

## Chapter 2

# Synthesis and Characterization of Tricarbonyl Rhenium Complexes\*

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## 2.1 Introduction

The rich photophysical, photochemical, and redox properties of polypyridyl transition metal complexes make them useful in a wide range of fields, including energy conversion<sup>1,2</sup>, medicine<sup>3-5</sup>, cellular imaging,<sup>6-9</sup> and DNA sensing.<sup>10-13</sup> The utility of these metal complexes stems from their stability in many different chemical environments, as well as their rich photophysical behavior and potent redox reactivity. In addition, the general synthetic flexibility and modularity of such molecules allows for easy and systematic modification of these properties.

Re complexes of the family *fac*-[Re(CO)<sub>3</sub>(diimine)(L)]<sup>n</sup>, where L is usually a cyclic imine or a halide, have been used as probes in time-resolved infrared (TRIR) spectroscopy. Vibrational modes involving the tricarbonyl ligand set provide three unique and specific transition moments that are well removed energetically from those of organic carbonyl groups. These are the totally symmetric in-phase  $\nu(\text{CO})$  vibration A'(1), which appears in ground state vibrational spectra near 2030 cm<sup>-1</sup>, and the totally symmetric out-of-phase A'(2) and equatorial asymmetric A'' modes, which appear near 1920 cm<sup>-1</sup>.<sup>14</sup> Elaborate photophysical and photochemical pathways can be elucidated by monitoring changes in the energies of these modes following electronic excitation of the complex.<sup>15-20</sup>

Because the carbonyl ligand stretching frequencies are energetically isolated from most organic vibrational modes, these complexes are especially suitable for use in the study of biomolecular photophysics and redox chemistry. For example, by coordinating Re<sup>I</sup>(CO)<sub>3</sub>(4,7-dimethyl-1,10-phenanthroline) to histidine 124 in *Pseudomonas Aeruginosa* azurin, researchers were able to follow the kinetics of charge transfer from the Re photooxidant to the Cu(I) center of the protein by observing changes in the vibrational frequencies of the Re CO ligands.<sup>21,22</sup> This work has shown that an intervening aromatic residue such as tryptophan can serve as an intermediate in a multistep tunneling mechanism between the photooxidant and the Cu center, increasing the rate of charge transfer by several orders of magnitude. Similarly, early studies have appeared in which tricarbonyl Re complexes were used to trigger the oxidation of DNA.<sup>23,24</sup> In such experiments, changes in the vibrational stretching frequencies of the CO ligands and the formation of oxidized guanine products

can be observed simultaneously.

Here, we report the synthesis and characterization of a pair of related tricarbonyl Re complexes,  $[\text{Re}(\text{CO})_3(\text{dppz})(\text{py}'\text{-OH})]^+$  and  $[\text{Re}(\text{CO})_3(\text{dppz})(\text{py}'\text{-OEt})]^+$  (dppz = di-pyrido[3,2-*a*:2',3'-*c*]phenazine; py'-OH = 3-(pyridin-4-yl)propanoic acid; py'-OEt = ethyl 3-(pyridin-4-yl)propanoate), (Scheme 2.1) designed for use as DNA photooxidants. These complexes share many photophysical characteristics with other tricarbonyl Re complexes that bear dppz, including an increase in luminescence in the presence of DNA. In addition, we show that the excited state reduction potential of these complexes is sufficiently strong to oxidize guanine.

## 2.2 Experimental Section

### 2.2.1 Materials

Unless indicated otherwise, all reagents and solvents were of reagent grade or better and were used as received without further purification. The ligand 3-(pyridin-4-yl)propanoic acid (py'-OH) was purchased from Chess GmbH (Mannheim, Germany).

### 2.2.2 Synthesis of $[\text{Re}(\text{CO})_3(\text{dppz})(\text{py}'\text{-OR})]^+$

The synthesis of  $[\text{fac-Re}(\text{CO})_3(\text{dppz})(\text{py}'\text{-OH})]\text{Cl}$  closely followed the procedure of Stoeffler, et al.<sup>25</sup> A mixture of 253 mg (0.7 mmol)  $\text{Re}(\text{CO})_5\text{Cl}$  and 147 mg (0.7 mmol) 1,10-phenanthroline-5,6-dione in 7 mL toluene was refluxed (110 °C) for 4.5 h. The crude solid product was collected by suction filtration, purified by silica gel using THF as an eluent, and dried under vacuum to yield  $\text{Re}(\text{CO})_3\text{Cl}(1,10\text{-phenanthroline-5,6-dione})$  as an orange microcrystalline solid.  $\text{Re}(\text{CO})_3\text{Cl}(\text{dppz})$  was formed by heating 160 mg (0.31 mmol)  $\text{Re}(\text{CO})_3\text{Cl}(1,10\text{-phenanthroline-5,6-dione})$  in 15 mL EtOH to reflux (85 °C), adding 55 mg (0.6 mmol) *o*-phenylenediamine, and refluxing the mixture for 1 h. The yellow-ochre solid product was collected by suction filtration. <sup>1</sup>H NMR (300 MHz) in DMSO indicated the presence of the dppz ligand:  $\delta$  8.22 (q, 2H), 8.31 (m, 2H), 8.55 (q, 2H), 9.58 (d, 2H), 9.88 (d, 2H). The desired product was obtained following substitution for the Cl ligand. A sus-

