Luminescent Electropolymerizable Ruthenium Complexes and **Corresponding Conducting Metallopolymers**

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S Supporting Information

ABSTRACT: Tris(2,2'-bipyridyl)ruthenium(II) dichloride $[Ru(bpy)_3Cl_2]$ and analogous complexes have been studied extensively in the literature due to their luminescent and photochemical properties as well as their excited-state lifetimes. Conducting polymers with similar ruthenium groups have also been investigated for various applications. In this study, syntheses of four ruthenium complexes with a polymerizable tridentate ligand, bis[4-[2-(3,4-diethylenedioxy)thiophene]pyrazol-1-yl]pyridine (EDOT₂NNN), and with bidentate ligands, two of which were anionic (hfac: 1,1,1,5,5,5-



hexafluoro-2,4-pentanedione; dbm: dibenzoylmethane) and two of which were neutral (bpy: 2,2'-bipyridyl; phen: 1,10phenanthroline), were achieved for potential OLED/PLED applications. Saturated CH₂Cl₂ solutions of monomers were oxidatively and electrochemically polymerized, and the scan rate dependences of the polymers were measured. UV-vis spectroscopic characterizations of the complexes and the EDOT-functionalized ligand were obtained. [Ru(EDOT₂NNN)- $(phen)(Cl)](PF_6)$ was electropolymerized on an ITO (indium tin oxide)-coated glass surface to obtain the solid-state absorption spectrum of the corresponding polymer. Photophysical data for each complex, i.e., excitation and emission spectra at 77 K and RT, in EtOH/MeOH (4:1) and in 2-MeTHF (dry, air-free, and aerated), quantum yield, and luminescence lifetime have been measured. The radiative and nonradiative decay constants as well as the oxygen quenching rate coefficient for each complex were calculated. $[Ru(EDOT_2NNN)(phen)(Cl)](PF_6)$, having the highest quantum yield of phosphorescence and the longest lifetime, was electropolymerized on an ITO-coated glass surface to obtain the solid-state excitation and emission spectra of the corresponding polymer. Luminescence studies of the polymer had promising results for photoluminescence.

INTRODUCTION

Tris(2,2'-bipyridyl)ruthenium(II) dichloride $[Ru(bpy)_3Cl_2]$ has been thoroughly studied and frequently employed due to its unique properties such as chemical stability, luminescence emission, excited-state lifetime, redox properties, and excitedstate reactivity.¹ This red crystalline salt is obtained as the hexahydrate from the reaction of an aqueous solution of ruthenium trichloride with 2,2'-bipyridine. Ru(III) is reduced to Ru(II) in the process by hypophosphorous acid.² The complex is a chiral, d^6 system with D_3 symmetry, and its enantiomers are kinetically stable. All of the properties of interest are in the cation $[\overset{\cdot}{Ru}(bpy)^3]^{2+}$ which has a noteworthy chemical stability; as a consequence, it can be stored in aqueous solutions for months. Furthermore, it is unaffected by boiling in concentrated HCl or 50% aqueous NaOH solutions.^{3,4} Excited solutions of the cation emit light both at room temperature (890 ns in CH_3CN , 650 ns in H_2O) and at 77 K (5 μ s) with relatively long lifetimes.^{1,5} When Ru(II)polypyridine complexes undergo one-electron oxidation, the process involves a metal-centered orbital with the formation of Ru(III) complexes which have a low-spin 4d⁵ configuration and inert to ligand substitution.⁶ Single electron reduction of Ru(II)-polypyridine complexes generally takes place on a

ligand orbital depending on either a sufficiently strong ligand field or easily reducible ligands. The reduced form in this case has a low-spin 4d⁶ configuration and is usually quite inert.⁷ Both single electron oxidation and reduction are reversible processes. The triplet excited state of Ru(bpy)32+ has both oxidizing and reducing properties. This remarkable situation arises because the excited state can be described as a Ru³⁺ complex containing a (bpy)⁻ ligand.¹⁰ Ru(bpy)₃²⁺ has been examined as a photosensitizer for both the oxidation and reduction of water.¹¹ The excited states of Ru(II)polypyridine complexes may involve three types of electronic transitions (Figure 1a).^{1,12-15} Polypyridine molecules possess σ -donor orbitals that are localized on the nitrogen atoms and the π -acceptor orbitals that are delocalized on aromatic rings. Promotion of an electron from a πM metal orbital to π^*L ligand orbitals results in metal-to-ligand charge transfer (MLCT) excited states, while promotion of an electron from πM to $\sigma^* M$ orbitals results in metal-centered (MC) excited states. The promotion of an electron from π L to π *L generates

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Figure 1. (a) Molecular orbital diagram for $\text{Ru}(\text{LL})_3^{2+}$ showing the three types of electronic transitions that occur (left). (b) Detailed representation of the MLCT transition in D_3 symmetry (right).¹

ligand-centered (LC) excited states. The presence of the heavy ruthenium atom causes spin-orbit coupling which leads to singlet-triplet mixing in the MC and MLCT excited states.¹²⁻¹⁵ Homo-tris-chelated complexes of ruthenium with bidentate polypyridine ligands exhibit a D_3 symmetry; the corresponding orbitals involved in electronic transitions are shown in Figure 1b.^{1,16-18}

Transition metal complexes in their high-energy excited states undergo fast nonradiative deactivation.¹⁹ Therefore, the lowest excited state and the states populated according to Boltzmann equilibrium law may result in luminescence emission and in bimolecular processes. The MC excited states of d⁶ octahedral complexes are strongly displaced with respect to the ground-state geometry. Therefore, such molecules undergo rapid nonradiative deactivation or ligand dissociation reactions. Consequently, no luminescence can be observed at room temperature from MC excited states.²⁰ Luminescence can generally be observed when the lowest excited states are LC and MLCT due to their small displacement from the ground-state geometry and therefore do not undergo fast nonradiative decay.

