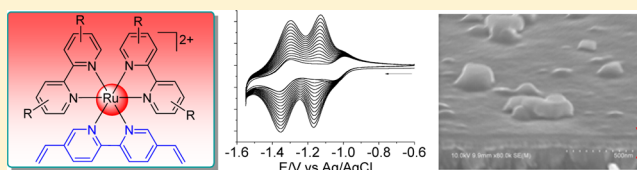# Synthesis and Reductive Electropolymerization of Metal Complexes with 5,5′-Divinyl-2,2′-Bipyridine

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S *Supporting Information*

ABSTRACT: Eight transition-metal complexes with 5,5′-divinyl-2,2′-bipyridine (5,5′-dvbpy) or 4,4′-divinyl-2,2′-bipyridine (4,4′-dvbpy) have been synthesized and studied. The ruthenium complexes $[Ru(5,5′-dvbpy)(bpy)_2]^{2+}$, $[Ru(5,5′-dvbpy)(4,4′-dpbpy)_2]^{2+}$, and $[Ru(5,5′-dvbpy)(5,5′-dpbpy)_2]^{2+}$ (bpy = 2,2′-bipyridine; dpbpy = diphenyl-2,2′-bipyridine) with one 5,5′-dvbpy ligand have been successfully deposited on electrode surfaces by reductive electropolymerization. The resulting films are stable and adherent and show well-defined redox processes. In contrast, the complex $[Ru(4,4′-dvbpy)(bpy)_2]^{2+}$ does not polymerize under the same conditions. Complexes $[Ru(5,5′-dvbpy)_2(bpy)]^{2+}$ and $[Ru(5,5′-dvbpy)_3]^{2+}$ with two or three 5,5′-dvbpy ligands have been polymerized as well. As a result of increasing degrees of entanglement, the resulting polymeric films show larger charge-trapping currents and smaller apparent diffusion constants than films of $[Ru(5,5′-dvbpy)(bpy)_2]^{2+}$. The electrochemical properties of the iridium complex $[Ir(5,5′-dvbpy)(ppy)_2]^+$ (ppy = 2-phenylpyridine) and the rhenium complex $[Re(5,5′-dvbpy)(CO)_3Cl]$ have been studied. The former complex can be polymerized, but the films show an irreversible anodic process. The latter complex does not polymerize under the same conditions. Additionally, characterizations of the above polymeric films using FTIR, SEM, and spectroscopic techniques are presented.

INTRODUCTION

Reductive electropolymerizations of vinyl-substituted polypyridine transition-metal complexes are well established for the in situ deposition of metallopolymeric films on electrode surfaces.[1] These films are stable, adherent, and electrochemically active. Their composition, electrochemistry, and thickness can be well controlled. These films are useful in a wide range of applications such as electrocatalysis,[2] photocatalysis,[3] electrochemiluminescence,[4] electrochromism,[5] ion and oxygen sensing,[6] and electrode coating.[7] It should be noted that two of the most popular vinyl-substituted polypyridine ligands for preparing such films are 4-methyl-4′-vinyl-2,2′-bipyridine[8] (vbpy, Figure 1) and 4′-vinyl-2,2′:6′,2″-terpyridine (vtpy),[9] although other sources have been studied as well.[10] Since the pioneering works of Murray, Meyer, and Abruña in the 1980s,[1] many transition-metal complexes with these two ligands, such as ruthenium,[1b,8a,c,9a] iron,[1b,9a] cobalt,[2a,9a,b] osmium,[8a,b] and

rhenium complexes,[11] have been synthesized and used for the preparations of electropolymerized films.

Recently we have embarked on a project to study bis-cyclometalating ligand-bridged open-shell bis-ruthenium complexes with redox-switching absorptions in the near-infrared (near-IR) region.[12] By using the above reductive electropolymerization strategy, two *bis-tridentate* complexes with vtpy ligands have been successfully deposited onto electrode surfaces, and the resulting films exhibited interesting near-IR electrochromic behaviors.[5b,c] Our next target is to prepare films with a *tris-bidentate* bisruthenium complex bridged by 1,4-bis(2-pyridyl)benzene.[13] This complex displayed redox-switching absorptions at 1300 nm, which is a region of particular interest for fiber-optic communications.[14] To this end, a vinyl-substituted bidentate polypyridine ligand is needed. The well-known compound vbpy is certainly a good choice. However, the synthesis of vbpy is somewhat tedious, which features an elimination of 4-methoxyethyl-4′-methyl-2,2′-bipyridine or an olefination of 4′-methyl-2,2′-bipyridine-4-carboxaldehyde as the key step.[5a,15] These two intermediates are in turn synthesized from a relatively expensive starting material, 4,4′-dimethyl-2,2′-bipyridine.[15,16] These difficulties prompted us to search for alternative options. We previously reported a facile method for the synthesis of vinyl-substituted polypyridine compounds via a Suzuki coupling between
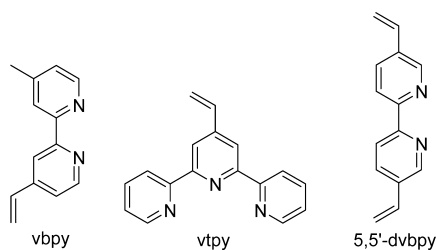
Figure 1. Vinyl-substituted polypyridine ligands.

