

## Title: Electron transport through a (terpyridine)ruthenium metallosurfactant containing a redox-active aminocatechol derivative

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**Figure S2.**  $^1\text{H}$ -NMR spectrum of 3,5-ditert-butyl-2-(phenylamino)catechol ( $\text{L}^{\text{H}_2}$ ) ligand

**Figure S3.** Full  $^1\text{H}$ -NMR spectrum of  $[\text{Ru}(\text{L}^{\text{terpy}})(\text{L}^{\text{H}_2})\text{Cl}]\text{PF}_6$  **1**

**Figure S4.**  $^{13}\text{C}$ -NMR spectrum of  $[\text{Ru}(\text{L}^{\text{terpy}})(\text{L}^{\text{H}_2})\text{Cl}]\text{PF}_6$  **1**

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**Figure S11.** AFM height images for 9-monolayers of complex **1** deposited on quartz substrate (a) 3D view (b) sectional analysis

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**Table T3.** Metal-ligand bond lengths for singlet, triplet, quintet, and septet states of the Ru complex optimized at the B3LYP+D3/SDD,6-311G\* level of theory as well as crystal structure data. The values in parentheses correspond to the optimized values in dichloromethane (PCM solvent model).

**Table T4.** : Energetics for singlet, triplet, quintet, and septet states of Complex **1** in dichloromethane (PCM solvent model)

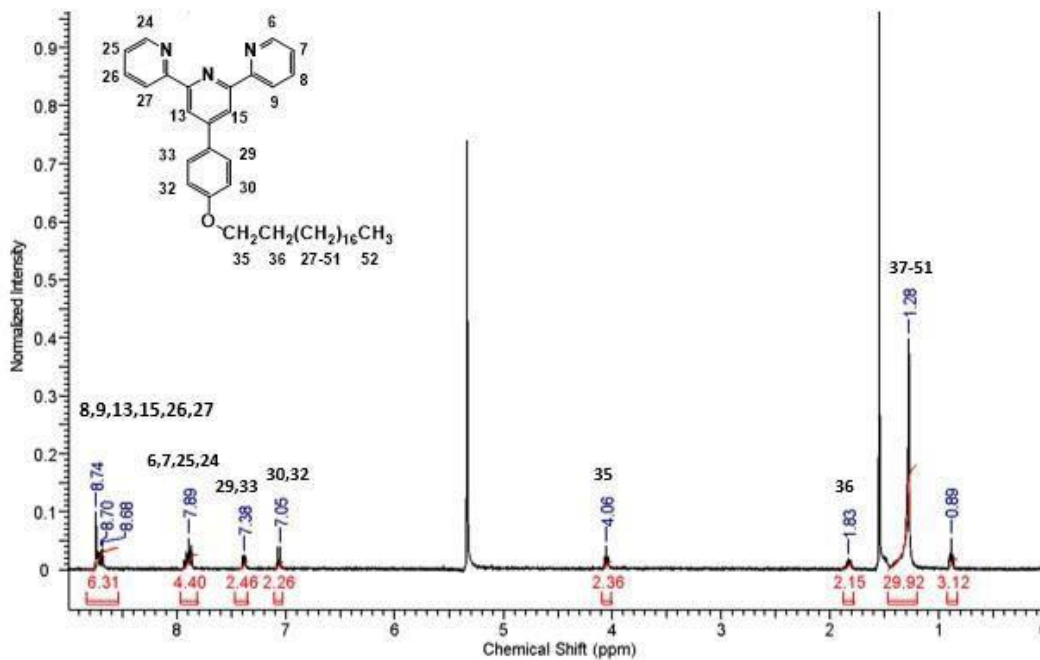
**Figure S13.** Calculated absorption spectrum with corresponding stick spectrum of  $[\text{Ru}(\text{L}^{\text{terpy}})(\text{L}^{\text{H}_2})\text{Cl}]\text{PF}_6$  **1**

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**Figure S14.** Singly-occupied natural orbitals of the oxidized and reduced species of  $[\text{Ru}(\text{L}^{\text{terpy}})(\text{L}^{\text{H}_2})\text{Cl}]\text{PF}_6$  **1** in dichloromethane

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**Figure S1:**  $^1\text{H-NMR}$  spectrum of 4'-(4-(octadecyloxy)phenyl)-2,2':6'2''-terpyridine ( $L^{\text{terpy}}$ ) ligand