Derivatives of $[Ru(bpy)_3]^{2+}$ are numerous, and such complexes of this type are widely used for applications in biodiagnostics, photovoltaics, and organic light-emitting diodes.^{1,21}

Because of their promising luminescence properties for materials applications, metal complexes were coordinated into the conducting polymer backbones.^{22–26} The N-donating ligands with bidentate and tridentate coordination modes have generally been used for such polymers with ruthenium(II) (Figure 2).^{27–35} Peng et al. reported a metallopolymer with increased photosensitivity upon incorporation of the metal complex that had a strong absorption in the visible region of the spectrum.^{36,37} Ruthenium(II) polypyridine complexes could enhance the charge mobility of the resulting metallopolymer, and processing of the material was easy.²⁷

In this study, the synthesis and characterization of four Ru(II) complexes with a polymerizable tridentate ligand, bis[4-[2-(3,4-diethylenedioxy)thiophene]pyrazol-1-yl]pyridine (EDOT₂NNN), and the bidentate ligands 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (hfac), dibenzoylmethane (dbm), 2,2'-bipyridine (bpy), and 1,10-phenanthroline (phen) are targeted. Subsequently, further studies of the complexes, i.e., electrochemistry/electropolymerization, UV-vis spectroscopy of complexes and one of the polymers (that has the highest molar extinction coefficient), luminescence studies of the monomer complexes in air free and aerated media, and luminescence study of one of the polymers (that has the best phosphorescence quantum yield), are planned. The reasons for selecting ruthenium-containing polymers are their chemical stability, luminescence emission, ease on processability, and high charge carrier mobility compared with monomers as well as the electronic interactions between the organic backbone and the ruthenium metals. Furthermore, having the bidentate ligands can enhance the light absorption. A possible application to these materials would be PLEDs.^{38,39}

EXPERIMENTAL SECTION

Instrumentation. ¹H and ¹³C{¹H} NMR spectra were recorded with a Varian 300 MHz spectrometer. ¹H NMR signals were referenced to residual proton resonances in deuterated solvents. ¹³C{¹H} NMR spectra were referenced relative to solvent peaks. All peak positions are listed in ppm, and all coupling constants are listed in hertz (Hz). UV–vis measurements were obtained by using a Varian Cary 6000i UV–vis–NIR spectrophotometer. Luminescence measurements were performed by a Photon Technology International QM 4 spectrophotometer. Innovative Technology Pure Solv solvent purifier was used to obtain dry solvents. Samples were freshly prepared prior to analysis.

Synthesis. General Methods. All chemicals were purchased from commercial suppliers and were used as received. The reactions were performed by using a Schlenk line which has a nitrogen atmosphere and using dry glassware. The ligand 3 (L = EDOT₂NNN) and the precursor 4 were prepared by Zhu's technique (The syntheses of 1 and 2 can be found in refs 24 and 31. The syntheses of 3 and 4 are included in this study due to having different yields and the different ε values than the reported literature values.^{24,31})

2,6-Bis[4-[2-(3,4-diethylenedioxy)thiophene]pyrazol-1-yl]pyridine [L = EDOT₂NNN] (3). 2,6-Bis(4-iodopyrazol-1-yl)pyridine (0.700 g, 1.511 mmol) and dichlorobis(triphenylphosphane)palladium(II) [Pd(PPh₃)₂Cl₂], (0.053 g, 0.0756 mmol) were added into a Schlenk flask. 60 mL of dry DMF was cannula-transferred into the Schlenk flask, and the mixture was stirred to dissolve while being heated to 120 °C to give a clear yellow solution. Meanwhile, 2-(tributylstannyl)-3,4-(ethylenedioxy)thiophene was dissolved in 20 mL of dry DMF, degassed by sparging with N₂, and subsequently cannula-transferred into the hot reaction mixture, and an immediate color change to dark was observed. The reaction mixture was stirred at 120 °C for 2 days. The reaction mixture was cooled to RT, and then DMF was evaporated under vacuum. The dark residue was redissolved in ethyl acetate and washed with H₂O three times. The



Figure 2. Electropolymerization of a ruthenium-containing polymer in which the donor atoms were N.³¹

organic phase was dried over MgSO₄ and vacuum filtered, and the filtrate was evaporated. The residue was further purified via column chromatography. The first fraction (impurities) was collected by CH₂Cl₂; afterward, the second fraction (product) was collected via ethyl acetate. The product was redissolved in CH₂Cl₂ with hexanes added to remove tributylstannyl impurities. The tan precipitate was collected as 0.355 g (48% yield). ¹H NMR (400 MHz, δ ppm, CDCl₃, 298 K): 8.72 (s, 2H), 8.00 (s, 2H), 7.92–7.97 (dd, 1H, ³J_{H,H} = 7.95 Hz, 1.80 Hz), 7.82–7.84 (d, 2H, ³J_{H,H} = 7.9 Hz), 6.25 (s, 2H), 4.36 (m, 4H), 4.24 (m, 4H). ¹³C{¹H} NMR (100 MHz, δ ppm, CDCl₃, 298 K): δ = 149.9, 141.9, 141.2, 140.1, 137.8, 122.8, 116.8, 109.4, 108.3, 96.4, 64.9, 64.6. MS (ESI) calculated for C₂₃H₁₈N₅O₄S₂ *m/z* = 492.08 ([M + H]⁺); found 492.12. UV–vis (CH₂Cl₂, nm (ε)): 277 (21969), 315 (24507) sh, 335 (29034).

 $Ru(L)Cl_3$ (4). RuCl₃·XH₂O (167 mg, 0.805 mmol) and 3 (202 mg, 0.411 mmol) were heated to reflux in ethanol (60 mL) for 12 h. After cooling, the precipitate was collected by filtration, washed with ethanol, and then dried under high vacuum to give a black insoluble solid (250 mg, 81.4%).

