# **Inorganic Chemistry**

# Cyclometalated Osmium–Amine Electronic Communication through the *p*-Oligophenylene Wire

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**Supporting Information** 

**ABSTRACT:** A series of bis-tridentate cyclometalated osmium complexes with a redox-active triarylamine substituent have been prepared, where the amine substituent is separated from the osmium ion by a *p*-oligophenylene wire of various lengths. X-ray crystallographic data of complexes  $3(PF_6)$  and  $4(PF_6)$  with three or four repeating phenyl units between the osmium ion and the amine substituent are presented. These complexes show two consecutive anodic redox couples between +0.1 and



+0.9 V vs Ag/AgCl, with the potential splitting in the range of 300–390 mV. A combined experimental and theoretical study suggests that, in the one-electron-oxidized state, the odd electron is delocalized for short congeners and localized on the osmium component for long congeners. The electronic coupling parameter  $(V_{ab})$  was estimated by the Marcus–Hush analysis. The distance dependence plot of  $\ln(V_{ab})$  versus the osmium–amine geometrical distance  $(R_{ab})$  gives a negative linear relationship with a decay slope of -0.19 Å<sup>-1</sup>, which is slightly steeper with respect to the previously reported ruthenium–amine series with the same molecular wire. DFT calculations with the long-range-corrected UCAM-B3LYP functional gave more reasonable results for the osmium complexes with respect to those with UB3LYP.

# INTRODUCTION

Photoinduced electron transfer occurs ubiquitously in natural systems and optoelectronic devices. One useful method to probe this fundamental process is mixed-valence chemistry,<sup>1</sup> which normally involves the synthesis of a bridged molecule containing two identical redox-active termini and performs the intervalence charge transfer (IVCT) analysis on the mixed-valent state generated by one-electron oxidation or reduction.<sup>2</sup> This analysis has been able to yield important parameters, such as reorganization energy ( $\lambda$ ) and electronic coupling parameter ( $V_{ab}$ ) of the involving electron transfer process. This field has been receiving continuous attention since the pioneering work by Creutz and Taube<sup>3</sup> and recently gained renewed interest due to the potential uses of mixed-valent molecules in molecular electronics,<sup>4</sup> electrochromism,<sup>5</sup> and information storage.<sup>6</sup>

Later studies have shown that the theories and analytical methods of mixed-valent chemistry can be applied for the analysis of common redox-active donor–acceptor systems provided that the transition dipole lies along the donor–acceptor axis and the donor–acceptor overlap can be ignored.<sup>7</sup> In this way, the concept of mixed-valence chemistry has been greatly expanded, and any two redox-active motifs, either inorganic or organic, can be used to build such nonsymmetric mixed-valent compounds in the broad sense.<sup>8</sup> We previously used the combination of cyclometalated ruthenium and triarylamine to build nonsymmetric donor–acceptor systems.<sup>9</sup> The obtained complexes showed strong electronic coupling and appealing electrochromism in the near-infrared (NIR) region.<sup>10</sup> Recently, we found that these two redox components can be

used to probe the long-range electronic communication through a *p*-oligophenylene molecular wire.<sup>11</sup> *p*-Oligophenylene is an important molecular wire that has received much attention in photoinduced electron/energy transfer processes.<sup>12</sup> However, the synthesis and studies of oligophenylene derivatives with more than four repeating phenyl units are limited.<sup>13</sup> It is well known that the electronic coupling of inorganic mixed-valent compounds is greatly dependent on the metal species and coordination environment.<sup>1,2</sup> We are interested in knowing the change of the metal–amine longrange electronic coupling properties upon replacing the cyclometalated ruthenium with the cyclometalated osmium ion. A previous study has shown that strong coupling is present between osmium and amine through a short phenyl bridge.<sup>14</sup>

The use of osmium complexes in mixed-valent chemistry has been known,<sup>15</sup> although it has received less attention with respect to its second-row analogue ruthenium. Osmium complexes generally have more inert metal–ligand bonds and stronger spin–orbit coupling relative to ruthenium complexes. This makes the optoelectronic properties of osmium complexes significantly different from those of ruthenium complexes.<sup>16</sup> We present herein the synthesis and electronic coupling studies of a series of cyclometalated osmium–triarylamine hybridized complexes  $1(PF_6)_2-5(PF_6)$ , where the osmium ion and the amine nitrogen atom are separated by the *p*-oligophenylene wire of various lengths (Scheme 1).

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#### RESULTS AND DISCUSSION

Synthesis and Single-Crystal Structures. Complexes  $1(PF_6)_2 - 5(PF_6)$  were prepared as outlined in Scheme 1. The reaction of the known ligand  $L1-L5^{11}$  with  $[Os(tpy)(H_2O)_3]$ - $(PF_6)_3^{17}$  (tpy = 2,2':6',2"-terpyridine) in ethylene glycol, followed by anion exchange using KPF<sub>6</sub>, afforded  $1(PF_6)_2$ - $5(PF_6)$ , respectively, in acceptable yield. Complexes  $2(PF_6)$ - $5(PF_6)$  were isolated with one counteranion. Complex  $1(PF_6)_2$ was isolated as the one-electron-oxidized form with two counteranions. Compound  $\mathbf{1}^{\scriptscriptstyle +}$  is more readily oxidized than the other members of the series, as determined by the electrochemical results discussed below. Complex  $1(PF_6)_2$  is paramagnetic, and no distinct <sup>1</sup>H NMR signals have been recorded. On the other hand, satisfactory <sup>1</sup>H NMR spectra have been obtained for complexes  $2(PF_6)-5(PF_6)$ . For the purpose of comparison, model complexes  $6(PF_6)$  and  $7(PF_6)$  were prepared in which the oligophenylene unit is present but the triarylamino group is lacking. These complexes were synthesized from ligand L6 or L7, respectively, which were obtained from the Suzuki coupling of 1,3-di(pyrid-2-yl)bromobenzene with phenyl boronic acid or 4-biphenyl boronic acid, respectively.

