ORGANOMETALLICS

Red-Shifts upon Metal Binding: A Di-Gold(I)-Substituted Bithiophene

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Supporting Information

ABSTRACT: 5,5'-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2'-bithiophene was metalated with (triphenylphosphine)gold(I) at the 5,5'-positions to yield a di-gold(I)-substituted bithiophene. The resulting complex was characterized by X-ray diffraction crystallography, optical spectroscopy, and elemental analysis. The digold bithiophene complex emits green, structured luminescence in chloroform. Its absorption profile is red-shifted from those of 2, 2'-bithiophene or the boronate ester starting material. Density-functional theory (DFT) calculations indicate that the frontier orbitals of the digold complex concentrate on the bithienyl bridge. Time-dependent DFT calculations find that the LUMO-HOMO promotion mostly accounts for the absorption onset in all three compounds and that configuration interaction with vacant orbitals on gold modulates this transition. This interaction contributes to red-shifted absorption profiles of σ -aurated gold(I) organometallics.



INTRODUCTION

Thiophene oligomers draw much study,¹⁻³ chiefly for their photophysical properties. A recent review⁴ surveys these compounds and their uses through 2007. Small oligothiophenes have been used in organic light-emitting diodes,⁵ organic solar cells,⁶ and organic field-effect transistors.^{7,8} Oligothiophenes have also served as spatial light modulators⁹ and electro-optic modulators.¹⁰ Thiophene oligomers are phototoxic to algae, nematodes, insect larvae, and human red blood cells. The phototoxicity results from sensitization of oxygen to form singlet oxygen.^{11,12}

Oxygen sensitization and use in light-emitting diodes exploit the triplet excited states of oligothiophenes. In oligomers of suitable length, visible light excitation leads to triplet-state dynamics. Bimolecular photoreactions can result, as shown by the sensitization of ${}^{3}O_{2}$ to ${}^{1}O_{2}$.

We have embarked on a program to access triplet excited states from aromatic molecules, including heterocycles, using relativistic effects.^{13–19} (Phosphine)- and (N-heterocyclic carbene)gold(I) centers are attached through σ -bonds to the aromatic rims of organic compounds.^{20–22} The heavy-atom character of $gold^{23-26}$ relaxes spin orthogonality between the singlet- and triplet-state manifolds. Intersystem crossing can follow and, with it, the population of triplet states.^{27,28}

RESULTS AND DISCUSSION

In this work, we show that the 2,2'-bithiophene core can be aurated in positions adjacent to sulfur. Metalation proceeds in high yield from a boron-based reagent. The synthesis, crystal structure, and absorption spectrum of a representative digold bithiophene are reported here. Density-functional theory calculations on a model bithiophene are discussed.

Reaction of boronate ester 1 with (triphenylphosphine)gold-(I) chloride and cesium carbonate in 2-propanol gave gold-substituted bithiophene 2 in 69% isolated yield, eq 1. Product formation was monitored by ${}^{31}P{}^{1}H$ NMR. A singlet at δ 43.7 ppm corresponds to bithiophene 2; no other peaks were detected in the ³¹P NMR spectrum. For comparison, the ³¹P NMR spectrum of Ph₃PAuCl shows a singlet at δ 33.7 ppm. This downfield shift upon carbon-gold bond formation is typical for arylation of (phosphine)gold(I) halides.^{13–15,17}



Vapor diffusion of diethyl ether into a chloroform solution of 2 produced yellow, diffraction-quality crystals. A thermal ellipsoid projection appears as Figure 1.²⁹ Complex 2 crystallizes in the monoclinic space group C2/c with Z = 4. The complex resides on a center of inversion, and the thiophene rings are coplanar. The C1-Au1-P1 angle is $174.7(3)^\circ$. The Au1-C1 bond length is 2.023(9) Å, and the Au1-P1 bond length is 2.277(2) Å. These metrics, and those of the bithienyl and phosphine ligands, are unremarkable. $^{13-22,30}$

The absorption spectra of free 2,2'-bithiophene, 1, and 2 in chloroform appear in Figure 2. All three compounds absorb in the near-ultraviolet. Band shapes are roughly the same. The absorption

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Figure 1. Thermal ellipsoid projection (50%, 100 K) of **2**. Selected interatomic distances (Å): Au1–C1: 2.023(9), Au1–P1: 2.277(2), S1–C1: 1.729(9), S1–C4: 1.735(8). Selected interatomic angles (deg): C1–Au1–P1: 174.7(3), C1–S1–C4: 94.1(4).

onset of 2, near 400 nm, is \sim 25 nm red-shifted from that of 1, which in turn is \sim 25 nm red-shifted from the absorption onset of the parent thiophene. Absorption maxima are 304 nm (2,2'-bithiophene), 334 nm (1), and 361 nm (2), respectively. Figure 2 also shows emission spectra of the three compounds. Emission spectra of 2,2'-bithiophene and 1 roughly mirror the absorption profiles; these emissions are unquenched by exposure to air. The emission of 2 is red-shifted and shows vibronic structure not seen for nonaurated compounds. Exposure to oxygen quenches the luminescence of 2.

