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Derivatization of Bichromic Cyclometalated Ru(II) Complexes with Hydrophobic Substituents

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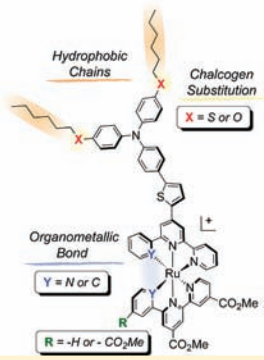
S *Supporting Information*

ABSTRACT: The syntheses and physical properties of cyclometalated Ru(II) complexes containing a triphenylamine (TPA) unit bearing aliphatic groups are reported. Each member of the series consists of an octahedral Ru(II) center coordinated by a tridentate polypyridyl ligand and a tridentate cyclometalating ligand. One of the chelating ligands contains electron-deficient methyl ester groups, while a TPA unit is attached to the central ring of the adjacent chelating ligand through a thiophene bridge. This study builds on our previous work (*Inorg. Chem.* **2011**, 50, 6019−6028; *Inorg. Chem.* **2011**, *50*, 5494−5508) by (i) outlining a synthetic protocol for installing aliphatic groups on the TPA substituents, (ii) examining the role that terminal −O-hexyl and −S-hexyl groups situated on the TPA have on the electrochemical properties, and (iii) demonstrating the potential benefit of installing the TPA on the *neutral* chelating ligand rather than the *anionic* chelating ligand. The results reported herein provide important synthetic advances for our broader goal of developing bis-tridentate cyclometalated Ru(II) complexes for light-harvesting applications.



■ INTRODUCTION

There has been a recent renaissance in the design and study of cyclometalated Ru(II) complexes in light of their proven utility in solar energy conversion schemes[1−7] and biological applications.[8−10] This interest is rooted in the broad absorption profiles and well-defined redox behavior stabilities for this class of compounds.[11−17] Moreover, the presence of a single anionic cyclometalating ligand about an octahedral Ru center that is coordinatively saturated by neutral polypyridal ligands induces an electronic asymmetry that offers acute control of the frontier molecular orbitals.[2,18] Consequently, the thermodynamic positions of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) can be easily modulated through judicious installation of substituents on the anionic and neutral ligands, respectively.[19] While this chemical control of the physicochemical properties translates to other metals,[20,21] it has proven to be particularly useful in developing Ru-based dyes that are capable of generating high power conversion efficiencies in the dye-sensitized solar cell[22] (DSSC).[1−3,523]

Bis-tridentate Ru(II) complexes bearing a cyclometalating ligand (e.g., pbpy = 6-phenyl-2,2′-bipyridine) have a rich history in the literature that extends back to the early work of Constable et al.[24] and Sauvage et al.[25] We recently added to this catalogue a series of cyclometalated Ru(II) complexes bearing triphenylamine (TPA) units (e.g., Figure 1d) to augment light absorption and enhance excited-state charge separation.[7,26,27] While these features had been previously observed for polypyridyl Ru(II) architectures,[28−31] the optical properties and thermodynamic energy levels of the frontier molecular orbitals of the cyclometalated derivatives are better positioned for sensitizing TiO_2.[7] Indeed, the high performance of these dyes in the DSSC was made possible by recognizing that the TPA and metal act as electrochemically isolated units in the ground state, thus enabling a desirable energy level gradient where the HOMO is confined to the TPA unit.

These promising results provided the impetus to further develop the chemistry of the TPA-substituted platform highlighted in Figure 1d. We therefore set out to investigate the syntheses and properties of complexes containing alkyl substituents on the TPA groups (**2**−**5**; Chart 1) in accordance with a well-documented approach for improving the power output and stability of the DSSC that involves placing hydrophobic groups on one of the bidentate polypyridyl ligands (Figure 1a and 1b).[34,35] The purported sensitivity of dye regeneration by electrolytes to chalcogenides on the metal complex also prompted us to develop a series where thiolates and alkoxy groups are positioned about the TPA unit.[36] This article also addresses how the position of the anionic ring relative to the TPA unit (e.g., **2** vs **4**; Chart 1) affects the optical and electrochemical properties. The syntheses and physical properties of these complexes are described herein and set the stage for studying the light-absorption and charge-separation events of bichromic cyclometalated complexes in future studies.

■ EXPERIMENTAL SECTION

Physical Methods. Elemental analysis (EA), electrospray ionization mass spectrometry (ESI-MS), and electron impact (EI) mass spectrometry data were collected at the Chemistry Instrumentation Facility of the University of Calgary. Electrochemical measurements were performed under anaerobic conditions with a Princeton Applied Research VersaStat 3 potentiostat using dry solvents, a glassy carbon

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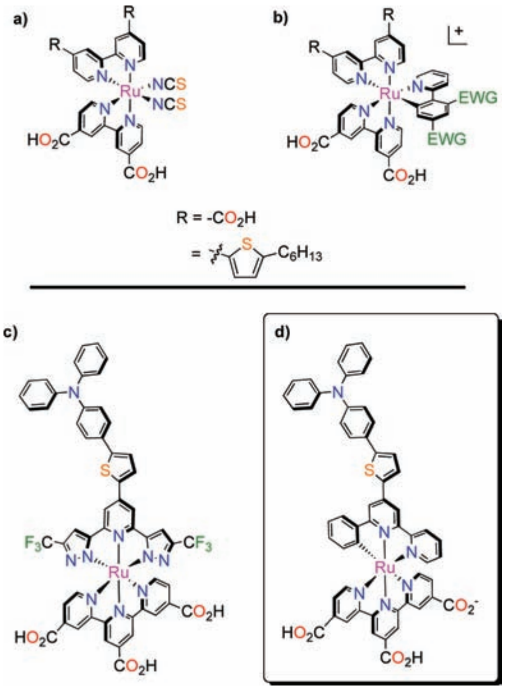


Figure 1. Listing of representative high-performance DSSC dyes that contain anionic (a) monodentate,[32,33] (b) bidentate,[1] and (c, d) tridentate ligands.[7,23] A common approach for improving the performance of bidentate Ru-based dyestuff in the DSSC is to install alkylated thiophenes at the R site.[34] The bichromic scaffold that serves as the foundation of this study is highlighted by the enclosure.[7,26]

