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Chromium(III) Bis-Arylterpyridyl Complexes with Enhanced Visible Absorption via Incorporation of Intraligand Charge-Transfer Transitions

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Supporting Information

ABSTRACT: A series of chromium(III) bis-arylterpyridyl complexes containing intraligand charge-transfer (ILCT) excited states were prepared and characterized. These complexes show significant absorption in the visible region due to the ILCT bands. The ILCT bands are tunable across the UV and visible spectrum via incorporation of electron-withdrawing and electron-donating groups on the aryl ring. The absorption of Cr(4'-(4-methoxyphenyl)-2,2':6',2"-terpyridine)₂³⁺ (4) in particular is much stronger in the visible region ($\varepsilon = 11\,900 \text{ M}^{-1} \text{ cm}^{-1}$ at 450 nm and $\varepsilon = 5090 \text{ M}^{-1} \text{ cm}^{-1}$ at 500 nm) than that of the parent complex Cr(tpy)₂³⁺ (tpy = 2,2':6',2"-terpyridine; $\varepsilon = 2160 \text{ M}^{-1} \text{ cm}^{-1}$ at 450 nm, and $\varepsilon = 170 \text{ M}^{-1} \text{ cm}^{-1}$ at 500 nm). Emission experiments on this series



reveal Cr(III)-based phosphorescence with lifetimes from 140 to 600 ns upon excitation into the ILCT bands, which indicates funneling of the excitation energy from ligand-localized excited states to Cr(III)-based excited states. Cyclic voltammograms exhibit at least three reversible ligand-based reductions. The first reduction shows shifts of up to -160 mV compared to $\text{Cr(tpy)}_2^{3^+}$. The excited-state reduction potential of these complexes ranges from +0.95 to +1.04 V vs the ferrocene/ferrocenium couple, making them potent photooxidants.

INTRODUCTION

Coordination complexes of Cr(III) have long been known as chromophores with rich photochemistry and redox chemistry.^{1–5} Recently, there has been renewed interest in the chemistry of these complexes, especially Cr(III) polypyridines.^{6–22} Most of the studies on Cr(III) polypyridines have focused on Cr(III) tris(2,2'-bipyridyl) and analogues with bidentate ligands. These complexes are potent photooxidants with excited-state reduction potentials of \geq +1.0 V vs the ferrocene/ferrocenium couple (Fc/Fc⁺) and excited-state lifetimes in the hundreds of microseconds.^{4,6,23,24} Chromium is an inexpensive, earth abundant metal. In light of these properties, Cr(III) chromophores are promising targets for use in schemes for solar energy conversion and photoredox catalysis.^{25–33}

Challenges to the widespread use of Cr(III) polypyridyl chromophores in a variety of applications include weak absorption bands in the visible portion of the solar spectrum and photoinduced ligand substitution reactions.⁴ Ligand variation has been a successful strategy for tuning the absorption properties of transition metal chromophores, especially chromophores with charge-transfer excited states.^{34–36} Additionally, incorporation of ligands or ligand-

appended groups with excited states of their own has led to chromophores with enhanced absorption properties.^{37–44} While Cr(III) polypyridyls generally absorb at $\lambda < 450$ nm, they phosphoresce at $\lambda > 700$ nm. Therefore, ligand-localized transitions that absorb visible light are expected to be energetically competent to sensitize the long-lived doublet excited states typical of Cr(III) polypyridyl complexes. However, we know of no previous systematic attempts to investigate the ability of visible-absorbing, ligand-localized transitions to funnel excitation energy into Cr(III)-based excited states.

Compared to Cr(III) tris-bipyridyl complexes, the electrochemical and photophysical properties of Cr(III) bis-terpyridyl complexes have received little attention.^{11,14,15,45–57} Many of those reports are aimed at understanding the relatively short (<200 ns) excited-state lifetimes of this family of complexes. Nonetheless, Cr(III) terpyridyl complexes present opportunities to address the challenges posed by the poor photostability and weak visible absorption of Cr(III) tris-bipyridyls. Addressing the first challenge, the increased denticity of the

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terpyridine ligand has the potential to stabilize the excited species toward ligand substitution. While recent reports reveal unexpected thermal lability for Cr(III) terpyridyl complexes, there have been no reports on the photolability for these complexes.^{14,15} Addressing the second challenge, terpyridines with an aryl substituent in the 4-position on the central pyridine ring are known to contain strongly absorbing charge-transfer (CT) states that are tunable via variation of the groups on the aryl substituent.^{58–60} Furthermore, complexes of arylterpyridines and metal centers (including Cr, Zn, Ru, Ir, Pt) are reported to exhibit intraligand charge-transfer (ILCT) bands in the visible region.^{59,61–66} A singular report details the synthesis of Cr(III) bis-arylterpyridyl complexes with identified ILCT bands but does not report on the photophysical properties of these complexes.¹⁵

Herein, we report the synthesis and photophysical characterization of a series of homoleptic Cr(III) complexes with 4'-aryl-2,2':6',2''-terpyridines as ligands. These complexes exhibit ILCT bands that greatly enhance the absorption properties of Cr(III) terpyridyls; the ILCT bands are tunable across the UV and visible region and absorb with ε of up to 56 000 M⁻¹ cm⁻¹. Emission spectroscopy indicates that, in all but one case, the excitation energy is funneled from the ILCT state into Cr(III)based doublet excited states, leading to phosphorescence with lifetimes up to 600 ns. These complexes are potent photooxidants with excited-state reduction potentials of up to +1.04 V vs Fc/Fc⁺.

EXPERIMENTAL SECTION

General Information. All manipulations involving CrCl₂ were performed using standard Schlenk techniques or in a MBRAUN Labstar glovebox under N2 atmosphere, until the oxidation step. 4'-(4-Bromophenyl)-2,2':6',2"-terpyridine (L2),⁶⁷ 4'-phenyl-2,2':6',2"-terpyridine (L1),⁶⁷ and $Cr(tpy)_2(PF_6)_3^{11}$ were synthesized via reported procedures. All other reagents were obtained from commercial sources. ¹H NMR spectra were obtained using a Bruker AVANCE III 400Mz NMR. All NMR spectra were recorded between 293 and 296 K in CDCl₃ and referenced to the residual solvent peak. IR spectra were recorded on a PerkinElmer Spectrum Two with UATR accessory. Elemental analyses were performed by Midwest Microlab, LLC, in Indianapolis, IN. Mass spectrometry was performed in either positive or negative ion mode on a Thermo Finnigan LCQ Deca quadrupole mass spectrometer equipped with an electrospray ion source. Tetrabutylammonium hexafluorophosphate (Sigma-Aldrich, 98%) was used as an electrolyte for electrochemical experiments and was recrystallized from 95% ethanol and dried under vacuum at 70 °C for at least 24 h. Acetonitrile used for electrochemical experiments was filtered through activated alumina and stored over molecular sieves prior to use. Ferrocene (Sigma-Aldrich, 98%) was sublimed under vacuum. Burdick and Jackson brand solvents were used for spectroscopic measurements. Acetonitrile (Burdick and Jackson brand) for steady-state and time-resolved emission experiments was dried over 4 Å molecular sieves for at least 48 h, freeze-pump-thaw degassed, and vacuum transferred before use.

