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Luminescent, Three-Coordinate Azadipyrromethene Complexes of d^{10} Copper, Silver, and Gold

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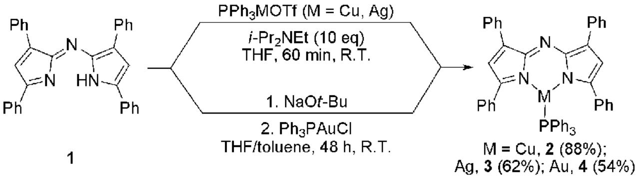
Boron azadipyrromethenes are red-light-absorbing dyes with chromophoric capabilities deriving from a conjugated, chelating framework. Reported here are tricoordinate copper(I), silver(I), and gold(I) complexes of a tetraphenylazadipyrromethene ligand. The new complexes are characterized by optical absorption and emission spectroscopy, multinuclear NMR, mass spectrometry, elemental analysis, and X-ray diffraction crystallography. Time-dependent density functional theory calculations indicate that the principal absorption features in azadipyrromethene complexes result from optically allowed intraligand transitions that undergo configuration interaction.

Boron azadipyrromethenes are long known,[1] but their optical properties have only lately provoked study.[2] These chromophores absorb visible light intensely, with absorption maximizing between 640 and 680 nm. Quantum yields of the ensuing fluorescence range from 0.23 to 0.36. These values increase upon rigidification of the chromophoric skeleton.[3] Their photoresponsivity toward red light commends azadipyrromethenes for applications in vivo, including drug discovery, assays, sensing, tumor imaging, and photodynamic therapy.[4,5] Tetraarylazadipyrromethene chelates of BF_2^+ exhibit triplet excited-state properties upon bromination at carbon. Oxygen sensitization was observed, as was in vitro photokilling of human cervical carcinoma (HeLa) cells.[2] Recently, mercury(II) ion sensing was demonstrated with a BF_2−azadipyrromethene flanked with *o*-pyridyl donors.[6]

Scheme 1. Syntheses of **2**−**4**[a]



[a] Isolated yields are in parentheses.

The optical properties of boron azadipyrromethenes derive from the delocalized π network; the bound BF_2^+ moiety is saturated and not itself photoactive. The full potential of azadipyrromethenes as chelating ligands is unrealized. Presented here are synthetic, structural, and preliminary optical studies of $(Ph_3P)M^I$ complexes (M = Cu, Ag, Au) of a tetraphenyl-substituted azadipyrromethene. All metal centers are three-coordinate in the solid state, and the gold complex is an unusual example of trigonally coordinated gold(I).[7,8] The complexes substantially retain the absorption characteristics of the free ligand and its BF_2^+ chelate.

Reaction of (triphenylphosphine)copper(I) triflate [prepared in situ from $(CuOTf)_2$·toluene] or (triphenylphosphine)silver(I) triflate[9] with 3,5-diphenyl-1*H*-pyrrol-2-yl-3,5-diphenylpyrrol-2-ylideneamine (tetraphenylazadipyrromethene, **1**)[2b] in the presence of diisopropylethylamine in tetrahydrofuran (THF) affords the corresponding $(Ph_3P)M^I$ azadipyrromethene complexes in good yields (Scheme 1). Attempted generation of a (phosphine)gold(I) azadipyrromethene com-

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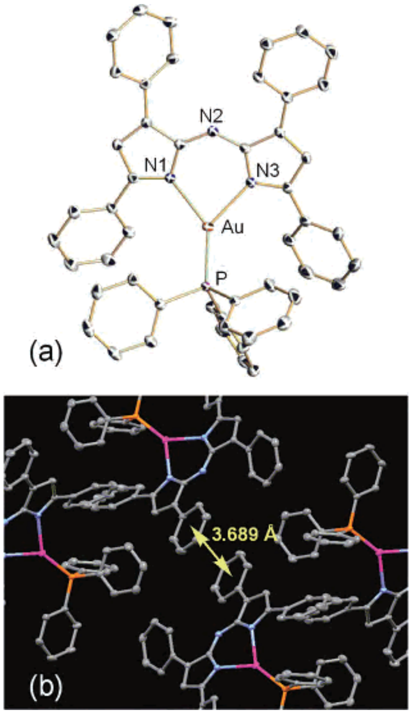

