Inorganic Chemistry

Article

pubs.acs.org/IC

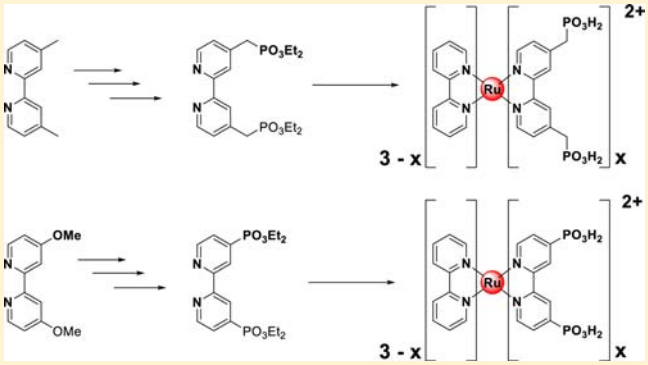
Synthesis of Phosphonic Acid Derivatized Bipyridine Ligands and Their Ruthenium Complexes

Michael R. Norris, Javier J. Concepcion, Christopher R. K. Glasson, Zhen Fang, Alexander M. Lapides, Dennis L. Ashford, Joseph L. Templeton, and Thomas J. Meyer*

Department of Chemistry, University of North Carolina at Chapel Hill, CB 3290, Chapel Hill, North Carolina 27599, United States

Supporting Information

ABSTRACT: Water-stable, surface-bound chromophores, catalysts, and assemblies are an essential element in dye-sensitized photoelectrosynthesis cells for the generation of solar fuels by water splitting and CO_2 reduction to CO, other oxygenates, or hydrocarbons. Phosphonic acid derivatives provide a basis for stable chemical binding on metal oxide surfaces. We report here the efficient synthesis of 4,4′-bis(diethylphosphonomethyl)-2,2′-bipyridine and 4,4′-bis-(diethylphosphonate)-2,2′-bipyridine, as well as the mono-, bis-, and tris-substituted ruthenium complexes, $[Ru(bpy)_2(Pbpy)]^{2+}$, $[Ru(bpy)(Pbpy)_2]^{2+}$, $[Ru(Pbpy)_3]^{2+}$, $[Ru(bpy)_2(CPbpy)]^{2+}$, $[Ru(bpy)(CPbpy)_2]^{2+}$, and $[Ru(CPbpy)_3]^{2+}$ [bpy = 2,2′-bipyridine; Pbpy = 4,4′-bis-(phosphonic acid)-2,2′-bipyridine; CPbpy = 4,4′-bis(methylphosphonic acid)-2,2′-bipyridine].



INTRODUCTION

Harnessing solar energy is one of the current grand challenges of science. Solar cell designs based on the attachment of ruthenium polypyridyl complexes to metal oxides such as TiO_2 have given rise to a family of solar cells based on the photosensitized injection of an electron from the ruthenium complex into the conduction band of the metal oxide.[1−7] The relatively long-lived excited states of ruthenium polypyridyl complexes allow the complexes to act as efficient sensitizers for electron injection upon light excitation.[8−11] Dye-sensitized solar cells (DSSCs) of this design generate electricity from sunlight, utilizing ruthenium complexes and other photosensitizers, with efficiencies approaching 12%.[12,13]

One drawback of DSSCs is that they do not provide a way to easily store the energy that is generated by sunlight. However, in dye-sensitized photoelectrosynthesis cells (DSPECs), the redox equivalents generated from photoexcitation and injection are used in a two-compartment cell to oxidize water and reduce H^+ or CO_2 into fuels.[14−17] The demands imposed by this application compel stringent requirements on the chromophore−catalyst combination. The chromophore should (1) absorb light broadly in the visible and near-IR, (2) be capable of either excited-state electron injection into the metal oxide conduction band in photoanode applications or excited-state hole injection for photocathodes, (3) have a redox potential sufficient to drive water oxidation (>1.23 V vs NHE at pH 0) or water/CO_2 reduction, and (4) have long-term stability at the oxide interface over a wide pH range in *aqueous solution*, under conditions of continuous *solar illumination* and *redox cycling*. Key to the final requirement is the nature of the chromophore anchoring links to the oxide surface.

In DSSCs, the ruthenium complexes are anchored to TiO_2 via ester formation at the surface utilizing derivatives functionalized with carboxylic acids.[4] Carboxylic acid groups are stable with respect to light and redox cycling in the acetonitrile environment typically used in DSSC applications. In aqueous environments, however, these anchoring groups quickly desorb from TiO_2 by hydrolysis of the surface ester bonds. Phosphonic acid derivatives have been shown to be far more stable than these carboxylic acids.[18,19] Other functional moieties including hydroxamates,[20,21] silanes,[22] silatrane,[23] and amides[24] have also been investigated as anchoring groups. A recent report has even combined phosphonate and carboxylate linkers to stabilize a dye on a metal oxide surface.[25] Implementation of each of these strategies has limitations. As noted above, carboxylates and maleonates are not stable under operating conditions in water. Siloxanes and amides present significant challenges in view of the synthetic requirements associated with synthesizing the derivatized ligands and subsequent complexes. Phosphonic acids are appealing in offering relatively stable surface binding in water at pH ≤5.[11,18,26,27]

Our work in chromophore−catalyst assemblies has been primarily based on polypyridyl complexes of ruthenium. Literature procedures exist for the functionalization of polypyridyl ligands with phosphonic acids, but still easy access to these ligands on large scales in only a few steps in high yield

Received: June 13, 2013
Published: October 21, 2013

remains a bottleneck to development in this area. We report here modifications to the syntheses of phosphonic acid derivatized bipyridine ligands at the 4 and 4′ positions, both directly on the aromatic ring and with a methylene spacer. These new procedures (i) have fewer number of synthetic steps, (ii) give higher yields, and (iii) negate the need for column chromatography. We have also developed or refined the coordination chemistry of these ligands with Ru^{II} through the synthesis of mono-, bis-, and tris-substituted complexes with both types of ligands. The ruthenium complexes synthesized in this work are shown in Figure 1.

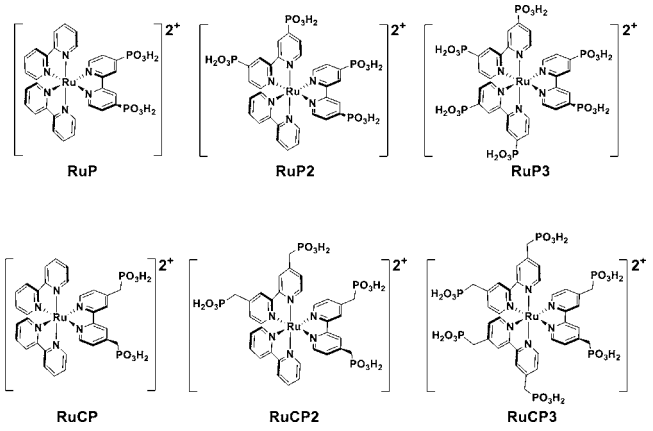


Figure 1. Structures of the six complexes synthesized and characterized in this study. Complexes with the methylene spacer are labeled "CP" followed by the number of functionalized bipyridines and with the ring directly functionalized by "P" followed by the number of phosphonate-substituted ligands.

EXPERIMENTAL SECTION

Materials and Methods. Distilled water was further purified using a Milli-Q Ultrapure water purification system. 4,4′-Dimethoxy-2,2′-bipyridine, 2,2′-bipyrimidine (bpm), and ruthenium trichloride trihydrate ($RuCl_3 \cdot 3H_2O$) were purchased from Aldrich and used as received. 4,4′-Dicarboxy-2,2′-bipyridine,[28] 4,4′-dihydroxymethyl-2,2′-bipyridine,[11] dichlororuthenium(II) cyclooctadiene polymer,[29] and $[(\eta^6\text{-}C_6H_6)RuCl]_2Cl_2$[30] were prepared as described in the literature. All other reagents were ACS grade and used without additional purification. Microwave reactions were carried out in Microwave Accelerated Reaction System, model MARS, 1200 W microwave oven with HP 500 plus Teflon vessels.

UV/vis absorption spectra were recorded on an Agilent Technologies model 8453 diode-array spectrophotometer. Electrochemical measurements were performed on a CH Instruments model 660D potentiostat/galvanostat. Voltammetric measurements were made with a planar CHI104 3 mm glassy carbon working electrode or FTO-coated glass slide, a platinum wire CHI115 counter electrode, and a Ag/AgCl CHI111 reference electrode (3 M NaCl, 0.207 V vs NHE) in buffered aqueous solutions with added 0.5 M KNO_3 or 0.5 M $NaClO_4$. The electrochemistry of the complexes was examined both in solution by dissolving them in a buffer (pH 1 and 7) and on a surface by immersing a planar FTO slide in a 1 mM solution (0.01 M HNO_3) of the complex for 1 h and using the modified slide as the working electrode in 0.1 M $HClO_4$. Potentials are reported versus NHE unless otherwise noted. ^1H and ^{31}P NMR spectra were recorded on a Bruker Avance 400 MHz or a Bruker 600 MHz spectrometer.

