ORGANOMETALLICS

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Cyclometalated Iridium(III) Complexes of Azadipyrromethene Chromophores

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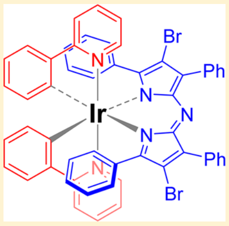
Supporting Information

ABSTRACT: Azadipyrromethenes are bidentate ligands that absorb in the red-orange region of the spectrum, with applications as tags, light harvesters, and sensitizers. Reported here are boron-transmetalation reactions that bind azadipyrromethenes to cyclometalated iridium(III). The new species absorb both near 590 nm and into the near-ultraviolet. Two examples have been crystallographically characterized. Both intra- and intermolecular aromatic stacking interactions are found. Cyclic voltammetry experiments show that azadipyrromethene complexes of iridium(III) undergo reduction and oxidation at potentials that depend little on the cyclometalating ligands on iridium. Density functional theory calculations indicate a LUMO that is azadipyrromethene-centered, whereas the HOMO may localize on either the Ir(C^N)$_2^+$ fragment or the azadipyrromethene.



INTRODUCTION

Boron azadipyrromethenes (Figure 1) are blue pigments that have been known since at least the Second World War.[1−3] Only in the past decade have they been appreciated for their excited-state properties. O'Shea and collaborators[4−7] have reported reliable syntheses of azadipyrromethenes and their BF_2^+ chelates. Absorption and luminescence spectra were disclosed for boron complexes substituted with bromine or methoxy on either phenyl set. An intense absorption band near 610 nm responds to remote substituents; shorter-wavelength features are less sensitive. Boron azadipyrromethenes fluoresce[8] with luminescence quantum yields commonly exceeding 20% if heavy-atom substituents are absent.[5,9] Zhao and Carriera[10] have produced chromophores rigidified by ring fusion along the azadipyrromethene perimeter. One such species is a fluorescence probe for cysteine.[11] The low-energy absorption red-shifts, but the fluorescence quantum yield is not enhanced relative to that of an unconstrained analogue. Boron azadipyrromethenes carrying trialkylammonium substituents stain gram-positive bacteria and are photoinducible antimicrobial agents.[12] Work on modified azadipyrromethenes has illustrated pH and toxin sensing.[13−15]

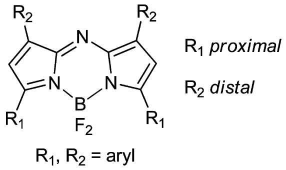


Figure 1. A boron azadipyrromethene chromophore.

Azadipyrromethenes have been embedded as repeat units in polymers.[16−18] Their electrochemical[19] and light-harvesting abilities have been surveyed for possible solar energy recovery. In recent years, ring-fused chromophores analogous to azadipyrromethenes have appeared.[20,21] These dyes have longer conjugated pathways and red-shifted optical spectra.

The development of *metalla*azadipyrromethenes has lagged behind that of boron chelates. Studies of copper, silver, and gold(I) azadipyrromethenes appeared from this laboratory in 2007 and after.[22−25] Bis(azadipyrromethene) complexes of zinc(II) and mercury(II) are heavily chromophoric.[26] Reports followed of homoleptic bis(azadipyrromethenes) of M(II) (M = Co, Ni, Cu) that are structurally and optically similar to the zinc analogues.[27−29] Boron azadipyrromethenes with distal 2-pyridyl rings are reported as optical sensors of Hg^{2+}, but the discrete complex is uncharacterized.[30] Complexes of heavier, non-d^{10} metals are uncommon. Gray and collaborators[31] have reported *fac*-$[Re(CO)_3]^+$ complexes that are electroactive; reductions are centered on the azadipyrromethene. Opportunities in metallaazadipyrromethene chemistry remain numerous.

Many cyclometalated iridium(III) complexes phosphoresce in colors across the spectrum.[32−35] Emission at room temperature typically persists for a few microseconds. Such lifetimes are ideal for organic light-emitting diodes. Emission originates from singlet and triplet excitons, but excited states decay quickly enough to evade saturation. Thompson and coworkers[36] reported seven bis(cyclometalated) iridium(III) dipyrromethene complexes that are redox active, with oxidation and reduction centered mainly on the dipyrrin ligand. These complexes are also luminescent and were applied in the building of organic light-emitting diodes (OLEDs). Cyclometalated Ir(III) complexes, both cations and anions, are the luminactive sites in light-emitting electrochemical cells, metal

Received: July 18, 2013
Published: January 16, 2014

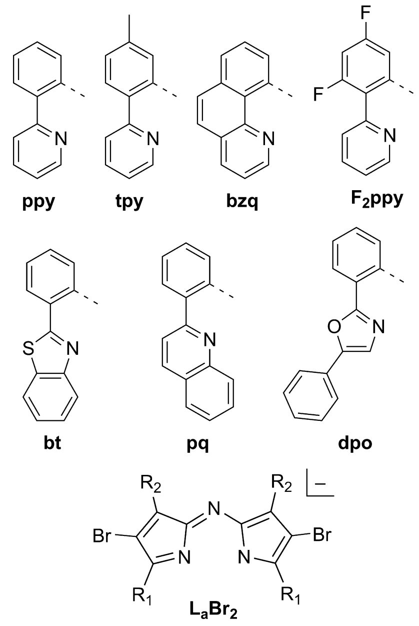
ion sensors, and biological tags. Iridium(III) cyclometalates have been evaluated as (pre)catalysts of photodriven water oxidation.[37,38] Common to most iridium(III) cyclometalates are optically allowed absorption bands at or below 550 nm.