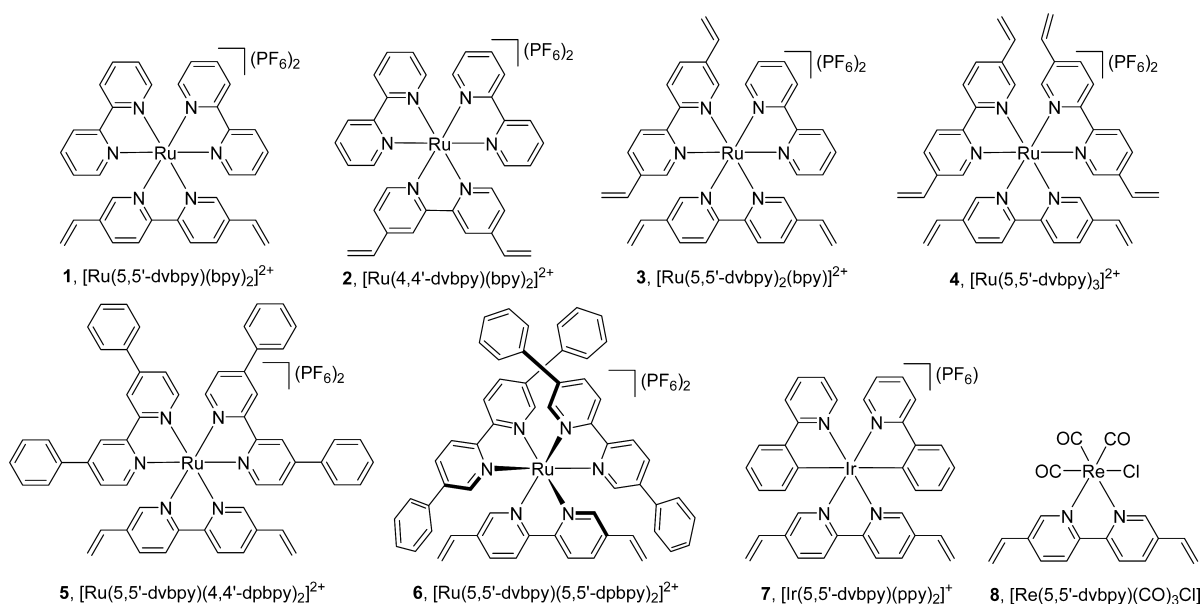vbpy   vtpy   5,5'-dvbpy

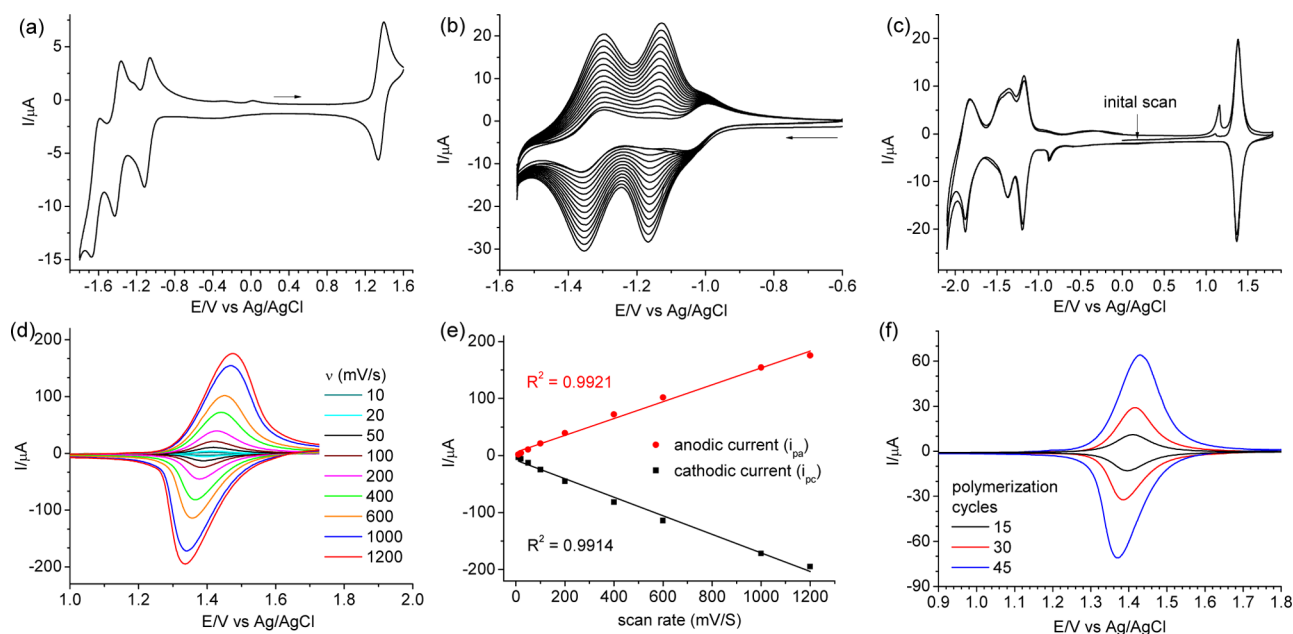**Figure 2.** Complexes studied in this paper.

Figure 3. (a) CV of **1** in CH₃CN at a Pt electrode. (b) Reductive electropolymerization of **1** (0.5 mM in CH₃CN) on a Pt-disk electrode ($d = 2$ mm) by 15 repeated cyclic potential scans at 100 mV/s between −0.60 and −1.55 V vs Ag/AgCl in 0.1 M Bu₄NClO₄/CH₃CN. (c) CV of the polymeric films obtained in (b) at a scan rate of 100 mV/s in a clean supporting electrolyte solution. (d) Anodic CVs of the polymeric films obtained in (b) at different scan rates from 10 to 1200 mV/s. (e) Linear dependence of the peak currents in (d) as a function of the scan rate. (f) CVs of polymeric films obtained after 15, 30, and 45 electropolymerization cycles. The scan rate was 100 mV/s.

potassium vinyltrifluoroborate and bromo-substituted polypyridines.[17] Among them, 5,5′-divinyl-2,2′-bipyridine (5,5′-dvbpy) can be readily obtained via two straightforward steps from a cheap starting material, 2,2′-bipyridine (bpy). In this paper, we present the synthesis and electropolymerization studies of a series of transition-metal complexes **1−8** (Figure 2) containing 5,5′-dvbpy or the related ligand 4,4′-divinyl-2,2′-bipyridine (4,4′-dvbpy).[17] As will be presented below, 5,5′-dvbpy is indeed a very efficient ligand to transform metal complexes into polymeric films and thus a good substitute for vbpy.

■ RESULTS AND DISCUSSION

Synthesis. Complexes **1−8** were synthesized by conventional methods. The reactions of [*cis*-Ru(bpy)₂Cl₂·2H₂O][18] with 5,5′-dvbpy or 4,4′-dvbpy, followed by anion exchange with KPF₆, afforded complexes **1** and **2** in good yield. The reaction of 2 equiv of 5,5′-dvbpy with RuCl₃·3H₂O gave [Ru(5,5′-dvbpy)₂Cl₂], which was then treated with bpy to afford complex **3** in 57% yield. The synthesis of [Ru(5,5′-dvbpy)₃]-(PF₆)₂ (**4**) has been reported previously.[17] Complexes **5** and **6** were prepared from the reactions of [Ru(4,4′-dpbpy)₂Cl₂] or [Ru(5,5′-dpbpy)₂Cl₂] with 5,5′-dvbpy, where 4,4′-dpbpy is 4,4′-diphenyl-2,2′-bipyridine[19] and 5,5′-dpbpy is 5,5′-diphenyl-

2,2′-bipyridine,[20] respectively. We were interested to know if complexes with substituents on the auxiliary ligands, such as **5** and **6**, could be electropolymerized or not. The ligand 5,5′-dpbby was previously synthesized from the homocoupling of 3-phenylpyridine[21] with 2-bromo-3-phenylpyridine.[20b] We prepared this compound via a Suzuki coupling between 5,5′-dibromo-2,2′-bipyridine[17,22] and phenylboronic acid in good yield, and we feel that this method is more straightforward and convenient for the preparations of bpy derivatives with aryl substituents on the 5,5′-positions.[23] The iridium complex **7** and rhenium complex **8** were synthesized from the reactions of 5,5′-dvbpy with [Ir(ppy)$_2$Cl]$_2$[24] (ppy = 2-phenylpyridine) and Re(CO)$_5$Cl, respectively. The details of synthesis and characterization data for all complexes are given in the Experimental Section.

