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Synthesis and Characterization of Tris(Heteroleptic) Ru(II) Complexes Bearing Styryl Subunits

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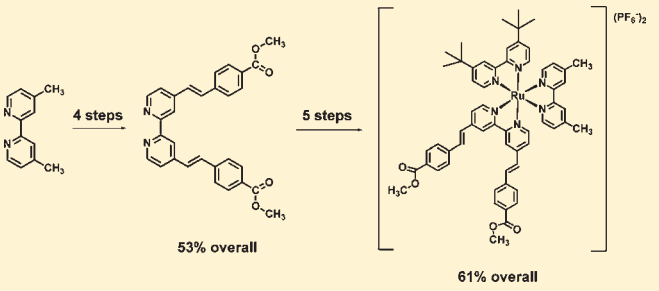
Supporting Information

ABSTRACT: We have developed and optimized a well-controlled and refined methodology for the synthesis of substituted π-conjugated 4,4′-styryl-2,2′-bipyridine ligands and also adapted the tris(heteroleptic) synthetic approach developed by Mann and co-workers to produce two new representative Ru(II)-based complexes bearing the metal oxide surface-anchoring precursor *4,4′-bis[E-(p-methylcarboxy-styryl)]-2,2′-bipyridine*. The two targeted Ru(II) complexes, (4,4′-dimethyl-2,2′-bipyridine)(4,4′-di-*tert*-butyl-2,2′-bipyridine)(4,4′-bis[*E*-(*p*-methylcarboxy-styryl)]-2,2′-bipyridine) ruthenium(II) hexafluorophosphate, [Ru(dmbpy)(dtbbpy)(*p*-COOMe-styryl-bpy)]$(PF_6)_2$ (**1**) and (4,4′-dimethyl-2,2′-bipyridine)(4,4′-dinonyl-2,2′-bipyridine)(4,4′-bis[*E*-(*p*-methylcarboxy-styryl)]-2,2′-bipyridine) ruthenium(II) hexafluorophosphate, [Ru(dmbpy)(dnbpy)(*p*-COOMe-styryl-bpy)]$(PF_6)_2$ (**2**) were obtained as analytically pure compounds in high overall yields (>50% after 5 steps) and were isolated without significant purification effort. In these tris(heteroleptic) molecules, NMR-based structural characterization became nontrivial as the coordinated ligand sets each sense profoundly distinct magnetic environments greatly complicating traditional 1D spectra. However, rational two-dimensional approaches based on both homo- and heteronuclear couplings were readily applied to these structures producing quite definitive analytical characterization and the associated methodology is described in detail. Preliminary photoluminescence and photochemical characterization of **1** and **2** strongly suggests that both molecules are energetically and kinetically suitable to serve as sensitizers in energy-relevant applications.



INTRODUCTION

Since the late 1980s, a variety of synthetic schemes have been developed with the purpose of producing tris(heteroleptic) Ru(II) complexes based on distinct diimine ligands, i.e. $[Ru(LL)(LL')(LL'')]^{2+}$, in high yields using the fewest number of steps, including a number of single pot reactions.[1−7] These efforts have been largely inspired by the fact that the associated ground and excited state properties of the charge transfer states can be finely tuned by synthetic modulation of the coordinated ligands.[8,9] Indeed this strategy has already produced black dyes potentially valuable for solar fuels photochemistry and metal oxide surface anchored dye sensitizers possessing broad-band visible light-harvesting properties.[10−13] As pointed out by Mann and co-workers,[7] these latter more general strategies are somewhat inconvenient, being limited by routinely accessible high purity reagents and high temperature (refluxing DMF) forcing conditions, respectively.[5,6] We recently became interested in pursuing a *tris*(heteroleptic) synthetic route that could be broadly applied to Ru(II) molecules bearing more sensitive π-conjugated diimine ligands. Such moieties lie at the heart of increasing oscillator strength in MLCT transitions[2,14−17] and possibly their associated two-photon cross sections.[18−21] The modern advent of upconversion photochemistry based on sensitized triplet−triplet annihilation mandates the development of new long wavelength/long lifetime Ru(II) sensitizers bearing π-conjugated subunits.[21−24] Of course, compatibility of these chromophores with metal oxide semiconductors in both solar fuels research and dye-sensitized solar cell applications demands a combination of light-harvesting properties and redox potentials concomitant with substituents such as carboxylic acids to enable surface anchoring chemistry.[25] In our opinion, the most promising and generic synthetic methodology with the potential to complement precious diimine ligands is that recently developed by Mann and co-workers.[7] However, to the best of our knowledge, this sequence has only been applied to the synthesis of heteroleptic Ru(II) chromophores bearing combinations of "simple" unsubstituted or methyl-substituted bipyridine and phenanthroline ligands.

Another goal of the present work intends to develop a refined and straightforward synthetic route toward π-conjugated styryl-bipyridine ligands starting from readily available precursors using the mildest possible reaction conditions. A comprehensive retrosynthetic and literature analysis suggests that functionalized 4,4′-styryl-2,2′-bipyridine ligands can be accessed using four different approaches, ranging from one-pot reactions to more

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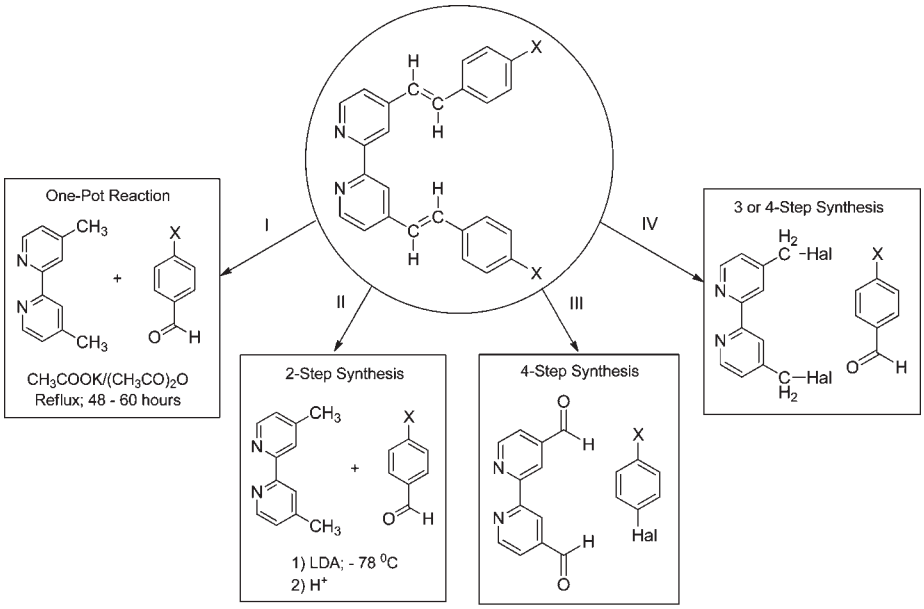
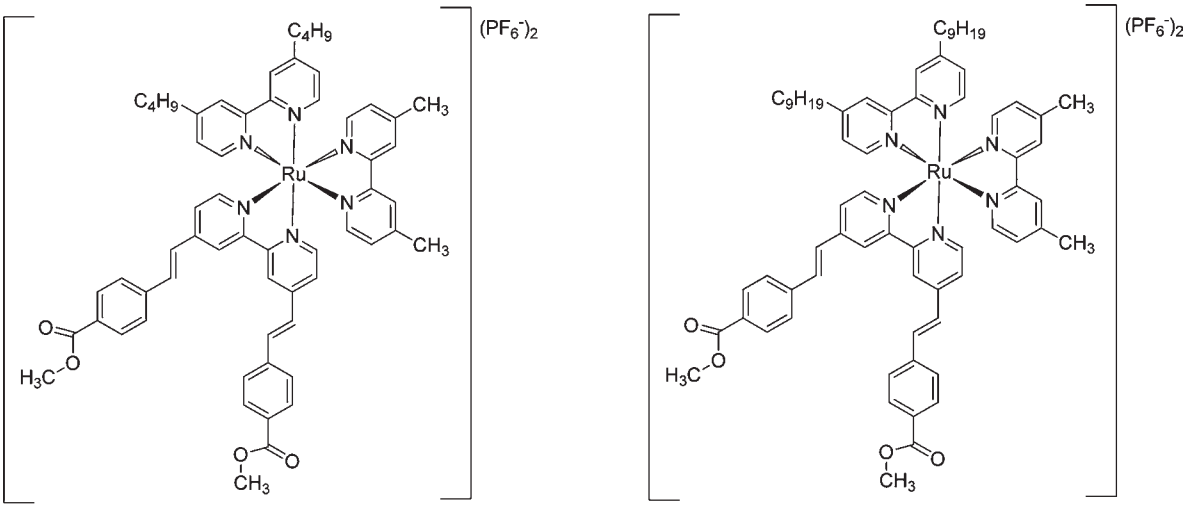
Scheme 1. Possible Synthetic Approaches Towards Functionalized 4,4′-Styryl-2,2′-bipyridine Ligands Based on Retrosynthetic and Literature Analysis[a]



[a] "X" denotes an arbitrary functional group, and "Hal" is a halogen. The common bipyridine precursor is 4,4′-dimethyl-2,2′-bipyridine (dmbpy).



1 **2**

Figure 1. Structures of model heteroleptic tris(polypyridyl) Ru(II) complexes: **1** (left), **2** (right). C_4H_9 denotes *tert*-butyl and C_9H_{19} is nonyl.

controlled multistep syntheses having well-defined intermediates (Scheme 1).[14,26−31] Each of these methodologies rely exclusively on the use of 4,4′-dimethyl-2,2′-bipyridine (dmbpy) as the synthetic departure point. Regardless of the variety of documented strategies, the preparation of these ligands remains nontrivial. For the sake of realistic and objective comparisons with available literature procedures, we found that routes I and II (Scheme 1) do not represent viable strategies if one desires high yields and minimal purification. While the one-pot reaction (route I, Scheme 1) could not be reproduced after several trials, we repeatedly encountered difficulties with diol dehydration in route II, which greatly compromised the overall reaction yield. Therefore, we decided to adopt the strategy presented as route IV to produce 4,4′-substituted styryl bipyridines in high overall yield. Although our main target is a metal oxide compatible carboxylated 4,4′-styryl-2,2′-bipyridine, the versatility of the heterocyclic synthetic approach was established by preparing distinct 4,4′-styryl-2,2′-bipyridines bearing electron-withdrawing and electron-donating substituents.

In conjunction with this effort, two new Ru(II) tris(heteroleptic) complexes bearing terminal methyl ester functionalities have been synthesized in high yield and were thoroughly characterized, [Ru(dmbpy)(dtbbpy)(*p*-COOMe-styryl-bpy)]$(PF_6)_2$ (**1**) and [Ru(dmbpy)(dnbpy)(*p*-COOMe-styryl-bpy)]$(PF_6)_2$ (**2**),

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with their corresponding chemical structures presented in Figure 1. Even though 1D NMR is typically sufficient for structural verification in many synthesized Ru(II) complexes, this was simply not the case in **1** and **2**. Here, multidimensional NMR spectroscopy was invaluable for the structural characterization of **1** and **2**, and we note that these techniques have been applied to the characterization of many classes of inorganic molecules.[7,32,33] Given the importance toward understanding the rationale of the approach, the complete structural assignment of **1** using 2D homo- and heteronuclear correlation NMR spectroscopy is described in detail. As both **1** and **2** were found to possess very similar structural and photophysical properties, the bulk of the discussion in this contribution is primarily dedicated to **1**.