Long-wavelength photoaction is troublesome with cyclometalated iridium(III). An intriguing prospect is joining the visible excitability of azadipyrromethenes with the triplet-state photoproperties of iridium(III). The synthesis of iridium(III) cyclometalates is muddled by substitutional inertness and an attendant need for harsh reaction conditions. Further, the proximal arms might clash with the cyclometalating ligands on iridium. Recent work from this laboratory has demonstrated transmetalation from boron as an efficient means of installing ligands on gold(I)[39−53] and iridium(III).[54] Bis(aquo)iridium(III) complexes react in the presence of base with boron azadipyrromethenes. Chelation to iridium results. Structural characterization of two complexes illustrates how the two proximal phenyl moieties coexist with C^N ligands in a mononuclear complex. The azadipyrromethene dominates the complexes' optical properties, and these are rationalized with density functional theory calculations.

■ EXPERIMENTAL SECTION

Materials. Solvents were purchased from Fisher Scientific and were used as received. $IrCl_3 \cdot H_2O$ and silver(I) triflate (AgOTf) were purchased from Strem Chemicals. The ligands 2-phenylpyridine (ppy), *p*-tolylpyridine (tpy), and 7,8-benzoquinoline (bzq) were purchased from Acros; 2,4-difluorophenylpyridine (F_2ppy), 2-phenylbenzothiazole (bt), 2,5-diphenyloxazole (dpo), and 2-phenylquinoline (pq) were purchased from Sigma-Aldrich and used without further purification (Chart 1). The azadipyrromethene $\mathbf{L_a}$[55] and BF_2-chelated azadipyrromethene ($BF_2 \cdot \mathbf{L_aBr_2}$) were synthesized following the procedure previously reported by O'Shea and co-workers.[5] The brominated adduct ($\mathbf{L_aBr_2}$) was prepared with *N*-bromosuccinimide.[24] Cyclometalated Ir(III) chloro-bridged dimers, $[Ir(C^\wedge N)_2(\mu\text{-}Cl)]_2$, were synthesized according to standard literature procedures.[56−58] The bis(aquo) complexes $[L_2Ir(H_2O)_2]OTf$ were prepared according to the method reported in the literature.[58,59] ^1H NMR spectra were recorded with a Varian AS-400 spectrometer operating at 399.7 MHz. Chemical shifts (δ) were determined in parts per million (ppm) relative to trimethylsilane and referenced to the solvent residual peaks. ^{19}F NMR spectra were measured using trichlorofluoromethane as an internal standard in $CDCl_3$. Microanalyses (C, H, and N) were performed by Midwest Microlabs, LLC. Mass spectrometry was performed at the University of Cincinnati Mass Spectrometry facility. Ultraviolet−visible spectra were collected on a Cary 500 spectrophotometer in HPLC grade or better solvents.

Chart 1. Cyclometalating Ligands and the Azadipyrromethene L_aBr_2



Syntheses. *$[Ir(bt)_2(H_2O)_2]OTf$.* Silver trifluoromethanesulfonate (57 mg, 0.22 mmol) was added to a solution of $[Ir(bt)_2(\mu\text{-}Cl)]_2$ (80 mg, 0.10 mmol) dimer in 10 mL of a 1/1 (v/v) mixture of ethanol and deionized water. The reaction mixture was then refluxed for 24 h at 100 °C. AgCl was removed by filtration, and the remaining solvent was removed by rotary evaporation. The residue was redissolved in dichloromethane and filtered through Celite. Dichloromethane was removed by rotary evaporation, and the resulting residue was washed with pentane. The isolated orange solids were dried under vacuum. Yield: 93 mg (72%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.68 (br s, 2H), 7.58 (d, 2H, *J* = 5.6 Hz), 7.64−7.52 (m, 6H), 6.87 (br s, 2H), 6.67 (br s, 2H), 6.13 (br s, 2H). Anal. Calcd for $C_{27}H_{20}F_3IrN_2O_5S_3 \cdot CH_2Cl_2$: C, 40.59; H, 2.65; N, 3.51. Found: C, 40.46; H, 2.69; N, 3.14.

*$[Ir(ppy)_2(\mathbf{L_aBr_2})]$ (**1**).* To a solution of $BF_2 \cdot \mathbf{L_aBr_2}$ (67 mg, 0.10 mmol) in THF (9 mL) was added a solution of potassium hydroxide (22 mg, 0.40 mmol) in deionized water (1 mL) under argon. The mixture was stirred for 30 min, and then *cis*-$[Ir(ppy)_2(H_2O)_2]OTf$ (69 mg, 0.10 mmol) in THF (2 mL) was added to the reaction mixture. After the mixture was stirred for 24 h at room temperature, the solvent was evaporated under vacuum, and the resulting violet residue was washed with 1 mL of water. The crude product was purified by column chromatography (diethyl ether/hexanes, 1/9, v/v) to afford **1**. Vapor diffusion of pentane into a concentrated solution of **1** in THF gave analytically pure **1** as a violet solid after filtration and vacuum drying. Yield: 71 mg (64%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.68 (d, 2H, *J* = 5.6 Hz), 7.59−7.52 (m, 10H), 7.31 (d, 4H, *J* = 7.2 Hz), 6.99−6.91 (m, 4H), 6.70 (t, 5H, *J* = 7.5 Hz), 6.40 (t, 5H, *J* = 7.4 Hz), 6.08 (t, 4H, *J* = 7.4 Hz), 5.36 (t, 2H, *J* = 7.6 Hz). HRMS (ESI): 1104.10159 (*m*/*z* calcd for $[M + H]^+$ 1104.10161). Anal. Calcd for $C_{54}H_{36}Br_2IrN_5$: C, 58.59; H, 3.28; N, 6.33. Found: C, 58.70; H, 3.42; N, 6.15.

