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Synthesis and Optical Properties of Bifunctional Thiophene Molecules Coordinated to Ruthenium

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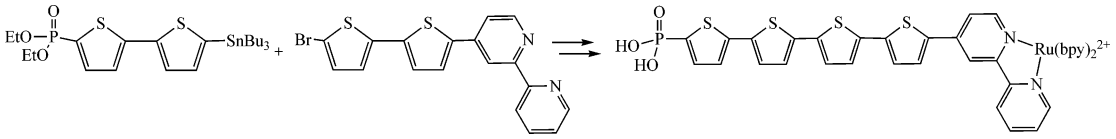

A series of unsymmetrical bi- and tetrathiophenes have been synthesized with bipyridine and phosphonic acid functional groups. To do this, phosphonic esters were bonded to thiophenes and the thiophenes coupled to bipyridine. After synthesis of the thienylbipyridines, bis(bipyridine) ruthenium was coordinated to them through the bipyridines. The thienylbipyridines absorb visible light and fluoresce; however, on attachment to ruthenium, both their fluorescence and that of ruthenium are quenched. An additional effect of coordinating ruthenium to the thiophenes is a new absorption band around 470 nm. Variation in oligothiophene length and bipyridine substitution position allowed comparison of the effect of these variables on electronic properties. The longer oligothiophenes display lower-energy absorptions and emissions than that of the shorter thiophenes. In contrast, the position of the bipyridine attachment does not have a large effect on the absorbance or emission wavelength, or on the fluorescence quantum yield.

Introduction

Oligothiophenes are a promising class of fluorescent molecules that have potential applications in photovoltaics and fluorescence sensing.[1] They are employed as conducting molecules because of their favorable optical and electronic properties and their environmental stability.[2,3] Electronic properties of oligothiophenes are tunable based on the number of conjugated subunits and types of substituents on the subunits. Aryl−aryl coupling reactions are used to synthesize oligothiophenes. The thiophenes can be attached to a conducting surface, which often results in highly ordered self-assembled monolayer. Recently, they have been attached to gold,[4] silicon,[5] indium tin oxide (ITO),[6] and CdSe nanocrystals.[7]

In addition to metal surfaces, oligothiophenes have been extensively studied in conjunction with one or more optically interesting groups, such as fullerenes,[8−16] porphyrins,[9−10] fer-

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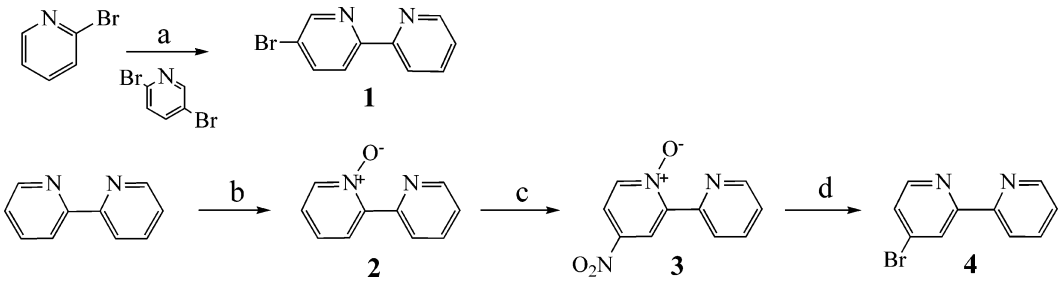
SCHEME 1. Synthesis of 5- and 4-Bromobipyridine[a]



[a] Reagents: (a) (1) n-BuLi, Bu_3SnCl; (2) 2,5-dibromopyridine, $Pd(PPh_3)_4$; (b) MMPP; (c) concd H_2SO_4, concd HNO_3; (d) (1) acetyl bromide; (2) PBr_3.

rocenes,[12] and ligand-coordinated transition metals, especially ruthenium.[17−26] Ruthenium complexes are commonly used as a source of photoexcited electrons for molecular devices. The many current applications include organic circuitry in solar cells,[27−29] fluorescent cation sensors,[30] and other energy transfer systems.[31−34]

We are interested in attaching oligothiophenes to photon-excitable molecules, such as Ru complexes, and using the oligothiophenes as conduits for electron transfer. Ideally, we desire oligothiophenes that have a Ru-binding group on one end and a surface-binding group on the other end. Although, Ru-binding groups have been attached to thiophenes and surface-binding groups have been attached to thiophenes, thiophenes with both have not been synthesized. Bipyridine (bpy) is known to complex well with ruthenium, so attachment of bpy to one end of the oligothiophene is a promising approach for the ruthenium binding group. The position of that attachment on bipyridine is important electronically.[17,22,33−37] The other functional group on the oligothiophene will be a surface binding phosphonic acid. We choose phosphonic acid because its oxygen atoms bind strongly to surface metal cations. Herein we report the synthesis of the first asymmetric bithiophenes and tetrathiophenes that contain bipyridine and phosphonic acid. These oligothiophenes have bipyridine attached to one end and phosphonic acid attached to the other end. We also synthesized the Ru complexes of the thiophenes and report their absorption and emission properties.

Results and Discussion

The planned procedure to prepare the unsymmetrical thiophenes involved preparing the di- and tetrathiophenes and then attaching bipyridine and phosphonic acid groups to them. This procedure worked for the bithiophenes, but was not effective for the tetrathiophenes because of the insolubility of tetrathiophene in common solvents. We planned to use Stille coupling to connect the thiophenes to bipyridine, requiring synthesis of the bromobipyridines. The synthesis of 5-bromopyridine (**1**) took one step and utilized catalytic coupling in a Stille fashion (Scheme 1).[38] The synthesis of 4-bromobipyridine (**4**) required three steps and several modifications to published procedures (Scheme 1).[39−41] To convert bipyridine to bipyridine *N*-oxide, magnesium monoperoxyphthalate (MMPP) was used instead of *m*-chloroperoxybenzoic acid because of its lower toxicity and expense. The reaction ran efficiently in ethanol and did not require glacial acetic acid.[39] The bipyridine *N*-oxide was easily separated from unreacted bipyridine by extraction and flash chromatography.

Next, the bipyridine *N*-oxide was nitrated by carefully controlling the temperature (100 °C) and rate of nitric acid addition. The yield of 4-nitrobipyridine *N*-oxide (**3**) was as large as if fuming sulfuric and nitric acids had been used (50%).[40] The slow rate of nitric acid addition and moderate temperature reduce the amount of dinitrobipyridine *N*-oxide formation. The transformation to the 4-bromobipyridine (**4**) was accomplished by adding acetyl bromide to replace the nitro group and PBr_3 to remove the oxide.[41] The 4-bromobipyridine was purified by extraction with $CHCl_3$ followed by sublimation.

Bithiophenes. To synthesize the bithiophene that could be coupled to bipyridine, the tin reagent of bithiophene was synthesized. After diethyl chlorophosphonate was used to attach a phosphonic ester group to bithiophene, lithium diisopropyla-

