SUPPORTING INFORMATION ACCOMPANYING:

Luminescent Electropolymerizable Ruthenium Complexes and Corresponding Conducting Metallopolymers

Seyma Goren Keskin,[*,†,a] Xunjin Zhu,[†,b], Xiaoping Yang[†,c], Alan H. Cowley[†], Bradley J. Holliday[d]

†Department of Chemistry, The University of Texas at Austin, NMS 3.316
2506 Speedway, Mailstop A5300, Austin, TX 78712-1224, United States

Corresponding author e-mail address: skeskin@utexas.edu

Electrochemistry/Electropolymerization

The polymerization scan of complex **5** (Figure S1a) had an oxidation at 0.31 V and reduction at 0.34 V (redox couple). An irreversible oxidation at 1.04V was observed. The peak at 0.31 V was assigned as the Ru(II)/Ru(III) oxidation, and the peak at 1.04 was assigned as oxidation of the monomer. New oxidation and reduction peaks grow at -0.04V and 0.71V respectively. Complex **6** has Ru (II)/Ru(III) redox couple at 0.04V and –0.40 V, and monomer oxidation is observed at 0.75 V (Figure S1b). Complex **6** was polymerized on a stainless-steel surface used as a working electrode. Because the surface area of the stainless-steel electrode was bigger than the platinum button, larger current density and broader peaks were observed (Figure S1b). All other complexes were polymerized on platinum button as the working electrode. Repeated cycling resulting in a linear increase of the peak currents with scan numbers, were due to the accumulation of the redox-active polymer onto the electrode surface. Polymerization profiles of complexes **5** and **6** both have a linear increase of peak currents with number of scans up to sixteen and twenty scans, respectively.

a) b)

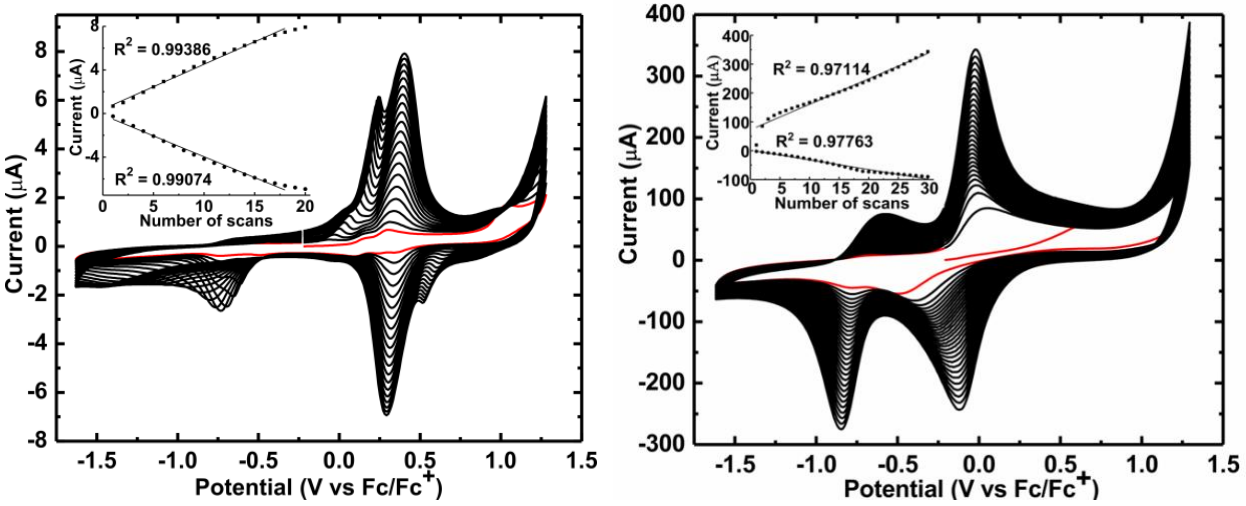

Figure S1. Electropolymerization of ruthenium complexes, initial scans shown in red. Insets: Current vs. number of scans. a) **5** (left) b) **6** (right).