*$[Ir(tpy)_2(\mathbf{L_aBr_2})]$ (**2**).* To a solution of $BF_2 \cdot \mathbf{L_aBr_2}$ (74 mg, 0.11 mmol) in THF (9 mL) was added a solution of potassium hydroxide (25 mg, 0.44 mmol) in deionized water (1 mL) under argon. The mixture was stirred for 30 min, and then *cis*-$[Ir(tpy)_2(H_2O)_2]OTf$ (79 mg, 0.11 mmol) in THF (2 mL) was added to the reaction mixture. After the mixture was stirred for 24 h at room temperature, the solvent was evaporated under vacuum, and the resulting violet residue was washed with 1 mL of water. The crude product was purified by column chromatography (diethyl ether/hexanes, 1/4, v/v) to afford **2** as a violet solid. Vapor diffusion of pentane into a concentrated solution of **2** in THF gave analytically pure product upon filtration. Yield: 72 mg (57%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.63 (d, 2H, *J* = 5.7 Hz), 7.67 (t, 2H, *J* = 6.1 Hz), 7.65 (d, 4H, *J* = 7.8 Hz), 7.58 (d, 2H, *J* = 8.2 Hz), 7.24 (s, 4H), 7.07 (t, 4H, *J* = 6.1 Hz), 6.95 (t, 2H, *J* = 7.5 Hz), 6.86 (d, 2H, *J* = 7.8 Hz), 6.72 (t, 4H, *J* = 7.9 Hz), 6.43 (br s, 4H), 6.23 (d, 2H, *J* = 9.2 Hz), 5.30 (s, 2H), 2.17 (s, 6H). Anal. Calcd for $C_{56}H_{40}Br_2IrN_5 \cdot C_5H_{12}$: C, 60.69; H, 4.34; N, 5.80. Found: C, 60.61; H, 4.30; N, 5.50.

*$[Ir(bzq)_2(\mathbf{L_aBr_2})]$ (**3**).* To a solution of $BF_2 \cdot \mathbf{L_aBr_2}$ (104 mg, 0.155 mmol) in THF (13.5 mL) was added a solution of potassium hydroxide (34 mg, 0.62 mmol) in deionized water (1.5 mL) under argon. The mixture was stirred for 30 min, and *cis*-$[Ir(bzq)_2(H_2O)_2]OTf$ (114 mg, 0.155 mmol) in THF (2 mL) was added to the reaction mixture. After the mixture was stirred for 24 h at room temperature, the solvent was evaporated under vacuum, and the resulting violet residue was washed with 1 mL of water. The crude product was purified by column chromatography (diethyl ether/hexanes, 2/3, v/v) to afford **3** as a violet solid. Vapor diffusion of pentane into a concentrated solution of **3** in chloroform gave analytically pure product upon filtration and vacuum drying. Yield: 85 mg (48%). ^1H NMR (400 MHz, $CDCl_3$): δ 9.01 (d, 2H, *J* = 5.3 Hz), 8.21 (d, 2H, *J* = 7.8 Hz), 8.04 (d, 2H, *J* = 7.0 Hz), 7.81 (d, 2H, *J* = 7.4 Hz), 7.65 (d,

3H, J = 7.2 Hz), 7.50−7.51 (m, 5H), 7.47 (s, 3H), 7.40−7.36 (m, 4H), 7.29 (s, 2H), 6.80 (d, 2H, J = 7.7 Hz), 6.63 (t, 2H, J = 7.3 Hz), 6.39 (br s, 3H), 6.24 (t, 2H, J = 7.6 Hz), 5.09 (d, 2H, J = 7.4 Hz). Anal. Calcd for $C_{58}H_{36}Br_2IrN_5 \cdot H_2O$: C, 59.39; H, 3.27; N, 5.97. Found: C, 59.59; H, 3.06; N, 5.82.

$[Ir(F_2ppy)_2(L_aBr_2)]$ (4). To a solution of $BF_2 \cdot \mathbf{L_aBr_2}$ (60 mg, 0.09 mmol) in THF (9 mL) was added a solution of potassium hydroxide (20 mg, 0.36 mmol) in deionized water (1 mL) under argon. The mixture was stirred for 30 min, and *cis*-$[Ir(F_2ppy)_2(H_2O)_2]$OTf (68 mg, 0.09 mmol) in THF (2 mL) was added to the solution. After the mixture was stirred for 24 h at room temperature, the solvent was evaporated under vacuum, and the resulting violet residue was washed with 1 mL of water. The crude product was purified by column chromatography (diethyl ether/hexanes, 3/17, v/v) to afford **4** as a violet solid. Analytically pure product was isolated by vapor diffusion of pentane into a concentrated solution of **4** in chloroform, followed by filtration and vacuum drying. Yield: 73 mg (69%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.66 (d, 2H, J = 5.7 Hz), 8.01 (d, 3H, J = 8.9 Hz), 7.81 (d, 3H, J = 7.4 Hz), 7.58 (d, 4H, J = 7.1 Hz), 7.18−7.06 (m, 7H), 6.83 (t, 5H, J = 7.6 Hz), 5.95 (t, 4H, J = 9.6 Hz), 4.83 (dd, 4H, J = 11.1 Hz, J = 6.7 Hz). ^{19}F NMR (376.1 MHz, $CDCl_3$): δ −109.56 (q, 2F, J = 9.5 Hz), −111.92 (t, 2F, J = 12.5 Hz). Anal. Calcd for $C_{54}H_{32}Br_2F_4IrN_5$: C, 55.02; H, 2.74; N, 5.94. Found: C, 55.36; H, 2.91; N, 5.67.