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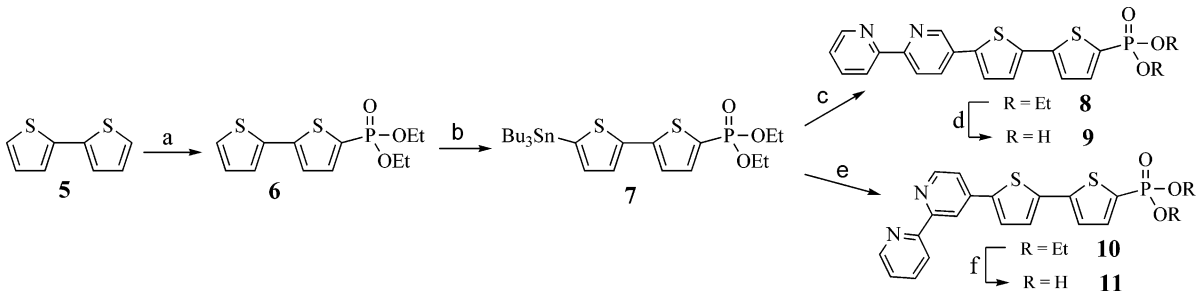
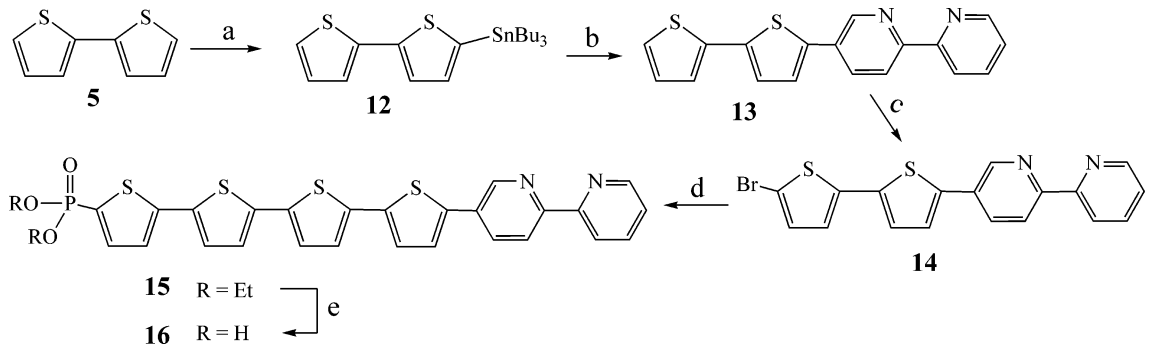
SCHEME 2. Synthesis of Bithiophene Compounds 9 and 11[a]



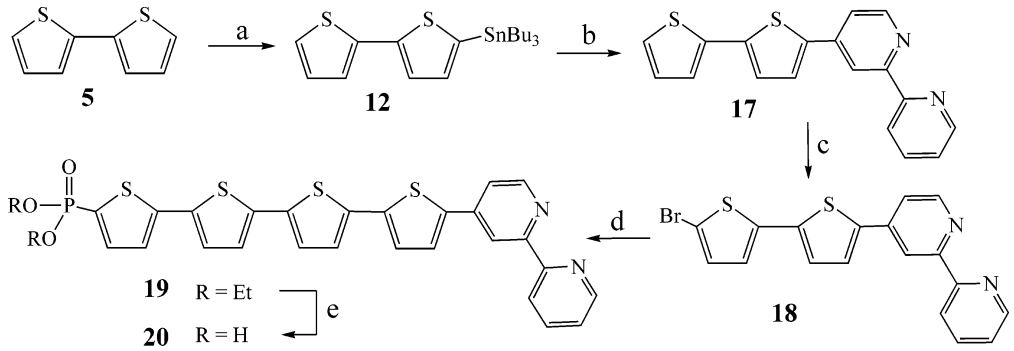
[a] Reagents: (a) (1) n-BuLi; (2) $(EtO)_2P(O)Cl$; (b) (1) LDA; (2) Bu_3SnCl; (c) **1**, $Pd(PPh_3)_4$; (d) (1) TMSBr; (2) H_2O; (e) **4**, $Pd(PPh_3)_4$; (f) (1) TMSBr; (2) H_2O.

SCHEME 3. Synthesis of Tetrathienylbipyridine 16[a]



[a] Reagents: (a) (1) n-BuLi; (2) Bu_3SnCl; (b) **1**, $Pd(PPh_3)_4$; (c) NBS; (d) **7**, $Pd(PPh_3)_4$; (e) (1) TMSBr; (2) H_2O.

SCHEME 4. Synthesis of Tetrathienylbipyridine 20[a]



[a] Reagents: (a) (1) n-BuLi; (2) Bu_3SnCl; (b) **4**, $Pd(PPh_3)_4$; (c) NBS; (d) **7**, $Pd(PPh_3)_4$; (e) (1) TMSBr; (2) H_2O.

mide (LDA) and tributyltin chloride were used to bond tributyltin to the other side of the bithiophene (Scheme 2).[42] This tin compound (**7**) was used to make both the 4- and 5-bithienybipyridines. The aryl−aryl coupling of **7** to 4- and 5-bromopyridine was catalyzed by palladium. Trimethylsilyl bromide (TMSBr) was used to promote the hydrolysis of the esters to acids.[7,43] The 4- and 5-bithienylbipyridines (**9** and **11**) have phosphonic acid groups and are ready to be coordinated to ruthenium.

Tetrathiophenes. Addition of bipyridine and phosphonic acid groups to bithiophene was straightforward, but because tetrathiophene was much less soluble than bithiophene, a new synthetic strategy was used to synthesize derivatives of tetrathiophene. The strategy entailed adding functional groups to bithiophene and then coupling the bithiophenes. The tributyltin phosphonic ester bithiophene (**7**) represents half of the needed tetrathiophene. It was thus necessary to synthesize the coupling partners of **7**, the thiophenes with bipyridine groups.

Because Stille coupling was the desired path to form the tetrathienylbipyridine compounds, the tin adduct of bithiophene was made (Scheme 3). This tributyltin bithiophene (**12**) was coupled to 4- and 5-bromobipyridines using a palladium catalyst and formed the bithienylbipyridines (**13** and **17**, Schemes 3 and 4).[22] These compounds were easily brominated with *N*-bromosuccinimide (NBS), after which the tributyltin phosphonic ester bithiophene (**7**) was coupled to them, again using a palladium catalyst. The hydrolysis of the esters to acids was facilitated with TMSBr. These tetrathienylbipyridine compounds (**16** and **20**) are less soluble than the bithienylbipyridines, and the 4-thienylbipyridines are somewhat more soluble than the 5-thienylbipyridines.

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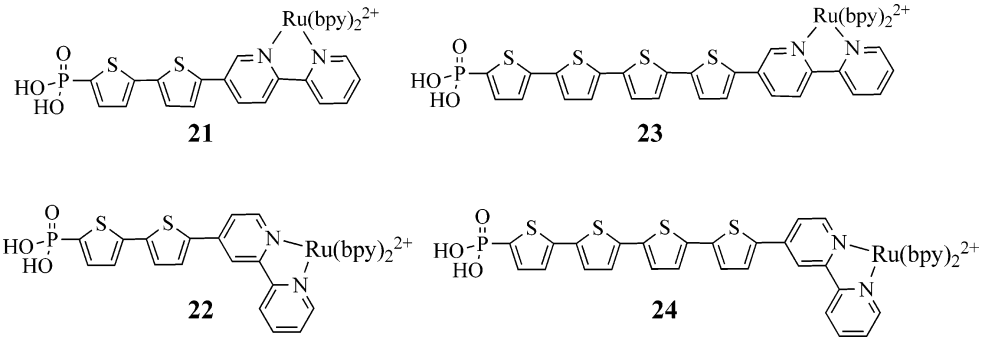

FIGURE 1. Ruthenium−thienylbipyridine complexes.

TABLE 1. Absorption and Emission Properties of Oligothiophenes and Oligothiophene−Ruthenium Complexes[a]

	absorption				emission	
compound	λ_{max}(nm) (ϵ_{max} (M^{-1} cm^{-1}))				λ_{em} (nm)[d]	ϕ_{em}(%)[e]
8	237 (12000)	261 (10000)	365 (43000)		416, 437	27
9[b]			377 (32000)		430, 449	
10	241 (11000)	274 (10000)	359 (20000)		408, 420	19
11[b]			363 (28000)		452	
13	238 (12000)	289 (12000)	363 (40000)		445	24
13[b]			374 (38000)		454	
15	250 (18000)	286 (16000)	422 (38000)		490, 514	20
15[b]			438 (22000)		503, 530	
17	242 (19000)	282 (16000)	357 (28000)		430	26
17[b]			362 (24000)		436	
19	240 (17000)	274 (17000)	420 (36000)		486, 508	28
19[b]			428 (28000)		497, 523	
21	244 (27000)	287 (78000)	397 (41000)	462 (18000)	445	0.23
22	245 (34000)	288 (75000)	384 (32000)	466 (28000)	436	0.13
23	245 (32000)	288 (75000)	446 (52000)	480 (39000)	486	0.12
24	245 (38000)	289 (75000)	437 (49000)	478 (46000)	452	0.17
tetrathiophene[c]	254 (8000)		393 (20000)		450, 478	
$Ru(bpy)_3(PF_6)_2$	244 (29000)	287 (95000)		450 (16000)	600	

[a] Dissolved in acetonitrile unless otherwise noted. Concentrations are 0.01 mM. [b] Dissolved in DMSO. [c] Dissolved in THF. [d] Excitation wavelengths at 350−400 nm. [e] Excitation wavelength 350 nm.