EXPERIMENTAL SECTION

General. Most synthetic manipulations were carried out under inert atmosphere (argon) using standard Schlenk techniques unless otherwise noted.[34] All solvents (ACS reagent grade) and reagents were purchased from either Sigma-Aldrich or Fisher Scientific and used as received unless otherwise specified. Tetrahydrofuran (THF) was dried over sodium/benzophenone and distilled fresh under argon prior to use.[35] Acetonitrile was dried and distilled fresh over CaH_2 under argon. *n*-Butyllithium (∼1.6 M solution in hexanes) was titrated with *N*-benzylbenzamide before use. Diisopropylamine (DIPA, 99+%) was stored over sodium under argon and used without any purification. Lithium diisopropylamide (LDA) was prepared fresh by adding *n*-BuLi (e.g., 6.6 mmol) dropwise to a solution of DIPA (e.g., 7.5 mmol) in 10 mL of THF (anh) cooled to −78 °C (dry ice/acetone), followed by stirring for 45 min. Photochemical reactions were carried out in a 100 mL quartz reactor (Chemglass) using the spectrally unfiltered output of a 450 W Hg vapor quartz immersion lamp. When necessary, bipyridine ligand purifications were carried out using flash chromatography on silica gel (Silica Gel 60, Geduran, 40−63 μm) deactivated with triethylamine (10% v/v solution in hexanes). *To ensure reproducibility and scalability, each reported reaction was repeated a minimum of two times.*

Characterization and Instrumentation. The structures of synthesized 4,4′-styryl-2,2′-bipyridine ligands and heteroleptic Ru(II) complexes were confirmed by high-resolution ^{1}H and ^{13}C NMR spectroscopy and MALDI-TOF mass spectrometry (MALDI-MS). 1D ^{1}H (500 MHz) and ^{13}C (125 MHz) and 2D correlation (^{1}H−^{1}H COSY, ^{1}H−^{1}H TOCSY, ^{1}H−^{13}C HSQC, ^{1}H−^{13}C HMBC) NMR spectra were recorded on a Bruker Avance III 500 spectrometer equipped with a cryoprobe. The acquired 1D and 2D NMR spectra were analyzed using MestReNova 6.1.1 and Sparky 3.113 software. All chemical shifts were referenced to the residual solvent signals [^{1}H NMR: $\delta(CDCl_3)$ = 7.27 ppm, $\delta(CD_3CN)$ = 1.94 ppm, δ(DMSO-d_6) = 2.50 ppm. ^{13}C NMR: $\delta(CDCl_3)$ = 77.23 ppm, $\delta(CD_3CN)$ = 1.39 and 118.69 ppm] and splitting patterns were assigned as s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). MALDI-TOF mass spectra were acquired using Bruker-Daltonics Omniflex spectrometer. Elemental analyses were provided by Midwest Microlab, LLC. All photophysical measurements were performed in anaerobic 1 cm^2 quartz cuvettes at room temperature in oxygen-free optically dilute acetonitrile solutions (spectrophotometric grade) with $[Ru(bpy)_3](PF_6)_2$ used as a reference. All samples were deoxygenated via freeze−pump−thaw technique. Ground-state absorption spectra were acquired on Cary 50 Bio UV−vis spectrophotometer (Varian). Steady-state photoluminescence spectra were measured on PTI single photon counting spectrofluorimeter. Photoluminescence lifetimes were measured using a nitrogen-pumped broadband dye laser as the excitation source (PTI GL-3300 Nitrogen laser, PTI GL-301dye laser, POPOP dye) and a detection system described elsewhere.[36] The excited-state lifetimes were obtained from the first-order decay fit of single wavelength emission transients using Origin 8.0 software. Photoisomerization (photostability) experiments were carried out in deaerated acetonitrile solutions contained in anaerobic 1 cm^2 quartz cuvettes using a 300 W xenon arc lamp equipped with 305 nm long pass filter.

Synthesis and Characterization. *4,4′-Bis(trimethylsilylmethyl)-2,2′-bipyridine.* This ligand was synthesized from commercially available 4,4′-dimethyl-2,2′-bipyridine (dmbpy) following the previously published procedure with slight modifications.[37] A 3.0 mmol (553 mg) portion of 4,4′-dimethyl-2,2′-bipyridine was dissolved in 18 mL of THF (anh) and then added dropwise over a 10-min period to a freshly prepared LDA solution (6.6 mmol in 10 mL of dry THF) cooled to −78 °C. The reaction mixture almost immediately turned dark red and was stirred at −78 °C for 1 h. Afterward, 1.0 mL (ca. 7.5 mmol) of chlorotrimethylsilane (TMS-Cl) was quickly added to the reaction mixture via syringe resulting in the reaction mixture color change to blue, followed by quenching with 2 mL of absolute ethanol 15 s later. The obtained clear yellow-colored solution was then poured cold into a separatory funnel containing 60 mL of saturated aqueous $NaHCO_3$ solution, allowed to warm to RT and extracted with dichloromethane (3 × 30 mL). The combined organic layers were washed with brine and dried over Na_2SO_4. After removal of solvent, the product was obtained as a white solid in 94% yield (927 mg). MALDI-MS: m/z = 329.20 ([M]$^+$). ^{1}H NMR (500 MHz, $CDCl_3$): 8.46 (2H, dd, J_1 = 5.0 Hz; J_2 = 0.6 Hz), 8.05 (2H, d, J = 1.1 Hz), 6.93 (2H, dd, J_1 = 5.0 Hz; J_2 = 1.8 Hz), 2.21 (4H, s), 0.04 (18H, s). We note that oversylilation was not found to be an issue under the employed reaction conditions. Although 4,4′-bis(trimethylsilylmethyl)-2,2′-bipyridine appears to be reasonably stable under ambient conditions, it is advisible to use it in the next step in a timely manner.

4,4′-Bis(chloromethyl)-2,2′-bipyridine. A 2.8 mmol (920 mg) portion of 4,4′-bis(trimethylsilylmethyl)-2,2′-bipyridine, 11.2 mmol (2.6515 g) of hexachloroethane, and 11.2 mmol (1.7469 g) of CsF were dissolved in 45 mL of acetonitrile (anh) under argon. The reaction mixture was then heated to 65 °C for 4 h. After cooling to RT, the reaction mixture was extracted with ethyl acetate (3 × 50 mL). The combined organic layers were dried over Na_2SO_4. After removal of solvent, the obtained crude was subjected to column chromatography on deactivated silica with the following elution order: (1) hexane, removed the unreacted hexachloroethane; (2) hexane/ethyl acetate =2/1, eluted both the remaining starting material (4,4′-bis(trimethylsilylmethyl)-2,2′-bipyridine, R_f = 0.81) and the main product (4,4′-bis(chloromethyl)-2,2′-bipyridine, R_f = 0.45). The main product was obtained as analytically pure white solid in 84% yield (595 mg). ^{1}H NMR (500 MHz, $CDCl_3$); 8.69 (2H, d, J = 5.0 Hz), 8.44 (2H, s), 7.38 (2H, dd, J_1 = 5.0 Hz, J_2 = 1.7 Hz), 4.64 (4H, s). ^{13}C NMR (125 MHz, $CDCl_3$): 156.15, 149.73, 147.05, 123.21, 120.47, 44.27. Our NMR data for both 4,4′-bis(trimethylsilylmethyl)-2,2′-bipyridine and 4,4′-bis(chloromethyl)-2,2′-bipyridine were found to be identical to the reported literature data.[37]

4,4′-Bis(diethylphosphonatomethyl)-2,2′-bipyridine. This ligand was synthesized via the Michaelis−Arbuzov reaction following a typical literature protocol.[38,39] A 4.58 mmol (1.159 g) portion of 4,4′-bis-(chloromethyl)-2,2′-bipyridine were dissolved in argon-saturated triethylphosphite (10 mL) upon heating to 140 °C. The reaction was allowed to proceed for 24 h. After cooling to RT, the reaction crude was purified on deactivated silica; the main product was eluted with ethyl acetate/methanol (4/1) as a colorless or slightly yellowish band. After solvent removal, the ligand was obtained as an off-white solid in 90% yield (1.88 g). ^{1}H NMR (500 MHz, $CDCl_3$): 8.61 (2H, d, J = 5.0 Hz), 8.32 (2H, s), 7.35−7.29 (2H, m), 4.08 (8H, dq, J_1 = 8.1 Hz, J_2 = 7.1 Hz), 3.24 (4H, d, J = 22.0 Hz), 1.28 (12H, t, J = 7.1 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): 156.00 (d, J = 2.5 Hz), 149.24 (d, J = 2.7 Hz), 142.18 (d, J = 8.6 Hz), 124.98 (d, J = 5.6 Hz), 122.50 (d, J = 6.8 Hz), 62.43 (d, J = 6.7 Hz), 34.14 + 33.05 (d, J = 137.0 Hz), 16.36 (d, J = 6.0 Hz).

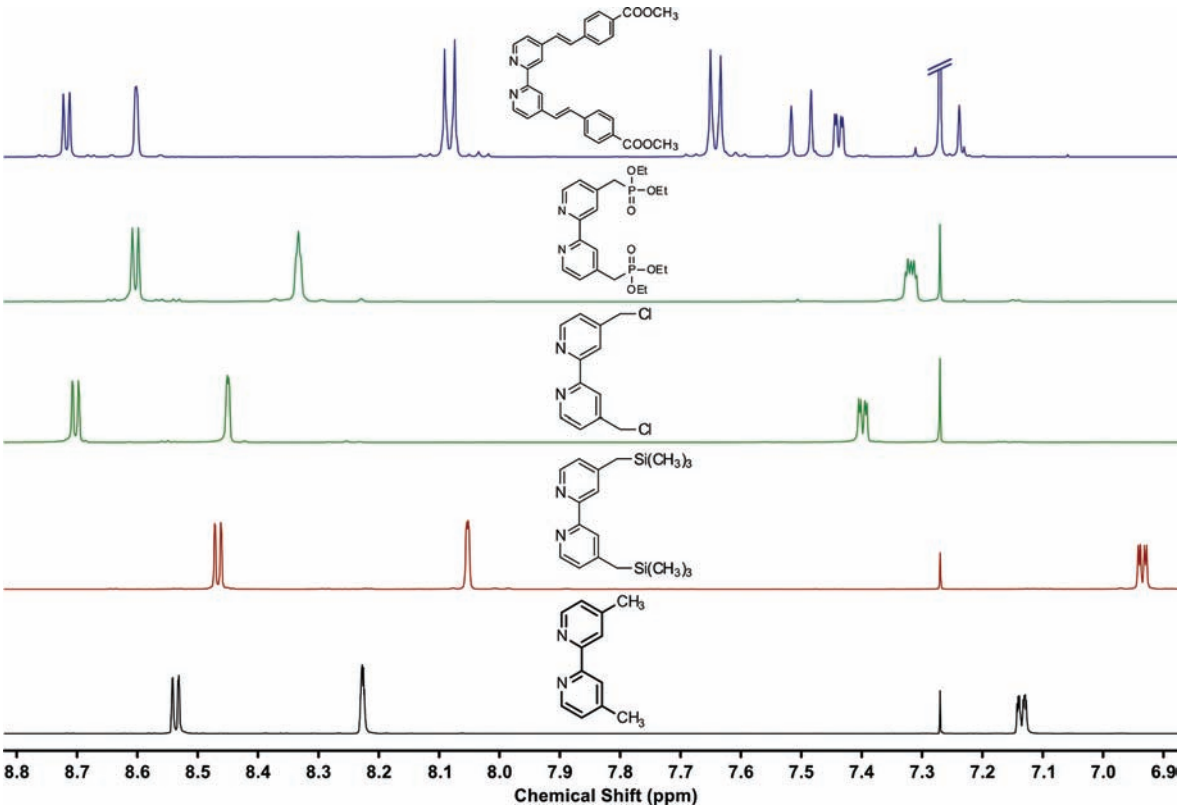

Figure 2. Stepwise transformation of 4,4′-dimethyl-2,2′-bipyridine into 4,4′-bis[*E*-(*p*-methylcarboxy-styryl)]-2,2′-bipyridine: evolution of the aromatic region (^{1}H NMR, 500 MHz, $\delta(CDCl_3)$ = 7.27 ppm) followed through each individual synthetic step.

4,4′-Bis[E-(p-methylcarboxy-styryl)]-2,2′-bipyridine. All target 4,4′-styryl-2,2′-bipyridines were synthesized via the Horner−Wadsworth−Emmons (HWE) coupling reaction of 4,4′-bis(diethylphosphonatomethyl)-2,2′-bipyridine with a corresponding functionalized benzaldehyde.[40] A suspension of potassium *tert*-butoxide (1.5 mmol, 168 mg) in 15 mL of THF (anh) was added dropwise under argon to a solution containing 0.5 mmol (228 mg) of 4,4′-bis(diethylphosphonatomethyl)-2,2′-bipyridine and 1.1 mmol (181 mg) of methyl-4-formylbenzoate in 5 mL of THF (anh) resulting in a nearly instantaneous formation of a precipitate. The yellow-brownish reaction mixture was then heated to a gentle reflux (70 °C) under argon for 24 h. After completion, the reaction was quenched by the addition of 30 mL of H_2O (DIUF grade). After removal of THF, the obtained white precipitate was filtered off, washed thoroughly with methanol, and dried under vacuum. The title compound was obtained as a white solid in analytically pure form in 74% yield (176 mg, overall yield 53%). Alternatively, the title compound can be isolated from the crude reaction mixture via the extraction with large amounts of dichloromethane following the typical workup protocol. If necessary, the product can be purified by recrystallization from hot 2-methoxyethanol. Anal. calcd (found) for $C_{30}H_{24}N_2O_4$ (%): C, 75.61 (75.44); H, 5.08 (5.06); N 5.88 (5.81). MALDI-MS: m/z = 477.30 ($[M]^+$). ^{1}H NMR (500 MHz, $CDCl_3$): 8.70 (2H, dd, J_1 = 5.0 Hz, J_2 = 0.5 Hz), 8.59 (2H, dd, J_1 = 1.5 Hz, J_2 = 0.5 Hz), 8.08 (4H, d, J = 8.0 Hz), 7.63 (4H, d, J = 8.0 Hz), 7.49 (2H, d, J = 16.0 Hz), 7.42 (2H, dd, J_1 = 5.0 Hz, J_2 = 1.5 Hz), 7.25 (2H, d, J = 16.0 Hz), 3.94 (6H, s). ^{13}C NMR (125 MHz, $CDCl_3$): 166.72, 156.50, 149.73, 145.19, 140.64, 132.26, 130.17, 129.96, 128.63, 126.92, 121.43, 118.39, 52.22. Among solvents tested, this ligand has low room temperature solubility in THF, $CHCl_3$ (sufficient for NMR spectroscopic characterization, Figure 2), and CH_2Cl_2.