Ligand Synthesis and Characterization. *4,4′-Dicarboxyethyl Ester 2,2′-Bipyridine.* This compound was synthesized by a modified literature procedure.[11] Concentrated sulfuric acid (10 mL) was added to a mixture of 4,4′-dicarboxy-2,2′-bipyridine (6.0 g, 0.025 mol) in absolute ethanol (EtOH; 150 mL). The reaction was heated under argon at reflux for 4 h. After cooling, the reaction was added to ice water (600 mL) and a white solid precipitated, which was filtered, washed with water, and dried in a vacuum oven. The product was used without further purification. Yield: 6.76 g (90%). Characterization data match literature values.[11]

4,4′-Dihydroxymethyl-2,2′-bipyridine. This compound was prepared as previously reported.[11]

4,4′-Bis(bromomethyl)-2,2′-bipyridine. This compound was synthesized by a modified literature procedure.[11] A solution of 4,4′-dihydroxymethyl-2,2′-bipyridine (2.34 g, 0.011 mol) in 48% HBr (60 mL) and concentrated sulfuric acid (20 mL) was heated at reflux overnight and then allowed to cool to room temperature. The addition of water (120 mL), followed by neutralization (pH 7) with a concentrated aqueous sodium hydroxide solution, led to the precipitation of a white solid. The solid was collected by filtration and washed with water. Yield: 2.58 g (75%). Characterization data match literature values.[11]

4,4′-Bis(diethylphosphonomethyl)-2,2′-bipyridine. This ligand was synthesized by a modified literature procedure that avoids the use of column chromatography for purification.[31] A solution of 4,4′-bis(bromomethyl)-2,2′-bipyridine (2.58 g, 7.5 mmol) in triethylphosphite (6.6 mL, 37.7 mmol) was purged with argon for 15 min and then heated at 80 °C for 12 h. The reaction mixture was allowed to cool to room temperature and pentane (30 mL) was added, causing the precipitation of an off-white solid. The product was collected by vacuum filtration and washed with pentanes to remove any excess triethylphosphite. Yield: 3.35 g (98%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.61 (d, 2H), 8.35 (t, 2H), 7.33 (dd, 2H), 4.09 (m, 8H), 3.25 (d, 4H), 1.29 (t, 12H). ^{31}P NMR (161 MHz, $CDCl_3$): δ 24.4.

4,4′-Dibromo-2,2′-bipyridine. Phosphorus oxybromide (52.8 g, 0.184 mol) was added dropwise to a stirred solution of 4,4′-dimethoxy-2,2′-bipyridine (5 g, 0.023 mol) in anhydrous *N,N*-dimethylformamide (DMF; 80 mL) at 0 °C. Stirring was continued at 0 °C for 1 h and then the mixture was heated to 105 °C for 18 h. Stirring was ceased, and the reaction mixture was cooled to room temperature. To this mixture was added water (160 mL), and the solution was neutralized with $NaHCO_3$. The resulting precipitate was isolated by filtration and washed with water. The product was used without further purification. Yield: 5.88 g (81%).

4,4′-Dihydroxy-2,2′-bipyridine. This ligand was prepared by modification of a literature procedure.[32] A suspension of 4,4′-dimethoxy-2,2′-bipyridine (4.00 g, 18.5 mmol) in a mixture of glacial acetic acid (200 mL) and 48% hydrobromic acid (30 mL) was heated at reflux for 15 h. The solvent was then removed, and the resultant residue was dissolved in water and neutralized (pH 7) with a 70% ammonium hydroxide solution. A white solid precipitated, which was filtered and washed with water. This product was used without further purification. Because of low solubility, ^1H NMR characterization was not possible. Yield: 1.65 g (47%).

4,4′-Ditrifluoromethanesulfonate-2,2′-bipyridine. This ligand was prepared in a manner similar to that of 2,2′:6′,2″-terpyridine-4′-trifluoromethanesulfonate.[33] Under an argon purge, 4,4′-dihydroxy-2,2′-bipyridine (0.88 g, 4.7 mmol) was dissolved in anhydrous pyridine (20 mL), and the reaction was cooled to 0 °C. Over 30 min, trifluoromethanesulfonic anhydride (1.6 mL, 2.6 g, 9.4 mmol) was added, and the reaction was allowed to warm to room temperature. After the reaction was stirred at room temperature for 16 h, it was poured into ice water (150 mL) and stirred for 30 min. A white solid precipitated, was filtered, washed with water, and dried in a vacuum oven. Yield: 1.9 g (89%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.77 (d, 1H), 8.40 (d, 1H), 7.30 (dd, 1H).

4,4′-Bis(diethylphosphonate)-2,2′-bipyridine. Using Schlenk techniques to prevent air and moisture from entering the reaction vessel, diethyl phosphite (2.6 g, 20 mmol), 4,4′-dibromo-2,2′-bipyridine, (2.8 g, 8.8 mmol), and tetrakis(triphenylphosphine)palladium(0) (0.946 g, 0.819 mmol) were added to a flask under argon. Anhydrous toluene (86 mL) and triethylamine (2.6 mL) were then added, and the reaction was heated to 110 °C for 4 h. The reaction mixture was filtered hot, and the toluene was removed under vacuum. Recrystallization of the resulting residue from refluxing hexanes gave

dx.doi.org/10.1021/ic4014976 | Inorg. Chem. 2013, 52, 12492−12501

light-yellow needles of pure 4,4′-bis(diethylphosphonate)-2,2′-bipyridine. Yield: 1.95 g (51%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (t, 2H), 8.75 (d, 2H), 7.70 (dd, 2H), 4.17 (m, 8H), 1.34 (t, 12H). ^{31}P NMR (161 MHz, $CDCl_3$): δ 14.73.

Metal Complex Synthesis and Characterization. *cis-[Ru(bpy)$_2$Cl$_2$].* Dichlororuthenium(II) cyclooctadiene polymer (11.2 g, 40 mmol) and 2,2′-bipyridine (12.5 g, 80 mmol) were suspended in *o*-dichlorobenzene (100 mL). The reaction was heated to 190 °C under argon for 2 h. The mixture was allowed to cool, and a dark solid precipitated, which was filtered and washed with diethyl ether. This product was used without further purification. Yield: 17.9 g (92%).

cis-[Ru(4,4′-(PO$_3$Et$_2$)$_2$bpy)$_2$Cl$_2$]. A suspension of $RuCl_3 \cdot 3H_2O$ (500 mg, 1.4 mmol), 4,4′-bis(diethylphosphonate)-2,2′-bipyridine (1.2 g, 2.8 mmol), and zinc granules (327 mg, 5.0 mmol) was heated at reflux in EtOH (200 mL) for 12 h. The reaction mixture was filtered hot, and the solvent was removed from the filtrate under vacuum. The resulting dark-purple solid was collected, washed with Et_2O, and dried. This product was used without further purification. Yield: 1.3 g (92%).

cis-[Ru(4,4′-(PO$_3$H$_2$)$_2$bpy)$_2$Cl$_2$]. In order to hydrolyze the ester groups, *cis*-[Ru(4,4′-$(PO_3Et_2)_2$bpy)$_2$Cl$_2$] (300 mg, 0.29 mmol) was dissolved in anhydrous acetonitrile (30 mL) and bromotrimethylsilane was added (8 equiv). The reaction was stirred at 70 °C for 48 h, after which anhydrous methanol (MeOH; 3 mL) was added and the reaction was stirred for 30 min. The solvent was then removed under reduced pressure. The dark purple/black solid was collected and used without further purification. Yield: 223 mg (95%).

[Ru(η^6-C$_6$H$_6$)(bpy)Cl]Cl. This complex was synthesized by modification of a literature preparation.[34] 2,2′-Bipyridine (1.00 g, 2.33 mmol) and [Ru(η^6-C_6H_6)Cl]$_2$Cl$_2$ (583 mg, 1.17 mmol) were suspended in MeOH (70 mL). The reaction was heated at reflux under argon for 3 h. The reaction was then filtered hot to remove any unreacted material, and the solvent was removed on a rotary evaporator. A yellow-brown solid resulted that was collected under diethyl ether and filtered. This product was used without further purification. Yield: 1.49 g (94%).

[Ru(η^6-C$_6$H$_6$)(bpy)OTf]OTf. [Ru(η^6-C_6H_6)(bpy)Cl]Cl (1.50 g, 3.69 mmol) was suspended in CH_2Cl_2 (50 mL) at room temperature, and the solution was degassed with argon. After the addition of a needle to vent HCl, trifluoromethanesulfonic acid (1.5 mL) was carefully added and the reaction was stirred for 2 h. Upon the addition of Et_2O (200 mL), a dark-green solid precipitated from solution. The solid was filtered and washed with Et_2O. Yield: 2.22 g (95%). ^{1}H NMR (600 MHz, CD_3OD): δ 9.84 (d, 2H), 8.59 (d, 2H), 8.38 (t, 2H), 7.91 (m, 2H), 6.38 (s, 6H).

General Procedure for the Complexes [Ru(NN)$_2$(N′N′)]$^{2+}$. *Method A.* A solution of the ligand [N′N′ = 4,4′-bis(diethylphosphonate)-2,2′-bipyridine, 4,4′-bis(diethylphosphonomethyl)-2,2′-bipyridine, or 2,2′-bipyridine; 1.03 mmol] and *cis*-[Ru(NN)$_2$Cl$_2$] [where NN = 4,4′-bis(diethylphosphonate)-2,2′-bipyridine or 2,2′-bipyridine; 1.03 mmol] in 1:1 (v/v) EtOH/H_2O (40 mL) was heated at reflux under an atmosphere of argon. The reaction was monitored by UV/vis absorption spectroscopy and stopped when spectra ceased to change (4−12 h.). The solvent was then removed on a rotary evaporator, and the solid was collected and rinsed with Et_2O.

Method B. A solution of [Ru(η^6-C_6H_6)(bpy)OTf]OTf (0.50 mmol) and the ligand [N′N′ = 4,4′-bis(diethylphosphonate)-2,2′-bipyridine, or 4,4′-bis(diethylphosphonomethyl)-2,2′-bipyridine; 1.00 mmol] in absolute EtOH (30 mL) was added to a Teflon vessel and heated in a microwave. The temperature was ramped to 150 °C over 5 min and then held at 150 °C for 20 min. After cooling to room temperature, EtOH was removed on a rotary evaporator.