Ruthenium Compounds. To make the ruthenium-bound thienylbipyridine complexes, the thienylbipyridines **9**, **11**, **16**, and **20** were refluxed with $RuCl_2(bpy)_2$[44] in basic water. Red ruthenium complexes (**21**, **22**, **23**, and **24**, Figure 1) were precipitated by acidifying the solution and exchanging the chlorides for hexafluorophosphates. The tetrathienylbipyridine ruthenium complexes required much longer reaction times than the bithienylbipyridines.

Optical Studies. Absorbance and emission measurements were made to know the relative energies of the orbital levels, the orbital overlap, and electronic communication between Ru and oligothiophene and to elucidate the differences between 4- and 5-substituted bipyridines. Table 1 summarizes UV−visible absorption and emission data. Acetonitrile was the principle solvent, but DMSO was also used for enhanced solubility. DMSO resulted in a small red shift (5 to 8 nm).

The oligothienylbipyridines, whether bithiophenes or tetrathiophenes, exhibit similar spectral features. They have a high-energy absorbance in the region of 240 nm, which is assigned to thiophene absorption. They also have an absorbance peak between 275 and 290 nm, which is assigned to bipyridine absorption. A third peak in the region of 350−430 nm is assigned to a $\pi-\pi^*$ transition for the entire thienylbipyridine unit. This lowest-energy absorption is the most intense and is the most red-shifted from the bithiophenes to the tetrathiophenes (58 nm from **8** to **15** and 61 nm from **10** to **19**). Three absorption peaks are observed for similar compounds.[24] The 4- and 5-substituted thienylbipyridines have similar absorbance wavelengths. This is the case for the bithiophenes (**8** and **10**) as well as the tetrathiophenes (**15** and **19**). The phosphonic ester and acid groups do not have a major affect on the absorbance peaks as can be seen by comparing the compounds with phosphonic groups (**8**, **9**, **10**, **11**) to those without (**13**, **17**).

Comparing the bithienylbipyridine compounds (**13** and **17**) to tetrathiophene shows the $\pi-\pi^*$ transition in tetrathiophene red-shifted. Thus, there is better conjugation when only thiophenes are connected. On the other hand, when tetrathiophene is compared to tetrathienylbipyridine compounds (**15** and **19**), its absorption is blue-shifted. This 30 nm shift can be explained by the increased conjugation over six aromatic rings compared to four for tetrathiophene alone.

An interesting observation may be made by comparing the known compounds 5,5′- and 4,4′-bis(bithienyl)bipyridines **25** and **26** (Figure 2)[22] to 5- and 4-tetrathienylbipyridines **15** and **19**. Each has a bipyridine and four thiophene rings, but **25** and **26** have bithiophene units on each side of the bipyridine, unlike **15** and **19** which have all of the thiophenes connected to each other. The absorption bands of **25** (396 nm) and **26** (361 nm)

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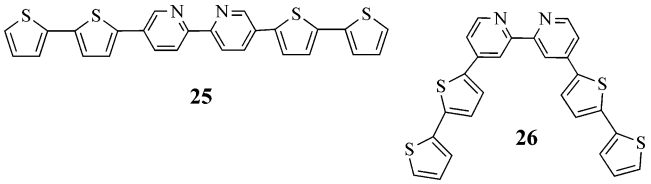


FIGURE 2. 5,5″-Bis(bithienyl)bipyridine (**25**) and 4,4′-bis(bithienyl)-bipyridine (**26**).

are at shorter wavelengths by 30−60 nm relative to **15** (432 nm) and **19** (420 nm). The energy transition is smaller when thiophenes are directly connected than when they are bound to bipyridine.

The thienylbipyridines fluoresce at wavelengths 70−80 nm lower in energy relative to their absorption (Figure 3, Table 1). As expected, the tetrathiophenes emit at longer wavelengths than the bithiophenes. Their fluorescence quantum yields are between 19 and 28% when they are excited at 350 nm. The emission of the 5-substituted bithienylbipyridine (**8**) is at slightly lower energy and more efficient than the emission of 4-substituted bithienylbipyridine (**10**). The fluorescent lifetimes of the thienylbipyridines are less than 2 ns; other oligothiophenes have fluorescent lifetimes near 1 ns.[45]

Ruthenium-Bound Thiophenes. The absorbance spectra of the four ruthenium-thienylbipyridine complexes (**21**−**24**) show one more peak than the non Ru-coordinated thiophenes (Figure 4). The new peak is due to the $Ru(bpy)_3$ unit. The two peaks at around 250 and 290 nm are due to thiophene and bipyridine, as they were with the metal free thiophenes. However, the 290 nm peak is much stronger than it was before Ru was coordinated, because there are now three bipyridines for each thiophene unit due to the added ancillary bipyridines on Ru. The next absorbance peaks between 384 and 446 nm, assigned to $\pi-\pi^*$ transitions, are red-shifted from where they were before Ru was coordinated to the thienylbipyridines. The magnitudes of the shifts for the compounds are: 32 nm (**21** from **8**), 25 nm (**22** from **10**), 24 nm (**23** from **15**), and 17 nm (**24** from **19**). This effect is common to Ru complexes of this type and has been ascribed to the "donor−acceptor" nature of the system.[14] As seen by the magnitudes of the shifts, when bipyridine is substituted at the 5-position, the red-shift is larger by 7 nm for both the bithiophene and tetrathiophene. Also, there is generally an increase in the molar absorptivity of the peaks after Ru coordination.

The lowest energy absorbance peaks for the compounds, found from 462 to 480 nm, are assigned to metal-to-ligand charge-transfer (MLCT) transitions. They are red-shifted from those of $Ru(bpy)_3^{2+}$ by 12−16 nm for the bithiophenes and 28−30 nm for the tetrathiophenes. No significant difference is observed between the 4- and 5-bipyridine positions. The red shift of the MLCT transitions can be explained by the negative charge being delocalized in a lower energy orbital originating from both bipyridine and thiophene. There is also observed an increase in the molar absorptivity of these absorbance bands compared to $Ru(bpy)_3^{2+}$.

The emission spectra of the ruthenium thienylbipyridine complexes show a dramatic quenching of both the thienylbipyridine and Ru-bpy fluorescence. The strongest emissions for the ruthenium thienylbipyridines are a hundred times weaker than the unbound thienylbipyridines. The fluorescence quenching indicates that nonradiative excited-state energy decay pathways become accessible when Ru is bound to the thienylbipyridines. Other ruthenium thiophene complexes also exhibit fluorescence quenching.[20]

Electrochemisty. Oxidation and reduction properties of the compounds were investigated using cyclic voltammetry. The bithienylbipyridines have two oxidation processes, **13**: 1.25 and 1.39 V, **17**: 1.36 and 1.49 V. The tetrathienylbipyridines (**15** and **19**) have at least three oxidation processes, which are observed at 1.15, 1.48, and 1.62 V (Figure 5). They also exhibit a reduction process at −1.82 V. The ruthenium-bound thienylbipyridines (**21**−**24**) have an oxidation process at around 1.4 V, which is attributed to the Rubpy moiety (Figure 6). $Ru(bpy)_3^{2+}$ has a reduction process at 1.38 V. Also, the ruthenium-bound bithienylbipyridines have an oxidation process at 1.7 V and a reduction process at around −1.4 V. Because of the poor solubility of the ruthenium-bound tetrathiophenes, weak signals are observed for their oxidation and reduction processes. However, besides the oxidation process from the Rubpy group, they exhibit oxidation processes at 1.1 and 1.5 V. And, **24** exhibits reduction processes at −0.99 and −1.25 V.

