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Organometallic Terthiophene Derivatives: Modulation of the Terthiophene Core of 5,5′′-Diphenyl-2,2′:5′2′′-Terthiophene via [CpRu]$^+$ and [Cp*Ru]$^+$ Substituents

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We have utilized electrochemical, UV−vis absorption/emission spectroscopy, and UV−vis spectroelectrochemistry to investigate the electronic structure of 5,5′′-diphenyl-2,2′:5′2′′-terthiophene (Ph$_2$Tth) and the complexes [Cp/Cp*Ru(η^6-Ph$_2$Tth)]PF$_6$ and [(Cp/Cp*Ru)$_2$(η^6,η^6-Ph$_2$Tth)](PF$_6$)$_2$ (Cp = cyclopentadienyl; Cp* = pentamethylcyclopentadienyl). Uncomplexed Ph$_2$Tth behaves as if the 2,2′:5′2′′-terthiophene (Tth) core has two weakly conjugated, sterically blocking phenyl group substituents. The nature of the phenyl substituents are altered by complexation with “Cp/Cp*Ru$^+$” to create [Cp/Cp*Ru(phenyl)]$^+$ substituents. Electrochemical studies show that Ph$_2$Tth exhibits two reversible oxidation processes that produce the radical cation and dication forms of the Tth core. The complexes of Ph$_2$Tth also exhibit localized Tth core oxidations that have $E°$s shifted to more positive potentials by about 150 mV per metal center. This shift is attributed to the positive charge of a [Cp/Cp*Ru(phenyl)]$^+$ substituent. The electronic absorption and emission spectra of the complexes are also indicative of the Tth chromophore. The $\lambda_{\max}$ of the $\pi-\pi^*$ transition for the Tth core is sensitive to the nature of the substituent and is red shifted by metal complexation. The complexes exhibit room temperature emission that is quenched by intramolecular processes involving the metal center and additionally by acetonitrile. For the Cp complexes in acetonitrile, quenching leads to decomplexation of Ph$_2$Tth; for the Cp* complexes, no decomplexation is observed. Spectroelectrochemical studies show that the radical cations of Ph$_2$Tth and the monoruthenated complexes exhibit a small degree of π-dimerization at room temperature; the diruthenated complexes show no evidence of π-dimerization. Studies of the complexes with [Cp/Cp*Ru(phenyl)]$^+$ substituents indicate that the properties of the Tth core can be modulated by the transition metal substituent(s).

Introduction

Recently we reported the synthesis and NMR (^{1}H and ^{13}C) spectroscopy studies of two types of novel oligothiophenes with organometallic substituents. One set features complexation of a thiophene ring by a CpRu$^+$ or Cp*Ru$^+$ group (Cp = cyclopentadienyl; Cp* = pentamethylcyclopentadienyl) that modulates the π-conjugation between the rings[1] while the other set uses complexation of a phenyl substituent of 5,5′′-diphenyl-2,2′:5′2′′-terthiophene (Ph$_2$Tth) to produce a new type of capping group for the 2,2′:5′,2′′-terthiophene (Tth) core of the molecule.[1] Further studies of the oligothiophenes that contain ruthenium-thiophene ring complexation will be the subject of a separate report; oligothiophenes with [Cp/Cp*Ru(phenyl)]$^+$ capping groups (see Figure 1) are of interest here.

NMR studies showed that the [Cp/Cp*Ru(phenyl)]$^+$ capping groups do not significantly change the conjugation of the Tth core. In this regard, they are similar to the alkyl, thiol, carboxylate, or silyl substituents of other α-capped oligothiophenes that have been extensively studied;[2−28] however, the organometallic cap has unique electrostatic, electrochemical, and photophysical/photochemical attributes that can lead to new oligothiophene properties that are otherwise unavailable. In this paper, we explore some of these ideas with electrochemical,

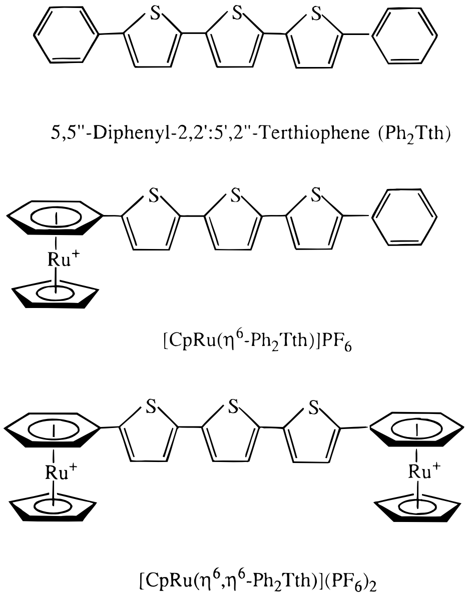

Figure 1. Structures of Ph$_2$Tth and ruthenated complexes.

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UV−vis absorption/emission, and spectroelectrochemical studies of the previously reported complexes: [CpRu(η^6-Ph$_2$Tth)]PF$_6$, [Cp*Ru(η^6-Ph$_2$Tth)]PF$_6$, [(CpRu)$_2$(η^6,η^6-Ph$_2$Tth)](PF$_6$)$_2$, and [(Cp*Ru)$_2$(η^6,η^6-Ph$_2$Tth)](PF$_6$)$_2$.[1]

Experimental Section

General Considerations. The syntheses of 5,5″-diphenyl-2,2′:5′,2″-terthiophene (Ph$_2$Tth), [CpRu(η^6-Ph$_2$Tth)]PF$_6$, [Cp*Ru(η^6-Ph$_2$Tth)]PF$_6$, [(CpRu)$_2$(η^6,η^6-Ph$_2$Tth)](PF$_6$)$_2$, and [(CpRu)$_2$(η^6,η^6-Ph$_2$Tth)](PF$_6$)$_2$ have been previously reported.[1] Solutions for UV−vis absorption studies were made with spectroscopic grade solvents as obtained from suppliers. Solutions for emission, electrochemical, and spectroelectrochemical studies were made with solvents dried by distilling acetonitrile from CaH$_2$ and dichloromethane from P$_2$O$_5$. Methanol for emission studies was dried over 3 Å sieves prior to use. Tetrabutylammonium hexafluorophosphate (TBA$^+$PF$_6^-$) was purchased from Southwestern Analytical Chemicals and stored in vacuum prior to use.

UV−Vis Studies. UV−vis spectra were recorded in undegassed solutions at room temperature with a Cary-17 spectrometer. Solutions were prepared by typically dissolving 2−4 mg of the compound in an appropriate volume of solvent and then diluting the solution until the highest measured absorbance was between 1.0 and 1.4 in the 1 cm path length quartz cell. Extinction coefficients were calculated from the experimentally determined absorbances and concentrations using Beer's law.

Emission Studies. Emission excitation profiles from solutions at ambient room temperature (25−27 °C) were recorded on a Spex F112x spectrofluorometer. All spectra were recorded with the front face detection mode to minimize reabsorption of the light emitted by the sample. Quantum yields (ϕ) for solutions were determined by the comparative method outlined by Demas and Crosby[29a] and utilizing eq 1. The quantum yields of the sample (ϕ_s) and reference compound

$$(\phi_s/\phi_r) = (f_r/f_s)(I_s/I_r)(\eta_s^2/\eta_r^2) \qquad (1)$$

(ϕ_r) are related to the fraction of light absorbed (f), the integrated intensity (I) of the emission band on an energy scale, and the refractive index (η) of the solvents (η(CH$_2$Cl$_2$) = 1.4242, η(CH$_3$CN) = 1.34423, and η(methanol) = 1.3288).[30] [Ru(bpy)$_3$](PF$_6$)$_2$ in methanol at 298 K was used as the standard (ϕ_r = 0.053).[29b] Solutions of Ph$_2$Tth, Ph$_2$Tth complexes and [Ru(bpy)$_3$](PF$_6$)$_2$ were prepared in dry solvents, degassed with Ar for 20 min, and diluted with degassed solvent until the measured absorbance at 420 nm was 0.05 ± 0.005.