Electrochemical Studies. We first carried out the electrochemical studies of complex **1** at a homemade Pt-disk electrode (d = 2 mm). This complex shows a Ru$^{II/III}$ wave at +1.37 V and three ligand reduction couples at −1.09, −1.40, and −1.63 V vs Ag/AgCl (Figure 3a and Table 1). When the

Table 1. Electrochemical Data

	$E_{1/2}$(monomer)^a		$E_{1/2}$(polymer)	
compd	anodic	cathodic	anodic	cathodic
[Ru(5,5′-dvbpy)(bpy)$_2$](PF$_6$)$_2$ (**1**)	+1.37	−1.09, −1.40, −1.63	+1.37	−1.18, −1.36, −1.85
[Ru(4,4′-dvbpy)(bpy)$_2$](PF$_6$)$_2$ (**2**)	+1.33	−1.19, −1.42, −1.65		
[Ru(5,5′-dvbpy)$_2$(bpy)](PF$_6$)$_2$ (**3**)	+1.40	−1.06, −1.20, −1.56	+1.32	−1.26, −1.47
[Ru(5,5′-dvbpy)$_3$](PF$_6$)$_2$ (**4**)	+1.39	−1.05, −1.19, −1.38	+1.37	−1.28, −1.47
[Ru(5,5′-dvbpy)(4,4′-dpbby)$_2$](PF$_6$)$_2$ (**5**)	+1.28	−1.12, −1.34, −1.56	+1.26	−1.19, −1.35, −1.84
[Ru(5,5′-dvbpy)(5,5′-dpbby)$_2$](PF$_6$)$_2$ (**6**)	+1.36	−1.10, −1.28, −1.48	+1.35	−1.08, −1.26
[Ir(5,5′-dvbpy)(ppy)$_2$](PF$_6$) (**7**)	+1.40	−1.06, −1.58	+1.41^b	−1.27
[Re(5,5′-dvbpy)(CO)$_3$Cl] (**8**)	+1.56^b	−1.09		

^{a}The potential is reported as the $E_{1/2}$ value vs Ag/AgCl unless otherwise noted. $^b E_{p,anodic}$, irreversible.

potential was scanned repeatedly between −0.60 and −1.55 V, the current increased gradually and continuously (Figure 3b), which indicated the in situ deposition of polymeric films on the electrode surface. Figure 3c displays the cyclic voltammogram (CV) of the polymeric film in a clean supporting electrolyte solution at a scan rate of 100 mV/s. The well-defined Ru$^{II/III}$ wave and three ligand reduction couples are retained. The Ru$^{II/III}$ potential remains unchanged after polymerization. However, the first reduction wave occurs at a more negative potential after polymerization (−1.18 vs −1.09 V). The first reduction event of the monomer is very likely associated with 5,5′-dvbpy. After polymerization, the vinyl groups of 5,5′-dvbpy were transformed into saturated carbon−carbon bond chains and the reduction became slightly more difficult. In addition, the CV of the polymeric film is more symmetric than that of the monomer. For instance, the potential separations between the anodic peak and cathodic peak (ΔE_{pa-pc}) of the Ru$^{II/III}$ wave are 20 and 60 mV for the polymer and monomer, respectively. Ideally, a surface-confined reversible wave should show a totally symmetric CV. The appearance of a slightly asymmetric profile reflects the charge repulsion effect between

neighboring metal components in the polymeric films. The anodic and cathodic currents of the polymer are linearly dependent on the scan rate (Figure 3d,e), which is characteristic of redox events confined on electrode surfaces. The surface coverage of the films can be simply varied by changing the potential cycle numbers during electropolymerization. For instance, Figure 3f shows the CVs of the films obtained after 15, 30, and 45 potential cycles between −0.60 and −1.55 V of 0.5 mM **1** in CH$_3$CN (the CVs for the polymerization processes are given in Figure S1 in the Supporting Information), which correspond to surface coverages of 2.3 × 10^{-9}, 5.7 × 10^{-9}, and 14.3 × 10^{-9} mol/cm^2, respectively, as measured by the charge under the Ru$^{II/III}$ wave. It should also be noted that the electropolymerization process took place equally well when the potential was scanned through the third reduction wave of **1**. However, no distinct electropolymerization was evident when the potential was scanned only through the first reduction wave (Figure S2, Supporting Information).

In stark contrast, the polymerization efficiency of complex **2** with 4,4′-dvbpy is very low, as indicated by the CVs shown in Figure S3 (Supporting Information). This is possibly caused by steric effects rather than electronic considerations. It is well-known that the ruthenium complex [Ru(bpy)(vbpy)$_2$]$^{2+}$ with vinyl substituents on the 4- or 4′-position of the auxiliary ligands can be smoothly polymerized by an electrochemical method.[8a,c] In the case of complex **2**, reductions of the ligands and vinyl groups possibly yield some dimetallic compounds as the major products via radical−radical coupling.[1c] However, due to the proximity of two vinyl groups, the chain propagation is inhibited. Since the synthesis of 4,4′-dvbpy is much more difficult than that of 5,5′-dvbpy,[25] we will focus on complexes with the latter ligand.

Complex **3** with two 5,5′-dvbpy ligands can be polymerized smoothly (Figure 4a), and the resulting polymers are stable (Figure 4b). However, the films of complex **4** with three 5,5′-dvbpy ligands obtained after electropolymerization are not as stable. Figure 4d shows the CV of a polymeric film of **4**. Both anodic and cathodic currents decreased considerably after repeated potential scans, which posed a serious problem for practical applications. The sharp prepeaks just before the metal-based oxidation and the ligand-based reduction are charge-trapping peaks, which were first observed for spatially segregated bilayer redox-active films by Murray and co-workers[1a,26] and later evidenced in numerous single- and multiple-component redox-acitve films.[27] The presence of charge-trapping peaks is attributed to redox sites trapped in the entangled polymeric films that are electronically isolated from the electrode surface, so that their charges are released at potentials just before the metal-based oxidation or the ligand-based reduction. By comparing Figures 3c and 4b,d, we find that the charge-trapping current becomes increasingly large from the films of complex **1** to **3** and **4**. This is reasonable, considering the fact that complex **1** has the smallest number of vinyl groups per metal component and the resulting polymeric films must has the lowest degree of entanglement.