Conclusion

Asymmetric bithiophene and tetrathiophene compounds were synthesized with bipyridine and phosphonic acid groups. During the synthesis, tin adducts were used and smaller thiophenes were coupled to make tetrathiophenes. The thiophenes were attached to 4- and 5-substituted bipyridines. The bi- and tetrathienylbipyridine compounds were coordinated to Ru, and their optical spectra were recorded. Absorption spectra indicate that longer thiophenes have smaller energy gaps between ground and excited states. Ruthenium coordination to the thiophenes causes the $\pi-\pi^*$ and MLCT transitions to be red-shifted. The $\pi-\pi^*$ transition is more red-shifted when the bipyridine is substituted at the 5 position. The free thiophenes fluoresce with quantum yields from 19−28%, while the Ru-bound thiophenes exhibit fluorescence quenching. The Ru-bound and unbound thienylbipyridines have oxidation processes in the range 1.1 to 1.7 V.

Experimental Section

Diethyl 5′-(2,2′-Bipyridin-5-yl)-2,2′-bithien-5-ylphosphonate (8). To 20 mL of dry toluene under N_2 were added **7** (0.88 g, 1.5 mmol), 5-Brbpy (0.350 g, 1.49 mmol) and $Pd(PPh_3)_4$ (0.089 g, 5.1 mol %). The solution was refluxed for 72 h. Toluene was evaporated, and the solid was chromatographed on silica with ethyl acetate as the eluent. The product was recovered and left under vacuum to remove volatile impurities. It (0.57 g, 1.2 mmol, 81%) was collected as a slightly sticky yellow solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.93 (dm, 1H, J = 3.0 Hz), 8.69 (dm, 1H, J = 5.0 Hz), 8.44 (d, 1H, J = 8.5 Hz), 8.42 (d, 1H, J = 7.0), 7.98 (dd, 1H, J = 2.5, 8.5 Hz), 7.82 (ddd, 1H, J = 2.0, 8.0 Hz), 7.58 (dd, 1H, J = 3.5, 8.0 Hz), 7.37 (d, 1H, J = 3.5 Hz), 7.32 (ddd, 1H, J = 1.0, 7.5, 5.0), 7.28 (d, 1H, J = 3.0 Hz), 7.26 (dd, 1H, J = 3.5, 3.5 Hz), 4.25−4.09 (m, 4H), 1.37 (t, 6H, J = 7.0 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 155.6, 155.3, 149.4, 146.1, 145.0 (d, J = 8.0 Hz), 140.8, 137.7 (d, J = 11.0 Hz), 137.1, 136.5 (d, J = 3.0 Hz), 133.6, 129.7, 126.7 (d, J = 210.0 Hz), 126.4, 125.4, 124.7 (d, J = 17.0 Hz), 124.0, 121.2, 121.2. ^{31}P NMR ($CDCl_3$, 121 MHz): δ 11.56 (s). UV−vis ($NCCH_3$) λ, nm (ϵ, M^{-1} cm^{-1}): 237 (12000), 261 (10000), 365 (43000). HRMS (ESI-TOF) *m*/*z* calcd for $C_{22}H_{21}N_2O_3PS_2$ $(M + Na)^+$ 479.0623; found 479.0623.

(45) Becker, R. S.; de Melo, J. S.; Macanita, A. L.; Elisei, F. *J. Phys. Chem.* **1996**, *100*, 18683−18695.

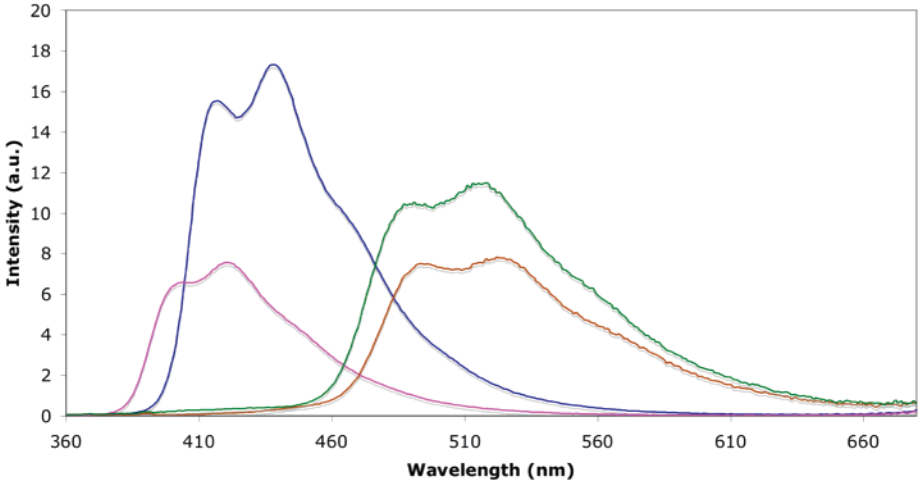


FIGURE 3. Emission spectra of bithienylbipyridines (**8**, blue; **10**, pink) and tetrathienylbipyridines (**15**, brown; **19**, green) excited at 350 nm. Taken at room temperature.

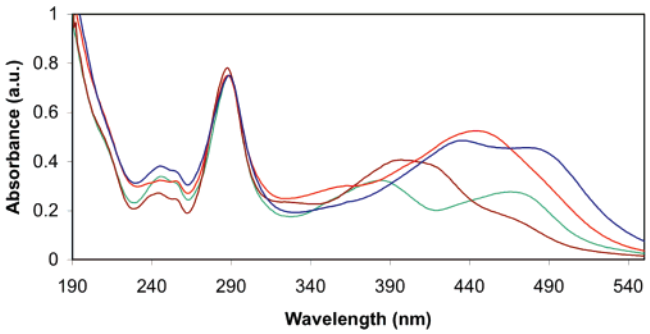


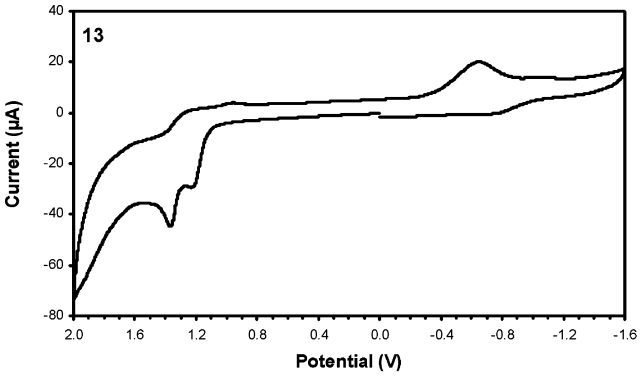
FIGURE 4. Absorbance spectra of the four Ru-oligothiophenes (**21**, brown; **22**, green; **23**, red; **24**, blue). Concentrations were 0.01 mM in acetonitrile.

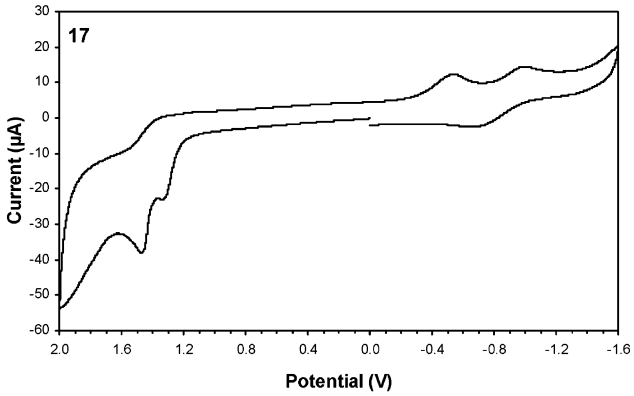
5′-(2,2′-Bipyridin-5-yl)-2,2′-bithien-5-ylphosphonic Acid (9). To **8** (0.479 g, 1.05 mmol) under N_2 was added TMSBr (1.0 mL, 7.6 mmol). The slurry was stirred for 2.5 h before being quenched with water. Excess water was removed under vacuum. Acetone was added, and the slurry was stirred vigorously and then filtered. The solid was washed with acetone and methanol until the filtrate ran colorless. The bright orange solid (mp 218−221 °C) was dried and collected (0.335 g, 0.77 mmol, 73%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.07 (d, 1H, J = 2.5 Hz), 8.74 (d, 1H, J = 4.5 Hz), 8.47 (d, 1H, J = 2.5, Hz), 8.46 (d, 1H, J = 2.5 Hz), 8.27 (dd, 1H, J = 2.5 Hz, 8.5 Hz), 8.07 (ddd, 1H, J = 8.0, 8.0, 0.5 Hz), 7.78 (d, 1H, J = 4.0 Hz), 7.55 (t, 1H, 6.0 Hz), 7.52 (d, 1H, J = 4.0 Hz), 7.43−7.39 (m, 2H). ^{31}P NMR (DMSO, 121 MHz): δ 5.36 (s). UV−vis (DMSO), λ, nm (ϵ, M^{-1} cm^{-1}): 377 (ϵ = 32000). HRMS (ESI-TOF) m/z calcd for $C_{18}H_{13}N_2O_3PS_2$ $(M + H)^+$ 401.0178; found: 401.0177.