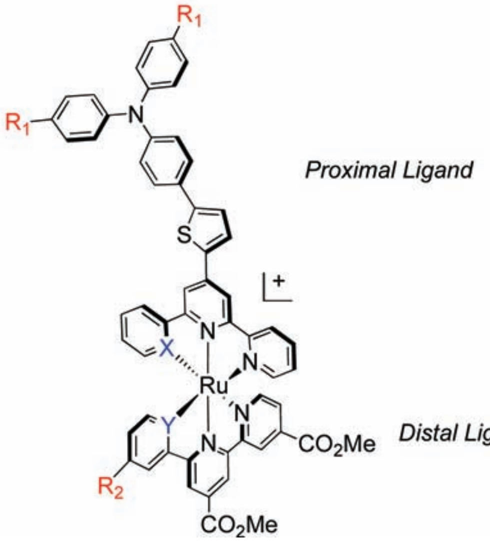
working electrodes, a Pt wire counter electrode, a Ag pseudoreference electrode, and 0.1 M NBu_4BF_4 MeCN supporting electrolyte solutions. Electronic spectroscopic data were collected on MeCN solutions collected using a Cary 5000 UV−vis spectrophotometer (Varian). Routine ^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively, on a Bruker AV 400 instrument at ambient temperature. Chemical shifts (δ) are reported in parts per million (ppm) from low to high field and referenced to residual nondeuterated solvent. Standard abbreviations indicating multiplicity are used as follows: s = singlet; d = doublet; t = triplet; m = multiplet. All proton assignments correspond to the generic molecular schemes that are provided (Figure 2).

Preparation of Compounds. All reactions and manipulations were performed using solvents passed through an MBraun solvent purification system prior to use. All reagents were purchased from Aldrich and used without further purification except for $RuCl_3{\cdot}3H_2O$ (Pressure Chemical Company) and trimethyl-4,4′,4″-tricarboxylate-2,2′:6′,2″-terpyridine (Me$_3$tctpy (**L6**); Helio Chemical Co., Switzerland). Purification by column chromatography was carried out using silica (Silicycle, Ultrapure Flash Silica). Analytical thin-layer chromatography (TLC) was performed on aluminum-backed sheets precoated with silica 60 F254 adsorbent (0.25 mm thick; Merck, Germany) and visualized under UV light. Organic and inorganic compounds 4-(hexyloxy)-*N*-(4-(hexyloxy)phenyl)-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (**P1**),[37] 4′-(5-bromo-2-thienyl)-2,2′:6′,2″-terpyridine (**P3**),[38] 4-(5-bromothiophen-2-yl)-6-phenyl-2,2′-bipyridine (**P4**),[26] dimethyl 6-phenyl-2,2′-bipyridine-4,4′-dicarboxylate (**L7H**),[5] Ru(**P3**)Cl$_3$,[38] Ru(**L6**)Cl$_3$,[39] and **1**[7] were prepared according to literature procedures. The experimental procedures for preparation of 4-(hexylthio)-*N*-(4-(hexylthio)phenyl)-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (**P2**) and its precursors (**P2b** and **P2bc**) and the ligands **L2H**−**L4H** are provided as Supporting Information.

[Ru(P4)(L6)]NO$_3$ (C1). A 250-mL round-bottom flask (RBF) containing Ru(**L6**)Cl$_3$ (0.200 g, 0.33 mmol) and 4-(5-bromothiophen-2-yl)-6-phenyl-2,2′-bipyridine (**P4**) (0.141 g, 0.36 mmol) was charged with a 120 mL of MeOH/H$_2$O (5:1 v/v) solution containing 0.5 mL of *n*-ethylmorpholine and then left at reflux for 14 h. After the reaction was cooled, AgNO$_3$ (0.166 g, 0.98 mmol) was added and the reaction mixture was set to reflux for an additional 2 h. The hot solution was filtered, and the solvent was removed in vacuo. The residue was purified by column chromatography [SiO$_2$, acetone/MeOH, 8:1; R_f = 0.50] to yield 0.252 g (80.6%) of the product as a dark black microcrystalline solid. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 9.13 (s, 2H,

Chart 1. Designation of Complexes and Ligands[a]

Complex	Proximal Ligand			Distal Ligand		
	Ligand	X	-R$_1$	Ligand	Y	-R$_2$
1	**L1**	-C	-OMe	**L6**	-N	-CO$_2$Me
2	**L2**	-C	-O-hexyl	**L6**	-N	-CO$_2$Me
3	**L3**	-C	-S-hexyl	**L6**	-N	-CO$_2$Me
4	**L4**	-N	-O-hexyl	**L7**	-C	-H
5	**L5**	-N	-S-hexyl	**L7**	-C	-H



[a] Counterion = NO$_3^-$ for **1** and **2** and HCO$_3^-$ for **3**−**5**. Proximal and distal are relative to the TPA unit.

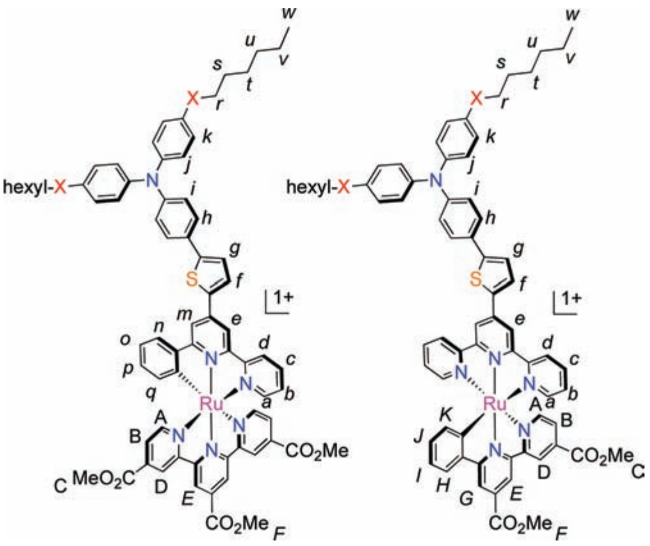


Figure 2. Generic labeling scheme for ^{1}H NMR signal assignments.