Single crystals of  $3(PF_6)$  and  $4(PF_6)$  were obtained by slowly diffusing *n*-hexane into their solutions in CH<sub>2</sub>Cl<sub>2</sub>. Figure 1 shows the thermal ellipsoid diagrams of the X-ray crystallographic structures of these two complexes. The osmium ion has an expected hexacoordinate octahedral configuration. The triarylamine motifs have a three-wheel propeller configuration. The Os-C bond of  $3(PF_6)$  and  $4(PF_6)$  has a length of 1.965(5) and 1.978(9) Å, respectively. The geometrical distance between the osmium ion and the amine nitrogen atom is 14.797 and 19.229 Å for  $3(PF_6)$  and  $4(PF_6)$ , respectively. The full crystallographic data are provided in the Experimental Section and Supporting Information (SI).

**Electrochemical Studies.** Figure 2 shows the cyclic voltammograms (CVs) and differential pulse voltammograms (DPVs) of  $1(PF_6)_2-5(PF_6)$ . The electrochemical data are summarized in Table 1. Complex  $1(PF_6)_2$  displays two anodic redox processes at +0.21 and +0.60 V vs Ag/AgCl, with a potential splitting ( $\Delta E$ ) of 390 mV. Complexes  $2(PF_6)-5(PF_6)$  show similar two redox waves. However, both waves shift to a slightly more positive region. In addition, the potential splitting becomes smaller ( $\Delta E = 320$ , 310, 300, and 300 mV for  $2(PF_6)$ ,  $3(PF_6)$ ,  $4(PF_6)$ , and  $5(PF_6)$ , respectively), and the difference of the potential splitting of these four complexes is small. By



**Figure 1.** Thermal ellipsoid diagram (30% probability) of the singlecrystal structure of (a)  $3(PF_6)$  and (b)  $4(PF_6)$ . Hydrogen atoms and anions are omitted for clarity. Atom color code: carbon, gray; nitrogen, blue; oxygen, red; osmium, navy.

comparing the potentials of these waves with the Os<sup>III/II</sup> potential of a model complex,  $[Os(dpb) (ttpy)](PF_6) (+0.36 V; dpb = 1,3-(pyrid-2-yl)benzene; ttpy = 4'-tolyl-2,2':6',2''-terpyridine; Figure S1 in the SI)<sup>18</sup> and the N<sup>•+/0</sup> potential of L2 (+0.70 V; L1–L5 have very similar N<sup>•+/0</sup> potential),<sup>11</sup> it is reasonable to assign the first anodic wave of 1(PF<sub>6</sub>)<sub>2</sub>–5(PF<sub>6</sub>) to the Os<sup>III/II</sup> process and the second one to the N<sup>•+/0</sup> process, respectively. Complexes 6(PF<sub>6</sub>) and 7(PF<sub>6</sub>) show an Os<sup>III/II</sup> process at +0.43 and +0.42 V vs Ag/AgCl, respectively (Figure S2).$ 

In the cathodic scan, a tpy-based reduction wave can be observed for all complexes. The comproportionation constant  $K_c$  for the equilibrium  $[Os^{II}-N] + [Os^{III}-N^{\bullet+}] \rightarrow 2[Os^{III}-N]$  ranges from  $1.2 \times 10^5$  to  $4.1 \times 10^6$  for  $1(PF_6)_2 - 5(PF_6)$ . This large comproportionation constant suggests that the one-electron-oxidized form  $[Os^{III}-N]$  has good thermodynamic stability, which will be beneficial for the following spectroelectrochemical measurements.

**Spectroscopic Studies.** The fact that complex  $1(PF_6)_2$  was isolated as the odd-electron form is also supported by its absorption spectrum, which shows an intense charge transfer transition at 950 nm. This band decreases upon either one-electron oxidation or one-electron reduction by stepwise electrolysis at a transparent indium–tin–oxide (ITO) glass



Figure 2. CVs (a–e) and DPVs (f) of  $1(PF_6)_2-5(PF_6)$  at a glassy carbon disk electrode in 0.1 M Bu<sub>4</sub>NClO<sub>4</sub>/CH<sub>2</sub>Cl<sub>2</sub>. The initial scan starts from 0 V and moves toward the positive potential.

### Table 1. Electrochemical Data

	$E_{1/2}/V (\Delta E_p/mV)$			
compound	anodic	cathodic	$\Delta E (mV)^{b}$	$K_{\rm c}^{\ c}$
$1(PF_6)_2$	+0.21 (180), + 0.60 (200)	-1.59 (180)	390	$4.1 \times 10^{6}$
$2(PF_6)$	+0.40 (230), + 0.72 (240)	-1.59 (210)	320	$2.7 \times 10^{5}$
$3(PF_6)$	+0.45 (200), + 0.76 (190)	-1.56 (200)	310	$1.8 \times 10^{5}$
$4(PF_6)$	+0.45 (200), + 0.75 (210)	-1.58 (200)	300	$1.2 \times 10^{5}$
$5(PF_6)$	+0.44 (190), + 0.74 (200)	-1.57 (180)	300	$1.2 \times 10^{5}$
[Os(dpb) (ttpy)](PF <sub>6</sub> )	+0.36 (70)	-1.48 (80)		
L2	+0.70 (100)			
<b>6</b> (PF <sub>6</sub> )	+0.43 (120)	-1.57 (120)		
7(PF <sub>6</sub> )	+0.42 (120)	-1.56 (110)		
			1-	

<sup>*a*</sup>Data in CH<sub>2</sub>Cl<sub>2</sub>. The electrochemical potentials are reported as the  $E_{1/2}$  value vs Ag/AgCl. Potentials vs ferrocene<sup>+/0</sup> can be estimated by subtracting 0.45 V.  $\Delta E_p$  refers to the peak-to-peak potential separation of each chemically reversible process. The relatively large  $\Delta E_p$  values of  $1(\text{PF}_6)_2 - 5(\text{PF}_6)$  are likely due to slow electron transfer kinetics under the current measurement conditions. <sup>*b*</sup>The potential splitting of two anodic waves. <sup>*c*</sup>K<sub>c</sub> =  $10^{\Delta E(\text{mV})/59}$ .