pension of 160 mg (0.27 mmol)  $\text{Re}(\text{CO})_3\text{Cl}(\text{dppz})$  was heated under Ar to 50 °C in 25 mL dry DMF. After addition of 280 mg (1.1 mmol)  $\text{AgPF}_6$ , the reaction mixture was heated at 50 °C for 5 min, then 250 mg (1.7 mmol)  $\text{py}'\text{-OH}$  was added and the mixture was refluxed at 70 °C under Ar for 6 h. The reaction was cooled, and the  $\text{AgCl}$  precipitate was removed by gravity filtration, yielding an orange-yellow solution. The crude product was purified by silica gel using 5% methanol in chloroform as the eluent, and then dried under vacuum to yield  $[\text{Re}(\text{CO})_3(\text{dppz})(\text{py}'\text{-OR})](\text{PF}_6)$ . The  $\text{PF}_6$  counter ion was exchanged for chloride using Sephadex QAE A-25 anion exchange resin, and the resulting solution was concentrated using a C18 Sep-Pak to yield *fac*- $[\text{Re}(\text{CO})_3(\text{dppz})(\text{py}'\text{-OR})]\text{Cl}$  as a bright yellow solid.  $^1\text{H}$  NMR ( $\text{PF}_6$  salt, 300 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  9.79 (dd, 2H), 9.65 (dd, 2H), 8.37 (dd, 2H), 8.23 (m, 4H), 8.09 (dd, 2H), 7.13 (d, 2H), 2.73 (t, 2H), 2.44 (t, 2H).  $^{13}\text{C}$  NMR ( $\text{PF}_6$  salt, 300 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  155.3, 155.0, 151.3, 149.0, 142.4, 136.5, 132.4, 129.3, 128.2, 126.3, 32.3, 28.9. ESI: calcd 703.7 for  $\text{C}_{29}\text{H}_{19}\text{N}_5\text{O}_5\text{Re}$  ( $\text{M}^+$ ), found 703.9.

The related ethyl ester was prepared in the same way following the Fischer esterification of  $\text{py}'\text{-OH}$ .  $^1\text{H}$  NMR ( $\text{PF}_6$  salt, 300 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  9.90 (dd, 2H), 9.65 (dd, 2H), 8.45 (dd, 2H), 8.26 (dd, 2H), 8.20 (dd, 2H), 8.13 (dd, 2H), 7.09 (d, 2H), 3.88 (q, 2H), 2.72 (t, 2H), 2.41 (t, 2H), 0.99 (t, 3H). ESI: calcd 731.8 for  $\text{C}_{31}\text{H}_{23}\text{N}_5\text{O}_5\text{Re}$  ( $\text{M}^+$ ), found 732.0.

### 2.2.3 Electrochemistry

Electrochemical measurements were carried out using an electrochemical workstation (CH Instruments 650A). Cyclic voltammetry (CV) was performed at ambient temperature using a standard three electrode apparatus with a glassy carbon working electrode, a Pt auxiliary electrode, and a  $\text{Ag}/\text{AgCl}$  reference electrode. The use of an internal ferrocene/ferrocenium standard for CV measurements facilitated conversion of the potentials referenced against  $\text{Ag}/\text{AgCl}$  to NHE. Immediately prior to measurement, samples were degassed rigorously with  $\text{N}_2$ . All samples were measured in the presence of 0.1 M tetra-n-butylammonium hexafluorophosphate electrolyte. All redox potentials are reported herein vs. NHE.

## 2.2.4 Spectroscopy

Steady-state absorption spectra were recorded on a Beckman DU 7400 diode array spectrophotometer. Steady-state emission spectra were recorded on a Fluorolog-3 spectrofluorometer (Jobin Yvon) using 2 mm slits. Scattered light was rejected from the detector by appropriate filters. Reported emission and excitation spectra are the average of at least five consecutive measurements. Low volume 1 cm path-length quartz cells were used for both spectrophotometric and luminescence experiments.

Fourier Transform Infrared (FT-IR) spectroscopy experiments were carried out on a Thermo-Nicolet NEXUX 670 FT-IR spectrometer. Samples were held in a 100  $\mu\text{m}$ -path-length cell between two  $\text{CaF}_2$  plates. Samples concentrations were approximately 1 mM in acetonitrile. Samples were degassed thoroughly before introduction into the sample cell.

