

## Effect of Electronic Structure on the Photoinduced Ligand Exchange of Ru(II) Polypyridine Complexes

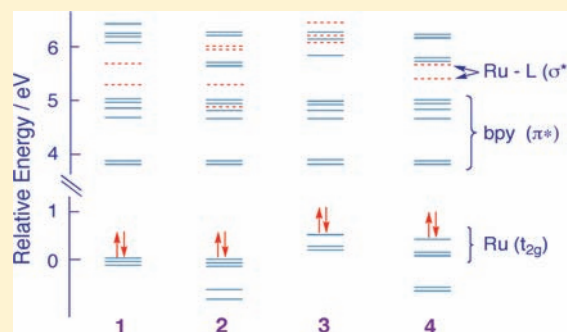
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Supporting Information

**ABSTRACT:** The series of complexes  $[\text{Ru}(\text{bpy})_2(\text{L})]^{2+}$ , where  $\text{bpy} = 2,2'$ -bipyridine and  $\text{L} = 3,6$ -dithiooctane (bete, **1**), 1,2-bis(phenylthio)ethane (bpte, **2**), ethylenediamine (en, **3**), and 1,2-dianilinoethane (dae, **4**), were synthesized, and their photochemistry was investigated. Photolysis experiments show that the bithioether ligands in **1** and **2** are more easily photosubstituted by chloride ions,  $\text{bpy}$ , and  $\text{H}_2\text{O}$  than the corresponding diammine complexes in **3** and **4** to generate the bisubstituted products. Electronic structure calculations show that bond elongation in the lowest energy triplet metal-to-ligand charge transfer ( $^3\text{MLCT}$ ) state compared to the ground state is greater for complexes containing bithioether ligands than those with coordinated bidentate nitrogen atoms. This elongation in the excited state is attributed to

$\text{Ru}-\text{S}$   $\pi$ -bonding character of the highest occupied molecular orbitals, which is not present in the diamine complexes. In the  $\text{Ru} \rightarrow \text{bpy}$   $^3\text{MLCT}$  state, the lower electron density on the metal-centered highest occupied molecular orbital (HOMO) weakens the  $\text{Ru}-\text{S}$  bond and results in the greater photoreactivity of **1** and **2** relative to that of **3** and **4**. The more efficient photoinduced ligand exchange of the complexes possessing thioether ligands results in binding of **1** and **2** to DNA upon irradiation.



## INTRODUCTION

Cisplatin,  $\text{cis-Pt}(\text{NH}_3)_2\text{Cl}_2$ , and related Pt(II) antitumor agents are typically activated by the thermal ligand exchange of the two chloride ligands for  $\text{H}_2\text{O}$  molecules followed by covalent binding of the metal to adjacent DNA bases, leading to inhibition of transcription and cell death.<sup>1–5</sup> Drawbacks of these complexes as anticancer drugs include their low selectivity for cancer cells and thermal activation, both of which result in toxicity toward healthy tissue, as well as acquired resistance to the drug.<sup>1–5</sup> The design of compounds that are activated by light, a field known as photodynamic therapy (PDT), permits the selective activation of complexes through irradiation of only the affected areas.<sup>6,7</sup> PDT is currently used in the treatment of endoscopically accessible cancers, such as lung, bladder, head and neck, and esophageal cancers; however, the mode of action of the drugs approved for clinical use are generally dependent on  $\text{O}_2$ .<sup>6–10</sup> This dependence represents a drawback of the technique because malignant tumors are often hypoxic.<sup>10–13</sup> It is now recognized that the discovery of new agents whose action is markedly different than that of typical drugs is required for significant improvements in PDT.<sup>14</sup> Such systems include those that are derived from transition metals instead of traditional organic molecules, as well as those for which the photoreactivity is independent of oxygen.<sup>14</sup>

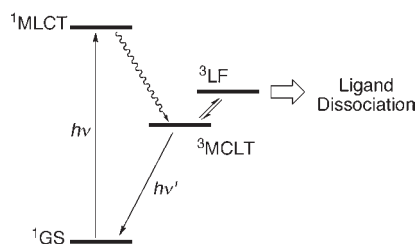
The quantum yields of sensitized  $^1\text{O}_2$  can be significantly greater for Ru(II) complexes than organic molecules owing to the fast intersystem crossing rate constants of the former, resulting in approximately unit yield of their long-lived triplet excited states.<sup>15,16</sup> These and related Os(II) complexes have

recently shown efficient DNA photocleavage with low energy light, making them promising PDT agents.<sup>17</sup> Furthermore, Ru(II) complexes possessing tridentate ligands with extended  $\pi$ -systems were shown to result in  $\sim 100\%$  production of  $^1\text{O}_2$  and to cross-link nuclear proteins and DNA upon irradiation with visible light.<sup>18</sup> Similarly, dirhodium(II,II) complexes enter the nucleus of HeLa and COLO-316 cancer cells and exhibit significantly greater toxicity upon irradiation with visible light.<sup>19</sup> In addition to high  $^1\text{O}_2$  yields, transition metal complexes whose PDT action is independent of oxygen have also been reported.<sup>20</sup> For example,  $\text{cis-}[\text{Ru}(\text{bpy})_2(\text{NH}_3)_2]^{2+}$  and  $\text{cis-}[\text{Rh}_2(\mu\text{-O}_2\text{CCH}_3)_2(\text{CH}_3\text{CN})_6]^{2+}$  were recently shown to covalently bind to double stranded DNA (ds-DNA) upon irradiation with near-UV light ( $\lambda_{\text{irr}} \geq 345$  nm) and visible light ( $\lambda_{\text{irr}} \geq 455$  nm), respectively.<sup>21,22</sup> The latter was shown to exhibit 34-fold greater toxicity toward Hs-27 human skin fibroblasts upon irradiation for 30 min with visible light than when the cell culture was exposed to the complex for the same period of time in the dark. Furthermore, the relatively high photoinduced ligand exchange quantum yield of  $\text{cis-}[\text{Ru}(\text{bpy})_2(\text{CH}_3\text{CN})_2]^{2+}$  makes this and related complexes potentially useful as oxygen-independent PDT agents.<sup>23</sup>