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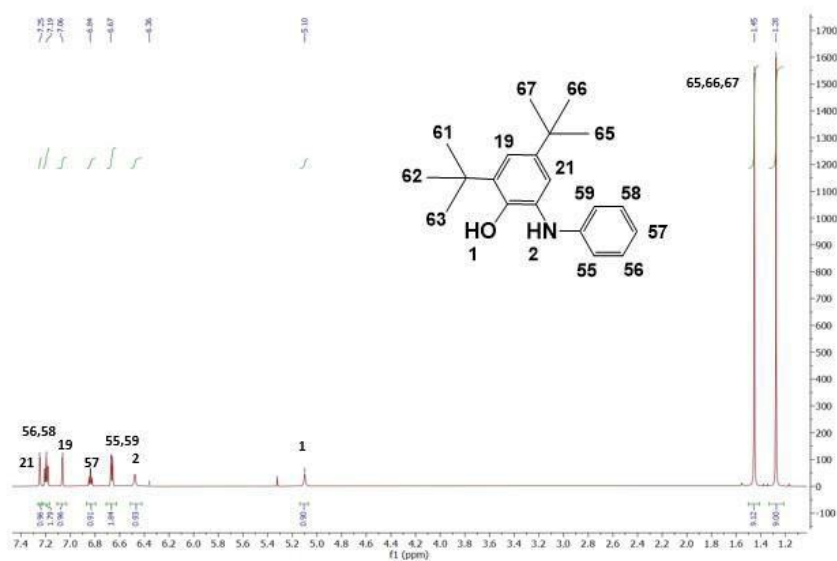


Figure S3: Full  $^1\text{H-NMR}$  spectrum of  $[\text{Ru}(\text{L}^{\text{terpy}})(\text{L}^2)\text{Cl}]\text{PF}_6$  **1**