Gratifyingly, complexes **5** and **6** with either 4,4′-dpbby or 5,5′-dpbby could be polymerized smoothly. The CVs recorded during the electropolymerization processes are shown in Figures S6 and S7 (Supporting Information). Figure 4e,f displays the CVs of representative polymeric films for these two compounds. It seems that the steric hindrance from the auxiliary ligands dose not inhibit the electropolymerization of these complexes. The iridium complex **7** can be polymerized as
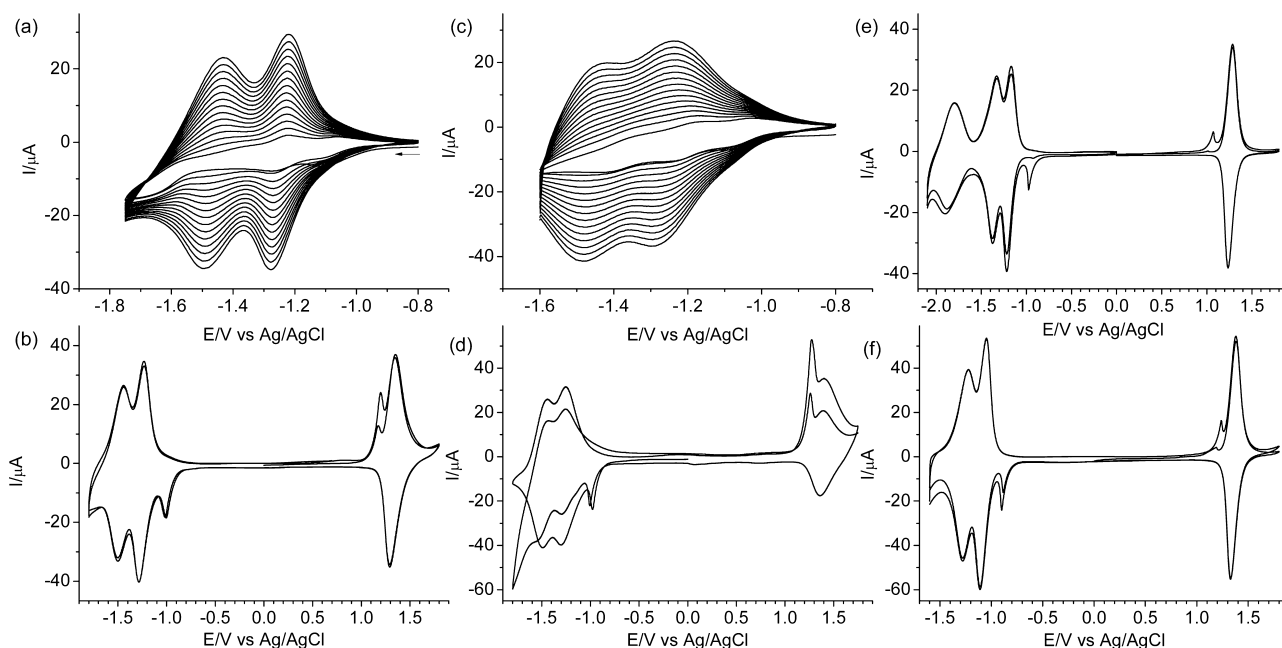
Figure 4. (a, c) Reductive electropolymerization of **3** and **4** by 15 repeated cyclic potential scans at 100 mV/s. (b, d) CVs at a scan rate of 100 mV/s of the polymeric films obtained in (a) and (c), respectively. (e, f) CVs at a scan rate of 100 mV/s of the polymeric films of **5** and **6** obtained after 15 repeated cyclic potential scans. The CVs of monomers **3**−**6** and those recorded during the electropolymerizations of **5** and **6** are given in Figures S4−S7 (Supporting Information).

well (Figure 5). The cathodic scan of the obtained polymeric films shows stable and reproducible CVs. However, in the anodic scan of the polymer, only an irreversible peak is observed in the initial cycle (Figure 5b). The rhenium complex **8** shows a chemically reversible reduction wave at −1.09 V vs Ag/AgCl and an irreversible reduction at a further negative potential (Figure S9a, Supporting Information). The latter peak

is possibly associated with reduction of the metal site (Re$^{I/0}$).[28] However, as demonstrated by Figure S9b (Supporting Information), the electropolymerization efficiency of **8** is quite low.

It is accepted[29] that charge transport process in redox polymeric films occur by self electron exchange between oxidized and reduced redox sites in proximity in combination with a charge-compensating flow of counterions, associated solvent, and involved polymer chain motions. It can be regarded as a diffusion process where coupled electron and ion movement controls the value of the apparent diffusion constant (D_{app}) for charge transport. Thus, the measurement of D_{app} will provide some useful information for this process. Potential step chronoamperometric experiments were carried out for three polymeric films prepared from **1**, **3**, and **4**. A linear relationship of current vs (time)$^{-1/2}$ is observed for all polymers at sufficiently short time (Figure 6). The slopes of three linear
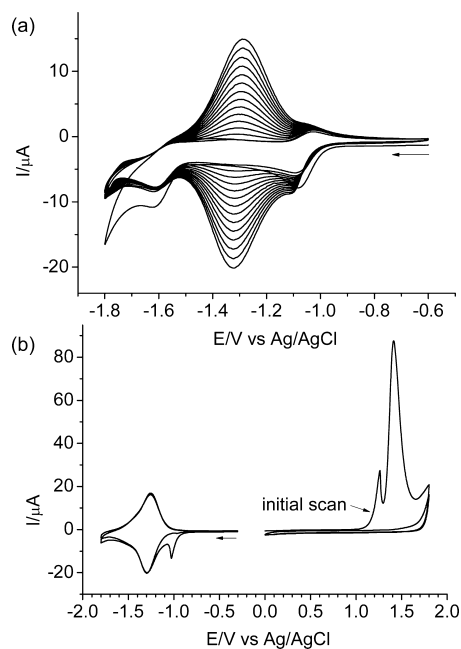