electrode (Figure 3). This phenomenon has been observed for related phen-1,4-diyl-bridged ruthenium or osmium–amine hybridized complexes<sup>9,14</sup> and forms the basis for theirs applications in NIR electrochromism.<sup>10</sup>

Figure 4 shows the absorption spectral changes of  $2(PF_6)$ – 4(PF<sub>6</sub>) upon one-electron (single) and the second one-electron (double) oxidations. In the single-oxidation step of  $2(PF_6)$ (potential was increased from +0.40 to +0.65 V vs Ag/AgCl), the metal-to-ligand charge transfer (MLCT) transitions in the visible decreased and new NIR absorptions around 1160 nm appeared (Figure 4a). The latter NIR transition is attributed to the donor-to-acceptor charge transfer (DACT) transitions in the odd-electron state ( $2^{2+}$ ). In the double-oxidation step (potential was increased from +0.65 to +1.0 V), the NIR transitions decreased and two absorption bands at 700 and 900 nm appeared (Figure 4b). The peak at 700 nm is characteristic of the N<sup>•+</sup>-localized transitions of triarylamine compounds.<sup>19</sup> This peak was also observed for  $3(PF_6)$  and  $4(PF_6)$  after double oxidation (Figure 4d and 4f). The peak at 900 nm of  $2^{3+}$  is possibly due to aminium-targeted charge transfer transitions. The appearance of some weak absorption at 2400 nm was observed in Figure 4a and 4b. These absorptions are very likely caused by the  $Os^{III}$  d-d transitions.<sup>20</sup>

During the oxidative spectroelectrochemical measurements of  $3(PF_6)$  and  $4(PF_6)$  (Figure 4c-f), the appearance of the DACT absorption can also be observed in the single-oxidation step, which decreases upon double oxidation. For complex  $4^{2+}$ , the DACT band is rather weak and severely overlaps with the higher energy side of the visible absorptions. The decrease of the DACT band upon double oxidation can be clearly distinguished as shown by the enlarged spectral changes in the NIR region in the inset of Figure 4f. No distinct NIR absorptions were observed when the model complexes  $8(PF_6)$ and  $9(PF_6)$  were subjected to oxidative electrolysis (Figure S3). In addition, when ligand L2 was subjected to similar oxidative electrolysis, the N<sup>•+</sup>-localized transitions at 750 nm appeared (Figure S4).<sup>11</sup> The absorptions with wavelength longer than 900 nm are negligible. These results support the assignment of



Figure 3. Absorption spectral changes of  $1(PF_6)_2$  upon one-electron oxidation (a) or reduction (b) in CH<sub>2</sub>Cl<sub>2</sub> upon stepwise oxidative electrolysis at an ITO glass electrode.

the above NIR absorptions of  $2^{2+}-4^{2+}$  to DACT absorptions. Some oligo-triarylamines are known to give NIR absorption bands in their oxidized forms,<sup>21</sup> which are attributable to intervalence charge transfer transitions between amine centers. This does not disagree with the interpretations of our results.

For the longer congener  $5(PF_6)$ , no distinct DACT band can be observed upon one-electron oxidation (Figure S5). Probably a very weak DACT band is buried inside the higher energy side of the visible absorptions of  $5^{2+}$ . However, the degree of osmium-amine electronic coupling in  $5^{2+}$  must be very weak

and difficult to estimate by spectroscopic analysis. The DACT bands of  $1^{2+}-4^{2+}$  are displayed in Figure 5a as a function of wavenumbers ( $\tilde{v}$ ). The DACT band of  $4^{2+}$  was



Figure 5. (a) DACT transitions of  $1^{2+}-4^{2+}$  in CH<sub>2</sub>Cl<sub>2</sub> as a function of wavenumbers. For complex  $4^{2+}$ , the Gussian-deconvoluted data is used. (b) Gaussian fitting of the NIR absorption spectra of  $4^{2+}$ . The black curve is the experimental data. The blue and green curves are the deconvoluted data. The blue curve is the deconvoluted DACT band of  $4^{2+}$ . The red curve is the sum of the deconvoluted data.

derived by Gaussian fitting of its NIR absorptions (Figure 5b). For complexes  $2^{2+}-4^{2+}$ , the DACT bands are symmetric. However, the DACT band of  $1^{2+}$  is nonsymmetric, with the lower energy side slightly narrower relative to the higher energy



Figure 4. Absorption spectral changes of  $2(PF_6)$  (a,b),  $3(PF_6)$  (c,d), and  $4(PF_6)$  (e,f) upon single (a,c,e) and double oxidation (b,d,f) in CH<sub>2</sub>Cl<sub>2</sub> upon stepwise oxidative electrolysis at an ITO glass electrode. The applied potential was referenced versus Ag/AgCl. (Inset in f) Enlarged plots in the NIR region.