Ru(L)(hfac)(Cl) (5). A mixture of 4 (101 mg, 0.144 mmol), triethylamine (0.81 mL, 5.81 mmol), and 1,1,1,5,5,5-hexafluoro-2,4pentanedione (hfac) (0.60 mL, 4.24 mmol) in 100 mL of absolute ethanol was heated at reflux under Ar for 12 h. The reaction mixture was allowed to cool, and the solvent was removed by rotary evaporation. The solid residue was redissolved in CH₂Cl₂ and filtered to remove insolubles. The filtrate was adsorbed on alumina to run a column chromatography with 0.5% CH₃OH in CH₂Cl₂ as the eluent. The second fraction was the product, but there were still triethylamine impurities. The product was then extracted between CH₂Cl₂ and H₂O. The organic phase was dried over MgSO₄ and vacuum filtered; the filtrate was evaporated and further dried under vacuum (81 mg, 67%). ¹H NMR (400 MHz, δ ppm, CD₂Cl₂, 298 K): 8.63 (s, 2H), 8.24 (s, 2H), 7.64 (t, 1H, J = 8.4 Hz), 7.47 (d, 2H, J = 8 Hz,), 6.34 (s, 2H), 6.10 (s, 1H), 4.26–4.34 (m, 8H). ¹⁹F NMR (376 MHz, δ ppm, CD₂Cl₂, 298 K): δ = -75.11, -75.62. MS (ESI) calculated for $C_{28}H_{18}ClF_6N_5O_6RuS_2$: m/z = 835.94 ([M + H]⁺), 799.96 ($[M - Cl]^+$); found 836 ($[M + H]^+$), 799 ($[M - Cl]^+$). UVvis (CH₂Cl₂, nm (ε)): 281 (29011), 316 (21986) sh, 354 (12247), 497 (6896). A solution of 5 in chloroform was slowly evaporated to obtain X-ray quality crystals.

Ru(L)(dbm)(Cl) (6). A mixture of 4 (127 mg, 0.182 mmol), triethylamine (0.95 mL, 6.82 mmol), and dibenzoylmethane (dbm) (55.3 mg, 0.254 mmol) in 127 mL of absolute ethanol was heated to reflux under Ar for 12 h. The reaction mixture was allowed to cool, and the solvent was removed by rotary evaporation. The solid residue was redissolved in CH2Cl2 and filtered to remove insolubles. The filtrate was washed with NH4Cl solution once, then dried over MgSO₄, and vacuum filtered. Hexanes was added into the filtrate to precipitate the product which was collected via vacuum filtration. The dark burgundy product was further dried under vacuum (97 mg, 63%). ¹H NMR (400 MHz, δ ppm, CD₂Cl₂, 298 K): 8.66 (s, 2H), 8.34 (m, 2H), 8.11 (s, 2H), 7.51-7.62 (6H), 7.17-7.14 (m, 3H), 7.06 (t, J = 8 Hz, 2H), 6.64 (s, 1H), 6.26 (s, 2H), 4.19–4.29 (m, 8H). MS (ESI) calculated for $C_{38}H_{28}ClN_5O_6RuS_2 m/z = 852.03$ ([M + $H]^+$, 816.05 ([M - Cl]⁺); found 852 ([M + H]⁺), 815 ([M - Cl]⁺). UV-vis $(CH_2Cl_2, nm(\varepsilon))$: 256 (35714), 279 (38713), 326 (52803), 486 (8153). A solution of 6 in chloroform was slowly evaporated to obtain X-ray quality crystals.

[*Ru*(*L*)(*bpy*)(*CI*)](*PF*₆) (7). 4 (100 mg, 0.143 mmol) and 2,2'bipyridene (bpy) (26 mg, 0.166 mmol) were refluxed for 12 h in 60 mL of EtOH/H₂O (3/1, v/v). The hot solution was filtered through Celite and evaporated to dryness. After dissolving the crude product in CH₂Cl₂, 26 mg of KPF₆ was added; the mixture was stirred overnight. The resulting brown precipitate was collected via vacuum filtration. The product was redissolved in CH₂Cl₂, and pentane was layered. The solid was collected a week later (60 mg, 45%). ¹H NMR (400 MHz, δ ppm, CD₃CN, 298 K): 10.25 (m, 1H), 8.92 (s, 2H), 8.56 (d, *J* = 8.0 Hz, 1H), 8.32 (d, *J* = 7.6 Hz, 1H), 8.23–8.27 (m, 1H), 8.18–8.22 (m, 1H), 8.01 (d, *J* = 8 Hz, 2H), 7.89–7.92 (m, 1H), 7.70–7.74 (m, 1H), 7.5 (s, 2H), 7.38 (d, *J* = 8.0 Hz, 1H), 6.96–7.00 (m, 1H), 6.35 (s, 2H), 4.17–4.25 (m, 8H). $^{13}C{^1H}$ NMR (500 MHz, δ ppm, CD₃CN, 298 K): 207.4, 160.4, 158.4, 154.5, 153.9, 151.4, 143.1, 142.8, 140.3, 139.0, 137.6, 136.9, 127.3, 127.2, 126.6, 124.1, 123.8, 119.8, 108.2, 106.0, 99.0, 65.96, 65.58. Elemental analysis calculated for C₃₃H₂₅ClF₆N₇O₄PRuS₂: C, 42.65; H, 2.71; N, 10.55; found: C, 42.11; H, 2.77; N, 10.62. MS (ESI) calculated for C₃₃H₂₅ClN₇O₄RuS₂ m/z = 784.01 ([M – PF₆]⁺); found 784. UV–vis (CH₂Cl₂, nm (ε)): 254 (30553), 290 (66486), 355 (21887), 455 (8894), 550 (4119).

[Ru(L)(phen)(Cl)](PF₆) (8). 4 (50 mg, 0.0713 mmol) and 1,10phenanthroline (phen) (14.5 mg, 0.08 mmol) were refluxed for 12 h in 30 mL of EtOH/H₂O (3/1, v/v) under N₂. The reaction mixture was filtered through Celite as hot. NH₄PF₆ (1g/10 mL) was added into filtrate and stirred for 1 h. The solvent was evaporated. The residue was redissolved in CH₂Cl₂ and then washed with H₂O once. The organic phase was dried over MgSO₄ and vacuum filtered; the filtrate was evaporated and further dried under vacuum to afford a reddish-brown solid (39 mg, 58%). ¹H NMR (400 MHz, δ ppm, CD₃CN, 298 K): 10.43 (dd, 1H), 8.90 (s, 2H), 8.78 (dd,1H), 8.23-8.29 (m, 4H), 8.04-8.08 (m, 3H), 7.74 (dd, 1H), 7.34 (s, 2H), 7.30 (dd, 1H), 6.28 (s, 2H), 4.11-4.19 (m, 8H). ¹³C{¹H} NMR (500 MHz, δ ppm, CD₃CN, 298 K): 207.4, 155.2, 154.4, 151.7, 150.8, 149.8, 143.1, 140.2, 139.0, 136.5, 135.8, 131.7, 131.0, 128.7, 128.1, 127.3, 126.4, 125.3, 119.7, 108.2, 105.9, 98.9, 65.89, 65.54. MS (ESI) calculated for $C_{35}H_{25}ClN_7O_4RuS_2 m/z ([M - PF_6]^+) = 808.01;$ found 808. UV-vis (CH₃CN, nm (ε)): 223 (53267), 265 (66997), 349 (18970), 443 (11820), 549 (4033).