## 2.3 Results and Discussion

### 2.3.1 Metal Complex Design

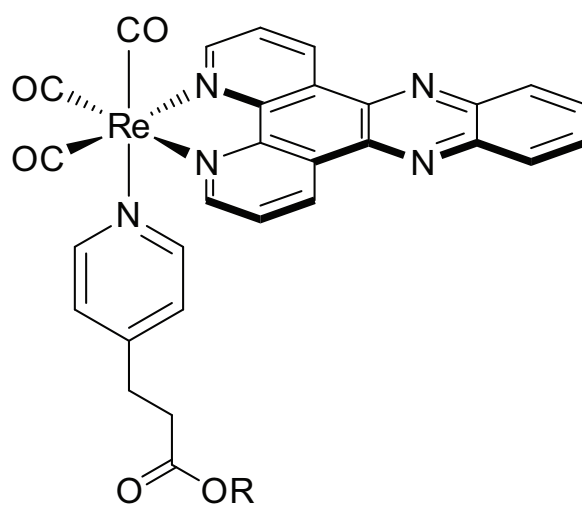
The Re complexes described here were designed specifically for use in TRIR experiments involving DNA. This intention led to the incorporation of two structural elements that facilitate interactions with the DNA duplex. The first of these is the polycyclic heteroaromatic ligand dppz, which allows the complex to bind to DNA by intercalation. In this binding mode, the intercalating ligand slides into the base stack, sandwiching itself between two neighboring bases.<sup>26</sup> Structural changes to the DNA duplex include a slight unwinding to accommodate the intercalator and a corresponding increase in length. Intercalation increases the binding affinity of the complex due to favorable  $\pi$  stacking interactions and hydrophobic forces. Because of the large surface area of dppz, these effects can be quite strong; the binding affinity of  $[\text{Ru}(\text{phen})_2(\text{dppz})]^{2+}$  is on the order of  $10^7 \text{ M}^{-1}$ , whereas that of  $[\text{Ru}(\text{phen})_3]^{2+}$  is closer to  $10^4 \text{ M}^{-1}$ .<sup>27</sup> Intercalation also facilitates strong electronic coupling between the metal complex and the base stack. It is this coupling that enables charge transport to occur through the DNA base stack over long distances<sup>28</sup> The second structural element is a carboxyalkyl chain, which is introduced via functionalization at the

4 position of a pyridine ligand. This modification allows for covalent attachment of the complex at specific sites on the DNA strand. By controlling the site of incorporation and intercalation, it is possible to determine the distance between the Re charge donor and the charge acceptor.

### 2.3.2 Metal Complex Synthesis

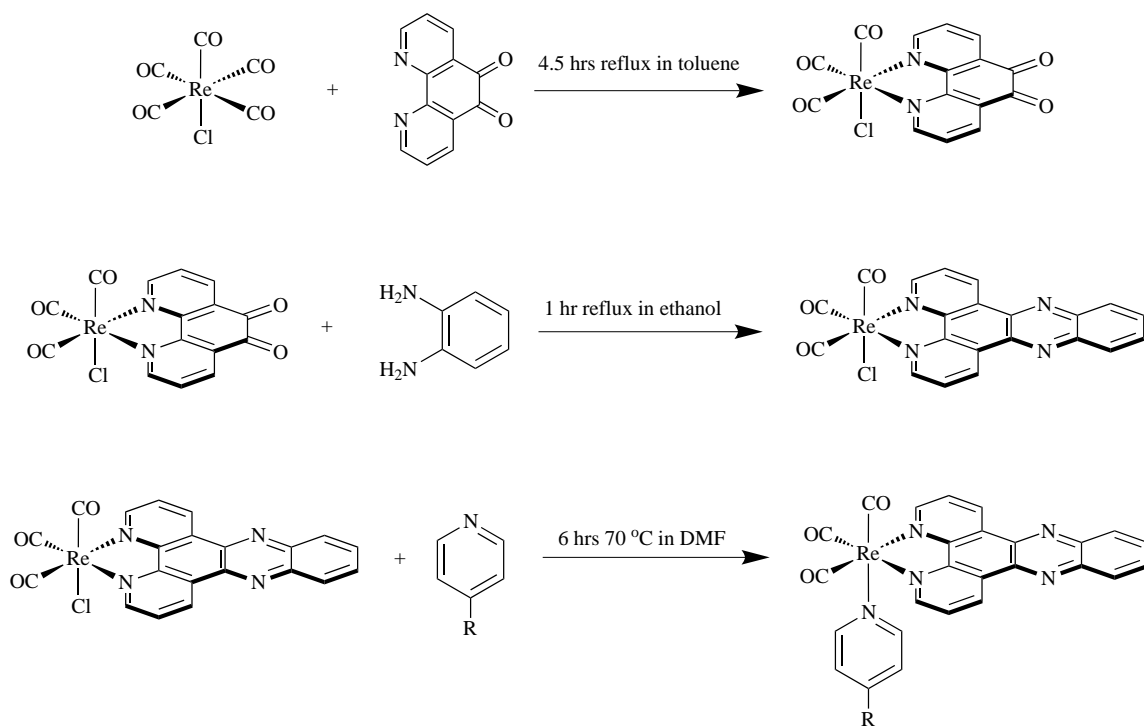
The synthetic strategy used for the preparation of  $[\text{Re}(\text{CO})_3(\text{dppz})(\text{py}'\text{-OR})]^+$  was based on the high-yielding and highly extensible methodology of Stoeffler et al.<sup>25</sup> The synthesis is outlined in Scheme 2.2. The first step involves substitution of 1,10-phenanthroline-5,6-dione for two carbonyl ligands of  $\text{Re}(\text{CO})_5\text{Cl}$ . Due to the trans effect, addition of the bidentate ligand results in the generation of only the *facial* stereoisomer. Following purification of the product by silica gel chromatography, formation of dppz is effected by condensation of *o*-phenylenediamine with the dione. The desired product is formed by substitution of the Cl ligand for pyridine or a derivative of pyridine in the presence of  $\text{AgPF}_6$ . If the pyridine ligand is functionalized with a hydrophilic group such as a carboxylate, purification of the crude product by silica gel chromatography can be difficult due to the high retention of the species on the solid phase. In such cases, it is advisable to protect the carboxylate with an ester prior to ligation of the ligand at the metal center. Pure, dry product forms a bright yellow powder that is insoluble in water. Salt metathesis on an anion exchange column can be used to generate the chloride salt, which is slightly more soluble in aqueous solution.