$[Ir(bt)_2(L_aBr_2)]$ (5). To a solution of $BF_2 \cdot \mathbf{L_aBr_2}$ (51 mg, 0.08 mmol) in THF (9 mL) was added a solution of potassium hydroxide (18 mg, 0.32 mmol) in deionized water (1 mL) under argon. The mixture was stirred for 30 min, and then *cis*-$[Ir(bt)_2(H_2O)_2]$OTf (64 mg, 0.08 mmol) in THF (2 mL) was added. After the mixture was stirred for 24 h at room temperature, the solvent was evaporated under vacuum, and the resulting violet residue was washed with 1 mL of water. The crude product was purified by column chromatography (diethyl ether/hexanes, 2/3, v/v) to afford **5** as a violet solid. Vapor diffusion of pentane into a concentrated solution of **5** in THF gave an analytically pure violet solid upon filtration and vacuum drying. Yield: 54 mg (56%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, 2H, J = 9.1 Hz), 7.50 (d, 2H, J = 8.1 Hz), 7.48−7.40 (m, 4H), 7.29 (d, 2H, J = 7.6 Hz), 7.19 (t, 6H, J = 7.4 Hz), 7.12 (d, 2H, J = 7.6 Hz), 6.88 (t, 2H, J = 6.2 Hz), 6.59 (t, 4H, J = 7.6 Hz), 6.47 (t, 4H, J = 7.3 Hz), 6.36 (d, 4H, J = 7.8 Hz), 6.09 (t, 2H, J = 6.0 Hz), 5.73 (d, 2H, J = 7.6 Hz). Anal. Calcd for $C_{58}H_{36}Br_2IrN_5S_2$: C, 57.10; H, 3.06; N, 5.74. Found: C, 57.34; H, 2.90; N, 5.55.

$[Ir(pq)_2(L_aBr_2)]$ (6). To a solution of $BF_2 \cdot \mathbf{L_aBr_2}$ (67 mg, 0.10 mmol) in THF (9 mL) was added a solution of potassium hydroxide (22 mg, 0.4 mmol) in deionized water (1 mL) under argon. The mixture was stirred for 30 min, and *cis*-$[Ir(pq)_2(H_2O)_2]$OTf (78.6 mg, 0.10 mmol) in THF (2 mL) was added. After the mixture was stirred for 24 h at room temperature, the solvent was evaporated under vacuum. The resulting violet residue was washed with 1 mL of water. The crude product was purified by column chromatography (diethyl ether/hexanes, 1/1, v/v) to afford **6** as a violet solid. Vapor diffusion of pentane into a concentrated solution of **6** in chloroform gave analytically pure product upon filtration. Yield: 81 mg (67%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (s, 2H), 8.32 (d, 2H, J = 9.6 Hz), 8.08 (d, 2H, J = 10.1 Hz), 7.87 (d, 2H, J = 7.9 Hz), 7.86 (d, 2H, J = 5.6 Hz), 7.52 (t, 2H, J = 6.3 Hz), 7.46 (t, 2H, J = 7.8 Hz), 7.20−7.14 (m, 10H), 6.79 (t, 2H, J = 6.2 Hz), 6.53 (t, 2H, J = 7.7 Hz), 6.48 (t, 2H, J = 6.9 Hz), 6.19 (d, 3H, J = 7.5 Hz), 6.12 (t, 3H, J = 7.4 Hz), 5.87 (d, 2H, J = 7.3 Hz), 5.59 (d, 2H, J = 5.8 Hz). Anal. Calcd for $C_{62}H_{40}Br_2IrN_5 \cdot H_2O \cdot CHCl_3$: C, 56.24; H, 3.30; N, 5.21. Found: C, 56.47; H, 3.43; N, 5.03.

$[Ir(dpo)_2(L_aBr_2)]$ (7). To a solution of $BF_2 \cdot \mathbf{L_aBr_2}$ (95 mg, 0.14 mmol) in THF (9 mL) was added a solution of potassium hydroxide (32 mg, 0.56 mmol) in deionized water (1 mL) under argon. The mixture was stirred for 30 min, and then *cis*-$[Ir(dpo)_2(H_2O)_2]$OTf (116 mg, 0.14 mmol) in THF (2 mL) was added to the solution. After the mixture was stirred for 24 h at room temperature, the solvent was evaporated under vacuum, and the resulting violet residue was washed with 1 mL of water. The crude product was purified by column chromatography (diethyl ether/hexanes, 3/4, v/v) to afford **7** as a violet solid. Analytically pure compound was isolated by vapor diffusion of pentane into a concentrated solution of **7** in chloroform, followed by filtration and vacuum drying. Yield: 80 mg (46%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, 4H, J = 9.1 Hz), 7.67 (d, 4H, J = 8.1 Hz), 7.56−7.51 (m, 6H), 7.44 (t, 3H J = 7.5 Hz), 7.30 (t, 4H, J = 7.4 Hz), 7.07 (t, 2H, J = 8.1 Hz), 6.98 (d, 3H, J = 6.8 Hz), 6.89 (t, 4H, J = 7.5 Hz), 6.62 (d, 4H, J = 6.9 Hz), 6.50 (t, 2H, J = 8.1 Hz), 6.27 (t, 2H, J = 7.7 Hz), 5.64 (d, 2H). Anal. Calcd for $C_{62}H_{40}Br_2IrN_5O_2 \cdot 0.5H_2O$: C, 59.57; H, 3.47; N, 5.60. Found: C, 59.56; H, 3.64; N, 5.44.