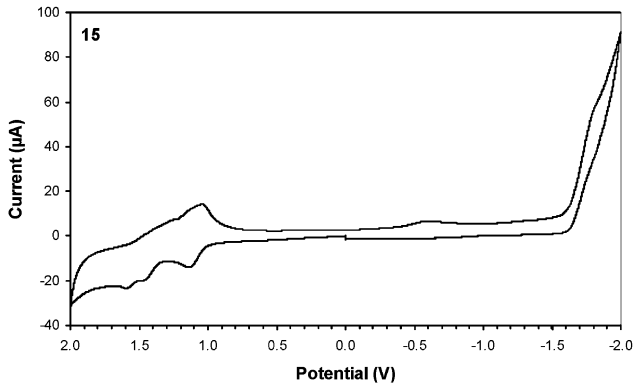
Diethyl 5′-(2,2′-Bipyridin-4-yl)-2,2′-bithien-5-ylphosphonate (10). Compound **7** (1.7 g, 2.9 mmol) was dissolved in 30 mL of dry toluene under N_2. Compound **4** (0.89 g, 4.0 mmol) and Pd-$(PPh_3)_4$ (0.173 g, 5 mol %) were added, and the solution was heated to reflux for 48 h. After cooling, the solution was extracted with 20 mL of water and then 20 mL of saturated NH_4Cl. The combined aqueous fractions were extracted with toluene (2 × 20 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and evaporated. The resulting crude orange oil was chromatographed on silica with hexanes:ethyl acetate (1:1) followed by ethyl acetate. The product (0.55 g, 1.2 mmol, 42%) was collected as an orange viscous oil. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.73 (dm, 1H, J = 5.0 Hz), 8.68 (d, 1H, J = 5.5 Hz), 8.63 (d, 1H, J = 1.5 Hz), 8.42 (d, 1H, J = 8.0 Hz), 7.85 (ddd, 1H, J = 2.0, 8.0, 8.0 Hz), 7.59 (d, 1H, J = 4.0 Hz), 7.59 (dd, 1H, J = 3.5, 8.5 Hz), 7.48 (dd, 1H, J = 2.0, 5.0 Hz), 7.35 (ddd, 1H, J = 1.0, 7.5, 5.5), 7.29 (d, 1H, J = 4.0 Hz), 7.28 (dd, 1H, J = 3.5, 3.5 Hz), 4.11−4.25 (m, 4H), 1.37 (t, 6H, J = 7.0 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 157.1, 155.8, 150.0, 149.3, 137.7 (C−P J = 11.0 Hz), 137.1, 128.7, 128.6, 127.0 (C−P J = 209.5), 126.6, 126.3, 125.0 (C−P J = 16.5 Hz), 124.1, 121.4, 119.6, 117.0, 63.0 (C−P J = 5.5 Hz), 16.4 (C−P J = 6.5 Hz). ^{31}P NMR ($CDCl_3$, 121 MHz); δ (ppm): 11.45 (s). UV−vis ($NCCH_3$) λ, nm (ϵ, M^{-1} cm^{-1}): 241 (11000), 274 (10000), 358 (20000). HRMS (ESI-TOF) m/z calcd for $C_{22}H_{21}N_2O_3PS_2$ $(M + Na)^+$ 479.0623; found: 479.0624.

5′-(2,2′-Bipyridin-4-yl)-2,2′-bithien-5-ylphosphonic Acid (11). Compound **10** (0.502 g, 1.1 mmol) was added to a Schlenk flask and thoroughly degassed with N_2. Trimethylsilyl bromide (TMSBr) (1.0 mL, 7.6 mmol) was added through a septum. The resultant slurry was stirred overnight under N_2. The reaction was quenched with water and stirred vigorously. The solid was filtered out and washed with acetone. Product (0.394 g, 0.97 mmol, 90%) was collected as an orange powder (mp 232−237 °C). ^{1}H NMR (DMSO, 500 MHz): δ 8.80 (d, 1H, J = 4.5 Hz), 8.75 (d, 1H, J = 5.0 Hz), 8.70 (d, 1H, J = 0.5 Hz), 8.57 (d, 1H, J = 8.0 Hz), 8.14 (ddd, 1H, J = 1.0, 8.0, 8.0 Hz), 8.06 (d, 1H, J = 4.0 Hz), 7.91 (dd, 1H, J = 1.5, 5.0 Hz), 7.64 (ddd, 1H, J = 1.0, 6.0, 6.0 Hz), 7.61 (d, 1H, J = 4.0 Hz), 7.52 (dd, 1H, J = 3.5, 3.5 Hz), 7.42 (dd, 1H, J = 3.5, 8.5 Hz). ^{31}P NMR (DMSO, 121 MHz): δ 5.20 (s). UV−vis (H_2O/OH^-) λ, nm (ϵ, M^{-1} cm^{-1}): 238 (13000), 278 (13000), 363 (31000). HRMS (ESI-TOF) m/z calcd for $C_{18}H_{13}N_2O_3PS_2$ $(M + H)^+$ 401.0178; found 401.0176.

5-(2,2′-Bipyridin-5-yl)-2,2′-bithiophene (13). Bithiophene (**5**) (2.00 g, 12.0 mmol) was dissolved in 50 mL of dry THF under N_2, and the solution was cooled to −78 °C. n-BuLi (7.5 mL, 12 mmol) was added dropwise, and the solution was stirred for 1 h at −78 °C. Tributyltin chloride (3.9 mL, 14 mmol) was added in one aliquot, and the mixture was left to stir and warm to room temperature overnight. The solvent was evaporated, and 50 mL of dry toluene was added. The precipitate was removed by vacuum filtration under air. The solution was returned to a Schlenk flask and purged with N_2. Compound **1** (2.76 g, 11.7 mmol) and Pd-$(PPh_3)_4$ (0.41 g, 2.9 mol %) were added, and the solution was heated to reflux for 72 h. The solvent was evaporated, and the solid was taken up in 200 mL of CH_2Cl_2 and 50 mL of 2 M NaOH. The layers were separated, and solid impurities in the organic layer were removed by filtration through celite. The solid was washed with CH_2Cl_2 until the filtrate ran pale, and then the solid was discarded.