The entire synthesis takes only a few days. In addition, the modular nature of the procedure allows for the rapid synthesis of a large number of related species. For example, by using 4- or 5-substituted *o*-phenylenediamine, it is possible to generate dppz ligands functionalized at the 11 and 12 positions. Similarly, any number of ligands, not just pyridine derivatives, can fill the last coordination site. Such strategies have been used to tease out the subtle photophysics of tricarbonyl Re complexes.<sup>14,17,20,29-31</sup>



R = H, CH<sub>2</sub>CH<sub>3</sub>

**Scheme 2.1:** [Re(CO)<sub>3</sub>(dppz)(py'-OR)]<sup>+</sup>



**Scheme 2.2:** Synthesis of  $[\text{Re}(\text{CO})_3(\text{dppz})(\text{py}')^+]$



### 2.3.3 Photophysical Characterization of $[\text{Re}(\text{CO})_3(\text{dppz})(\text{py}'\text{-OR})]^+$

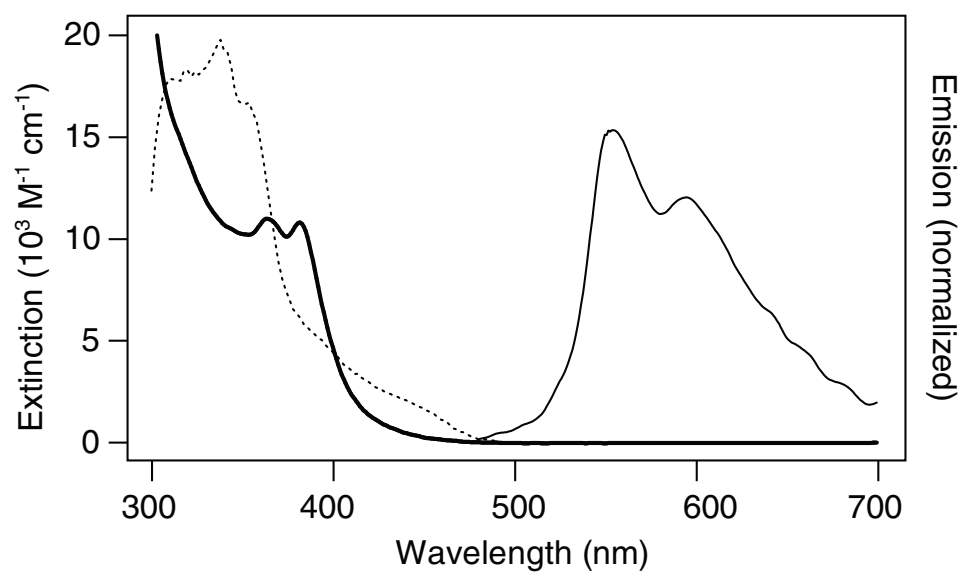
Spectroscopically, the Re complexes resemble other dppz-bearing tricarbonyl Re complexes (Figure 2.1).<sup>19,25,29,31–38</sup> The complex displays absorption maxima at 364 nm and 382 nm ( $\epsilon_{388} \approx 11\,000 \text{ M}^{-1} \text{ cm}^{-1}$ ),<sup>25,34</sup> with a weak tail extending into the visible region. The emission spectrum ( $\lambda_{ex} = 355 \text{ nm}$ ) in acetonitrile is bifurcated, exhibiting maxima at 555 nm and 595 nm. The excitation spectrum of  $[\text{Re}(\text{CO})_3(\text{dppz})(\text{py}'\text{-OEt})]^+$  in acetonitrile ( $\lambda_{em} = 550 \text{ nm}$ ) indicates the evolution of prominent luminescence at 570 nm upon excitation between 300 nm and 370 nm, with less emission at higher excitation wavelengths.