Luminescence Studies

The luminescence measurements were performed initially at RT then at 77 K in a quartz EPR tube. For complexes **5** and **6**, both excitation and the emission peaks were found to be weak (Figure S2). Complex **5** did not even display an emission peak at RT in an EPR tube. However, upon cooling to 77 K, a shoulder appeared. Complex **6** yielded better results at both temperatures, but the peaks still appeared as weak and noisy. The emission of **6** was enhanced upon cooling and blue shifted. Both complexes did not indicate good emission peaks for the measurements that were carried out in a cuvette at RT.

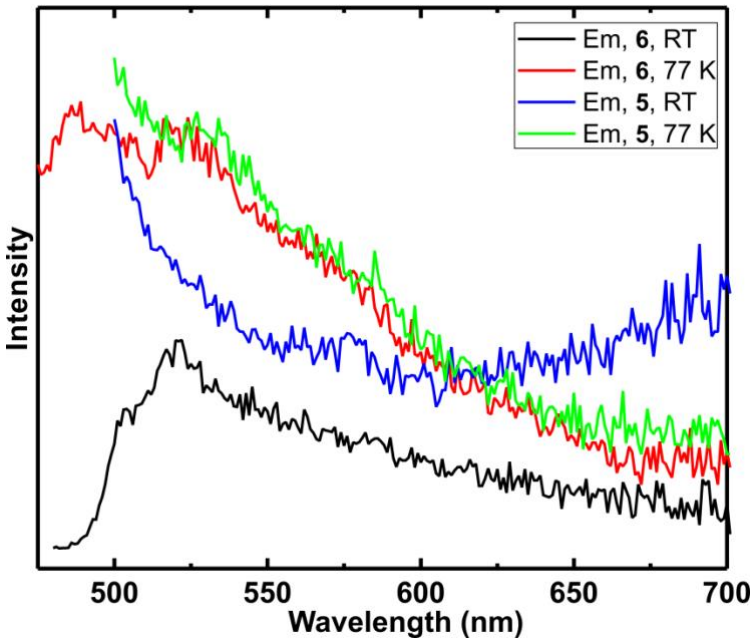

Figure S2. Emission spectra of ^{3}MLCT phosphorescence of complexes **5** and **6** at RT and at 77 K in a dry, air-free EtOH/MeOH (4:1) solution in a quartz EPR tube.

The excitation and emission spectra for **7** and **8** in a quartz cuvette at RT revealed broad unstructured bands as was observed for the measurements that were carried out in an EPR tube at RT (Figures S3 and S4, respectively). The peak maxima for complex **8** were also blue shifted by 10–15 nm with respect to **7** and the standard.

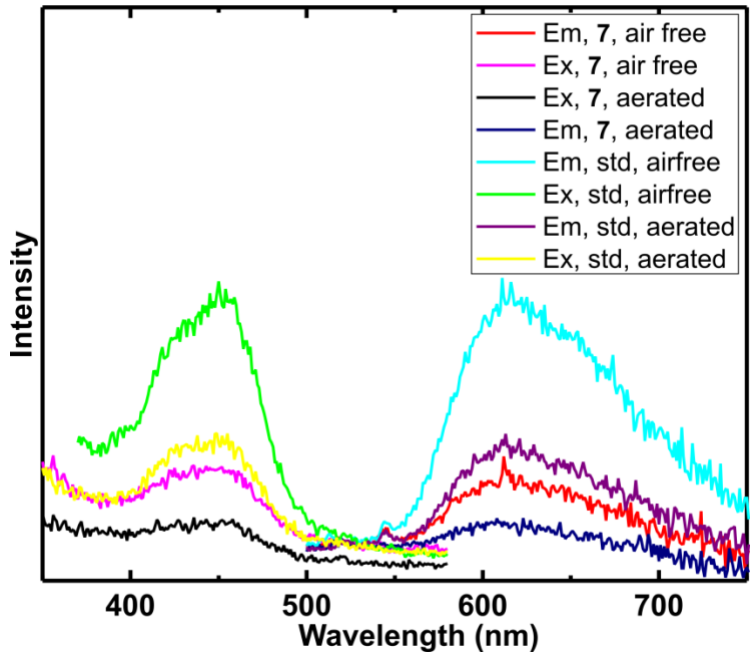

Figure S3. Excitation and emission spectra of ^{3}MLCT phosphorescence of complex **7** and $Ru(bpy)_3^{2+}$ as the standard at RT in air-free and aerated EtOH/MeOH (4:1) solution in an airtight quartz cuvette.