Method C. A solution of the ligand [N′N′ = 4,4′-bis(diethylphosphonate)-2,2′-bipyridine (1.03 mmol), 4,4′-bis(diethylphosphonomethyl)-2,2′-bipyridine (1.03 mmol), or 2,2′-bipyridine (3.09 mmol)] and *cis*-[Ru(NN)$_2$Cl$_2$] [where NN = 4,4′-bis(diethylphosphonate)-2,2′-bipyridine or bipyridine; 1.03 mmol] in absolute EtOH (30 mL) was added to a Teflon vessel and heated in a microwave. The temperature was ramped to 150 °C over 5 min and then held at 150 °C for 20 min. After cooling to room temperature, EtOH was removed.

Hydrolysis. The isolated [Ru(NN)$_2$(N′N′)]$^{2+}$ complexes were hydrolyzed after isolation without any prior purification. [Ru(NN)$_2$(N′N′)]$^{2+}$ (0.50 mmol) was dissolved in 30 mL of anhydrous CH_3CN under an argon atmosphere. Trimethylsilyl bromide (1.02 equiv per −OEt group) was then added, and the reaction was heated at 70 °C for 48 h or until completion (as assessed by ^{1}H NMR of an aliquot of the reaction mixture). After cooling the reaction to room temperature, anhydrous MeOH (1.0 mL) was added and an orange solid precipitated from the reaction. The orange solid was filtered and washed with cool CH_3CN and Et_2O.

[Ru(bpy)$_2$(4,4′-(PO$_3$H$_2$)$_2$bpy)](Cl)$_2$ ***(RuP).*** This complex was prepared as in Method A or Method C starting with *cis*-[Ru(bpy)$_2$Cl$_2$] and 4,4′-bis(diethylphosphonate)-2,2′-bipyridine. After hydrolysis of the ester groups, the product was isolated as an orange solid and was found to be pure by NMR. Yield: method A, 75%; method C, 85%. Both methods gave identical ^{1}H and ^{31}P NMR spectra. ^{1}H NMR (400 MHz, D_2O): δ 8.75 (d, 2H), 8.51 (d, 4H), 8.03 (t, 4H), 7.91 (m, 2H), 7.79 (dd, 4H), 7.55 (dd, 2H), 7.35 (t, 4H). ^{31}P NMR (161 MHz, D_2O): δ 6.78. Anal. Found (calcd) for $C_{30}H_{26}Cl_2N_6O_6P_2Ru \cdot 5H_2O$: C, 40.15 (40.46); H, 3.94 (4.07); N, 9.45 (9.44).

[Ru(bpy)(4,4′-(PO$_3$H$_2$)$_2$bpy)$_2$](Cl)$_2$ ***(RuP2).*** This complex was prepared as in Method C starting with *cis*-[Ru(4,4′-$(PO_3H_2)_2$bpy)$_2$Cl$_2$] and 2,2′-bipyridine or as in Method B starting with 4,4′-bis(diethylphosphonate)-2,2′-bipyridine. The pure product was isolated upon hydrolysis. Yield: method B, 80%; method C, 88%. Both methods gave identical ^{1}H and ^{31}P NMR spectra. ^{1}H NMR (400 MHz, D_2O): δ 8.75 (d, 4H), 8.51 (d, 2H), 8.04 (t, 2H), 7.88 (m, 4H), 7.74 (d, 2H), 7.56 (dd, 4H), 7.37 (t, 2H). ^{31}P NMR (161 MHz, D_2O): δ 6.74. Anal. Found (calcd) for $C_{30}H_{28}Cl_2N_6O_{12}P_4Ru \cdot 5H_2O \cdot 2CH_3OH$: C, 34.19 (34.48); H, 4.17 (4.16); N, 7.77 (7.54).

[Ru(4,4′-(PO$_3$H$_2$)$_2$bpy)$_3$](Cl)$_2$ ***(RuP3).*** This complex was prepared as in Method A starting with *cis*-[Ru(4,4′-$(PO_3H_2)_2$bpy)$_2$Cl$_2$] and hydrolyzed 4,4′-bis(phosphonic acid)-2,2′-bipyridine, although better results were found for an alternative synthesis as follows. A solution of hydrolyzed 4,4′-bis(phosphonic acid)-2,2′-bipyridine (150 mg, 0.47 mmol) and $RuCl_3 \cdot 3H_2O$ (31 mg, 0.12 mmol) in 1:1 (v/v) EtOH/H_2O (20 mL) was heated in a microwave reactor. The reaction was heated at 160 °C for 15 min with a 5 min ramp to temperature. After the reaction was allowed to cool, EtOH (30 mL) was added, and the product precipitated as a red microcrystalline solid that was collected by filtration and washed with EtOH and Et_2O. Yield: 46 mg (94%). ^{1}H NMR (400 MHz, D_2O): δ 8.76 (d, 6H), 7.86 (dd, 6H), 7.58 (dd, 6H). ^{31}P NMR (161 MHz, D_2O): δ 6.28. Anal. Found (calcd) for $C_{30}H_{30}Cl_2N_6O_{18}P_6Ru \cdot H_2O$: C, 31.90 (31.65); H, 3.19 (2.83); N, 7.37 (7.38).

[Ru(bpy)$_2$(4,4′-(CH$_2$PO$_3$H$_2$)$_2$bpy)](Cl)$_2$ ***(RuCP).*** This complex was prepared as in Method A or Method C starting with *cis*-[Ru(bpy)$_2$Cl$_2$] and 4,4′-bis(diethylphosphonomethyl)-2,2′-bipyridine. After hydrolysis, the complex was run down a Sephadex LH-20 column, eluting with H_2O. Yield: method A, 55%; method C, 68%. Both methods gave identical ^{1}H and ^{31}P NMR. ^{1}H NMR (400 MHz, D_2O): δ 8.36 (d, 4H), 8.27 (t, 2H), 7.87 (tdd, 4H), 7.77 (dd, 2H), 7.67 (dd, 2H), 7.51 (d, 2H), 7.19 (m, 4H), 7.10 (dt, 2H), 3.03 (d, 4H). ^{31}P NMR (161 MHz, D_2O): δ 19.03. Anal. Found (calcd) for $C_{32}H_{30}Cl_2N_6O_9P_2Ru \cdot 4H_2O$: C, 42.91 (42.68); H, 4.55 (4.25); N, 9.36 (9.33).

[Ru(bpy)(4,4′-(CH$_2$PO$_3$H$_2$)$_2$bpy)$_2$](Cl)$_2$ ***(RuCP2).*** This complex was prepared using Method B starting with 4,4′-bis(diethylphosphonomethyl)-2,2′-bipyridine. After hydrolysis, this complex was run down a Sephadex LH-20 column, eluting with H_2O. Yield: 62%. ^{1}H NMR (400 MHz, D_2O): δ 8.36 (d, 2H), 8.28 (s, 4H), 7.87 (t, 2H), 7.77 (d, 2H), 7.62 (d, 2H), 7.54 (d, 2H), 7.20 (t, 2H), 7.10 (t, 4H), 3.09 (d, 8H). ^{31}P NMR (161 MHz, D_2O): δ 17.35, 17.23. Anal. Found (calcd) for $C_{34}H_{36}Cl_2N_6O_{12}P_4Ru \cdot 4H_2O$: C, 37.79 (37.51); H, 4.33 (4.07); N, 7.52 (7.72).

[Ru(4,4′-(CH$_2$PO$_3$H$_2$)$_2$bpy)$_3$]Cl$_2$ ***(RuCP3).*** A solution of ligand 4,4′-bis(diethylphosphonomethyl)-2,2′-bipyridine (500 mg, 1.5 mmol), $RuCl_3 \cdot 3H_2O$ (126 mg, 0.48 mmol), and zinc granules (65 mg, 1 mmol) was added to 1:1 (v/v) EtOH/H_2O (30 mL) and heated at

dx.doi.org/10.1021/ic4014976 | Inorg. Chem. 2013, 52, 12492−12501

reflux under dinitrogen overnight. The reaction was allowed to cool, and the solvent was removed on a rotary evaporator. The product was then hydrolyzed with trimethylsilyl bromide in CH_3CN. After hydrolysis, the product was purified on a Sephadex LH-20 column, eluting with water. Like fractions were combined, and the solvent was removed to give a dark-orange powder. Yield: 434 mg (75%). ^{1}H NMR (600 MHz, D_2O): δ 8.27 (s, 6H), 7.61 (d, 6H), 7.10 (d, 6H), 3.11 (d, 12H). ^{31}P NMR (242 MHz, D_2O): δ 18.07. Anal. Found (calcd) for $C_{36}H_{42}Cl_2N_6O_{18}P_6Ru{\cdot}3H_2O{\cdot}2CH_3OH$: C, 34.17 (34.51); H, 4.20 (4.27); N, 6.26 (6.35).

RESULTS

Ligand Synthesis. *Synthesis of 4,4″-($CH_2PO_3Et_2$)$_2$bpy.* The route to this ligand that proved to be most successful resulted in a significant improvement over two modified literature procedures.[11,31] First, 4,4′-dimethyl-2,2′-bipyridine was oxidized by allowing it to react with potassium dichromate in concentrated sulfuric acid, followed by treatment with nitric acid to give 4,4′-dicarboxy-2,2′-bipyridine. Esterification of the carboxylic acid groups was accomplished in absolute EtOH by the addition of a catalytic amount of sulfuric acid. After 12 h, a white solid precipitated from the mixture. Isolation of the precipitate, followed by dissolution in water and neutralization with base gave the desired product as a white, crystalline solid. Reduction of the ester groups was accomplished with sodium borohydride in MeOH to give 4,4′-dihydroxymethyl-2,2′-bipyridine. 4,4′-Dihydroxymethyl-2,2′-bipyridine was then converted into 4,4′-dibromomethyl-2,2′-bipyridine in a mixture of 48% HBr and sulfuric acid. Finally, 4,4′-bis-(diethylphosphonomethyl)-2,2′-bipyridine was synthesized by heating 4,4′-dibromomethyl-2,2′-bipyridine in neat triethyl phosphite. The product precipitated upon the addition of excess pentane to give analytically pure 4,4′-bis(diethyl phosphonomethyl)-2,2′-bipyridine in greater than 90% yield without either high vacuum distillation of the excess triethyl phosphite or column chromatography. The desired compound was obtained in 68% overall yield from 4,4′-dimethyl-2,2′-bipyridine.