The high degree of similarity between the absorption spectra of complexes of the type *fac*- $[\text{Re}(\text{CO})_3(\text{dppz})(\text{L})]^{n+}$  and the free dppz ligand suggests that the absorption maxima observed near 360 nm and 380 nm result from a  $\pi \rightarrow \pi^*$  (dppz) intraligand (IL) transition.<sup>19,25</sup> However, the long, low-intensity tail into the visible region, as well as a slight red shift of these bands compared to the free dppz ligand, indicates the presence of an underlying  $d\pi(\text{Re}) \rightarrow \pi^*$  (dppz) metal-to-ligand charge transfer (MLCT) transition.<sup>19,32</sup> The complexes  $[\text{Re}(\text{CO})_3(\text{dppz})(\text{py}'\text{-OR})]^+$  share these characteristics, suggesting that irradiation with light in the near-UV populates several excited states in this species, namely MLCT states and IL transitions centered on the phenanthrene ( $\text{IL}_{\text{phen}}$ ) and phenazine ( $\text{IL}_{\text{phz}}$ ) parts of dppz.<sup>18,19,31,35,36</sup> Over time, the initially excited singlet states are expected to decay to  $^3\text{MLCT}$ ,  $^3\text{IL}_{\text{phen}}$  and  $^3\text{IL}_{\text{phz}}$  states.<sup>19</sup>

The FT-IR spectrum of  $[\text{Re}(\text{CO})_3(\text{dppz})(\text{py}'\text{-OEt})]^+$  is shown in Figure 2.2 on page 68. The spectrum consists of two strong bands. The band at  $2036 \text{ cm}^{-1}$  corresponds to absorbance of the  $A'(1)$  mode, and the band at  $1932 \text{ cm}^{-1}$  corresponds to overlapping absorption of the  $A'(2)$  and  $A''$  modes. The low intensity shoulders at  $2025 \text{ cm}^{-1}$  and  $1905 \text{ cm}^{-1}$  are likely due to impurities.

### 2.3.4 Interactions with DNA

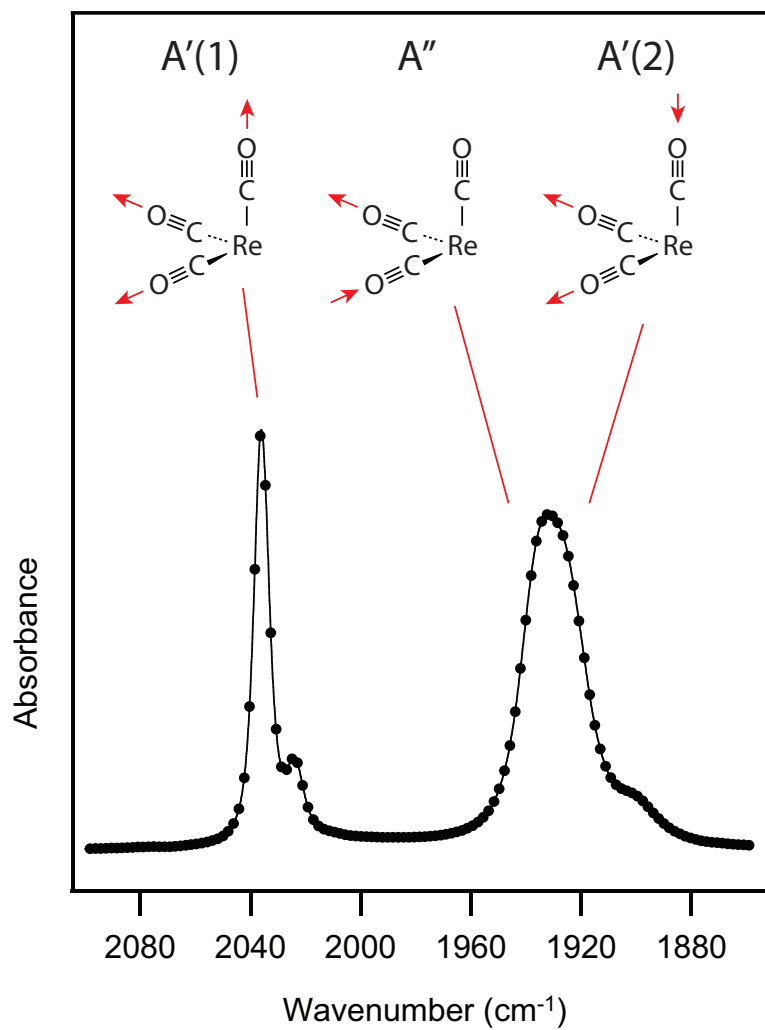
Addition of DNA to a solution of  $[\text{Re}(\text{CO})_3(\text{dppz})(\text{py}'\text{-OEt})]^+$  results in a decrease and slight redshift of the IL absorption bands near 360 and 390 nm. This change is illustrated in Figure 2.3 for the addition of 30-mer duplexes containing only A·T or only G·C base