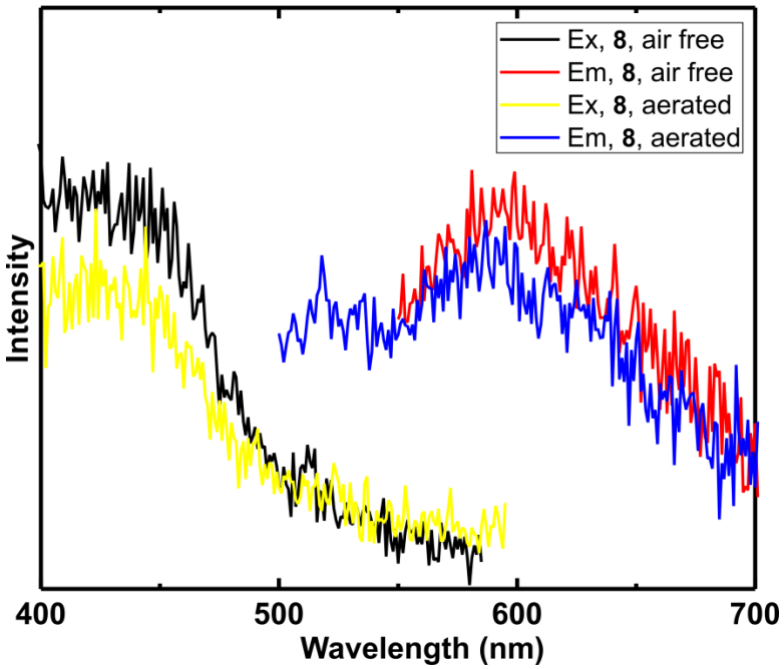

Figure S4. Excitation and emission spectra of ^{3}MLCT phosphorescence of complex **8** at RT in air-free and aerated EtOH/MeOH (4:1) solution in an airtight quartz cuvette.

Crystal Structure

Crystal data and structure refinement for complexes **5** and **6** can be found in Table S1. The complex **5** crystalizes in the triclinic space group *P-1* with two molecules per unit cell. The central Ru ion of the complex is six-coordinate, bound to three nitrogen atoms of the ligand **3**, two oxygen atoms of the hfac ligand and one Cl^- anion. The average distances for Ru-N and Ru-O are 2.026 Å and 2.068 Å, respectively. While the Ru-Cl bond length is 2.385 Å, which is much longer than those of Ru-N and Ru-O. Selected bond lengths and angles for **5** are presented in Table S2.

Complex **6** crystallizes in the monoclinic space group $P2_1/c$ with four independent molecules in the unit cell. The central Ru ion of the complex has a six-coordinate environment, bound to three nitrogen atoms of the ligand **3**, two oxygen atoms of the dbm ligand and one Cl^- anion. The average distances for Ru-N and Ru-O are 2.017 Å and 2.052 Å, respectively. While the Ru-Cl bond length is 2.411 Å, which is much longer than those of Ru-N and Ru-O. Selected bond lengths and angles for **6** are presented in Table S3.

Table S1. Crystal data and structure refinement for complexes **5** and **6**

	5	**6**
CCDC #	1557063	1557064
Formula	$C_{28}H_{18}N_5O_6Cl_1F_6S_2Ru$, $3(C_1H_1Cl_3)$	$C_{38}H_{28}N_5O_6ClS_2Ru$
Fw	1193.22	851.29
Cryst syst.	triclinic	monoclinic
Space group	P−1	$P2_1/c$
a, Å	10.3010(4)	14.6005(6)
b, Å	15.0820(8)	18.1804(8)
c, Å	15.2570(8)	13.3305(8)
α, deg	81.325(3)	90
β, deg	78.617(3)	99.7260(18)
γ, deg	71.005(2)	90
V, $Å^3$	2187.56(18)	3487.6(3)
Z	2	4
D_{calc}, g cm^{-3}	1.812	1.621
temp, K	153(2)	153(2)
F(000)	1180	1728
μ, mm^{-1}	1.139	0.703
θ rang, deg	2.07-27.47	1.80-25.70
reflns meads	14187	12059
reflns used	9868	6583
params	567	478
R^a ($I > 2\sigma(I)$)	R1 = 0.0658	R1 = 0.0556
	wR2 = 0.1466	wR2 = 0.0926
R^a (all data)	R1 = 0.1034	R1 = 0.1337
	wR2 = 0.1689	wR2 = 0.1147
S	1.070	1.031

[a] $R1 = \Sigma||F_o| - |F_c||\Sigma|F_o|$. $wR2 = [\Sigma w[(F_o^2 - F_c^2)^2]/\Sigma|[w(F_o^2)^2]]^{1/2}$. $w=1/[\sigma^2(F_o^2)+(0.075P)^2]$, where $P = [\max(F_o^2,0)+2F_c^2]/3$.