Figure 1. (a) Thermal ellipsoid projection of **4**. (b) Packing diagram of **4** along *b*. An intermolecular π-stacking interaction between distal phenyl groups of neighboring molecules is indicated. Data were collected at 100 ± 2 K; ellipsoids are shown at 50% probability. Hydrogen atoms are omitted for clarity.

plex by dehalogenation of (phosphine)gold(I) halides gave no evidence of binding. However, the reaction of sodium *tert*-butoxide with azadipyrromethene **1** and (triphenylphosphine)gold(I) chloride in a 1:10 (v:v) THF/toluene mixture yields gold(I) azadipyrromethene **4**. ^{1}H NMR measurements in $CDCl_3$ show that azadipyrromethene resonances are largely insensitive to metal-ion complexation. The most conspicuous change is a 0.3-ppm upfield shift of the ortho and meta protons of the proximal azadipyrromethene phenyl substituents (i.e., the phenyl groups deriving from acetophenone).[2a,b] $^{31}P\{^1H\}$ NMR exhibits singlet resonances at δ 3.8 (**2**), 14.4 (**3**), and 30.7 (**4**) ppm. All three products are deep blue in solution; in the solid state, they appear violet, black, or (for **4**) gold.

Vapor diffusion of pentane into concentrated THF solutions affords diffraction-quality platelike crystals.[10] Figure 1a depicts a thermal ellipsoid plot of gold complex **4**. Structures of **2** and **3** appear as Supporting Information. Trigonal-planar coordination of gold is evident. Au−N bond lengths are 2.2349(12) and 2.2448(12) Å. The near-C_{2v} microsymmetry of gold in **4** contrasts with the asymmetric structure of $[(Ph_3P)Au(bpy)](PF_6)$, where Au−N distances are 2.166 and 2.406 Å (estimated standard deviations are said to range from 0.001 to 0.003).[11] At 2.2088(3) Å, the Au−P bond length is unremarkable.[12−14] Structural comparisons with copper(I) and silver(I) bipyridine and phenanthroline complexes suggest that metal−ligand bond metrics in **2** and **3** (Supporting Information) are normal.[15,16] Azadipyrromethene complexes undergo intermolecular π stacking in the crystalline state. For example, symmetry-related molecules of **4** approach within 3.69 Å (Figure 1b).

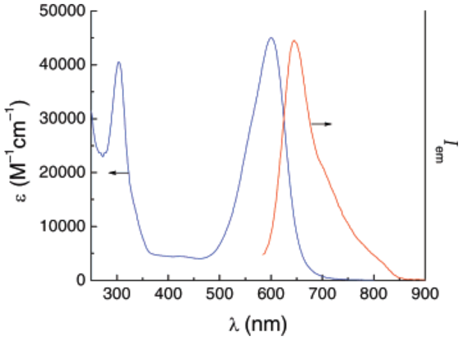

Figure 2. Absorption (blue) and emission (550-nm excitation, red) spectra of gold complex **4** in deoxygenated $CHCl_3$ (298 ± 2 K).

Backbone $C{-}N_{meso}{-}C$ angles in metallaazadipyrromethenes are distended compared to those in difluoroboron complexes. O'Shea and co-workers[2a,b] report crystal structures of two BF_2−azadipyrromethenes. In these, the $C{-}N_{meso}{-}C$ angles are 119.7(3)° and 119.5(3)°. In the group 11 complexes reported here, this angle has widened: the range is 127.46(12)° in the gold complex **4** to 130.1(2)° in one independent molecule of **3**. The azadipyrromethene chromophore is sufficiently flexible that chelation distorts the remote nitrogen from idealized sp^2 hybridization.