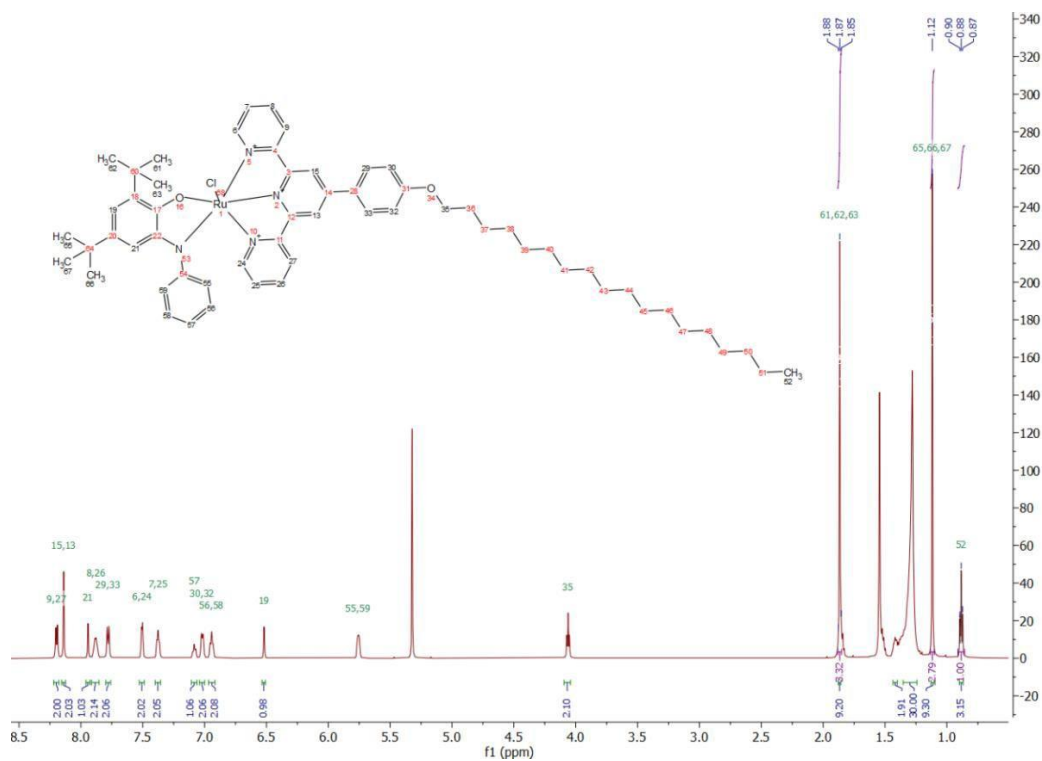


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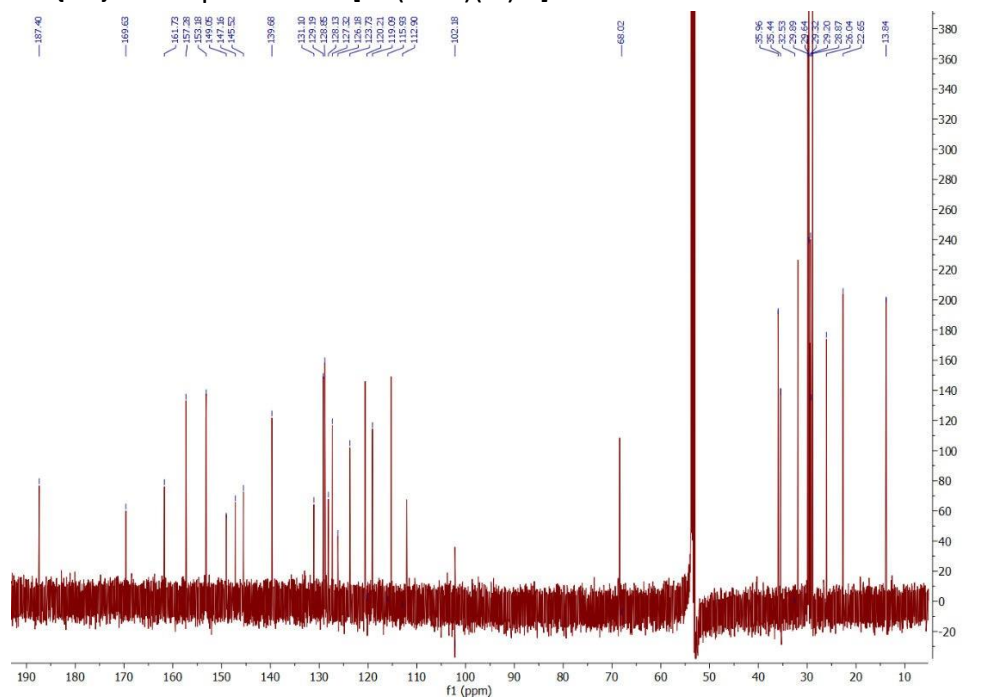


Figure S5: HSQC NMR spectrum of  $[\text{Ru}(\text{L}^{\text{terpy}})(\text{L}^2)\text{Cl}]\text{PF}_6$  **1**