The ligand was found to be pure by ^{1}H and ^{31}P NMR (Figure 2). The ^{1}H NMR spectrum consists of three resonances in the aromatic region for the three ring protons. Of note is the large doublet at 3.25 ppm due to the $-CH_2-$ spacer between the bipyridine and phosphonate groups that has a $^2J_{HP}$ of 24 Hz. The ester groups of the phosphonates appear at 4.09 and 1.29 ppm. The proton-decoupled ^{31}P NMR spectrum shows only a singlet at 24.4 ppm.

Synthesis of 4,4′-(PO_3Et_2)$_2$bpy. This ligand was synthesized by two different routes from 4,4′-dimethoxy-2,2′-bipyridine. In the first method, 4,4′-dimethoxy-2,2′-bipyridine was refluxed in a mixture of acetic acid and 48% hydrobromic acid to form 4,4′-dihydroxy-2,2′-bipyridine. A white crystalline solid precipitated from the reaction mixture, which was filtered, dissolved in water, and precipitated by neutralization of the solution with ammonium hydroxide to yield clean 4,4′-dihydroxy-2,2′-bipyridine. It was converted to 4,4′-ditrifluoromethanesulfonate-2,2′-bipyridine by reaction with trifluoromethanesulfonic anhydride in anhydrous pyridine at 0 °C following a procedure similar to the one reported for a related terpyridine derivative.[33] The addition of the reaction mixture to ice water precipitated clean product in good yield.

In the second method, 4,4′-dimethoxy-2,2′-bipyridine was converted directly to 4,4′-dibromo-2,2′-bipyridine. Phosphorus oxybromide was carefully added to a solution of 4,4′-dimethoxy-2,2′-bipyridine in anhydrous DMF at 0 °C. After stirring for 1 h, the reaction was heated to 105 °C overnight. The product was isolated by aqueous workup as pure 4,4′-dibromo-2,2′-bipyridine. It must be noted, however, that better results in the following step were achieved if the 4,4′-dibromo-2,2′-bipyridine product was run down a plug of silica, which likely removes a small amount of an inorganic impurity that is not observable in the ^{1}H NMR spectrum.

In both methods, the corresponding triflate- or bromo-functionalized bipyridine compound was reacted with diethyl phosphite using a tetrakis(triphenlyphosphine)palladium(0) catalyst followed by recrystallization from hexanes to give analytically pure 4,4′-bis(diethylphosphonate)-2,2′-bipyridine. We have found the purity of the palladium catalyst to be crucial. The use of pure tetrakis(triphenlyphosphine)palladium(0) negates the use of excess triphenylphosphine in the cross-coupling reaction, which not only improves the purity of the product but also prevents the need for column chromatography. The synthesis of these ligands is summarized in Scheme 1.

Recrystallization results in pure ligand as demonstrated by ^{1}H and ^{31}P NMR spectra (Figure 3). There is no evidence for

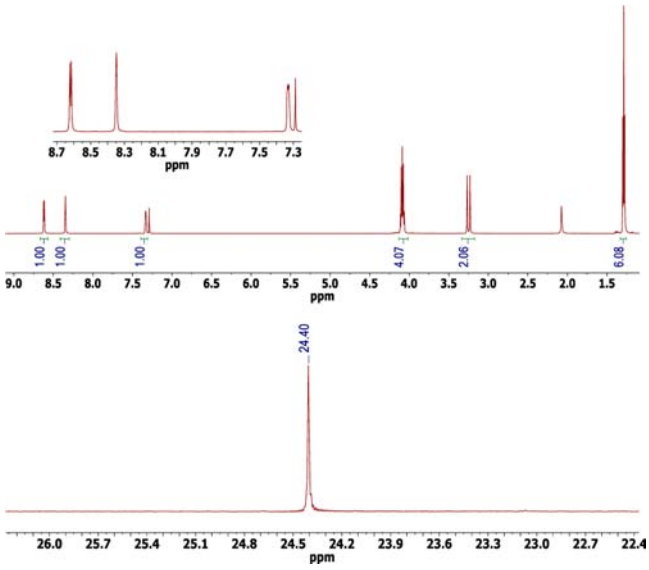
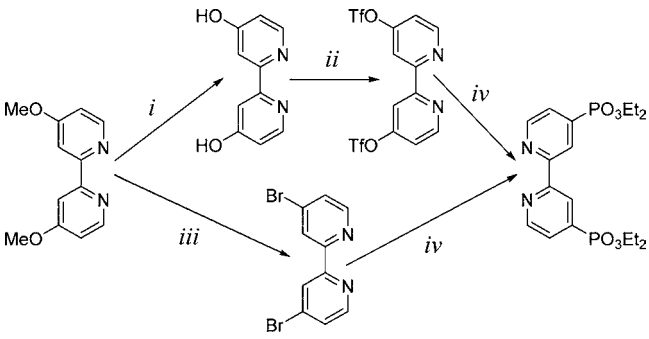


Figure 2. ^{1}H and ^{31}P NMR spectra in $CDCl_3$ at 22 °C of 4,4′-bis(diethylphosphonomethyl)-2,2′-bipyridine showing the expected aromatic and aliphatic resonances.

Scheme 1. Synthesis of 4,4′-Bis(diethylphosphonate)-2,2′-bipyridine by Two Routes[a]



[a](i) HOAc, HBr (47%); (ii) TfOTf, pyridine (89%); (iii) DMF, $POBr_3$ (81%); (iv) $P(O)H(OEt)_2$, $Pd(PPh_3)_4$, NEt_3, toluene (51%).

dx.doi.org/10.1021/ic4014976 | Inorg. Chem. 2013, 52, 12492−12501

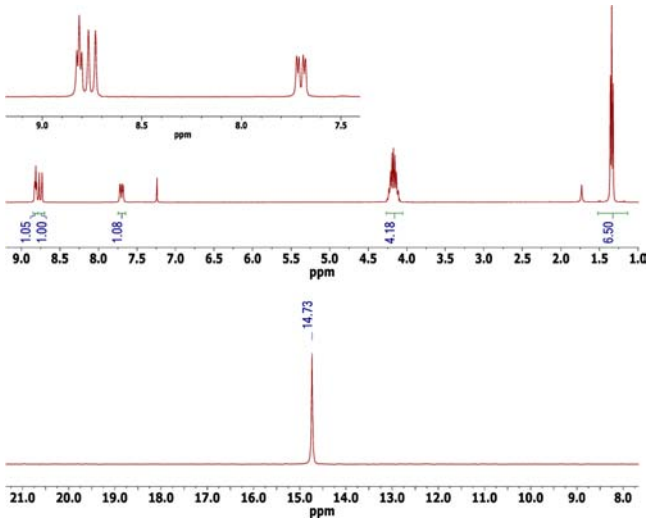


Figure 3. ^{1}H NMR (top) and ^{31}P NMR (bottom) in $CDCl_3$ at 22 °C of 4,4′-bis(diethyl phosphonate)-2,2′-bipyridine showing aromatic and aliphatic signals.

excess triphenylphosphine or triphenylphosphine oxide in the product. These are impurities that are seen when excess PPh_3 is used in the synthesis, and both are difficult to separate from the desired product by column chromatography. The ^{1}H NMR spectrum shows three aromatic peaks (a triplet at 8.81 ppm, a doublet at 8.75 ppm, and a doublet of doublets at 7.70 ppm), as well as the characteristic ethyl ester resonances from the phosphonates, with the $-P-O-CH_2-$ group appearing as a complex multiplet at 4.17 ppm because of the diastereotopic nature of the protons and coupling to the phosphorus. The proton-decoupled ^{31}P NMR spectrum consists of a singlet at 14.7 ppm.

Although most reactions with ruthenium were carried out using the ligand as the phosphonate ester, the ligand can also be hydrolyzed prior to complexation. Hydrolysis was achieved by stirring the ligand in anhydrous CH_3CN with trimethylsilyl bromide at room temperature. Hydrolyzed ligand [4,4′-bis(phosphonic acid)-2,2′-bipyridine] is more reactive toward coordination in $EtOH/H_2O$ mixtures because of the electron-donating nature of the deprotonated acid groups under these conditions relative to the electron-withdrawing esters. The ^{1}H NMR spectrum of the 4,4′-bis(phosphonic acid)-2,2′-bipyridine ligand (Figure S1 in the Supporting Information) is similar to that of the nonhydrolyzed ligand (Figure 3).

Metal Complex Synthesis. *Synthesis of the Ruthenium Complexes with One Phosphonate-Derivatized Ligand $[Ru(bpy)_2(NN)]^{2+}$, Where NN is 4,4′-Bis(phosphonic acid)-2,2′-bipyridine or 4,4′-Bis(methylphosphonic acid)-2,2′-bipyridine.* Essential to the synthesis of pure $[Ru(bpy)_2(NN)]^{2+}$ analogues is the use of pure *cis*-$[Ru(bpy)_2Cl_2]$. The reaction of $[Ru(COD)Cl_2]_n$ (COD = 1,5-cyclooctadiene) with 2 equiv of 2,2′-bipyridine in *o*-dichlorobenzene at 190 °C under argon for 2 h results in pure *cis*-$[Ru(bpy)_2Cl_2]$, free of $[Ru(bpy)_3]^{2+}$. The neutral product was isolated in >90% yield by the addition of diethyl ether to the cooled reaction mixture.