Electrochemistry. All cyclic voltammetry experiments were performed at room temperature with an Epsilon EClipse BASi electrochemical analyzer and a C3 cell stand. A three-electrode setup consisting of a glassy carbon working electrode (3 mm diameter), Ptwire auxiliary electrode, and a Ag-wire quasi-reference electrode was used, and electrodes were polished with alumina prior to each experiment. Samples consisted of the chromium complex analyte dissolved in a nitrogen-purged 0.1 M $^{\rm nBu}_4{\rm NPF}_6$ solution in acetonitrile. All cyclic voltammograms were collected at a scan rate of 100 mV/s. Ferrocene was added as an internal reference, and under the experimental conditions, the Fc/Fc⁺ couple exhibited reversible behavior.

Photophysical Measurements. Absorption spectra were obtained using a Shimadzu UV-2450 spectrophotometer with samples in 1 cm quartz cuvettes at room temperature. Extinction coefficients were determined from plots of absorbance versus concentration for five or more samples prepared via dilution of a stock solution. Samples for emission experiments were sealed in screw-top cuvettes with silicone septa under a nitrogen atmosphere. This method produced sufficiently low oxygen concentrations to yield repeatable emission lifetimes and quantum yield measurements for these samples.

Emission spectroscopy was performed on a Horiba Jobin Yvon Fluorolog-3 equipped with a red-sensitive Hamamatsu R928 PMT. Steady-state emission experiments were performed with a 455 nm long pass filter between the sample and the emission monochromator. Relative emission yields were obtained from optically dilute (OD < 0.1) samples of a standard, $Cr(tpy)_2(PF_6)_3$, and the unknown measured in succession. The relative emission intensity was calculated from eq 1:⁶⁸

$$\operatorname{rel}\operatorname{em} = \left(\frac{I_{\operatorname{unk}}}{I_{\operatorname{std}}}\right) \left(\frac{A_{\operatorname{std}}}{A_{\operatorname{unk}}}\right) \tag{1}$$

where *I* is the integrated emission intensity of the phosphorescence band and *A* is the absorption of the sample at the excitation wavelength. Emission spectra were corrected for PMT response, and a solvent background was subtracted from each spectrum. The emission spectra of **6** were further adjusted to yield a baseline at zero. The emission spectra of **4** were each fit to a Gaussian function from 625 to 715 nm; a representative emission spectrum and Gaussian function are shown in Figure S1. To determine the integrated doublet emission intensity for **4**, the area under this function was subtracted from the area under the emission spectrum from 600 to 825 nm.

Time-resolved emission experiments were performed using a Fluorolog-3, equipped with a time-correlated single photon counting module using the same detector and emission channel as the steady-state emission experiments. The excitation source was a 454 nm Horiba NanoLED with a 1.2 ns pulse width. A 715 nm long pass filter was placed between the sample and the emission monochromator for lifetimes monitored at $\lambda > 720$ nm. Emission experiments were performed on at least three samples for each complex, and the reported lifetime is the average of the three samples. Lifetimes were found by fitting the decay traces to a single exponential function over 5τ . In the case of 4 and 6 a fast feature decayed with the instrument response function; time points that include the rapid feature were excluded from the fit. Inspection of the residuals confirmed the appropriateness of the fits. Absorption spectra of the samples showed no change before and after the emission measurements.

Synthesis of Ligands and Chromium Complexes. 4'-(4-Methylphenyl)-2,2':6',2"-terpyridine (L3). Toluylbenzaldehyde (4.72 mL, 0.0400 mol), 2-acetylpyridine (10.5 mL, 0.0936 mol), and NaOH (s) (12.0 g, 0.300 mol) were combined using a mortar and pestle until the sticky aggregate became a pale orange powder (ca. 30 min). The powder was added to a suspension of ammonium acetate (21.6 g, 0.280 mol) in 120 mL of glacial acetic acid and was refluxed for 2 h. Upon the addition of 650 mL of water, a brown precipitate formed, was collected via filtration, and was washed with water. The brown solid was >98% pure by ¹H NMR and used without further purification (10.045 g, 0.0311 mol, 77.7%). ¹H NMR: δ = 8.74 (m, 4H), 8.67 (d, *J* = 8 Hz, 2H), 7.88 (td, *J* = 7.7 Hz, *J* = 1.7 Hz, 2H), δ = 7.83 (d, *J* = 8 Hz, 2H), δ = 7.35 (m, 2H), δ = 7.32 (d, *J* = 8 Hz, 2H), δ = 2.43 (s, 3H). ¹H NMR data is consistent with a previous report for the same compound.⁵⁸

4'-(4-Methoxyphenyl)-2,2':6',2"-terpyridine (L4). p-Anisaldehyde (6.10 mL, 0.050 mol), 2-acetylpyridine (10.5 mL, 0.0936 mol), and NaOH (s) (11.8 g, 0.295 mol) were combined using a mortar and pestle until the sticky aggregate became an orange powder (ca. 1 h). The powder was added to a suspension of ammonium acetate (21.6 g, 0.280 mol) in 150 mL of glacial acetic acid and was refluxed for 2 h. Upon the addition of 650 mL of water, a black precipitate formed and was collected via filtration. The resulting sticky, black solid was triturated with ethanol, yielding a dark green solid. The green solid was used without further purification (3.061 g, 0.00902 mol, 18.0%). ¹H NMR: δ = 8.73 (m, 2H), 8.70 (s, 2H), 8.66 (d, *J* = 8 Hz, 2H), 7.89–7.85 (m, 4H), 7.34 (m, 2H), 7.02 (d, *J* = 8.8 Hz, 2H), δ = 3.88 (s, 3H). ¹H NMR data is consistent with a previous report for the same compound.⁵⁸

4⁻-(4-Dimethylaminophenyl)-2,2':6',2"-terpyridine (L5). 4-Dimethylaminobenzaldehyde (5.97 g, 0.0400 mol), 2-acetylpyridine (10.5 mL, 0.0936 mol), and NaOH (s) (11.8 g, 0.295 mol) were combined using a mortar and pestle until the sticky aggregate became an orangeyellow powder (ca. 30 min). The powder was added to a suspension of ammonium acetate (21.6 g, 0.280 mol) in 150 mL of glacial acetic acid and was refluxed for 2 h. Upon the addition of 650 mL of water, a dark precipitate formed, was collected via filtration, and was washed with water. The dark brown solid was >98% pure by ¹H NMR and used without further purification (7.867 g, 0.0231 mol, 55.8% yield). ¹H NMR: δ = 8.73 (m, 2H), 8.69 (s, 2H), 8.65 (d, *J* = 8 Hz, 2H), 7.88–7.84 (m, 4H), 7.34 (m, 2H), 6.81 (d, *J* = 8 Hz, 2H), δ = 3.04 (s, 6H). ¹H NMR data is consistent with a previous report for the same compound.⁵⁸

4⁻-(2,4,6-Trimethylphenyl)-2,2':6',2"-terpyridine (L6). Mesitaldehyde (5.9 mL, 0.0400 mmol), 2-acetylpyridine (10.5 mL, 0.0936 mmol), and NaOH (s) (12.0 g, 0.300 mol) were combined using a mortar and pestle until the sticky aggregate became a caramel-colored powder (ca. 45 min). The powder was added to a suspension of ammonium acetate (21.6 g, 0.280 mol) in 100 mL of glacial acetic acid and was refluxed for 2.5 h. Upon the addition of 650 mL of water, a green precipitate formed, was collected via filtration, and was washed with water. The resulting sticky, green solid was triturated with ethanol, yielding a pale solid, which was used without further purification (5.149 g, 0.0147 mol, 34.2%). ¹H NMR: δ = 8.68 (m, 4H), 8.31 (s, 2H), 7.88 (td, *J* = 7.6 Hz, *J* = 2.0 Hz, 2H), 7.35–7.31 (m, 2H), 6.95 (s, 2H), 2.34 (s, 3H), 2.07 (s, 6H) ¹H NMR data is consistent with a previous report for the same compound.⁶²