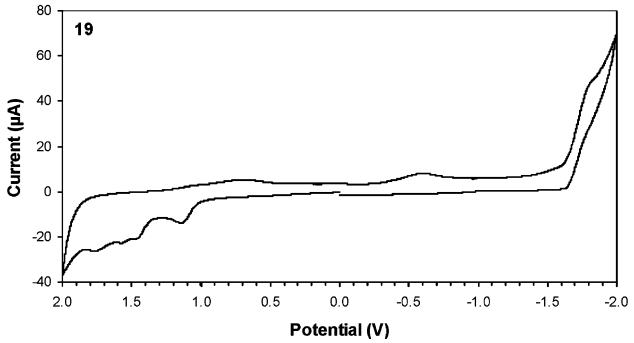
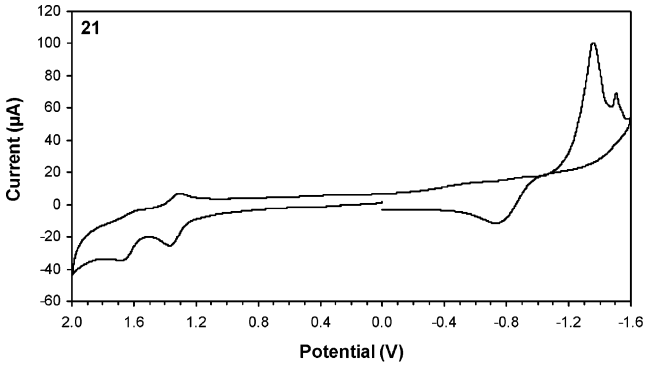
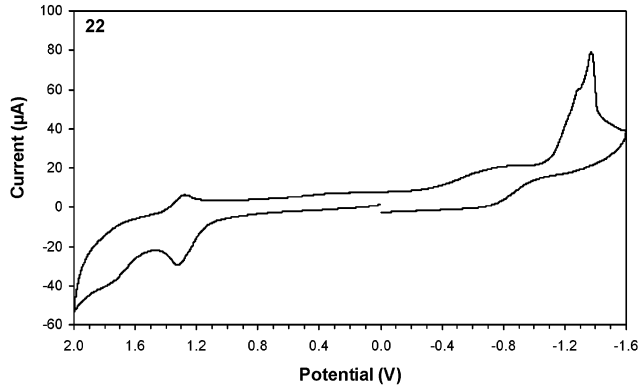
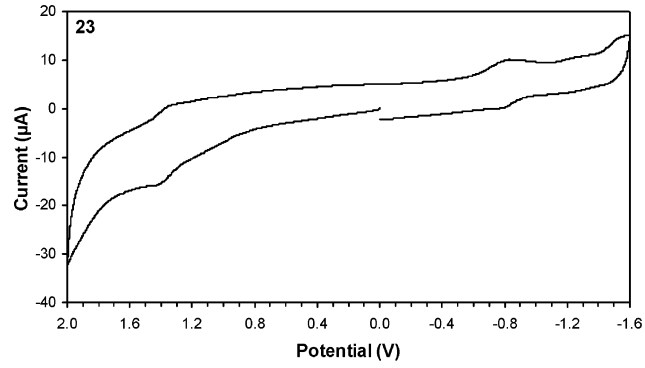


FIGURE 5. Cyclic voltammograms of bithienylbipyridines **13** and **17** in acetonitrile and tetrathienylbipyridines **15** and **19** in dichloromethane. Compound concentrations were 0.5 mM and NBt_4PF_6 was 0.1 M.







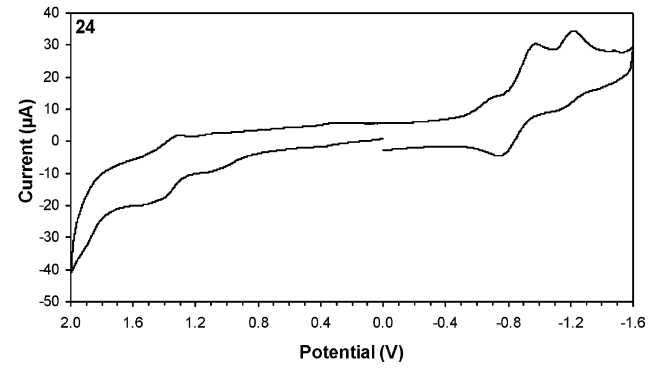


FIGURE 6. Cyclic voltammograms of Ru-thienylbipyridines **21**−**24** in acetonitrile. Compound concentrations were 0.5 mM or less and NBt_4PF_6 was 0.1 M.

The solvent was evaporated and the residual solid was chromatographed with silica and 0.5% methanol in ethyl acetate increasing to 2% methanol. Product (1.47 g, 4.6 mmol, 39%) was collected as a brown solid (mp 145−148 °C). Sublimation yields a pure yellow solid, but some material is lost to decomposition. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.94 (d, 1H, J = 2.0 Hz), 8.69 (d, 1H, J = 4.0 Hz), 8.43 (m, 2H), 7.99 (dd, 1H, J = 2.5, 8.5 Hz), 7.83 (ddd, 1H, J = 1.5, 7.5, 7.5 Hz), 7.36 (d, 1H, J = 4.0 Hz), 7.32 (ddd, 1H, J = 1.0 Hz, 6.5, 5.0 Hz), 7.25 (dd, 1H, J = 1.0, 5.0 Hz), 7.24 (dd, 1H, J = 1.0, 3.5 Hz), 7.20 (d, 1H, J = 3.5 Hz), 7.05 (dd, 1H, J = 5.0, 3.5 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 155.8, 155.0, 149.4, 146.1, 139.1, 138.3, 137.1, 133.4, 130.2, 128.2, 125.2, 125.1, 125.0, 124.3, 123.9, 121.2, 121.2. UV−vis ($NCCH_3$) λ, nm (ϵ, M^{-1} cm^{-1}):

238 (12000), 289 (12000), 363 (40000). HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{12}N_2S_2$ $(M + H)^+$ 321.0515; found 321.0513.

5-Bromo-5′-(2,2′-bipyridin-5-yl)-2,2′-bithiophene (14). To 200 mL of 1:1 $CHCl_3$:acetic acid was added **13** (1.00 g, 3.12 mmol) and *N*-bromosuccinimide (NBS) (0.56 g, 3.14 mmol). The reaction was heated to 60 °C and was maintained at that temperature for 15 min before cooling. The mixture was poured into 50 mL of water, and the layers were separated. The aqueous layer was extracted with $CHCl_3$ (2 × 50 mL), and the combined organic extracts were washed with K_2CO_3(aq) until neutral. The organic layer was then dried over $MgSO_4$, filtered, and evaporated. Product (1.21 g, 3.00 mmol, 96%) was collected as an orange solid (mp 175−179 °C, with partial decomposition). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.92 (dm, 1H, J = 2.5 Hz), 8.69 (dm, 1H, J = 3.5 Hz), 8.43 (dd, 1H, J = 0.5 Hz, 8.5 Hz), 8.42 (ddd, 1H, J = 1.0 Hz, 1.0 Hz, 8.5 Hz), 7.97 (dd, 1H, J = 2.5 Hz, 8.5 Hz), 7.83 (ddd, 1H, J = 2.0 Hz, 8.0 Hz, 8.0 Hz), 7.34 (d, 1H, J = 4.0 Hz), 7.32 (ddd, 1H, J = 1.5, 7.5, 5.5 Hz), 7.13 (d, 1H, J = 4.0 Hz), 7.02 (d, 1H, J = 4.0 Hz), 6.97 (d, 1H, J = 4.0 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 155.8, 155.3, 149.5, 146.2, 139.7, 138.7, 137.2, 137.2, 133.6, 131.0, 130.0, 125.3, 124.4, 124.0, 121.3, 121.3, 111.8. HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{11}N_2S_2Br$ $(M - H)^+$ 398.9620; found 398.9619.