Qualitative photolysis experiments were carried out by dissolving the complex in the appropriately dried solvent (protected from light) and then degassing with Ar for 30 min. The excitation wavelength was set to 420 nm, the sample was placed in the spectrometer, and the initial spectrum was recorded. The shutter was left open, and photolysis of the sample was monitored by a computer program that recorded spectra every 45 min.

Electrochemical Measurements. Electrochemical experiments were performed with a BAS 100 electrochemical analyzer. Cyclic voltammetry (CV) and chronocoulometry (CC) experiments were performed at room temperature (23−24 °C) with a normal three-electrode configuration consisting of a highly polished glassy-carbon working electrode (A = 0.07 cm^2), a Pt auxiliary electrode, and a Ag/AgCl reference electrode containing 1.0 M KCl. The 5 mL working compartment was separated from the reference compartment by a modified Luggin capillary. All three compartments were filled with a 0.1 M solution of tetrabutylammonium hexafluorophosphate (TBA$^+$PF$_6^-$). In all experiments, the electrolyte solution was passed down a column of activated alumina prior to the electrochemical experiments. The working compartment of the cell was bubbled with solvent-saturated argon to deaerate the solution. In most cases, the working solutions were prepared by recording the background cyclic voltammograms of the electrolyte solution prior to addition of the solid sample.

Potentials are reported vs aqueous Ag/AgCl and are not corrected for the junction potential. In order to assess the reproducibility, reliability, and referencing of our cell, the $E^{\circ\prime}$ values and diffusion coefficients for the ferrocenium/ferrocene couple were determined for solutions and concentrations similar to that used in the study of these complexes. For a 1.1 mM dichloromethane solution of ferrocene, the peak separation was 123 mV and the $E^{\circ\prime}$ value was +511 mV. For a 1.1 mM acetonitrile solution of ferrocene, the peak separation was 69 mV and the $E^{\circ\prime}$ value was +390 mV.

UV−Vis Spectroelectrochemical Studies. Spectroelectrochemical studies were performed in a flow through thin layer cell previously described.[31] Spectra were recorded with a Tracor Northern TN-6500 rapid-scan diode-array apparatus with a Xe arc lamp as the light source. Electrolyses were controlled by a BAS-100 bulk electrolysis program. The solutions used for these studies were prepared as for the electrochemical studies and then transferred to the thin layer cell via glass syringe. A CV of the sample in the thin-layer cell was used to determine the applied potential needed for the bulk electrolysis. Spectra were recorded at periodic intervals during the electrolysis.

Results

Electrochemical Studies. Two oxidative processes occur at +947 and +1325 mV (Table 1) for dichloromethane solutions of Ph$_2$Tth. Both of these oxidations appear to be quasi-reversible. A standard measure of reversibility, the i_a/i_p ratio, is not strictly applicable because the reduction processes coupled to the oxidations exhibit a small current "spike" that is indicative of insolubility of one or more of the oxidized forms at the electrode. Repeated scanning from 0.0 to +1.8 V yielded identical CVs and indicates that no polymerization or decomposition occurs for the oxidized forms of Ph$_2$Tth. The chemical reversibility of both oxidations is further supported by UV−vis spectroelectrochemical studies (vida infra). Unfortunately, the low solubility of Ph$_2$Tth in common electrochemical solvents prevented an accurate determination of the number of electrons transferred for these processes. On the basis of previous reports for other α-capped Tth molecules and other oligothiophenes in general, the oxidations of Ph$_2$Tth are consistent with one-electron processes that sequentially form the radical cation and dication.[2−19,32−37]

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Table 1. Cyclic Voltammetry Data for Ph_2Tth and Complexes[a]

	CH_2Cl_2 solutions			CH_3CN solutions		
	$E°'$ (mV)	$E°'$ (mV)	$E_{p,c}$ (mV)[b]	$E°'$ (mV)	$E_{p,a'}$ (mV)[b]	$E_{p,c}$ (mV)[b]
Ph_2Tth	+947	+1325	*c*	*d*		
$[CpRu(Ph_2Tth)]PF_6$	+1095	+1476	−1593	+1051	+1383	−1479
$[Cp^*Ru(Ph_2Tth)]PF_6$	+1090	+1480	−1650	+1053	+1428	−1695
$[(CpRu)_2(Ph_2Tth)](PF_6)_2$	+1244	+1553	−1437	+1256	+1551	−1383
$[(Cp^*Ru)_2(Ph_2Tth)](PF_6)_2$	+1265	+1595	−1536	+1200	+1506	−1499[e]

[a] Measured at room temperature with a scan rate of 100 mV/s in 0.1 M $TBA^+PF_6^-$. [b] Cathodic peak potentials for these irreversible processes. [c] No reduction processes were observed for this compound between 0 and −1.8 V. [d] Due to extremely low solubility, Ph_2Tth was not studied in acetonitrile. [e] $E°'$ for this reversible peak.

Table 2. Chronocoulometry Data for the Oxidation of Ph_2Tth Complexes

	step (V)[a] E_{int}/E_{final}	$10^3 nD^{1/2}$ (cm/s$^{1/2}$)[b]	($n = 1$) $10^5 D$ (cm^2/s)	($n = 2$) $10^5 D$ (cm^2/s)
		CH_2Cl_2 Solutions		
$[CpRu(Ph_2Tth)]PF_6$[c]	0.00/1.35	3.9	1.5	
	0.00/1.70	7.8		1.5
$[Cp^*Ru(Ph_2Tth)]PF_6$[d]	0.00/1.30	3.8	1.4	
	0.00/1.65	7.8		1.5
ferrocene[c]	0.00/0.80	5.0	2.5	
		CH_3CN Solutions		
$[CpRu(Ph_2Tth)]PF_6$[c]	0.00/1.20	5.1	2.6	
	0.00/1.55	10.2		2.6
$[Cp^*Ru(Ph_2Tth)]PF_6$[d]	0.70/1.20	4.4	1.9	
	0.70/1.48	8.2		1.7
$[(CpRu)_2(Ph_2Tth)](PF_6)_2$[d]	1.00/1.40	4.6	2.1	
	1.00/1.55	8.7		1.9
$[(Cp^*Ru)_2(Ph_2Tth)](PF_6)_2$[d]	1.00/1.30	4.7	2.2	
	1.00/1.48	9.4		2.2
ferrocene[c]	0.00/0.60	5.3	2.8	

[a] Measured for $\tau = 400$ ms pulse in a 0.1 M $TBA^+PF_6^-$ solution. [b] Calculated from the slope of a linear Anson plot (Q vs $t^{1/2}$) which had a correlation coefficient of at least 0.998 or better. [c] 1.1 mM solution. [d] 1.0 mM solution.

In addition to the two oxidative processes between 0.0 and +1.8 V, the complexes of Ph_2Tth exhibit a reductive process between 0.0 and −1.8 V that is not present for free Ph_2Tth (Table 1). In dichloromethane, the first and second oxidative processes of the mono and diruthenated complexes are chemically reversible as evidenced by repeated CV scans in the range of 0.0 to +1.8 V and from spectroelectrochemical studies (vida infra). The monoruthenated complexes exhibit higher solubility than free Ph_2Tth enabling chronocoulometry experiments for the first and second oxidation process. For the first oxidation, the calculated diffusion coefficients (Table 2) are consistent with a one-electron process, as compared to a ferrocene standard. Chronocoulometry step experiments across the first *and* second oxidations give calculated diffusion coefficients (Table 2) that are consistent with a net two-electron transfer (compared to a ferrocene standard); each oxidation is a one-electron process. Due to the low solubility of the diruthenated complexes in dichloromethane, the diffusion coefficients were not determined in this solvent, but the comparisons of the CV data to those of the monoruthenated complexes indicate that the oxidations are each one-electron processes.