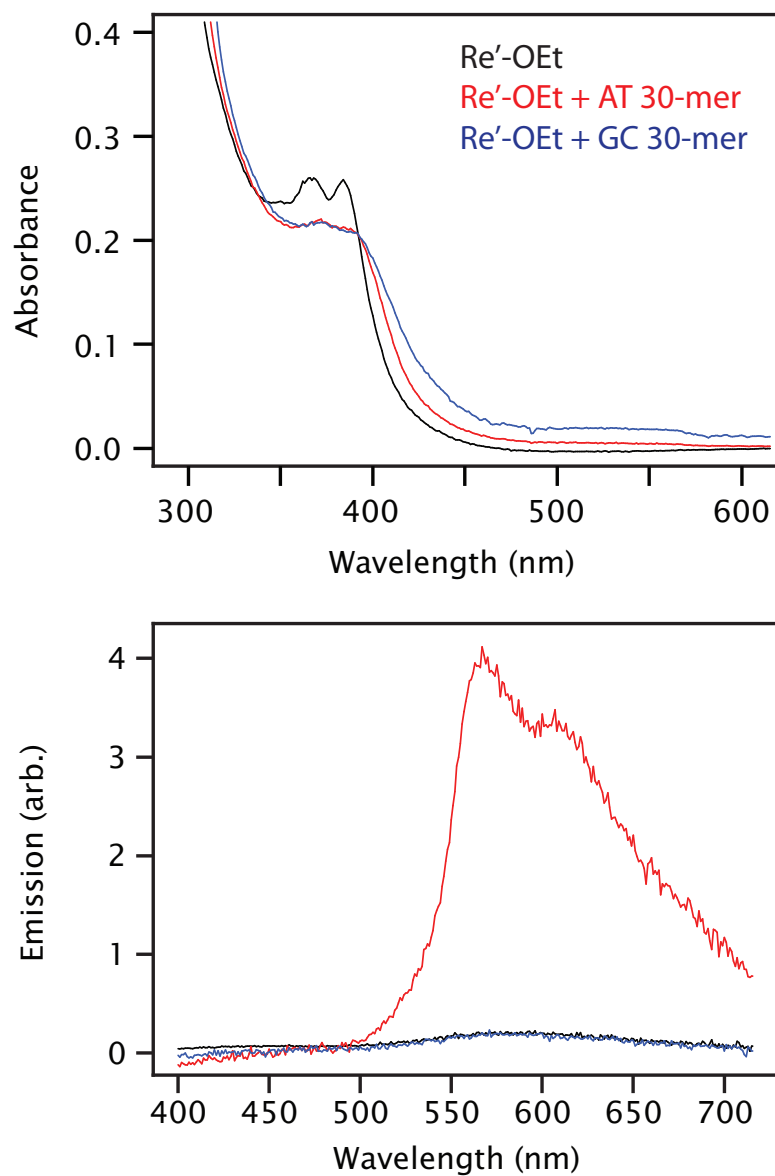
**Figure 2.1:** UV/visible steady-state characteristics of  $[\text{Re}(\text{CO})_3(\text{dppz})(\text{py}')^+]^+$ . The absorbance spectrum (bold), emission spectrum ( $\lambda_{ex} = 355$  nm; solid), and excitation spectrum ( $\lambda_{em} = 570$  nm; dotted) of the complex ( $18 \mu\text{M}$ ) in degassed acetonitrile are shown.

pairs. Hypochromicity is observed in both sequence contexts, showing that the identity of the bases has a negligible effect on binding. The change in absorption observed upon the addition of DNA is common for transition metal complexes that contain polycyclic aromatic ligands and is indicative of intercalative binding.<sup>26,39–43</sup>