4,4′-Bis[E-(p-diphenylamino-styryl)]-2,2′-bipyridine. A suspension of potassium *tert*-butoxide (0.6 mmol, 67 mg) in 8 mL of THF (anh) was added dropwise under argon to a solution containing 0.2 mmol (91 mg) of 4,4′-bis(diethylphosphonatomethyl)-2,2″-bipyridine and 0.45 mmol (123 mg) of 4-diphenylaminobenzaldehyde in 4 mL of THF (anh). The reaction mixture was then heated to a gentle reflux (70 °C) under argon for 24 h. After completion, the reaction was quenched by the addition of 15 mL of H_2O (DIUF grade). After removal of THF, the reaction mixture was extracted with dichloromethane (3 × 25 mL). The combined organic layers were washed with brine and dried over Na_2SO_4. After solvent removal, the title compound was obtained as an analytically pure yellow solid in 92% yield (127 mg, overall yield 68%). MALDI-MS: m/z = 694.32 ($[M]^+$). ^{1}H NMR (500 MHz, $CDCl_3$): 8.66 (2H, dd, J_1 = 5.0 Hz, J_2 = 0.4 Hz), 8.51 (2H, d, J = 1.5 Hz), 7.43 (4H, d, J = 8.5 Hz), 7.41 (2H, d, J = 16.0 Hz), 7.36 (2H, dd, J_1 = 5.0 Hz, J_2 = 1.5 Hz), 7.28 (8H, m), 7.13 (8H, m), 7.06 (8H, m), 7.01 (2H, d, J = 16.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): 156.48, 149.48, 148.41, 147.31, 146.12, 132.87, 129.96, 129.40, 128.01, 124.91, 124.08, 123.46, 122.86, 120.88, 118.06.

4,4′-Bis[E-(p-trifluoromethyl-styryl)]-2,2′-bipyridine. This ligand was synthesized via the procedure identical to the one used for the synthesis of 4,4′-bis[*E*-(*p*-diphenylamino-styryl)]-2,2′-bipyridine. The title compound was obtained as analytically pure off-white solid in 89% yield (88 mg, overall yield 63%). MALDI-MS: m/z = 497.10 ($[M]^+$). ^{1}H NMR (500 MHz, $CDCl_3$): 8.71 (2H, d, J = 5.0 Hz), 8.60 (2H, s), 7.67 (8H, d, J = 2.0 Hz), 7.49 (2H, d, J = 16.0 Hz), 7.43 (2H, dd, J_1 = 5.0 Hz, J_2 = 0.5 Hz), 7.23 (2H, d, J = 16.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): 156.66, 149.93, 145.29, 139.88, 132.03, 128.82, 127.37, 126.09, 126.03, 121.64, 118.59, 66.08.

Dichloro(η^6-benzene)ruthenium(II) dimer, ([Ru(Bz)Cl$_2$]$_2$). The synthesis of this ruthenium(II) complex was accomplished following the previously published procedure with slight modifications.[41,42] A 4.07 mmol (1.065 g) portion of hydrated ruthenium(III) chloride ($RuCl_3x3H_2O$) was dissolved in 50 mL of 90% v/v ethanol followed by

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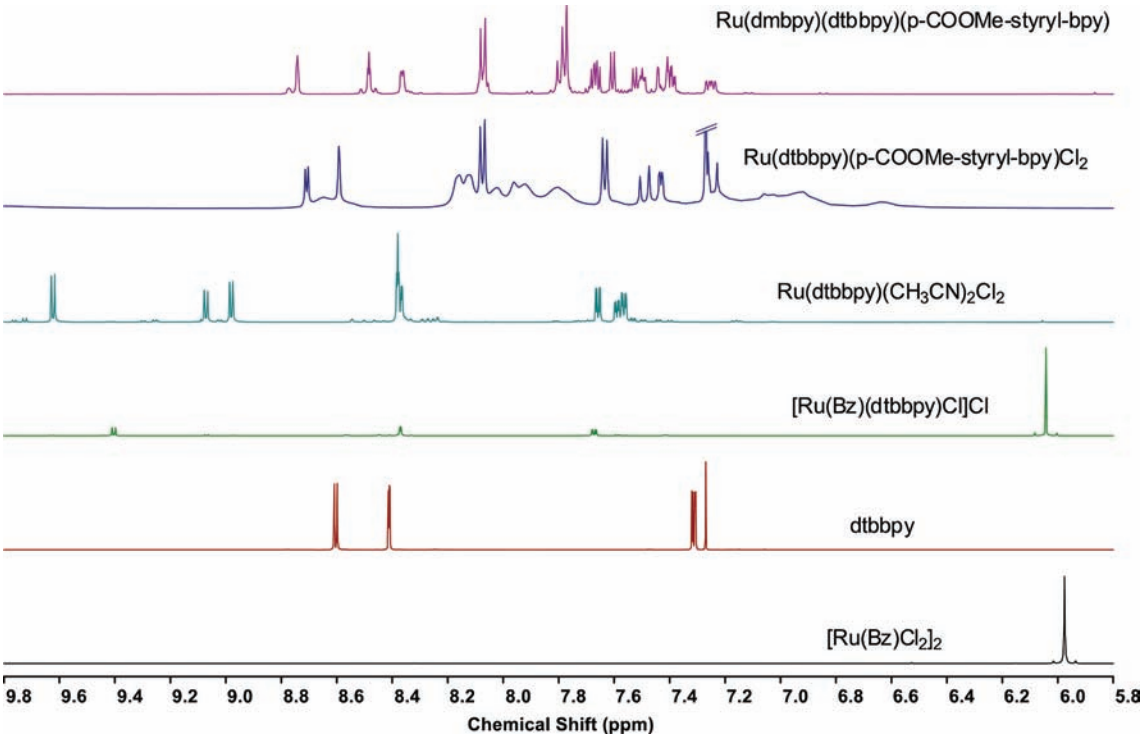

Figure 3. Stepwise transformation of $[Ru(Bz)Cl_2]_2$ into $[Ru(dmbpy)(dtbbpy)(p\text{-COOMe-styryl-bpy})](PF_6)_2$ (**1**): evolution of aromatic region (^{1}H NMR, 500 MHz) followed through each individual synthetic step.

dropwise addition of excess 1,3-cyclohexadiene (5.0 mL). The deep blue reaction mixture was heated to reflux (85 °C) for 4 h under ambient conditions resulting in the formation of product in the form of a bright red precipitate. The product was isolated by filtration, washed with copious amount of ethanol, and dried under vacuum (1.83 g, 90% yield). MALDI-MS: m/z = 464.13 ($[M - Cl]^+$). ^{1}H NMR (500 MHz, DMSO-d_6): 5.98 (6H, s).

Chloro(η^6-benzene)(4,4′-ditert-butyl-2,2′-bipyridine)ruthenium(II) Chloride, ([Ru(Bz)(dtbbpy)Cl]Cl). A 0.2 mmol (100 mg) portion of $[Ru(Bz)Cl_2]_2$ and 0.42 mmol (113 mg) of 4,4′-di-*tert*-butyl-2,2′-bipyridine (dtbbpy) were suspended in 30 mL of acetonitrile (anh) and purged with dry argon for 30 min. Subsequently, the reaction mixture was heated to reflux (90 °C) under argon overnight. Then, the reaction mixture was placed in a freezer for several hours to precipitate out the unreacted dtbbpy. The reaction mixture was filtered, and the filtrate was collected and concentrated to dryness to yield orange-brownish solid. The obtained solid was washed with ether and dried under vacuum to give title compound in 90% yield (186 mg). MALDI-MS: m/z = 483.17 ($[M - Cl]^+$). ^{1}H NMR (500 MHz, CD_3CN): 9.41 (2H, d, J = 6.0 Hz), 8.37 (2H, d, J = 2.0 Hz), 7.67 (2H, dd, J_1 = 6.0 Hz, J_2 = 2.0 Hz), 6.04 (6H, s), 1.44 (18H, s). ^{13}C NMR (125 MHz, CD_3CN): 166.13, 156.74, 156.12, 125.85, 122.55, 88.33, 36.89, 30.79. [Ru(Bz)(dtbbpy)Cl]Cl was found to be reasonably stable if stored under anhydrous conditions.

Chloro(η^6-benzene)(4,4′-dinonyl-2,2′-bipyridine)ruthenium(II) Chloride, [Ru(Bz)(dnbpy)Cl]Cl. A 0.2 mmol (100 mg) portion of $[Ru(Bz)Cl_2]_2$ and 0.42 mmol (172 mg) of 4,4′-dinonyl-2,2′-bipyridine (dnbpy) were suspended in 30 mL of acetonitrile (anh) and purged with argon for 30 min. After that, the reaction mixture was heated to reflux (90 °C) under argon overnight. Then, the reaction mixture was placed in a freezer for several hours to precipitate out the unreacted dnbpy. The reaction mixture was filtered, and the filtrate was collected and concentrated to dryness to yield orange-brownish solid. The obtained solid was washed with ether and dried under vacuum to give title compound in 92% yield (242 mg). ^{1}H NMR (500 MHz, CD_3CN): 9.43 (2H, d, J = 6.0 Hz), 8.28 (2H, d, J = 1.5 Hz), 7.51 (2H, dd, J_1 = 6.0 Hz, J_2 = 1.5 Hz), 6.07 (6H, s), 2.84−2.81 (4H, m), 1.73−1.69 (4H, m), 1.35−1.28 (24H, m), 0.89−0.86 (6H, m). ^{13}C NMR (125 MHz, CD_3CN): 157.95, 156.49, 155.71, 128.50, 124.91, 87.94, 35.76, 32.65, 30.87, 30.24, 30.09, 30.07, 29.92, 23.44, 14.46.

Dichlorobis(acetonitrile)(4,4′-ditert-butyl-2,2′-bipyridine)ruthenium(II), Ru(CH_3CN)$_2$(dtbbpy)Cl$_2$). A 0.21 mmol (112 mg) portion of [Ru(Bz)-(dtbbpy)Cl]Cl were placed in a 100 mL quartz reactor followed by the addition of dry acetonitrile (50 mL). The reaction mixture was purged with dry argon for 1 h, sealed airtight, and then photolyzed for 24 h using the spectrally unfiltered output of 450 W Hg vapor lamp as a light source. After reaction completion, the reaction mixture was concentrated to approximately 5 mL, and the product was precipitated by the addition of ether (∼200 mL). The solvent layer was gently decanted and the obtained product was dried under vacuum to yield orange solid (104 mg, 95% yield). ^{1}H NMR (500 MHz, CD_3CN): 9.63 (2H, d, J = 6.0 Hz), 9.08 (2H, d, J = 6.0 Hz), 8.99 (2H, d, J = 6.0 Hz), 8.38 (4H, t, J = 2.0 Hz), 8.36 (2H, d, J = 2.0 Hz), 7.66 (2H, dd, J_1 = 6.0 Hz, J_2 = 2.0 Hz), 7.59 (2H, dd, J_1 = 6.0 Hz, J_2 = 2.0 Hz), 7.56 (2H, dd, J_1 = 6.0 Hz, J_2 = 2.0 Hz), 1.46 (50H, s). ^{13}C NMR (125 MHz, CD_3CN): 154.88, 154.24, 126.11, 125.94, 124.26, 123.90, 123.36, 121.40, 121.20, 120.98, 36.28, 36.21, 30.72, 30.66, 4.97, 4.23. In acetonitrile solution, the product is likely to exist as a mixture of two interconverting complexes: bis(acetonitrile)dichloro(4,4′-di-*tert*-butyl-2,2′-bipyridine)ruthenium(II) and tris(acetonitrile)chloro(4,4′-di-*tert*-butyl-2,2′-bipyridine)ruthenium(II) chloride, Figure 3.