The electrochemical properties of the Ph_2Tth complexes (but not Ph_2Tth because of low solubility) were also studied in acetonitrile where again the analogous two oxidative processes occur between 0.0 and +1.8 V and the reductive process occurs between 0.0 and −1.8 V (Table 2). Under these conditions, the monoruthenated complexes exhibit an irreversible second oxidation process but a reversible first oxidation process. Repeated CV scans from 0.0 to +1.8V and spectroelectrochemical studies (vida infra) are consistent with these results. For the diruthenated complexes, the second oxidative process is irreversible while the first oxidative process is quasi-reversible; the first oxidative process is reversible if the applied potential is below that of the second oxidation and irreversible if the applied potential is at or above the second oxidation potential. The number of electrons transferred for each oxidative process was determined from chronocoulometry experiments. For each of the Ph_2Tth complexes, the calculated diffusion coefficient (Table 2) for the first oxidative process is consistent with a one-electron transfer process (compared to a ferrocene standard). Further, the calculated diffusion coefficients (Table 2) for chronocoulometry steps across both oxidative processes are consistent with two electrons being transferred, indicating two separate one-electron oxidation processes.

The reductive processes exhibited by the Ph_2Tth complexes were also studied in dichloromethane and acetonitrile. In dichloromethane, all of the complexes exhibit an irreversible reductive process between 0.0 and −1.8 V; in acetonitrile only the reduction of $[(Cp^*Ru)_2(Ph_2Tth)](PF_6)_2$ is reversible while the reduction of all other complexes exhibit some degree of irreversibility. For example, the reduction of $[(CpRu)_2(Ph_2Tth)](PF_6)_2$ at −1383 mV is coupled to an oxidative process at −1236 mV. This coupled process is probably not the oxidation of the originally reduced species because the peak separation ($\Delta E_p = 147$ mV) between these two processes is nearly twice that found for the reversible oxidation at 1256 mV ($\Delta E_p = 72$ mV). Chronocoulometry studies of the reduction processes of the monoruthenated complexes in dichloromethane and acetonitrile

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Table 3. Chronocoulometry Data for the Reduction of Ph_2Tth Complexes

	step (V)[a] E_{int}/E_{final}	$10^3nD^{1/2}$ (cm/s$^{1/2}$)[b]	($n = 1$) 10^5D (cm^2/s)	($n = 2$) 10^5D (cm^2/s)
		CH_2Cl_2 Solution		
[CpRu(Ph_2Tth)]PF_6[c]	0.00/−1.60	5.2	2.7	0.67
[Cp*Ru(Ph_2Tth)]PF_6[d]	0.00/−1.70	5.9	3.4	0.86
		CH_3CN Solution		
[CpRu(Ph_2Tth)]PF_6[c]	−1.00/−1.70	5.0	2.9	0.72
[Cp*Ru(Ph_2Tth)]PF_6[d]	−1.30/−1.75	5.6	3.2	0.79
[$(CpRu)_2$(Ph_2Tth)]$(PF_6)_2$[d]	−1.00/−1.55	6.9	4.7	1.2
[$(Cp*Ru)_2$(Ph_2Tth)]$(PF_6)_2$[d]	−1.20/−1.70	6.8	4.6	1.2

[a] Measured for $\tau = 250$ ms pulse in a 0.1 M $TBA^+PF_6^-$ solution. [b] Calculated from the slope of a linear Anson plot (Q vs $t^{1/2}$) which had a correlation coefficient of at least 0.998. [c] 1.1 mM solution. [d] 1.0 mM solution.

Table 4. UV−Vis Data for Ph_2Tth and Complexes

	λ_{max} (nm) (ϵ (10^3 M^{-1} cm^{-1}))[a]			
	CH_2Cl_2 solutions		CH_3CN solutions	
Ph_2Tth	262 (19)[b]	408 (44)	258[c]	402[c]
[CpRu(Ph_2Tth)]PF_6	262 (16)[b]	422 (36)	256 (14)[b]	408 (35)
[Cp*Ru(Ph_2Tth)]PF_6	262 (16)[b]	424 (35)	255 (17)[b]	414 (41)
[$(CpRu)_2$(Ph_2Tth)]$(PF_6)_2$	263 (18)[b]	418 (40)	255 (16)[b]	408 (45)
[$(Cp*Ru)_2$(Ph_2Tth)]$(PF_6)_2$	258 (16)[b]	426 (41)	254 (17)[b]	418 (42)

[a] Reported values of ϵ are not corrected for overlap with other absorption bands. [b] Shoulder on solvent absorption edge. [c] Due to very low solubility, the ϵ values were not obtained in this solvent.

yielded calculated diffusion coefficients (Table 3) that are slightly larger than expected for a one electron process. The slightly larger value of these diffusion coefficients may arise from the catalytic reduction of trace amounts of oxygen in the system or more likely from the proximity of the reduction to that of the solvent and electrolyte (*ca.* −1.8 V). Chronocoulometry experiments performed with the diruthenated complexes in acetonitrile yielded calculated diffusion coefficients that are slightly below those expected for a two electron process.

CV's covering the range of +1.8 to −1.8 V were obtained in acetonitrile to further assess whether the reductions of the complexes involve one or two electrons. For the monoruthenated complexes, the ratio of the anodic to cathodic peak currents is about 1.1−1.4 in dichloromethane and 1.0−1.2 in acetonitrile. For the diruthenated complexes, the ratio is about 2.1−2.3 in dichloromethane and 2.0−2.2 in acetonitrile. The reduction in the monoruthenated complexes is most likely a one electron reduction of the metal center while it is likely that the diruthenated complexes undergo a one electron reduction of *each* metal center (a net two-electron reduction).

UV−Vis Absorption Studies. The electronic spectrum of uncomplexed Ph_2Tth in dichloromethane exhibits a moderately intense high-energy transition at 262 nm and a very intense, lower energy transition at 408 nm (Table 4, Figure 2). These two bands are generally observed for oligothiophenes; the narrow, high-energy band is attributed to a π-π^* local excitation of the heteronucleus[38] while the broader, lower energy band is attributed to $\pi-\pi^*$ transitions in the conjugated thiophene π-system.[39] The lower energy band actually consists of a larger transition centered at the λ_{max} and several smaller, high-energy shoulders which give rise to a distinctive, asymmetric high-energy tail (Figure 2). The electronic spectra of the Ph_2Tth complexes in dichloromethane also exhibit two bands: a moderately intense, high-energy band and an intense, lower energy band with an asymmetric high-energy tail (Table 4). The

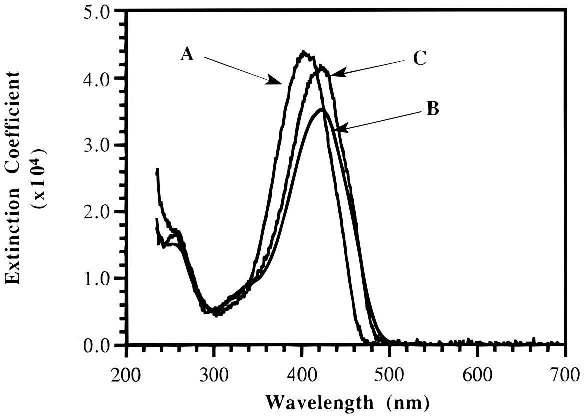

Figure 2. UV−vis spectra recorded in dichloromethane for (A) Ph_2Tth, (B) [Cp*Ru(Ph_2Tth)]PF_6, and (C) [$(Cp*Ru)_2$(Ph_2Tth)]$(PF_6)_2$.