Electrochemistry. Tetrabutylammonium hexafluorophosphate (Fluka) was recrystallized from ethyl acetate and ether and was dried thoroughly under vacuum and stored in a nitrogen drybox. Ferrocene (Aldrich) was purified via sublimation and stored under nitrogen. Cyclic voltammetry experiments were performed in a nitrogen-filled Vacuum Atmospheres drybox outfitted with a CH Instrument Workstation at room temperature. A glassy-carbon working electrode was polished with 0.05 μm alumina and was cleaned and dried before use. A silver wire served as a quasi-reference electrode, and a platinum wire was the counter electrode. Scans were performed at a scan rate of 100 mV s^{-1}.

Crystallography. Crystals of $[Ir(ppy)_2(\mathbf{L_aBr_2})]$ and $[Ir(bt)_2(\mathbf{L_aBr_2})]$ were affixed to nylon filament loops with Paratone-N oil and cooled to 100 K. Data were collected using Bruker diffractometers: for $[Ir(ppy)_2(\mathbf{L_aBr_2})]$, an APEXII (CCD) D8 platform; for $[Ir(bt)_2(\mathbf{L_aBr_2})]$, a Photon (CMOS) system. Structure solution was achieved by direct methods, which revealed all non-hydrogen atoms. Hydrogen atoms were treated as idealized contributions. All aspects of data processing used standard routines available in the Bruker and SHELXL libraries (Bruker AXS, Madison, WI). Non-hydrogen atoms were refined anisotropically during the last few refinements.

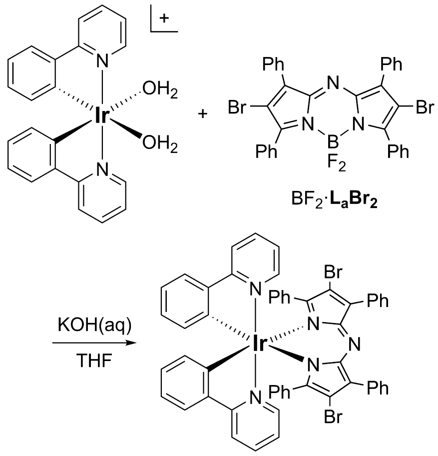
Calculations. Spin-restricted density functional theory computations were carried out with Gaussian09 rev. A.02.[60] Geometries were fully optimized, and converged structures were confirmed to be potential energy minima by harmonic frequency calculations. Calculations used the exchange and correlation functionals of Perdew, Burke, and Ernzerhof[61] and the TZVP basis set of Godbelt, Andzelm, and co-workers for nonmetals.[62] For iridium, the Stuttgart−Dresden effective core potential and basis set were used;[63] scalar relativistic effects are included implicitly. Dielectric continuum solvation in chloroform was included with the integral equation formalism of the polarizable continuum model.[64−67] Population analyses[68] proceeded with the AOMix software of Gorelsky.[69,70]

■ RESULTS AND DISCUSSION

Syntheses. The aquo complex *cis*-$[Ir(ppy)_2(H_2O)_2]^+$ (ppy = 2-phenylpyridyl), reported by Bernhard and co-workers, is one member of a family of iridium(III) synthons.[59] We have demonstrated that reactions of (aquo)iridium(III) complexes with boronic acids and esters yield chelated complexes in boron to iridium transmetalations.[54] The reaction is base-promoted, with KOH and K_3PO_4 being effective. Addition of *cis*-$[Ir(ppy)_2(H_2O)_2](OTf)$ to a solution of $BF_2 \cdot \mathbf{L_aBr_2}$ and KOH in 10/1 (v/v) THF/H_2O proceeded with a color change from green to violet (Scheme 1). Silica gel column chromatography, followed by vapor diffusion crystallization, yielded analytically pure products. Isolated yields range from 46 to 69%. The brominated azadipyrromethene was chosen for ease of purification of complexes from residual free ligand. Complexes of $\mathbf{L_aBr_2}$ were separated from the free ligand by silica gel column chromatography, whereas complexes of unbrominated $\mathbf{L_a}$ required, in our hands, preparative thin-layer chromatography followed by vapor diffusion crystallization (Supporting Information). Also, the flanking bromo groups provided ready handles for cross-coupling or other functionalization reactions.