Figure 5. (a) Reductive electropolymerization of the iridium complex **7** (0.5 mM in CH$_3$CN) on a Pt-disk electrode (*d* = 2 mm) by 15 repeated cyclic potential scans at 100 mV/s between −0.60 and −1.80 V vs Ag/AgCl in 0.1 M Bu$_4$NClO$_4$/CH$_3$CN. (b) CV of the polymeric films obtained in (b) at a scan rate of 100 mV/s.
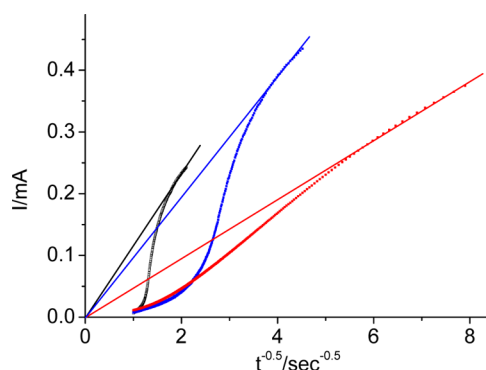

Figure 6. Cottrell plots of current vs (time)$^{-1/2}$ of poly-**1** (black line), poly-**3** (blue line), and poly-**4** (red line) films on a Pt-disk electrode (*d* = 2 mm). The surface coverages are 2.6 × 10^{-8}, 1.3 × 10^{-8}, and 0.9 × 10^{-8} mol/cm^2, respectively.

curves are 11.6×10^{-5}, 9.7×10^{-5}, and 4.7×10^{-5}, respectively, which give the $D_{app}^{1/2}C$ values of 6.7×10^{-8}, 5.6×10^{-8}, and 2.7×10^{-8} mol/(cm^{2}s$^{1/2}$) for above three polymeric films, according to the Cottrell equation $i = nFAD_{app}^{1/2}C/(\pi t)^{1/2}$.[1b,30] If the ruthenium concentration C is taken to be 1.6×10^{-3} mol/cm^3 as $[Ru(vbpy)_3]^{2+}$ polymers,[1b] the D_{app} values are 17.5×10^{-10}, 12.2×10^{-10}, and 2.8×10^{-10} cm^2/s for poly-**1**, poly-**3**, and poly-**4** films, respectively. It is reasonable that poly-**1** has a higher D_{app} value than poly-**3** and poly-**4** films, because poly-**1** has the lowest degree of entanglement. The D_{app} value of the poly-**4** film is comparable to that of a poly-$[Ru(vbpy)_3]^{2+}$ film reported by Murray and co-workers (2.2×10^{-10} cm^2/s).[1b]

FTIR Spectroscopy of Polymeric Films. Figure 7 shows the infrared spectra of $[Ru(bpy)_3](PF_6)_2$, **4**, and a poly-**4**
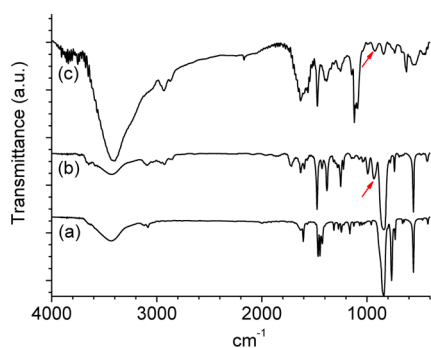

Figure 7. FTIR plots of (a) $[Ru(bpy)_3(PF_6)_2]$, (b) **4**, and (c) poly-**4**. The vinyl group peaks are indicated with a red arrow.

sample obtained from scratching a polymeric film on a Pt electrode surface. The intense peak at 844 cm^{-1} for $[Ru(bpy)_3](PF_6)_2$ and **4** is due to the PF_6^- stretches,[5a] which is not observed in poly-**4** because the PF_6^- anion is largely replaced by ClO_4^- from the supporting electrolyte during electropolymerization. This is evidenced by the appearance of a new intense peak at 1110 cm^{-1} for poly-**4**. The peak at 935

cm^{-1} for **4** (indicated by a red arrow in Figure 7) is assigned to the out-of-plane deformation vibration of the vinyl groups.[31] This peak is not observed for $[Ru(bpy)_3](PF_6)_2$. However, the poly-**4** sample evidences the presence of a similar peak, albeit with much weaker intensity. This suggests that some of the vinyl groups of **4** are preserved during electropolymerization. The same situation applies to complex **3** with four vinyl groups and poly-**3** (Figure S10, Supporting Information). However, both vinyl groups in complex **1** are believed to be completely consumed during electropolymerization, as supported by the disappearance of the vinyl group peaks in poly-**1** (Figure S11, Supporting Information).

Scanning Electron Microscopy (SEM) Characterizations. Complexes have also been successfully deposited on indium−tin oxide (ITO) glass electrode surfaces in order to study the morphology of these films. Figure 8 shows representative SEM images of the polymeric films of **1** (a and b), **3** (c and d), and **4** (e and f) on ITO surfaces. Some small domains of irregular shapes are observed on the top of all polymeric films, and their sizes vary from tens of nanometers to a few micrometers. Apart from these irregular domains, the film surface of poly-**1** is uniform and flat (Figure 8b). However, the polymeric films of **3** and **4** exhibit higher surface roughness. In addition, the film of poly-**1** was found to adhere tightly to the ITO surface (Figure 8b). However, the contact between the substrate and the films of poly-**3** and poly-**4** is much looser (Figure 8d−f).

Absorption and Emission Spectra of Polymeric Films. The electronic absorption and emission spectra of polymeric films of **1** and **3**−**6** on ITO glass electrodes are displayed in Figure 9. The metal-to-ligand charge-transfer (MLCT) transitions are well preserved, with low-energy tails extending beyond 700 nm. Poly-**5** and poly-**6** display red-shifted MLCT bands in comparison to the others, which are consistent with their monomeric behaviors.[19,20] Poly-**1**, poly-**5**, and poly-**6** films show weak emissions at 613, 631, and 632 nm. However, no distinct emission spectra could be recorded for poly-**3** and poly-
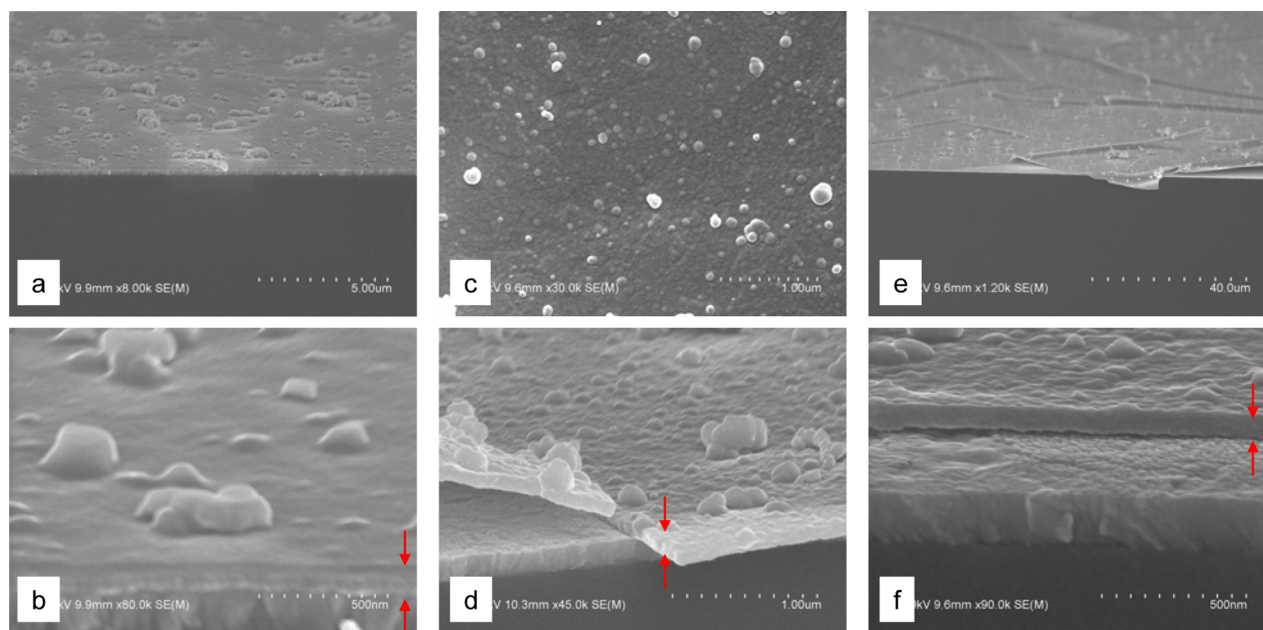