λ_{max} of the high-energy band in the monoruthenated complexes is nearly unshifted from that in Ph_2Tth while the lower energy band is red shifted by 815 and 925 cm^{-1} for the Cp and Cp* complexes of Ph_2Tth, respectively (Table 4, Figure 2). The extinction coefficients of the bands in the complexes are 16−20% less than in free Ph_2Tth. The λ_{max} of the high-energy band in the diruthenated complexes is unshifted to that in Ph_2Tth while the λ_{max} of the lower energy band is red shifted by 585 and 1035 cm^{-1} for the Cp and Cp* complexes, respectively (Table 4). The extinction coefficients for the diruthenated complexes are 6−9% less than in free Ph_2Tth.

The electronic spectra of Ph_2Tth and the complexes were also recorded in acetonitrile (Table 4). The λ_{max} of the high-energy and low-energy bands of uncomplexed Ph_2Tth are blue shifted by 592 and 366 cm^{-1}, respectively, from their values in dichloromethane. Binding one ruthenium to Ph_2Tth results in λ_{max} values for the high-energy band that are blue shifted by 300 and 450 cm^{-1} for the Cp and Cp* complexes, respectively. In the monoruthenated complexes, the low-energy band red shifts by 366 and 721 cm^{-1} for the Cp and Cp* complexes, respectively. For the diruthenated complexes, the λ_{max} of the high-energy band blue shifts by about 600 cm^{-1} while the low-energy band red shifts by 366 and 953 cm^{-1} for the Cp and Cp* complexes, respectively. In addition, the λ_{max} for the mono- and diruthenated Cp complexes is the same but the extinction coefficient is greater by 27% for the diruthenated complex. For the Cp* complexes, the lower energy λ_{max} of the diruthenated complex is red shifted by 232 cm^{-1} from that of the monoruthenated complex and the intensities are nearly the same for both complexes.

UV−Vis Emission Studies. The emissive properties of Ph_2Tth were studied in dichloromethane and acetonitrile (Table 5). In both solvents, excitation (420 nm) of the low energy band of Ph_2Tth leads to an intense, structured emission consisting of two bands and a lower energy shoulder which mirrors the high

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Table 5. Emission[a] Data for Ph_2Tth and Complexes

	ϕ[b]	λ_{max} (nm) (intensity ratio of peaks)[c]
	CH_2Cl_2 Solutions	
Ph_2Tth	0.26	464 (100), 493 (75), 534[d] (25)
$[CpRu(Ph_2Tth)]PF_6$	0.047	566[e]
$[Cp^*Ru(Ph_2Tth)]PF_6$	0.055	534[e]
$[(CpRu)_2(Ph_2Tth)](PF_6)_2$	0.019	508[e]
$[(Cp^*Ru)_2(Ph_2Tth)](PF_6)_2$	0.053	478 (100), 508 (92), 548 (40)
	CH_3CN Solutions	
Ph_2Tth	0.24	458 (100), 486 (88), 520 (29)
$[CpRu(Ph_2Tth)]PF_6$	0.039	500[e]
$[Cp^*Ru(Ph_2Tth)]PF_6$	*f*	510[e]
$[(CpRu)_2(Ph_2Tth)](PF_6)_2$	*f*	494[e]
$[(Cp^*Ru)_2(Ph_2Tth)](PF_6)_2$	*f*	470 (100), 498 (91), 535 (45)

[a] Measured at room temperature with $\lambda_{ex} = 420$ nm. [b] Quantum yields were determined for Ar: degassed solutions at 298 K with excitation at 420 nm. Values quoted have variances of ±10%. [c] The ratio of peak intensities is calculated based on the most intense peak and does not account for overlap of the individual bands of the emission. [d] Broad shoulder. [e] Broad, nearly featureless bands as described in the text. [f] Quantum yield could not be determined reliably due the large degree of backscatter as discussed in the text.

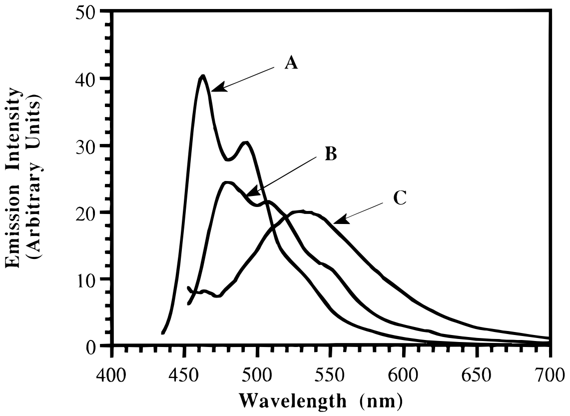

Figure 3. Room temperature emission spectra of (A) Ph_2Tth, (B) $[(Cp^*Ru)_2(Ph_2Tth)](PF_6)_2$ (×4), and (C) $[Cp^*Ru(Ph_2Tth)]PF_6$ (×4), for dichloromethane solutions with $A_{420} = 0.05$ and $\lambda_{ex} = 420$ nm.

energy tail of the absorption band (Figure 3). Room-temperature fluid solution emission was also observed from dichloromethane and acetonitrile solutions of the Ph_2Tth complexes. Emission was observed at longer wavelengths than for free Ph_2Tth when the low-energy band of the complexes was excited at 420 nm. For the monoruthenated complexes, this emission band is almost structureless with a weak, low energy tail that is red shifted from the structured emission of Ph_2Tth (*ca.* 480 nm) by about 3165 and 2106 cm^{-1} for the Cp and Cp* complexes, respectively (Figure 3). A relatively intense, structureless emission is also observed for $[(CpRu)_2(Ph_2Tth)](PF_6)_2$. This band is blue shifted by 2017 cm^{-1} from that of $[CpRu(Ph_2Tth)]PF_6$ and red shifted by 1150 cm^{-1} from the center of the structured emission of Ph_2Tth (*ca.* 480 nm). The analogous diruthenated Cp* complex exhibits a structured emission band (*ca.* 490 nm) blue shifted from that of the monoruthenated complex by about 1681 cm^{-1} (Figure 3). Each component of the emission is red shifted by about 600 cm^{-1} from its corresponding component in free Ph_2Tth.

In acetonitrile solutions, excitation of $[Cp^*Ru(Ph_2Tth)]PF_6$ at 420 nm leads to a moderately intense, featureless emission similar in shape to that observed in dichloromethane but red shifted from free Ph_2Tth (*ca.* 475 nm) by about 1450 cm^{-1}. Excitation of $[(Cp^*Ru)_2(Ph_2Tth)](PF_6)_2$ at 420 nm in acetonitrile leads to a structured emission (as in dichloromethane) that is red shifted from that of free Ph_2Tth by about 500−550 cm^{-1} for each component of the emission. Excitation of the mono- and diruthenated Cp complexes at 420 nm leads to a very broad and featureless emission that is red shifted from that of free Ph_2Tth by 1053 and 810 cm^{-1}, respectively.

The quantum yields of Ph_2Tth and complexes were investigated in dichloromethane for excitation at 420 nm. The quantum yield for the mono- and di-Cp* complexes are similar but 5 times less than for Ph_2Tth. The quantum yield of the mono-Cp complex is 2.5 times larger than for the di-Cp complex and 5 times smaller than for Ph_2Tth. These results indicate that binding the metal partially quenches the emission, most likely by an intramolecular process involving the metal.

Acetonitrile solutions of the CpRu complexes were observed to undergo a photochemical reaction: prolonged excitation (14 h) of the mono- and diruthenated Cp complexes at 420 nm leads to nearly complete conversion to free Ph_2Tth and $[CpRu(CH_3CN)_3]^+$. The Cp* analogs do not appear to be photoactive as there is no evidence for the formation of free Ph_2Tth after 12 h of photolysis at 420 nm. The steric bulk of the Cp* group likely slows or inhibits this photochemical reaction. There are no photochemical reactions observed for any of the complexes in dichloromethane.