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side. As discussed in the Introduction, the Marcus–Hush theory of mixed-valence chemistry should be applicable to  $1^{2+}-4^{2+}$ . The electronic coupling parameter  $V_{ab}$  was thus calculated to be 2310, 960, 460, and 190 cm<sup>-1</sup> for  $1^{2+}$ ,  $2^{2+}$ ,  $3^{2+}$ , and  $4^{2+}$ , respectively, according to  $V_{ab} = (\mu_{ge}\tilde{v}_{max})/eR_{ab}^{22}$  where  $\mu_{ge}$  is the transition dipole moment of the DACT band, e is the elementary charge, and  $R_{ab}$  is the diabatic electron transfer distance which was taken to be the DFT-calculated Os–N geometrical distance (Table 2). This equation is applicable to the CT band of any shape, and  $\mu_{ge}$  can be calculated from the integrated absorbance of the CT band.<sup>23</sup>

Table 2	Parameters	for NIR	Charge	Transfer	Transitions <sup>a</sup>
Table 2.	Parameters	IOP INTE	Charge	Transfer	Transitions

$\tilde{v}_{\rm max}~({\rm cm}^{-1})$	$\varepsilon_{\rm max}~({ m M}^{-1}~{ m cm}^{-1})$	$R_{ab}$ (Å) <sup>b</sup>	$V_{\rm ab}~({\rm cm}^{-1})^c$
10 530	9550	6.1	2310
8650	8600	10.5	960
9510	2970	14.8	460
9630	1030	19.2	190
	$\tilde{v}_{max} (cm^{-1})$ 10 530 8650 9510 9630	$\begin{array}{c} \tilde{v}_{\max} \ (\mathrm{cm}^{-1}) & \varepsilon_{\max} \ (\mathrm{M}^{-1} \ \mathrm{cm}^{-1}) \\ 10 \ 530 & 9550 \\ 8650 & 8600 \\ 9510 & 2970 \\ 9630 & 1030 \end{array}$	$ \begin{array}{c} \tilde{v}_{\max} \ (\mathrm{cm}^{-1}) & \varepsilon_{\max} \ (\mathrm{M}^{-1} \ \mathrm{cm}^{-1}) & R_{\mathrm{ab}} \ (\mathrm{\AA})^b \\ \\ 10 \ 530 & 9550 & 6.1 \\ \\ 8650 & 8600 & 10.5 \\ \\ 9510 & 2970 & 14.8 \\ \\ 9630 & 1030 & 19.2 \\ \end{array} $

<sup>*a*</sup>On the basis of the spectroelectrochemical results in CH<sub>2</sub>Cl<sub>2</sub>. <sup>*b*</sup>Estimated by the DFT-optimized Os–N geometrical distance. <sup>*c*</sup>V<sub>ab</sub> values calculated by ( $\mu_{ge} \tilde{\nu}_{max}$ )/eR<sub>ab</sub>.

Figure 6 shows the distance dependence plot of  $\ln(V_{ab})$  versus  $R_{ab}$  of  $1^{2+}-4^{2+}$ , where the four data can be well fitted to a



**Figure 6.** Distance dependence plot of  $\ln(V_{ab})$  as a function of  $R_{ab}$  (Å) from data in Table 2. The data was fitted to a linear equation with a slope of -0.19 Å<sup>-1</sup> and adjusted  $R^2$  of 0.99.

negative linear equation with a decay slope  $(-\gamma)$  of -0.19 Å<sup>-1</sup>. This suggests a tunneling-dominated electron-transfer mechanism. Such a linear relationship is well known for a series of related donor-acceptor compounds with a tunneling-dominated superexchange mechanism.<sup>12</sup> Note that the decay slope of the  $1^{2+}-4^{2+}$  series is slightly steeper with respect to the previously reported ruthenium-amine series with the same molecular wire,<sup>11</sup> where the decay slope was calculated to be -0.14 Å<sup>-1</sup>. We conjecture that this difference is caused by the different redox asymmetry of these two series compounds. As has been discussed in the electrochemical analysis, the cyclometalated osmium model complex [Os(dpb) (ttpy)](PF<sub>6</sub>) shows the Os<sup>III/II</sup> process at +0.36 V vs Ag/AgCl, while the  $N^{\bullet+/0}$  process of  $\hat{L1}\text{--}L5$  occurs at +0.70 V. In contrast, the corresponding cyclometalated ruthenium model complex  $[Ru(dpb) (tpy)](PF_6)$  shows the  $Ru^{III/II}$  process at +0.56 V.<sup>24</sup> This suggests that the osmium-amine series compounds have larger redox asymmetry relative to the ruthenium-amine series compounds, which may lead to the steeper decay slope of the osmium–amine series. Another possibility for the steeper slope of the osmium series is that the osmium series complexes may have a larger tunneling energy gap with respect to the ruthenium series.<sup>25</sup> The tunneling energy gap is difficult to determine; however, the redox state of cyclometalated osmium, cyclometalated ruthenium, and the bridging oligophenylene increases in an ascending order. This means that the energy gap between osmium and the bridge should be larger with respect to that between ruthenium and the bridge, which will lead to a larger tunneling energy gap for the osmium series relative to the ruthenium series.

It should be noted that  $R_{ab}$  may be much shorter with respect to the geometrical distance between redox sites due to a high degree of charge delocalization. This means that the calculated  $V_{ab}$  values are underestimated. However, this may have little influence on the comparison of the decay slope between two series because both series complexes were studied using the same method. The decay slopes of both ruthenium and osmium series are comparable to the attenuation factor ( $\beta = 0.46 \text{ Å}^{-1}$ ) of the oligophenylene wire determined by charger transfer dynamics by Wasielewski and co-workers.<sup>12e</sup> Note that the  $\beta$ value determined by charger transfer dynamics and the  $\gamma$  value determined by electronic coupling differ by a factor of 2, namely, the  $\beta$  value of 0.46 Å<sup>-1</sup> corresponds to a  $\gamma$  value of 0.23 Å<sup>-1</sup>.