X-ray Crystallography. Data were collected on a Rigaku MiniFlex II CCD diffractometer with graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) at 223 K. The data set was corrected for absorption based on multiple scans and reduced using standard methods. The structures were solved by direct methods and refined anisotropically using full-matrix least-squares methods with the SHELX 97 program package.⁴⁰ Coordinates of the non-hydrogen atoms were refined anisotropically, while hydrogen atoms were included in the calculation isotropically but not refined. Neutral atom scattering factors were taken from Cromer and Waber.⁴¹

Electrochemistry/Electropolymerization. The GPES system from Eco. Chemie was used to carry out electrochemistry and electropolymerization experiments in the glovebox with three electrodes, i.e., Ag/AgNO₃ as the reference electrode, a Pt wire coil as the counter electrode, and a Pt button as the working electrode. For the UV-vis and luminescence measurements of the polymers, Delta Technologies ITO-coated glass was used as a working electrode instead of the Pt button. The reference electrode consists of a Ag wire which was in a 0.01 M AgNO₃ solution with 0.1 M $[(n-Bu)_4N][PF_6]$ (TBAPF₆) in CH₃CN. Potentials measured were relative to the reference electrode which needed to be calibrated by external reference ferrocene. Calibrations were performed before and after experiments were performed. The average of the ferrocene measurements was determined and used to correct the measured potentials. Solution of 0.1 M (TBAPF₆) in CH₂Cl₂ was used as the electrolyte. ${\sim}1~{\times}~10^{-3}~M$ monomer solutions were prepared for electropolymerizations. The potential windows were between ~ -1.6 and ~1.25 V at the scan rate of 100 mV s⁻¹. The polymer films were washed with dry CH₂Cl₂ in the glovebox to remove any monomer or electrolyte left on the films before further experiments. TBAPF₆ had to be purified. Hot ethanol was used to recrystallize TBAPF₆ three times, and then the white crystals were dried for 3 days above 100 °C under active vacuum.

Luminescence Studies. Optical density of all complexes was about 0.1 absorbance unit to exclude any excimer formation and concentration quenching effect. After having a proper range of optical density (0.05-0.1 A), fresh stock solutions were transferred into capped and parafilmed quartz EPR (electron paramagnetic resonance) tubes as well as airtight quartz cuvettes in the glovebox. Measurements with airtight cuvettes could only be performed at RT (no dewar available), but samples in EPR tubes were suitable for both RT and 77 K measurements. Dry solvents of 2-MeTHF, EtOH, and MeOH were degassed by freeze–pump–thaw technique for 4–5 cycles and then

Scheme 1. Synthesis of the Polymerizable Ligand and the Ruthenium Precursor



Scheme 2. Complex Synthesis



Figure 3. (a) A view of the crystal structure of 5 (left). (b) A view of the crystal structure of 6 (right). The H atoms have been omitted for clarity, and the thermal ellipsoids were drawn at the 30% probability level.

transferred into the glovebox which has a N_2 atmosphere. EtOH/ MeOH (4:1) solution was prepared to make stock solutions of each complex in it, and then a sample of each complex solution was taken to measure its optical density (~0.1 A) by using a UV-vis spectrophotometer.

To find the excitation and emission spectra of complexes, solutions of each complex were excited at their UV–vis absorption maxima. The resulting emission maxima were used to obtain excitation maxima; finally, samples were excited at the excitation maxima found to obtain the maximized emission spectra.

RESULTS AND DISCUSSION

Synthesis. The ligand 3 (L = EDOT₂NNN) was prepared by Zhu's technique and obtained in 48% yield (Scheme 1).^{24,31} Subsequently, 3 was reacted with RuCl₃·XH₂O to obtain the precursor 4 as an insoluble black powder in 81.4% yield



Figure 4. Electropolymerization of ruthenium complexes with initial scans shown in red. Insets: current vs number of scans. (a) 7 (left); (b) 8 (right).



Figure 5. Electrochemical scan rate dependence of (a) poly-7 (left) and (b) poly-8 (right). Insets: current vs scan rate.

(Scheme 1). The ruthenium complexes 5 and 6 based on β diketonate ligands and 2,6-bis(*N*-pyrazolyl)pyridine were synthesized according to methods reported by Jameson and co-workers (Scheme 2).⁴² Complexes 7 and 8 were prepared as deep burgundy salts by the reaction of 4 with the appropriate diimine ligand (bpy and phen) in boiling EtOH/ H₂O. While Ru(III) was reduced, ethanol was oxidized. KPF₆ or NH₄PF₆ was added to exchange the uncoordinating chloride with the [PF₆]⁻ anion to obtain the complex salts.

Crystal Structure. X-ray quality crystals were obtained by slow evaporation of saturated solutions of **5** and **6** in chloroform. The central Ru(II) ion of both complexes is six-coordinate and bound to three nitrogen atoms of the ligand **3**, two oxygen atoms of the diketone ligand (hfac and dbm, respectively), and one Cl⁻ anion (Figure 3). Details of the X-ray crystallography, tables, and bond lengths and distances can be found in the Supporting Information.