Diethyl 5‴-(2,2′-Bipyridin-5-yl)-2,2′-5′,2″-5″,2‴-tetrathien-5-ylphosphonate (15). Compounds **7** (2.63 g, 4.4 mmol) and **14** (1.15 g, 2.9 mmol) were dissolved in 90 mL of dry toluene under N_2. $Pd(PPh_3)_4$ (0.17 g, 5 mol %) was added, and the mixture was heated to reflux for 16 h. The reaction mixture was poured into 200 mL of hexanes, and a precipitate was allowed to form for several minutes. The solid was collected by filtration, and the filtrate was discarded. The solid was then dissolved in THF, and the residual solid was removed by filtering through celite and was discarded. The THF solution was evaporated to an orange/brown sticky solid which was stirred vigorously in ∼100 mL of ether for 0.5 h. The dry solid (0.770 g, 1.2 mmol, 41%) was collected by filtration (dec ∼200 °C). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.93 (d, 1H, J = 2.5 Hz), 8.69 (dm, 1H, J = 2.5), 8.43 (dd, 2H, J = 8.5, 8.5 Hz), 7.98 (dd, 1H, J = 8.5, 2.5 Hz), 7.83 (ddd, 1H, J = 7.75, 7.75, 2.0 Hz), 7.56 (dd, 1H, J = 8.5, 4.0 Hz), 7.36 (d, 1H, 3.5 Hz), 7.31 (ddd, 1H, J = 1.0, 7.0, 5.0 Hz), 7.21 (d, 1H, J = 3.5 Hz), 7.20 (dd, 1H, J = 3.0, 3.0 Hz), 7.18 (d, 1H, J = 3.5 Hz), 7.16 (d, 1H, J = 3.5 Hz), 7.13 (d, 1H, J = 4.0 Hz), 7.12 (H_{11-14}, d, 1H, J = 3.0 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 155.9, 155.2, 149.5, 146.2, 139.6, 137.8, 137.7, 137.2, 136.6, 136.1, 135.0, 133.5, 130.1, 126.2, 125.7, 125.4, 125.2, 125.1, 125.0, 124.8, 124.6, 124.4, 124.0, 121.3, 121.3, 63.0 (C−P J = 5.5 Hz), 16.5 (C−P J = 6.0 Hz). ^{31}P NMR ($CDCl_3$, 121 MHz): δ 11.44 (s). UV−vis ($NCCH_3$) λ, nm (ϵ, M^{-1} cm^{-1}): 250 (18000), 286 (16000), 422 (38000). HRMS (ESI-TOF) *m/z* calcd for $C_{30}H_{25}N_2O_3PS_4$ $(M + H)^+$ 621.0558; found 621.0559. Anal. Calcd for $C_{30}H_{25}N_2O_3PS_4$: C, 58.04; H, 4.06; N, 4.51. Found C, 57.71; H, 4.02; N, 4.29.

5-Bromo-5′-(2,2′-bipyridin-4-yl)-2,2′-bithiophene (18). To 200 mL of 1:1 $CHCl_3$:acetic acid were added **17** (1.00 g, 3.12 mmol) and NBS (0.56 g, 3.14 mmol). The reaction was heated to 60 °C and was maintained at that temperature for 15 min before cooling. The mixture was poured into 50 mL of water, and the layers were separated. The aqueous layer was extracted with $CHCl_3$ (2 × 50 mL), and the combined organic extracts were washed with K_2CO_3(aq) until neutral. The organic layer was then dried over $MgSO_4$, filtered, and evaporated. Product (1.20 g, 3.00 mmol, 96%) was collected as an orange solid (mp 137−141 °C, with partial decomposition). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.72 (dm, 1H, J = 4.0 Hz), 8.64 (dd, 1H, J = 5.0, 1.0 Hz), 8.60 (dm, 1H, J = 2.0 Hz), 8.42 (ddd, 1H, J = 8.0, 1.0, 1.0 Hz), 7.83 (ddd, 1H, J = 2.0, 8.0, 8.0 Hz), 7.53 (d, 1H, J = 4.0 Hz), 7.44 (dd, 1H, J = 3.0, 5.0 Hz), 7.33 (dd, 1H, J = 1.0, 8.0, 5.0), 7.12 (d, 1H, J = 4.0 Hz), 7.00 (d, 1H, J = 4.0 Hz), 6.97 (d, 1H, J = 4.0 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 157.1, 156.0, 150.0, 149.3, 142.0, 140.5, 138.5, 138.2, 137.2, 131.0, 126.6, 125.1, 124.6, 124.2, 121.4, 119.6, 117.0, 112.1. HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{13}N_2S_2Br$ $(M + H)^+$ 398.9620; found 398.9621.

Diethyl 5‴-(2,2′-bipyridin-4-yl)-2,2′-5′,2″-5″,2‴-tetrathien-5-ylphosphonate (19). To 25 mL of dry toluene under N_2 in a Schlenk flask were added **7** (1.02 g, 1.72 mmol), **18** (0.715 g, 1.79 mmol), and $Pd(PPh_3)_4$ (0.101 g, 5.1 mol %). The solution was heated to reflux and stirred for 72 h. After cooling, the mixture was poured into 100 mL of hexane, which precipitated a red/orange solid (mp/dec ∼150 °C). Product (0.877 g, 1.41 mmol, 82%) was collected by filtration and washed with hexanes. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.72 (dm, 1H, J = 5.0 Hz), 8.66 (d, 1H, J = 5 Hz), 8.63 (d, 1H, J = 2.0 Hz), 8.44 (d, 1H, J = 8.0 Hz), 7.83 (ddd, 1H, J = 2.0, 7.5, 7.5 Hz), 7.57 (d, 1H, J = 4.0 Hz), 7.55 (dd, 1H, J = 8.5, 3.5 Hz), 7.47 (dd, 1H, J = 2.0, 5.5 Hz), 7.34 (ddd, 1H, J = 1.0, 8.0, 5.0 Hz), 7.22 (d, 1H, J = 4.0 Hz), 7.20 (dd, 1H, J = 3.0, 3.0 Hz), 7.18 (d, 2H, J = 4.0 Hz), 7.14 (d, 1H, J = 7.0 Hz), 7.13 (d, 1H, J = 6.5 Hz), 4.22−4.12 (m, 4H), 1.37 (t, 6H, J = 7.0 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 157.1, 156.0, 150.0, 149.4, 142.1, 140.4, 138.8, 137.6, 137.2, 136.4, 136.4, 126.7, 126.2, 125.1, 124.9, 124.2, 121.5, 119.6, 117.0. ^{31}P NMR ($CDCl_3$, 121 MHz): δ 11.63 (s). UV−vis ($NCCH_3$) λ, nm (ϵ, M^{-1} cm^{-1}): 240 (17000), 274 (17000), 420 (36000). HRMS (ESI-TOF) *m/z* calcd for $C_{30}H_{25}N_2O_3PS_4$ $(M + 2H)^{2+}$ 311.0316; found 311.0316. Anal. Calcd for $C_{30}H_{25}N_2O_3PS_4$: C, 58.04; H, 4.06; N, 4.51. Found C, 58.19; H, 4.10; N, 4.44.

[5′-(2,2′-Bipyridin-5-yl)-2,2′-bithien-5-ylphosphonic acid]bis-(bipyridyl)ruthenium(II) Hexafluorophosphate (21). To 25 mL of H_2O were added **9** (0.204 g, 0.510 mmol), $RuCl_2(bpy)_2$ (0.249 g, 0.514 mmol), and NaOH (21.3 mg, 0.533 mmol). The mixture was refluxed for 3 h. After cooling, the mixture was acidified with 1 M HCl and filtered to remove unreacted starting material. KPF_6 (0.427 g, 2.32 mmol) in 10 mL of water was added which precipitated a red solid. The solid was collected by centrifugation. It was then dissolved in acetone, transferred to a round-bottom flask, and evaporated to dryness. The product (0.490 g, 0.444 mmol, 87%) was collected as a red/brown solid (dec >180 °C). ^{1}H NMR (DMSO, 500 MHz): δ 8.91−8.84 (m, 6H), 8.46 (d, 1H, J = 8.0 Hz), 8.28 (dd, 1H, J = 8.0, 8.0 Hz), 8.21−8.16 (m, 4H), 7.94 (d, 1H, J = 5.0 Hz), 7.85 (d, 1H, J = 5.0 Hz), 7.77−7.74 (m, 3H), 7.66−7.61 (m, 2H), 7.56−7.52 (m, 5H), 7.46 (d, 1H, J = 4.0 Hz), 7.38 (dd, 1H, J = 3.5, 7.5 Hz), 7.35 (d, 1H, J = 3.0 Hz). ^{31}P NMR (DMSO, 121 MHz): δ 4.83 (s). UV−vis ($NCCH_3$) λ, nm (ϵ, M^{-1} cm^{-1}): 244 (27000), 287 (78000), 397 (41000), 462 (18000). HRMS (ESI-TOF) *m/z* calcd for $C_{38}H_{29}N_6O_3PS_2Ru$ $(M)^{+2}$ 407.0256; found 407.0264. Anal. Calcd for $C_{38}H_{29}N_6O_3F_{12}P_3S_2Ru$: C, 41.35; H, 2.65; N, 7.61. Found C, 41.49; H, 2.80; N, 7.62.