To synthesize the complex with the phosphonate-derivatized ligand, *cis*-$[Ru(bpy)_2Cl_2]$ was reacted either thermally with 1 equiv of ligand [4,4′-bis(diethylphosphonate)-2,2′-bipyridine or 4,4′-bis(diethylphosphonomethyl)-2,2′-bipyridine] in refluxing 1:1 (v/v) EtOH:H_2O or in a microwave reactor with 3 equiv of ligand [4,4′-bis(diethylphosphonate)-2,2′-bipyridine or 4,4′-bis(diethylphosphonomethyl)-2,2′-bipyridine] in absolute EtOH at 150 °C to give $[Ru(bpy)_2(NN)]^{2+}$. Hydrolysis of the ester groups was accomplished either by heating the crude product with trimethylsilyl bromide under anhydrous conditions in CH_3CN at 70 °C or by heating the crude product at reflux in 4 M HCl. In both cases, complete hydrolysis took 48 h.

Synthesis of the Ruthenium Complexes with Two Phosphonate-Derivatized Ligands $([Ru(N'N')(NN)_2]^{2+}$, Where N′N′ Is a Bidentate Ligand and NN Is 4,4′-Bis(phosphonic acid)-2,2′-bipyridine or 4,4′-Bis-(methylphosphonic acid)-2,2′-bipyridine). For phosphonate-derivatized bipyridine ligands, the straightforward procedure used to prepare the parent *cis*-$[Ru(bpy)_2Cl_2]$ described above was not successful in forming bis-ligand complexes. High-temperature reactions either cause oligomerization through the formation of P−O−P bonds or create synthetic problems because of solubility complications.

Two viable routes to the effective synthesis of these complexes have been discovered. The first involves the reaction of $[(\eta^6\text{-}C_6H_6)Ru(N'N')OTf]OTf$ with 2 equiv of 4,4′-bis(diethylphosphonate)-2,2′-bipyridine or 4,4′-bis(diethylphosphonomethyl)-2,2′-bipyridine in 1:1 (v/v) $EtOH/H_2O$ under refluxing conditions. The use of the triflate complex allows for thermal removal of benzene at lower temperatures conducive to the synthesis of phosphonate-derivatized complexes. This procedure can also be carried out in a microwave at 150 °C in the same solvent mixture but using 3 equiv of 4,4′-bis(diethylphosphonate)-2,2′-bipyridine or 4,4′-bis(diethylphosphonomethyl)-2,2′-bipyridine.

An alternate procedure involves the synthesis of $[Ru(4,4'\text{-}(PO_3Et_2)_2bpy)_2Cl_2]$, which can be used in many downstream reactions analogous to reactions available with *cis*-$[Ru(bpy)_2Cl_2]$. This complex can be prepared by refluxing $RuCl_3{\cdot}3H_2O$ with 2 equiv of 4,4′-bis(diethylphosphonate)-2,2′-bipyridine with zinc powder in EtOH. The reaction was monitored by UV/vis absorption spectroscopy to detect any appearance of $[Ru(4,4'\text{-}(PO_3Et_2)_2bpy)_3]^{2+}$. For 4,4′-bis(diethylphosphonate)-2,2′-bipyridine, the addition of ligands with electron-withdrawing groups decreases the rate of substitution for a third ligand. Over 12 h, no $[Ru(4,4'\text{-}(PO_3Et_2)_2bpy)_3]^{2+}$ was formed and pure $[Ru(4,4'\text{-}(PO_3Et_2)_2bpy)_2Cl_2]$ was isolated. This procedure was also attempted with 4,4′-bis(diethylphosphonomethyl)-2,2′-bipyridine, but because of the more electron-rich nature of these ligands and the correspondingly facile substitution chemistry at the metal, $[Ru(4,4'\text{-}(CH_2PO_3Et_2)_2bpy)_2Cl_2]$ could not be cleanly separated from $[Ru(4,4'\text{-}(CH_2PO_3Et_2)_2bpy)_3]^{2+}$.

Because of the difficulty in adding a third ligand to $[Ru(4,4'\text{-}(PO_3Et_2)_2bpy)_2Cl_2]$, which allowed for its clean preparation, it proved necessary to carry out reactions of $[Ru(4,4'\text{-}(PO_3Et_2)_2bpy)_2Cl_2]$ with another ligand in a microwave reactor in absolute EtOH at 150 °C with an excess of the to-be-added bidentate ligand. This procedure is general and can be used to add a variety of bidentate, polypyridyl ligands. The incorporation of bpm as the third ligand illustrates this strategy. Additionally, bpm addition does not result in the formation of dimers, with bpm acting as a bridge. Rather, clean conversion to $[Ru((PO_3Et_2)_2bpy)_2(bpm)]^{2+}$ occurs.

If a thermal reaction is preferable for the addition of a third ligand, the ester groups of $[Ru((PO_3Et_2)_2bpy)_2Cl_2]$ can be hydrolyzed to give the more reactive $[Ru((PO_3H_2)_2bpy)_2Cl_2]$, with deesterification achieved by using trimethylsilyl bromide.

dx.doi.org/10.1021/ic4014976 | *Inorg. Chem.* 2013, 52, 12492−12501

Refluxing in 4 M HCl is effective, but yields for the addition of the third ligand were low with this method. We suspect that this may be due to partial oxidation of the metal to Ru^{III} during hydrolysis, and it does not readily add a third ligand. After hydrolysis, a third ligand is easily added in refluxing 1:1 (v/v) $EtOH/H_2O$, and the resulting complex can be purified by column chromatography.

Synthesis of the Ruthenium Complexes with Three Phosphonate-Derivatized Ligands ($[Ru(NN)_3]^{2+}$, Where NN Is 4,4′-Bis(phosphonic acid)-2,2′-bipyridine or 4,4′-Bis-(methylphosphonic acid)-2,2′-bipyridine). To make complexes with three phosphonate-derivatized ligands, *cis*-$[Ru(4,4'\text{-}(PO_3H_2)_2bpy)_2Cl_2]$ was first prepared as previously described. This intermediate was then reacted with hydrolyzed 4,4′-bis(phosphonic acid)-2,2′-bipyridine in refluxing 1:1 (v/v) $EtOH/H_2O$. This method was found to be more efficacious than the direct synthesis of trisubstituted complexes using unhydrolyzed 4,4′-bis(diethylphosphonate)-2,2′-bipyridine because of slow ligand substitution of the ester complexes as noted above. An alternate preparative method that gave better yields involved the reaction between $RuCl_3{\cdot}3H_2O$ and hydrolyzed 4,4′-bis(phosphonic acid)-2,2′-bipyridine in 1:1 (v/v) $EtOH/H_2O$ by the microwave technique at 160 °C. Upon cooling and the addition of excess EtOH, the product precipitated as a red microcrystals.

Because the ester derivative of 4,4′-bis-(diethylphosphonomethyl)-2,2′-bipyridine is much more reactive than 4,4′-bis(diethylphosphonate)-2,2′-bipyridine, synthesis of **RuCP3** was achieved by a direct reaction between $RuCl_3{\cdot}3H_2O$ and 4,4′-bis(diethylphosphonomethyl)-2,2′-bipyridine. Overnight reflux of $RuCl_3{\cdot}3H_2O$ and 3.3 equiv of 4,4′-bis(diethylphosphonomethyl)-2,2′-bipyridine in a 1:1 (v/v) mixture of $EtOH/H_2O$ with added zinc to reduce Ru^{III} gave **RuCP3** in good yield. The crude product was isolated, and the ligands were hydrolyzed in anhydrous CH_3CN with added trimethylsilyl bromide. After hydrolysis, the product was purified by column chromatography.

Spectroscopic and Electrochemical Characterization. UV/vis absorption measurements of **RuP(1−3)** and **RuCP(1−3)** were obtained in 0.1 M $HClO_4$ containing a 1.0×10^{-5} M complex (Figure 4). Typical of ruthenium polypyridyl complexes, all six complexes have characteristic absorption bands in the visible region of the spectrum due to metal-to-ligand charge-transfer (MLCT) transitions. The band shape of each complex is similar with maxima that vary slightly from 456 to 464 nm. For the **RuP** series (**RuP**, **RuP2**, and **RuP3**), the low-energy edge of the MLCT absorption sharpens with each consecutive addition of a phosphonate-derivatized ligand. Similarly, the ligand-centered transition around 290 nm also red shifts slightly. Further, with the consecutive addition of 4,4′-bis(phosphonic acid)-2,2′-bipyridine ligands, the molar absorptivity increases from 13300 M^{-1} cm^{-1} at 457 nm to 17300 M^{-1} cm^{-1} at 463 nm. For the **RuCP** series (**RuCP**, **RuCP2**, and **RuCP3**), all of the absorption spectra are similar to one another with extinction coefficients and MLCT and interligand $\pi \rightarrow \pi^*$ bands nearly constant across the series.