Ligand photodissociation plays a crucial role in the reactivity of complexes that bind to DNA and other biomolecules upon excitation; therefore, it is important to understand the dominant factors that govern this process to design improved systems. As

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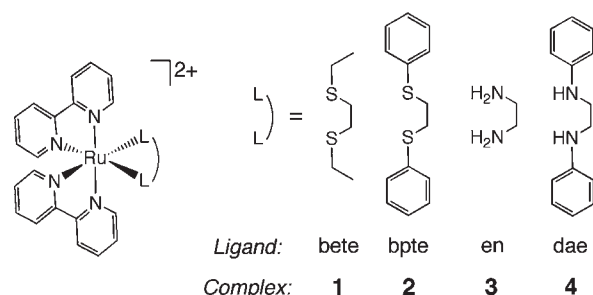
**Figure 1.** Typical Jablonski diagram of Ru(II) complexes that undergo photochemical ligand dissociation.

proposed by Ford and others, excited state ligand dissociation from Ru(II) polypyridyl complexes is believed to proceed via population of low-lying ligand field (LF) state(s) that possess  $M-L(\sigma^*)$  character, schematically shown in Figure 1.<sup>24,25</sup> In such complexes, absorption of a photon into the  $^1MLCT$  (metal-to-ligand charge transfer) excited state undergoes intersystem crossing (isc) to the corresponding  $^3MLCT$  state very quickly, a process that occurs within  $\sim 40$  fs in  $[Ru(bpy)_3]^{2+}$ .<sup>15</sup> Thermal population of the  $^3LF$  state(s) from the  $^3MLCT$  state in these systems generally results in ligand exchange quantum yields that are dependent on the energy gap between these states. For complexes with low energy MLCT absorption, where the  $^3MLCT$ - $^3LF$  gap is large, low photoinduced ligand substitution quantum yields are typically observed. For example,  $cis-[Ru(bpy)_2(NH_3)_2]^{2+}$  exhibits  $\lambda_{abs} = 490$  nm and photoaquation quantum yields of 0.024 and 0.018 measured with 350 and 400 nm irradiation, respectively.<sup>22</sup> In contrast,  $cis-[Ru(bpy)_2(CH_3CN)_2]^{2+}$  exhibits  $^1MLCT$  absorption at 425 nm and  $\Phi_{350} = 0.38$  and  $\Phi_{450} = 0.22$  for the generation of the bis-aqua complex.<sup>23</sup> The magnitude of photoinduced ligand exchange quantum yield in  $cis-[Ru(bpy)_2(CH_3CN)_2]^{2+}$  is comparable to the  $S \rightarrow O$  photoisomerization yields measured for some Ru-sulfoxide complexes, such as  $[Ru(tpy)(pic)(dmsO)]^+$  ( $tpy = 2,2':6'2''$ -terpyridine,  $pic = 2$ -pyridine carboxylate,  $dmsO =$  dimethyl sulfoxide) with  $\Phi_{S \rightarrow O} = 0.25$ .<sup>26</sup> It has been shown that in these dmsO complexes, the Ru-S bonding character in the occupied metal  $t_{2g}(d\pi)$  set plays a prominent role in the observed isomerization yields.<sup>27</sup> Based on these findings, a question of interest is the direct comparison of the photochemistry of sulfur- and nitrogen-containing ligands coordinated to a Ru(II) center.

In the present work, the photochemistry of  $[Ru(bpy)_2(L)]^{2+}$ , where  $L = 3,6$ -dithiaoctane (**1**), 1,2-bis(phenylthio)ethane (**2**), ethylenediamine (**3**), and 1,2-dianilinoethane (**4**), is compared. The former two complexes possess sulfur-coordination and the latter contains nitrogen-chelating ligands. The molecular structures of the complexes and ligands are schematically shown in Figure 2. The minimized ground state and  $^3MLCT$  excited state structures of **1–4** were calculated using density functional theory (DFT) to aid in the understanding of the experimental observations. The results provide evidence in support of an active role of the  $^3MLCT$  state in the photoinduced ligand exchange of the sulfur-coordinated complexes.

## EXPERIMENTAL SECTION

**Materials.** The ligands 2,2'-bipyridine, 3,6-dithiaoctane (**1**), and 1,2-ethylenediamine (**en**), as well as sodium phosphate, gel loading buffer (0.05% (w/v) bromophenol blue, 40% (w/v) sucrose, 0.1 M EDTA (pH = 8.0, 0.5% (w/v) sodium lauryl sulfate), Tris base, Tris/HCl,



**Figure 2.** Schematic representation of the molecular structures of **1–4**.

and ethidium bromide were purchased from Sigma and used as received. 1,2-Bis(phenylthio)ethane (**bpte**) and 1,2-dianilinoethane (**dae**) were purchased from Alfa Aesar. The pUC18 and pUC19 plasmids were purchased from Bayou Biolabs and purified using the QIAprep miniprep spin system from Qiagen. *Sma*I and REact 4 buffer were purchased from Invitrogen, and the removal of *Sma*I was performed with the QIAquick gel extraction kit from Qiagen. *Cis*- $[Ru(bpy)_2Cl_2]^{2+}$  and  $[Ru(bpy)_2(en)]^{2+}$  (**3**)<sup>29</sup> were prepared by procedures previously reported.

**$[Ru(bpy)_2(bete)]^{2+}$  (**1**).**  $[Ru(bpy)_2(bete)]^{2+}$  was prepared by a modification of published procedures,<sup>30,31</sup> where 100 mg (0.20 mmol) of *cis*- $[Ru(bpy)_2Cl_2]$  was dissolved in 15 mL of ethylene glycol, and 0.5 mL of 3,6-dithiaoctane was added to the reaction mixture. The reaction was allowed to proceed for 4 h at 140 °C, was cooled to room temperature, and a saturated  $NH_4PF_6$  solution in 30 mL of water was added to the reaction mixture. The yellow precipitate was collected by filtration, washed with cold deionized water and ether, and dried under vacuum. Elem. anal. calcd. for  $[Ru(C_{10}H_8N_2)_2(C_6H_{14}S_2)](PF_6)_2$ : C, 36.6%; H, 3.55%; N, 6.56%. Found: C, 36.4%; H, 3.66%; N, 6.21%.  $^1H$  NMR (400 MHz) in acetone- $d_6$   $\delta$  (splitting, integration): 1.01 (t, 6H), 1.95 (q, 4H), 2.75 (d, 2H), 3.65 (d, 2H), 7.51 (t, 2H), 7.92 (d, 2H), 8.01 (t, 2H), 8.17 (t, 2H), 8.43 (t, 2H), 8.75 (d, 2H), 8.85 (d, 2H), 9.58 (d, 2H).