Emission measurements also show evidence of intercalative binding. In aqueous solution, complexes of the type  $[\text{Re}(\text{CO})_3(\text{dppz})(\text{L})]^{n+}$  behave as a DNA light switches,<sup>44</sup> emitting only in the presence of DNA.<sup>18,19,25,29,31,33,35,36</sup> This phenomenon is a result of a decrease in solvent accessibility to the intercalated dppz ligand. In solution, hydrogen bonding between water and the phenazine nitrogens of the dppz ligand enable a facile non-radiative decay pathway for excited state relaxation, shutting off luminescence. Upon intercalation, solvent is excluded from interactions with dppz, and fluorescence is restored.<sup>45</sup> Changes in the luminescence of  $[\text{Re}(\text{CO})_3(\text{dppz})(\text{py}'\text{-OEt})]^+$  upon binding to DNA are shown in Figure 2.3. When the complex is bound to a DNA sequence containing only A·T pairs or a mixed sequence, its luminescence spectrum displays a maximum at 570 nm and a shoulder near 610 nm. This spectrum is typical of dppz-containing tricarbonyl Re complexes. By comparison with the emission of  $[\text{Ru}(\text{bpy})_3]^{2+}$  in deaerated acetonitrile, the emission quantum yield of  $[\text{Re}(\text{CO})_3(\text{dppz})(\text{py}'\text{-OEt})]^+$  in the presence of the A·T 30-mer in buffer is 0.008 (compared to 0.062 for  $[\text{Ru}(\text{bpy})_3]^{2+}$ ).<sup>46</sup> Interestingly, when bound to a 30-mer consisting of only G·C base pairs, or to DNA with high GC content, emission of the complexes is almost completely quenched, and the maximum is shifted to 585 nm.<sup>47</sup> This dependence of emission on GC content has been observed before. In early experiments, the origin of this effect was unknown. It was suggested that dppz complexes of Re bind more strongly to A·T sequences than to G·C sequences due to more facile propeller twisting of the A and T bases. This flexibility was presumed to decrease unfavorable steric interactions between the DNA backbone and the ancillary (non-intercalating) ligands of the metal complex.<sup>33</sup> More recently, it was suggested that the difference in luminescence in the two sequence contexts is instead due to quenching of the  $\text{Re}^*$  excited state by guanine.<sup>32</sup> This more straightforward explanation is supported by biochemical and spectroscopic experiments.<sup>23,24,47</sup>



**Figure 2.2:** FT-IR spectrum of  $[\text{Re}(\text{CO})_3(\text{dppz})(\text{py}'\text{-OEt})]^+$  saturated in degassed acetonitrile. The solid line shows a cubic spline fit to the data points. Vibrational assignments are based on those of Vlček.<sup>14</sup> For this complex, the A'' and A'(2) bands overlap.



**Figure 2.3:** Steady-state optical absorption and emission spectra of 25  $\mu\text{M}$   $[\text{Re}(\text{CO})_3(\text{dppz})(\text{py}'\text{-OEt})]^+$  and 25  $\mu\text{M}$  DNA 30-mer in  $\text{D}_2\text{O}$  buffer (10 mM  $\text{NaP}_i$ , 50 mM  $\text{NaCl}$ ; pD 7.0). Top: optical absorption of the Re complex without (black) and with AT-30 (red) or GC-30 (blue). Bottom: emission of Re without (black) or with AT-30 (red) or GC-30 (blue) following excitation at 355 nm. Luminescence spectra have been corrected for emission from DNA alone.