Dichlorobis(acetonitrile)(4,4′-dinonyl-2,2′-bipyridine)ruthenium-(II), Ru(CH_3CN)$_2$(dnbpy)Cl$_2$. A 0.17 mmol (115 mg) portion of [Ru(Bz)(dnbpy)Cl]Cl was placed in a 100 mL quartz reactor followed by the addition of dry acetonitrile (40 mL). The reaction mixture was purged with argon for 1 h, sealed airtight, and then photolyzed for 24 h using the spectrally unfiltered output of 450 W Hg vapor lamp as a light source. After reaction completion, the reaction mixture was concentrated to approximately 5 mL, and the product was precipitated by the

addition of ether (~200 mL). The solvent layer was gently decanted, and the obtained product was dried under vacuum to yield orange solid (96 mg, 85% yield). ^{1}H NMR (500 MHz, CD_3CN): 9.61 (2H, d, J = 6.0 Hz), 9.05 (2H, d, J = 6.0 Hz), 8.95 (2H, d, J = 6.0 Hz), 8.27 (3H, s), 8.25 (1H, s), 7.49 (2H, dd, J_1 = 6.0 Hz, J_2 = 2.0 Hz), 7.44 (6H, m), 2.86−2.82 (12H, m), 1.78−1.72 (12H, m), 1.41−1.26 (72H, m), 0.89−0.85 (18H, m). Similar to the above-described $Ru(CH_3CN)_2(dtbbpy)Cl_2$, the product is likely to exist in acetonitrile solution as a mixture of two interconverting complexes: bis(acetonitrile)dichloro(4,4′-dinonyl-2,2′-bipyridine)ruthenium(II) and tris(acetonitrile)chloro(4,4′-dinonyl-2,2′-bipyridine)ruthenium(II) chloride.

Dichloro(4,4′-ditert-butyl-2,2′-bipyridine)(4,4′-bis[E-(p-methylcarboxy-styryl)]-2,2′-bipyridine) Ruthenium(II), [$RuCl_2$(dtbbpy)(p-COOMe-styryl-bpy)]. A 0.19 mmol (100 mg) portion of $Ru(CH_3CN)_2(dtbbpy)Cl_2$ and 0.21 mmol (100 mg) of 4,4′-bis[*E*-(*p*-methylcarboxy-styryl)]-2,2′-bipyridine were suspended in 55 mL of THF (anh) under argon. The obtained brownish suspension was purged with dry argon for 30 min and then heated to a gentle reflux (70 °C) for 24 h under argon. Along the reaction course, the reaction mixture turned into a clear deep blue solution. After cooling to RT, the reaction mixture was placed in a freezer for several hours to precipitate out the unreacted starting materials. After filtration and solvent removal, the obtained dark blue (almost black) solid was washed with ether and dried under vacuum (162 mg, 93% yield). MALDI-MS: m/z = 916.06 ($[M]^+$). ^{1}H NMR (500 MHz, $CDCl_3$): 8.75−8.50 (4H, broad m), 8.22−7.70 (24H, broad m), 7.63 (4H, d, J = 8.0 Hz), 7.49 (2H, d, J = 16.0 Hz), 7.42 (2H, d, J = 4.0 Hz), 7.24 (2H, d, J = 16.0 Hz), 7.10−6.80 (8H, broad m), 6.69−6.55 (2H, broad s), 3.96−3.91 (12H, m), 1.47−1.26 (36H, m).

Dichloro(4,4′-dinonyl-2,2′-bipyridine)(4,4′-bis[E-(p-methylcarboxy-styryl)]-2,2′-bipyridine) Ruthenium(II), $RuCl_2$(dnbpy)(p-COOMe-styryl-bpy). A 0.106 mmol (70 mg) portion of $Ru(CH_3CN)_2(dnbpy)Cl_2$ and 0.12 mmol (57 mg) of 4,4′-bis[*E*-(*p*-methylcarboxy-styryl)]-2,2′-bipyridine were added to 30 mL of THF (anh) under argon. The obtained brownish suspension was purged with argon for 30 min and then heated to a gentle reflux (70 °C) for 24 h under argon. Along the reaction course, the reaction mixture turned into a clear deep blue solution. After filtration and solvent removal, the obtained dark blue (almost black) solid was washed with ether and dried under vacuum (108 mg, 97% yield). MALDI-MS: m/z = 1021.76 ($[M - Cl]^+$). ^{1}H NMR (500 MHz, $CDCl_3$): 8.71−8.59 (4H, broad m), 8.47 (2H, broad s), 8.15−8.06 (8H, m), 7.92−7.62 (14H, m), 7.54−7.42 (4H, broad m), 7.32−7.00 (10H, broad m), 6.88−6.84 (2H, broad s), 6.64 (2H, broad s), 6.53 (2H, broad s), 3.97−3.91 (12H, m), 2.84−2.81 (4H, m), 1.85−1.67 (6H, m), 1.49−1.19 (54H, m), 0.94−0.82 (12H, m).

*(4,4′-Dimethyl-2,2′-bipyridine)(4,4′-ditert-butyl-2,2′-bipyridine)-(4,4′-bis[E-(p-methylcarboxy-styryl)]-2,2′-bipyridine) Ruthenium(II) Hexafluorophosphate, [Ru(dmbpy)(dtbbpy)(p-COOMe-styryl-bpy)]-$(PF_6)_2$ (**1**).* A 0.1 mmol (92 mg) portion of $RuCl_2$(dtbbpy)(*p*-COOMe-styryl-bpy) and 0.12 mmol (22 mg) of 4,4′-dimethyl-2,2′-bipyridine (dmbpy) were dissolved in 25 mL of absolute ethanol. The reaction mixture was purged with argon for 30 min and then brought to reflux conditions (85 °C) for 24 h under argon. During the reaction course, the color changed from deep blue to dark red. After cooling to RT, the reaction mixture was filtered and the product was precipitated out by the addition of excess NH_4PF_6 (aq). The obtained precipitate was filtered off, washed with a copious amount of H_2O (DIUF grade) and ether, and dried under vacuum to give analytically pure red solid in 86% yield (113 mg, 61% overall yield). Anal. calcd (found) for $C_{60}H_{60}F_{12}N_6O_4P_2Ru$ (%): C, 54.59 (54.42); H, 4.58 (4.44); N 6.37 (6.30). MALDI-MS: m/z = 1175.28 ($[M - PF_6]^+$). ^{1}H NMR (500 MHz, CD_3CN): 8.73 (2H, s, *p-COOMe-styryl-bpy*), 8.48 (2H, dd, *dtbbpy*, J = 2.0 Hz), 8.37 (2H, ss, *dmbpy*), 8.07 (4H, d, J = 8.0 Hz, *p-COOMe-styryl-bpy*), 7.81−7.77 (6H, m, *p-COOMe-styryl-bpy*), 7.68−7.65 (3H, m, *p-COOMe-styryl-bpy* + *dtbbpy*), 7.61 (2H, d, J = 6.0 Hz, *dtbbpy* + *dmbpy*), 7.52−7.49 (3H, m, *p-COOMe-styryl-bpy* + *dmbpy*), 7.44−7.39 (4H, m, *p-COOMe-styryl-bpy* + *dtbbpy*), 7.27−7.24 (2H, dd, J = 6.0 Hz, *dmbpy*) 3.88 (6H, s, *p-COOMe-styryl-bpy*), 2.55 (3H, s, *dmbpy*), 2.53 (3H, s, *dmbpy*), 1.42 (9H, s, *dtbbpy*), 1.40 (9H, s, *dtbbpy*). ^{13}C NMR (125 MHz, CD_3CN): *p-COOMe-styryl-bpy* 167.59, 158.79, 158.76, 152.13, 152.07, 147.07, 141.56, 136.15, 131.35, 128.80, 127.97, 125.92, 122.20, 122.18, 53.23; *dtbbpy* 158.14, 158.09, 152.83, 152.74, 151.66, 151.65, 125.92, 122.86, 36.68, 36.67, 30.84, 30.82; *dmbpy* 157.85, 157.82, 151.66, 152.07, 151.94, 129.63, 126.22, 21.65, 21.63. The complete structural assignment was performed based on 2D homo- and heteronuclear correlation NMR data[43] (Figures 4−6 and S1) and is discussed below in more detail.

*(4,4′-Dimethyl-2,2′-bipyridine)(4,4′-dinonyl-2,2′-bipyridine)(4,4′-bis[E-(p-methylcarboxy-styryl)]-2,2′-bipyridine) Ruthenium(II) Hexafluorophosphate, [Ru(dmbpy)(dnbpy)(p-COOMe-styryl-bpy)]$(PF_6)_2$ (**2**).* A 0.05 mmol (53 mg) portion of [$RuCl_2$(dnbpy)(*p*-COOMe-styryl-bpy)] and 0.06 mmol (11 mg) of 4,4′-dimethyl-2,2′-bipyridine were dissolved in 10 mL of absolute ethanol. The reaction mixture was purged with argon for 30 min and then brought to reflux conditions (85 °C) for 24 h under argon. During the reaction course, the color changed from deep blue to dark red. After cooling to RT, the reaction mixture was filtered and the product was precipitated out by the addition of excess NH_4PF_6 (aq.). The precipitate was filtered off, washed thoroughly with H_2O (DIUF grade) and ether and dried under vacuum to give analytically pure red solid in 84% yield (61 mg, 57% overall yield). Anal. calcd (found) for $C_{70}H_{80}F_{12}N_6O_4P_2Ru$ (%): C, 57.57 (57.73); H, 5.52 (5.45); N 5.75 (5.62). MALDI-MS: m/z = 1315.56 ($[M - PF_6]^+$). ^{1}H NMR (500 MHz, CD_3CN): 8.73 (2H, s), 8.36 (4H, s), 8.06 (4H, d, J = 8.0 Hz), 7.77 (6H, m), 7.67 (2H, m), 7.62 (2H, m), 7.55−7.48 (4H, m), 7.42 (2H, d, J = 16.0 Hz), 7.24 (4H, m), 3.88 (6H, s), 2.82−2.77 (4H, m), 2.55 (3H, s), 2.54 (3H, s), 1.73−1.65 (4H, m), 1.38−1.24 (24H, m), 0.89−0.83 (6H, m). ^{13}C NMR (125 MHz, CD_3CN): 167.32, 158.50, 157.77, 157.58, 155.72, 152.50, 151.94, 151.83, 151.64, 151.32, 148.73, 141.32, 135.79, 131.66, 131.02, 129.31, 128.51, 127.73, 125.92, 125.54, 125.22, 121.93, 52.92, 35.79, 32.67, 32.64, 30.98, 30.95, 30.23, 30.20, 30.08, 30.06, 30.03, 29.91, 29.85, 23.46, 23.43, 21.33, 14.47, 14.44.

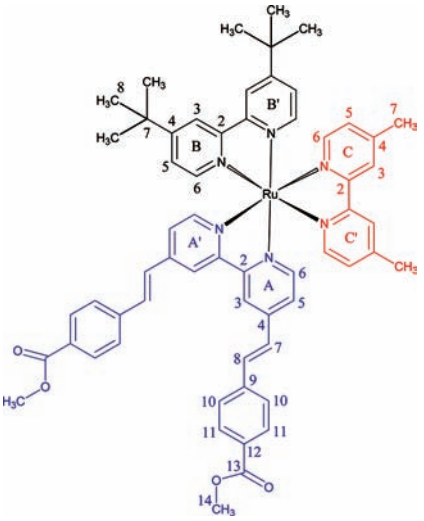

Figure 4. Labeling scheme for the structural assignment of **1**.

RESULTS AND DISCUSSION

Synthesis of π-Conjugated 4,4′-Styryl-2,2′-bipyridine Ligands. The developed stepwise synthesis of a series of π-conjugated 4,4′-styryl-2,2′-bipyridine ligands is presented in

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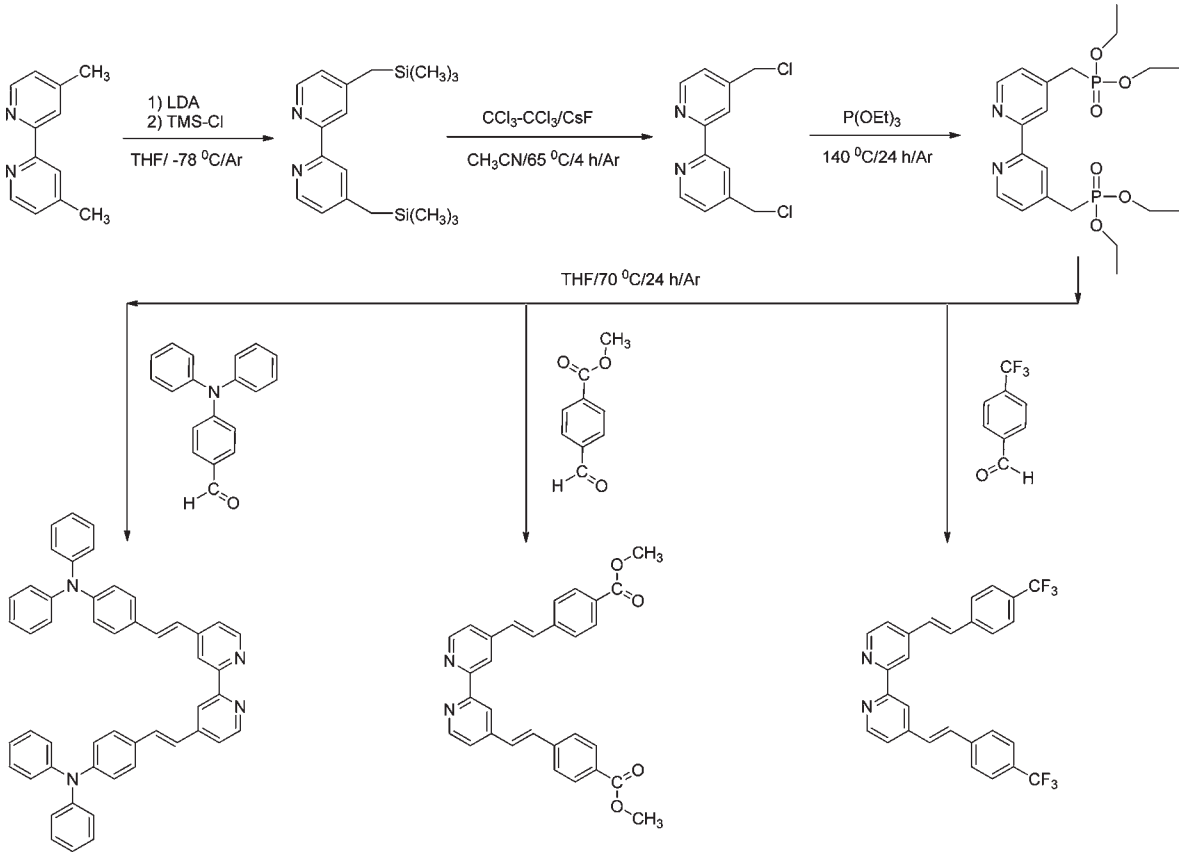
Scheme 2. Stepwise Synthetic Route Towards Functionalized 4,4′-Styryl-2,2′-bipyridine Ligands



Scheme 2, starting from commercially available 4,4′-dimethyl-2,2′-bipyridine (dmbpy).