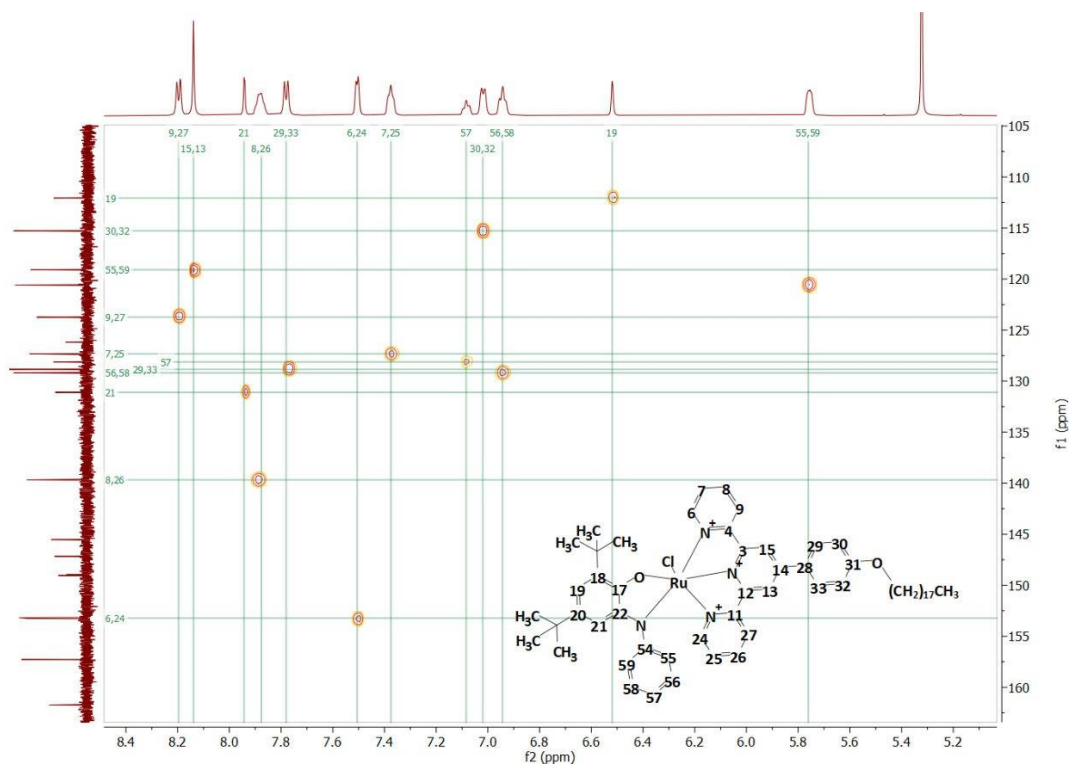
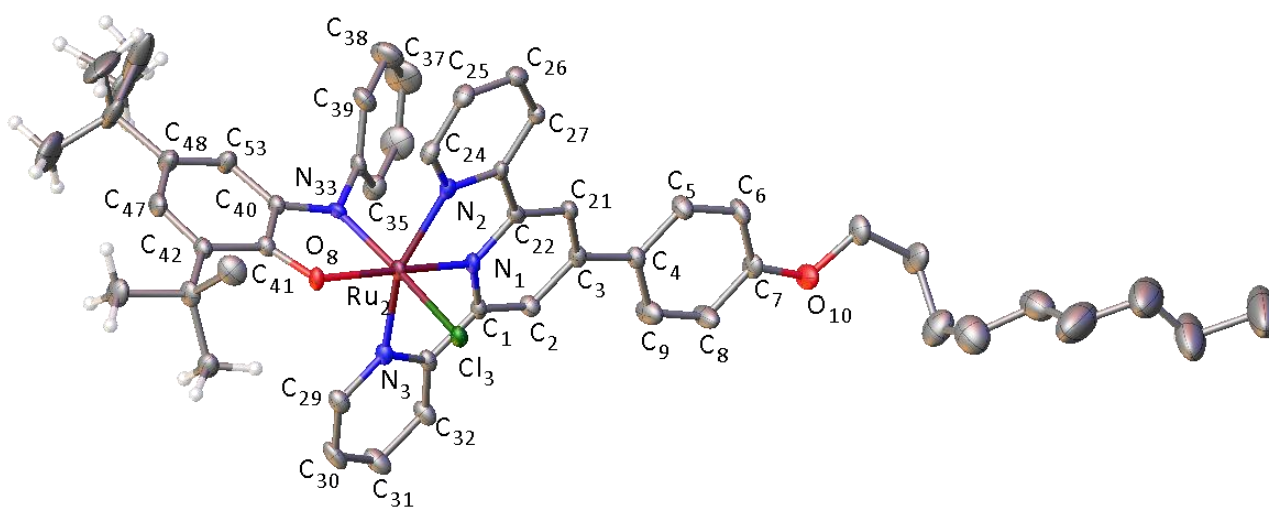


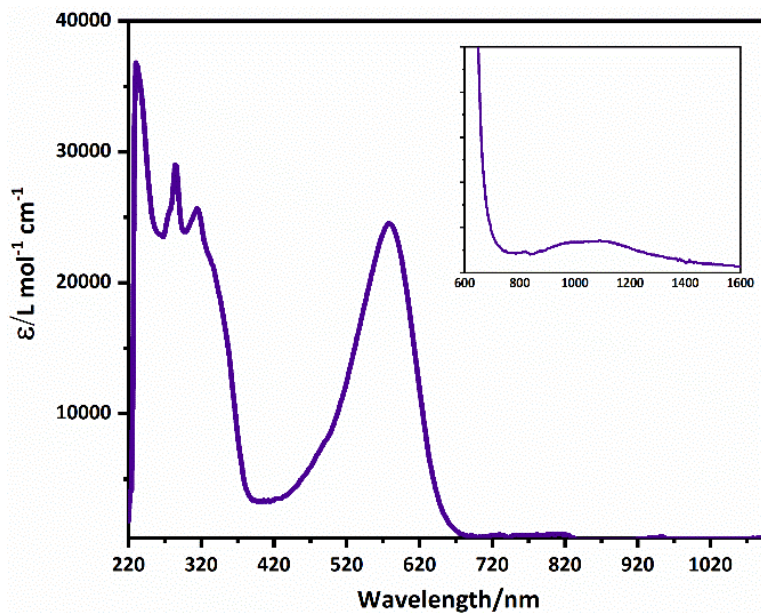
Figure S6: Crystal structure of complex **1** with 50% probability