**$[Ru(bpy)_2(bpte)]^{2+}$  (**2**).**  $[Ru(bpy)_2(bpte)]^{2+}$  was prepared in a manner similar to that described for **1**.<sup>30,31</sup>  $^1H$  NMR (400 MHz) in acetone- $d_6$   $\delta$  (splitting, integration): 3.45 (d, 2H), 4.10 (d, 2H), 6.57 (d, 4H), 6.95 (t, 4H), 7.27 (t, 2H), 7.47 (t, 2H), 8.00 (m, 6H), 8.20 (m, 6H), 9.85 (d, 2H). Elem. anal. calcd. for  $[Ru(C_{10}H_8N_2)_2(C_{14}H_{14}S_2)](PF_6)_2$ : C, 43.0%; H, 3.19%; N, 5.90%. Found: C, 42.9%; H, 3.30%; N, 5.55%.

**$[Ru(bpy)_2(dae)]^{2+}$  (**4**).**  $[Ru(bpy)_2(dae)]^{2+}$  was synthesized by refluxing 100 mg of (0.20 mmol) *cis*- $[Ru(bpy)_2Cl_2]$  and 425 mg of (2.0 mmol) 1,2-dianilinoethane in a 10 mL mixture of 1:1 methanol and water (v:v) for 12 h, during which time the dark purple solution became bright red. The reaction mixture was evaporated to dryness, redissolved in water, and precipitated with  $NH_4PF_6$ . The mixture was filtered, washed with ether, and dried under vacuum. Elem. anal. calcd. for  $[Ru(C_{10}H_8N_2)_2(C_{14}H_{16}N_2)](PF_6)_2 \cdot 2C_3H_6O$ : C, 46.5%; H, 4.38%; N, 8.14%. Found: C, 46.1%; H, 4.31%; N, 8.40%.  $^1H$  NMR (400 MHz) in acetone- $d_6$   $\delta$  (splitting, integration): 3.42(d, 4H), 6.14 (d, 4H), 6.37 (s, 2H), 6.67 (t, 4H), 6.88 (t, 2H), 7.07 (t, 2H), 7.50 (d, 2H), 7.56 (t, 2H), 7.73 (d, 2H), 8.00 (m, 4H), 8.14 (t, 2H), 9.60 (d, 2H).

**Instrumentation.** Electronic absorption measurements were performed on a Hewlett-Packard diode array spectrophotometer with HP 8453 Win System software. A 150 W Xe lamp housed in a Milliarc compact arc lamp housing (PTI) and powered by a PTI model LPS-220 power supply was used in the steady-state photolysis experiments; the wavelength of the light reaching the sample was controlled with colored glass long-pass and band-pass filters (Newport).  $^1H$  NMR spectra were recorded on a Bruker DRX-400 spectrometer, and electrochemical studies were performed on a BAS CV-50W voltammetric analyzer. Ethidium bromide stained gels were imaged on a Gel Doc 2000 (Biorad) transilluminator with Quantity One software.

**Table 1.** Absorption Maxima and Molar Extinction Coefficients in CH<sub>2</sub>Cl<sub>2</sub>, Ligand Exchange Quantum Yields, and Redox Potentials of 1–4

complex	$\lambda_{\text{abs}}/\text{nm}$ ( $\epsilon/\times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ )	$\Phi_{\text{H}_2\text{O}}^a$	$\Phi_{\text{Cl}^-}^b$	$E_{1/2}/\text{V}^c$
1	242 (20), 283 (55), 422 (7.6) <sup>d</sup>	0.024(2)	0.019(1)	+1.43, -1.31, -1.53
2	236 (42.3), 284 (33.2), 404 (6.4)	0.022(3)	0.016(3)	+1.48, -1.35, -1.55
3	291 (57.5), 344 (7.58), 485 (9.75) <sup>e</sup>	<i>f</i>	0.002(1)	+0.98, -1.47, -1.70
4	293 (47.5), 330 (7.13), 469 (9.30)	<i>f</i>	0.003(1)	+1.49, -1.35, -1.52

<sup>a</sup> For the formation of *cis*-[Ru(bpy)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup> ( $\lambda_{\text{irr}} = 400 \text{ nm}$ ). <sup>b</sup> For the formation of *cis*-Ru(bpy)<sub>2</sub>Cl<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> with excess (*n*-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NCl ( $\lambda_{\text{irr}} = 400 \text{ nm}$ ). <sup>c</sup> vs SCE in CH<sub>3</sub>CN with 0.1 M N(*n*-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>PF<sub>6</sub>. <sup>d</sup> From ref 22. <sup>e</sup> From ref 30. <sup>f</sup> Spectral overlap of reactant and product precluded the determination of photoaquation quantum yields.

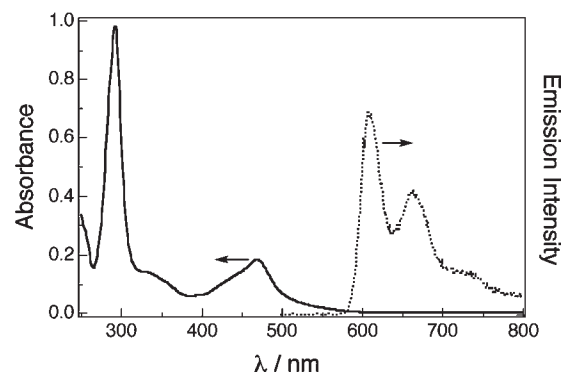
**Methods.** The solutions for the photolysis experiments were deoxygenated by bubbling with N<sub>2</sub> for 15 min prior to irradiation. Photosubstitution quantum yields were determined using ferrioxalate actinometry as previously described in detail.<sup>32</sup> Cyclic voltammetry measurements were performed using a three electrode cell with a glassy carbon working electrode, a platinum wire auxiliary electrode, and a Ag/AgCl reference electrode, using distilled CH<sub>3</sub>CN containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate as the supporting electrolyte. At the end of each experiment, a small amount of ferrocene (Fc) was added as an internal standard, and  $E_{1/2}(\text{Fc}^{+/0}) = 0.389 \text{ V}$  vs SCE was used as reference for calculating the oxidation and reduction potentials of each complex.<sup>33</sup>