Cyclic voltammograms of **RuP**, **RuP2**, and **RuP3** anchored to FTO are shown in Figure 5A, with square-wave voltammograms shown in Figure 5B. Each complex displays a characteristic $Ru^{III/II}$ reversible redox couple with $E_{1/2}$ ranging from 1.29 V for **RuP** to 1.40 V (vs NHE) for **RuP3**. The peak-to-peak separation is <60 mV, characteristic of a surface-bound redox couple. Of note, **RuP3** displays several additional waves

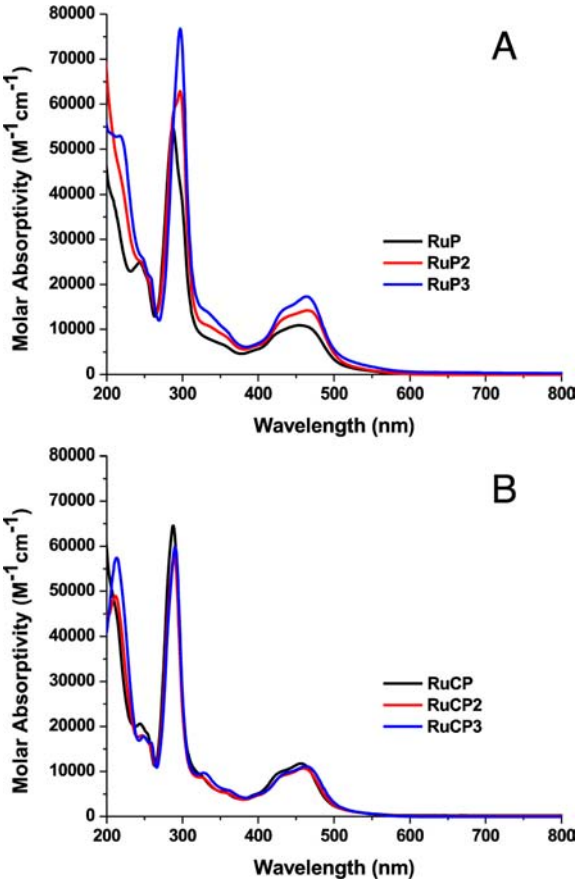


Figure 4. UV/vis absorption spectra for the **RuP** series [A: **RuP** (black), **RuP2** (red), and **RuP3** (blue)] and **RuCP** series [B: **RuCP** (black), **RuCP2** (red), and **RuCP3** (blue)] with an MLCT absorption appearing at ∼460 nm for each complex.

in the cyclic voltammogram at lower potentials than the $Ru^{III/II}$ wave. These waves are present from the first cycle and are likely due to small amounts of impurity polypyridyl complexes where a polypyridyl ligand has been substituted by water or anions (Cl^- or NO_3^-).

In voltammograms of the **RuCP** series anchored to FTO-coated glass slides in 0.1 M $HClO_4$, reversible $Ru^{III/II}$ waves appear but with differences from the **RuP** series. For these complexes, the trend of increasing the redox potentials with the addition of phosphonic acid derivatized ligands is reversed with $E_{1/2}$ for the $Ru^{III/II}$ couple for **RuCP** at 1.19 V and $E_{1/2}$ for **RuCP3** at 1.15 V (vs NHE). $E_{1/2}$ values for the $Ru^{III/II}$ couples for the entire series also occur at much less positive potentials than their **RuP** analogues with differences of 100−250 mV. Spectroscopic and electrochemical data are summarized in Table 1.

DISCUSSION

Synthesis of Ligands and Metal Complexes. Phosphonic acid substituents are desirable for DSPEC applications because of their documented stability in anchoring ruthenium polypyridyl complexes to metal oxide surfaces under conditions of irradiation and potentials leading to electrochemical oxidation.[35] Our focus in this manuscript is the improvement of synthetic routes to phosphonate-derivatized bipyridine ligands and their complexation with Ru^{II}. As $[Ru(bpy)_3]^{2+}$ analogues, they have proven to behave as effective photo-

dx.doi.org/10.1021/ic4014976 | Inorg. Chem. 2013, 52, 12492−12501

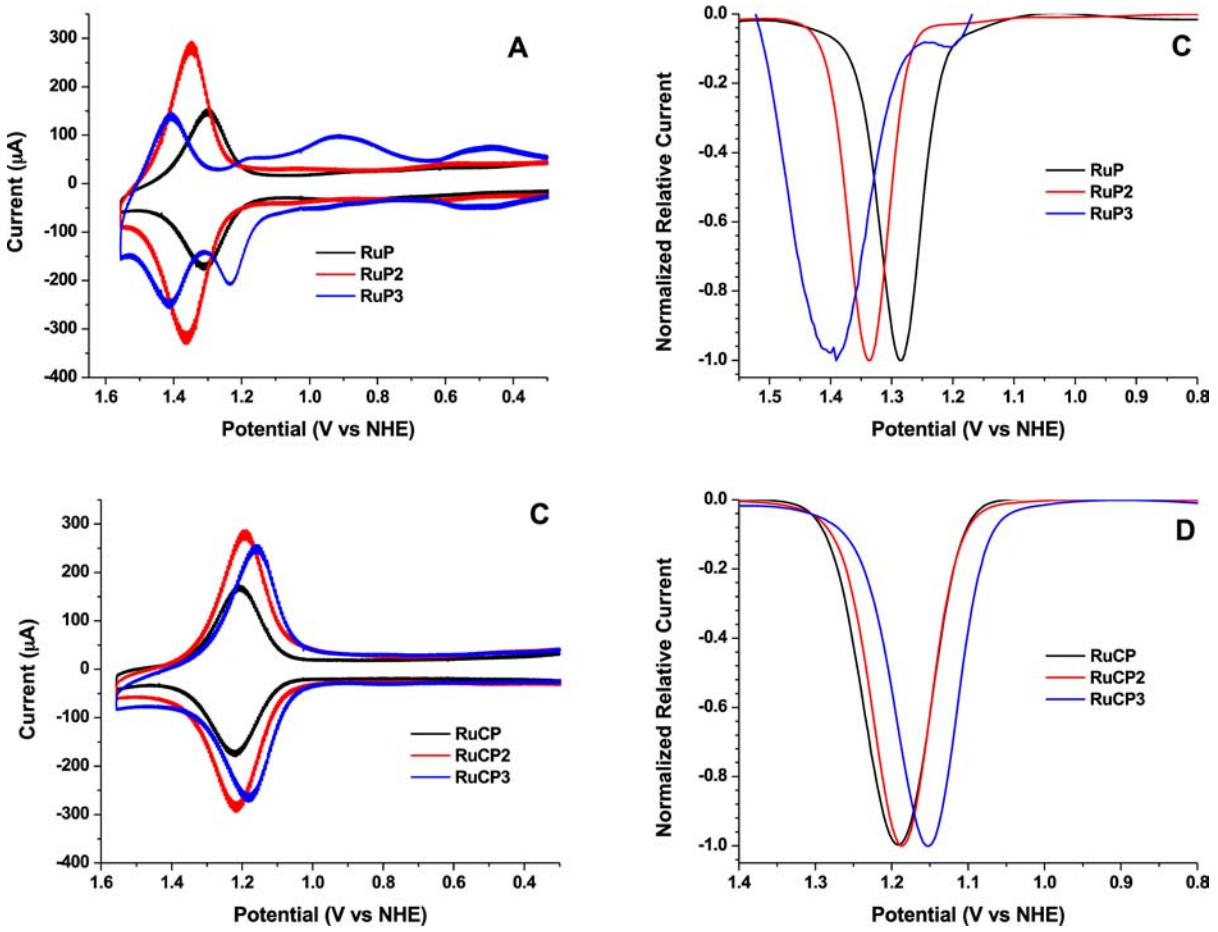


Figure 5. (A) Cyclic voltammagrams of **RuP** (black), **RuP2** (red), and **RuP3** (blue), (B) square-wave voltammagrams of **RuP** (black), **RuP2** (red), and **RuP3** (blue), (C) cyclic voltammagrams of **RuCP** (black), **RuCP2** (red), and **RuCP3** (blue), and (D) square-wave voltammagrams of **RuCP** (black), **RuCP2** (red), and **RuCP3** (blue) loaded on a planar FTO-coated glass slide (1×10^{-10} mol cm^{-2}) in 0.1 M $HClO_4$ with a 100 mV s^{-1} scan rate at 298 ± 3 K.

Table 1. Summary of Spectroscopic and Electrochemical Properties of the Ruthenium Complexes

		$E_{1/2}(Ru^{III/II})$ (V vs NHE)		
complex	λ_{abs} max[a] (nm) [ε (M^{-1} cm^{-1})]	pH 1.0[b]	pH 7.49[c]	pH 1.0 on FTO[d]
$[Ru(bpy)_3]Cl_2$	453 [14700]	1.26	1.26	
$[Ru(bpy)_2(CPbpy)]Cl_2$ (**RuCP**)	456 [11800]	1.21	1.12	1.19
$[Ru(bpy)(CPbpy)_2]Cl_2$ (**RuCP2**)	460 [10700]	1.15	1.02	1.19
$[Ru(CPbpy)_3]Cl_2$ (**RuCP3**)	462 [11200]	1.12	0.96	1.15
$[Ru(bpy)_2(Pbpy)]Cl_2$ (**RuP**)	457 [13300]	1.26	1.16	1.29
$[Ru(bpy)(Pbpy)_2]Cl_2$ (**RuP2**)	464 [14200]	1.31	1.16	1.34
$[Ru(Pbpy)_3]Cl_2$ (**RuP3**)	463 [17300]	1.36	1.39	1.40

[a]Spectra were obtained in 0.1 M $HClO_4$ with a 1.0×10^{-5} M complex. [b]Numbers from differential pulse voltammetry in 0.1 M $HClO_4$ with a 1 mM complex. [c]Numbers from differential pulse voltammetry in 0.1 M phosphate buffer (pH 7.49) with 0.5 M $NaClO_4$ and a 1 mM complex. [d]0.1 M $HClO_4$.

sensitizers and have desirable properties as light-absorbing dyes in DSPEC applications.

In the syntheses, two options for functionalization of bipyridine with phosphonate groups were available from the literature: conversion of a $-CH_2Br$ group on an aromatic ring to form a $-CH_2-$ phosphonate ester or conversion of a heteroaryl−X bond to a phosphonate ester directly bound to the ring through a cross-coupling reaction.

Literature procedures for the synthesis of phosphonate-derivatized ligands with $-CH_2-$ spacers are available through 4,4′-$(CH_2Br)_2$-2,2′-bpy as the starting material. Its synthesis has been reported from commercially available 4,4′-dimethyl-2,2′-bipyridine by reaction with *N*-bromosuccinimide (NBS) and azobis(isobutyronitrile) in CCl_4.[36] However, we have not been able to produce significant yields with the published procedure. Further, our overall yield for 4,4′-$(CH_2PO_3Et_2)_2$-2,2′-bipyridine through an alternate route to 4,4′-$(CH_2Br)_2$bpy is higher than the reported yield for 4,4′-$(CH_2Br)_2$bpy by direct bromination using NBS. Another approach to 4,4′-$(CH_2Br)_2$bpy is to first synthesize the trimethylsilyl adduct followed by reaction with an electrophilic bromide source in the presence of cesium fluoride.[37] Although the preparation we report has more steps, the overall yields are high, and relatively pure product is obtained after straightforward recrystallization of the final phosphonate-derivatized ligand.