 $[Cr(L1)_2](PF_6)_3$ (1). CrCl₂ (0.1 g, 0.9 mmol) was dissolved in 25 mL of water and added via cannula to a suspension of L1 (0.529 g, 1.71 mmol) in 50 mL of methanol. The dark purple reaction mixture was stirred at room temperature. After 20 h, air was bubbled through the mixture for 20 min, resulting in an orange-brown mixture. The mixture was filtered, and excess NaPF₆ was added to the filtrate to precipitate an orange solid (0.2866 g, 31% crude yield). The orange solid (ca. 0.2 g) was chromatographed on silica gel with ACN:H₂O (7:1). After a purple band eluted, ACN:H2O:sat. aq KNO3 (7:1:0.5) was used to elute the product as an orange band. The eluent was concentrated, NaPF₆ (0.203 g, 1.21 mmol) in 5 mL of water was added, and the solution was cooled to 2 °C to precipitate an orange crystalline solid (0.1011 g, 0.090 mmol, 50% yield for purification steps). ES-MS $(CH_3CN): m/z \ 1250.14 ([Cr(L1)_2(PF_6)_4]^-). ES+MS (CH_3CN): m/z \ 223.37 ([Cr(L1)_2]^{3+}), 344.57 ([Cr(L1)_2F]^{2+}), 707.84 ([Cr(L1)_2F_2]^+).$ Anal. Calcd for C42H30N6CrP3F18: C, 45.62; H, 2.74; N, 7.60. Calcd for 1 0.5CH₃CN: C, 45.86; H, 2.82; N, 8.09. Found: C, 45.67; H, 3.09; N, 8.01. IR (solid, ATR): v_{Ar,Py} 1610, 1596, 1570, 1550, 1482, 1449, 1422, 1366 $\rm cm^{-1}$

 $[Cr(L2)_2](PF_6)_3$ (2). CrCl₂ (0.018 g, 0.15 mmol) was dissolved in 5 mL of water and added via cannula to a suspension of L2 (0.12 g, 0.31 mmol) in 50 mL of methanol. The dark purple mixture was stirred at room temperature. After 20 h, air was bubbled through the mixture for 15 min, resulting in a yellow-brown mixture. The mixture was filtered, and excess NaPF₆ was added to the filtrate to precipitate a yelloworange solid. The crude product was washed with water, diethyl ether, and acetone (0.120 g). The product was recrystallized three times by slow diffusion of diethyl ether into a concentrated acetonitrile solution to yield bright yellow crystals (0.049 g, 24% yield). ES-MS (CH₃CN): m/z 1407.91 ([Cr(L2)₂(PF₆)₄]⁻). ES+MS (CH₃CN): m/z 275.97 $([Cr(L2)_2]^{3+})$, 423.46 $([Cr(L2)_2F]^{2+})$, 865.65 $([Cr(L2)_2F_2]^+)$. Anal. Calcd for C42H28N6CrP3F18Br2: C, 39.93; H, 2.23; N, 6.65. Calcd for 2.2CH3CN: C, 41.06; H, 2.55; N, 8.33. Found: C, 40.99; H, 2.69; N, 8.19. IR (solid, ATR): ν_{Ar,Py} 1610, 1587, 1571, 1545, 1500, 1480, 1435, 1396, 1371 cm⁻¹

 $[Cr(L3)_2](PF_6)_3$ (3). CrCl₂ (0.332 g, 2.70 mmol) was dissolved in 100 mL of water and added via cannula to a suspension of L3 (1.84 g, 5.68

mmol) in 200 mL of methanol. The reaction mixture was stirred at room temperature. After 3 days, air was bubbled through the mixture for 20 min, the mixture was filtered, and excess sodium hexafluorophosphate was added to the filtrate, resulting in a brown precipitate (1.144 g; 34% yield of crude product). 0.595 g of the brown solid was chromatographed on silica gel with ACN:H₂O (7:1). After a purple band eluted, ACN:H2O:sat. aq KNO3 (7:1:0.5) was used to elute the product as a yellow band. The eluent was concentrated, and NaPF₆ (0.482 g, 2.87 mmol) in 5 mL of water was added to precipitate a yellow-orange solid. The solid was collected via filtration and recrystallized from acetonitrile via slow diffusion of diethyl ether, yielding yellow crystals (0.144 g, 0.0127 mmol, 24.2% yield for purification). ES-MS (CH₃CN): m/z 1278.17 ([Cr(L3)₂(PF₆)₄]⁻). ES+MS (CH₃CN): m/z 232.71 ([Cr(L3)₂]³⁺), 358.56 ([Cr-(L3) $_{2}F$]²⁺), 735.88 ([Cr(L3) $_{2}F_{2}$]⁺). Anal. Calcd for C₄₄H₃₄N₆CrP₃F₁₈: C, 46.61; H, 3.02; N, 7.41. Calcd for 3.2.5CH₃CN: C, 47.60; H, 3.38; N, 9.63. Found: C, 47.85; H, 3.36; N; 9.46. IR (solid, ATR): $\nu_{Ar,Pv}$ 1618, 1601, 1570, 1548, 1480, 1435, 1407, 1367 cm⁻¹.

 $[Cr(L4)_2](PF_6)_3$ (4). CrCl₂ (0.201g, 1.64 mmol) was dissolved in 25 mL of water and added via cannula to a suspension of L4 (1.19 g, 3.49 mmol) in 50 mL of methanol. The brown-red mixture was stirred at room temperature. After 21 h, air was bubbled through the mixture for 20 min, resulting in an orange-red mixture. The mixture was filtered, and NaPF₆ (0.964 g, 5.84 mmol) was added to the filtrate to precipitate a red-orange solid (0.910 g, 44% yield of crude product). The product was recrystallized three times by vapor diffusion of diethyl ether into a concentrated acetonitrile solution. The resulting red solid was triturated with methylene chloride (10 mL) and recrystallized a fourth time to yield red crystals (0.0448 g, 0.0354 mmol, 2.2% yield). Crystallizations were performed until successive solids gave identical UV-vis absorption spectra. ES-MS (CH₃CN): m/z 1310.18 ([Cr(L4)₂(PF₆)₄]⁻). ES+MS (CH₃CN): m/z 243.37 $([Cr(L4)_2]^{3+})$, 374.56 $([Cr(L4)_2F]^{2+})$, 767.87 $([Cr(L4)_2F_2]^{+})$. Anal. Calcd for $C_{44}H_{34}N_6O_2CrP_3F_{18}$: C, 45.33; H, 2.94; N, 7.21. Calcd for 4-H₂O·2CH₃CN: C, 45.54; H, 3.34; N, 8.85. Found: C, 45.26; H, 3.12; N, 8.61. IR (solid, ATR): $\nu_{Ar,Py}$ 1608, 1590, 1574, 1545, 1525, 1479, 1440, 1419, 1365 cm⁻¹.