Density-functional theory calculations were performed on 1 and on model compound 2', with methyl groups in place of phenyls on phosphorus. A calculation was run on the parent bithiophene for comparison. Geometries were optimized, and harmonic frequency calculations confirmed the final structures to be energy minima. Chloroform solvation was modeled with the PCM protocol of Tomasi and co-workers.^{31,32}

Figure 3 depicts a frontier orbital energy-level diagram of 2'. Plots of a few orbitals appear at right. The three highest occupied Kohn–Sham orbitals (HOMOs) are predominantly bithienyl π -functions. On this basis, excitations from the three highest occupied orbitals to the LUMO are predicted to be mainly intraligand, with some thienyl-to-gold charge transfer.

Time-dependent DFT calculations indicate that excitation to the first singlet excited state is optically allowed and that it dominates the absorption spectrum through the near-ultraviolet. This conclusion holds for 1, 2', and the parent bithiophene. For digold complex 2', this first absorption transition consists of several excitations that mingle through configuration interaction. Promotions from the HOMO dominate: LUMO \leftarrow HOMO (78%) and LUMO+4 \leftarrow HOMO (10%). Both components have bithienyl-to-gold ligand-to-metal charge transfer (LMCT) character. A Mulliken population analysis³³ ascribes 13% of the electron density to gold in the LUMO and 47% in the LUMO+4. Figure S1, Supporting Information, plots the LUMO+4 of 2' and the corresponding orbitals on the bare (Me₃PAu)₂²⁺ fragment.

The excited states of the parent bithiophene and 1 are unaffected by gold (neither compound carries gold). TDDFT calculations find that for these compounds the LUMO \leftarrow HOMO promotion dominates the first excited singlet by itself. There is no possibility of configuration interaction with gold-based orbitals. For these unmetalated compounds, absorption blue-shifts compared to that calculated for 2' and seen experimentally for 2. We attribute the red-shifted absorption spectrum of 1 relative to 2,2'-bithiophene to the inductive effect of boron and conjugation of the vacant boron $p\pi$ orbitals with the bithienyl core. Red-shifts brought about by (pinacolato)boron esters are less than those



Figure 2. Absorption and emission spectra of (a) 2,2'-bithiophene, (b) boronate ester 1, and (c) gold complex 2 in chloroform. Spectra were collected at room temperature.

from (triphenylphosphine)gold(I), both experimentally and theoretically.

(Triphenylphosphine)gold(I) has been bound to the 2,2'bithienyl backbone to yield a complex that is centrosymmetric in the solid state. This complex is luminescent at room temperature, $\lambda_{em} = 488$ nm, upon excitation at 422 nm in CHCl₃. The absorption spectra of the digold complex, its pinacol boronate precursors, and the unsubstituted bithiophene are similar. Absorption spectra red-shift upon boron substitution, and more so upon auration. TDDFT calculations find that the LUMO⁺-HOMO transition dominates the absorption spectra up to the solvent cutoff.



Figure 3. Partial Kohn–Sham orbital energy level diagram of model complex 2'. Chloroform solvation is included with the polarizable continuum model (PCM). Isodensity plots (contour level 0.03 au) of selected orbitals appear at right.

With gold substitution, this LUMO \leftarrow HOMO promotion engages in configuration interaction with at least one other state. For model 2', a transition to the gold-heavy LUMO+4 adds LMCT character. We propose that this configuration interaction stabilizes the first singlet excited state of 2 and lowers the first absorption energy.

These results add nuance to the effects of metalation on optical spectra. We and others^{13–18,21,22,34} have shown that substitution with gold(I) red-shifts the absorption spectra of aromatic molecules. These compounds gain triplet-state emission through the heavy-atom effect. Gold also introduces empty 6s and 6p orbitals that can accept electron density from aryl ligands. Configuration interaction between the first excited singlet and states involving these metal-based orbitals can contribute to red-shifted absorptions, without making the carbon—gold bonds themselves chromophoric. A similar red-shifting appears in the platinum(II) σ -pyrenyls of Yip and co-workers,²² suggesting that the effect is not specific to gold(I).

EXPERIMENTAL SECTION

5,5'-Bis[(triphenylphosphine)gold(I)]-2,2'-bithiophene. (Triphenylphosphine)gold(I) chloride was prepared using reported methods.³⁵ To a 50- mL round-bottom flask were added (PPh₃)AuCl (257 mg, 0.52 mmol), 2,2'-bithiophene-5,5'-diboronic acid bis(pinacol) ester (110 mg, 0.26 mmol), and Cs₂CO₃ (345 mg, 1.06 mmol) under an argon atmosphere. The reactants were suspended in 15 mL of dry, degassed 2-propanol, and the resulting yellow mixture was stirred under argon at 40 °C for 24 h. 2-Propanol was removed by rotary evaporation. The remaining pale yellow residue was extracted into dry dichloromethane and filtered twice through Celite pads to yield a golden solution. Dichloromethane was removed by rotary evaporation. Pentane was used to triturate the resultant residue, and a yellow solid was collected by filtration. Yield: 389 mg (69%). ³¹P{¹H} NMR (CDCl₃): δ 43.7 (s) ppm. Anal. Calcd for C₄₄H₃₄Au₂P₂S₂: C, 48.81; H, 3.17. Found: C, 48.90; H, 3.03.

ASSOCIATED CONTENT

Supporting Information. X-ray and computational details; plot of the LUMO+4 of 2'; crystallographic data for 2 in CIF

format. This material is available free of charge via the Internet at http://pubs.acs.org.

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