

Nonlinear Optical Properties of Molecular Gold Complexes

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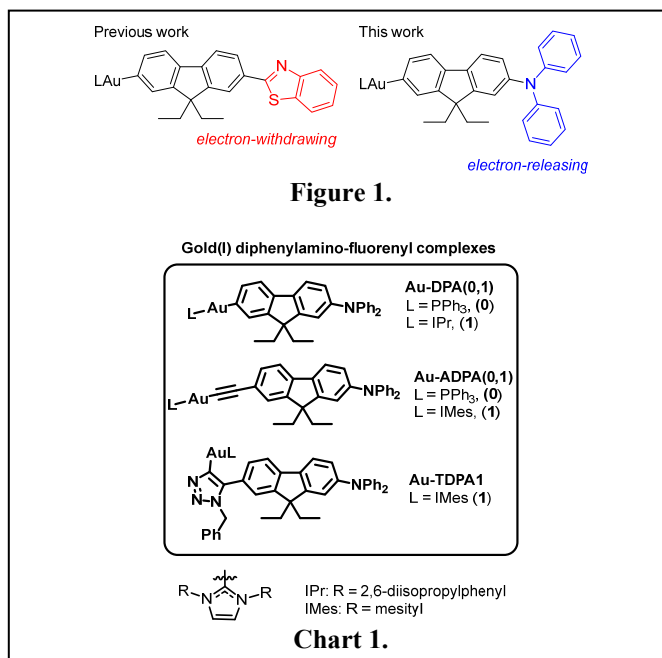
Abstract—Recent advances in the structure, optical spectroscopy, and excited-state dynamics of amine-substituted gold(I) fluorenyls are described. Excited-state kinetic parameters are sensitive to the mode of attachment of gold(I) to fluorenyl (direct attachment, or through alkynyl or triazolyl spacers) and to the ancillary phosphine or carbene ligand on gold. Density-functional theory calculations indicate that the frontier orbitals are dominated by the fluorenyl carbocycle and amine substituent.

Keywords—gold, nonlinear optics, ultrafast spectroscopy, charge transfer, density-functional theory

I. INTRODUCTION (HEADING I)

Nonlinear optical (NLO) materials support a range of applications, including laser beam compression, spatial light modulation, laser mode locking, optical switching, bioimaging, and human photodynamic therapy. Crystalline solids, complex mixtures,[1] and discrete molecules can act as nonlinear light absorbers. *Molecular* NLO chromophores offer advantages: they can be embedded in transparent matrices, such as glass or polymeric media, with optical properties intact. The full armamentarium of organic synthesis can be applied to improve solubility, crystallinity, or manufacturability. Recent work in our laboratories has investigated molecular organogold chromophores for their fundamental excited-state dynamics. Structure-function correlations are sought for the rational design of these third-order NLO materials. Recent progress is summarized.

Our earlier research[2]–[6] emphasized organogold(I) complexes where gold(I) attaches to a fluorenyl carbocycle through direct Au–sp² C σ -bonds or through alkynyl or triazolyl linkers, Figure 1. Benzothiazolyl acts as an electron-



withdrawing substituent. The juncture of the six-membered terminal ring of fluorenyl with the five-membered heterocycle allows coplanarity between rings. Cross-molecule charge transfer is enhanced.

In this work, the diphenylamine moiety is attached to fluorenyl at the site opposite gold. This amine moiety is electron-releasing. Our guiding hypothesis is that amine-for-benzothiazolyl substitution promotes charge transfer toward

gold, leading to solvatochromism and excited-state behavior that is solvent-sensitive. We further conjecture that metalation through an alkynyl spacer affords absorption (ground- and excited-state) and emission profiles that are red-shifted from those of σ -aryls, because of the longer π -conjugation pathway of the carbanionic ligand.

II. RESULTS AND DISCUSSION

A. Synthesis of Complexes.

Complexes were prepared as in ref [6]. New compounds were purified by recrystallization and characterized by nuclear magnetic resonance spectroscopy and combustion analysis. Chart 1 enumerates compounds.

B. Optical Spectra.

Alkynyl and triazolyl complexes have similar ground-state absorption spectra that have two distinct transitions near 370 and 310 nm. Absorption profiles of the alkynyl and triazolyl complexes closely parallel those of the free alkyne, indicating absorption from π - π^* transitions. Absorption spectra of aryl complexes **AuDPA0–1** show absorption spectra blue-shifted from those of alkynyl and triazolyl counterparts; carbene ligation again exerts a red-shifting effect. Metal-aryl absorption spectra are similar to those of the free fluorenyl ligand, indicating π - π^* transitions.

Excitation from 345–355 nm in deoxygenated toluene solution elicits broad, structured emission. Figure 2 reproduces normalized steady-state luminescence spectra and 1931 C.I.E. color coordinates. Complexes show dual emission of fluorescence and phosphorescence in rigorously degassed toluene. Vibronic structure in both fluorescence and phosphorescence profiles suggest that emissions arise from ligand-centered π - π^* states. Fluorescence quantum yields range

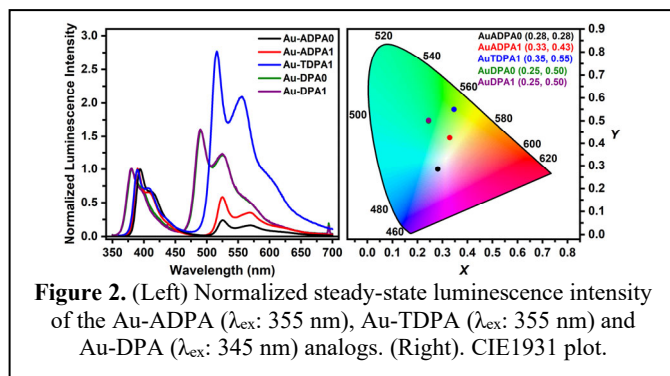


Figure 2. (Left) Normalized steady-state luminescence intensity of the Au-ADPA (λ_{ex} : 355 nm), Au-TDPA (λ_{ex} : 355 nm) and Au-DPA (λ_{ex} : 345 nm) analogs. (Right) CIE1931 plot.

from < 0.01 (**Au-TDPA1**) to 0.20 ± 0.02 (**Au-ADPA0**). For all compounds, fluorescence lifetimes are less than 200 ps. Quantum yields of phosphorescence range from < 0.05 (**Au-TDPA1**) to 0.21 (**Au-DPA1**). Phosphorescence lifetimes of all complexes exceed 500 μ s at 298 K.

C. Density-functional theory calculations.

Density-functional theory calculations find frontier orbitals localized on the carbanionic ligand, and the observation of vibronically structured optical spectra serve to validate this

conclusion. The calculations indicate amine orbital density on the highest-occupied Kohn-Sham orbital (HOMO) that attenuates in the lowest unoccupied Kohn-Sham orbital (LUMO). This result is consistent with carbanionic ligands that support charge-transfer excited states.

III. CONCLUSION.

A single gold atom suffices to populate triplet excited states in these substituted fluorenyl-diphenyl amine chromophores. Both singlet and triplet excited states derive from ligand-based transitions; gold acts as a non-chromophoric spectator that promotes intersystem crossing through the heavy-atom effect.

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