These results indicated that acetonitrile might quench the emission of the complexes. To verify this, solutions of $[CpRu(Ph_2Tth)]PF_6$ with constant absorbance at 420 nm but with varying ratios of dichloromethane to acetonitrile were prepared. The emission blue shifts as the ratio of CH_2Cl_2:CH_3CN is decreased from pure dichloromethane to a 7:3 solvent mixture, 3:7 solvent mixture and pure acetonitrile. The quantum yield of the emission in acetonitrile is only 83% of that in dichloromethane. For comparison, the quantum yield of Ph_2Tth in acetonitrile is only 92% of that in dichloromethane. Quantitative comparisons of quantum yields for other complexes in both solvents could not be determined reliably as the close proximity of the emission bands to the excitation wavelength led to a large degree of scatter for the acetonitrile solutions. This backscatter largely masked the emission from the complexes at higher energy wavelengths.

UV−Vis Spectroelectrochemical Studies. The UV−vis spectra of the oxidized forms of free Ph_2Tth and complexes were investigated in dichloromethane and acetonitrile with thin layer bulk electrolysis techniques. One-electron oxidation of free Ph_2Tth in dichloromethane results in significant spectral changes. The $\pi-\pi^*$ band at 408 nm disappears as two new bands grow in isosbestically: a narrow band at 662 nm and a broad, bumpy band at about 560 nm with a distinct shoulder at about 520 nm (Figure 4a). This oxidation process is chemically reversed by reduction of the oxidized species at 0.0 V. Reduction produces the original spectrum with >95% of the original intensity.

The spectra of the one-electron oxidized species show evidence of reversible oligomerization. Studies of the π-dimerization of an analog of Ph_2Tth, 5,5″-diphenyl-3′,4′-dibutyl-2,2′:5′2″-terthiophene, have been investigated,[41] and these results indicate that the π-dimer of Ph_2Tth should exhibit a band around 560−590 nm that overlaps with the absorption shoulder of the

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(41) The UV−vis λ_{max} values for neutral and oxidized 5,5″-diphenyl-3′,4′-dibutyl-2,2′:5′2″-terthiophene in dichloromethane are as follows: 264 and 384 nm (neutral); 654 and 585(sh) nm (radical cation); 590 nm (cation radical dimer, broad absorption band). The similarity of the λ_{max} for the neutral and cation radicals for Ph_2Tth and 5,5″-diphenyl-3′,4′-dibutyl-2,2′:5′2″-terthiophene indicate the π-dimer of Ph_2Tth should exhibit an absorption band around 560−590 nm. Graf, D. D.; Duan, R. D.; Campbell, J. C.; Miller, L. L.; Mann, K. R. Unpublished results.

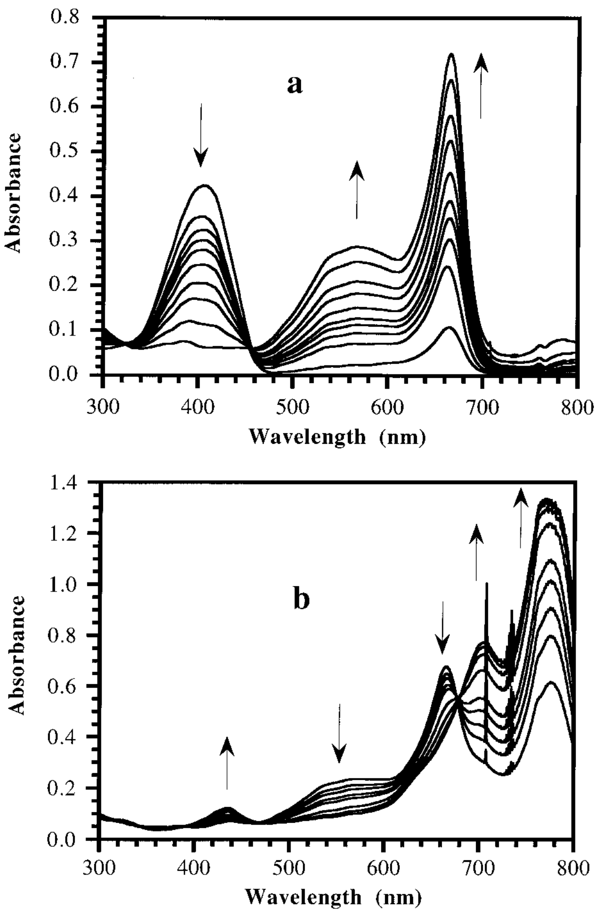

Figure 4. UV−vis spectra (room temperature in 0.1 M $TBA^+PF_6^-$/CH_2Cl_2) recorded during the spectroelectrochemical oxidation of Ph_2Tth ($[Ph_2Tth]_{initial}$ = 0.11 mM; T = 22 °C). Spectra were recorded approximately every 10 s (A) during the passage of 1 e^-/molecule at $E_{applied}$ = 0.9 V and (B) during the passage of a second $1e^-$/molecule at $E_{applied}$ = 1.4 V (vs the pseudo Pt reference of the thin layer cell).

monomeric cation radical. To investigate whether π-dimerization occurs for Ph_2Tth, the absorbance ratio (A_{650nm}/A_{560nm}) was determined after the removal of 1 e^-/mol from solutions with various initial concentrations of Ph_2Tth (0.1−0.01 mM). The absorbance ratio decreases as the initial concentration of Ph_2Tth is increased, indicative of the growth of a band around 560−590 nm due to the π-dimer of the cation radical of Ph_2Tth. In addition, the absorbances at 560 and 650 nm were monitored during the bulk electrolysis of each Ph_2Tth solution. For each spectroelectrochemical experiment, a plot of log(A_{560}) vs log(A_{650}) gave a straight line with slope of about one for the early stages of bulk electrolysis but at later stages, the data exhibit a small curvature to larger slope values (see Supporting Information). The curvature is less pronounced for lower initial concentrations of Ph_2Tth than for the higher initial concentrations. The curvature of the plots and the dependence of the curvature on initial concentrations of Ph_2Tth are consistent with the results for the alkylated analog 5,5″-diphenyl-3′,4′-dibutyl-2,2′:5′2″-terthiophene which is known to π-dimerize.[42] The

Table 6. UV−Vis Data for Oxidized Ph_2Tth and Complexes[a]

	λ$_{max}$ (nm), CH2Cl$_2$		λ$_{max}$ (nm), CH_3CN	
	1 e^- oxidized	2 e^- oxidized	1 e^- oxidized	2 e^- oxidized
Ph_2Tth	662, 560[b]	778, 702[c]	*f*	*f*
[CpRu(Ph_2Tth)]PF_6	640, 570[c]	762[d]	643[g], 575[g]	*i*
[Cp*Ru(Ph_2Tth)]PF_6	659, 580[c]	778, 712[c]	652[g], 560[g]	*i*
[$(CpRu)_2$(Ph_2Tth)]$(PF_6)_2$	630, 560[c]	683[d]	650[h]	*i*
[$(Cp*Ru)_2$(Ph_2Tth)]$(PF_6)_2$	652, 575[c]	*e*	649, 575[c]	*i*

[a] Determined by thin layer cell UV−vis spectroelectrochemistry with 0.1 M $TBA^+PF_6^-$ supporting electrolyte. [b] This is the center of a broad band which overlaps with the 662 nm band and has a shoulder at 520 nm. [c] Shoulder. [d] No shoulder could be discerned due to the overlap of the shoulder region with the peak for the one-electron oxidized species. [e] The spectrum of this oxidized form was not obtained due to passivation of the electrode as discussed in the text. [f] The low solubility of Ph_2Tth in acetonitrile precluded its study. [g] These two peaks overlap but have distinct maxima. [h] This peak is relatively weak since only a small amount (ca. 10%) of the complex was oxidized as discussed in the text. [i] This species was not observed due to the irreversibility of this oxidation process.

spectroelectrochemical results for Ph_2Tth indicate that π-dimers form at later stages of the oxidation when the concentration of the oxidized species is high.