Electropolymerization of Ruthenium Complexes. Solutions of monomers with an $\sim 1 \times 10^{-3}$ M concentration in CH₂Cl₂ including 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as the electrolyte were oxidatively and electrochemically polymerized. The potential of the electrode was swept between -1.75 and +1.25 V versus ferrocene/ ferrocenium (Fc/Fc⁺) at a scan rate of 100 mV/s. The polymerization profiles for complexes 7 and 8 are displayed in Figure 4 (the polymerization profiles for complexes 5 and 6 can be found in the Supporting Information). The polymerization profiles of all the complexes were similar in terms of Ru(II)/Ru(III) redox couples and monomer oxidations. Although it was not practical or sufficient to compare the potentials reported in the literature, it should be mentioned that the Ru(II)/Ru(III) potentials of the polypyridine complexes were around 1.25 V with respect to the normal hydrogen electrode (NHE) (0.62 V vs Fc/Fc⁺).^{1,31,43} The substitution of polypyridine ligands could drastically change these potentials. For example, when one of the bpy ligands of Ru(bpy)₃²⁺ was changed by 2Cl⁻ ligands, the potential decreased by 0.35 V.¹

Complex 7 had a Ru(II)/Ru(III) redox couple at 0.51 and 0.41 V (Figure 4). The monomer oxidation was observed at 0.78 V, and a new oxidation (1.04 V) peak and a reduction (0.85 V) peak were observed in subsequent scans. Complex 8 had a Ru(II)/Ru(III) redox couple at 0.53 and 0.46 V. The monomer oxidation was observed at 0.8 V, and a new oxidation (1.05 V) peak and a reduction (0.96 V) peak were observed in subsequent scans. The peak around -0.75 V that appeared during the polymerization of all complexes might be due to the reduction of short oligomers that had not been incorporated into the polymer film.³¹ Repeated cycling resulting in linear increase of the peak currents with scan numbers (Figure 4a,b insets) might be due to the electrode

surface. Complexes 7 and 8 both had a linear increase in peak currents with number of scans (Figure 4). Accordingly, all polymers were redox-active.

The resulting insoluble polymer films that deposited on the anode were then rinsed with fresh CH₂Cl₂ in a glovebox to rinse any monomers or oligomers (which were soluble in CH_2Cl_2) away from the polymers. The reddish-brown films that were confined to the working electrode (anode) were cycled in a monomer free electrolyte solution of 0.1 M TBAPF₆ at scan rates that varied from 10 to 500 mV/s (Figure 5). Poly-7 had reversible peaks at 0.53 and 0.45 V; poly-8 had reversible peaks at 0.60 and 0.46 V. Peak currents increased with increasing scan rate for both poly-7 and for poly-8. Scan rate dependence of the polymers was measured for characterization. It was quite linear up to 100 mV for both polymerization processes, indicating that the electroactive material was not limited by the ionic flux of counterions. Because there was a decrease in charge mobility through the polymer backbone at higher scan rates, less facile ion transport and a deviation from the linear relationship occurred. A very similar ruthenium containing conducting polymer has been reported in the literature, and it had consistent results.³

Complexes 5–8 have also been polymerized on a stainless steel surface as well as an ITO on glass substrate for X-ray photoelectron spectroscopy (XPS) measurement. However, the ruthenium peak coincided with the carbon peak in XPS, and the percentages for the Ru atoms in the analysis were exaggerated. Another problem concerning the XPS data was that some of the TBAPF₆ (solution of which is the electrolyte) remained in the polymer film, despite the fact that the polymers were rinsed out with CH_2Cl_2 after the polymerization process was complete. As a conseqence, the percentages for the N, F, and P atoms were also difficult to interpret.

UV–Vis Studies. All four complexes feature Ru^{2+} which is a d⁶ system. For most Ru(II) complexes in the literature, the lowest excited state is a ³MLCT which undergoes slow radiationless transitions and therefore exhibits long lifetimes and intense luminescence emissions.¹ UV–vis spectroscopic characterizations of the complexes **5–8** and ligand **3** were obtained. The complexes adopted a maroon to reddish-brown color, and the ligand adopted a tan color. The molar extinction coefficient values vs wavelength for these complexes are displayed in Figure 6. Complexes **5–7** and the ligand **3** were



Figure 6. Molar extinction coefficient values vs wavelength for the complexes 5-8 and the ligand 3.

dissolved in CH₂Cl₂, and complex 8 was dissolved in CH₂CN (due to its lower solubility in CH_2Cl_2) to prepare stock solutions for UV-vis absorption spectra. The maximum absorptions fell below 300 nm for complexes 5, 7, and 8, and the maximum absorptions found above 300 nm for complex 6 and ligand 3 are due to LC π to π^* transitions.^{1,44} The ligand 3 and complex 5 had relatively smaller molar extinction coefficient values (29034 and 29011, respectively) than complexes 6, 7, and 8, which had molar extinction coefficient values of 52803, 66486, and 66997 M⁻¹ cm⁻¹, respectively. Intense visible absorption bands around 450–600 nm were assigned as ¹MLCT for the complexes,⁴⁴ and clearly there is no such band in the UV-vis spectrum of ligand 3. Furthermore, no peak was observed for the ³MLCT absorption at RT. Overall, the results are consistent with those of the $Ru(bpy)_{3}^{2+}$ complex which has reported values of LC transition at 285 nm, MLCT transitions at 240 and 450 nm, and MC transition at 344 nm (shoulder).¹

The ³MLCT of $Ru(bpy)_3^{2+}$ complex was observed at ~550 nm ($\varepsilon \sim 600$) when the measurement was performed in an ethanol–methanol glass at 77 K.¹ Ligand 3 had an absorption maximum at 335 nm (Figure 6). The molar extinction coefficients and the absorption maxima for the bidentate ligands, i.e., hfac, dbm, bpy, and phen, have been reported in the literature (measured in CH_2Cl_2) as follows: for phen λ_{max} = 264 nm and $\varepsilon = 31000 \text{ M}^{-1} \text{ cm}^{-1};^{45}$ for bpy $\lambda_{\text{max}} = 302 \text{ nm and}$ $\varepsilon = 14125 \text{ M}^{-1} \text{ cm}^{-1};^{46}$ for dbm $\lambda_{\text{max}} = 337 \text{ nm and}$ $\varepsilon = 26646 \text{ M}^{-1} \text{ cm}^{-1};^{47}$ for hfac $\lambda_{\text{max}} = 275 \text{ nm}^{48,49}$ and $\varepsilon = 7000 \text{ M}^{-1}$ cm^{-1,49} For all the complexes, the absorption maxima were found to be blue-shifted upon Ru²⁺ coordination with respect to ligand 3. On the other hand, complex 6 had only a 9 nm blue-shift, while other complexes typically had larger blueshifts: 54 nm for complex 5, 45 nm for complex 7, and 70 nm for complex 8. When the absorption maxima of each complex were compared with the absorption maxima of the corresponding bidentate ligand, the shift in λ_{max} upon coordination was relatively small. For example, 5 was redshifted by 6 nm, 6 was blue-shifted by 17 nm, and 7 was blueshifted by 12 nm. On the other hand, 8 was unchanged.