[5′-(2,2′-Bipyridin-4-yl)-2,2′-bithien-5-ylphosphonic acid]bis-(bipyridyl)ruthenium(II) Hexafluorophosphate (22). To 25 mL of H_2O were added **11** (0.199 g, 0.499 mmol), $RuCl_2(bpy)_2$ (0.264 g, 0.545 mmol), and NaOH (24.4 mg, 0.61 mmol). The mixture was refluxed for 2.5 h. After cooling, the mixture was acidified with about 1.0 mL of 1 M HCl and filtered to remove unreacted starting material. KPF_6 in 10 mL of H_2O (0.49 g, 2.7 mmol) was added, which precipitated a red solid. The mixture was filtered through a medium fritted filter. Product (0.410 g, 0.371 mmol, 74%) was washed with ether and dried (mp 232−237 °C). ^{1}H NMR (DMSO, 500 MHz): δ 9.14 (d, 1H, J = 8.5 Hz), 9.08 (d, 1H, J = 2.0 Hz), 8.88−8.85 (m, 4H), 8.24−8.16 (m, 6H), 7.90 (d, 1H, J = 2.5 Hz), 7.77−7.74 (m, 4H), 7.71 (dd, 1H, J = 2.0, 6.0 Hz), 7.66 (d, 1H, J = 3.5 Hz), 7.62 (d, 1H, J = 6.5 Hz), 7.57−7.53 (m, 5H), 7.49 (dd, 1H, J = 3.0, 3.0 Hz), 7.42 (dd, 1H, J = 3.5, 8.0 Hz). ^{31}P NMR (DMSO, 121 MHz): δ 5.12 (s). UV−vis ($NCCH_3$) λ, nm (ϵ, M^{-1} cm^{-1}): 245 (34000), 288 (75000), 384 (32000), 466 (28000). HRMS (ESI-TOF) *m/z* calcd for $C_{38}H_{29}N_6O_3PS_2Ru$ $(M)^{2+}$ 407.0256; found 407.0256. Anal. Calcd for $C_{38}H_{29}N_6O_3F_{12}P_3S_2Ru$: C, 41.35; H, 2.65; N, 7.61. Found C, 41.06; H, 2.73; N, 7.85.

[5‴-(2,2′-Bipyridin-5-yl)-2,2′-5′,2″-5″,2‴-tetrathien-5-ylphosphonic acid]bis(bipyridyl)ruthenium(II) Hexafluorophosphate (23). Compound **15** (0.213 g, 0.343 mmol) was placed in a Schlenk flask under N_2. TMSBr (1.0 mL, 7.6 mmol) was added by syringe. The slurry was stirred for 16 h. Some of the TMSBr evaporated, leaving a thick slurry. Three milliliters of $CHCl_3$ was added, and it was quenched with water. The slurry was filtered with difficulty, washed with acetonitrile, and dried to form **16**, a dark red solid (0.155 g, 0.27 mmol, 80%, dec 250 °C).

To 25 mL of water in a round-bottom flask were added **16** (0.147 g, 0.26 mmol), $RuCl_2(bpy)_2$ (0.130 g, 0.27 mmol), and NaOH (17 mg, 0.425 mmol). The mixture was refluxed for 4 h. After cooling, a solution of KPF_6 (0.29 g, 1.6 mmol) in 10 mL of 0.3 M HCl was added and a red precipitate formed. The solid was collected by centrifugation, and the mother liquor was decanted. The solid was dissolved in DMF and collected in a round-bottom flask, and the DMF was evaporated. Product, 0.252 g (0.20 mmol, 76%), was collected as a dark red solid (dec ∼210 °C). ^{1}H NMR (DMSO, 500 MHz): δ 8.93 (d, 1H, J = 8.5 Hz), 8.90−8.85 (m, 5H), 8.47 (d, 1H, J = 8.5 Hz), 8.32 (t, 1H, J = 8.0 Hz), 8.22−8.16 (m, 4H), 7.97 (m, 1H), 7.88 (d, 1H, J = 5.5 Hz), 7.78 (m, 2H), 7.75 (d, 1H, J = 5.5 Hz), 7.66 (t, 1H, J = 6.5 Hz), 7.61 (s, 1H), 7.56 (m, 5H), 7.46 (d, 1H, J = 3.5 Hz), 7.42 (d, 1H, J = 3.5 Hz), 7.40−7.38 (m, 4H), 7.36 (d, 1H, J = 3.5 Hz). ^{31}P NMR (DMSO, 121 MHz): δ 4.83 (s). UV−vis ($NCCH_3$) λ, nm (ϵ, M^{-1} cm^{-1}): 245 (32000), 288 (75000), 446 (52000), 480 (39000). HRMS (ESI-TOF) *m*/*z* calcd for $C_{46}H_{33}N_6O_3PS_4Ru$ $(M)^{+2}$ 489.0134; found 489.0136. Anal. Calcd for $C_{46}H_{33}N_6O_3F_{12}P_3S_4Ru$: C, 43.57; H, 2.62; N, 6.63. Found C, 43.27; H, 2.87; N, 6.44.

[5‴-(2,2′-Bipyridin-4-yl)-2,2′-5′,2″-5″,2‴-tetrathien-5-ylphosphonic acid]bis(bipyridyl)ruthenium(II) Hexafluorophosphate (24). Compound **19** (0.152 g, 0.245 mmol) was placed in a Schlenk flask under N_2, and TMSBr (1.0 mL, 7.6 mmol) was added by syringe. The slurry was left to stir overnight. Some TMSBr had evaporated, leaving a thick slurry. One milliliter of $CHCl_3$ was added, followed by 1 mL of acetonitrile. The reaction was then quenched with water, and a precipitate formed. The product (**20**, 0.123 g, 89%, dec 245 °C) was washed extensively with acetonitrile and then dried. NMR and MS spectra were not recorded because of the insolubility of the product.

To 30 mL of H_2O in a round-bottom flask were added **20** (76.2 mg, 0.135 mmol), $RuCl_2(bpy)_2$ (66.0 mg, 0.136 mmol), and NaOH (5 mg, 0.1 mmol). The mixture was heated to reflux for 16 h. After cooling, the mixture was filtered through celite to remove unreacted starting material. The solid was washed with basic water until the filtrate ran pale. KPF_6 (0.20 g, 1.1 mmol) in 5 mL of H_2O was added to the filtrate with no result. A 10 mL amount of 1 M HCl was added, which caused a red/orange solid to precipitate. The solid was collected by centrifugation and washed once with water. The solid was then suspended in acetonitrile and transferred to a round-bottom flask. The solvent was evaporated, leaving **24** as a red solid (0.109 g, 0.086 mmol, 64%, dec >190 °C). ^{1}H NMR (DMSO, 500 MHz): δ 9.17 (d, 1H, J = 8.0), 9.09 (s, 1H), 8.86 (m, 4H), 8.24−8.15 (m, 6H), 7.90 (d, 1H, J = 5.5 Hz), 7.76−7.73 (m, 4H), 7.68 (d, 1H, J = 6.5 Hz), 7.61 (d, 2H, J = 5.0 Hz), 7.56−7.53 (m, 5H), 7.48 (d, 1H, J = 4.0 Hz), 7.42−7.37 (m, 5H). ^{31}P NMR (DMSO, 121 MHz): δ 5.32 (s). UV−vis ($NCCH_3$) λ, nm (ϵ, M^{-1} cm^{-1}): 245 (38000), 289 (75000), 437 (49000), 478 (46000). HRMS (ESI-TOF) *m*/*z* calcd for $C_{46}H_{33}N_6O_3PS_4Ru$ $(M)^{+2}$ 489.0134; found 489.0135. Anal. Calcd for $C_{46}H_{33}N_6O_3F_{12}P_3S_4Ru$: C, 43.57; H, 2.62; N, 6.63. Found C, 43.76; H, 2.64; N, 6.54.

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Supporting Information Available: General procedures, synthetic procedures for **2**, **3**, and **6**, and ^{1}H NMR spectra of selected compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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