Plasmid linearization was accomplished by incubating 50 units of *Sma*I with 10  $\mu\text{g}$  of pUC18 plasmid and 10  $\mu\text{L}$  of REact 4 buffer at 30 °C for 1 h followed by 10 min at 65 °C. The linearized DNA was subsequently separated from the enzyme using a QIAquick gel extraction kit. The concentration of plasmid DNA was determined from its absorption at 260 nm using an extinction coefficient of 6,600 M<sup>-1</sup> cm<sup>-1</sup> in accordance with the Qiagen protocol. The DNA mobility experiments were carried out using 20  $\mu\text{L}$  total sample volume in 0.5 mL transparent Eppendorf tubes containing 50  $\mu\text{M}$  linearized pUC18 plasmid, 10 mM sodium phosphate buffer, and the concentration of each metal complex was varied. Following irradiation or dark incubation, 4  $\mu\text{L}$  of DNA gel loading buffer was added to each sample. The electrophoresis was carried out in 1  $\times$  TBE buffer (TBE = tris-borate/EDTA, 0.09 M tris-borate, 0.002 M EDTA, pH = 8.3) using a 0.75% agarose gel, run at 92 V for 1 h. Staining was performed after electrophoresis by soaking the gel in a 0.5  $\mu\text{g}/\text{mL}$  aqueous ethidium bromide solution followed by washing in water for 30 min.

Calculations were performed with density functional theory (DFT) using the Gaussian 03 program.<sup>34</sup> The B3LYP<sup>35–37</sup> functional along with the 6-31G\* basis set for H, C, N, and S,<sup>38</sup> and the SDD energy-consistent pseudopotentials for Ru were used.<sup>39</sup> Geometries were fully optimized using the criteria of the respective programs. Orbital analysis was completed with GaussView.<sup>40</sup> Electronic transitions were calculated using the TDDFT methods implementation within Gaussian 03. Mulliken population analyses were completed using Gaussian 03 and were analyzed for molecular orbital percent contribution of sulfur and nitrogen atoms with GaussSum 2.4.<sup>41</sup>

## RESULTS AND DISCUSSION

**Electronic Absorption, Emission, and Electrochemistry.** Complexes 1–4 show characteristic  $\pi\pi^*$  transitions localized on the bpy ligands in the 283–293 nm range (Table 1). The lowest energy band for each complex is assigned as metal-to-ligand charge transfer (<sup>1</sup>MLCT) arising from Ru(*t*<sub>2g</sub>)  $\rightarrow$  bpy( $\pi^*$ ) transitions with maxima in the 404–485 nm range. <sup>1</sup>MLCT transitions at higher energy are also observed at 344 nm for 3 and as a shoulder at 330 nm for 4.<sup>30,42</sup> This second MLCT peak in 1

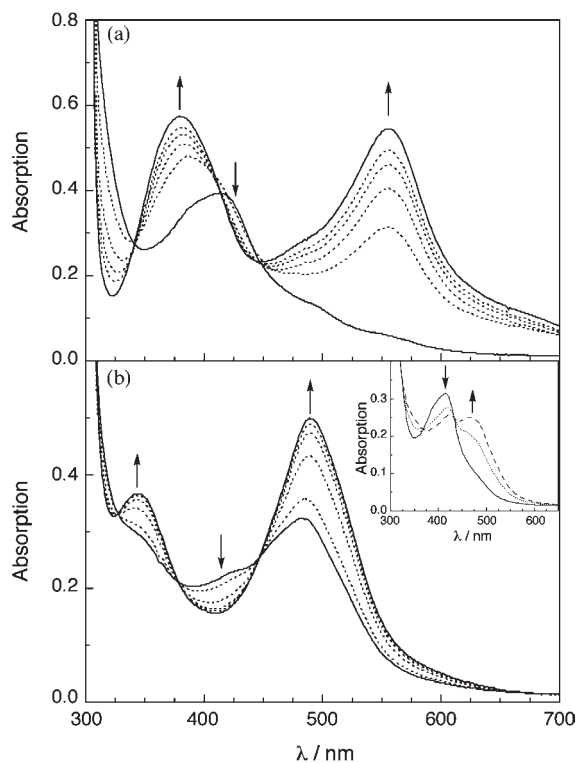


**Figure 3.** Electronic absorption spectrum of 4 at 298 K in H<sub>2</sub>O (solid line) and emission spectrum (dotted line) at 77 K in an ethanol/methanol glass (4:1, v:v).

and 2 is blue-shifted, and is likely masked by the intense bpy  $\pi\pi^*$  transition.<sup>30</sup> The electronic absorption spectrum of the new complex 4 is shown in Figure 3. Although 1, 2, and 4 are not emissive in H<sub>2</sub>O or CH<sub>3</sub>CN at 298 K, luminescence was detected at 77 K in ethanol:methanol (4:1, v:v) glasses. The 77 K emission spectrum of 4 is shown in Figure 3, and those of 1 and 2 are displayed in Supporting Information, Figure S1. The spectrum of each complex exhibits a high energy  $E_{00}$  peak and vibronic structure with spacing of 1351, 1356, and 1360 cm<sup>-1</sup> for 1, 2, and 4, respectively. These values are similar to those of [Ru(bpy)<sub>3</sub>]<sup>2+</sup> and related bpy-containing complexes, whose emission is known to arise from the Ru $\rightarrow$ bpy <sup>3</sup>MLCT excited state.<sup>43–45</sup> The emission of 3 has been previously reported at 298 K in CH<sub>3</sub>CN with maximum at 682 nm and in a butyronitrile glass at 77 K at 662 nm.<sup>42,46</sup>