**Table T1:** Crystal structure data and selected bond lengths for complex **1**

	<b>1</b>
Formula	C <sub>57</sub> H <sub>64.7</sub> ClF <sub>6</sub> N <sub>4</sub> O <sub>2</sub> PRu
FW	1157.66
Space group	P-1
a(A°)	12.8026(6)
b(A°)	15.0623(8)
c(A°)	19.8264(10)
α(deg)	68.182(3)
β(deg)	88.474(3)
γ(deg)	66.262(3)
V(A°) <sup>3</sup>	3214.9(3)
Z	2
Temp(K)	100
λ(A°)	0.71073
ρ(g m <sup>-3</sup> )	1.196
μ(mm <sup>-1</sup> )	0.368
R(F)(%)	5.60
Rw(F)(%)	14.2

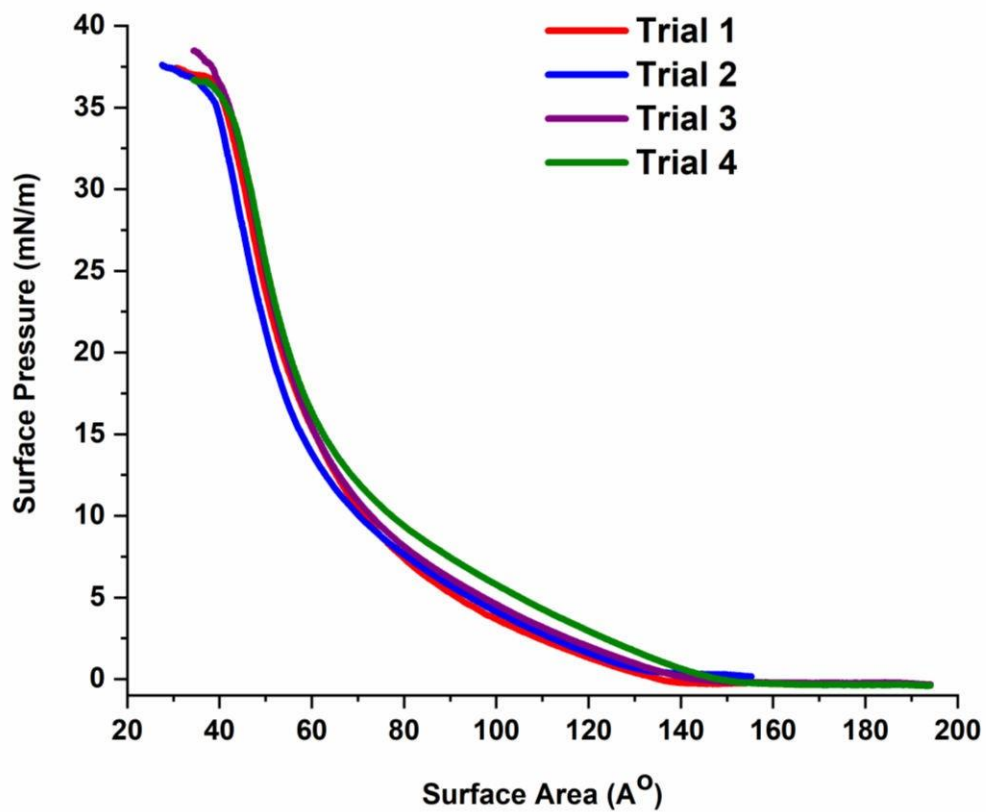
Bond length(A°)	<b>1</b>
Ru-N1	1.972(2)
Ru-N2	2.073(3)
Ru-N3	2.068(2)
Ru-O8	2.0365(19)
Ru-N33	1.971(2)
Ru-Cl	2.3875(7)
C40-N33	1.347
C41-O8	1.281
C40-C41	1.444
C41-C42	1.443
C42-C47	1.362
C47-C48	1.438
C48-C53	1.366
C53-C40	1.412
Diameter(C31-C13)	10.244
Area(A°) <sup>2</sup> (Circular)	82.45
Volume	2042
Length (C46-C10)	24.768