 $[Cr(L5)_2](PF_6)_3$ (5). CrCl₂ (0.144 g, 1.17 mmol) was dissolved in 25 mL of water and added via cannula to a suspension of L5 (0.966 g, 2.59 mmol) in 50 mL of methanol. The dark purple-red reaction mixture was stirred at room temperature. After 20 h, air was bubbled through the mixture for 30 min, and the mixture turned green-purple. The mixture was filtered, and NaPF₆ (0.806 g, 4.80 mmol) was added to the filtrate to precipitate the dark product (0.4508 g, 31% yield of crude product). The product was recrystallized twice by vapor diffusion of diethyl ether into a concentrated acetonitrile solution to give a green crystalline powder (0.0917 g, 0.0731 mmol, 6.2% yield). ES-MS (CH₃CN): m/z 1335.80 ([Cr(L5)₂(PF₆)₄]⁻). Anal. Calcd for C₄₆H₄₀N₈CrP₃F₁₈: C, 46.36; H, 3.38; N, 9.40. Calcd for 5·3.5H₂O: C, 44.03; H, 3.78; N, 8.93. Found: C, 43.70; H, 3.41; N, 8.87. IR (solid, ATR): $\nu_{Ar,Py}$ 1607, 1578, 1563, 1539, 1476, 1445, 1420, 1382, 1363 cm⁻¹.

[*Cr*(*L6*)₂](*PF*₆)₃ (6). CrCl₂ (0.114 g, 0.928 mmol) was dissolved in 25 mL of water and added via cannula to a suspension of *L*6 (0.686 g, 1.95 mmol) in 50 mL of methanol. The brown mixture was stirred at room temperature. After 17 h, air was bubbled through the mixture for 30 min with no significant color change. The mixture was filtered, and excess NaPF₆ (0.772 g, 4.60 mmol) was added to the filtrate to precipitate a dark yellow solid (0.500 g, 45.2% crude yield). 0.434 g of the dark yellow solid was recrystallized from acetonitrile/diethyl ether to yield dark red crystals (0.371 g, 0.312 mmol, 85.5% yield for purification steps). ES–MS (CH₃CN): *m*/*z* 1334.26 ([Cr-(L6)₂(PF₆)₄]⁻). ES+MS (CH₃CN): *m*/*z* 251.41 ([Cr(L6)₂]³⁺), 386.61 ([Cr(L6)₂F]²⁺), 791.93 ([Cr(L6)₂F₂]⁺). Anal. Calcd for C₄₈H₄₂N₆CrP₃F₁₈: *C*, 48.45; H, 3.56; N, 7.07. Found *C*, 48.49; H, 3.72; N, 7.34. IR (solid, ATR): $\nu_{Ar,Py}$ 1607, 1570, 1540, 1480, 1449, 1425 cm⁻¹.

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RESULTS AND DISCUSSION

Synthesis and Characterization of Compounds. L1-L6 are known compounds that are typically synthesized via one of two methods: condensation of a substituted benzaldehyde with 2-acetylpyridine in the presence of base in solvent, followed by ring closure using an appropriate nitrogen source, or Suzuki coupling of 4-bromoterpyridine with an appropriate aryl boronic acid.^{59,60,69} We prepared these complexes via a solventless condensation of 2-acetylpyridine and an appropriate benzaldehyde followed by refluxing the resulting 1,5-diketone with ammonium acetate in acetic acid. This method developed by Raston extends the principles of green chemistry to terpyridine synthesis. L1 and L2 have been prepared by this method previously.⁶⁷ For this study we extended this method to prepare L3-L6 via a solventless condensation and subsequent ring closing with ammonium acetate for the first time. Ligands L1-L5 were selected to incorporate a range of electron-donating groups that serve to modulate the energy of the CT transitions in the target chromium complexes; L6 was chosen to prevent planarization between the 4'-aryl ring and the central pyridyl ring. A previous report gives a value of 67.5° for the dihedral angle between the mesityl group and central terpyridine ring in L6 in contrast to 11° for the dihedral angle between the toluyl group and central terpyridine ring in L3.⁶ The lack of planarity between the aryl ring and the central terpyridyl ring should serve to inhibit conjugation between these two moieties in both the ground and excited states.

Cr(III) complexes 1-6 are synthesized via the complexation of arylterpyridyl ligands to a Cr(II) salt in stoichiometric amounts, followed by oxidation in air and a salt metathesis with excess sodium hexafluorophosphate to yield the hexafluorophosphate salts (Scheme 1). Complexes 1-3 have been

Scheme 1. Synthesis of Cr(III) Arylterpyridyl Complexes



synthesized previously, but their photophysical properties have not been fully characterized; 4-6 are novel complexes.^{15,48,56} Purification of these complexes is achieved via column chromatography in the case of 1, column chromatography followed by recrystallization from an acetonitrile–ether solution in the case of 3, and recrystallization from acetonitrile–ether solutions in the cases of 2 and 4-6. The low yields (<40%) for these compounds can be attributed in part to the extensive purification required to obtain samples that are sufficiently pure for emission spectroscopy. In contrast to the bright yellow $[Cr(tpy)_2](PF_6)_3$, these complexes range from orange-yellow, 1–3, to bright orange, 4, to red-orange, 6, to dark green (vivid purple in solution), 5. The purity and identity of these compounds are established via elemental analysis, mass spectrometry, and IR spectroscopy.

Photostability Studies. Cr(III) bis-terpyridyls have been recently shown to undergo both thermal ligand substitution by selected solvents over a period of several hours, and rapid ligand substitution by OH^{-} in aqueous solution at pH >7.^{14,15} We investigated the photostability of $Cr(tpy)_2^{3+}$ to evaluate the potential of Cr(III) bis-terpyridyls as a platform for the design of photostable chromophores. Solutions of $Cr(tpy)_2(PF_6)_3$ or $Cr(bpy)_3(PF_6)_3$ in 1 M HCl were irradiated with UV light (26) W CFL black light bulb, $\lambda_{max} = 370$ nm) over a period of 24 h. The UV-visible absorption spectrum of $Cr(tpy)_2^{3+}$ remained unchanged during 24 h of irradiation, while under the same conditions, $Cr(bpy)_3^{3+}$ was completely consumed (Figure 1). It is worth noting that for $Cr(bpy)_{3}^{3+}$ the Φ for photosubstitution is reported to be 0.007 at this pH.⁷¹ The previously proposed mechanism for the photoaquation of Cr(III) polypyridyls involves an initial coordination of water-likely water that is preorganized in the intraligand pocket-to the Cr center, followed by deprotonation by OH- and subsequent water coordination/loss of the polypyridine ligand. Even the short ${}^{2}E_{\sigma}$ (O_h) lifetime for Cr(tpy)₂³⁺ (~50 ns in 1 M HCl) should be sufficient for the first step to occur efficiently; the short excitedstate lifetime of $Cr(tpy)_2^{3+}$ compared to $Cr(bpy)_3^{3+}$ does not explain the discrepancy in photostability.^{49,71,72} These results suggest that Cr(III) terpyridyls are a promising platform for design of photostable Cr(III) polypyridyl complexes.