H_E), 9.07 (d, 1H, ^3J = 7.9 Hz, H_d), 9.03 (s, 1H, H_e), 8.90 (d, 2H, ^4J = 1.7 Hz, H_D), 8.09 (d, 1H, ^4J = 1.4 Hz, H_m), 8.07 (d, 1H, ^3J = 3.9 Hz, H_f), 7.93 (t, 1H, ^3J = 6.4 Hz, H_c), 7.74 (d, 1H, ^3J = 7.8 Hz, H_n), 7.72 (d, 2H, ^3J = 5.9 Hz, H_A), 7.65 (d, 2H, ^3J = 5.9 Hz, H_B), 7.28 (d, 1H, ^3J = 4.0 Hz, H_g), 7.15 (d, 1H, ^3J = 5.1 Hz, H_a), 7.02 (ddd, 1H, ^3J = 7.4, ^3J = 5.4, ^4J = 0.9 Hz, H_b), 6.67 (t, 1H, ^3J = 7.5 Hz, H_o), 6.46 (t, 1H, ^3J = 7.4 Hz, H_p), 5.34 (d, 1H, ^3J = 7.5 Hz, H_q), 4.20 (s, 3H, H_F), 3.94 (s, 6H, H_C). HRMS (ESI): m/z = 894.0083 [(M)$^+$] (calcd for $C_{41}H_{29}N_5O_6RuS^+$, m/z = 894.0098). Anal. Calcd for $C_{41}H_{29}N_6O_9RuS \cdot 2H_2O$: C, 49.41; H, 3.33; N, 8.41. Found: C, 49.80; H, 3.29; N, 8.09.

[Ru(L2)(L6)]NO$_3$ (2). To a 100-mL RBF containing **C1** (0.160 g, 0.17 mmol) and 4-(hexyloxy)-*N*-(4-(hexyloxy)phenyl)-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (**P1**) (0.100 g, 0.17 mmol) was added 25 mL of anhydrous DMF. After the mixture was sparged with N_2 for 20 min, K_2CO_3 (0.230 g, 1.66 mmol) and Pd(PPh$_3$)$_4$ (0.020 g, 0.02 mmol) were added and left to stir for 20 h at 70 °C. The solvent was removed in vacuo, leaving a residue that was dissolved in CH_2Cl_2. The white precipitate (K_2CO_3) was removed by filtration, and the solvent was removed in vacuo. The residue was purified by column chromatography [SiO$_2$, acetone/MeOH, 8:1; R_f = 0.35] to yield 0.173 g (78.4%) of the product as a dark black microcrystalline solid. The yield was decreased due to formation of the saponified product, [Ru(**L2**)(Me$_2$tctpy)], (Me$_2$tctpy = dimethyl-4,4′,4″-tricarboxylate-2,2′:6′,2″-terpyridine). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 9.13 (s, 2H, H_E), 8.99 (d, 1H, ^3J = 8.2 Hz, H_d), 8.96 (s, 1H, H_e), 8.91 (s, 2H, H_D), 8.21 (s, 1H, H_m), 8.17 (d, 1H, ^3J = 3.9 Hz, H_f), 7.97 (t, 1H, ^3J = 7.0 Hz, H_c), 7.78 (d, 1H, ^3J = 7.9 Hz, H_n), 7.73 (d, 2H, ^3J = 5.9 Hz, H_A), 7.65 (dd, 2H, ^3J = 5.9, ^4J = 1.6 Hz, H_B), 7.51 (d, 2H, ^3J = 8.7 Hz, H_h), 7.40 (d, 1H, ^3J = 3.9 Hz, H_g), 7.19 (d, 1H, ^3J = 5.4 Hz, H_a), 7.08 (d, 4H, ^3J = 8.8 Hz, H_j), 7.05 (t, 1H, ^3J = 6.4 Hz, H_b), 6.95 (d, 2H, ^3J = 8.7 Hz, H_i), 6.85 (d, 4H, ^3J = 8.9 Hz, H_k), 6.77 (t, 1H, ^3J = 7.7 Hz, H_o), 6.46 (t, 1H, ^3J = 7.5 Hz, H_p), 5.34 (d, 1H, ^3J = 7.5 Hz, H_q), 4.20 (s, 3H, H_F), 3.95 (s, 6H, H_C), 3.94 (t, 4H, ^3J = 6.6 Hz, H_r), 1.81–1.74 (m, 4H, H_s), 1.50–1.42 (m, 4H, H_t), 1.36–1.32 (m, 8H, H_u, H_v), 0.90 (t, 6H, ^3J = 7.0 Hz, H_w). HRMS (ESI): m/z = 1265.3768 [(M)$^+$] (calcd for $C_{71}H_{67}N_6O_8RuS^+$, m/z = 1265.3798). Anal. Calcd for $C_{71}H_{67}N_7O_{11}RuS \cdot H_2O \cdot MeOH$: C, 62.78; H, 5.34; N, 7.12. Found: C, 62.46; H, 5.19; N, 6.76.