Figure 8. Representative SEM images of polymeric films of (a, b) **1**, (c, d) **3**, and (e, f) **4** on ITO glass electrodes with surface coverages of 1.0×10^{-8}, 1.3×10^{-8}, and 0.3×10^{-8} mol/cm^2, respectively. The polymeric layers are indicated by arrows.
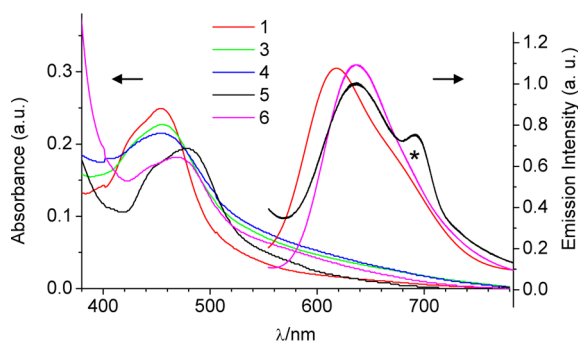
Figure 9. Representative absorption and emission spectra of polymeric films of **1** and **3–6** on optically transparent ITO glass electrodes immersed in CH$_3$CN. The surface coverage is about 1×10^{-8} mol/cm^2. The asterisk denotes noise due to a nonperfect background compensation.

4 films under ambient conditions using the fluorimeter at hand. More detailed emission studies will be carried out in the future for the above polymeric films. Previous studies have demonstrated that the emissions of poly-[Ru(vbpy)$_3$]$^{2+}$ films are largely inhibited by intrastrand energy transfer and self-quenching at low-energy trap sites.[32]

■ CONCLUSION

In conclusion, ruthenium and iridium complexes with one or two 5,5′-divinyl-2,2′-bipyridine ligands have been found to undergo reductive electropolymerization efficiently. The resulting polymeric films are stable and show reproducible and well-defined redox processes. Importantly, the electropolymerization occurs equally well for complexes with aromatic substituents on the auxiliary ligands, such as **5** and **6**. Taking into account the simplicity of the synthetic procedure for 5,5′-divinyl-2,2′-bipyridine,[17] this ligand will be a good substitute for 4-methyl-4′-vinyl-2,2′-bipyridine in the electropolymerization of polypyridine metal complexes. The synthesis and studies of tris-bidentate bisruthenium complexes[13] and other mixed-valence systems[33] with 5,5′-divinyl-2,2′-bipyridine are underway and will be reported in due course. The rhenium complex **8** with 5,5′-divinyl-2,2′-bipyridine did not undergo efficient electropolymerization. However, we believe that our chemistry will be suitable for iron,[1b,9a] osmium,[8a,b] and cobalt[2a,9a,b] complexes, as has been studied for those with vbpy ligands.

■ EXPERIMENTAL SECTION

Electrochemical Measurements. All cyclic voltammetric measurements were taken using a CHI620D potentiostat with a one-compartment electrochemical cell under an atmosphere of nitrogen. All measurements were carried out in 0.1 M Bu$_4$NClO$_4$/acetonitrile. The working electrode was a Pt-disk electrode, which was polished prior to use with 0.05 μm 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 a Ag/AgCl electrode in saturated aqueous NaCl without regard for the liquid junction potential.

SEM Measurements. Prior to measurement, an ultrathin conductive Au coating was deposited on the top of the polymeric films on ITO glass electrodes by low-vacuum sputter coating of the sample. Images were obtained using a field-emission microscope (JEOL S-4800) operated at an acceleration voltage of 10 kV.

Spectroscopic Measurements. Absorption spectra were obtained using a TU-1810DSPC spectrometer from Beijing Purkinje General Instrument Co. Ltd. at room temperature. Emission spectra were recorded using a F-380 spectrofluorimeter of Tianjin Gangdong

Sic. & Tech Development Co. Ltd., with an R928F red-sensitive photomultiplier tube. The polymeric films on ITO glass electrodes were immersed in CH$_3$CN in a 1.0 cm quartz cell for all spectroscopic measurements.

Other Measurements. NMR spectra were recorded in the designated solvent on Bruker Avance 400 MHz spectrometer. Spectra are reported in ppm from residual protons of the deuterated solvent. Mass data were obtained with a Bruker Daltonics Inc. Apex II FT-ICR or Autoflex III MALDI-TOF mass spectrometer. The matrix for MALDI-TOF measurement is α-cyano-4-hydroxycinnamic acid. Microanalysis was carried out using a Flash EA 1112 or Carlo Erba 1106 analyzer at the Institute of Chemistry, Chinese Academy of Sciences.