Complex 8, which had the highest molar extinction coefficient value, was electropolymerized on an ITO-coated glass surface to obtain the solid-state absorption spectrum of the corresponding polymer (Figure 7). A plain ITO-coated



Figure 7. Absorption spectrum of poly-8 electropolymerized on an ITO-coated glass surface.

Table 1. Photophysical Data for the Ruthenium Complexes

| | complex | | | |
|---------------------------------------------------------------------------------|---------------------------------------------------------|-----------------------------------------------------|--------------------------------------------------------------------|---------------------------------------------------------------------|
| | 5 | 6 | 7 | 8 |
| $\lambda_{\mathrm{Abs/nm}}$ (ϵ , M^{-1} cm ⁻¹) | 281 (29011), 316 (21986) sh, 354 (12247), 497 (6896) | 256 (35714), 279 (3873), 326 (52803), 489 (8151) | 254 (30553),290 (66486), 355 (21887), 455 (8894), 550 (4119) | 223 (53267), 265 (66997), 349 (18970), 443 (11820) 549 (4033) |
| $\lambda_{\rm Em~(Ex)/nm}$ at 77 K | 310, 400, 630, 750 (276); 450 (400) | 306, 400, 635, 760 (278); 485 (450) | 315, 400, 620, 750 (277); 581 (456) | 312, 400, 618, 750 (278); 566 (453) |
| $_{\lambda Em \ (Ex)/nm}$ at RT | 318, 640 (276) | 316, 650 (276) | 327, 650 (277); 610 (450) | 316, 618 (275); 580 (445) |
| $	au_{0/\mu s}$ (³ MLCT) in 2-MeTHF (air-free, dry) | 6 ± 3 | 7.2 ± 0.4 | 11 ± 1 | 14 ± 1 |
| $	au_{0/\mu s}$ (³ MLCT) in EtOH/ MeOH (4:1) (air-free, dry) | 6 ± 2 | 8 ± 3 | 10 ± 3 | 14 ± 1 |
| $	au_{0/\mu s}$ (³ MLCT) in EtOH/ MeOH (4:1) (aerated) | 6 ± 2 | 7 ± 2 | 10 ± 4 | 14 ± 3 |
| $	au_{0/\mu s}$ (³ MC) in EtOH/MeOH (4:1) (aerated) | 5 ± 1 | 4 ± 2 | 9 ± 6 | 7 ± 3 |
| $\Phi_{\rm Em}$ (%) of phosphorescence (³ MLCT) (air-free, dry) | 1.07 | 1.4 | 7.94 | 10.6 |
| $\Phi_{\rm Em}(\%)$ of phosphorescence (³ MLCT) (aerated) | 1.13 | 1.3 | 6.98 | 7.99 |
| $\Phi_{\rm Em}$ (%) of fluororescence (air-free, dry) | 35.8 | 14.4 | 19.3 | 22.5 |
| $\Phi_{\rm Em}$ (%) of fluororescence (aerated) | 34.4 | 14.2 | 19.2 | 13.7 |
| $k_{\rm r}$ (s ⁻¹), air-free (aerated) | 1783.33 (1883.33) | 1750 (1857.14) | 7940 (6980) | 7571.43 (5707.1) |
| $k_{\rm nr}~({\rm s}^{-1})$, air-free (aerated) | 164883.33 (164783.33) | 123250 (141000) | 92060 (93020) | 63857.14 (65721.43) |
| $k_q (M^{-1} s^{-1}) (O_2 $ quenching) | 4.68×10^{6} | 1.287×10^{7} | 8.49×10^{6} | 1.353×10^{7} |

glass was used as a blank in a double-beam instrument. The solid-state UV-vis spectrum of **Poly-8** revealed peaks at 289 and 355 nm and a shoulder at 441 nm. Absorbance measurement was performed up to 285 nm as a cutoff wavelength due to the absorption coming from the substrate. The monomer complex **8** had peaks at 223, 265, 349, and 443 nm. The peaks at 265 and 349 nm in the monomer **8** were slightly red-shifted to 289 and 355 nm upon polymerization due to the extended aromatic system that formed between the monomer units. The peak at 443 nm was shifted to 441 nm.

Luminescence Studies. Photophysical data for each complex have been obtained and are listed in Table 1. The measurements of each complex and the standard were performed in an EPR tube in the following order: air-free, RT; air-free, 77 K; aerated, RT; and aerated, 77 K. The resulting luminescence spectra have been presented in Figures 8 and 9. All complexes have excitation maxima at 276-278 nm both at RT and at 77 K (Figure 8) although all have different absorption maxima in UV-vis spectra. Corresponding emission maxima are also more or less the same, i.e., 310-320 nm and a broad peak ~550-750 nm. Emissions around 310-320 nm correspond to ligand fluorescence because of both a small Stokes shift and a short excited-state lifetime. Emission around ~550-750 nm should come from ligand phosphorescence due to intersystem crossing after having a singlet excited state. When cooled to 77 K in EtOH/MeOH (4:1) glass, emission intensity increased for all complexes and for $Ru(bpy)_3^{2+}$ standard; the broad peak at ~550-750 nm became structured a little bit and blue-shifted. Furthermore, a new structured peak appeared around ~350-550 nm. These observations are due to the reduction of thermal nonradiative pathways available for energy loss.

The luminescence spectra of all samples and the standard in airtight cuvettes were also obtained at RT (Supporting Information). Subsequently, the airtight cuvettes were aerated

by bubbling air and using a Pasteur pipet for the corresponding measurements.