Spectroelectrochemical oxidations of the mono- and diruthenated complexes of Ph_2Tth in dichloromethane also result in isosbestic behavior: decrease of the band for the reactant (*ca.* 400 nm) and the growth of a new band around 630−660 nm with a broad, bumpy shoulder centered at about 560−580 nm (Table 6). For the monoruthenated complexes, bulk electrolysis caused the reactant band (*ca* 400 nm) to completely disappear at the expense of the new low energy bands (Figure 5a) but for the diruthenated complexes, bulk electrolysis decreased the intensity of the reactant band by only 50−80%. We believe that the diruthenated oxidation products passivate the Pt electrode. For all complexes, the first oxidation is chemically reversible; reduction of the oxidized solution at 0.0V results in regeneration of the starting spectrum with >95% of the initial intensity. In acetonitrile, oxidation of the complexes by one electron leads to a decrease in the reactant band (*ca.* 420 nm) and the appearance and growth of two overlapping bands at around 650 and 570 nm. These peaks are in nearly the same positions as those found for the oxidized species in dichloromethane but the higher energy band is not a shoulder but is a distinct, broad band. As in the dichloromethane case, the one-electron oxidation in acetonitrile is chemically reversible. Bulk reduction of the oxidized species (0.0 V) regenerates the starting spectra with >95% of the initial intensity.

The spectra of the one-electron oxidized forms of the complexes were also analyzed to determine if π-dimerization occurs at room temperature. The absorbances at 560 and 650 nm were monitored during the bulk electrolyses of each complex. For each spectroelectrochemical experiment with [Cp*Ru(Ph_2Tth)]PF_6 in dichloromethane or acetonitrile, the plot of log(A_{560}) vs log(A_{650}) is similar to that for Ph_2Tth: the data form straight lines with a slope of about 1 during the early stages of bulk electrolysis, but at later stages, the data exhibit a small curvature to larger slope values. For [CpRu(Ph_2Tth)]PF_6, a similar curvature of the data is observed for plots of log(A_{560}) vs log(A_{650}). For [$(CpRu)_2$(Ph_2Tth)]$(PF_6)_2$ and [$(Cp*Ru)_2$(Ph_2Tth)]$(PF_6)_2$ in dichloromethane, plots of log(A_{560}) vs log(A_{650}) give straight lines of slope 1 with no curvature, even at the highest concentration studied. This strict Beer's law behavior is consistent with the simple conversion of the diruthenated complex to the oxidized forms with no observable formation of the π-dimers at the temperature and concentrations studied.

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(42) The spectroelectrochemical oxidation (1 F/mol) of 5,5″-diphenyl-3′,4′-dibutyl-2,2′:5′2″-terthiophene (0.2 mM) was carried out as for Ph_2Tth in 0.1 M $TBA^+PF_6^-$/CH_2Cl_2. A plot of log(A_{550}) vs log(A_{670}) gave a straight line with slope of about one for the early stages of bulk electrolysis, but at later stages, the data exhibit a small curvature to larger slope values. As the cation radical of 5,5″-diphenyl-3′,4′-dibutyl-2,2′:5′2″-terthiophene is known to π-dimerize[41] and the log−log plots are similar for this compound and Ph_2Tth, π-dimerization most likely occurs for Ph_2Tth. Graf, D. D.; Duan, R. D.; Campbell, J. C.; Miller, L. L.; Mann, K. R. Unpublished results.

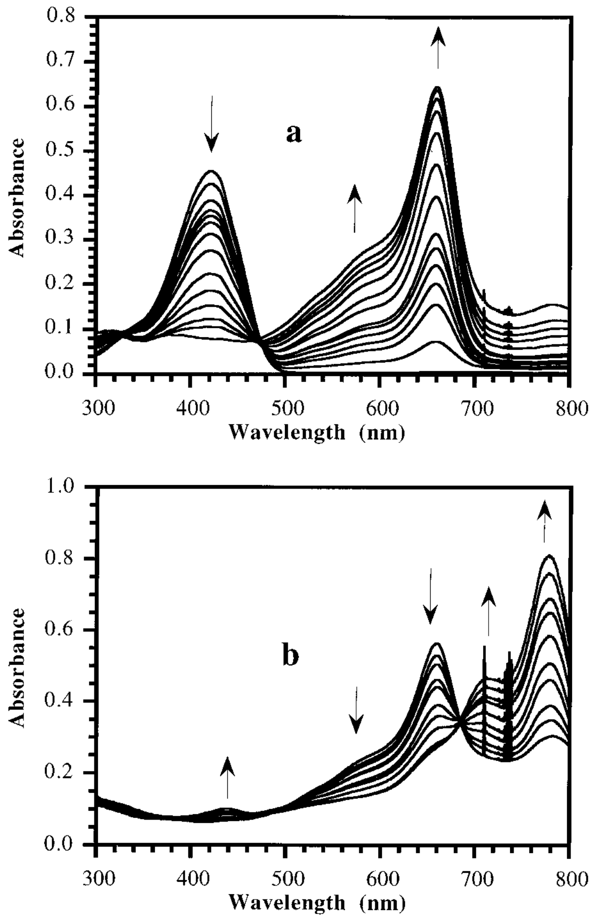

Figure 5. UV−vis spectra recorded during the spectroelectrochemical oxidation of [Cp*Ru(Ph$_2$Tth)]PF$_6$ at room temperature in 0.1 M TBA$^+$PF$_6^-$ /CH$_2$Cl$_2$ ([[Cp*Ru(Ph$_2$Tth)]PF$_6$]$_{\text{initial}}$ = 0.14 mM; T = 22 °C). The spectra were recorded approximately every 10 s (A) during the passage of 1 e$^-$/molecule at E_{applied} = 0.85 V and (B) during the passage of a second 1e$^-$/molecule at E_{applied} = 1.5 V (vs the pseudo Pt reference of the thin layer cell).

The second oxidation process exhibited by Ph$_2$Tth and complexes was also studied in dichloromethane. For Ph$_2$Tth and [Cp*Ru(Ph$_2$Tth)]PF$_6$, the removal of the second electron caused the 650 and 570 nm bands to disappear as new bands grew in isosbestically around 760−785 nm with distinct shoulders around 700−710 nm (Figures 4b and 5b). Unfortunately, electrode passivation severely limited the extent (10−50%) of the second oxidation of the [CpRu(Ph$_2$Tth)]PF$_6$ and the diruthenated complexes of Ph$_2$Tth. In all cases, the second oxidation process is chemically reversible: bulk reduction at 0.0 V regenerates the reactant spectrum with only slight changes in the intensity. The chemical reversibility of the processes suggest that the passivation of the Pt electrode most likely results from precipitation of the highly charged oxidized species at the electrode surface. This is further supported by the CV data which shows that the oxidations of the oxidized complexes with net charges of +3 and +4 in dichloromethane lead to a desorption current spike in the CV reduction process. The observation of this current spike indicates that the electrooxidized species precipitates on the electrode surface.