Absorption Spectroscopy. The absorption spectrum of $\operatorname{Cr}(\operatorname{tpy})_2^{3^+}$ has been reported previously to exhibit an intense absorption band in acetonitrile at 364 nm ($\varepsilon = 23\,000\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$), with vibrational structure on the blue edge of the band (Figure 2); this band is assigned as a terpyridine-localized $\pi \to \pi^*$ transition, which is singlet with respect to the terpyridine ligand and quartet with respect to the complex, ${}^4[{}^1(\pi \to \pi^*)]$.⁵⁰ Additionally, in the blue region there is a structured feature centered at 443 nm ($\varepsilon = 2540 \,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$). The intensity of this feature is greater than expected for chromium-localized ligand-field transitions, even considering the lack of a center of inversion in $\operatorname{Cr}(\operatorname{tpy})_2^{3^+}$, and has been assigned to a terpyridine-localized ${}^3(\pi \to \pi^*)$ transition coupled with a spin flip in the ${}^4A_{2g}(O_h)$ ground state of $\operatorname{Cr}(\operatorname{III})$, resulting in a quartet excited state, ${}^4[{}^3(\pi \to \pi^*)]$, though this assignment is uncertain.⁵⁷

Previous studies on unligated arylterpyridines assign the lowest energy absorption bands to a $(\pi \rightarrow \pi^*)$ transition within the terpyridine π -system and a ¹CT transition from the aryl π -system to terpyridine π^* -orbitals.⁵⁸ The energy of the ¹CT transition has been shown to be sensitive to the nature of the groups on the aryl substituent, while the energy of the $1(\pi$ $\rightarrow \pi^*$) transition is nearly unperturbed by substitution of the aryl ring. Density functional theory calculations on arylterpyridines indicate that the donor orbitals involved in the ¹CT transitions are delocalized over both the aryl π -system and the substituents on the aryl ring. For arylterpyridines with electronwithdrawing groups or moderately electron-donating groups (such as L1-L3), the lowest energy absorption band has been assigned to the ${}^{1}(\pi \to \pi^{*})$ transition; for arylterpyridines with strongly electron-donating groups (such as L4 and, L5), the order of the ${}^{1}(\pi \rightarrow \pi^{*})$ and ${}^{1}CT$ transitions is inverted, and the



Figure 1. Absorption spectra of $Cr(bpy)_3^{3+}$ (a) and $Cr(tpy)_2^{3+}$ (b) in 1 M HCl after irradiation with a 26 W CFL bulb ($\lambda_{max} = 370$ nm) for 0 h (black), 8 h (red), and 24 h (blue).



Figure 2. Electronic absorption spectra in acetonitrile for Cr- $(tpy)_2(PF_6)_3$ (black), 5 (gray), and 6 (brown).

lowest energy absorption band has been assigned to the ¹CT transition.^{58,60} Additionally, coordination of arylterpyridines to metals (e.g., Cr, Zn, Ru, Ir, Pt) has been reported to lead to substantial red shifts of both the ¹($\pi \rightarrow \pi^*$) and ¹CT bands.^{15,59,61-66} As described in this study, the electronic absorption spectra of **1**–**6** exhibit features characteristic of both Cr(tpy)₂³⁺ and ILCT transitions.

1–5 all display features that are attributed to terpyridinelocalized $\pi \to \pi^*$ and ILCT transitions in acetonitrile. The ⁴[¹($\pi \to \pi^*$)] band appears at $\lambda_{max} = 364 \pm 4$ nm for all compounds studied; this band appears nearly unshifted from the analogous feature in $Cr(tpy)_2^{3+}$ (Table 1). In some cases this band is observed primarily as a shoulder on the edge of an ILCT band (Figure 3). Additionally, a structured ${}^4[{}^3(\pi \to \pi^*)]$



Figure 3. Electronic absorption spectra in acetonitrile for 1 (red), 2 (green), 3 (blue), 4 (purple), and 5 (gray). The arrows mark the location of the ILCT band in each spectrum. Note the shared feature near $\lambda = 363$ nm in all spectra.

band is evident for 1–3 that is nearly unshifted compared with $Cr(tpy)_2^{3+}$. 4 and 5 exhibit intense bands in this region that obscure the ${}^{4}[{}^{3}(\pi \rightarrow \pi^*)]$ band. 1–5 display an additional

Table 1. Electron Absorption Data for Cr(III) Terpyridyl Complexes

	$\lambda_{ m max}/ m nm~(arepsilon/ m M^{-1}~ m cm^{-1})$					
complex	${}^4[{}^1(\pi{ ightarrow}\pi^*)]$	${}^{4}[{}^{3}(\pi \rightarrow \pi^{*})]$	ILCT			
$Cr(tpy)_2^{3+a}$	364 (23 000), 350 (18 700), 326 (12 700), 314 (10 600)	421 (2320), 443 (2540), 473 (1560)				
1 ^{<i>a,b</i>}	365 (35 500)	444 (3210), 471 (1760),	349 (44 200)			
$2^{a,b}$	365 (50 200)	443 (4190), 473 (2080)	353 (51 900)			
3 ^{<i>a,b</i>}	367 (51 800)	441 (5280), 469 (3210)	357 (47 900)			
4 ^{<i>a,b</i>}	366 (35 200), 347 (27 600), 325 (20 400), 313 (20 900)		406 (43 900), 499 (5140)			
5 ^{<i>a</i>}	360 (25 800)		532 (56 500), 691 (13 600)			
6 ^{<i>a</i>}	362 (25 500), 348 (22 300), 325 (15 900), 313 (13 900)	438 (3990), 472 (2150)				
$[Cr(L5-H^+)_2]^{5+c}$	367	444, 472	331			

^{*a*}In acetonitrile. ^{*b*}These spectra exhibit substantial overlap between ($\pi \rightarrow \pi^*$) and ILCT bands. Reported ε values should be understood to arise from a combination of both bands. ^{*c*}In 1 M HCl.

intense band that is not present in $[Cr(tpy)_2]^{3+}$. The location of this band is strongly dependent on the electron-donating nature of the groups on the aryl substituent and exhibits a red shift as the electron-donating ability of these groups increases. It is found at 347 nm in 1 and 532 nm in 5, which is consistent with an assignment of an ILCT transition from the aryl ring to a terpyridyl-localized π^* -orbital. This band is assigned as a ${}^{4}[^{1}\text{ILCT}]$ transition that is singlet with respect to the terpyridine ligand and quartet with respect to the complex. These ${}^{4}[^{1}\text{ILCT}]$ bands are intense with $\varepsilon = 40\,000-56\,000$ M⁻¹ cm⁻¹, though the ${}^{4}[^{1}\text{ILCT}]$ and ${}^{4}[^{1}(\pi \to \pi^*)]$ bands overlap substantially in 1–4 and the contribution to ε from the ${}^{4}[^{1}\text{ILCT}]$ band is lower than these values.

Complexes 1-5 all show enhanced visible absorption compared to $Cr(tpy)_2^{3+}$. In the case of 4 and 5 the visible absorption is greatly enhanced. 4 absorbs visible light with $\varepsilon =$ 11 900 M⁻¹ cm⁻¹ at 450 nm and $\varepsilon = 5090$ M⁻¹ cm⁻¹ at 500 nm, compared to $\varepsilon = 1960$ M⁻¹ cm⁻¹ at 450 nm and $\varepsilon \sim 1000$ M⁻¹ cm⁻¹ at 500 nm for the Cr(III) tris-bipyridyl complex that has the strongest previously reported visible absorption profile.⁶ 5 is a remarkably strong absorber of visible light with $\varepsilon > 7500$ M⁻¹ cm⁻¹ for the entire visible region. However, unlike 4, there is no evidence that the excitation energy in 5 is funneled to the Cr(III) doublet state, ${}^{2}E_{g}$ (O_{h}), vide infra. 1–5 represent a series of Cr(III) arylterpyridyl complexes with intense ILCT absorption bands that are tunable across the near UV to visible region via judicious selection of the substituents on the aryl ring.