Table S2. Selected Bond Lengths (Å) and Angles (°) for **5**.

Ru(1)-N(1)	1.946(4)
Ru(1)-N(3)	2.055(4)
Ru(1)-O(1A)	2.067(3)
Ru(1)-O(2A)	2.068(4)
Ru(1)-N(5)	2.076(4)
Ru(1)-Cl(1)	2.3850(13)
N(1)-Ru(1)-N(3)	79.42(17)
N(1)-Ru(1)-O(1A)	92.10(16)
N(3)-Ru(1)-O(1A)	90.47(15)
N(1)-Ru(1)-O(2A)	174.11(16)
N(3)-Ru(1)-O(2A)	96.32(16)
O(1A)-Ru(1)-O(2A)	92.01(14)
N(1)-Ru(1)-N(5)	78.65(17)
N(3)-Ru(1)-N(5)	157.86(18)
O(1A)-Ru(1)-N(5)	87.29(15)
O(2A)-Ru(1)-N(5)	105.77(16)
N(1)-Ru(1)-Cl(1)	89.41(12)
N(3)-Ru(1)-Cl(1)	90.82(12)
O(1A)-Ru(1)-Cl(1)	178.17(11)
O(2A)-Ru(1)-Cl(1)	86.57(11)
N(5)-Ru(1)-Cl(1)	92.00(12)

Table S3. Selected Bond Lengths (Å) and Angles (°) for **6**.

Ru(1)-N(1)	1.936(4)
Ru(1)-N(3)	2.028(4)
Ru(1)-O(2A)	2.034(4)
Ru(1)-O(1A)	2.070(3)
Ru(1)-N(5)	2.087(4)
Ru(1)-Cl(1)	2.4108(15)
N(1)-Ru(1)-N(3)	79.41(16)
N(1)-Ru(1)-O(2A)	88.09(15)
N(3)-Ru(1)-O(2A)	88.75(15)
N(1)-Ru(1)-O(1A)	174.37(15)
N(3)-Ru(1)-O(1A)	95.00(15)
O(2A)-Ru(1)-O(1A)	91.14(14)
N(1)-Ru(1)-N(5)	79.21(16)
N(3)-Ru(1)-N(5)	158.39(16)
O(2A)-Ru(1)-N(5)	87.49(15)
O(1A)-Ru(1)-N(5)	106.33(14)
N(1)-Ru(1)-Cl(1)	92.95(13)
N(3)-Ru(1)-Cl(1)	91.76(13)
O(2A)-Ru(1)-Cl(1)	178.91(10)
O(1A)-Ru(1)-Cl(1)	87.86(11)
N(5)-Ru(1)-Cl(1)	92.39(12)

REFERENCES

1) Zhu, X. J.; Holliday, B. J. Electropolymerization of a Ruthenium(II) Bis(pyrazolyl)pyridine Complex to Form a Novel Ru-Containing Conducting Metallopolymer. *Macromolecular Rapid Communications* **2010**, 31, 9-10, 904-909.

2) Stanley, J. M.; Zhu, X.; Yang, X.; Holliday, B. J. Europium Complexes of a Novel Ethylenedioxythiophene-derivatized Bis(pyrazolyl)pyridine Ligand Exhibiting Efficient Lanthanide Sensitization. *Inorganic Chemistry* **2010**, 49, 5, 2035-2037.

3) G. H. Sheldrick, SHELX 97, A software package for the solution and refinement of X-ray data; University of Göttingen: Göttingen, Germany, 1997.

4) D. T. Cromer and J. T. Waber, International Tables for X-Ray Crystallography, Kynoch Press, Birmingham, vol. 4, 1974, Table 2.2A.