First, dmbpy was converted into its bis(chloromethyl) derivative via the two-step methodology developed by Fraser and coworkers.[37] The dihalogenated bipyridine is readily isolated by flash chromatography on deactivated silica, while its precursor, the silylated bpy, is obtained in excellent yields and can be used without any further purification. In terms of product distribution, isolation, and yields, this route turns out to be more efficient and better controlled when compared to a direct radical halogenation (e.g., with *N*-bromosuccinimide) where the reported product yields are typically near 40%.[15,44] In addition, both the silylation (step 1) and halogenation (step 2) reactions are easily scalable without noticeably affecting the product yields. In a broad sense, 4,4′-bis(chloromethyl)-2,2′-bpy can be viewed as a versatile intermediate for synthesizing other classes of bipyridine ligands, for example, via well-established transition metal-catalyzed chemistry.[45]

In the next step, 4,4′-bis(chloromethyl)-2,2′-bpy was cleanly and efficiently converted into 4,4′-bis(diethylphosphonatomethyl)-2,2′-bipyridine by refluxing with excess triethylphosphite, the Michaelis−Arbuzov reaction.[30,38] The obtained product, 4,4′-bis(diethylphosphonatomethyl)-2,2′-bipyridine, can be readily isolated by column chromatography on deactivated silica. The attachment of the two phosphonate groups to the bipyridine skeleton was confirmed by ^{1}H NMR spectroscopy where the methylene (CH_2) group directly attached to a phosphorus atom gave rise to a doublet, with a characteristic coupling constant of 22.0 Hz (^{1}H NMR, 500 MHz). In addition, all carbon peaks in proton-decoupled ^{13}C NMR spectra appeared as doublets with coupling constants ranging between 2.5 and 137.0 Hz (see the Experimental Section). In terms of the formation of a trans (*E*-isomer) C═C double bond, 4,4′-bis(diethylphosphonatomethyl)-2,2′-bpy should be considered the most important intermediate in our synthetic sequence, as it can be coupled with a wide variety of commercially available functionalized benzaldehydes via the Horner−Wadsworth−Emmons (HWE) reaction (Scheme 2), selectively producing the target *E*-isomer. Even though the classical Wittig reaction has been reported to produce the disubstituted product,[46] it failed in our case, as only monosubstituted phosphonium salts were obtained—as soon as the first chloromethyl group reacted with triphenylphosphine (PPh_3), the product immediately precipitated, thereby rendering the second substitution step inefficient. In addition, the Wittig reaction is considered inferior to the HWE reaction in terms of the ultimate product stereochemical control.[40] In some cases, the HWE coupling reaction has been reported to operate at room temperature in DMF; however, the reported product yields were only ∼50%, and it is not obvious why DMF was the solvent of choice.[30] From the product isolation point of view, high-boiling solvents should be substituted with low-boiling alternatives if possible. As we discovered, more favorable reaction conditions do indeed exist and carrying out the HWE coupling reaction in refluxing THF achieves notably higher product yields by approximately 20−25%, i.e., from ∼50% to >70% (see the Experimental Section), a significant improvement over the previously reported methodologies. For all 4,4′-styryl-2,2′-bipyridines reported herein, the selective formation of the *E*-isomer was confirmed

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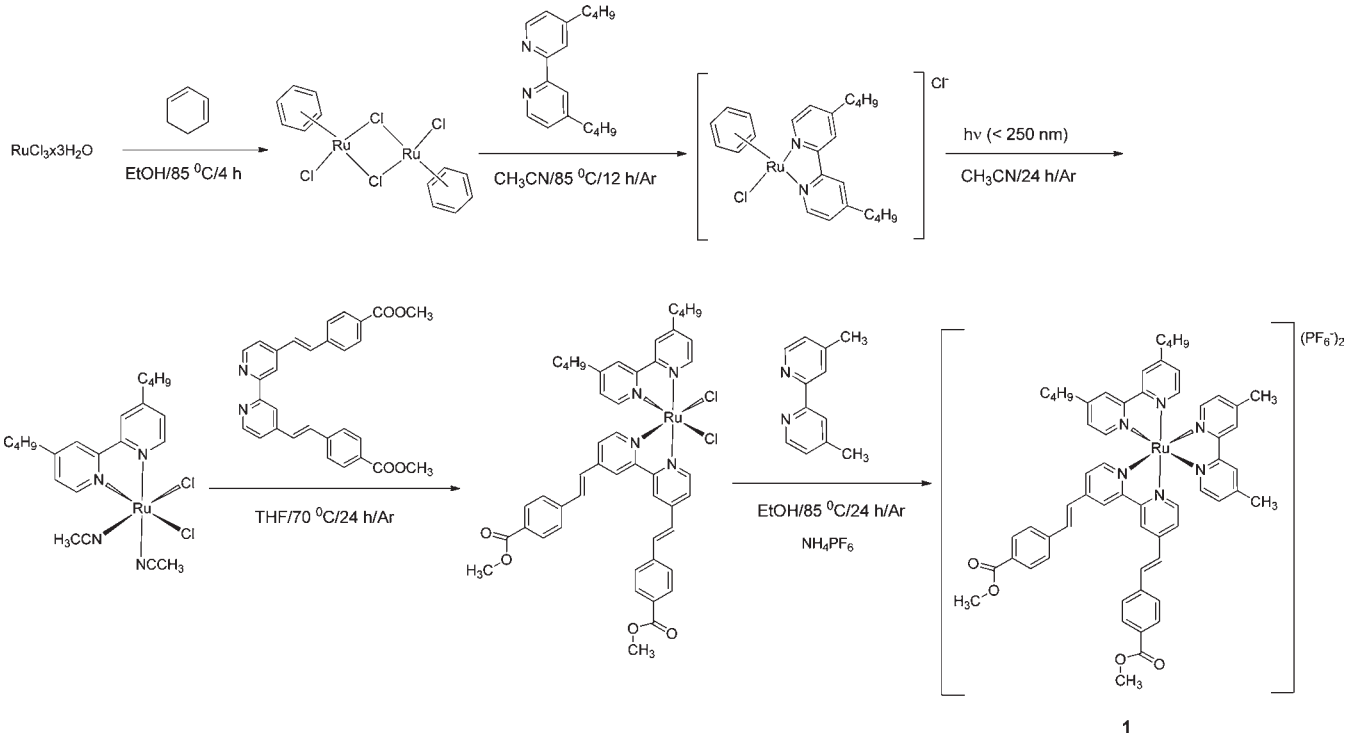
Scheme 3. Stepwise Synthetic Route Towards Tris(heteroleptic) Ru(II) Complexes Incorporating a π-Conjugated Carboxylated 4,4′-Styryl-2,2′-bipyridine Ligand Using Target 1 as a Representative Example



through careful analysis of ^{1}H NMR spectra, where the olefinic protons typically gave rise to a pair of doublets with a coupling constant of 16.0 Hz (see the Experimental Section), which falls well into the expected range for the trans isomer.[40] We also note that while the bis(phosphonate)-bpy, the appropriately functionalized benzaldehyde, and base (*t*-BuOK) can in principle be added in any arbitrary order, the dropwise addition of *t*-BuOK suspension in THF to a solution of the bis(phosphonate)bpy and benzaldehyde derivative yielded the best results.

Our main target ligand was the 4,4′-bis[*E*-(*p*-methylcarboxy-styryl)]-2,2′-bipyridine, since its acid form can be used for covalent binding to the surface of metal oxide semiconductors, e.g., TiO_2.[47] To the best of our knowledge, this ligand has been used sparingly to date as its alternative synthesis via the one-pot reaction has not gained popularity.[14,26] We note that the reliability of this one-pot methodology remains questionable as the reported structural data were found to be inconsistent with the findings presented herein. The structural analysis of 4,4′-bis[*E*-(*p*-methylcarboxy-styryl)]-2,2′-bipyridine predicts that the molecule is symmetric, and thus, a set of 8 peaks in the ^{1}H NMR spectrum is expected and was observed in our case: three peaks from the bipyridine ring (all doublets of doublets in a 1:1:1 ratio), four resonances from the styryl moieties (all doublets in a 2:2:1:1 ratio), and one peak (singlet) from the methyl carboxylates. Our ^{1}H NMR data are also in excellent agreement with the associated ^{13}C NMR (13 observed resonances) in addition to the MALDI-MS data, thereby confirming the formation of the target ligand, 4,4′-bis[*E*-(*p*-methylcarboxy-styryl)]-2,2′-bipyridine (see the Experimental Section).

Overall, the utility of the developed methodology for the synthesis of various 4,4′-styryl-2,2′-bipyridines is that the entire synthetic sequence is well-controlled and at each individual step the product is formed in good to excellent yield, the product is isolated in analytically pure form as evident from the stacked NMR spectra presented in Figure 2, which uses the synthesis of 4,4′-bis[*E*-(*p*-methylcarboxy-styryl)]-2,2′-bipyridine as a representative example. We note that the overall yields of the synthesized 4,4′-styryl-2,2′-bipyridines always exceeded 50% using the current methodology (see the Experimental Section). In addition, the versatility and efficiency of this strategy was demonstrated by synthesizing styryl-bipyridine ligands bearing both electron-donating and electron-withdrawing groups, namely 4,4′-bis[*E*-(*p*-diphenylamino-styryl)]-2,2′-bipyridine and 4,4′-bis[*E*-(*p*-trifluoromethyl-styryl)]-2,2′-bipyridine (see the Experimental Section).

Synthesis of Heteroleptic Tris(polypyridyl) Ru(II) Complexes Bearing Styryl-Bipyridines. The overall synthetic sequence toward tris(heteroleptic) Ru(II) complexes bearing the π-conjugated carboxylated 4,4′-styryl-2,2′-bipyridine ligand is outlined in Scheme 3. As a representative example, the overall synthesis of **1** is presented in detail.