[Ru(L3)(L6)]HCO$_3$ (3). To a 100-mL RBF containing **C1** (0.151 g, 0.16 mmol) and 4-(hexylthio)-*N*-(4-(hexylthio)phenyl)-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (**P2**) (0.100 g, 0.17 mmol) was added 25 mL of anhydrous DMF. After the mixture was sparged with N_2 for 20 min, K_2CO_3 (0.217 g, 1.57 mmol) and Pd(PPh$_3$)$_4$ (0.020 g, 0.02 mmol) were added and left to stir for 20 h at 70 °C. The solvent was removed in vacuo, leaving a residue that was dissolved in CH_2Cl_2. The white precipitate (K_2CO_3) was removed by filtration, and the solvent was removed in vacuo. The residue was purified by column chromatography [SiO$_2$, CH_2Cl_2/MeOH, 9:1; R_f = 0.23] to yield 0.106 g (50.7%) of the product as a dark black microcrystalline solid. The low yield is due to formation of the saponified product, [Ru(**L3**)(Me$_2$tctpy)]. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 9.60 (d, 1H, ^3J = 8.2 Hz, H_d), 9.39 (s, 1H, H_e), 9.12 (s, 2H, H_E), 8.90 (s, 2H, H_D), 8.66 (d, 1H, ^3J = 3.9 Hz, H_f), 8.20 (s, 1H, H_m), 8.02 (t, 1H, ^3J = 7.2 Hz, H_c), 7.77 (d, 1H, ^3J = 7.7 Hz, H_n), 7.73 (d, 2H, ^3J = 5.9 Hz, H_A), 7.64 (dd, 2H, ^3J = 5.9, ^4J = 1.7 Hz, H_B), 7.59 (d, 2H, ^3J = 8.6 Hz, H_h), 7.46 (d, 1H, ^3J = 3.9 Hz, H_g), 7.30–7.23 (m, 5H, H_a, H_k), 7.14–7.03 (m, 7H, H_j, H_b, H_i), 6.76 (t, 1H, ^3J = 7.1 Hz, H_o), 6.45 (t, 1H, ^3J = 7.4 Hz, H_p), 5.31 (d, 1H, ^3J = 7.0 Hz, H_q), 4.19 (s, 3H, H_F), 3.94 (s, 6H, H_C), 2.88 (t, 4H, ^3J = 7.3 Hz, H_r), 1.68–1.60 (m, 4H, H_s), 1.43–1.38 (m, 4H, H_t), 1.30–1.23 (m, 8H, H_u, H_v), 0.87 (t, 6H, ^3J = 6.9 Hz, H_w). HRMS (ESI): m/z = 1291.3345 [(M)$^+$] (calcd for $C_{71}H_{67}N_6O_6RuS_3{}^+$, m/z = 1291.3360). Anal. Calcd for $C_{72}H_{68}N_6O_9RuS_3 \cdot 4H_2O$: C, 60.45; H, 5.35; N, 5.87. Found: C, 60.45; H, 4.94; N, 5.65.

[Ru(P3)(L7)]NO$_3$ (C2). A 250-mL RBF containing Ru(**P3**)Cl$_3$ (0.424 g, 0.71 mmol) and dimethyl 6-phenyl-2,2′-bipyridine-4,4′-dicarboxylate (**L7H**) (0.234 g, 0.67 mmol) was charged with 120 mL of a MeOH/H$_2$O (5:1 v/v) solution containing 0.5 mL of *n*-ethylmorpholine and then left at reflux for 14 h. After the reaction was cooled, AgNO$_3$ (0.359 g, 2.12 mmol) was added and the reaction mixture was set to reflux for an additional 2 h. The hot solution was filtered, and the solvent was removed in vacuo. The residue was purified by column chromatography [SiO$_2$, CH_2Cl_2/MeOH, 9:1; R_f = 0.26] to yield 0.196 g (32.3%) of the product as a dark black microcrystalline solid. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.89 (s, 1H, H_D), 8.84 (s, 2H, H_e), 8.82 (s, 1H, H_E), 8.65–8.63 (m, 3H, H_G, H_d) 8.15 (d, 1H, ^3J = 4.0 Hz, H_f), 7.87 (d, 1H, ^3J = 7.8 Hz, H_H), 7.81 (d, 1H, ^3J = 5.2 Hz, H_A), 7.76–7.69 (m, 3H, H_c, H_B), 7.28 (d, 1H, ^3J = 3.86 Hz, H_g), 7.09 (d, 2H, ^3J = 4.7 Hz, H_a), 6.91 (t, 2H, ^3J = 6.0 Hz, H_b), 6.86 (t, 1H, ^3J = 6.8 Hz, H_I), 6.66 (t, 1H, ^3J = 7.3 Hz, H_J), 5.98 (d, 1H, ^3J = 6.5 Hz, H_K), 4.18 (s, 3H, H_F), 3.96 (s, 3H, H_C). HRMS (ESI): m/z = 842.0007 [(M)$^+$] (calcd for $C_{39}H_{27}BrN_5O_4RuS^+$, m/z = 842.0010). Anal. Calcd for $C_{39}H_{27}BrN_6O_7RuS \cdot 2H_2O$: C, 49.79; H, 3.32; N, 8.49. Found: C, 49.39; H, 3.04; N, 8.59.

[Ru(L4)(L7)]HCO$_3$ (4). To a 100-mL RBF containing **C2** (0.100 g, 0.11 mmol) and 4-(hexyloxy)-*N*-(4-(hexyloxy)phenyl)-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (**P1**) (0.066 g, 0.12 mmol) was added 25 mL of anhydrous DMF. After the mixture was sparged with N_2 for 20 min, K_2CO_3 (0.153 g, 1.11 mmol) and Pd(PPh$_3$)$_4$ (0.013 g, 0.01 mmol) were added and left to stir for 20 h at 70 °C. The solvent was removed in vacuo, leaving a residue that was dissolved in CH_2Cl_2. The white precipitate (K_2CO_3) was removed by filtration, and the solvent was removed in vacuo. The residue was purified by column chromatography [SiO$_2$, acetone/MeOH, 8:1; R_f = 0.32] to yield 0.040 g (28.5%) of the product as a dark black microcrystalline solid. The low yield is due to formation of the saponified product, [Ru(**L4**)(ph-Medcbpy)] (ph-Medcbpy = methyl 6-phenyl-2,2′-bipyridine-4,4′-dicarboxylate). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.96 (s, 2H, H_e), 8.87 (s, 1H, H_D), 8.81 (s, 1H, H_E), 8.79 (d, 2H, ^3J = 8.2 Hz, H_d), 8.64 (s, 1H, H_G), 8.51 (d, 1H, ^3J = 3.9 Hz H_f), 7.84 (d, 1H, ^3J = 7.7 Hz, H_H), 7.73 (t, 2H, ^3J = 7.7 Hz, H_c), 7.69–7.65 (m, 2H, H_A, H_B), 7.42 (d, 2H, ^3J = 8.7 Hz, H_h), 7.27 (d, 1H, ^3J = 3.9 Hz, H_g), 7.07–7.05 (m, 6H, H_a, H_j), 6.91–6.88 (m, 4H, H_b, H_i), 6.85–6.79 (m, 5H, H_k, H_I), 6.63 (t, 1H, ^3J = 7.5 Hz, H_J), 6.00 (d, 1H, ^3J = 7.5 Hz, H_K), 4.15 (s, 3H, H_F), 3.94 (s, 3H, H_C), 3.92 (t, 4H, ^3J = 6.6 Hz, H_r), 1.79–1.72 (m, 4H, H_s), 1.48–1.41 (m, 4H, H_t), 1.36–1.30 (m, 8H, H_u, H_v), 0.89 (t, 6H, ^3J = 7.0 Hz, H_w). HRMS (ESI): m/z = 1207.3742 [(M)$^+$] (calcd for $C_{69}H_{65}N_6O_6RuS^+$, m/z = 1207.3742). Anal. Calcd for $C_{70}H_{66}N_6O_9RuS \cdot 3H_2O$: C, 63.67; H, 5.49; N, 6.35. Found: C, 64.01; H, 5.45; N, 6.40.