**Figure S7:** UV-visible spectrum of complex **1** in dichloromethane. Inset shows the magnification of 600-1600 nm region of the UV-visible spectrum

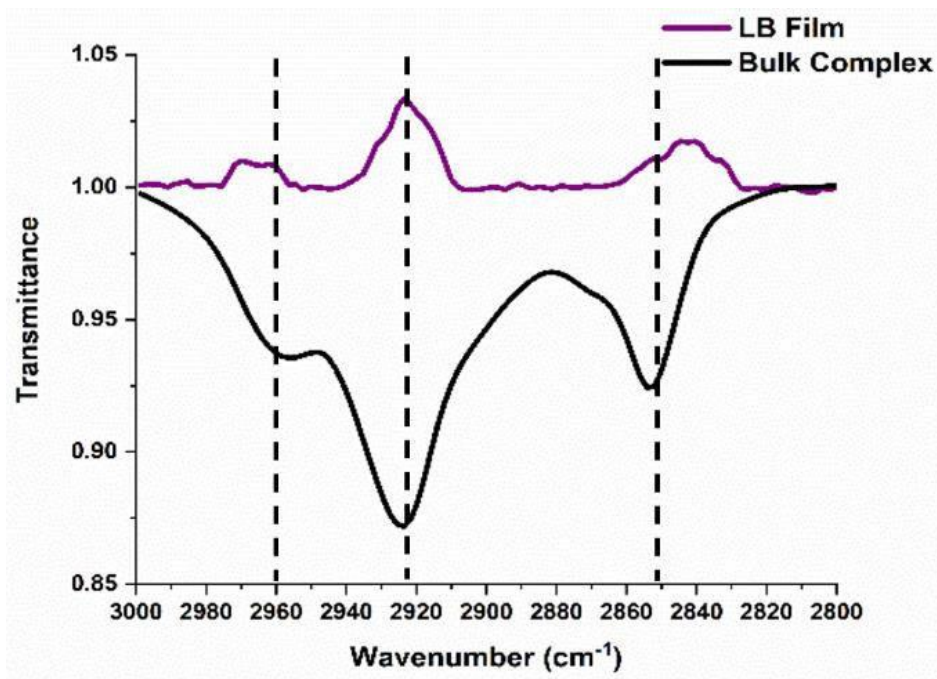
**Table T2:** Electrochemical data recorded in dichloromethane for complex **1**

Peak Assignment	$E_{1/2}(\Delta E_p)/V$ $ I_{pa}/I_{pc} $	$E_{1/2}(\Delta E_p)/V$ $ I_{pa}/I_{pc} $	$E_{1/2}(\Delta E_p)/V$ $ I_{pa}/I_{pc} $	$E_{1/2}(\Delta E_p)/V$ $ I_{pa}/I_{pc} $
Complex <b>1</b>	0.76 (90)  1.18	-0.76 (72)  0.95	-1.60 (74)  1.11	-2.20