DFT Studies. DFT calculations are known to provide useful information on the spin density distributions of mixed-valent compounds. We first performed the geometrical optimization of  $1^{2+}-4^{2+}$  on the level of theory of UB3LYP/LANL2DZ/6-31G\*/CPCM (see details in the Experimental Section). The left panel of Figure 7 shows the Mulliken spin density distributions  $(\alpha - \beta)$  and segmental analysis of these compounds optimized with this method. Compounds  $1^{2+}$  and  $2^{2+}$ show delocalized spin density distributions. To our surprise, the spin density of  $3^{2+}$  and  $4^{2+}$  are more biased toward or localized on the triarylamine segment. This result seems contradicting with the above electrochemical findings, which suggest that the one-electron oxidation of  $1^+-4^+$  is more likely associated with the  $\mathrm{Os}^{\mathrm{III/II}}$  process. In addition, we found that no electron paramagnetic resonance (EPR) signals could be recorded for  $\mathbf{\hat{1}}^{2+} - \mathbf{4}^{2+}$  either at room or low temperature. This also suggests that  $\mathbf{1}^{2+}{-}\mathbf{4}^{2+}$  are dominated by or have a large contribution from the Os(III) forms because common Os(III) complexes are known not to show distinct EPR signals due to the strong spin-orbital coupling effect.<sup>15</sup>

Being aware of the fact that DFT results are significantly dependent on the calculation method, we used the long-rangecorrected version of B3LYP, CAM-B3LYP functional,<sup>26</sup> to reperform geometrical optimization of  $1^{2+}-4^{2+}$ . The results obtained with UCAM-B3LYP show reasonable spin density distributions (right panel of Figure 7), where compounds  $1^{2+}$ are delocalized and the spin density of  $2^{2+}-4^{2+}$  are more biased toward or localized on the osmium component. These results make us question the reliability of the previously reported DFT calculations on the ruthenium-amine series compounds,<sup>11</sup> where UB3LYP was used and the spin density of long congeners was also found to localize on the triarylamine segment. Although the EPR results gave consistent information in this case, we are interested to know whether the use of UCAM-B3LYP will make a difference. The spin density distributions of three of the ruthenium-amine compounds calculated with UCAM-B3LYP are shown in Figure S6, which indeed gives very similar information with respect to those

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Figure 7. DFT-calculated spin density distributions and segmental analysis of  $1^{2+}-4^{2+}$  by using the UB3LYP (left) or UCAM-B3LYP (right) functional.

calculated with UB3LYP. These results suggest that DFT calculations in some circumstances are highly dependent on the functional and method used. Theoretical results alone may lead to incorrect information. It would be better to combine both experimental and theoretical data for the interpretation of a specific system.

# CONCLUSION

In summary, the electronic communication between cyclometalated osmium and redox-active triarylamine through the poligophenylene molecular wire has been investigated. Electrochemical and spectroelectrochemical measurements suggest that the osmium component was oxidized prior to the amine oxidation. The electron transfer from the neutral amine site to the oxidized osmium(III) component occurs via a tunnelingdominated mechanism with a decay slope of -0.19 Å<sup>-1</sup>, which is slightly steeper with respect to the previously reported ruthenium-amine series with the same molecular wire. This difference is possibly caused by the relative larger redox asymmetry or larger tunneling energy gap of the osmiumamine series compounds. In addition, DFT calculations with UCAM-B3LYP gave more reasonable results for the osmium complexes with respect to those with the UB3LYP functional. This suggests that the choice of functional is important for obtaining useful information consistent with experimental findings.

# EXPERIMENTAL SECTION

**Synthesis.** NMR spectra were recorded in the designated solvent on a Bruker Avance 300 or 400 MHz spectrometer. Spectra are reported in ppm values from residual protons of deuterated solvent. Mass data were obtained with a Bruker Daltonics Inc. Autoflex III MALDI-TOF mass spectrometer (Germany). The matrix for MALDI-TOF measurement is  $\alpha$ -cyano-4-hydroxycinnamic acid. Microanalysis was carried out using a Thermo Scientific Flash EA 1112 analyzer (USA) at the Institute of Chemistry, Chinese Academy of Sciences.  $[Os(tpy)(H_2O)_3](PF_6)_3$  was prepared according to the known procedure.<sup>17</sup> Ligands L1–L5 were prepared according to a previous report.<sup>11</sup>

**Synthesis of Complex 1(PF<sub>6</sub>)<sub>2</sub>.** To 7 mL of dry ethylene glycol were added  $[Os(tpy)(H_2O)_3](PF_6)_3$  (68.4 mg, 0.075 mmol) and ligand L1 (23.0 mg, 0.050 mmol). The mixture was refluxed for 1 h under microwave heating (power = 600 W). After cooling to room temperature, an excess of aq. KPF<sub>6</sub> was added. The resulting precipitate was collected by filtrating and washing with water and Et<sub>2</sub>O. The obtained solid was subjected to flash column chromatography on silica gel (eluent: acetone/H<sub>2</sub>O/aq. KNO<sub>3</sub>, 100/5/1), followed by anion exchange using KPF<sub>6</sub>, to give 28.0 mg of complex  $1(PF_6)_2$  in 48% yield as a brown solid. MALDI-MS (*m*/*z*): 883.5 for  $[M - 2PF_6]^{2+}$ . Anal. Calcd for C<sub>45</sub>H<sub>35</sub>F<sub>12</sub>N<sub>6</sub>O<sub>2</sub>P<sub>2</sub>Os·3H<sub>2</sub>O: C, 44.08, H, 3.37, N, 6.85. Found: C: 44.37, H, 3.07, N, 7.02.

**Synthesis of Complex 2(PF<sub>6</sub>).** This complex was prepared from  $[Os(tpy)(H_2O)_3](PF_6)_3$  and ligand L2 as a red solid in 58% yield using the similar procedure for the synthesis of complex  $1(PF_6)_2$  (eluent for column chromatography: acetone/CH<sub>2</sub>Cl<sub>2</sub>, 5/1). <sup>1</sup>H NMR (400 MHz, acetone- $d_6$ ): 3.84 (s, 6H), 6.67 (td, J = 6.5, 1.2 Hz, 2H), 6.05–7.05 (m, 6H), 7.07 (t, J = 6.6 Hz, 2H), 7.10–7.20 (m, 6H), 7.28 (d, J = 5.6 Hz, 2H), 7.60 (td, J = 7.6, 1.6 Hz, 2H), 7.71 (td, J = 8.0, 1.6

Hz, 2H), 7.80–7.95 (m, 3H), 8.49 (d, J = 8.0 Hz, 2H), 8.70 (d, J = 8.4 Hz, 2H), 8.74 (s, 2H), 9.00 (d, J = 8.0 Hz, 2H). MALDI-MS (m/z): 959.2 for  $[M - PF_6]^+$ . Anal. Calcd for  $C_{51}H_{39}F_6N_6O_2POs \cdot H_2O: C$ , 54.64; H, 3.69; N, 7.50. Found: C, 54.61; H, 3.59; N, 7.64.