[Ru(L5)(L7)]HCO$_3$ (5). To a 100-mL RBF containing **C2** (0.164 g, 0.18 mmol) and 4-(hexylthio)-*N*-(4-(hexylthio)phenyl)-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (**P2**) (0.115 g, 0.19 mmol) was added 25 mL of anhydrous DMF. After the mixture was sparged with N_2 for 20 min, K_2CO_3 (0.250 g, 1.81 mmol) and Pd(PPh$_3$)$_4$ (0.022 g, 0.02 mmol) were added and left to stir for 20 h at 70 °C. The solvent was removed in vacuo, leaving a residue that was dissolved in CH_2Cl_2. The white precipitate (K_2CO_3) was removed by filtration, and the solvent was removed in vacuo. The residue was purified by column chromatography [SiO$_2$, CH_2Cl_2/MeOH, 9:1; R_f = 0.36] to yield 0.110 g (47.2%) of the product as a dark black microcrystalline solid. The low yield is due to formation of the saponified product, [Ru(**L5**)(ph-Medcbpy)]. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 9.02 (s, 2H, H_e), 8.88–8.81 (m, 4H, H_D, H_E, H_d), 8.64 (s, 1H, H_G), 8.61 (d, 1H, ^3J = 3.9 Hz, H_f), 7.85 (d, 1H, ^3J = 7.5 Hz, H_H), 7.74–7.66 (m, 4H, H_A, H_B, H_c), 7.53 (d, 2H, ^3J = 8.6 Hz, H_h), 7.39 (d, 1H, ^3J = 3.9 Hz, H_g), 7.23 (d, 4H, ^3J = 8.6 Hz, H_k), 7.04–7.00 (m, 8H, H_a, H_i, H_j), 6.90 (t, 2H, ^3J = 6.3 Hz, H_b), 6.82 (t, 1H, ^3J = 7.2 Hz, H_I), 6.64 (t, 1H, ^3J = 7.2 Hz, H_J), 6.00 (d, 1H, ^3J = 7.2 Hz, H_K), 4.16 (s, 3H, H_F), 3.94 (s, 3H, H_C), 2.87 (t, 4H, ^3J = 7.4 Hz, H_r), 1.67–1.60 (m, 4H, H_s), 1.45–1.38 (m, 4H, H_t), 1.31–1.26 (m, 8H, H_u, H_v), 0.87 (t, 6H, ^3J = 6.8 Hz, H_w). HRMS (ESI): m/z = 1239.3249 [(M)$^+$] (calcd for $C_{69}H_{65}N_6O_4RuS_3{}^+$, m/z = 1239.3290). Anal. Calcd for $C_{70}H_{66}N_6O_7RuS_3 \cdot 3H_2O$: C, 62.07; H, 5.36; N, 6.20. Found: C, 62.09; H, 4.96; N, 6.50.

■ RESULTS AND DISCUSSION

This study details the syntheses and physicochemical properties of four new cyclometalated Ru(II) complexes bearing hydrophobic TPA substituents (Chart 1 and Table 1). The ensuing sections will address, in sequence, (i) a synthetic protocol for installing aliphatic groups on the TPA substituent, (ii) the benefit of placing the TPA on the neutral chelating ligand rather than the anionic ligand, and (iii) the role that terminal −O-hexyl and −S-hexyl substituents have on the physicochemical properties.

Table 1. Summary of Spectroscopic and Electrochemical Properties for Complexes C1−C2 and 1−5

compound	UV−vis absorbance data (nm)[a] λ_{max} ($\varepsilon \times 10^3$ M^{-1} cm^{-1})	$E_{1/2}^{ox}$ (V vs NHE)[b] Ru(III)/Ru(II)	TPA$^{\bullet+}$/TPA^0
C1	523 (21.1), 431 (29.5), 327 (53.0)	1.03	c
1	524 (34.5), 435 (42.3), 330 (48.4)	1.03	0.93
2	526 (34.4), 435 (44.5), 330 (48.4)	1.04	0.92
3	526 (28.0), 432 (40.0), 327 (54.7)	1.03	1.03
C2	561 (25.3), 389 (18.4)	0.89	c
4	572 (36.0), 421 (38.1)	0.87	0.95
5	571 (32.2), 418 (36.7)	0.87	1.05

[a] Data collected in MeCN; ε values indicated in parentheses with units of $\times 10^3$ M^{-1} cm^{-1}; shoulders at ca. 690 nm and select high-energy maxima are not listed. [b] Data collected using 0.1 M NBu_4BF_4 MeCN solutions at 100 mV/s and referenced to a [Fc]/$[Fc]^+$ internal standard followed by conversion to NHE; [Fc]/$[Fc^+]$ = +640 mV vs NHE in MeCN. [c] Not observed.