Synthesis of [Ru(5,5′-dvbpy)(bpy)$_2$](PF$_6$)$_2$ (1). To a mixture of 20 mL of ethanol and 10 mL of water were added cis-Ru(bpy)$_2$Cl$_2$·2H$_2$O (125 mg, 0.24 mmol) and 5,5′-divinyl-2,2′-bipyridine (50 mg, 0.24 mmol). The mixture was refluxed for 4 h under a N$_2$ atmosphere. After the mixture was cooled to room temperature, ethanol was removed under reduced pressure, followed by the addition of an excess of KPF$_6$. The resulting precipitate was collected by filtering and washing with water and Et$_2$O. The obtained solid was subjected to flash column chromatography on silica gel (eluent saturated aq.ueous KNO$_3$/H$_2$O/CH$_3$CN, 1/15/150) followed by anion exchange with KPF$_6$ to give 145 mg of **1** in a yield of 65%. ^{1}H NMR (400 MHz, CD$_3$CN): δ 5.46 (d, J = 11.0 Hz, 2H), 5.84 (d, J = 17.6 Hz, 2H), 6.54 (dd, J = 17.6, 11.0 Hz, 2H), 7.39 (t, J = 6.4 Hz, 4H), 7.60 (s, 2H), 7.71 (d, J = 5.5 Hz, 2H), 7.76 (d, J = 5.5 Hz, 2H), 8.05 (t, J = 7.8 Hz, 4H), 8.16 (d, J = 8.5 Hz, 2H), 8.43 (d, J = 8.6 Hz, 2H), 8.48 (d, J = 8.2 Hz, 4H). MALDI-MS: 767.2 for [M − PF$_6$]$^+$, 621.1 for [M − 2PF$_6$]$^{2+}$. Anal. Calcd for C$_{34}$H$_{28}$F$_{12}$N$_6$P$_2$Ru·H$_2$O: C, 43.93; H, 3.25; N, 9.04. Found: C, 43.90; H, 3.24; N, 8.92.

Synthesis of [Ru(4,4′-dvbpy)(bpy)$_2$](PF$_6$)$_2$ (2). Compound **2** was prepared from cis-Ru(bpy)$_2$Cl$_2$·2H$_2$O (125 mg, 0.24 mmol) and 4,4′-divinyl-2,2′-bipyridine (50 mg, 0.24 mmol) in a yield of 80% using the same procedure as for the synthesis of **1**. ^{1}H NMR (400 MHz, CD$_3$CN): δ 5.74 (d, J = 10.9 Hz, 2H), 6.33 (d, J = 17.6 Hz, 2H), 6.88 (dd, J = 17.5, 10.9 Hz, 2H), 7.39 (m, 6H), 7.63 (d, J = 5.9 Hz, 2H), 7.71 (d, J = 5.6 Hz, 2H), 7.76 (d, J = 5.5 Hz, 2H), 8.05 (t, J = 7.8 Hz, 4H), 8.49 (d, J = 8.1 Hz, 4H), 8.58 (s, 2H). MALDI-MS: 767.2 for [M − PF$_6$]$^+$, 621.1 for [M − 2PF$_6$]$^{2+}$. Anal. Calcd for C$_{34}$H$_{28}$F$_{12}$N$_6$P$_2$Ru·5H$_2$O: C, 40.77; H, 3.82; N, 8.39. Found: C, 40.91; H, 3.37; N, 8.72.

Synthesis of [Ru(5,5′-dvbpy)$_2$(bpy)](PF$_6$)$_2$ (3). To 10 mL of dimethylformamide (DMF) was added 5,5′-divinyl-2,2′-bipyridine (50 mg, 0.24 mmol), RuCl$_3$·3H$_2$O (31 mg, 0.12 mmol), and LiCl (51 mg, 1.2 mmol). The mixture was stirred at 140 °C for 20 h under an N$_2$ atmosphere. After the mixture was cooled to room temperature, DMF was removed under reduced pressure. To the residue were added 20 mL of ethanol, 10 mL of water, and 2,2′-bipyridine (28 mg, 0.18 mmol). The mixture was refluxed for 4 h under an N$_2$ atmosphere. After the mixture was cooled to room temperature, ethanol was removed under reduced pressure, followed by the addition of an excess of KPF$_6$. The resulting precipitate was collected by filtering and washing with water and Et$_2$O. The obtained solid was subjected to flash column chromatography on silica gel (eluent saturated aqueous KNO$_3$/H$_2$O/CH$_3$CN, 1/15/150) followed by anion exchange with KPF$_6$ to give 40 mg of **3** in a yield of 57%. ^{1}H NMR (400 MHz, CD$_3$CN): δ 5.46 (d, J = 10.9 Hz, 4H), 5.84 (dd, J = 17.6, 11.1 Hz, 4H), 6.54 (m, 4H), 7.39 (t, J = 6.6 Hz, 2H), 7.57 (s, 2H), 7.64 (s, 2H), 7.75 (d, J = 5.2 Hz, 2H), 8.05 (t, J = 7.8 Hz, 2H), 8.16 (t, J = 7.2 Hz, 4H), 8.42 (d, J = 8.6 Hz, 4H), 8.47 (d, J = 7.9 Hz, 2H). MALDI-MS: 819.0 for [M − PF$_6$]$^+$, 674.1 for [M − 2PF$_6$]$^{2+}$. Anal. Calcd for C$_{38}$H$_{32}$F$_{12}$N$_6$P$_2$Ru·3H$_2$O: C, 44.84; H, 3.76; N, 8.26. Found: C, 44.54; H, 3.33; N, 8.24.

Synthesis of [Ru(5,5′-dvbpy)(4,4′-dpbpy)$_2$](PF$_6$)$_2$ (5). To 10 mL of DMF were added 4,4′-diphenyl-2,2′-bipyridine (50 mg, 0.16 mmol), RuCl$_3$·3H$_2$O (21 mg, 0.08 mmol), and LiCl (34 mg, 0.8 mmol). The mixture was stirred at 140 °C for 20 h under an N$_2$ atmosphere. After the mixture was cooled to room temperature, DMF was removed under reduced pressure. To the residue were added 20

mL of ethanol, 10 mL of water, and 5,5′-divinyl-2,2′-bipyridine (14 mg, 0.07 mmol). The mixture was refluxed for 8 h under an N_2 atmosphere. After the mixture was cooled to room temperature, ethanol was removed under reduced pressure, followed by the addition of an excess of KPF_6. The resulting precipitate was collected by filtering and washing with water and Et_2O. The obtained solid was subjected to flash column chromatography on silica gel (eluent saturated aqueous $KNO_3/H_2O/CH_3CN$, 1/20/1000) to give 51 mg of **5** in a yield of 77%. ^{1}H NMR (400 MHz, CD_3CN): δ 5.47 (d, J = 10.8 Hz, 2H), 5.89 (d, J = 17.6 Hz, 2H), 6.61 (dd, J = 17.6, 11.2 Hz, 2H), 7.60 (t, J = 6.6 Hz, 12H), 7.70 (d, J = 6 Hz, 4H), 7.76 (s, 2H), 7.85 (d, J = 6 Hz, 2H), 7.87 (d, J = 6 Hz, 2H), 7.93 (d, J = 6 Hz, 8H), 8.21 (d, J = 8.4 Hz, 2H), 8.49 (d, J = 8.8 Hz, 2H), 8.93 (s, 4H). MALDI-MS: 1071.0 for $[M - PF_6]^+$, 925.0 for $[M - 2PF_6]^{2+}$. Anal. Calcd for $C_{58}H_{44}F_{12}N_6P_2Ru\cdot3H_2O$: C, 54.85; H, 3.97; N, 6.62. Found: C, 54.87; H, 3.99; N, 7.04.