The well-resolved absorption features in 5 provide an opportunity to further investigate the assignment of the lowest energy UV and visible bands (Figure 2). 5 displays an absorption band in the UV at 360 nm (ε = 25 800 M⁻¹ cm⁻¹) that is similar in location and intensity to the ${}^{4}[{}^{1}(\pi \rightarrow$ π^*)] band in Cr(tpy)₂³⁺, though any vibrational structure on the blue edge of the band is obscured by an intense feature that we cannot definitively assign.⁷³ Two broad bands at 532 nm (ε = 56 500 M⁻¹ cm⁻¹) and 689 nm (ε = 13 700 M⁻¹ cm⁻¹) dominate the visible region. The higher energy band is assigned to a ⁴[¹ILCT] transition. Possible assignments for the lowest energy band include vibrational progression within the ⁴[¹ILCT] transition and a triplet ILCT transition that is coupled to a spin flip in the Cr(III) quartet state, ⁴[³ILCT], analogous to the ${}^{4}[3(\pi \rightarrow \pi^{*})]$ band in $Cr(tpy)_{2}^{3+}$. The relatively large energy difference between these bands (4300 cm⁻¹) suggests a ⁴[³ILCT] assignment over vibrational progression. An analogous band is observed at 499 nm for 4, and a similar feature may in fact be present in all the arylterpyridyl chromium complexes studied, but the congested nature of the absorption spectra of 1-3 prevents definitive identification of this feature.

The ⁴[¹ILCT] assignment for the feature at 532 nm in acetonitrile in **5** can be further confirmed by investigating it both in other solvents and upon protonation. The ⁴[¹ILCT] band in **5** shows a weak, negative solvatochromism, though solvents with protic hydrogens are notably out of order, presumably due to the effect of hydrogen bonding with the amino group (Figure S2). Weak solvatochromism is consistent with previous studies on ILCT bands in homoleptic arylterpyridyl Ir(III) complexes.⁶² Due to the limited solubility of **5** in the solvents used, it is difficult to make definitive statements about the solvatochromism of the band near 690 nm. Protonation of the amino groups in **5** forms [Cr(L5-

 $H^+)_2]^{5+}$, which contains the strongly electron-withdrawing $-NMe_2H^+$ in place of the strongly electron-donating $-NMe_2$. The ⁴[¹ILCT] band for $[Cr(L5-H^+)_2]^{5+}$ in 1 M HCl shows a large blue shift from 532 to 331 nm compared with 5 in water



Figure 4. Electronic absorption spectra for 5 in water (gray) and 1 M HCl (black).

(Figure 4). This band is higher in energy than any of the ⁴[¹ILCT] bands in 1–4, consistent with the strongly electronwithdrawing ability of $-NMe_2H^+$. This significant blue shift upon protonation is consistent with the aryl-ring-to-terpyridyl- π^* -system character of the ILCT transition, with substantial electron delocalization over the aryl π -system and the dimethylamino substituent. $[Cr(L5-H^+)_2]^{5+}$ also displays a ${}^{4}[{}^{1}(\pi \to \pi^{*})]$ band at 367 nm and a structured ${}^{4}[{}^{3}(\pi \to \pi^{*})]$ band in the blue region, similar to those observed in $Cr(tpy)_{2}^{3+}$. Upon addition of NaOH to $[Cr(L5-H^+)_2]^{5+}$ in 1 M HCl, the ${}^{4}[^{1}ILCT]$ band at 331 nm decreases in intensity and the ⁴[¹ILCT] band from **5** at 530 nm grows with increasing pH. Basic pH results in the decomposition of 5, as reported previously for Cr(III) terpyridyls (Figure S3).¹⁴ The significant blue-shift of the ${}^{4}[{}^{1}ILCT]$ band for $[Cr(L5-H^{+})_{2}]^{5+}$ containing strongly electron-withdrawing groups-in 1 M HCl compared to 5-containing strongly electron-donating groups—in water further confirms the ⁴[¹ILCT] assignment.

The electronic absorption spectrum of **6** is striking in its similarity to that of $Cr(tpy)_2^{3+}$ (Figure 2). The absorption features for $Cr(tpy)_2^{3+}$ and **6** at wavelengths longer than 300 nm occur with λ_{max} within 2 nm of each other, and ε values are 10–20% higher for **6**. **6** lacks a defined ILCT transition in this region, suggesting that substantial mixing between the aryl and the terpyridyl π -systems is necessary for low energy ILCT transitions. However, the ${}^{4}[{}^{1}(\pi \rightarrow \pi^{*})]$ transition is left unaffected by this mixing. This provides additional insight into strategies to design Cr(III) polypyridyl complexes with desired absorption properties.

Emission Spectroscopy. The emission spectra of Cr(III) tris-bipyridyl complexes are well-known and consist of a sharp emission feature assigned to a ${}^{2}E_{g} \rightarrow {}^{4}A_{2g}(O_{h})$ transition and a broader, less intense feature to the blue assigned to a ${}^{2}T_{1g} \rightarrow {}^{4}A_{2g}$ transition (O_{h}) ; these features are commonly referred to in octahedral symmetry $(O_{h} \text{ or } O)$, though D_{3} is a more appropriate descriptor of the symmetry of these compounds.^{6,50} Many fewer examples of Cr(III) bis-terpyridyl complexes exist. The reduced symmetry of Cr(III) bisterpyridyl complexes may be expected to significantly alter the excited state manifold with respect to Cr(III) tris-bipyridyl

complexes. In D_{2d} symmetry the ²E_g (O_h) state splits into a pair of singly degenerate states, ²A₁ (D_{2d}) and ²B₁ (D_{2d}), while the ²T_{1g} (O_h) state splits into ²A₂ (D_{2d}) and ²E (D_{2d}) states. Fluorescence line-narrowing spectroscopy has previously been used to find a value of ~23 cm⁻¹ for the splitting between the ²A₁ (D_{2d}) and ²B₁ (D_{2d}) excited states for Cr(tpy)₂^{3+,74} The splitting of the ²T_{1g} (O_h) state for Cr(tpy)₂^{3+ in} D_{2d} symmetry is expected to be greater than the ~23 cm⁻¹ splitting of the ²E_g (O_h) state. In a previous study on *trans*-CrN₄X₂ complexes, where N is an amine or pyridine, the ²T_{1g} (O_h) state splits into two states. The magnitude of this splitting is large enough when X = F⁻ that one of the doublet states of ²T_{1g} (O_h) parentage.⁷⁵ In all of the complexes studied here, a ²E_g (O_h) band is the lowest energy feature observed in the emission spectra and there is at most one discernible ²T_{1g} (O_h) band, *vide infra*. Due to the similarity to Cr(III) tris-bipyridyl complexes, state labels from O_h symmetry are appropriate to approximate the doublet excited states for Cr(tpy)₂³⁺ and **1**-6.

Emission spectra were obtained upon excitation of acetonitrile solutions of 1–5 at λ_{max} of the ⁴[¹ILCT] band and of 6 at λ_{max} of the ⁴[¹($\pi \rightarrow \pi^*$)] band (see Table 1 for λ_{max} of ⁴[¹ILCT] and ⁴[¹($\pi \rightarrow \pi^*$)] bands). Complexes 1–4 and 6 each display a sharp emission feature with λ_{max} between 776 and 796 nm; 1–4 also display a weak shoulder on the blue edge of this band at ~750 nm (Figure 5).⁷⁶ Complex 5 is



Figure 5. (top) Relative emission spectra for $Cr(tpy)_2^{3+}$ (black), **1** (red), **2** (green), **3** (blue), and **6** (brown) in acetonitrile under N₂ and (bottom) emission spectrum for **4** (purple) in acetonitrile under N₂. λ_{ex} for **1**-**4** is the absorbance maximum for the ILCT band (Table 1); λ_{ex} for **6** is 363 nm.

nonemissive. The shapes of emission bands and shoulders found in 1–4 and 6 are similar to those found for Cr(III) trisbipyridyl complexes. The sharp, prominent features in 1–4 and 6 are assigned to the ${}^{2}E_{g} \rightarrow {}^{4}A_{2g}$ (O_{h}) Cr(III) ligand-field transitions, and the broader shoulders near 750 nm in 1–4 are assigned to the ${}^{2}T_{1g} \rightarrow {}^{4}A_{2g}$ (O_{h}) ligand-field transitions. In the case of 1–4, an alternative assignment for the shoulder near 750 nm is emission from one component of the split ${}^{2}T_{1g}$ (O_{h})

state with emission from the other component obscured under the ${}^{2}E_{e}$ (O_{h}) emission.