Metal ions within structurally characterized azadipyrromethene complexes are trigonal planar, but the coordination plane is canted relative to the plane of the azadipyrromethene complex. Here the canting angle Θ is defined as the angle between the best-fit plane of the ligand (excluding substituted phenyl groups) and the plane of the two chelating nitrogens and metal(I). For **4**, Θ is 29.8°. This is the largest such tilt encountered here; the smallest is 18.3° for one crystallographically independent molecule of **3**. Ligand bite angles, defined as $\angle N{-}M{-}N$, are 94.49(6)° for **2**, 86.30(7)°, 82.89(7)°, and 82.20(6)° for the three independent molecules of **3**, and 81.51(4)° for **4**.

Arguably the leading feature of azadipyrromethenes is their absorption of orange or red light, at wavelengths to which human tissue is partly transparent. Figure 2 depicts

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[10] Crystallographic data for **4**: violet irregular chunk, crystal dimensions $0.44 \times 0.42 \times 0.18$ mm^3, space group $P2_1/n$, $a = 12.3616(2)$ Å, $b = 12.9923(2)$ Å, $c = 23.7047(5)$ Å, $\beta = 90.6780(10)°$, $V = 3806.84(12)$ Å^3, $Z = 4$, $\rho_{calc} = 1.584$ g m^{-3}, μ(Mo Kα) = 3.947 mm^{-1}, data measured on a Bruker AXS SMART APEX II CCD-based diffractometer (Mo Kα, $\lambda = 0.710\,73$ Å) at 100(2) K; structure solved by direct methods, 119 551 reflections collected, 10 670 independent reflections (R(int) = 0.0232), data/restraints/parameters 10 670/0/496, final R indices [$I > 2\sigma(I)$] R1 = 0.0157 and wR2 = 0.0401, R indices (all data) R1 = 0.0180 and wR2 = 0.0413, largest difference peak and hole +1.177 and −0.560 e Å^{-3}. Data for other complexes appear as Supporting Information.

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absorption and emission spectra of the representative complex **4**. Spectra of all complexes appear as Supporting Information. An intense absorption at 597 nm ($\epsilon \sim 30\,000$ M^{-1} cm^{-1}; $CHCl_3$) is characteristic of the free azadipyrromethene. This absorption red shifts slightly (1−19 nm) upon metalation. It also intensifies markedly: for silver complex **3**, the extinction coefficient at λ_{max} more than doubles ($\epsilon = 65\,000$ M^{-1} cm^{-1}; $CHCl_3$). Resolution is improved at 77 K in 2-methyltetrahydrofuran (2-MeTHF) glasses. At low temperature, distinct absorption maxima emerge for **4** at 576 and 617 nm; a third transition appears as a shoulder near 637 nm. Broadly similar observations pertain to copper and silver analogues **2** and **3**.

Compounds **2**−**4** are luminescent in fluid solution at room temperature and at 77 K in 2-MeTHF. Figure 2 reproduces the 298 K emission spectrum of **4** in chloroform; spectra of **1**−**3** are deposited as Supporting Information. The mean Stokes shift for the four compounds is 41 nm, and an approximate mirror-image symmetry relates the emission profile and the absorption features near 600 nm. Room-temperature emission quantum yields (±10%) for the three complexes are 0.0025 (**2**), 0.0039 (**3**), and 0.0024 (**4**); these are comparable to a 0.0014 emission quantum yield of ligand **1**. Structured luminescence appears in 2-MeTHF glass at 77 K (Supporting Information) for **2**−**4**. The average peak-to-peak separations for **2** and **4** are 657 and 651 cm^{-1}, respectively, consistent with vibronic activation of azadipyrromethene skeletal modes.[17] For silver complex **3**, two 77 K emissions are resolved at 642 and 693 nm, with the longer-wavelength emission showing vibronic progression (mean peak-to-peak spacing of 610 cm^{-1}).