An important aspect of utilizing a dye molecule in DSPEC applications is efficient excited-state electron injection into TiO_2. For this purpose, literature results point to the

dx.doi.org/10.1021/ic4014976 | *Inorg. Chem.* 2013, 52, 12492−12501

importance of having the phosphonate groups bound directly to the aromatic ring. As reported by Meyer and co-workers, bipyridines with phosphonates directly bound to the 4 and 4′ positions have nearly 40% higher incident photon-to-current efficiencies (IPCEs) than phosphonate-derivatized bipyridines with methylene spacers, at least when evaluated on the nanosecond time scale.[11]

Often phosphonate-derivatized bipyridines with methylene spacers are used because of their accessibility and higher synthetic yields. With our modified procedures, however, the derivatives with phosphonates directly bound are more easily accessible in high yields and with fewer steps than previously reported. Either 4,4′-trifluoromethanesulfonate-2,2′-bipyridine or 4,4′-dibromo-2,2′-bipyridine can be used in the coupling step with good yield. In general, using 4,4′-dibromo-2,2′-bipyridine gives overall better yields than the triflate intermediate because it involves fewer synthetic steps. However, it does require the use of a reagent, $POBr_3$, which is more expensive and more difficult to handle than the reagents in the triflate synthesis. 4,4′-Dibromo-2,2′-bipyridine can also be purchased directly from suppliers at similar or lower cost than the reagents required for the synthesis, which makes the phosphonate derivative only one step away from a commercially available reagent. This is perhaps the most economical route to 4,4′-$(PO_3Et_2)_2$-2,2′-bipyridine.

Our most significant finding in the synthesis of 4,4′-$(PO_3Et_2)_2$-2,2′-bipyridine is the care required for the palladium-catalyzed cross-coupling reaction in the final step. Pure $Pd(PPh_3)_4$ and rigorously air-free conditions are necessary in order to avoid excess PPh_3. In typical cross-coupling reactions catalyzed by $Pd(PPh_3)_4$ or $Pd(PPh_3)_2Cl_2$, an excess of PPh_3 is used to increase the turnover number of the palladium catalyst; however, this excess of PPh_3 is not required for this reaction. The addition of excess PPh_3 is detrimental to the yield and complicates isolation of pure 4,4′-$(PO_3Et_2)_2$-2,2′-bipyridine because at the end of the reaction the excess PPh_3 and triphenylphosphine oxide byproducts must be removed by careful column chromatography. When the reaction is run without excess PPh_3, 4,4′-$(PO_3Et_2)_2$-2,2′-bipyridine can be recrystallized from hexanes in excellent yield in high purity. In fact, the purity of 4,4′-$(PO_3Et_2)_2$-2,2′-bipyridine synthesized in this manner is better (as determined by ^{1}H NMR) than that after using column chromatography for purification (after the addition of excess PPh_3).

The synthesis of ruthenium complexes with phosphonate-derivatized ligands is challenging. We have discovered discrepancies in literature reports for the synthesis, characterization, and properties of these complexes. For example, **RuP2** has been reported to have a negligible IPCE in a DSSC configuration in acetonitrile,[38] in contrast to our results.[35] Moreover, the reported ^{1}H NMR spectrum of **RuP2** in D_2O/NaOD consists of three unresolved multiplets, while λ_{max} for its MLCT transition was reported at 488 nm, values significantly different from those reported here. The product synthesized by our procedure has IPCE characteristics that are similar to those of analogues **RuP** and **RuP3**.[35] For this complex, the low-energy MLCT visible maximum occurs at λ_{max} = 464 nm, and its ^{1}H NMR spectrum shows seven clearly resolved resonances (Figure 6, middle). In addition, the phosphonate-derivatized complexes are highly soluble in aqueous media without the addition of NaOD(H).

A comparison of ^{1}H NMR spectra for **RuP**, **RuP2**, and **RuP3** is shown in Figure 6. There are four clear resonances for the

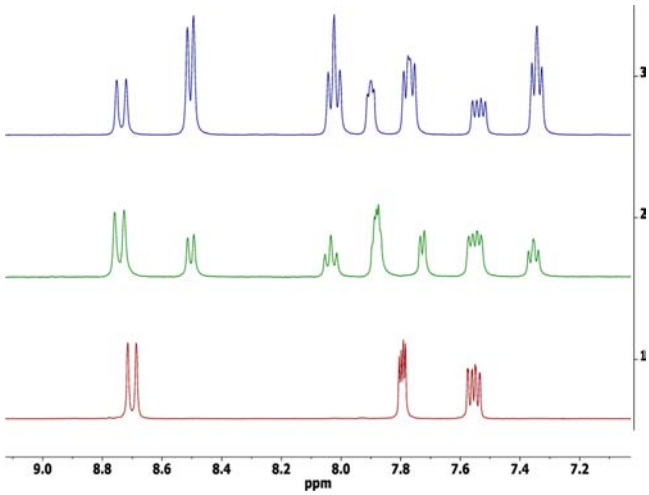


Figure 6. ^{1}H NMR spectra in D_2O at 22 °C for **RuP** (top), **RuP2** (middle), and **RuP3** (bottom) showing the aromatic region of the spectra.

eight aromatic bipyridine protons at 8.51, 8.02, ∼7.75, and 7.32 ppm and three distinct resonances for the three aromatic protons on the functionalized 4,4′-$(PO_3H_2)_2$-bipyridine at 8.73, ∼7.85, and 7.55 ppm. Their chemical shifts remain relatively constant as more phosphonate-derivatized ligands are added. Further, all resonances are sharp and have well-defined splitting patterns.

Spectroscopic and Electrochemical Characterization of Complexes. The UV/vis absorption spectra of the **RuP** and **RuCP** complexes are relatively unremarkable. They all share typical visible MLCT absorptions that are red-shifted from $[Ru(bpy)_3]^{2+}$ by 4−10 nm (193−523 cm^{-1}). This is the expected result given the electron-withdrawing substituent effect of the phosphonate groups in lowering the π^* levels on 4,4′-$(PO_3H_2)_2$-2,2′-bipyridine with respect to unfunctionalized bipyridine. The same red shift of MLCT absorptions was also observed for **RuCP** derivatives with the absorption maxima red-shifted by 3−9 nm (145−430 cm^{-1}).

The redox potentials for the $Ru^{III/II}$ couples in the series **RuP**, **RuP2**, and **RuP3** are more positive than those for the $Ru^{III/II}$ couple in $[Ru(bpy)_3]^{2+}$, again because of the effect of the phosphonic acid derivatized ligands upon stabilization of the $d\pi_{Ru^{II}}$ levels at Ru^{II}. From known solution pK_a values at pH 1, the phosphonic acid substituents not bound to the FTO surface are likely protonated. Consistent with this observation, the trend in the redox potentials from **RuP** to **RuP2** and finally to **RuP3** becomes more positive as more electron-withdrawing substituents are added to the bpy ligands. The same trend was also observed in solution at pH 1.

In solution at pH 7, the potentials for the $Ru^{III/II}$ couples are all ∼100 mV less positive. Under these conditions, the phosphonic acid substituents are completely deprotonated, the ligands become electron-donating relative to bipyridine, and the charge types of the couples are changed. For pH 7, there is no difference in the $Ru^{III/II}$ couples for **RuP** and **RuP2**, although **RuP3** has a $Ru^{III/II}$ couple 230 mV more positive than **RuP** or **RuP2**.

The redox potentials for the $Ru^{III/II}$ couples in the **RuCP** series all occur at less positive potentials than that of the $Ru^{III/II}$ couple of $[Ru(bpy)_3]^{2+}$ under all experimental conditions, which is opposite to the trend observed for the **RuP** series. The trend in the redox potentials with added **CP** ligands is also

dx.doi.org/10.1021/ic4014976 | Inorg. Chem. 2013, 52, 12492−12501

opposite to that found for the **RuP** series, with each additional ligand causing a decrease in potential by ~50−100 mV. These lower potentials and the reversal of the trend with added substituents can be attributed to the electron-donating nature of the alkyl substituents on the **RuCP** complexes. The more electron-rich ruthenium centers are easier to oxidize, and the alkyl spacer between the functional group and aromatic ring also lessens the inductive effects of the protonation state of the phosphonic acids. These trends are in agreement with the σ-donating and π-accepting nature of the substituents on the bipyridine ligands affecting the ruthenium redox potentials as previously reported[39] and originally reported by Lever.[40]

Changing the number of phosphonate-derivatized ligands around the metal center should also have little to no effect on the injection efficiency into TiO_2, and we have shown this to be the case,[35] while other reports show a difference that is dependent on the number of ligands.[38] Although significant differences exist between **RuP** and **RuCP** with respect to photoinjection into TiO_2, which is understandable given their electronic differences, earlier reports of significant differences as the number of 4,4′-$(PO_3H_2)_2$-2,2′-bipyridine or 4,4′-$(CH_2PO_3H_2)_2$-2,2′-bipyridine ligands is an unexpected result.