In the majority of recent cases, heteroleptic Ru(II) complexes of the general forms $RuCl_2(LL)'(LL)''$ or $Ru(LL)'(LL)''(NCS)_2$ are synthesized starting from the commercially available dichloro(*p*-cymene)ruthenium(II) dimer ($[Ru(p\text{-cymene})Cl_2]_2$).[14,16,17,48,49] However, in the present cases, the use of this synthon proved to be inefficient, as the *p*-cymene ligand turned out to be inert to photosubstitution with acetonitrile, as we demonstrate for the [Ru(*p*-cymene)(dnbpy)Cl]Cl complex in Supporting Information Figure S2. This particular observation agrees well with previously reported results.[50] However, the related η^6-benzene π-complex derivative undergoes facile photosubstitution and is easily prepared from $RuCl_3$ via the redox reaction with 1,3-cyclohexadiene in refluxing aqueous

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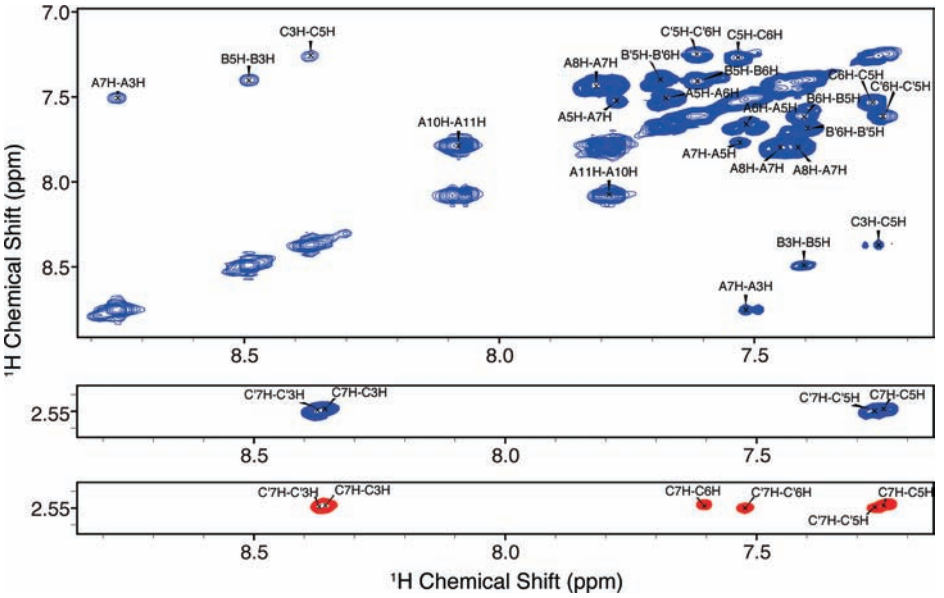

Figure 5. $^1H-^1H$ correlation NMR spectrum (500 MHz, CD_3CN) of **1** with complete peak assignments: COSY (blue) selected aromatic (top) and aliphatic (middle) regions; TOCSY (red) selected aliphatic region (bottom).

ethanol.[41,42] Under the employed reaction conditions, the formed dimer, $[Ru(Bz)Cl_2]_2$, precipitates out as a bright red solid in excellent yield (90%). The η^6-benzene resonance in the ^1H NMR spectrum (measured in DMSO-d_6) lies at δ = 5.98 ppm (see the Experimental Section). The assignment of the benzene chemical shift in $[Ru(Bz)Cl_2]_2$ at δ = 5.98 ppm is supported by comparison with [Ru(*p*-cymene)(dnbpy)Cl]Cl where *p*-cymene gives rise to a pair of doublets in the same region of the ^1H NMR spectrum (measured in CD_3CN, Supporting Information Figure S2) with chemical shifts of δ_1 = 5.98 (J = 6.4 Hz) and δ_2 = 5.80 (J = 6.4 Hz) ppm, respectively.

The first bipyridine ligand, 4,4′-di-*tert*-butyl-2,2′-bipyridine (dtbbpy) in the present case, was coordinated by reacting with $[Ru(Bz)Cl_2]_2$ in refluxing acetonitrile overnight. The initial choice of bipyridine ligand depends largely on the design of the ultimate Ru(II) complex, as other functionalized diimines can be also used at this stage. We are interested in dtbbpy ligands as they have revealed clear evidence of Stark effects in dye-sensitized titania.[51,52] For comparison, we also tested 4,4′-dinonyl-2,2′-bipyridine (dnbpy) and the obtained results were identical to dtbbpy in terms of product yield and purity (see the Experimental Section). We note that if the chosen diimine ligand is not sufficiently soluble in acetonitrile at RT, the uncoordinated portion can be easily removed (precipitated) from the product, thereby yielding analytically pure complex in this particular instance as [Ru(Bz)(dtbbpy)Cl]Cl.

In the next step, the η^6-benzene was photolytically substituted using UV excitation in the presence of acetonitrile to yield the solvato complex as $Ru(CH_3CN)_2(dtbbpy)Cl_2$, with final product isolation accomplished by precipitation with ether. This type of photosubstitution reaction has been extensively investigated previously and can notably be used for the synthesis of both Ru(II)- and Os(II)-based complexes.[7,53] Distinguishable with respect to the reported reaction conditions,[7] the present chemistry takes place under homogeneous conditions, as both the starting material, [Ru(Bz)(dtbbpy)Cl]Cl, and the reaction product, $Ru(CH_3CN)_2(dtbbpy)Cl_2$, were soluble in acetonitrile at RT. The photosubstitution reaction step is crucial in our synthetic sequence as it allows one to insert labile acetonitrile ligands that can be selectively removed in the next step. It is important to note the observation that the benzene π-complex in [Ru(Bz)(dtbbpy)Cl]Cl does not undergo ligand substitution with acetonitrile through simple thermal activation. The successful photosubstitution was confirmed by ^1H NMR spectroscopy where the quantitative disappearance of the η^6-benzene peak was readily apparent (see the Experimental Section and Figure 3). However, as also evident from NMR data, the obtained product likely exists in acetonitrile solution as a mixture of two interconverting complexes, presumably the neutral $Ru(CH_3CN)_2(dtbbpy)Cl_2$ and ionic $[Ru(CH_3CN)_3(dtbbpy)Cl]Cl$ as has been reported in related literature.[7] Nevertheless, we found that this ill-defined precursor successfully underwent the coordination of the second bipyridine ligand, 4,4′-bis[*E*-(*p*-methylcarboxy-styryl)]-2,2′-bipyridine. In a broader context, we would like to emphasize that the π-conjugated ligand should be preferentially coordinated into the complex framework as the second or third polypyridyl ligand in order to avoid exposure to UV-photolysis thereby circumventing any chemistry related to photodecomposition and/or cis/trans isomerization.

The incorporation of the second (π-conjugated) bipyridine ligand was accomplished by refluxing the mixture of Ru(II) acetonitrile complexes with 4,4′-bis[*E*-(*p*-methylcarboxy-styryl)]-2,2′-bipyridine in anhydrous THF for 24 h to yield the desired Ru(II) dichloride complex, $RuCl_2(dtbbpy)$(*p*-COOMe-styryl-bpy). The choice of the solvent and reaction conditions was primarily dictated by the fact that 4,4′-bis[*E*-(*p*-methylcarboxy-styryl)]-2,2′-bipyridine was very stable under the employed conditions (identical to the original ligand synthesis). In addition, we had to keep in mind that 4,4′-bis[*E*-(*p*-methylcarboxy-styryl)]-2,2′-bipyridine is somewhat soluble only in a handful of solvents. Even though all starting materials exhibited low solubility in THF at RT, the initially formed brownish suspension, as the reaction proceeded, gradually became a clear solution accompanied by a color change to deep blue which is characteristic of dichloride Ru(II) complexes structurally similar to

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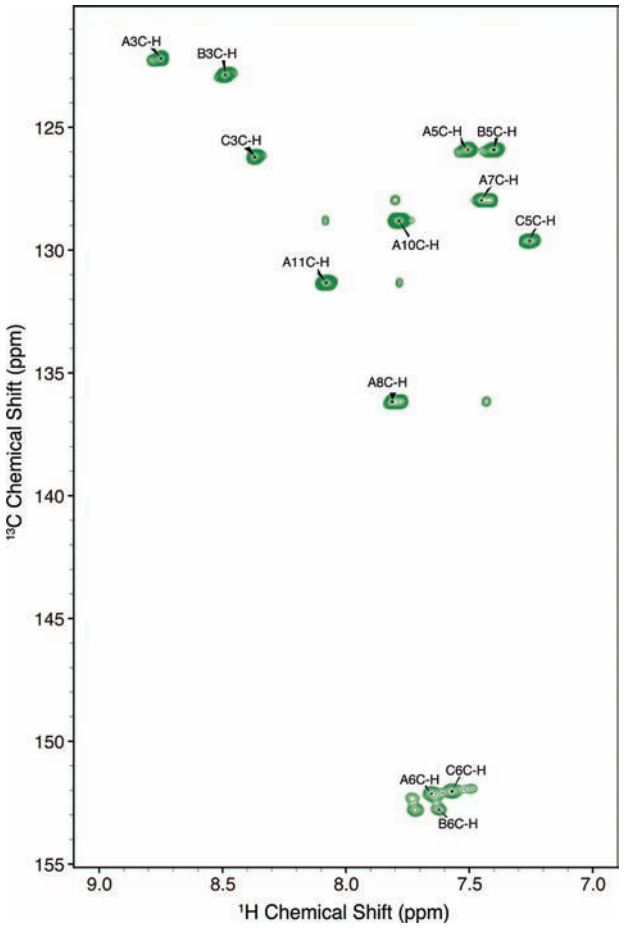

Figure 6. $^{1}H-^{13}C$ correlation NMR spectrum (HSQC) of **1** with complete peak assignments presented (500 MHz, CD_3CN). For clarity, only the aromatic region is presented.

$RuCl_2$(dtbbpy)(*p*-COOMe-styryl-bpy). The isolation of the target complex was very straightforward, as all unreacted starting materials were precipitated out at low temperature (−15 °C). On the basis of MALDI-MS data and observed changes during the reaction course (e.g., changes in color and product solubility), the formation of the desired Ru(II) dichloride complex appeared certain. However, the observed ^{1}H NMR spectra were somewhat puzzling as most peaks appeared to be quite broad concomitant with a significant degree of spectral overlap resulting in the loss of the spectral resolution. The origin of this effect is still not understood; however, we can speculate that the product was formed as a mixture of two structurally proximate complexes, neutral $RuCl_2$(dtbbpy)(*p*-COOMe-styryl-bpy) and ionic [RuCl(CH_3CN)(dtbbpy)(*p*-COOMe-styryl-bpy)]Cl, thereby inducing broadening of the observed ^{1}H resonances. In addition, we cannot also exclude the formation of solvato-complexes as this reaction step was carried out in THF. Nevertheless, as discussed below, in the next synthetic step the obtained product was efficiently converted into the ultimate tris(heteroleptic) Ru(II) complex **1**.

In the final step of this synthetic sequence, the above product, $RuCl_2$(dtbbpy)(*p*-COOMe-styryl-bpy), was converted into the tris(heteroleptic) Ru(II) complex **1** in high yield (86%) via the facile reaction with dmbpy in refluxing absolute ethanol followed by precipitation with aqueous NH_4PF_6. The introduction of 4,4′-dimethyl-2,2′-bipyridine was selected merely as a proof of synthetic concept, whereas a variety of different polypyridyl ligands can be used at this stage depending on the desired structural design of the ultimate Ru(II) complex. All acquired analytical data (NMR and MALDI-MS) were found to be consistent with the structure of the target complex, [Ru(dmbpy)(dtbbpy)(*p*-COOMe-styryl-bpy)]$(PF_6)_2$ (**1**). We would also like to emphasize at this point that the desired Ru(II) complexes **1** and **2** were obtained as analytically pure compounds in high overall yields (>50% after 5 steps) and, most importantly, isolated without significant purification effort.

Table 1. Complete Structural Assignment of 1[a]

	bis(*p*-COOMe-styryl-bpy)		dtbbpy		dmbpy	
atom #	A	A′	B	B′	C	C′
			^{1}H (ppm)			
3	8.75	8.75	8.49	8.48	8.36	8.37
5	7.51	7.49	7.42	7.40	7.25	7.27
6	7.65	7.67	7.68	7.62	7.61	7.53
7	7.43	7.43			2.53	2.55
8	7.81	7.81	1.40	1.42		
10	7.78	7.78				
11	8.08	8.08				
14	3.89	3.89				
			^{13}C (ppm)			
2	158.79	158.76	158.09	158.14	157.82	157.85
3	122.20	122.18	122.86	122.86	126.22	126.22
4	147.07	147.04	151.65	151.66	151.66	151.66
5	125.92	125.92	125.92	125.92	129.63	129.63
6	152.07	152.13	152.74	152.83	151.94	152.07
7	127.97	127.97	36.67	36.68	21.63	21.65
8	136.15	136.15	30.82	30.84		
9	147.07	147.07				
10	128.80	128.80				
11	131.35	131.35				
12	141.56	141.56				
13	167.59	167.59				
14	53.23	53.23				

[a] The labeling scheme is presented in Figure 4.