In addition to these sharp features, the emission spectrum of 4 exhibits a broad band centered at ~725 nm. No other complex studied exhibits a similar feature in this wavelength range. The excitation spectrum for emission from 4 at 670 nm reveals peaks at the same wavelengths as those found in the absorption spectrum. However, the intensity of the 4 [$^{1}(\pi \rightarrow$ π^*) band in the excitation spectrum is enhanced with respect to those from ILCT transitions (Figure S4). The broad emission profile of this band suggests that it arises from a ligand-localized transition. Additionally, this feature exhibits an emission lifetime of ≤ 250 ps, vide infra, which suggests fluorescence versus phosphorescence. One possible assignment for this emission is fluorescence from the ${}^{4}[^{1}ILCT]$ state. If this assignment is correct, it represents a Stokes shift of ~10 000 cm⁻¹. The observed Stokes shift for L5 fluorescence has been reported as 8300 cm⁻¹ in CH₂Cl₂; Stokes shifts as large as 11 000 cm⁻¹ have been previously reported for CT fluorescence in unligated 4'-arylterpyridines.58,60

Two additional aspects of the ${}^{2}E_{g}\left(O_{h}\right)$ phosphorescence in 1-4 and 6 bear noting. First, the sole previous investigation of the room temperature steady-state emission of $Cr(tpy)_2^{3+}$ reports ${}^{2}T_{1g}(O_{h})$ emission at 710 nm (in 1 M HCl) and a ${}^{2}E_{g}-{}^{2}T_{1g}(O_{h})$ energy gap of ~1100 cm⁻¹ compared to ~600 cm⁻¹ for Cr(III) bipyridyls.⁵⁰ We do not observe ${}^{2}T_{1g}$ emission from acetonitrile solutions of either $Cr(tpy)_2^{3+}$ or 6 (Figure 5). Curiously, we do observe ${}^{2}T_{1g}$ (O_{h}) emission for the Cr(III) arylterpyridyl complexes 1-4, with an energy difference between the ${}^{2}E_{g}(O_{h})$ and ${}^{2}T_{1g}(O_{h})$ features of ~600 cm⁻¹. We do not currently have an explanation as to why $Cr(tpy)_2^{3+}$ and 6 do not display ${}^{2}T_{1g}$ (O_{h}) emission. Second, the phosphorescence of 1–4 and 6 is red-shifted compared to $Cr(tpy)_{2}^{3+}$ and the magnitude of this red shift depends on the substitution on the aryl ring. These red shifts of up to 26 nm are large compared to the red shifts observed for arylsubstitution on Cr(III) tris-bipyridyls. This is mildly surprising considering the t_{2g}^{3} electron configuration of both the ${}^{2}E_{g}(O_{h})$ excited state and the ${}^{4}A_{2g}(O_{h})$ ground state. One possible explanation has been offered previously for the red-shifted ${}^{2}E_{g}$ emission in a Cr(III) complex with a phenyl-substituted phenanthroline ligand. In that case, the authors suggested that spin-pairing effects between electrons in individual metal orbitals become less significant as the electron delocalization is increased upon extension of the aromatic system.⁶ The emission in $Cr(tpy)_2^{3+}$ is already red-shifted 42 nm from that of $Cr(bpy)_2^{3+}$, which would imply greater t_{2g} electron delocalization in $Cr(tpy)_2^{3+}$ compared to $Cr(bpy)_3^{3+,50}$ Aryl substitution in 1-4 leads to a significant red shift from $Cr(tpy)_2^{3+}$ emission. This red shift increases with an increase in the electron-donating ability of the aryl substituents (Table 2). It is curious that 1 and 2 emit at the same wavelength, though 2 contains electron-donating Br substituents. The origin of this red shift upon increased conjugation is in need of further study. In comparison, the emission from 6—containing electronically isolated mesityl groups-is red-shifted by only 6 nm from $Cr(tpy)_2^{3+}$. Therefore, the Cr(III) terpyridyl platform may be a useful one for the tuning of primarily Cr(III)-based excited states via ligand modification utilizing both steric and electronic effects.

The energy of the ${}^{2}E_{g}(O_{h})$ excited state, E_{00} , is approximated by λ_{em} . This approximation is valid due to the shared t_{2g}^{3} electronic configuration between the ${}^{2}E_{g}(O_{h})$ excited state and

Table 2. Electrochemical and Emission Data for Cr(III) Complexes

	emission data				electrochemical data ^{a,b}			
complex	$\lambda_{ m em}/ m nm$	E_{00}/eV^c	rel em ^d	τ/ns^e	$E_{1/2}^{3+/2+}/V$	$E_{1/2}^{2+/1+}/V$	$E_{1/2}^{1+/0}/V$	$E_{1/2}^{3+*/2+}/V^{f}$
$Cr(tpy)_2^{3+}$	770	1.61	1.0	140	-0.53	-0.94	-1.44	1.08
1	785	1.58	2.6	280	-0.55	-0.92	-1.42	1.03
2	785	1.58	1.9	300	-0.54	-0.89	-1.42^{g}	1.04
3	788	1.57	2.8	400	-0.60	-0.95	-1.44^{g}	0.97
4	796	1.56	4.3	600 ^h	-0.61	-0.98	-1.45	0.95
5					-0.69	-1.03	-1.46	
6	776	1.60	0.8	140 ^h	-0.59	-0.98	-1.48	1.01

^aPotentials reported vs Fc/Fc⁺. ^bMeasurements conducted at room temperature with 0.1 M [NBu₄][PF₆] in acetonitrile. ^cE₀₀ is estimated from the emission energy. ${}^{d}\lambda_{ex}$ is ILCT absorption maximum for 1-4; λ_{ex} is ${}^{4}[{}^{1}(\pi \to \pi^{*})]$ absorption maximum for 6; relative emission intensity vs $Cr(typ)_{2}(PF_{6})_{3}$ in acctonitrile with matching $\lambda_{ex} {}^{e}\pm 5\%$. ${}^{f}Calculated$ from eq 1. ${}^{g}Limited$ solubility in the electrolyte solution for electrochemical experiments resulted in larger than expected ΔE_{o} values for the third reduction wave. ^hThis value represents the long-lived component. An additional component with a τ < 250 ps is observed for these complexes.

the ${}^{4}A_{2g}(O_h)$ ground state, and the sharp profile of ${}^{2}E_{g}(O_h)$ emission. 24,50 Previous calculations of E_{00} , using the energy and bandwidth of emission from Cr(III) bipyridyl complexes, yield a E_{00} that differs at most by 0.01 eV from the value estimated using the emission energy alone.⁶ For the complexes in this study, E_{00} is found to be between 1.56 and 1.60 eV compared to 1.61 eV in $Cr(tpy)_2^{3+}$ (Table 2).