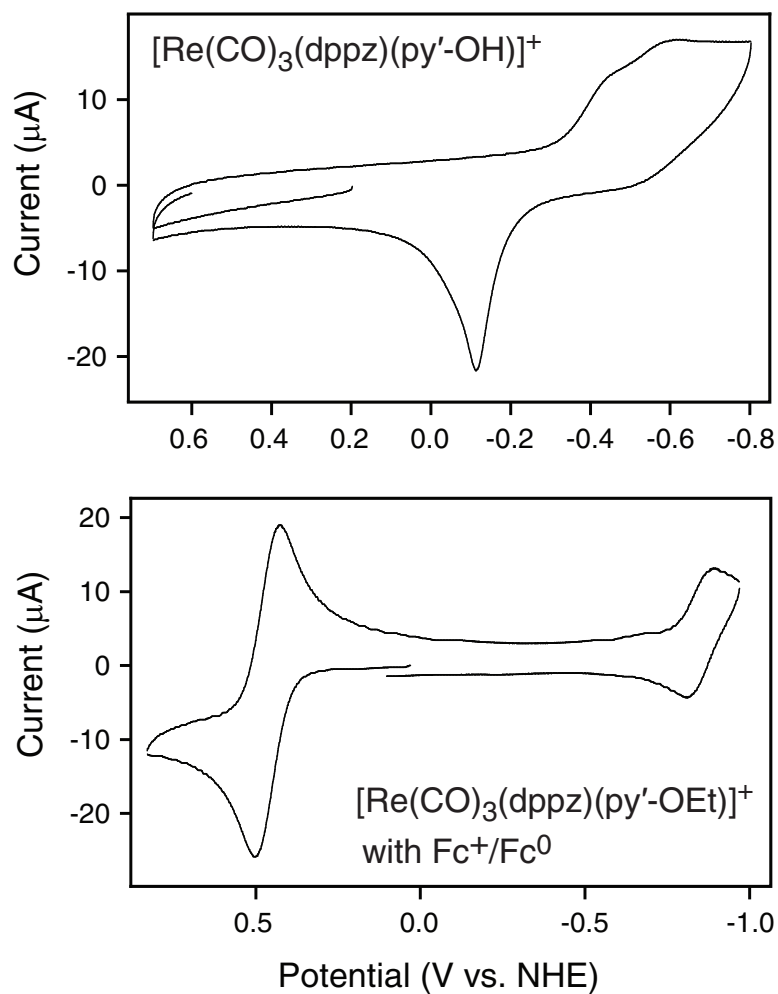
### 2.3.5 Electrochemistry

In order to understand the redox properties of the Re complexes, their electrochemical behavior was studied by CV. The CV trace of  $[\text{Re}(\text{CO})_3(\text{dppz})(\text{py}'\text{-OH})]^+$  shows several overlapping peaks upon reduction and one sharp peak upon reoxidation, indicating aggregation of the complex at the electrode surface, while the CV of  $[\text{Re}(\text{CO})_3(\text{dppz})(\text{py}'\text{-OEt})]^+$  is much cleaner, showing one reversible redox wave at  $-850$  mV (Figure 2.4). Because the carboxylate functionality is so far removed from the metal center, the ground state redox properties of the ester are expected to be identical to those of the carboxylic acid. Further reduction of  $[\text{Re}(\text{CO})_3(\text{dppz})(\text{py}'\text{-OEt})]^+$  to  $-1.8$  V shows several additional irreversible reduction waves. The excited state reduction potential of  $[\text{Re}(\text{CO})_3(\text{dppz})(\text{py}'\text{-OEt})]^+$ ,  $E^\circ(\text{Re}^{+*}/\text{Re}^0)$ , was estimated using the formula

$$E^\circ(\text{Re}^{+*}/\text{Re}^0) = E_{00} + E^\circ(\text{Re}^+/\text{Re}^0),$$

where  $E_{00}$  is the zero-zero excited-state energy and  $E^\circ(\text{Re}^+/\text{Re}^0)$  is the ground state reduction potential.<sup>48</sup> Since DNA-mediated CT may occur from several excited states in these Re complexes, depending on the relative rates of CT and conversion between excited states,<sup>19</sup>  $E_{00}$  is best approximated as a range of values. The lower bound for  $E_{00}$  can be estimated as the emission maximum (570 nm in aqueous solution, or 2.18 eV), and the upper bound can be estimated as the crossover point between the emission and excitation spectra (480 nm, or 2.58 eV). Thus, for  $E^\circ(\text{Re}^+/\text{Re}^0) = -850$  mV,  $E^\circ(\text{Re}^{+*}/\text{Re}^0)$  is estimated to lie between 1.33 V and 1.73 V. Considering the redox potentials of the base nucleosides ( $E^\circ[\text{G}^{\bullet+}/\text{G}] = 1.29$  V;  $E^\circ[\text{A}^{\bullet+}/\text{A}] = 1.42$  V;  $E^\circ[\text{T}^{\bullet+}/\text{T}] = 1.6$  V;  $E^\circ[\text{C}^{\bullet+}/\text{C}] = 1.7$  V),<sup>49</sup> the oxidation strength of excited  $[\text{Re}(\text{CO})_3(\text{dppz})(\text{py}'\text{-OR})]^+$  is indeed sufficient to oxidize guanine.

Since the only difference between samples that showed aggregation at the electrode and samples that did not is the presence of a carboxylic acid functionality instead of a protective ethyl ester at the same position, it is clear that the ethyl ester improves the solubility of the complex in some way. In aqueous solution, the carboxylic acid may become deprotonated, leading to the formation of a zwitterionic species that has no net charge. In this case,  $\pi$ -stacking interactions between dppz ligands and a lack of electrostatic repulsion between neighboring molecules may lead to dimerization or aggregation of the complexes.



**Figure 2.4:** Cyclic voltammograms for 20  $\mu\text{M}$   $[\text{Re}(\text{CO})_3(\text{dppz})(\text{py}'\text{-OH})]^+$  (top) and 20  $\mu\text{M}$   $[\text{Re}(\text{CO})_3(\text{dppz})(\text{py}'\text{-OEt})]^+$  (bottom) in acetonitrile. Samples were thoroughly degassed with  $\text{N}_2$  prior to measurement. Measurements were made using a glassy carbon working electrode, a Pt auxiliary electrode, and a Ag/AgCl reference electrode.  $[\text{Re}(\text{CO})_3(\text{dppz})(\text{py}'\text{-OEt})]^+$  was measured in the presence of a ferrocene/ferrocenium ( $\text{Fc}^+/\text{Fc}^0$ ) internal standard. A scan rate of 0.2 V/s was used.

It is unclear whether the aggregation at the electrode is due to a similar process, but it cannot be ruled out.

## 2.4 Conclusions

Well-tested techniques were employed to synthesize the complexes  $[\text{Re}(\text{CO})_3(\text{dppz})(\text{py}'\text{-OH})]^+$  and  $[\text{Re}(\text{CO})_3(\text{dppz})(\text{py}'\text{-OEt})]^+$ . The ease and speed with which these syntheses can be carried out verifies the generality of the procedure. The properties of the new complexes are consistent with those of similar complexes: they bind to DNA by intercalation, they exhibit light switch behavior, they have two strong, well-resolved IR absorption bands, and they are strong enough oxidants from the excited state to oxidize guanine. These characteristics ensure that the Re complexes synthesized will be valuable probes for the study of DNA-mediated CT.



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