Structures. Two representative compounds were characterized by X-ray diffraction crystallography.[71] Pentane vapor

Scheme 1



diffusion into THF solution yielded violet blades of [Ir($ppy)_2$($\mathbf{L_aBr_2}$)] and [Ir($bt)_2$($\mathbf{L_aBr_2}$)]. The complex [Ir($ppy)_2$($\mathbf{L_aBr_2}$)] crystallizes in the centrosymmetric space group $P\bar{1}$. Crystals of [Ir($bt)_2$($\mathbf{L_aBr_2}$)] are monoclinic, $P2_1/c$, with two of each enantiomer per unit cell. A thermal ellipsoid plot of [Ir($ppy)_2$($\mathbf{L_aBr_2}$)] appears as Figure 2 and that of [Ir($bt)_2$($\mathbf{L_aBr_2}$)] as Figure 3. Both enantiomers of each complex occur in the unit cell, as does a THF of crystallization in the cell of [Ir($ppy)_2$($\mathbf{L_aBr_2}$)]. Nitrogen atoms in the C^N ligands are trans to each other; azadipyrromethene nitrogens are trans to carbon. Bonds between iridium and the azadipyrromethene nitrogens are longer than those to carbon or nitrogen of the cyclometalating ligands. Geometric parameters of the C^N ligands are unexceptional. The meso nitrogens of the azadipyrromethene core dilate from an idealized sp^2 geometry. For [Ir($ppy)_2$($\mathbf{L_aBr_2}$)], the angle C−N_{meso}−C is 127.9(8)°; for [Ir($bt)_2$($\mathbf{L_aBr_2}$)], it is 128.1(3)°. For comparison, the backbone angle in BF_2·$\mathbf{L_aBr_2}$ is 119.5(2)°[5] and that in $\mathbf{L_a}$$Ir^I$(COD) (COD = (1Z,5Z)-cycloocta-1,5-diene) is 125.3(3)°.[72] The greater meso-nitrogen distention in the iridium(III) complex suggests steric hindrance between the azadipyrromethene phenyls and the cyclometalating ligands. The azadipyrromethene is more strained than when it is complexed to the larger iridium(I).

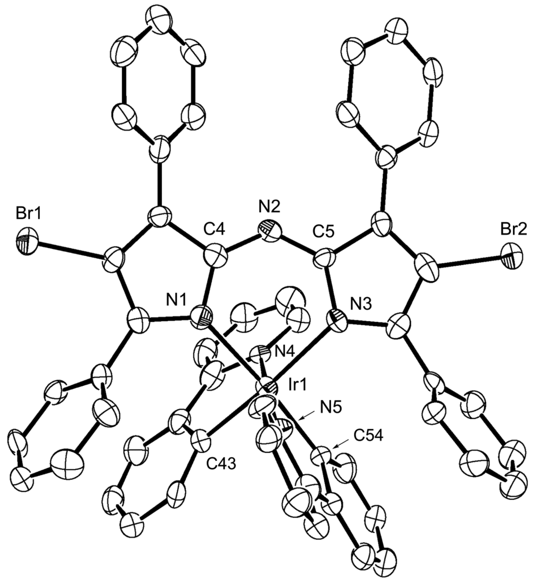


Figure 2. Crystal structure of [Ir($ppy)_2$($\mathbf{L_aBr_2}$)] (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. Carbon atoms are unlabeled. Selected interatomic distances (Å): Ir1−C43, 2.017(9); Ir1−C54, 2.024(9); Ir1−N5, 2.029(9); Ir1−N4, 2.040(8); Ir1−N1, 2.187(8); Ir1−N3, 2.183(7). Selected angles (deg): N1−Ir1−N3, 85.1(3); C43−Ir1−N4, 81.0(4); C54−Ir1−N5, 81.1(4); C4−N2−C5, 127.9(8).

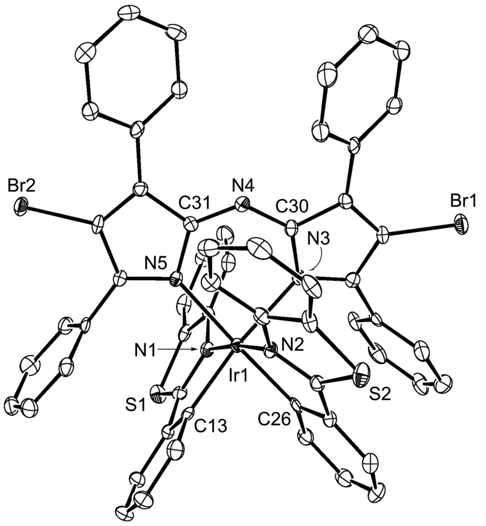


Figure 3. Crystal structure of [Ir($bt)_2$($\mathbf{L_aBr_2}$)] (50% probability ellipsoids). H atoms and solvent of crystallization are omitted for clarity. A partial atom labeling scheme is shown; carbon atoms are unlabeled. Selected interatomic distances (Å): Ir1−C13, 2.014(4); Ir1−C26, 2.024(4); Ir1−N1, 2.027(3); Ir1−N2, 2.074(3); Ir1−N5, 2.159(3); Ir1−N3, 2.197(3). Selected angles (deg): N5−Ir1−N3, 85.12(11); C13−Ir1−N1, 79.74(14); C26−Ir1−N2, 79.52(13); C31−N4−C30, 128.1(3).