Previous reports reveal that $Cr(tpy)_2^{3+}$ is weakly emissive in room temperature solution ($\phi \sim 10^{-5}$ in 1 M HCl).⁷⁷ We report the relative phosphorescence intensity of complexes 1-4 and 6 compared to $Cr(tpy)_2^{3+}$ (Table 2). To isolate the intensity of the phosphorescence from emission of the broad feature centered at ~725 nm in 4, vide supra, we fit the blue edge of the broad emission to a Gaussian function and subtracted this function from the overall emission band (Figure S1). The emission from 6 is slightly weaker than that from $Cr(tpy)_2^{3+}$. 1–4 are stronger emitters than $Cr(tpy)_2^{3+}$. This further indicates migration of the excitation energy from the arylterpyridine-localized ⁴[¹ILCT] state to the emissive, Cr-(III)-based ²E state. The excitation spectrum of 4 in acetonitrile overlays the absorption spectrum at $\lambda > 400$ nm (Figure S4), confirming that excitation into both ILCT features leads to population of the ${}^{2}E_{g}$ (O_{h}) excited state. Complexes 1-4 demonstrate that judicious modification of ligands in Cr(III) complexes is capable of introducing strongly absorbing ILCT states that funnel excitation energy into the Cr(III) localized ${}^{2}\mathrm{E}_{\mathrm{g}}(O_{h})$ state.

Time-resolved emission measurements for $Cr(tpy)_{2}^{3+}$ and 1–3 (monitored at λ_{em} from Table 2) exhibit single exponential decays with lifetimes in the hundreds of nanoseconds, while 4 and 6 (monitored at λ_{em} from Table 2) each exhibit a fast component (at least as fast as the instrument response function; $\tau \leq 250$ ps) in addition to a long-lived component with a lifetime in the hundreds of nanoseconds (Figure S5). The emission of 4 monitored at 675 nm-where only the broad feature emits, vide supra-also decays with the instrument response function yielding an emission lifetime of \leq 250 ps; the two-component decay of 4 upon monitoring at 796 nm is likely due to overlapping emission from both the phosphorescence bands and the tail of a broad feature to the blue of the phosphorescence. The sub-nanosecond lifetime for the fast component in 4 is shorter than expected for ${}^{2}E_{\sigma}(O_{h})$ phosphorescence and likely originates from a quenched fluorescence pathway. The longer-lived component is consistent with ${}^{2}E_{g}(O_{h})$ phosphorescence.

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The emission lifetimes of complexes 1-4 are all longer than the emission lifetime for $Cr(tpy)_2^{3+}$, and they increase with an increase in the electron-donating ability of aryl substituents, ranging from 280 to 600 ns (Table 2). Curiously, this increase in emission lifetime is accompanied by a decrease in emission energy, which is contrary to what is expected from the energy gap law. By contrast, the emission lifetime of 6 was found to be the same as that of $Cr(tpy)_2^{3+}$. One possible explanation is that increased electron delocalization onto the arylterpyridyl ligands in the ${}^{2}E_{g}(O_{h})$ excited state leads to elongation of the emission lifetime. Particularly noteworthy is the 600 ns emission lifetime of 4. While this lifetime is shorter than the $\sim 1-700 \ \mu s$ emission lifetimes typical of Cr(III) bipyridyls, it is on the order of lifetimes exhibited by Ru and Ir chromophores.^{4,6,24,34,35} As such, 4 has an excited-state lifetime that is sufficiently long for use as a photoredox sensitizer.

Electrochemistry. The cyclic voltammograms of 1-6 each exhibit at least three reversible reduction waves within the solvent window (Figures S6 and S7). These waves are assigned to successive reductions into terpyridine-localized π^* -orbitals, as has been found previously for $Cr(tpy)_2^{3+11}$ The cyclic voltammogram of 5 exhibits an additional reversible oxidation wave at +0.69 V vs Fc/Fc⁺ that is presumably due to oxidation of the dimethylamino group, analogous to a similar feature found previously for the diphenylamino analogue.¹⁵ No oxidative features were observed for 1-4 or 6. The first reduction shifts to negative potentials as the substituents on the aryl ring become more electron-donating (Table 2). This shift is less pronounced for the second reduction and is nearly absent for the third reduction. The presence of o-methyls on the mesityl ring in 6 has no notable effect on the first reduction potential in comparison to 3, which contains a toluyl ring. This suggests that the shift to negative potentials for the first reduction is due more to inductive effects than to mixing between the terpyridyl and aryl π systems. These results are consistent with previous studies on Pt(4'-Ar-tpy)Cl⁺ and Ir(4'- $Ar-tpy)_2^{3+}$ complexes, which show that aryl substitution has a small effect on terpyridine-localized reduction potentials.^{61,78}

The excited-state reduction potential, $E_{1/2}^{3+\frac{3}{2}/2+}$, for Cr(III) complexes can be calculated according to eq 2, using the first reduction potential for the ground state, $E_{1/2}^{3+/2+}$, and the energy of the excited state, E_{00} :

$$E_{1/2}^{3+*/2+} = E_{00} + E_{1/2}^{3+/2+}$$
(2)

 $E_{1/2}^{3+/2+}$ and E_{00} both decrease as the substituents on the aryl ring increase in electron-donating ability. These two effects combine to lower $E_{1/2}^{3+*/2+}$; the effects are relatively small in the series studied, contributing to a decrease in $E_{1/2}^{3+*/2+}$ for 4 by 0.13 V compared to $Cr(tpy)_2^{3+}$.

CONCLUSIONS

We have synthesized and characterized a series of Cr(III) arylterpyridines with intensely absorbing ILCT transitions. The location of the ILCT bands in the absorption spectra of these complexes is tunable via judicious selection of the substituents on the aryl ring. The ILCT bands are found in the visible region when strongly electron-donating substituents are used; this is most pronounced in **5**, which absorbs strongly across the entire visible region. The absorption properties of this series of chromophores represent a marked improvement over previously reported Cr(III) polypyridines and validate the strategy of incorporating visible-absorbing, ligand-localized excited states to improve the absorption characteristics of Cr(III) complexes.

Most of the Cr(III) arylterpyridines studied exhibit Cr(III)localized ${}^{2}E_{g}$ (O_{h}) phosphorescence upon excitation into the terpyridine-localized ILCT bands. This demonstrates the ability of Cr(III) bis-arylterpyridyl complexes to funnel excitation energy from ligand-localized excited states into Cr(III)-based excited states. These complexes emit with larger emission quantum yields and longer excited-state lifetimes than Cr-(tpy)₂³⁺. This is most pronounced in 4, which absorbs strongly in the blue with significant visible absorption that extends to 560 nm. Excitation of 4 leads to ${}^{2}E_{g}$ (O_{h}) phosphorescence with a lifetime of 600 ns and an excited-state reduction potential of +0.95 V vs Fc/Fc⁺. 4 is an example of the promise of using ligand-localized absorptions in the visible region to generate photooxidizing excited states in Cr(III) polypyridyl complexes.

Additionally, we report enhanced photostability of $Cr(tpy)_2^{3+}$ compared to $Cr(bpy)_3^{3+}$ in 1 M HCl. In light of this photostability and the excited-state properties discussed above, Cr(III) terpyridyl complexes are worth consideration as candidates for use in solar energy harvesting schemes and photoredox catalysis. These complexes are potent excited-state oxidants with excited-state reduction potentials up to +1.04 V vs Fc/Fc⁺, excited-state lifetimes up to 600 ns, and moderate to strong absorption bands in the visible region of the solar spectrum. Further challenges facing these complexes include addressing their surprising thermal lability and further extending their excited-state lifetimes. Considering the low cost and high abundance of chromium compared to metals in the second and third transition series, these complexes are worthy of further study.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b00953.

Cyclic voltammograms of $Cr(tpy)_2^{3+}$ and **1–6**, absorption spectra of **5**, time-resolved emission decay traces, and emission and excitation spectrum of **4** (PDF)

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Notes

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