bearing electron-withdrawing benzothiazolyl (**IBTF**) or electron-releasing diphenylamino (**IDPA**) moieties, along with synthesis, structural authentication, and optical characterization of their (bromo)gold(I) complexes. Gold(I) binds to the carbene center with linear stereochemistry; packing diagrams show an absence of aurophilic contacts in the crystalline state. The new gold complexes absorb light at wavelengths below 400 nm in π-π* (**IBTF-AuBr**) or metal-perturbed intraligand charge transfer (**IDPA-AuBr**) transitions. TDDFT calculations indicate substantial participation of the fluorenyl carbocycle in Franck-Condon S1 states of both complexes.

The new gold species are dual fluorescence/phosphorescence emitters in rigorously deoxygenated toluene at 298 K. The fluorescence profile of benzothiazolyl derivative **IBTF-AuBr** shows vibronic structure, whereas that of amine analogue **IDPA-AuBr** is unstructured. The occurrence of structured emission indicates π-π* fluorescence from **IBTF-AuBr**, while unstructured emission indicates charge-transfer fluorescence in **IDPA-AuBr**. Hence, the first singlet excited state is alterable by remote substitution of the carbene ligand. The phosphorescence of both complexes is vibronically structured, indicative of metal-perturbed π-π* character in the triplet excited-state of **IBTF-AuBr** and **IDPA-AuBr**. The room-temperature phosphorescence lifetimes of both complexes are longer than 100 μs with the phosphorescence lifetime of **IDPA-AuBr** near 300 μs and the phosphorescence lifetime of **IBTF-AuBr** near 1 ms. Intersystem crossing is the primary decay mode of the singlet excited state for both complexes, with quantum yields of ISC near 50%. Density-functional theory calculations find delocalized frontier orbitals with substantial density on fluorenyl, and relatively little on either gold or bromine. TDDFT calculations indicate that the lowest-energy Franck-Condon singlet excited state arises from a LUMO←HOMO one-particle transition, whereas the lowest triplet consists of multiple one-particle transitions, mostly ligand based, engaging in configuration interaction. The presence of the NHC diminishes the values of k_{ISC} and $k_{r,P}$ relative to complexes with direct Au(I) coordination to the fluorenyl carbocycle.[40,42] This leads to reduced phosphorescence in the NHC complexes but does not exclude phosphorescence. A similar observation has been made in Au(I) complexes where the Au atom is linked to fluorenyl benzothiazole[44] or fluorenyl diphenyl amine[40] units by way of a triazolyl linkage We believe embedding gold as a heavy atom through a strongly σ-donating and moderately π-accepting NHC provides a foundation for enabling phosphorescence in chromophoric NHC ligands. The influence of structural changes to the chromophoric NHC ligand and the coordinated metal atom on the excited state dynamics in organometallic complexes containing chromophoric NHC ligands will allow the design of complexes with tunable dual luminescent properties.

Supporting Information Available: Photochemical characterization including instrumentation, methodology, fluorescence quantum yield data, phosphorescence quantum yield data, singlet oxygen phosphorescence quantum yield data, fluorescence lifetime data, and phosphorescence lifetime data. Material characterization including synthetic details, ^{1}H and ^{13}C NMR spectra, mass spectrometry, and geometry-optimized structures (.xyz). Complete crystallographic data, in CIF format, have been deposited with the Cambridge Crystallographic Data Centre. CCDC 2208456 and 2208457 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Conflict of Interest: Case Western Reserve University has filed for provisional patent protection for the new ligands and complexes.

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