Synthesis of 5,5′-Diphenyl-2,2′-bipyridine. In an oven-dried Schlenk flask were added phenylboronic acid (194 mg, 1.6 mmol), 5,5′-dibromo-2,2′-bipyridine (200 mg, 0.6 mmol), 20 mL of toluene, and 6 mL of an aqueous solution of Na_2CO_3 (2 M) under a N_2 atmosphere. The mixture was bubbled with N_2 for 15 min before 37 mg of $Pd(PPh_3)_4$ was added. The system was refluxed for 14 h. After the mixture was cooled to room temperature, the mixture was extracted with CH_2Cl_2 (50 mL × 3). The combined organic phase was washed with 20 mL of brine and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the crude product was purified by column chromatography on silica gel (eluent petroleum ether/ethyl acetate, 17/1) to give 150 mg of 5,5′-diphenyl-2,2′-bipyridine as a white solid in 77% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (t, J = 7.4 Hz, 2H), 7.52 (m, 4H), 7.68 (d, J = 7.6 Hz, 4H), 8.05 (d, J = 8.4 Hz, 2H), 8.52 (d, J = 8.0 Hz, 2H), 8.95 (s, 2H). EI-HRMS for $C_{22}H_{16}N_2$: calcd 308.1313, found: 308.1318.

Synthesis of $[Ru(5,5′-dvbpy)(5,5′-dpbpy)_2](PF_6)_2$ (6). Compound **6** was prepared from 5,5′-diphenyl-2,2′-bipyridine (50 mg, 0.16 mmol), $RuCl_3\cdot3H_2O$ (21 mg, 0.08 mmol), LiCl (34 mg, 0.8 mmol), and 5,5′-divinyl-2,2′-bipyridine (14 mg, 0.07 mmol) in a yield of 58% using the same procedure as for the synthesis of **5**. ^{1}H NMR (400 MHz, CD_3CN): δ 5.44 (d, J = 14.7 Hz, 2H), 5.86 (d, J = 23.6 Hz, 2H), 6.56 (dd, J = 23.6, 14.9 Hz, 2H), 7.43 (m, 20H), 7.83 (s, 2H), 7.94 (d, J = 7.5 Hz, 4H), 8.19 (d, J = 11.4 Hz, 2H), 8.32 (t, J = 10.4 Hz, 4H), 8.47 (d, J = 11.5 Hz, 2H), 8.58 (t, J = 10.5 Hz, 4H). MALDI-MS: 1070.5 for $[M - PF_6]^+$, 925.4 for $[M - 2PF_6]^{2+}$. Anal. Calcd for $C_{58}H_{44}F_{12}N_6P_2Ru\cdot5H_2O$: C, 52.97; H, 4.22; N, 6.39. Found: C, 52.58; H, 3.75; N, 6.90.

Synthesis of $[Ir(5,5′-dvbpy)(ppy)_2](PF_6)$ (7). To a mixture of 10 mL of CH_2Cl_2 and 5 mL of MeOH were added 5,5′-divinyl-2,2′-bipyridine (50 mg, 0.24 mmol) and $[Ir(ppy)_2Cl]_2$ (129 mg, 0.12 mmol). The mixture was refluxed for 6 h under an N_2 atmosphere. After the mixture was cooled to room temperature, an excess of KPF_6 was added. The suspension was stirred for 30 min, and the insoluble inorganic salts were removed by filtering. The filtrate was concentrated to dryness under reduced pressure. The residue was dissolved in the proper amount of CH_2Cl_2, followed by washing with copious amounts of H_2O. The organic phase was dried with anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the crude product was purified by column chromatography on silica gel (eluent CH_2Cl_2/MeOH, 100/1) to give 95 mg of **7** in a yield of 93%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.42 (d, J = 11.0 Hz, 2H), 5.70 (d, J = 17.6 Hz, 2H), 6.30 (d, J = 7.5 Hz, 2H), 6.44 (dd, J = 11.0, 17.6 Hz, 2H), 6.91 (t, J = 7.3 Hz, 2H), 7.03 (m, 4H), 7.51 (d, J = 5.6 Hz, 2H), 7.68 (d, J = 7.7 Hz, 2H), 7.76 (t, J = 6.7 Hz, 2H), 7.81 (s, 2H), 7.93 (d, J = 8.1 Hz, 2H), 8.10 (d, J = 8.5 Hz, 2H), 8.53 (d, J = 8.5 Hz, 2H). MALDI-MS: 708.8 for $[M - PF_6]^+$. Anal. Calcd for $C_{36}H_{28}F_6N_4PIr$: C, 50.64; H, 3.31; N, 6.56. Found: C, 50.24; H, 3.42; N, 6.54.

Synthesis of $[Re(5,5′-dvbpy)(CO)_3Cl]$ (8). To 10 mL of toluene were added 5,5′-divinyl-2,2′-bipyridine (50 mg, 0.24 mmol) and $Re(CO)_5Cl$ (104 mg, 0.29 mmol). The mixture was refluxed for 8 h under an N_2 atmosphere. After the mixture was cooled to room temperature, toluene was removed under reduced pressure. The

obtained solid was subjected to flash column chromatography on silica gel (eluent CH_2Cl_2/ethyl acetate, 50/1) to give 71 mg of **8** in a yield of 57%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.68 (d, J = 11.0 Hz, 2H), 6.05 (d, J = 17.6 Hz, 2H), 6.78 (dd, J = 11.0, 17.6 Hz, 2H), 8.06 (m, 4H), 8.98 (s, 2H). MALDI-MS: 514.4 for $[M]^+$, 478.8 for $[M - Cl]^+$. Anal. Calcd for $C_{17}H_{12}ClN_2O_3Re\cdot0.5H_2O$: C, 39.04; H, 2.51; N, 5.36. Found: C, 39.16; H, 2.50; N, 5.56.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures giving cyclic voltammograms and electropolymerization studies of complexes **1−8**, FTIR spectra of **1**, **3**, poly-**1**, and poly-**3** films, and ^{1}H NMR and mass spectra of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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