**Synthesis of Complex 3(PF<sub>6</sub>).** This complex was prepared from  $[Os(tpy)(H_2O)_3](PF_6)_3$  and ligand L3 as a red solid in 73% yield using the similar procedure for the synthesis of complex  $1(PF_6)_2$  (eluent for column chromatography: acetone/CH<sub>2</sub>Cl<sub>2</sub>, 5/1). <sup>1</sup>H NMR (400 MHz, acetone- $d_6$ ): 3.83 (s, 6H), 6.70 (td, J = 6.4, 1.2 Hz, 2H), 6.92–7.05 (m, 8H), 7.08 (td, J = 6.6, 1.2 Hz, 2H), 7.12–7.18 (m, 4H), 7.30 (d, J = 6.0 Hz, 2H), 7.62 (td, J = 8.0, 1.6 Hz, 2H), 7.67 (d, J = 8.8 Hz, 2H), 7.72 (td, J = 7.6, 1.6 Hz, 2H), 7.84–7.92 (m, 3H), 8.13 (d, J = 8.4 Hz, 2H), 8.55 (d, J = 8.4 Hz, 2H), 8.72 (d, J = 8.0 Hz, 2H), 8.86 (s, 2H), 9.02 (d, J = 8.0 Hz, 2H). MALDI-MS (m/z): 1035.2 for [M – PF<sub>6</sub>]<sup>+</sup>. Anal. Calcd for C<sub>37</sub>H<sub>43</sub>F<sub>6</sub>N<sub>6</sub>O<sub>2</sub>POs·H<sub>2</sub>O: C, 57.18; H, 3.79; N, 7.02. Found: C, 57.13; H, 3.66; N, 7.26.

**Synthesis of Complex 4(PF<sub>6</sub>).** This complex was prepared from  $[Os(tpy)(H_2O)_3](PF_6)_3$  and ligand L4 as a red solid in 70% yield using the similar procedure for the synthesis of complex  $1(PF_6)_2$  (eluent for column chromatography: acetone/CH<sub>2</sub>Cl<sub>2</sub>, 5/1). <sup>1</sup>H NMR (300 MHz, acetone- $d_6$ ): 3.83 (s, 6H), 6.70 (t, J = 6.3 Hz, 2H), 6.90–7.20 (m, 14H), 7.31 (d, J = 5.4 Hz, 2H), 7.62 (m, 4H), 7.72 (t, J = 7.2 Hz, 2H), 7.79 (d, J = 8.4 Hz, 2H), 7.84–7.92 (m, 3H), 7.97 (d, J = 8.1 Hz, 2H), 8.19 (d, J = 8.4 Hz, 2H), 8.56 (d, J = 8.1 Hz, 2H), 8.72 (d, J = 8.1 Hz, 2H), 8.89 (s, 2H), 9.02 (d, J = 7.8 Hz, 2H). MALDI-MS (m/z): 1111.6 for [M – PF<sub>6</sub>]<sup>+</sup>. Anal. Calcd for C<sub>63</sub>H<sub>47</sub>F<sub>6</sub>N<sub>6</sub>O<sub>2</sub>POs·H<sub>2</sub>O: C, 59.43; H, 3.88; N, 6.60. Found: C, 59.46; H, 3.82; N, 6.88.

**Synthesis of Complex 5(PF<sub>6</sub>).** This complex was prepared from  $[Os(tpy)(H_2O)_3](PF_6)_3$  and ligand L5 as a red solid in 65% yield using the similar procedure for the synthesis of complex  $1(PF_6)_2$  (eluent for column chromatography: acetone/CH<sub>2</sub>Cl<sub>2</sub>, 5/1). <sup>1</sup>H NMR (300 MHz, acetone- $d_6$ ): 3.82 (s, 6H), 6.71 (t, J = 7.2 Hz, 2H), 6.90–7.20 (m, 14H), 7.31 (d, J = 5.7 Hz, 2H), 7.55–7.65 (m, 4H), 7.65–7.80 (m, 4H), 7.84 (d, J = 5.1 Hz, 2H), 7.84–7.92 (m, 3H), 7.95 (d, J = 5.1 Hz, 2H), 8.00 (d, J = 5.1 Hz, 2H), 8.21 (d, J = 8.4 Hz, 2H), 8.57 (d, J = 8.4 Hz, 2H), 8.72 (d, J = 8.1 Hz, 2H), 8.90 (s, 2H), 9.02 (d, J = 8.1 Hz, 2H). MALDI-MS (m/z): 1187.3 for  $[M - PF_6]^+$ . Anal. Calcd for C<sub>69</sub>H<sub>51</sub>F<sub>6</sub>N<sub>6</sub>O<sub>2</sub>POs·H<sub>2</sub>O: C, 61.42; H, 3.96; N, 6.23. Found: C, 61.00; H, 3.47; N, 6.39.

**Synthesis of Ligand L6.** To a suspension of 1,3-di(pyrid-2-yl)bromobenzene (311 mg, 1.0 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (58 mg, 0.050 mmol), and K<sub>2</sub>CO<sub>3</sub> (690 mg, 5.0 mmol) in a mixed solvent of degassed THF/H<sub>2</sub>O (18 mL/2 mL) was added phenylboronic acid (146 mg, 1.2 mmol). The mixture was stirred at 90 °C for 12 h. The solvent was evaporated under reduced procedure. The crude product was purified through column chromatography on silica gel (eluent: CH<sub>2</sub>Cl<sub>2</sub>/EtOAc, 15/1) to give 200 mg of 3,5-di(pyrid-2-yl)-1,1'-biphenyl (L6) as a pale yellow solid in 65% yield. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.25–7.35 (m, 2H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 2H), 8.60 (t, *J* = 1.5 Hz, 1H), 8.75 (d, *J* = 4.2 Hz, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  120.84, 122.39, 124.49, 126.42, 127.43, 127.58, 128.79, 136.79, 140.47, 140.96, 142.38, 149.74, 157.19. EI-MS: 308 for [M]<sup>+</sup>.