Intramolecular π interactions are prominent in both structures. The proximal arms of $\mathbf{L_aBr_2}$ stack with the phenyl rings of both 2-phenylpyridyl ligands in the structure of [Ir($ppy)_2$($\mathbf{L_aBr_2}$)]. Centroid to centroid distances are 3.501 and 3.607 Å (Figure S2, Supporting Information). No stacking interactions occur between neighbors within the unit cell. In the structure of [Ir($bt)_2$($\mathbf{L_aBr_2}$)], stacking is both intra- and intermolecular. The proximal phenyl groups stack with the benzenoid rings of bt. Centroid to centroid distances within the same complex are 3.536 and 3.599 Å (Figure S3, Supporting Information). Intermolecular π stacking occurs between proximal phenyls, with a centroid to centroid separation of 3.874 Å. Within one unit cell, a four-tiered π stack forms, as shown in Figure 4. The structures prove that tetraarylazadi-

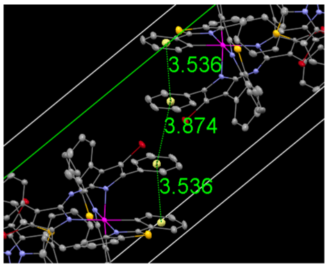


Figure 4. Intermolecular π-stacking interactions in [Ir($bt)_2$($\mathbf{L_aBr_2}$)]. Distances between benzene ring centroids (yellow spheres) are given in Å.

pyrromethenes accommodate six-coordination if planar, chelating ligands are opposite each other. This favorable outcome is not intuitive; the implication is that azadipyrromethene complex synthesis is not obstructed by the jutting phenyl arms.

Optical Spectra. Electronic absorption spectra all show an azadipyrromethene π–π^* transition near 590 nm (Figure 5). This feature is the optical hallmark of azadipyrromethenes; it appears in the spectra of metal and boron complexes.[4−14,23−27,31] Overlapping charge-transfer bands of the cyclometalated core appear at shorter wavelengths and extend into the ultraviolet. No luminescence is observed at room temperature upon excitation at 590 nm. Excitation at 260 nm gives weak luminescence; emission spectra appear as given in Figure S1 (Supporting Information). Attempted measurements of luminescence lifetimes gave evidence of decomposition. The azadipyrromethene ligand quenches the emission native to cyclometalated iridium(III).

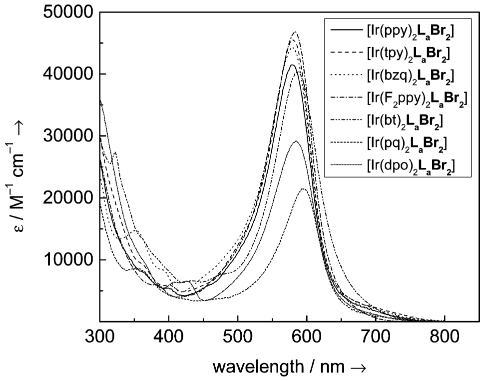


Figure 5. Absorption spectra of iridium(III) complexes in chloroform solution.

The new complexes were characterized by cyclic voltammetry. Voltammograms collected in dichloromethane appear as Figure 6, along with that of the boron chelate $\mathrm{BF_2}\cdot\mathbf{L_aBr_2}$. Potentials are referenced to the ferrocene/ferrocenium couple.

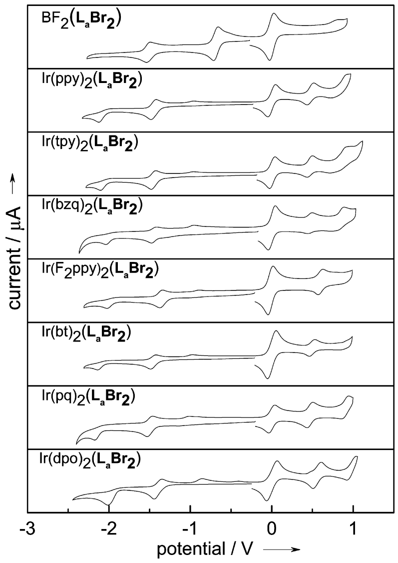


Figure 6. Cyclic voltammograms of iridium(III) azadipyrromethene complexes in dichloromethane. Voltammograms were recorded at 100 mV s^{-1} and are referenced to internal Fc/Fc$^+$.

The boron complex shows two reversible reductions at $E_{1/2}$ = −0.7 and −1.5 V. Regardless of the C^N ligands, iridium complexes show one reversible and one irreversible reduction, each at potentials more negative than the respective first or second reductions of $\mathrm{BF_2}\cdot\mathbf{L_aBr_2}$. The second reduction is irreversible for Ir complexes and varies with the cyclometalating ligand. Iridium complexes undergo reversible or quasi-reversible oxidations near +0.5 V that depend weakly on the cyclometalating ligands. These have no clear counterpart in the voltammograms of $\mathrm{BF_2}\cdot\mathbf{L_aBr_2}$, except for an irreversible event near +0.6 V. The complexes ([Ir(tpy)$_2$($\mathbf{L_aBr_2}$)], [Ir(pq)$_2$($\mathbf{L_aBr_2}$)]) show irreversible oxidations at potentials between +0.5 and +1.0 V. Combined, these measurements indicate that the azadipyrromethene is the site of one-electron reduction of the neutral complexes.