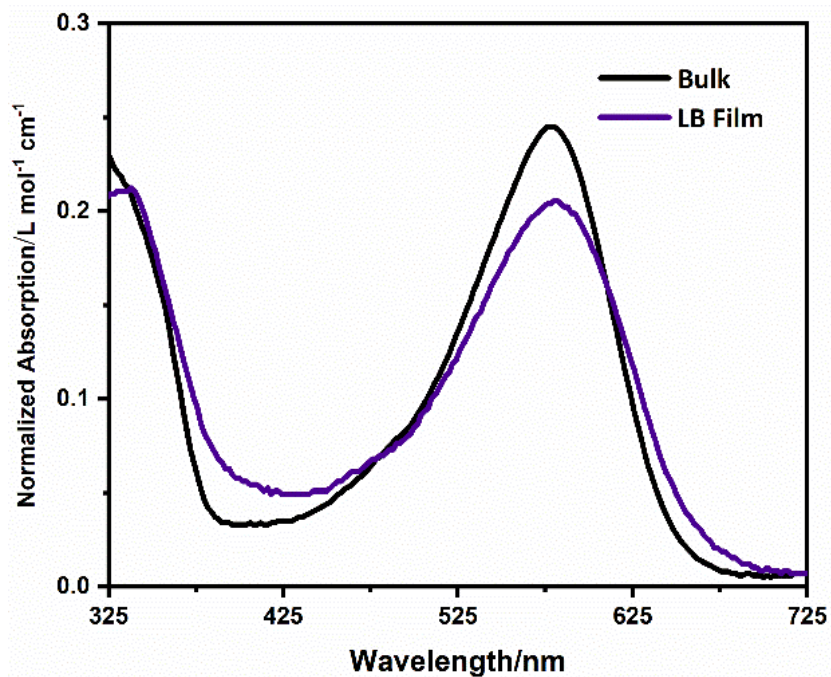
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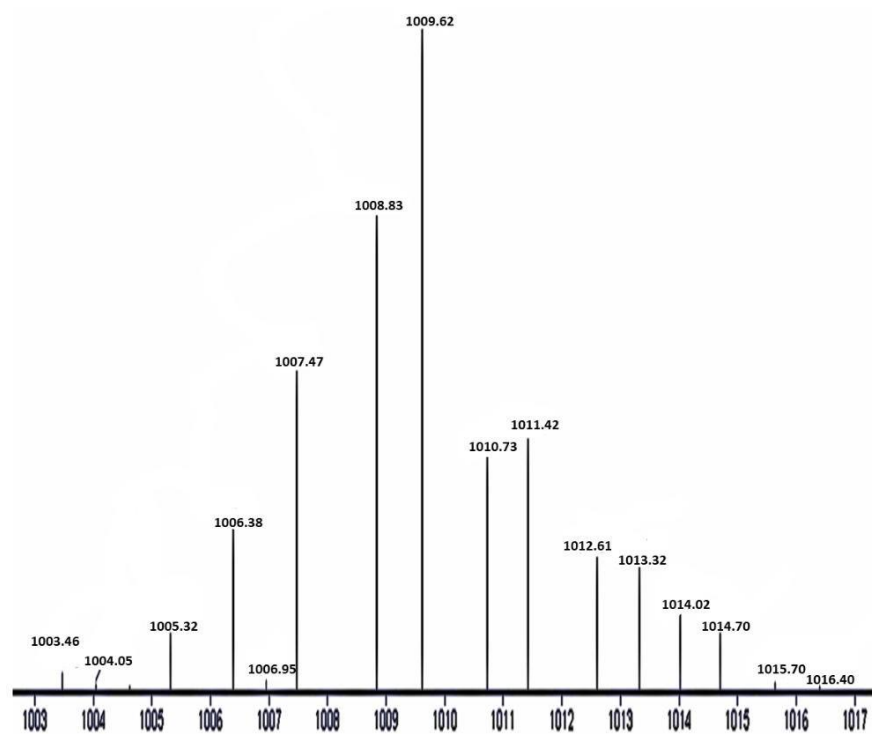


**Figure S9:** Comparison of IRRAS spectrum of 57 layers of LB film and IR spectrum of  $[\text{Ru}(\text{L}^{\text{terpy}})(\text{L}^2)\text{Cl}]\text{PF}_6$  **1**

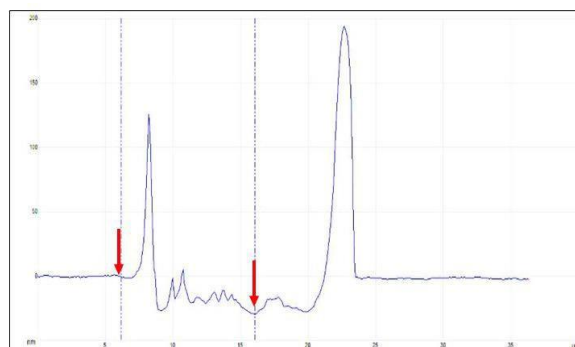
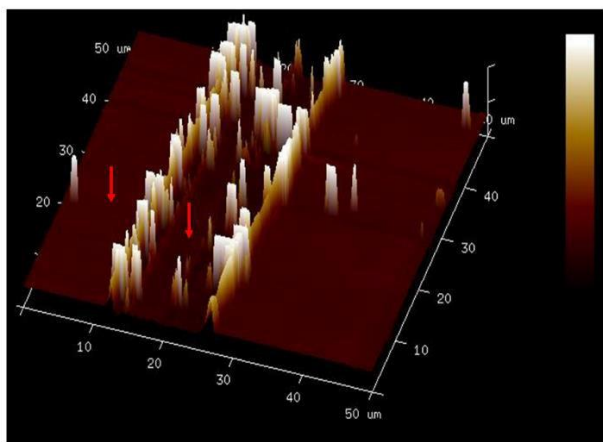