Synthesis of Ligand L7. To a suspension of 1,3-di(pyrid-2yl)bromobenzene (311 mg, 1.0 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (58 mg, 0.050 mmol), and K<sub>2</sub>CO<sub>3</sub> (690 mg, 5.0 mmol) in a mixed solvent of degassed THF/H<sub>2</sub>O (18 mL/2 mL) was added 4-biphenylboronic acid (238 mg, 1.2 mmol). The mixture was stirred at 90 °C for 12 h. The solvent was evaporated under reduced procedure. The crude product was purified through column chromatography on silica gel (eluent: CH<sub>2</sub>Cl<sub>2</sub>/EtOAc, 15/1) to give 212 mg of 3,5-di(pyrid-2-yl)-1,1':4',1''terphenyl (L7) as a pale yellow solid in 55% yield. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.25–7.35 (m, 2H), 7.37 (t, J = 7.2 Hz, 1H), 7.48 (t, J = 7.2 Hz, 2H), 7.68 (d, J = 7.2 Hz, 2H), 7.71 (d, J = 8.1 Hz, 2H), 7.81 (td, J = 7.5, 1.8 Hz, 2H), 7.87 (d, J = 8.1 Hz, 2H), 7.92 (d, J = 7.8 Hz, 2H), 8.36 (d, J = 1.5 Hz, 2H), 8.61 (s, 1H), 8.76 (d, J = 4.8 Hz, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  120.87, 122.43, 124.58, 126.28, 127.10, 127.42, 127.51, 127.79, 128.87, 136.82, 139.82, 140.40, 140.54, 140.71, 141.82, 149.77, 157.17. EI-MS: 384 for [M]<sup>+</sup>.

Synthesis of Complex 6(PF<sub>6</sub>). To a mixture of 2 mL of DMF and 3 mL of ethylene glycol were added  $[Os(tpy)Cl_3]$  (0.10 mmol, 53 mg) and ligand L6 (0.10 mmol, 31 mg). The mixture was refluxed under microwave heating for 30 min at a power of 375 W and then another 10 min at a power of 600 W. After cooling to room temperature, an excess of aqueous KPF<sub>6</sub> was added. The resulting precipitate was collected by filtering and washing with water and Et<sub>2</sub>O. The crude solid was purified through flash column chromatography on silica gel, followed by anion exchange using  $KPF_{6}$  to give 57 mg of  $6(PF_6)$  in 65% yield as a red solid. <sup>1</sup>H NMR (300 MHz, acetone- $d_6$ ):  $\delta$  6.67 (t, J = 6.3 Hz, 2H), 7.00 (d, J = 5.7 Hz, 2H), 7.10 (t, J = 6.0 Hz, 2H), 7.35–7.45 (m, 3H), 7.60 (d, J = 7.8 Hz, 2H), 7.63 (d, J = 7.8 Hz, 2H), 7.71 (td, J = 7.8, 1.5 Hz, 2H), 7.88 (t, J = 7.8 Hz, 1H), 8.03 (d, J = 7.2 Hz, 2H), 8.51 (d, J = 8.4 Hz, 2H), 8.71 (d, J = 8.1 Hz, 2H), 8.82 (s, 2H), 9.01 (d, J = 7.8 Hz, 2H). MALDI-MS (m/z): 732.2 for [M - M]PF<sub>6</sub>]<sup>+</sup>. Anal. Calcd for C<sub>37</sub>H<sub>26</sub>F<sub>6</sub>N<sub>5</sub>POs·H<sub>2</sub>O: C, 49.72; H, 3.16; N, 7.84. Found: C, 50.10; H, 3.23; N, 7.68.

**Synthesis of Complex 7(PF<sub>6</sub>).** This complex was prepared from  $[Os(tpy)Cl_3]$  (0.10 mmol, 53 mg) and ligand L7 (0.10 mmol, 38 mg) as a red solid in 71% yield (67 mg of product was obtained) using the similar procedure for the synthesis of complex **6**(PF<sub>6</sub>). <sup>1</sup>H NMR (300 MHz, acetone-*d*<sub>6</sub>):  $\delta$  6.70 (td, *J* = 6.6, 1.5 Hz, 2H), 7.00–7.15 (m, 4H), 7.30 (d, *J* = 5.7 Hz, 2H), 7.42 (t, *J* = 4.5 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 2H), 7.62 (td, *J* = 7.5, 1.5 Hz, 2H), 7.72 (td, *J* = 7.8, 1.5 Hz, 2H), 7.80–7.86 (m, 2H), 7.86–7.95 (m, 3H), 8.18 (d, *J* = 8.4 Hz, 2H), 8.56 (d, *J* = 8.1 Hz, 2H), 8.71 (d, *J* = 8.1 Hz, 2H), 8.87 (s, 2H), 9.01 (d, *J* = 8.1 Hz, 2H). MALDI-MS (*m*/*z*): 808.3 for  $[M - PF_6]^+$ . Anal. Calcd for C<sub>43</sub>H<sub>30</sub>F<sub>6</sub>N<sub>5</sub>POs·2H<sub>2</sub>O: C, 52.28; H, 3.47; N, 7.09. Found: C, 52.34; H, 3.44; N, 6.74.