Synthetic Protocol for Installing the Aliphatic Groups. The Suzuki reagent **P1** was synthesized according to documented methodologies.[37] Attempts to synthesize the thiolate-substituted TPA units **P2b** and **P2c** by similar methods proved unsuccessful. An alternative route stemming from a literature procedure[40] provided access to the boronic ester **P2** (Scheme S1, Supporting Information). Reagents (**P1** and/or **P2**) could then be coupled to the appropriate chelating ligands (**P3** and/or **P4**) via Suzuki cross-coupling methods to furnish the hydrophobic TPA-functionalized tridentate ligands **L2H**, **L3H**, and **L4** in high yields (Scheme S2, Supporting Information). The seemingly trivial task of binding these ligands to the Ru center, however, was made difficult by the inherently poor solubility of the ligands in polar media being in discord with the need for a high dielectric solvent (e.g., MeOH/H_2O 5:1 v/v) to induce halide displacement and cyclometalation.[41] While the solubility of TPA-appended pbpy ligands can be enhanced with a small amount of THF (e.g., MeOH/H_2O/THF 5:1:1 v/v/v[7,26]), the long alkyl chains of **L2H** and **L3H** demanded a greater fraction of THF, thus yielding a mixture of cyclometalated/noncyclometalated products that were not easily separated by column chromatography (Figure 3; Route A). We also tried to carry out the cyclometalation step with **L2H** and $[Ru(C_6H_6)Cl_2]_2$ prior to chelation of the Me_3tctpy (**L6**) ligand;[3] but this strategy proved unsuccessful with myriad solvent combinations at variable temperatures (Figure 3; Route B).

With the aforementioned synthetic routes exhausted, we turned our attention to less conventional cross-coupling reactions involving the bis-tridentate Ru coordination complex (Figure 3; Route C).[42] This approach, which proved to be remarkably facile, involved the chelation of *pro*-ligand **P4**[7] to Ru(**L6**)Cl_3 to furnish the brominated precursor complex **C1**, which, in turn, was reacted with Suzuki reagents **P1**/**P2** in anhydrous basic DMF to yield **2** and **3**. Complexes **4** and **5** were prepared from **C2** following a similar protocol. One consequence of this synthesis was partial saponification of the product (i.e., one of the methylesters could be converted into the corresponding carboxylic acid derivative); however, these two products could be readily separated by column chromatography. While **1** is soluble in a wide range of organic solvents (e.g., CH_2Cl_2, $CHCl_3$, MeOH, EtOH, DMF, DMSO), the complexes bearing the long aliphatic chains about the TPA unit were significantly more soluble in less polar solvents (e.g., THF).

In overcoming a major synthetic roadblock, we were able to isolate and fully characterize the redox and spectroscopic properties of pure phases of the title complexes. The inherent asymmetry of each of the complexes enables an accurate assignment of the aromatic signals by ^{1}H NMR (1D and 2D) spectroscopy. Sample purity was verified by mass spectrometry

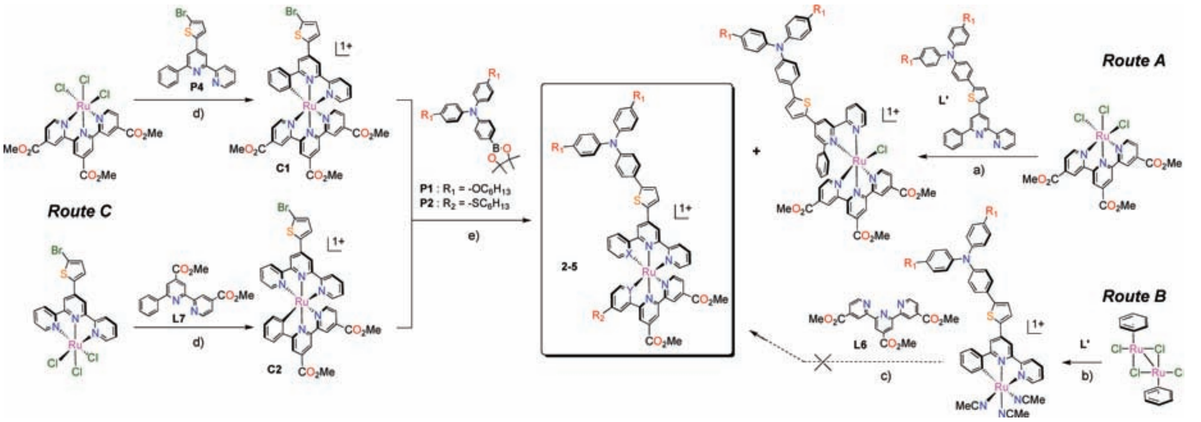


Figure 3. Synthetic pathways used to isolate **2**−**5** (Route C). Route A produced an inseparable byproduct, and Route B did not yield the desired product. Reaction conditions: (a) $AgNO_3$, *n*-ethylmorpholine, MeOH/H_2O/THF (5:1:>1, v/v/v), reflux, 16 h; (b) KPF_6, NaOH, MeCN, 40 °C, 18 h; (c) desired product was not generated in a variety of solvents (i.e., MeOH, EtOH, MeCN, CH_2Cl_2, $CHCl_3$, CCl_4, DMF, DMSO, $OHCH_2CH_2OH$); (d) $AgNO_3$, *n*-ethylmorpholine, MeOH/H_2O (5:1, v/v/v), reflux, 16 h; (e) K_2CO_3, $Pd(PPh_3)_4$, DMF, 70 °C, 20 h.

and elemental analyses. We note that many of the complexes contain waters of hydration.

A full assessment of the electrochemical and spectroscopic data recorded in MeCN was augmented by the extensive catalogue of compounds reported in our previous studies.[7,26] The broad and intense absorption profiles of related compounds have been previously shown to arise from overlapping metal-to-ligand charge-transfer (MLCT) and intraligand charge-transfer (ILCT) absorption bands.[7] For complexes containing **L6**, for example, the lower energy MLCT bands (i.e., shoulder at ~580 nm and maximum at ~520 nm) involve promotion of an electron from metal-based orbitals that are delocalized over the anionic ring of the chelating ligand to the π^* orbital of the neutral chelating ligand; the higher energy bands (e.g., 431 nm) arise from MLCT transitions involving the π^* network of the cyclometalating ligand. A comparison of the spectra of **C1** and **2** illustrates explicitly how the TPA unit enhances light absorption (Figure S1, Supporting Information), and provides confirmation that the absorption bands in bichromic complexes of this type are both MLCT and ILCT in character.[7,26] The low-energy ILCT transitions emanating from the TPA unit involve excited-state character on the π^* system of the adjacent chelating ligand. Introduction of long alkyl chains has a negligible effect on the spectroscopic properties of the complexes (e.g., **1** vs **2**; Figure S1a, Supporting Information). Note that the absorption traces of **C1** and **2** extend beyond 800 nm regardless of whether a TPA unit is present. We assign the low-energy shoulder centered at ~690 nm to direct population of the ^{3}MLCT state facilitated by the heavy Ru atom.[43]