The cyclic voltammograms of 1–3 are in close agreement with previous reports.<sup>30,42</sup> Complex 4 exhibits two reduction waves at -1.35 and -1.52 V vs SCE that are similar to those observed in 1 and 2 and other ruthenium bpy complexes, and are therefore attributed to the sequential reduction of each bpy ligand.<sup>30,42,44</sup> One oxidation peak is observed in 4 at +1.49 V vs SCE, which is also observed in 1 and 2 at a similar potential, and is typical of the Ru<sup>III/II</sup> couple.<sup>30,42,44</sup>

**Photochemistry.** The photolysis reactions of 1–4 were performed under various conditions and were typically monitored by changes to the electronic absorption spectrum of each complex and, in some cases, the progress of the reaction was followed by <sup>1</sup>H NMR spectroscopy. Figure 4a shows the photo-induced exchange of the beta ligand upon irradiation of 50  $\mu\text{M}$  1 in the presence of 0.5 M tetrabutylammonium chloride (TBACl) in CH<sub>2</sub>Cl<sub>2</sub> ( $\lambda_{\text{irr}} > 495 \text{ nm}$ ). It is evident from Figure 4a that the



**Figure 4.** Changes to the electronic absorption spectrum of 50 μM **1** upon photolysis in (a) CH<sub>2</sub>Cl<sub>2</sub> with 0.5 mM TBACl at  $t_{\text{irr}} = 0, 5, 10, 20, 30, 45$  s ( $\lambda_{\text{irr}} > 495$  nm) and (b) H<sub>2</sub>O  $t_{\text{irr}} = 4, 5, 10, 15, 20, 30$  min; inset:  $t_{\text{irr}} = 0, 1, 2$  min ( $\lambda_{\text{irr}} > 395$  nm).

absorption peaks of *cis*-Ru(bpy)<sub>2</sub>Cl<sub>2</sub>, with maxima at 383 and 553 nm, increase in intensity during the 45 s photolysis, with the concomitant decrease of the reactant <sup>1</sup>MLCT peak at 422 nm. The spectral features of the product in Figure 4a are similar to those of *cis*-Ru(bpy)<sub>2</sub>Cl<sub>2</sub> prepared independently and shown in the Supporting Information, Figure S2, with maxima at 383 and 553 nm in CH<sub>2</sub>Cl<sub>2</sub>.<sup>44</sup> The quantum yield of the formation of *cis*-Ru(bpy)<sub>2</sub>Cl<sub>2</sub> from **1**,  $\Phi_{\text{Cl}}$  ( $\lambda_{\text{irr}} = 400$  nm) was measured to be 0.019(1). It should be noted that a mixture of 50 μM **1** and 0.5 M TBACl in CH<sub>2</sub>Cl<sub>2</sub> kept in the dark over a period of 54 h at room temperature did not result in changes to the electronic absorption spectrum, consistent with the expected stability of the complex in the absence of light. The related complex *cis*-[Ru(phen)<sub>2</sub>(bete)]<sup>2+</sup> (phen = 1,10-phenanthroline) was shown to undergo clean photoinduced ligand exchange with Cl<sup>-</sup> in the presence of tetraethylammonium chloride in 1,2-dichloroethane to generate *cis*-Ru(phen)<sub>2</sub>Cl<sub>2</sub> within 30 s of 345 nm irradiation; however, quantum yields were not reported.<sup>31</sup>

Similarly, the changes to the electronic absorption spectrum of 50 μM **1** as a function of irradiation time in the presence of 0.5 mM bpy in CH<sub>2</sub>Cl<sub>2</sub> ( $\lambda_{\text{irr}} > 495$  nm) show the formation of the <sup>1</sup>MLCT peak of the [Ru(bpy)<sub>3</sub>]<sup>2+</sup> product with maximum at 450 nm during the photolysis (0–60 s). Changes in the <sup>1</sup>H NMR spectrum for this reaction were also observed upon irradiation of 2.5 mM **1** and 20 mM bpy in DMSO ( $\lambda_{\text{irr}} \geq 395$  nm, 0–30 min), which resulted in a decrease in the intensities of the aromatic resonances of the reactant at 7.49, 7.58, 7.90, 8.12, 8.35, 8.72, 8.83, and 9.20 ppm and the concomitant formation of peaks typical of [Ru(bpy)<sub>3</sub>]<sup>2+</sup> at 7.3, 7.6, 8.2, and 8.9 ppm. However, <sup>1</sup>H NMR peaks consistent with the formation of

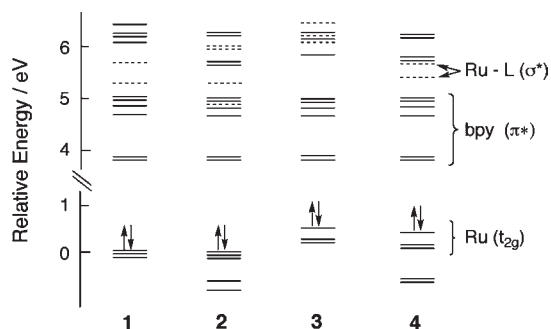
*cis*-[Ru(bpy)<sub>2</sub>(dmsO)]<sup>2+</sup> were also observed when the photolysis was carried out in this solvent.<sup>47</sup> When left in the dark at room temperature, this reaction mixture did not result in changes to the <sup>1</sup>H NMR spectrum over the same time period.

Figure 4b displays the changes to the electronic absorption spectrum of 30 μM **1** upon photolysis in water ( $\lambda_{\text{irr}} > 395$  nm). At early irradiation times,  $t_{\text{irr}} = 0$ –2 min, the <sup>1</sup>MLCT peak of **1** at 422 nm decreases in intensity with the growth of a band at lower energy resulting and two isosbestic points at 366 and 433 nm (Figure 4b, inset). The spectral changes at early times can be ascribed to the formation of the mono aqua species, *cis*-[Ru(bpy)<sub>2</sub>(η<sup>1</sup>-bete)(H<sub>2</sub>O)]<sup>2+</sup> from **1**. As shown in Figure 4b, after 4 min of irradiation, three new isosbestic points are observed at 327, 377, and 446 nm, indicating the conversion of the mono-aqua species to the bis-aqua product, *cis*-[Ru(bpy)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup>, with known <sup>1</sup>MLCT maximum at 490 nm.<sup>48</sup> The quantum yield for the formation of the *cis*-[Ru(bpy)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup> from **1** with  $\lambda_{\text{irr}} = 400$  nm was measured to be 0.024(2). It should be noted that the electronic absorption spectrum of **1** in water did not change over a period of 54 h when the solution was kept in the dark at 298 K.