X-ray Crystallography. The X-ray diffraction data were collected using a Rigaku Saturn 724 diffractometer on a rotating anode (Mo K $\alpha$ radiation, 0.71073 Å) at 173 K. The structure was solved by direct method using SHELXS-97<sup>27</sup> and refined with Olex2.<sup>28</sup> The structure graphics were generated using Olex2. Crystallographic data for  $3(PF_6)$ (CCDC: 1403263):  $C_{57}H_{43}F_6N_6O_2OsP$ , M = 1179.14, monoclinic, space group  $P_1 2_1/c1$ , a = 14.214(3) Å, b = 15.470(3) Å, c = 24.639(5)Å,  $\alpha = 90^{\circ}$ ,  $\beta = 99.784(2)^{\circ}$ ,  $\gamma = 90^{\circ}$ , U = 5339.2(19) Å<sup>3</sup>, T = 173 K, Z = 4, 42 007 reflections measured, radiation type Mo K $\alpha$ , radiation wavelength 0.71073 Å, final R indices R1 = 0.0573, wR2 = 0.1302, R indices (all data) R1 = 0.0649, wR2 = 0.1346. Crystallographic data for 4(PF<sub>6</sub>) (CCDC: 1403264): 2( $C_{63}H_{47}F_6N_6O_2O_8P$ )·5(CH<sub>2</sub>Cl<sub>2</sub>), M = 2935.10, monoclinic, space group  $P_1 2_1/c1$ , a = 52.130(18) Å, b =8.757(2) Å, c = 26.681(9) Å,  $\alpha = 90^{\circ}$ ,  $\beta = 93.943(4)^{\circ}$ ,  $\gamma = 90^{\circ}$ , U =12151(7) Å<sup>3</sup>, T = 173 K, Z = 4, 106 506 reflections measured, radiation type Mo K $\alpha$ , radiation wavelength 0.71073 Å, final R indices R1 = 0.0885, wR2 = 0.1535, R indices (all data) R1 = 0.1040, wR2 = 0.1598. It should be mentioned that single crystals of  $3(PF_6)$  and  $4(PF_6)$  were obtained after several attempts by slowly diffusing *n*hexane into their solutions in CH2Cl2. No solvate of water was found on the crystal structures. However, the samples for elemental analysis were directly obtained after column chromatography where water was added in the eluent. It is reasonable to compensate the microanalysis data with water solvate.

**Spectroscopic Measurement.** Absorption spectra were recorded on a PE Lambda 750 UV/vis/NIR spectrophotometer at room temperature. Spectroelectrochemical measurements were performed in a thin layer cell (optical length 0.2 cm), in which a transparent ITO glass electrode (<10  $\Omega$ /square) was set in the indicated solvent that contained the compound to be studied (about 5 × 10<sup>-5</sup> M) and 0.1 M Bu<sub>4</sub>NClO<sub>4</sub> as the supporting electrolyte. A platinum wire and Ag/AgCl in saturated aqueous NaCl was used as the counter electrode and reference electrode, respectively. The cell was put into the spectrometer to monitor the spectral change during electrolysis.

**Electrochemical Measurement.** All electrochemical measurements were taken using a CHI 660D potentiostat with a onecompartment electrochemical cell under an atmosphere of nitrogen. All measurements were carried out in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M "Bu<sub>4</sub>NClO<sub>4</sub> as the supporting electrolyte at a scan rate of 100 mV/s (for cyclic voltammetry). The working electrode was a glassy carbon disk electrode (d = 3 mm). The electrode was polished prior to use

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with 0.05  $\mu$ m alumina and rinsed thoroughly with water and acetone. A large area platinum wire coil was used as the counter electrode. All potentials are referenced to Ag/AgCl electrode in saturated aqueous NaCl without regard for the liquid junction potential. Potentials vs ferrocene<sup>+/0</sup> can be deduced by subtracting 0.45 V.

**Computational Methods.** DFT calculations were carried out using the B3LYP<sup>29</sup> or CAM-B3LYP<sup>26</sup> exchange correlation functional and implemented in the Gaussian 09 program package. The electronic structures of complexes were determined using a general basis set with the Los Alamos effective core potential LanL2DZ basis set for osmium and 6-31G\* for other atoms.<sup>30</sup> No symmetry constraints were used in the optimization (nosymm keyword was used). Solvent effects (CH<sub>2</sub>Cl<sub>2</sub>) are included in all calculations with the conductor-like polarizable continuum model (CPCM).<sup>31</sup> Frequency calculations have been performed with the same level of theory to ensure the optimized geometries to be local minima. All orbitals have been computed at an isovalue of 0.02 e/bohr<sup>3</sup>.

### ASSOCIATED CONTENT

#### **S** Supporting Information

CVs of L2,  $[Os(dpb) (ttpy)](PF_6)$ ,  $6(PF_6)$ , and  $7(PF_6)$ ; absorption spectral changes of  $6(PF_6)$ ,  $7(PF_6)$ , L2, and  $5(PF_6)$ upon oxidative electrolysis; DFT-calculated spin density distribution of the ruthenium–amine series compounds using the UCAM-B3LYP functiona;, Cartesian coordinates of DFToptimized structures; NMR and mass spectra of new compounds; X-ray crystallographic data of  $3(PF_6)$  and  $4(PF_6)$ in cif format. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/ acs.inorgchem.5b01828.

CVs of L2,  $[Os(dpb) (ttpy)](PF_6)$ ,  $6(PF_6)$ , and  $7(PF_6)$ ; absorption spectral changes of  $6(PF_6)$ ,  $7(PF_6)$ , L2, and  $5(PF_6)$  upon oxidative electrolysis; DFT-calculated spin density distribution of the ruthenium–amine series compounds using the UCAM-B3LYP functiona;, Cartesian coordinates of DFT-optimized structures; NMR and mass spectra of new compounds (PDF)

X-ray crystallographic data of  $3(PF_6)$  in cif format (CIF) X-ray crystallographic data of  $4(PF_6)$  in cif format (CIF)

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#### Notes

The authors declare no competing financial interest.

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