Cyclic voltammograms of **1** and **2** reveal two distinctive and quasi-reversible oxidation processes (Figure S1, Supporting Information). The first process corresponds to oxidation of the TPA unit (i.e., $E_{1/2}$, $\text{TPA}^{\bullet+}/\text{TPA}^0 \approx +0.9$ V vs NHE) with a closely spaced Ru(III)/Ru(II) redox couple at ~+1.0 V vs NHE for both **1** and **2**.[7,44,45] Note that the cyclic voltammograms of complexes **C1** and **2** (Figure S1b, Supporting Information) indicate a lack of communication between the two redox-active sites on the basis of the static Ru(III)/Ru(II) couple remains static (i.e., ~+1.03 V vs NHE).[7,26] The length of the alkyl chains has a negligible effect on the optical and electrochemical properties. The assignment of the redox waves observed in the cyclic voltammetry experiments was aided by previous studies and spectroelectrochemical experiments (Figure S3, Supporting Information). Upon application of a fixed potential of +0.95 V vs NHE (which is not expected to oxidize the Ru(II) center), several changes are observed in the absorption spectrum. In particular, growth of the low-energy absorption band centered at ~750 nm is attributed to a radical species $\mathbf{2}^{\bullet 2+}$, which is the product of a one-electron oxidation of $\mathbf{2}^+$.[30,46] This absorption band is specifically assigned to a species where the radical is localized to the TPA fragment of the complex.

Position of the Organometallic Bond. We previously demonstrated that the anionic ring of dyes related to **1** should be in the flanking position of the chelating ligand to engender optical and electrochemical properties appropriate for sensitizing n-type semiconductors.[7,26] A point we did not explicitly address in these studies, however, is whether the phenyl ring should be on the chelating ligand attached to the TPA unit as opposed to the adjacent chelate. (Note that the latter scheme was recently reported[5]). While we situated the TPA on the cyclometalating ligand to leave all three acid modalities on 4,4′,4″-tricarboxylate-2,2′:6′,2″-terpyridine (tctpy) accessible for binding to TiO_2, only two acid groups are, in principle, needed for binding and electron injection.[47] Thus, we include in this study a synthetic route to furnish derivatives where the TPA groups are attached to the neutral chelate (e.g., **4** and **5**; Scheme S1, Supporting Information). An attractive feature of this particular arrangement is that the anionic ring is trans to the pyridine containing the (potential) anchoring groups to potentially promote more efficient electron injection.[48] Moreover, **4** and **5** do not contain the Me_3tctpy ligand, which currently stands as an expensive component of commercial DSSC dyes.

The protocol used to prepare **2** and **3** also worked effectively in preparing **4** and **5**, thereby demonstrating the versatility of using C−C cross-coupling methodologies to attach the aliphatic TPA unit to the coordinatively saturated metal complexes. The ^{1}H NMR spectra of **2**−**4** reveal a clear response of chemical shifts to the position of the Ru−C bond (Figure 4). Confirmation of cyclometalation by the pbpy chelate is provided in the form of the distinctively upfield shift of the proton ortho to the Ru−C bond (i.e., H_q and H_K for **2** and **4**, respectively). The H_K resonance of **4** is downfield relative to that of H_q for **2** due to the electron-withdrawing $-CO_2Me$ group being trans to the anionic phenyl ring.

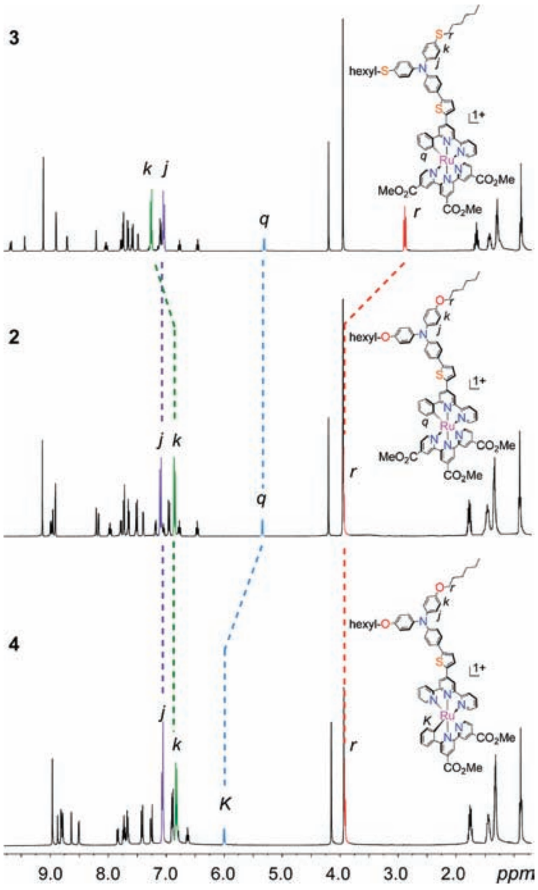


Figure 4. ^{1}H NMR spectra for $CDCl_3$ solutions of **2**−**4** at ambient temperatures highlighting how the terminal substitutents and the position of the Ru−C bond affect the proton resonances. Color scheme: green = H_k; red = H_r; blue = H_q/H_K; purple = H_j; dashed lines are provided to guide the reader.