Discussion

Oligothiophenes typically undergo two one electron oxidations at different potentials to form the radical cation and dication species.[2−26,32−37,42] Generally these oxidations are irreversible due to polymerization of the oxidized species to a conducting film on the electrode surface. Previous studies have also shown that this polymerization can be slowed by capping the α positions of the oligothiophenes[2−19] with −CH$_3$ −SCH$_3$, −COO$^-$, and −Si(CH$_3$)$_3$. In the complexes we have studied, the α positions of the Tth core are substituted with phenyl groups to provide binding sites for metal centers. Previous studies have suggested that the phenyls have only a relatively small degree of conjugation with the Tth core π-system.[1] Furthermore, the phenyl conjugation is expected to be relatively weak compared to that of the thiophene ring conjugation of the Tth core. The small degree of phenyl conjugation is supported by the comparison of the electrochemical and optical properties of Ph$_2$-Tth and 5,5′′-dimethyl-2,2′:5′:2′′-terthiophene (Me$_2$Tth) which exhibits two oxidations (E°(+1/0) = +975 (reversible), $E_{\text{p,a}}$ = +1348 mV, (irreversible)) and a $\pi-\pi^*$ band at 368 nm.[43] The similarity of the electrochemical data for Me$_2$Tth and Ph$_2$Tth indicate the phenyls are not highly conjugated while the somewhat lower energy $\pi-\pi^*$ band (red shift of 2600 cm^{-1}) of Ph$_2$Tth indicates that the phenyls may have a somewhat larger degree of conjugation, most likely in the excited state. The small degree of conjugation between the phenyls and the Tth core is further supported by the relatively small changes in the electrochemical and optical properties upon complexation of the phenyl rings: if the phenyls were highly conjugated, then complexation should lead to very large changes. In addition to electronic effects, the α-phenyl groups are important in stabilizing the oxidized forms of the Tth core so that the first and second oxidations are chemically reversible on the CV time scale. As there is no evidence for substantial delocalization of the charge onto the phenyl rings, the most likely cause of the stabilization of the oxidized forms is an inhibition of polymerization by the steric bulk of the phenyl substituents. In summary, Ph$_2$Tth behaves most like a Tth core, stabilized by weakly conjugated, steric blocking groups. On the basis of this model, the binding of metals to the phenyl groups should modulate the properties of the Tth core by converting one or both of the phenyl groups into the positively charged [Cp/Cp*Ru(phenyl)]$^+$ substituents.

Ph$_2$Tth and its complexes exhibit the electrochemical behavior of a Tth unit whose properties are governed by the nature of the end groups. Comparison of the electrochemical data for Ph$_2$Tth and monoruthenated complexes in dichloromethane shows an increase in the E° for the first and second oxidation processes of about 150 mV for both the Cp and Cp* complexes. For the diruthenated complexes in dichloromethane, the E°s for the first oxidation increase by about 300 and 320 mV for the Cp and Cp* complexes, respectively, while those for the second oxidation potential increase by about 230 and 270 mV, respectively. E°s for the first and second oxidations of the monoruthenated complexes are increased by about 150 mV *per metal center*; for the diruthenated complexes, a similar increase of about 150 mV per metal center occurs for the first process, but there is only an increase of 115 and 135 mV per metal center for the second process for the Cp and Cp* complexes, respectively. Direct comparison of the data for Ph$_2$Tth and the complexes in acetonitrile is not possible due to the extremely low solubility of Ph$_2$Tth; however, the first oxidation of the diruthenated complexes is about 200 and 150 mV, respectively, more positive than those for the monoruthenated Cp and Cp* complexes, respectively. The second oxidation process follows trends similar to those observed in the dichloromethane data although direct comparison is somewhat ambiguous due to the

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[43] The peak potentials for the oxidations of 5,5′′-dimethyl-2,2′:5′,2′′-terthiophene (1.1 mM) were measured by CV with the same electrochemical cell and conditions as for Ph$_2$Tth: 0.1M TBA$^+$PF$_6^-$/CH$_2$Cl$_2$ and scan rate of 100 mV/s.

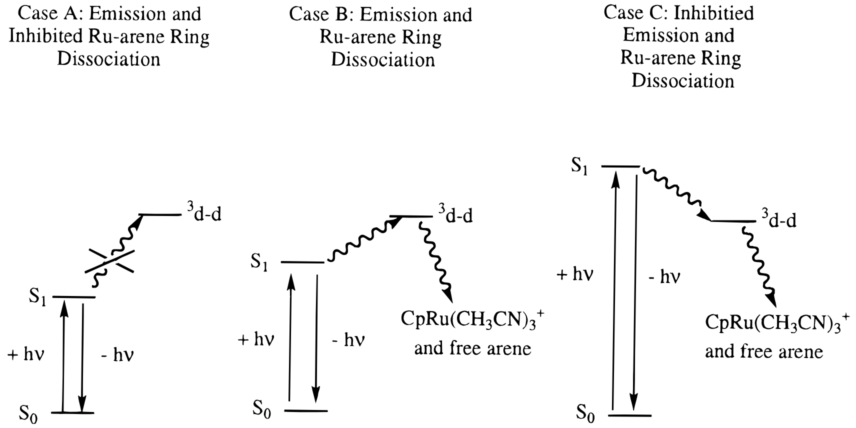

Figure 6. Qualitative state diagrams for the relative energies of the fluorescent S_1 state and the reactive d−d a^3E_1 state for ruthenium complexes of highly fluorescent arenes.

irreversibility of the second process. The positive shift for the oxidation processes that occur upon binding the metal may arise from either (1) placement of the positively charged ruthenium center near the Tth core and/or (2) a change in the electronic character of the phenyl substituent upon binding the metal. As the phenyl group is not significantly conjugated to the Tth core and there is a fairly consistent $E°$ shift upon the addition of a CpRu or Cp*Ru group, the presence of the positive charge is likely the dominant factor. Compared to free Ph_2Tth, the 150 mV increase in $E°$ for the first and second oxidation processes of the monoruthenated complexes reflects the addition of the positive charge from each metal while the increase observed for the second oxidation process of the diruthenated complexes may also reflect additional electronic and/or steric contributions.

The reduction processes associated with the complexes are also consistent with the model presented for the oxidations. The absence of these processes in uncomplexed Ph_2Tth indicates they reside on the $[Cp/Cp^*Ru(phenyl)]^+$ substituent. In a similar case ($[CpRu(Bz)]PF_6$),[44] the analogous reductions occur at −1968 mV in dichloromethane and −1929 mV in acetonitrile, about 400 mV more negative than those observed for the $[(Cp/Cp^*Ru)_n(Ph_2Tth)]^{n+}$ complexes. For the monoruthenated complexes, the $E_{p,c}$ values for reduction of the more electron rich Cp* complexes are about 60 and 115 mV more than those for the Cp complexes in dichloromethane and acetonitrile, respectively. For the diruthenated complexes, the $E_{p,c}$ for the reduction of the more electron rich Cp* complex is about 100 mV more negative than the Cp analog in dichloromethane or acetonitrile. Further, the $E_{p,c}$ for the reduction of the monoruthenated complexes is more negative than the $E_{p,c}$ of the highly positively charged diruthenated complexes. These results indicate that the reductive process is localized on the metal center and is the equivalent process observed for the reduction of $[CpRu(Bz)]^+$. The lower potential for the $[Cp/Cp^*Ru(phenyl)]^+$ substituents than for $[CpRu(Bz)]^+$ most likely results from the benzene ring being substituted in our complexes.

The electronic structure of the complexes can be further discerned from the UV−vis absorption and emission spectra. The absorption spectra of the complexes and free Ph_2Tth exhibit a low- and a high-energy band in nearly the same position, with similar intensities, and with similar band shapes. The emission bands observed for Ph_2Tth and complexes also exhibit a high degree of similarity. These results suggest that the Tth core is the common chromophore in all cases. The observed red shift and changes in intensity of the absorption and emission bands all correlate with the number of metal centers, the ancillary ligand, and solvent. Further, these results agree with previous studies of highly conjugated arene metal complexes. In these cases, binding a metal to a phenyl substituent not directly involved in the chromophore leads to changes in the position and intensity, but not the shape, of the absorption and emission bands, as compared to the free arene.[45,46] In these previous studies, the absorption and emission band red shift upon binding the electropositive $[CpRu]^+$ group to a phenyl substituent, and this has been attributed to excited state stabilization via an inductive effect.[46] This type of excited state stabilization is consistent with our results for the Tth systems. We find that binding the first metal center red shifts the absorption and emission bands significantly but binding the second metal leads to a smaller red shift in almost every case. It is reasonable that a single polar substituent at the end of the Tth group creates a strong inductive effect while placing two identical substituents at opposite ends of the Tth unit partially cancels the net effect.