The photolysis reactions of **2**–**4** were also investigated, and  $\Phi_{400 \text{ nm}} = 0.016(3)$  was measured for the formation of *cis*-Ru(bpy)<sub>2</sub>Cl<sub>2</sub> from 53 μM **2** and 0.5 mM TBACl in CH<sub>2</sub>Cl<sub>2</sub>, and the generation of *cis*-[Ru(bpy)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup> was determined to have  $\Phi_{400 \text{ nm}} = 0.022(3)$  from the photolysis of **2** in water (Table 1). These values are similar to those listed in Table 1 measured for **1** under similar experimental conditions, as expected given the presence of bis-thioether leaving ligands in both complexes. The photolysis of **2** was also followed by <sup>1</sup>H NMR spectroscopy in D<sub>2</sub>O, which results in a decrease in intensity of the peak at 3.9 ppm assigned to the protons of the ethylene group of the coordinated bpte ligand and the simultaneous increase in intensity of a new peak at 2.7 ppm, known to correspond to free bpte. The integrations of these resonances indicate 50% ligand exchange after 1 h of irradiation. Similar results are observed in the aromatic region for the bpy resonances of the reactant and product.

The complexes containing diammine leaving ligands, **3** and **4**, exhibit significantly lower photoreactivity than their bis-thioether counterparts, **1** and **2**. As listed in Table 1, **3** undergoes ligand photosubstitution under the experimental conditions described above for **1** and **2** with  $\Phi_{\text{Cl}} = 0.002(1)$ , consistent with a previous report.<sup>49</sup> Photolysis of 20 μM **4** in the presence of 0.5 mM TBACl in CH<sub>2</sub>Cl<sub>2</sub> ( $\lambda_{\text{irr}} = 400$  nm) results in the formation of Ru(bpy)<sub>2</sub>Cl<sub>2</sub> with  $\Phi_{\text{Cl}} = 0.003(1)$ , which is also significantly smaller than the corresponding quantum yields measured for **1** and **2** (Table 1). The photoaquation quantum yields of **3** and **4** could not be measured because of spectral overlap between the initial and final species. The data presented here clearly shows that the bis-thioether ligands of **1** and **2** are more easily photosubstituted than the corresponding diammine ligands of **3** and **4**.

**Electronic Structure Calculations.** Computational studies were undertaken to gain further understanding of the differences observed in ligand exchange photochemistry between the sulfur coordinated complexes **1** and **2** relative to those with nitrogen chelators, **3** and **4**. The calculated molecular orbital diagrams of **1**–**4** are shown in Figure 5. The lowest unoccupied molecular orbital (LUMO) of each complex is bpy( $\pi^*$ ) in character, and these orbitals were set to equal energies on the molecular orbital (MO) diagram since the first reduction potential is relatively invariant among the complexes (Table 1). In addition, the highest



**Figure 5.** Molecular orbital diagrams of 1–4, where dashed lines represent Ru–L ( $\sigma^*$ ) orbitals.

occupied molecular orbital (HOMO) of **1** was set equal to 0.0 eV as an arbitrary reference. The electron densities of the HOMO, HOMO-1, and HOMO-2 of 1–4 are mostly centered on the metal, and represent the Ru( $d\pi$ )  $t_{2g}$ -type set (Figure 5). Complexes **2** and **4** each have two orbitals with electron density on the phenyl rings of the bpte and dae ligand, respectively, below the Ru( $d\pi$ ) MOs, also shown in Figure 5. In addition, 1–4 also have filled bpy( $\pi$ ) orbitals at lower energies that are not shown in Figure 5.

The unoccupied molecular orbitals of each complex are composed of six bpy( $\pi^*$ ) orbitals that comprise the LUMO to LUMO+5 in **1**, **3**, and **4**. These orbitals in **2** are the LUMO to LUMO+3, LUMO+5, and LUMO+6. The LUMO+4 and LUMO+7 in **2** can be ascribed to Ru–L( $\sigma^*$ ), where L represents the bpte ligand, and the LUMO+4 lies 1.09 eV above the LUMO (Figure 5). The lowest energy Ru–L( $\sigma^*$ ) MOs are calculated as the LUMO+6 in **1** and **4**, at 1.48 eV (L = bpte) and 1.64 eV (L = dae) higher in energy than the LUMO of each complex, respectively (Figure 5). In **3**, the lowest energy Ru–en( $\sigma^*$ ) orbital is the LUMO+7, 2.35 eV above the corresponding LUMO. Two phenyl  $\pi^*$  unoccupied MOs are present in **2** and **4** as the LUMO+8 and LUMO+9, respectively. Two additional bpy( $\pi^*$ ) MOs are also calculated for each complex at higher energies, along with at least one other Ru–L( $\sigma^*$ ) MO, where L represents the diammine or thioether ligand 1–4.

The Ru–L( $\sigma^*$ ) orbitals are expected to contribute to the dissociative metal-centered ligand-field (LF) states of each complex, whereas the bpy( $\pi^*$ ) orbitals, including the LUMO, are involved in the MLCT transitions. The energy difference between the HOMO and the lowest energy Ru–L( $\sigma^*$ ) MO, may be related to the energy of the LF state(s),  $\Delta E_{LF}$ , whereas the HOMO–LUMO gap may be related to that of the MLCT state(s),  $\Delta E_{MLCT}$ . Therefore, if population from the  $^3MLCT$  state to the  $^3LF$  state(s) is operative in photoinduced ligand dissociation, then the difference between these two energies,  $\Delta E = \Delta E_{LF} - \Delta E_{MLCT}$ , may provide some indication of the ability of ligand substitution to take place. The values of  $\Phi_{Cl}$  for 1–4 listed in Table 1 generally follow this trend, where the values of **1** and **2** are similar and within the error of the measurement, those of **3** and **4** are  $\sim 5$  to  $\sim 10$ -fold smaller. Complexes **1** and **2** exhibit the smallest values of  $\Delta E$ , 1.48 and 1.09 eV, respectively, followed by **4** ( $\Delta E = 1.64$  eV) and **3**, for which  $\Delta E$  is significantly greater, 2.35 eV. However, the similarity between the  $\Delta E$  values of **1** and **4** does not correlate well with the experimental  $\sim 6$ -fold difference  $\Phi_{Cl}$  (Table 1). It should also be noted that calculations were also run for  $[Ru(bpy)_2(L)]^{2+}$  (L = N,N'-diethylenediamine), resulting in  $\Delta E = 2.31$  eV, making the value similar to **3** and