Figure 5 illustrates how the position of the organometallic bond affects the optical properties. The low-energy shoulder in

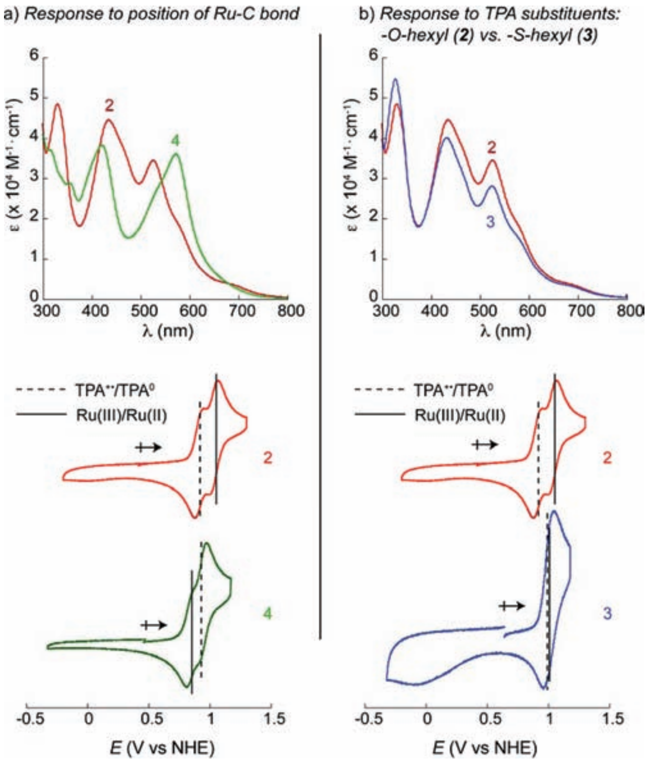


Figure 5. UV−vis spectra and cyclic voltammograms of select compounds in MeCN highlight the effect on the optical and electrochemical properties upon (a) altering the position of the Ru−C bond (R_1 = -O-hex) and (b) substitution of the chalcogen (O vs S) para to the N of the TPA.

2 (∼580 nm) becomes more pronounced in the case of **4**, which is notable in the collective pursuit of dyes that absorb at the maximum of the solar flux at ca. 600 nm.[49] While it is difficult to accurately discriminate how the position of the organometallic bond affects the electrochemical properties because of the disparate number of $-CO_2Me$ groups for **2** and **4**, the Ru(III)/Ru(II) redox couple does appear to be affected to some extent because the +170 mV shift for **4** relative to **2** cannot be fully accounted for by a single $-CO_2Me$ group (e.g., loss of two $-CO_2Et$ groups has been shown to only affect the Ru(III)/Ru(II) redox potential by +140 mV[3]). The TPA oxidation potential is not significantly affected by the position of the Ru−C bond in **2** and **4** (e.g., +0.92 and +0.95 V vs NHE for **2** and **4**, respectively), which is again consistent with the metal and TPA units being electrochemically isolated in the ground state.[7,26]

Effect of Terminal Chalcogenide Substituents (O vs S) on the TPA. Isolation of the alkoxy- and thiolate-substituted TPAs was achieved following the aforementioned cross-coupling schemes (Figure 3; Route C). An examination of the ^{1}H NMR spectra of **2** and **3** indicate that the protons ortho to the chalcogen on the TPA (e.g., H_k) and the methylene protons (i.e., H_r) of the aliphatic chain are affected the most by the different chalcogens about the TPA (Figure 4). The divergence of the chemical shifts (i.e., H_k and H_r are shifted downfield and upfield, respectively, for **2** relative to **3**) indicates that the larger S orbitals better shield the methylene protons than the corresponding O atom of the alkoxy group but display inferior orbital overlap with the π system of the TPA unit. Consequently, the S atom donates less electron density into the π system of the TPA relative to the O atom. Less electron donation of the S atom into the aromatic system of the TPA was authenticated by electrochemical measurements: the $TPA^{\bullet+}/TPA^0$ redox couple appears at +0.92 and +1.03 V vs NHE for **2** and **3**, respectively (Figure 5) (The Ru(III)/Ru(II) redox couple was not affected). The different intensities of the optical spectra for **2** and **3** (Figure 5) also appear to be manifest in this electron donation into the aromatic systems of the TPA units affecting the transition dipole of the ILCT transitions.

■ SUMMARY

The primary objective of this study was to develop a protocol for isolating *hydrophobic* bichromic cyclometalated Ru(II) complexes related to **1**.[7,26] Functionalization of the TPA units with aliphatic chains gave rise to a host of solubility issues that rendered our previously established synthetic methodologies unsuccessful. Fortunately, it was found that Pd-catalyzed C−C cross-coupling reactions between appropriately functionalized bis-tridentate Ru metal complexes (**C1** and **C2**) and TPA units were remarkably efficient for making the target complexes. This synthetic endeavor also enabled us to position the organometallic bond within the scaffold of **1** from the ligand bearing the TPA unit to the anchoring chelate. Not only does this arrangement induce a bathochromically shifted absorption envelope better matched to the incident solar flux but it also sidesteps the use of the expensive tctpy ligand.

While the TPA unit is a common constituent in organic DSSC dyes,[50,51] there is currently no example of an organic or metal sensitizer where the TPA has been substituted with thiolate groups. This observation prompted us to develop a synthetic scheme for isolating Ru complexes bearing TPA units that have been functionalized with thiolate groups. Characterization of these dyes, however, reveals that the thiolates are weaker donors than the alkoxy groups because of the less favorable orbital interactions with the phenyl rings of the TPA group. This finding has consequences when inducing intramolecular charge transfer, namely, there will be a lower thermodynamic driving force for the thiolate-substituted TPA group to reduce the photo-oxidized metal fragment. Consequently, we do not expect the sensitization of *n*-type semiconductors with bichromic sensitizers bearing thiolate-substituted TPA groups to be enhanced (if kinetic parameters are held at parity). Studies are underway to verify this claim.

With the synthetic chemistry for bichromic cyclometalated Ru(II) complexes now fully developed, future studies will focus exclusively on probing the interaction between the chalcogenide-substituted TPA units and the I^--based electrolyte species in the DSSC. We are also evaluating whether the aliphatic chains enhance the stability of these complexes in the DSSC as they do with dyes bearing bidentate ligands (e.g., **Z907**[35]).[52] The device performance for this entire suite of complexes in liquid-junction and solid-state DSSCs will be disseminated in future studies.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthetic schemes for **P2** and ligands **L2H−L3H** and **L4** and experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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