The quantum yield measurements/calculations were performed by a relative quantum yield technique in which previously reported values for a reference is needed. Ru-(bpy)₃Cl₂ was used as the reference. The measurements were performed both in 2-MeTHF and in EtOH/MeOH (4:1). The latter was used in the literature where the values for the reference were reported. The relative quantum yield for each complex was calculated by using eq 1,⁵⁰ where the integration was the area under emission peak. $\Phi_{\rm reference}$ was reported as 0.35 and 0.328 in the literature, and the latter was used in our calculations.^{44,51}

$$\Phi_{\text{sample}} = \Phi_{\text{ref}} \times \frac{\text{integration}_{\text{sample}}}{\text{integration}_{\text{ref}}} \frac{\text{absorbance}_{\text{ref}}}{\text{absorbance}_{\text{sample}}}$$
(1)

Radiative (k_r) and nonradiative (k_{nr}) decay constants as well as the oxygen quenching rate coefficient (k_q) for each complex were calculated by using eqs 2–4,^{52,53} in which the relative quantum yields of emission $(\Phi_{\rm Em})$, measured phosphorescence lifetimes (τ_0) , and measured intensity of emissions (I) were used. The oxygen concentration in the alcohol mixture was obtained from the literature.⁵⁴

$$k_{\rm r} = \Phi_{\rm Em} / \tau_0 \tag{2}$$

$$k_{\rm nr} = (1 - \Phi_{\rm Em})/\tau_0 \tag{3}$$

$$I/I' = 1 + (k_q \tau_0[O_2])$$
⁽⁴⁾

The luminescent properties of a complex depend on the ordering of its low-energy excited states and the orbital nature of its lowest excited state. As a consequence, the energy positions of MC, MLCT, and LC are important. The energies of the MC excited states depend on the ligand field strength which is related to the σ -donor and π -acceptor properties of the ligands, the steric crowding around the metal, and the bite



Figure 8. Excitation and emission spectra of the complexes (a) 5, (b) 6, (c) 7, and (d) 8 and $Ru(bpy)_3^{2+}$ as the standard in dry, air-free EtOH/MeOH (4:1) solution at RT and at 77 K in a quartz EPR tube.



Figure 9. (a) Excitation and emission spectra of ³MLCT phosphorescence using complex 7 and Ru(bpy)₃²⁺ as the standard at RT and at 77 K in a dry, air-free EtOH/MeOH (4:1) solution in a quartz EPR tube (left). (b) Excitation and emission spectra of ³MLCT phosphorescence using complex 8 and Ru(bpy)₃²⁺ as the standard at RT and at 77 K in a dry, air-free EtOH/MeOH (4:1) solution in a quartz EPR tube (right).

angle of the polydentate ligands. The energy of the MLCT excited states depends on the reduction potential of the ligand that is involved in the MLCT, the oxidation potential of the metal in the complex, and the charge separation caused by the transition. The energy of the LC excited states depends on the intrinsic properties of the ligands, such as the energy gap

between the HOMO–LUMO levels and singlet–triplet splitting. Ru(II) polypyridine complexes generally have ³MLCT as its lowest excited state and demonstrate long lifetimes and intense luminescence properties.¹

To confirm that the orbital nature of the emission occurred from \sim 350 to 550 nm appeared upon cooling to 77 K (Figure



Figure 10. (a) Emission spectrum of poly-8 was excited at 276 nm (left). (b) Excitation (black) and emission spectra (red and blue) of poly-8 in the visible region of the spectrum (right).

8a-d), emission spectra of all complexes and the standard were compared with the emission spectrum of the free ligand 3 which has been reported previously.²⁴ The RT absorption and the emission of 3 have been reported as 339 and 378 nm, respectively. These values were higher than the absorption and emission values for the complexes. The ligand phosphorescence of 3 was observed in between 484 and 650 nm. There was no peak around that region for the emission of complexes. All complexes and the standard had the same structured emissions from ~375 to 550 nm upon cooling. However, the only common component among complexes 5 and 6 and the standard was Ru^{2+} , despite the fact that emissions from ~350 to 550 nm overlapped. The common components among complexes 7 and 8 and the standard are Ru2+ and the bpy ligand (phen is similar to bpy in complex 8). Furthermore, the lifetimes of the emissions fell in the same range, i.e., a few microseconds (Table 1). Assignment of the peak was made as ³MC emission. The literature supports the idea as follows: in d⁶ octahedral complexes, MC excited states are strongly displaced with respect to the ground-state geometry along metal-ligand vibration coordinates. As the lowest excited state is MC, it undergoes fast nonradiative pathway to the ground state, or ligand dissociation reactions. As a result, no luminescence can be observed at RT. Because LC and MLCT excited states are not strongly displaced compared with the ground state, the nonradiative pathways do not occur, and luminescence can be observed. Luminescence coming from the ³LC and ³MLCT states is usually structured. The ³LC emission usually occurs close to the free ligand emission. On the other hand, the ³MLCT emission occurs at lower energies. Moreover, ³LC emission is less influenced by the heavy metal ion; hence, the emission lifetime is longer than that for ³MLCT. Luminescence arising from a ³MC excited state appears as a Gaussian-shaped emission band that is red-shifted compared with the lowest energy absorption bands. The excited-state lifetimes and the intensity decrease with increasing temperature. Furthermore, the ³MC emissions cannot be observed in fluid solutions at RT.¹

To find luminescence originating from the MLCT transition, the excitation spectra of complexes were obtained by having the emission maxima at \sim 630 nm. The complexes were then excited at the excitation maxima found at 450 nm. The resulting maximized emission spectra were assigned as the ³MLCT emissions.^{1,44}

The ³MLCT emissions of complexes 7 and 8 in an EPR tube at RT revealed small bumps (Figure 9). However, upon cooling to 77 K, both complexes revealed a highly structured excitation and emission bands as expected for a MLCT transition. Furthermore, the emission maxima for 7 and 8 were found to be blue-shifted when cooled to 77 K. Having a broad structureless spectra at RT and structured spectra upon cooling suggests that the thermal nonradiative pathways are reduced due to the energy loss. The excitation and emission spectra of complex 7 for the MLCT transition overlapped with the excitation and emission spectra for the standard. On the other hand, the emission spectra for the MLCT transition of complex 8 was 15 nm blue-shifted with respect to the standard.

The emission lifetimes for all complexes in both air-free and aerated solutions were measured at 77 K and are presented in Table 1. The lifetime of the standard was also measured and found to be consistent with the literature value of 5 μ s.^{1,21} The complexes had mean lifetime values that range from 6 to 14 μ s. Complex 5 had the shortest lifetime, and complex 8 had the longest lifetime. The lifetime values of complexes did not change either by changing the solvent from 2-MeTHF to EtOH/MeOH (4:1) or by introducing air into the solutions. The lifetimes of phosphoresce due to the ³MC transition of complexes were also measured. The corresponding values were almost the same as, but slightly lower than, the ³MLCT phosphorescence for all complexes.