**Table 2.** Calculated Percent Sulfur or Nitrogen Character to the HOMO,  $\%(S/N)$ , and Average of the Three Highest Occupied MOs,  $\%(S/N)_{ave}$ , Selected Bond Lengths of the Minimized Singlet Ground State (S), Lowest Energy Triplet State (T), and the Difference ( $\Delta r$ )

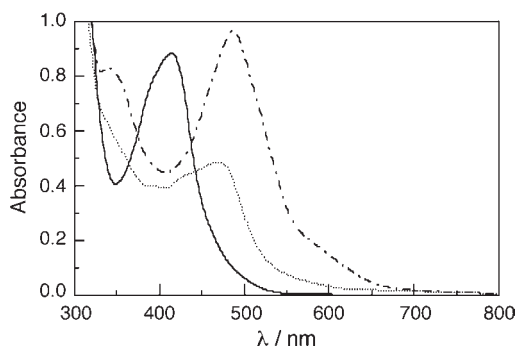
complex	$\%(S/N)^a$	$\%(S/N)_{ave}$	bond <sup>b</sup>	S/Å	T/Å	$\Delta r/\text{Å}$
1	5	5.7	Ru–S1	2.447	2.890	0.443
			Ru–S2	2.447	2.895	0.448
2	12	8.0	Ru–S1	2.448	2.833	0.385
			Ru–S2	2.449	2.926	0.477
3	1	0.3	Ru–N5	2.188	2.481	0.293
			Ru–N6	2.188	2.483	0.295
4	1	1.0	Ru–N5	2.269	2.595	0.326
			Ru–N6	2.269	2.590	0.321

<sup>a</sup> Nitrogen or sulfur atom character of the diammine or thioether ligand, respectively; only whole numbers are provided by the calculation. <sup>b</sup> S1 and S2 represent sulfur atoms in thioether ligand and N5 and N6 are the nitrogen atoms in diammine ligand.

showing that the difference in  $\Delta E$  between **1** and **3** is not related to the presence of the ethyl groups on the bpte ligand.

The comparison of the optimized geometries of the ground state (S) and lowest energy triplet state (T) can be used to understand the differences in photosubstitution yields among the complexes. The calculated Ru–L bond distances of 1–4 in S and T are summarized in Table 2, where L represents the sulfur atoms in the bis-thioether ligands in **1** and **2** or the nitrogen atoms in the diammine ligands in **3** and **4**. It is evident from Table 2 that the Ru–L bond distance for each complex is elongated in the triplet state compared to the ground state ( $\Delta r$ ). However, the elongation is greater in **1** and **2**, with average elongation,  $\Delta r_{ave}$ , of 0.44 Å, compared to those in **3** ( $\Delta r_{ave} = 0.29$  Å) and **4** ( $\Delta r_{ave} = 0.32$  Å). It should also be noted that the changes in the Ru–N bond length for the ancillary bpy ligands ranges from +0.099 to –0.020 Å in 1–4 between S and T. Because sulfur has low-lying unoccupied d-orbitals that can participate in  $\pi$ -backbonding with the filled  $t_{2g}$ -set of transition metals,<sup>50,51</sup> the percent sulfur character to the HOMO of **1** and **2** was calculated,  $\%(S)$ , and compared to the percent nitrogen character from the diammine ligands in **3** and **4**,  $\%(N)$ , and the resulting values are listed in Table 2. In addition, the average contributions of these atoms to the three highest occupied orbitals, the Ru( $d$ )  $t_{2g}$ -type set, are also listed in Table 2,  $\%(S/N)_{ave}$ . It is evident from the values in Table 2 that indeed the HOMO, HOMO-1, and HOMO-2 of **1** and **2** have significant greater Ru–S  $\pi$ -bonding character than nitrogen contribution from the corresponding  $\sigma$ -donor diammine ligands of **3** and **4**. Therefore, the Ru–S bond elongation calculated for the triplet states of **1** and **2** may be explained by the removal of electron density from the metal  $t_{2g}$ -type set in the Ru $\rightarrow$ bpy MLCT state, thus weakening the Ru–S bonds in the excited state. A similar finding was recently reported for the photoisomerization of Ru(II) complexes with sulfur-bound dmsol ligands.<sup>27</sup> The greater elongation of **1** and **2** in the triplet state can aid in their ability to undergo ligand dissociation upon excitation, consistent with the observed trend in photodissociation quantum yields (Table 1).

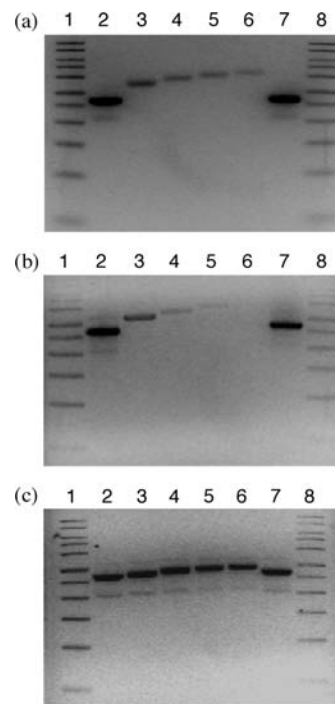
**Photoinduced DNA Binding.** Since **1** exhibits the largest photosubstitution quantum yields among the complexes, its photoinduced binding to guanosine 5-monophosphate (GMP) was explored. A solution of 140  $\mu\text{M}$  **1** in water in the presence of



**Figure 6.** Electronic absorption spectrum of 140  $\mu\text{M}$  **1** in  $\text{H}_2\text{O}$  in the presence of 14 mM GMP prior to photolysis (solid line), irradiated with  $\lambda_{\text{irr}} > 395$  nm for 10 min (dot-dashed line), and then incubated in the dark at 37  $^\circ\text{C}$  for 4 h (dotted line).