Scalar-relativistic density functional theory (DFT) and time-dependent DFT calculations[18] on **3′**, a truncated model of **3**, were undertaken. Here, PH_3 ligands replace PPh_3 for computational tractability; all computations preserve the full tetraphenylazadipyrromethene. The calculations find the highest occupied Kohn−Sham orbital (HOMO) and the lowest unoccupied Kohn−Sham orbital (LUMO) to be centered on the azadipyrromethene and similarly for the HOMO−1 and HOMO−2. These frontier orbitals bear minimal silver character, each being derived from a corresponding a_2 (HOMO and HOMO−2) and b_1 (LUMO and HOMO−1) orbital of the free ligand. Figure 3 depicts a partial Kohn−Sham orbital energy level diagram of the (phosphine)silver(I) adduct of **3′**. Vertical excitation energies were calculated for optimized geometries. Time-dependent DFT calculations on **3′** predict an intense absorption near 591 nm having two constituent excitations. These are the LUMO ← HOMO and LUMO ← HOMO−2 one-electron transitions. In idealized C_{2v} symmetry, both are $b_1 \leftarrow a_2$ excitations, leading to B_2 states that engage in configuration interaction. The transition dipole vector associated with the LUMO ← HOMO transition dominates the lowest-energy vertical excitation. The other one-electron transition, LUMO ← HOMO−2, is the primary component of a second allowed B_2 excitation, calculated at 525 nm, which undergoes configuration interaction with the $^1B_2$ state that is the lowest singlet excited state. For **3′**, an absorption transition calculated at 541 nm also contributes absorption intensity (LUMO ← HOMO−1; $^1A_1$ state). The calculations indicate that optically allowed intraligand transitions govern the electronic spectra of azadipyrromethene chelates. Low-lying singlet excited states undergo configuration interaction with oscillator strengths determined by constitutive transition dipole vectors.

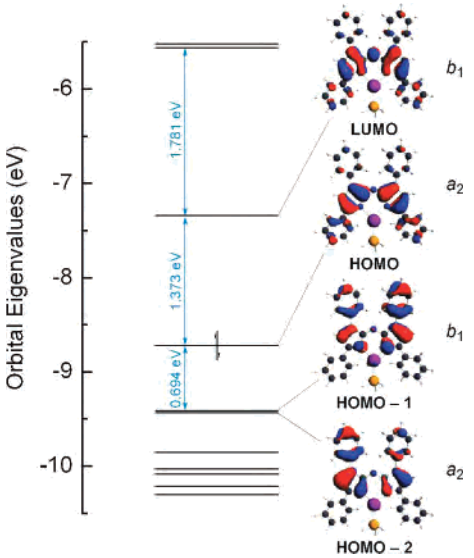

Figure 3. Partial Kohn−Sham orbital energy-level diagram of **3′**, the H_3PAg^I complex of ligand **1**. Plots of selected orbitals are inset (contour level 0.03 au). Irreducible representations of orbitals in idealized C_{2v} symmetry appear at the right.

In conclusion, copper(I), silver(I), and gold(I) complexes of azadipyrromethene ligands have been prepared and structurally characterized. Metal chelates of azadipyrromethenes share the qualitative absorption features of BF_2^+ complexes. The new complexes are weakly luminescent in solution at room temperature. At 77 K, a vibronic structure appears in the emission profile. Time-dependent DFT calculations indicate allowed transitions to $^1B_2$ states (in C_{2v} symmetry) that undergo configuration interaction. Further experiments, including cellular uptake studies, are ongoing.

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Supporting Information Available: Full experimental procedures and crystallographic (CIF) and computational data. This material is available free of charge via the Internet at http://pubs.acs.org.

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