The fluorescence and phosphorescence quantum yields of the complexes were calculated by using eq 1 for both dry airfree and aerated solutions of the complexes. The quantum yield of ligand fluorescence was the highest for **5**. However, the quantum yield of phosphorescence due to the ³MLCT was the highest for **8**. The emission intensities of both fluorescence and phosphorescence values for all complexes decreased upon exposure to air. The corresponding quantum yield calculations were also decreased up to 2.61% for the phosphorescence and 8.8% for the fluorescence of **8**.

The quenching of the emission by dissolved molecular oxygen was also investigated. The preparation of degassed solution of complexes and introduction of air into samples has been described previously. Farley et al. reported a very efficient quenching of dissolved oxygen on their series of platinum complexes by the same technique that was used here, with the exception that the $[O_2]$ was used as 0.0022 M in their calculations rather than the value used here of 0.0019099 M.^{54,55} In this study, oxygen quenching resulted in a little

decrease in the emission intensities and a k_q value in the order of 10^6-10^7 M⁻¹ s⁻¹, in contrast to the values reported by Farley et al. as in the order of 10^9 M⁻¹ s⁻¹. The calculated values of the quantum yield also indicated that the oxygen quenching was minimal (Table 1). The reason for having this much difference in the quenching might be due to the empty axial position of the metal in square-planar platinum(II) complexes that Farley et al. made, which were relatively accessible for interaction with a quencher. On the other hand, it was difficult to reach to metal center of an octahedral ruthenium(II) complex that was coordinatively saturated. Another technique for oxygen quenching has been reported by Rusak et al. In their technique, oxygen quenching of Ru(bpy)₃²⁺ was studied by introducing SO₃²⁻ anions into the Ru(bpy)₃²⁺ solution to adjust the O₂ concentration by the reaction

$$2SO_3^{2-} + O_2 \rightarrow 2SO_4^{2-}$$

Subsequently, the measurements were performed at RT since the lifetimes are shorter than those at 77 K.⁵³ Measurements were made in an aqueous solution of Ru(bpy)₃²⁺ without any degassing procedure. This was because the luminescence without SO_3^{2-} anions was measured first and then added to decrease the O₂ concentration to obtain an enhanced luminescence.

Complex 8 was selected to be electropolymerized on an ITO-coated glass surface to obtain the solid-state excitation and emission spectra of the corresponding polymer because 8 has the highest quantum yield of phosphorescence and the longest lifetime. Initially, **poly-8** was excited at 276 nm, which corresponds to the excitation wavelength of monomer complexes that are mainly for fluorescence emission. The corresponding emission spectra were recorded at 77 K (Figure 10a). The emission peaks are located at approximately 312 and 728 nm. The peak at 312 nm appeared in the same region as that of the monomer. However, the broad peak at ~728 nm had a considerable red-shift in comparison with that of the monomer emission that appeared at ~630 nm. The reason for this might be the extended π conjugation that occurred during polymerization.

The peak at 312 nm has a lower intensity than that of the broad peak at 747 nm. The emission spectrum of the monomer was the opposite in terms of the intensity; i.e., the peak at \sim 310 nm was significantly more intense than that of the MLCT emission peak at ~630 nm. The reason for this might be that the singlet excited state of the polymer encounters an efficient intersystem crossing that causes the triplet emission to be enhanced. Poly-8 was also excited to obtain the MLCT emission. However, the excitation at 453 nm, which was the monomer excitation wavelength, did not result in any emission. Two excitation maxima were found to obtain an emission at 747 nm (531 and 639 nm, Figure 10b, black). Poly-8 was then excited at these two wavelengths to obtain the emission spectra (Figure 10b, red and blue). The lifetime of the 747 nm emission was measured as $13 \pm 8 \ \mu$ s. This value was very close to that of the monomer lifetime $(14 \pm 1 \ \mu s)$ that has an emission at 566 nm at 77 K. However, the standard deviation was significantly higher than that of the monomer. An ITOcoated glass substrate was also excited at 456 nm to determine whether the emission originated from the ITO. The emission maximum of the ITO surface was found to be 730 nm, which was a close, but different, value than that for the poly-8 emission at 747 nm.

CONCLUSIONS

In summary, the syntheses, characterization, electropolymerization, and absorption and luminescence properties of EDOTfunctionalized ruthenium(II) complexes in which two of the ligands are anionic (hfac and dbm) and two of the ligands are neutral (bpy and phen) have been reported for their luminescent and photophysical properties. All the complexes are electropolymerizable, and the polymers are electroactive. Moreover, complexes are emissive with relatively long lifetimes, and oxygen quenching of emission is minimal. Complex 8 was polymerized on an ITO-coated glass substrate for the luminescence studies of the resulting polymer which has shown promising results for photoluminescence.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macro-mol.8b00959.

Electropolymerization profiles for ruthenium complexes 5 and 6 (and insets: current vs number of scans); the figure for emission spectra of ³MLCT phosphorescence of complexes 5 and 6 at RT and at 77 K in a quartz EPR tube; figures for excitation and emission spectra of ³MLCT phosphorescence of complexes 7 and 8 at RT in an airtight quartz cuvette; tables for crystal data and structure refinement, selected bond lengths and angles for 5 and 6 (PDF)

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Notes

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ABBREVIATIONS

 $[Ru(bpy)_3Cl_2]$, tris(2,2'-bipyridyl)ruthenium(II) dichloride; L, ligand; MLCT, metal-to-ligand charge transfer; MC, metal centered; LC, ligand centered; EDOT, 3,4-diethylene-

dioxythiophene; ITO, indium tin oxide; EDOT₂NNN, bis[4-[2-(3,4-diethylenedioxy)thiophene]pyrazol-1-yl]pyridine; hfac, 1,1,1,5,5,5-hexafluoro-2,4-pentanedione; dbm, dibenzoylmethane; bpy, 2,2'-bipyridine; phen, 1,10-phenanthroline; OLED, organic light-emitting diode; PLED, polymer lightemitting diode; TBAPF₆, tetrabutylammonium fluoride hexafluorophosphate; Fc/Fc⁺, ferrocene/ferrocenium; NHE, normal hydrogen electrode; XPS, X-ray photoelectron spectroscopy; EPR, electron paramagnetic resonance; HOMO, highest occupied molecular orbital; LUMO, lowest unoccupied molecular orbital; RT, room temperature; std, standard.

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