The two crystallographically characterized compounds were chosen for density functional theory (DFT) computations; both are representative. Figure 7 depicts a partial energy-level diagram of [Ir(ppy)$_2$($\mathbf{L_aBr_2}$)], with orbital plots inset at the right. The highest occupied Kohn–Sham orbital (HOMO) has 40% Ir and 48% ppy character; percentages are of electron density according to Mulliken.[68] The HOMO-1 lies just 0.02 eV below the HOMO and is derived (97%) from $\mathbf{L_aBr_2}$. The lowest unoccupied Kohn–Sham orbital (LUMO) is also $\mathbf{L_aBr_2}$-centered (98%). The calculated energy gap between the LUMO and the LUMO+1 is 40% that of the HOMO–LUMO gap. Given the new compounds' reducibility, the calculated properties of the LUMO are unsurprising. Energy levels and frontier orbital compositions of [Ir(bt)$_2$($\mathbf{L_aBr_2}$)] are similar to those of the ppy analogue, except that an azadipyrromethene π orbital is the HOMO with a nearby [Ir(bt)$_2$]$^{2+}$-centered HOMO-1. An energy-level diagram for this compound appears as Figure S4 (Supporting Information).

Time-dependent DFT calculations were performed on [Ir(ppy)$_2$($\mathbf{L_aBr_2}$)] and [Ir(bt)$_2$($\mathbf{L_aBr_2}$)], both in their optimized, ground-state (singlet) geometries. Thus, excited singlets or triplets are Franck–Condon states. For [Ir(ppy)$_2$($\mathbf{L_aBr_2}$)], the first singlet excited state results from a single-particle LUMO ← HOMO-1 transition; both orbitals center on the azadipyrromethene. For [Ir(bt)$_2$($\mathbf{L_aBr_2}$)], the first excited singlet derives from a combination of LUMO ← HOMO and LUMO ← HOMO-1 transitions that mix through configuration interaction. A state of mixed intraligand and metal–ligand to ligand charge transfer is suggested. Triplet states and higher singlet states show extensive configuration interaction. That is, these states are built up of linear combinations of transitions between orbitals.

■ CONCLUSIONS

Cyclometalated iridium(III) complexes have been prepared having a chromophoric azadipyrromethene ligand. The common four-aryl geometry of azadipyrromethenes is preserved, yet the ligand comports with six-coordinate iridium(III). The syntheses disclosed here show that base-assisted transmetalation from boron extends to complexes of N^N chelating ligands. We had earlier demonstrated its use in preparing C^N chelates.[54] Visible spectra are dominated by azadipyrromethene absorption bands. The new complexes are electroactive, with reversible reductions and oxidations near −1.3 and +0.5 V, respectively. Other redox events are irreversible and depend on the cyclometalating ligands. DFT calculations return a LUMO that is azadipyrromethene-centered and is isolated in energy. An azadipyrromethene π

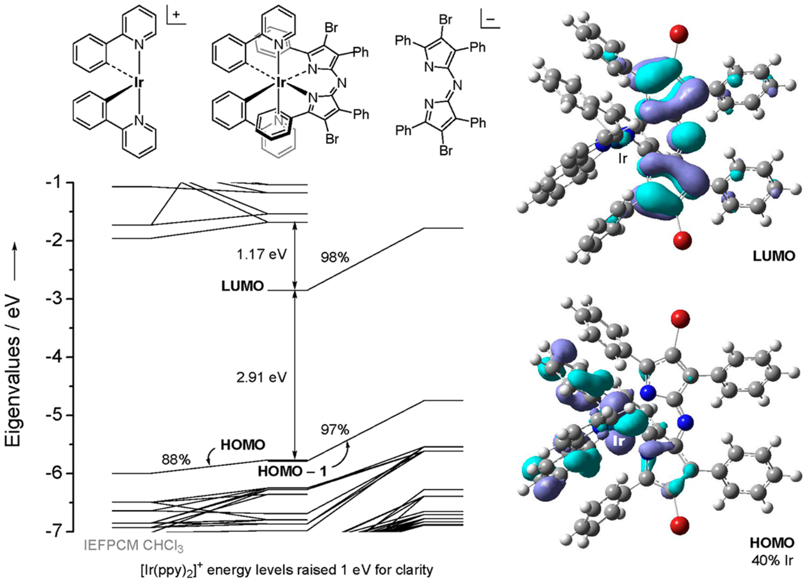


Figure 7. Partial Kohn−Sham orbital energy diagram of $[Ir(ppy)_2(\mathbf{L_aBr_2})]$ with continuum (IEFPCM) chloroform solvation. Frontier orbital images appear at the right (contour level 0.03 au).

orbital is the HOMO or very near it. The azadipyrromethene $\pi-\pi^*$ transition that colors BF_2^+ complexes also governs the optical properties of Ir(III) complexes.

Like the unsubstituted dipyrromethene complexes of Thompson and co-workers,[36] Ir(III) azadipyrromethenes exhibit oxidative and reductive electrochemistry. Their signature absorption features, a structureless absorption band near 590 nm, is red-shifted from a similar band in the dipyrromethene complexes, which appears near 480 nm. Unlike dipyrromethene complexes, the new metallaazadipyrromethenes are not luminescent in the visible region in room-temperature solutions.

This work demonstrates rational syntheses of red-absorbing iridium complexes. The electrooptical properties of azadipyrromethene ligands may carry over to other metal complexes and to materials that assimilate them. Experiments that test these conjectures are ongoing.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthesis and characterization of $[Ir(typ)_2(\mathbf{L_a})]$ (**8**), X-ray data in CIF format, tables of crystallographic data, photophysical properties, and optimized Cartesian coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Science and Engineering, under Award DE-FG02-13ER46977 to T.G.G. We thank the Republic of Turkey for a fellowship to N.D. and Professor J. D. Protasiewicz, Case Western Reserve, for access to instrumentation.

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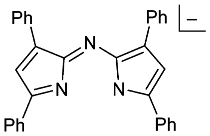

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