CONCLUSIONS

We describe here improved procedures and new synthetic methods for the synthesis of phosphonate-derivatized polypyridyl ligands. These include new column-chromatography-free routes to 4,4′-(PO_3Et_2)-2,2′-bipyridine through a two-step, high-yield process from commercially available materials. Additionally, we have developed reaction conditions for clean conversion to the corresponding Ru^{II} complexes. We have also noted the importance of mild reaction conditions in the synthesis of phosphonate-derivatized ruthenium complexes to ensure pure products free of oligomeric forms. These synthetic approaches have allowed phosphonate-derivatized ligands to be added to a variety of complexes that have value as components in the design and synthesis of more complex molecular assemblies for DSPEC applications, for example. The key feature is the aqueous solution stability of the resulting surface linkages, which is an essential element in applications such as water splitting or solar-driven reduction of CO_2 by water.[41−43]

ASSOCIATED CONTENT

Supporting Information

NMR spectra of intermediates and additional voltammograms. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: tjmeyer@email.unc.edu.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Funding from the UNC Energy Frontier Research Center (EFRC) "Center for Solar Fuels", an EFRC funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Award DE-SC0001011, supporting M.R.N., J.J.C., and Z.F. is gratefully acknowledged. A.M.L. acknowledges support from the Chemical Sciences, Geosciences and Biosciences Division of the Office of Basic Energy Sciences, U.S. Department of Energy, Grant DE-FG02-06ER15788. We acknowledge funding by UVA EFRC: CCHF EFRC through Grant DE-SC0001298 supporting C.R.K.G. D.L.A. acknowledges support from a fellowship from the Department of Energy Office of Science Graduate Fellowship Program (DOE SCGF), made possible in part by the American Recovery and Reinvestment Act of 2009, administered by ORISE-ORAU under Contract DE-AC05-06OR23100.

REFERENCES

(1) Bignozzi, C. A.; Schoonover, J. R.; Scandola, F. In *Progress in Inorganic Chemistry*; John Wiley & Sons, Inc.: New York, 2007; p 1.
(2) Grätzel, M. *J. Photochem. Photobiol. C* **2004**, *4*, 145.
(3) Heimer, T. A.; D'Arcangelis, S. T.; Farzad, F.; Stipkala, J. M.; Meyer, G. J. *Inorg. Chem.* **1996**, *35*, 5319.
(4) Nazeeruddin, M. K.; Kay, A.; Rodicio, I.; Humphry-Baker, R.; Mueller, E.; Liska, P.; Vlachopoulos, N.; Graetzel, M. *J. Am. Chem. Soc.* **1993**, *115*, 6382.
(5) O'Regan, B.; Grätzel, M. *Nature* **1991**, *353*, 737.
(6) Trammell, S. A.; Moss, J. A.; Yang, J. C.; Nakhle, B. M.; Slate, C. A.; Odobel, F.; Sykora, M.; Erickson, B. W.; Meyer, T. J. *Inorg. Chem.* **1999**, *38*, 3665.
(7) Zakeeruddin, S. M.; Nazeeruddin, M. K.; Pechy, P.; Rotzinger, F. P.; Humphry-Baker, R.; Kalyanasundaram, K.; Grätzel, M.; Shklover, V.; Haibach, T. *Inorg. Chem.* **1997**, *36*, 5937.
(8) Myahkostupov, M.; Piotrowiak, P.; Wang, D.; Galoppini, E. *J. Phys. Chem. C* **2007**, *111*, 2827.
(9) Ardo, S.; Meyer, G. J. *Chem. Soc. Rev.* **2009**, *38*, 115.
(10) Piotrowiak, P.; Galoppini, E.; Wei, Q.; Meyer, G. J.; Wiewiór, P. *J. Am. Chem. Soc.* **2003**, *125*, 5278.
(11) Gillaizeau-Gauthier, I.; Odobel, F.; Alebbi, M.; Argazzi, R.; Costa, E.; Bignozzi, C. A.; Qu, P.; Meyer, G. J. *Inorg. Chem.* **2001**, *40*, 6073.
(12) Gao, F.; Wang, Y.; Zhang, J.; Shi, D.; Wang, M.; Humphry-Baker, R.; Wang, P.; Zakeeruddin, S. M.; Grätzel, M. *Chem. Commun.* **2008**, *0*, 2635.
(13) Han, L.; Islam, A.; Chen, H.; Malapaka, C.; Chiranjeevi, B.; Zhang, S.; Yang, X.; Yanagida, M. *Energy Environ. Sci.* **2012**, *5*, 6057.
(14) Meyer, T. J. *Acc. Chem. Res.* **1989**, *22*, 163.
(15) Concepcion, J. J.; Jurss, J. W.; Brennaman, M. K.; Hoertz, P. G.; Patrocinio, A. O. v. T.; Murakami Iha, N. Y.; Templeton, J. L.; Meyer, T. J. *Acc. Chem. Res.* **2009**, *42*, 1954.
(16) Alstrum-Acevedo, J. H.; Brennaman, M. K.; Meyer, T. J. *Inorg. Chem.* **2005**, *44*, 6802.
(17) Lewis, N. S.; Nocera, D. G. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 15729.
(18) Hanson, K.; Brennaman, M. K.; Luo, H.; Glasson, C. R. K.; Concepcion, J. J.; Song, W.; Meyer, T. J. *ACS Appl. Mater. Interfaces* **2012**, *4*, 1462.
(19) Bae, E.; Choi, W.; Park, J.; Shin, H. S.; Kim, S. B.; Lee, J. S. *J. Phys. Chem. B* **2004**, *108*, 14093.
(20) McNamara, W. R.; Milot, R. L.; Song, H.-e.; Snoeberger , R. C., III; Batista, V. S.; Schmuttenmaer, C. A.; Brudvig, G. W.; Crabtree, R. H. *Energy Environ. Sci.* **2010**, *3*, 917.
(21) Brewster, T. P.; Konezny, S. J.; Sheehan, S. W.; Martini, L. A.; Schmuttenmaer, C. A.; Batista, V. S.; Crabtree, R. H. *Inorg. Chem.* **2013**, *52*, 6752.
(22) Ghosh, P.; Spiro, T. G. *J. Am. Chem. Soc.* **1980**, *102*, 5543.
(23) Brennan, B. J.; Keirstead, A. E.; Liddell, P. A.; Vail, S. A.; Moore, T. A.; Moore, A. L.; Gust, D. *Nanotechnology* **2009**, *20*, 505203/1.
(24) Moses, P. R.; Murray, R. W. *J. Electroanal. Chem.* **1977**, *77*, 393.
(25) Brown, D. G.; Schauer, P. A.; Borau-Garcia, J.; Fancy, B. R.; Berlinguette, C. P. *J. Am. Chem. Soc.* **2013**, *135*, 1692.
(26) Gallagher, L. A.; Serron, S. A.; Wen, X.; Hornstein, B. J.; Dattelbaum, D. M.; Schoonover, J. R.; Meyer, T. J. *Inorg. Chem.* **2005**, *44*, 2089.

(27) Youngblood, W. J.; Lee, S.-H. A.; Kobayashi, Y.; Hernandez-Pagan, E. A.; Hoertz, P. G.; Moore, T. A.; Moore, A. L.; Gust, D.; Mallouk, T. E. *J. Am. Chem. Soc.* **2009**, *131*, 926.
(28) Hoertz, P. G.; Staniszewski, A.; Marton, A.; Higgins, G. T.; Incarvito, C. D.; Rheingold, A. L.; Meyer, G. J. *J. Am. Chem. Soc.* **2006**, *128*, 8234.
(29) Doi, T.; Nagamiya, H.; Kokubo, M.; Hirabayashi, K.; Takahashi, T. *Tetrahedron* **2002**, *58*, 2957.
(30) Bennett, M. A.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1974**, 233.
(31) Jang, S.-R.; Lee, C.; Choi, H.; Ko, J. J.; Lee, J.; Vittal, R.; Kim, K.-J. *Chem. Mater.* **2006**, *18*, 5604.
(32) Hong, Y.-R.; Gorman, C. B. *J. Org. Chem.* **2003**, *68*, 9019.
(33) Holbrey, J. D.; Tiddy, G. J. T.; Bruce, D. W. *J. Chem. Soc., Dalton Trans.* **1995**, *0*, 1769.
(34) Freedman, D. A.; Evju, J. K.; Pomije, M. K.; Mann, K. R. *Inorg. Chem.* **2001**, *40*, 5711.
(35) Hanson, K.; Brennaman, M. K.; Ito, A.; Luo, H.; Song, W.; Parker, K. A.; Ghosh, R.; Norris, M. R.; Glasson, C. R. K.; Concepcion, J. J.; Lopez, R.; Meyer, T. J. *J. Phys. Chem. C* **2012**, *116*, 14837.
(36) Dong, Y.; Koken, B.; Ma, X.; Wang, L.; Cheng, Y.-X.; Zhu, C.-J. *Inorg. Chem. Commun.* **2011**, *14*, 1719.
(37) Ward, R. S.; Branciard, D.; Dignan, R. A.; Pritchard, M. C. *Heterocycles* **2002**, *56*, 157.
(38) Park, H.; Bae, E.; Lee, J.-J.; Park, J.; Choi, W. *J. Phys. Chem. B* **2006**, *110*, 8740.
(39) Dovletoglou, A.; Adeyemi, S. A.; Meyer, T. J. *Inorg. Chem.* **1996**, *35*, 4120.
(40) Lever, A. B. P. *Inorg. Chem.* **1990**, *29*, 1271.
(41) Song, W.; Glasson, C. R. K.; Luo, H.; Hanson, K.; Brennaman, M. K.; Concepcion, J. J.; Meyer, T. J. *J. Phys. Chem. Lett.* **2011**, *2*, 1808.
(42) Treadway, J. A.; Moss, J. A.; Meyer, T. J. *Inorg. Chem.* **1999**, *38*, 4386.
(43) Xu, Y.; Eilers, G.; Borgström, M.; Pan, J.; Abrahamsson, M.; Magnuson, A.; Lomoth, R.; Bergquist, J.; Polívka, T.; Sun, L.; Sundström, V.; Styring, S.; Hammarström, L.; Åkermark, B. *Chem.—Eur. J.* **2005**, *11*, 7305.