14 mM GMP was photolyzed with  $\lambda_{\text{irr}} > 395$  nm for 10 min and then incubated in the dark at 37  $^\circ\text{C}$  for 4 h, and the resulting spectral changes are shown in Figure 6. After irradiation, the formation of the  $[\text{Ru}(\text{bpy})_2(\text{H}_2\text{O})_2]^{2+}$  is observed with maximum at 490 nm (10 min), and after 4 h in the dark the  $^1\text{MLCT}$  peak blue shifts to 475 nm. The absorption at 475 nm has been previously assigned to the related complex  $[\text{Ru}(\text{bpy})_2(9\text{-MeG})_2]^{2+}$  (9-MeG = 9-methylguanine).<sup>52</sup> Similar results are observed when the GMP is added to the solution of **1** in water after irradiation and incubated at 37  $^\circ\text{C}$  for 4 h. These results are similar to the photoinitiated binding of 9-ethylguanine and 9-methylguanine to the related compound  $[\text{Ru}(\text{bpy})_2(\text{NH}_3)_2]^{2+}$ .<sup>22</sup> When **1** is incubated in the presence of GMP at room temperature for 4 h in the dark, no significant changes are observed in the electronic absorption spectrum. These results clearly indicate that the binding of **1** to GMP must proceed via the photochemically generated bis-aqua intermediate to form the product.

Covalent binding of cisplatin to double-stranded DNA, ds-DNA, has been previously shown to decrease the mobility of linearized plasmid in agarose gel electrophoresis.<sup>21,22,53</sup> Therefore, agarose shift mobility gels were utilized to evaluate the ability of **1** and **2** to undergo covalent binding to ds-DNA upon irradiation, and these results are compared to those of **3**. In the gels presented in Figure 7, lanes 1 and 8 show the mobility of commercially available 1 kb DNA molecular weight standard ladder, and lanes 2 and 7 are controls showing the mobility of linearized pUC18 plasmid in the absence of metal complex. Figures 7a and 7c compare the abilities of **1** and **3** to shift the mobility of 50  $\mu\text{M}$  linearized pUC18 plasmid DNA (10 mM phosphate buffer, pH = 8.3,  $\lambda_{\text{irr}} > 395$  nm,  $t_{\text{irr}} = 4$  min). It is evident from Figure 7c that there is only a slight shift in mobility for **3** as the concentration of complex is increased across lanes 3–6 (25  $\mu\text{M}$ –250  $\mu\text{M}$ ), while keeping the DNA concentration constant. In contrast, a dramatic reduction in mobility is observed for **1** in Figure 7a over the same complex concentration range and irradiation conditions. This difference in covalent DNA binding and reduced mobility between the thioether and amino analogues can be explained by the greater quantum yield of photoinduced ligand exchange of **1** compared to that of **3**. In addition, the photolysis of **2** in the presence of linearized pUC18 plasmid results in a decreased mobility of the ds-DNA (Figure 7b); however, in this gel the complex/DNA mixture was irradiated for 20 min, resulting in greater covalent binding and reduced mobility than that of **1** in Figure 7a ( $t_{\text{irr}} = 4$  min).



**Figure 7.** Imaged ethidium bromide stained agarose gel of 50  $\mu\text{M}$  linearized pUC18 plasmid (10 mM phosphate buffer, pH = 8.3) irradiated with  $\lambda_{\text{irr}} > 395$  nm in the presence of various concentrations of (a) **1** ( $t_{\text{irr}} = 4$  min), (b) **2** ( $t_{\text{irr}} = 20$  min), and (c) **3** ( $t_{\text{irr}} = 4$  min). Lanes 1 and 8, 1 kb DNA molecular weight standard; lanes 2 and 7, linearized plasmid alone; lanes 3–6, 25  $\mu\text{M}$ , 75  $\mu\text{M}$ , 150  $\mu\text{M}$ , 250  $\mu\text{M}$  complex.

In contrast, no change in the mobility was observed for samples of **2** incubated with plasmid in the dark at 24  $^\circ\text{C}$  for 20 min (Supporting Information, Figure S3). The effect of **4** on the DNA mobility is lower than that of the corresponding thioether complex **2** under similar irradiation conditions and does not induce a mobility shift in the dark, as shown in Supporting Information, Figure S4. It should be noted that the ligands alone, at the highest concentration used for the complexes, do not result in DNA mobility shift in the dark or upon irradiation (Supporting Information, Figure S5).

## CONCLUSIONS

The thioether ligands in the sulfur chelated complexes  $[\text{Ru}(\text{bpy})_2(\text{bete})]^{2+}$  (**1**) and  $[\text{Ru}(\text{bpy})_2(\text{bpte})]^{2+}$  (**2**) are photosubstituted by  $\text{Cl}^-$ , bpy, and  $\text{H}_2\text{O}$  when irradiated with visible light and are stable to ligand exchange under similar conditions in the dark. Complexes **1** and **2** are able to bind guanine 5-monophosphate and linearized ds-DNA through the initial photosubstitution of the bis-thioether ligands with water molecules, which then undergo thermal substitution resulting in coordination to nucleobases. The relatively greater ligand exchange quantum yields of **1** and **2** relative to the analogous nitrogen chelated complexes, **3** and **4**, can be explained by the greater Ru–L bond elongation in the lowest energy triplet states of the former relative to the latter attributed to weakening of the Ru–S bonds in the  $\text{Ru} \rightarrow \text{bpy}$  MLCT excited state. This work provides better understanding of the electronic properties of Ru(II) complexes that lead to greater photoinduced yields of ligand exchange.

## ■ ASSOCIATED CONTENT

**S Supporting Information.** Emission spectra at 77 K, comparison of photolysis product to synthetic compound, additional DNA mobility shift assays, and percent contributions and Cartesian coordinates of optimized geometries calculated for 1–4. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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