NMR Structural Assignment of Tris(heteroleptic) Ru(II) Complexes. Along with X-ray crystallography, multidimensional high-resolution NMR spectroscopy provides a powerful analytical tool for the structural characterization/assignment of complex molecules including polypyridyl transition metal complexes.[7,32] As a result of the ambiguities observed in the 1D ^{1}H NMR spectrum of **1** (and **2**), we performed complete structural assignments using an array of multidimensional homo- and heteronuclear (^{1}H, ^{13}C) correlation NMR techniques.[43] To simplify the interpretation and assignment of the obtained 2D NMR data, structural aspects of **1** are labeled and color-coded according to the scheme presented in Figure 4. Most of the protons have been assigned based on $^{1}H-^{1}H$ correlation COSY and TOCSY experiments (Figure 5) whereas proton-attached carbons and quaternary carbons have been assigned via $^{1}H-^{13}C$ correlation HSQC (Figure 6) and HMBC (Supporting Information Figure S1) experiments, respectively. All structurally assigned ^{1}H and ^{13}C resonances are summarized in Table 1. We

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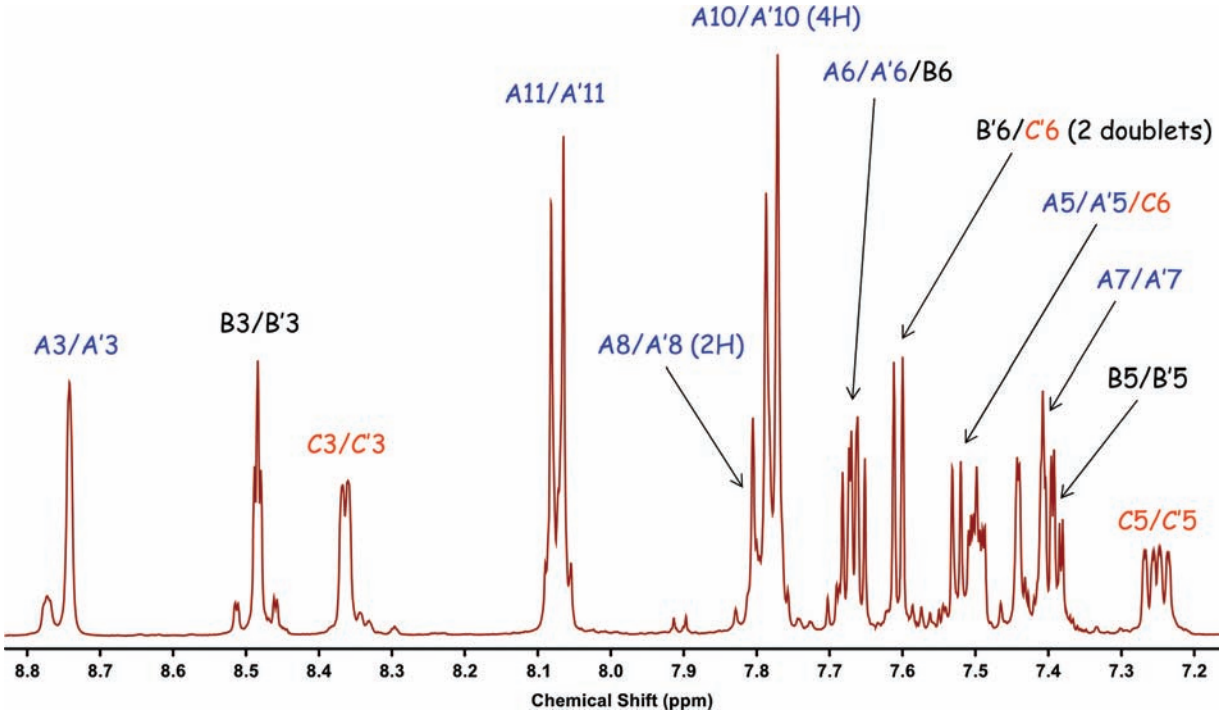

Figure 7. Complete assignment of the aromatic region in the 1D ^{1}H NMR spectrum of **1** (500 MHz, CD_3CN) using the combined 2D NMR data. The color- and letter-labeling scheme is presented in Figure 4.

note here that both homo- (^{1}H−^{1}H) and heteronuclear (^{1}H−^{13}C) correlations were necessitated as proper assignments could not be completed using only ^{1}H−^{1}H correlations (COSY, TOCSY). The most important steps encountered during the structural assignment of **1** are described below.

Note that there are several substituents within **1** that can be used as a departure point for structural assignments, specifically, the styryl fragments from the bis(*p*-COOMe-styryl-bpy) ligand (A7−A12, A′7−A′12), the *tert*-butyl groups from the dtbbpy ligand (B7−B8, B′7−B′8), and the methyl groups from the dmbpy ligand (C7, C′7). As evident from the combined 1 and 2D NMR data (see Figures 5−7), both dmbpy (C, C′) and dtbbpy (B, B′) ligand constituents became asymmetric upon coordination to the metal center due to the heteroleptic nature of the complex; however, the bis(*p*-COOMe-styryl-bpy) ligand (A, A′) remained in a pseudosymmetric geometry, presumably caused by the free rotation of the styryl moieties about their respective C−C single bonds. The observed asymmetry of the dmbpy and dtbbpy ligands became initially apparent upon the examination of the 1D ^{1}H NMR spectra where the methyl groups from both dmbpy (C7, C′7) and dtbbpy (B8, B′8) each gave rise to a set of two singlets of nearly equal intensity, rather than the one expected singlet if they retained their intrinsic symmetry. The pseudosymmetry of the *p*-COOMe-styryl-bpy subunit was also deduced based on ^{1}H NMR (see the Experimental Section and Figure 7) where the styryl moiety (A7−11, A′7−11) simply gave rise to a set of 4 peaks rather than 8, in a 1:1:2:2 ratio.

In the coordinated bis(*p*-COOMe-styryl-bpy) ligand, phenyl ring protons (A10−11, A′10−11) were primarily assigned based on their correlation with the neighboring trans double bond spin system (A7−8, A′7−8), phenyl ring protons at δ 8.08 (A11, A′11) were found to correlate only with protons at δ 7.78 (A10, A′10), while protons at δ 7.78 (A10, A′10) correlated with both A11 (A′11) and A8 (A′8) protons (Figure 5). The successful assignment of the styryl fragment then led to a straightforward assignment of atoms from the bipyridyl section of the ligand. On the dmbpy fragment, the methyl group protons at δ 2.53−2.55 (C7, C′7) revealed two equal intensity 4-bond correlations in the COSY spectrum with protons at both the 3(3′)- and 5(5′)-positions of its bipyridine ring, δ 8.36−8.37 and δ 7.25−7.27, respectively (Figure 5, Table 1). In addition, the TOCSY experiment (Figure 5) revealed a 5-bond scalar correlation between C7, C′7 and C6, C′6 protons.

Similarly, protons at the C3 and C′3 positions (δ 8.36−8.37) possess correlations with two sets of protons (C5,7; C′5,7) whereas the protons at C5 and C′5 were found to correlate with all three sets of protons within the spin system of dmbpy (Figure 5). The remaining bipyridine ligand, dtbbpy, then had its protons assigned following an identical strategy.

Once the structural assignment of **1** was completed, several interesting electronic effects clearly surfaced. First, the protons at the 6,6′-positions of both dmbpy (C6, C′6) and dtbbpy (B6, B′6) exhibited the highest degree of magnetic inequality (Table 1, Figure 7); however, this effect agrees well with the octahedral arrangement of the target complex as the 6,6′-positions are relatively exposed to the neighboring ligands and are therefore most sensitive to any induced changes in the local magnetic environment. Second, the protons at the 3,3′-positions of each polypyridyl ligand became the most deshielded upon metal coordination and were observed as three pseudosinglets across the 8.3−8.8 ppm spectral range (Figure 3). In concert with our assignment of chemical shifts, protons at the 3,3′-positions of dtbbpy (B3, B′3) appear in the 1D ^{1}H NMR spectrum (Figure 7) as a doublet of doublets (dd, δ 8.48−8.49) with a coupling constant of 2.0 Hz which is characteristic of 4-bond scalar coupling between protons at the 3,3′- and 5,5′-positions. The

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Table 2. Photophysical Properties of Ru(II) Complexes 1 and 2

Ru(II) complex	abs λ_{max} (nm) (ε (M^{-1} cm^{-1}))	em λ_{max} (nm) (nm)	τ (ns)
1	490 (15 000)	690	750
	324 (55 800)		
	290 (62 200)		
2	490 (15 000)	690	640
	320 (48 600)		
	290 (64 000)		
$[Ru(bpy)_3](PF_6)_2$	450 (13 800)	610	920
	288 (77 600)		

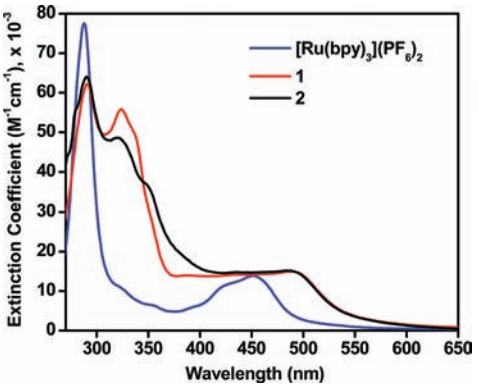

Figure 8. Ground-state absorption spectra of **1** (red), **2** (black), and $[Ru(bpy)_3](PF_6)_2$ (blue) measured in acetonitrile at RT.

same scalar coupling pattern was observed in case of the noncoordinated bipyridine ligands (see the Experimental Section). Evidently, in heteroleptic Ru(II) complexes, the electron density distribution in metal-coordinated polypyridyl ligands differs substantially from the noncoordinated "free" ligands where the most deshielded protons normally occur at the 6,6′-positions.

Photophysical Properties of the Tris(heteroleptic) Ru(II) Complexes. Steady-state and time-resolved photoluminescence measurements in oxygen-free acetonitrile solutions were carried out to evaluate the fundamental photophysical properties of **1** and **2** complexes using $[Ru(bpy)_3](PF_6)_2$ as a reference compound.[54] The combined data are summarized in Table 2. As shown in Figure 8, both **1** and **2** display broad and featureless low energy absorption bands spanning the near-visible and visible region from ~370 to 600 nm with a maximum centered near 490 nm. These bands are characteristic of metal-to-ligand charge transfer (MLCT) transitions from a metal-based t_{2g} orbital to ligand-based π^* orbitals.[55] Due to the tris(heteroleptic) nature of **1** and **2**, the observed MLCT absorption band possesses mixed character with transitions terminating on all three bipyridine ligands. Apparently, the intensity of the MLCT band responded weakly to the incorporation of the styryl-bipyridine moiety in the structure of these heteroleptic Ru(II) complexes as its extinction coefficient (ε) was only slightly enhanced in comparison to $[Ru(bpy)_3](PF_6)_2$, from 13 800 to 15 000 M^{-1} cm^{-1} (see Table 2). Nevertheless, the MLCT bands in **1** and **2** displayed a pronounced bathochromic shift (~40 nm) relative to our reference compound which agrees well with the extension of π-conjugation in the presence of the 4,4′-bis[*E*-(*p*-methylcarboxy-styryl)]-2,2′-bipyridine ligand. Similar effects

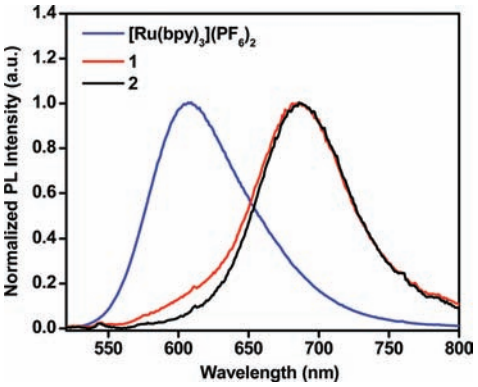

Figure 9. Steady-state photoluminescence spectra of **1** (red), **2** (black), and $[Ru(bpy)_3](PF_6)_2$ (blue) measured in acetonitrile at RT.

have also been observed in the case of polypyridyl Ru(II) complexes bearing various conjugated bipyridine ligands.[56−58] The intense absorption band (ε = 64 000 M^{-1} cm^{-1}) centered at 290 nm is a sum of $\pi-\pi^*$ electronic transitions primarily originating from dmbpy and dtbbpy ligands. Another intense band ($\varepsilon \approx$ 49 000−55 000 M^{-1} cm^{-1}) in the UV region is centered at 320 nm and is assigned to the $\pi-\pi^*$ electronic transition of the styryl-bipyridine ligand. The origin of this band can be confirmed by the comparison with the absorption spectrum of the noncoordinated ligand (Supporting Information Figure S3).

Room-temperature steady-state photoluminescence spectra of **1** and **2** were measured in oxygen-free acetonitrile solutions using 490 nm excitation. As demonstrated in Figure 9, both complexes display broad and featureless emission profiles typical of polypyridyl Ru(II) complexes.[55] However, as compared to $[Ru(bpy)_3](PF_6)_2$, their emission maxima are red-shifted by ~80 nm suggesting a compression of the energy gap. The observed behavior is consistent with the changes in the ground-state absorption spectra and correlates well with the incorporation of the π-conjugated styryl subunits into the structures of **1** and **2**. The measured excited-state lifetimes in oxygen-free acetonitrile solutions were all found to be on the order of hundreds of nanoseconds (Table 2). Even though the measured excited-state lifetimes were somewhat shorter relative to $[Ru(bpy)_3](PF_6)_2$, they remain consistent with triplet MLCT excited state character in both instances. In the presence of oxygen (data not shown), there was pronounced quenching of the steady-state photoluminescence intensity and their corresponding excited-state lifetimes were substantially shortened as anticipated for molecules exhibiting a lowest triplet charge transfer excited state.

Inspired by studies on styryl-bearing complexes of Re(I) and Pt(II),[59−61] we decided to explore the possibility of initiating photoinduced cis/trans isomerization of the styryl moiety in the present Ru(II) complexes. These isomerization reactions typically proceed through the lowest energy triplet excited state, requiring the ^{3}CT state to lie above that of the relevant styryl moiety to promote sensitization. Given the low excited state energies in **1** and **2**, it is not surprising that no quantitative changes were observed in either the static absorption or the ^{1}H NMR spectra even after prolonged 30 min broadband photolysis (λ > 305 nm), Supporting Information Figures S4 and S5. Importantly, both complexes **1** and **2** appear to exhibit sufficient photochemical stability, important for their translation into a variety of photonics applications.