The quenching of the Ph_2Tth emission by binding the metal and then the further quenching of the complex emission by acetonitrile are quite curious and give insight into the electronic structure of the complexes. The energetics of Forster energy transfer or electron transfer quenching involving the solvent are expected to be quite unfavorable and are unlikely quenching mechanisms. Furthermore, the significant degree of quenching is unlikely a result of intermolecular quenching as the solutions studied were very dilute (10^{-6} M). Reasonable mechanisms for the quenching by metal complexation and the addition of acetonitrile[47,48] involve internal energy transfer from the Tth emitting core to the $[Cp/Cp^*Ru(phenyl)]^+$ substituent which can undergo rapid arene decomplexation in the presence of nucleophiles (i.e. acetonitrile). These quenching mechanisms are supported by the similarity of the extinction coefficients for the absorption bands of the complexes and Ph_2Tth (relatively unperturbed by the metal), the lower quantum yield for the complexes (due to internal energy transfer), and the photochemical reactivity of the Cp complexes in acetonitrile.

Previous reports have shown that when a “$CpRu^+$” is bound to a pendant group which is weakly coupled to the emissive chromophore, three possible qualitative Jablonski diagrams can be drawn (Figure 6).[46] These diagrams show the relative energy ordering of the S_0 and S_1 states of the Tth core and the triplet

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[44] The $E_{p,c}$ for the reduction of $[CpRu(Bz)]PF_6$ (1.0 mM) was measured by CV with the same electrochemical cell and conditions as for the complexes of Ph_2Tth: 0.1M $TBA^+PF_6^-$ in CH_3CN or CH_2Cl_2 and scan rate of 100 mV/s.

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d−d state (a^3E_1) of the metal which has been implicated as the excited state involved in the loss of the arene ring in photochemical reactions.[49] In cases B and C, excitation to the ligand-based S_1 state can lead to intersystem crossing to the metal-based a^3E_1 state which then can undergo an arene displacement reaction in coordinating solvents. Thus, the efficiency of the arene labilization is dependent on the ease of intersystem crossing from the S_1 to the a^3E_1 state and the rate of the arene displacement reaction. As the Cp complexes of Ph$_2$Tth exhibit emission *and* arene labilization, they most likely fall into case B where the d−d state is slightly higher in energy than the S_1 state. Further, the Cp* complexes also fall into case B because the d−d state is only slightly higher in energy due to replacing the Cp with the more electron donating Cp* ring. Excitation of the Cp complexes leads to efficient arene labilization to produce Ph$_2$Tth and [CpRu(CH$_3$CN)$_3$]PF$_6$ while for the Cp* complexes, there is no observable production of free Ph$_2$Tth. With similar intersystem rates expected for the Cp and Cp* complexes, the rate of arene displacement should be the dominant factor. This is consistent as the Cp complexes typically undergo more rapid photochemical arene displacement than Cp* complexes that are sterically protected from nucleophilic attack.[49,50] Further studies of these complexes are in progress to determine whether the decrease in the arene displacement quantum yield for the Cp* complexes is accompanied by a similar decrease in quenching by acetonitrile.

The spectroelectrochemical properties of uncomplexed Ph$_2$Tth are similar to those observed for other α-capped oligothiophenes.[2−9,17−19,32,34−37] The positions of the two bands (662 and 560 nm) observed for the cation radical (Ph$_2$Tth$^+$) are similar to those reported for other α-capped oligothiophenes. As in these previous cases, the electron hole appears to be localized on the Tth core.[2−9,17−19,32,34−37] For the complexes, we also observe bands for the cation radical that are blue shifted by 10−30 nm from those in free Ph$_2$Tth$^+$. The similarity of the position, shape, and intensities of these bands indicates that the electron hole is also localized on the Tth core and is not significantly delocalized onto the phenyl groups or (Cp/Cp*Ru)$^+$ substituents. Removal of the second electron from Ph$_2$Tth produces a new band at 785 nm with a higher energy shoulder. The position of this band is also in agreement with the band reported for other 2e$^-$ oxidized, α-capped terthiophene molecules.[2,3,5−8,18] For the complexes, the removal of the second electron also produces bands in the 680−760 nm region. These results are consistent with the localization of the two electron holes on the Tth core and not on the phenyl substituents or metal centers.

The spectroelectrochemical studies of Ph$_2$Tth show that a small amount of π-dimerization occurs at room temperature over the very low concentration range studied (< 0.2 mM). Additionally, the nonplanarity of the phenyl rings may sterically inhibit π-dimerization,[51] as has been noted for other oligothiophenes with bulky substituents.[8] Studies that show distinct spectra for π-dimers have typically involved alkyl-substituted oligothiophenes that are more soluble and less sterically hindered than Ph$_2$Tth.[2−6,16−19,32,34,35] Monoruthenated complexes π-dimerize late in the bulk electrolysis experiments when the concentration of the oxidized form is high. The formation of π-dimers is particularly unfavorable in this case because of the sterically large [Cp/Cp*Ru(phenyl)]$^+$ substituent and because of the increased coulombic repulsion between the radical cations. The diruthenated complexes show no evidence of π-dimerization. Dimerization of these net triply charged radical cations will be particularly unfavorable because of the presence of two large [Cp/Cp*Ru(phenyl)]$^+$ substituents.

Conclusions

We have found that the oligothiophene Ph$_2$Tth behaves as a Tth unit with two weakly conjugated, sterically blocking phenyl groups. The nature of the phenyl substituents can be altered by "Cp/Cp*Ru$^+$" complexation to create [Cp/Cp*Ru(phenyl)]$^+$ substituents. Studies of complexes with one and two [Cp/Cp*Ru(phenyl)]$^+$ substituents indicate that the properties of the Tth core are modulated by the transition metal substituent(s). Electrochemical studies show that Ph$_2$Tth exhibits two reversible oxidation processes that produce the radical cation and dication forms of the Tth core. The complexes of Ph$_2$Tth exhibit oxidations localized on the Tth core. The *E*°s of the oxidation processes are shifted to more positive potentials by about 150 mV per metal center. This shift is mainly due to the positive charge associated with the [Cp/Cp*Ru(phenyl)]$^+$ substituents. The low energy bands in the electronic absorption and emission spectra of the complexes arises from the Tth chromophore but the λ_{max} values are red shifted. The complexes exhibit room temperature emission that is quenched by intramolecular processes involving the metal center and additionally by acetonitrile. For the Cp complexes, this quenching leads to decomplexation of Ph$_2$Tth in acetonitrile. Spectroelectrochemical studies show that the radical cations of Ph$_2$Tth and the monoruthenated complexes exhibit a small degree of π-dimerization at room temperature; the diruthenated complexes show no evidence of π-dimerization. The incorporation of [Cp/Cp*Ru(phenyl)]$^+$ substituents presents a novel and rational method for modulating the properties of the oligothiophene and for introducing new properties unavailable with purely organic substituents. Further studies will be directed toward the isolation and characterization of the oxidized forms of the oligothiophene complexes.

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Supporting Information Available: Figures showing (1) cyclic voltammograms for Ph$_2$Tth, [Cp*Ru(Ph$_2$Tth)]PF$_6$, and [(Cp*Ru)$_2$(Ph$_2$Tth)](PF$_6$)$_2$, (2) cyclic voltammograms of the behavior of the first oxidation of [(Cp*Ru)$_2$(Ph$_2$Tth)](PF$_6$)$_2$ in acetonitrile when the potential is scanned positive of the second oxidation process and between the first and the second oxidation processes, (3) emission spectra of [CpRu(Ph$_2$Tth)]PF$_6$ for solutions with varying ratios of CH$_2$Cl$_2$:CH$_3$CN, and (4) a plot of the log(A_{560}) vs log(A_{650}) recorded during the spectroelectrochemical oxidation of [Cp*Ru(Ph$_2$Tth)]PF$_6$ (4 pages). Ordering information is given on any current masthead page.

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