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CONCLUSIONS

We have developed and optimized a well-controlled and refined methodology for the synthesis of substituted π-conjugated 4,4′-styryl-2,2′-bipyridine ligands and their heteroleptic tris(polypyridyl) Ru(II)-based counterparts. Notably, NMR-based structural characterization becomes nontrivial when the coordinated ligand sets sense profoundly distinct magnetic environments. However, rational two-dimensional approaches typically utilized in more complex molecules can be readily applied to these Ru(II) heteroleptic structures producing quite definitive analytical characterization. The preliminary photoluminescence characterization of **1** and **2** strongly suggest that both molecules are energetically and kinetically suitable to serve as sensitizers in energy-relevant applications. The described synthetic methodology and associated structural characterizations can be used as a reliable guide toward the synthesis of novel heteroleptic Ru(II) complexes with designed and improved photophysical, photochemical, and electrochemical properties, targeted specifically for applications in photonics, dye-sensitized solar cell technology, and solar fuels photochemistry.

ASSOCIATED CONTENT

Supporting Information. 2D heteronuclear correlation NMR spectrum (^{1}H−^{13}C HMBC) of **1**, the ^{1}H NMR spectra of [Ru(*p*-cymene)(dnbpy)Cl]Cl before and after photolysis in acetonitrile solution, the steady-state absorption and photoluminescence spectra of 4,4′-bis[*E*-(*p*-methylcarboxy-styryl)]-2,2′-bipyridine (measured in $CHCl_3$), and the steady-state absorption spectra of **1** and **2** and the ^{1}H NMR spectrum of **1** over a 30 min period of photolysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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REFERENCES

(1) Spiccia, L.; Deacon, G. B.; Kepert, C. M. *Coord. Chem. Rev.* **2004**, *248*, 1329–1341.
(2) Strouse, G. F.; Anderson, P. A.; Schoonover, J. R.; Meyer, T. J.; Keene, F. R. *Inorg. Chem.* **1992**, *31*, 3004–3006.
(3) Juris, A.; Campagna, S.; Balzani, V.; Gremaud, G.; Vonzelewsky, A. *Inorg. Chem.* **1988**, *27*, 3652–3655.
(4) Thummel, R. P.; Lefoulon, F.; Chirayil, S. *Inorg. Chem.* **1987**, *26*, 3072–3074.
(5) Anderson, P. A.; Deacon, G. B.; Haarmann, K. H.; Keene, F. R.; Meyer, T. J.; Reitsma, D. A.; Skelton, B. W.; Strouse, G. F.; Thomas, N. C.; Treadway, J. A.; White, A. H. *Inorg. Chem.* **1995**, *34*, 6145–6157.
(6) Zakeeruddin, S. M.; Nazeeruddin, M. K.; Humphry-Baker, R.; Gratzel, M.; Shklover, V. *Inorg. Chem.* **1998**, *37*, 5251–5259.
(7) Freedman, D. A.; Evju, J. K.; Pomije, M. K.; Mann, K. R. *Inorg. Chem.* **2001**, *40*, 5711–5715.
(8) Meyer, G. J. *Inorg. Chem.* **2005**, *44*, 6852–6864.
(9) Robertson, N. *Angew. Chem., Int. Ed.* **2006**, *45*, 2338–2345.
(10) Polo, A. S.; Itokazu, M. K.; Iha, N. Y. M. *Coord. Chem. Rev.* **2004**, *248*, 1343–1361.
(11) Gratzel, M. *Inorg. Chem.* **2005**, *44*, 6841–6851.
(12) Nazeeruddin, M. K.; Kay, A.; Rodicio, I.; Humphrybaker, R.; Muller, E.; Liska, P.; Vlachopoulos, N.; Gratzel, M. *J. Am. Chem. Soc.* **1993**, *115*, 6382–6390.
(13) Nazeeruddin, M. K.; De Angelis, F.; Fantacci, S.; Selloni, A.; Viscardi, G.; Liska, P.; Ito, S.; Takeru, B.; Gratzel, M. *J. Am. Chem. Soc.* **2005**, *127*, 16835–16847.
(14) Jang, S. R.; Yum, J. H.; Klein, C.; Kim, K. J.; Wagner, P.; Officer, D.; Gratzel, M.; Nazeeruddin, M. K. *J. Phys. Chem. C* **2009**, *113*, 1998–2003.
(15) Jang, S. R.; Lee, C.; Choi, H.; Ko, J. J.; Lee, J.; Vittal, R.; Kim, K. J. *Chem. Mater.* **2006**, *18*, 5604–5608.
(16) Kuang, D. B.; Ito, S.; Wenger, B.; Klein, C.; Moser, J. E.; Humphry-Baker, R.; Zakeeruddin, S. M.; Gratzel, M. *J. Am. Chem. Soc.* **2006**, *128*, 4146–4154.
(17) Kuang, D. B.; Klein, C.; Ito, S.; Moser, J. E.; Humphry-Baker, R.; Zakeeruddin, S. M.; Gratzel, M. *Adv. Func. Mater.* **2007**, *17*, 154–160.
(18) Castellano, F. N.; Malak, H.; Gryczynski, I.; Lakowicz, J. R. *Inorg. Chem.* **1997**, *36*, 5548–5551.
(19) Montgomery, M. A.; Damrauer, N. H. *J. Phys. Chem. A* **2007**, *111*, 1426–1433.
(20) Rebane, A.; Makarov, N. S.; Drobizhev, M.; Spangler, B.; Tarter, E. S.; Reeves, B. D.; Spangler, C. W.; Meng, F. Q.; Suo, Z. Y. *J. Phys. Chem. C* **2008**, *112*, 7997–8004.
(21) Singh-Rachford, T. N.; Castellano, F. N. *J. Phys. Chem. A* **2009**, *113*, 9266–9269.
(22) Singh-Rachford, T. N.; Castellano, F. N. *Coord. Chem. Rev.* **2010**, *254*, 2560–2573.
(23) Islangulov, R. R.; Kozlov, D. V.; Castellano, F. N. *Chem. Commun.* **2005**, 3776–3778.
(24) Singh-Rachford, T. N.; Nayak, A.; Muro-Small, M. L.; Goeb, S.; Therien, M. J.; Castellano, F. N. *J. Am. Chem. Soc.* **2010**, *132*, 14203–14211.
(25) Hagfeldt, A.; Boschloo, G.; Sun, L. C.; Kloo, L.; Pettersson, H. *Chem. Rev.* **2010**, *110*, 6595–6663.
(26) Balasubramanian, K. K.; Cammarata, V.; Wu, Q. *Langmuir* **1995**, *11*, 1658–1665.
(27) Leidner, C. R.; Sullivan, B. P.; Reed, R. A.; White, B. A.; Crimmins, M. T.; Murray, R. W.; Meyer, T. J. *Inorg. Chem.* **1987**, *26*, 882–891.
(28) Maury, O.; Guegan, J. P.; Renouard, T.; Hilton, A.; Dupau, P.; Sandon, N.; Toupet, L.; Le Bozec, H. *New J. Chem.* **2001**, *25*, 1553–1566.
(29) Aranyos, V.; Hjelm, J.; Hagfeldt, A.; Grennberg, H. *J. Chem. Soc., Dalton Trans.* **2001**, 1319–1325.
(30) Klein, C.; Baranoff, E.; Nazeeruddin, M. K.; Gratzel, M. *Tetrahedron Lett.* **2010**, *51*, 6161–6165.
(31) Lohio, O.; Viau, L.; Maury, O.; Le Bozec, H. *Tetrahedron Lett.* **2007**, *48*, 1229–1232.
(32) Sun, Y. L.; Onicha, A. C.; Myahkostupov, M.; Castellano, F. N. *ACS Appl. Mater. Interfaces* **2010**, *2*, 2039–2045.
(33) Pastor, A.; Martinez-Viviente, E. *Coord. Chem. Rev.* **2008**, *252*, 2314–2345.
(34) Mohrig, J. R.; Hammond, C. N.; Schatz, P. F. *Techniques in Organic Chemistry*; 2nd ed.; W. H. Freeman and Co., 2006.
(35) Armarego, W. L. F.; Perrin, D. D. *Purification of Laboratory Chemicals*; 4th ed.; Butterworth-Heinemann, 1996.
(36) Tyson, D. S.; Castellano, F. N. *J. Phys. Chem. A* **1999**, *103*, 10955–10960.

(37) Fraser, C. L.; Anastasi, N. R.; Lamba, J. J. S. *J. Org. Chem.* **1997**, *62*, 9314–9317.
(38) Gillaizeau-Gauthier, I.; Odobel, F.; Alebbi, M.; Argazzi, R.; Costa, E.; Bignozzi, C. A.; Qu, P.; Meyer, G. J. *Inorg. Chem.* **2001**, *40*, 6073–6079.
(39) Boutagy, J.; Thomas, R. *Chem. Rev.* **1974**, *74*, 87–99.
(40) Furniss, B. S.; Hannaford, A. J.; Smith, P. W. G.; Tatchell, A. R. *Vogel's Textbook of Practical Organic Chemistry*, 5th ed.; Longman Group UK Ltd., 1989.
(41) Zelonka, R. A.; Baird, M. C. *Can. J. Chem.* **1972**, *50*, 3063–3072.
(42) Bennett, M. A.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1974**, 233–241.
(43) Claridge, T. D. W. *High-Resolution NMR Techniques in Organic Chemistry*; Elsevier: New York, 2000.
(44) Gould, S.; Strouse, G. F.; Meyer, T. J.; Sullivan, B. P. *Inorg. Chem.* **1991**, *30*, 2942–2949.
(45) Yin, L. X.; Liebscher, J. *Chem. Rev.* **2007**, *107*, 133–173.
(46) Karthikeyan, C. S.; Thelakkat, M. *Inorg. Chim. Acta* **2008**, *361*, 635–655.
(47) Galoppini, E. *Coord. Chem. Rev.* **2004**, *248*, 1283–1297.
(48) Snaith, H. J.; Karthikeyan, C. S.; Petrozza, A.; Teuscher, J.; Moser, J. E.; Nazeeruddin, M. K.; Thelakkat, M.; Gratzel, M. *J. Phys. Chem. C* **2008**, *112*, 7562–7566.
(49) Wang, P.; Klein, C.; Humphry-Baker, R.; Zakeeruddin, S. M.; Gratzel, M. *J. Am. Chem. Soc.* **2005**, *127*, 808–809.
(50) Schrenk, J. L.; Mcnair, A. M.; Mccormick, F. B.; Mann, K. R. *Inorg. Chem.* **1986**, *25*, 3501–3504.
(51) (a) Staniszewski, A.; Ardo, S.; Sun., Y.; Castellano, F. N.; Meyer, G. J. *J. Am. Chem. Soc.* **2008**, *130*, 11586–11587. (b) Ardo, S.; Sun, Y.; Staniszewski, A.; Castellano, F. N.; Meyer, G. J. *J. Am. Chem. Soc.* **2010**, *132*, 6696–6709.
(52) Ardo, S.; Sun, Y. L.; Castellano, F. N.; Meyer, G. J. *J. Phys. Chem. B* **2010**, *114*, 14596–14604.
(53) Freedman, D. A.; Magneson, D. J.; Mann, K. R. *Inorg. Chem.* **1995**, *34*, 2617–2624.
(54) Montalti, M.; Credi, A.; Prodi, L.; Gandolfi, T. M. *Handbook of Photochemistry*, 3rd ed.; CRC Press: Boca Raton, FL, 2006.
(55) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; Vonzelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85–277.
(56) Galoppini, E.; Guo, W. Z.; Zhang, W.; Hoertz, P. G.; Qu, P.; Meyer, G. J. *J. Am. Chem. Soc.* **2002**, *124*, 7801–7811.
(57) Wang, D.; Mendelsohn, R.; Galoppini, E.; Hoertz, P. G.; Carlisle, R. A.; Meyer, G. J. *J. Phys. Chem. B* **2004**, *108*, 16642–16653.
(58) Myahkostupov, M. Ultrafast Photoinduced Electron Transfer from Azulene- and Ru(II)-based Chromophores into Semiconductor Nanoparticles. Ph. D. Dissertation, Rutgers—Newark, The State University of New Jersey, 2008.
(59) Yam, V. W.-W.; Lau, V. C.-Y.; Wu, L.-X. *J. Chem. Soc., Dalton Trans.* **1998**, 1461–1468.
(60) Yam, V. W.-W.; Yang, Y.; Zhang, J.; Chu, B. W.-K.; Zhu, N. *Organometallics* **2001**, *20*, 4911–4918.
(61) Haskins-Glusac, K.; Ghiviriga, I.; Abboud, K. A.; Schanze, K. S. *J. Phys. Chem. B* **2004**, *108*, 4969–4978.