**Figure S10:** (a) Comparison of UV-vis spectrum of 57 layers of LB film and solution state UV-vis spectrum of complex **1** (b) Mass spectrum of **1** recovered from LB films



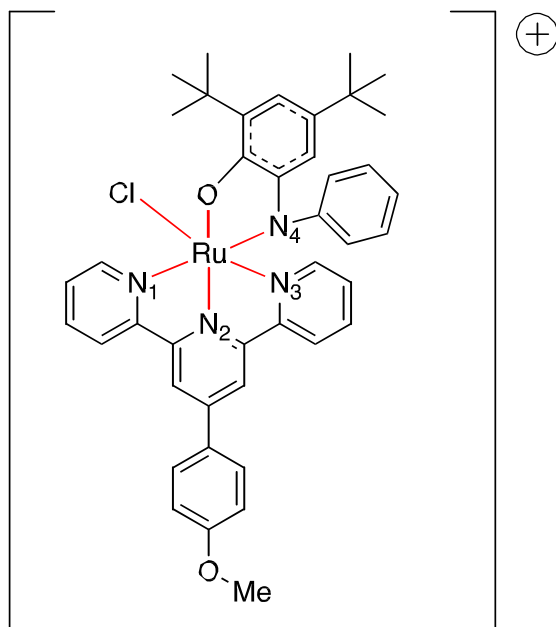


**Figure S11:** AFM height images for 9-monolayers of complex **1** deposited on quartz substrate (a) 3D view (b) sectional analysis





**Figure S12:** Geometric parameters for [Ru(L<sup>terpy</sup>)(L<sup>2</sup>)Cl]PF<sub>6</sub> **1** coordination environment



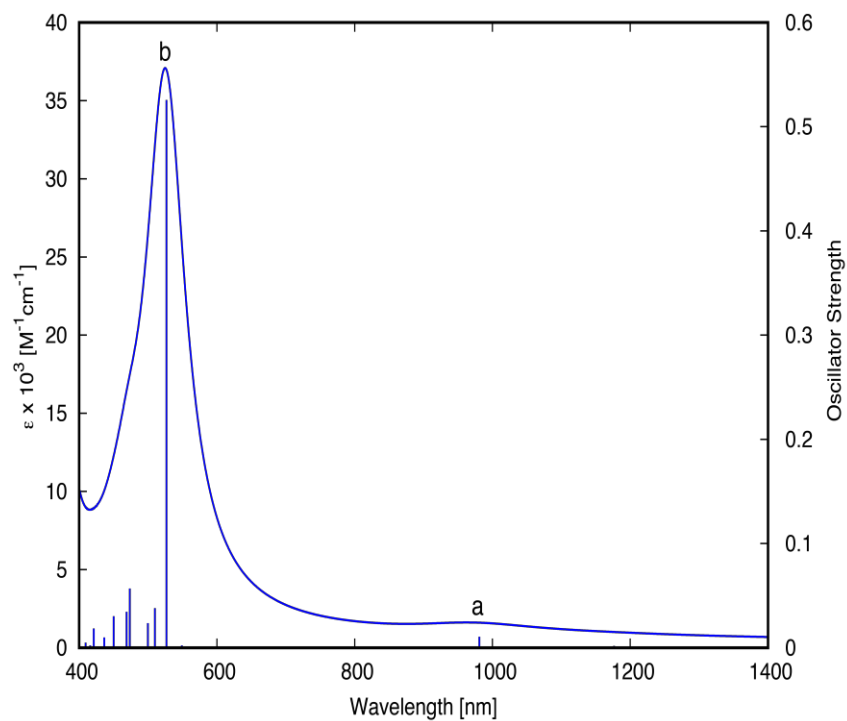
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Bond lengths (Å)	Experimental	Singlet	Triplet	Quintet	Septet
Ru-Cl	2.39	2.42	2.39	2.32	2.31
Ru-N <sub>1</sub>	2.07	2.08	2.09	2.08	2.08
Ru-N <sub>2</sub>	1.97	1.97	2.00	1.94	1.95
Ru-N <sub>3</sub>	2.07	2.09	2.08	2.09	2.08
Ru-N <sub>4</sub>	1.97	1.98	2.03	2.05	2.05
Ru-O	2.04	2.07	2.02	2.04	2.03

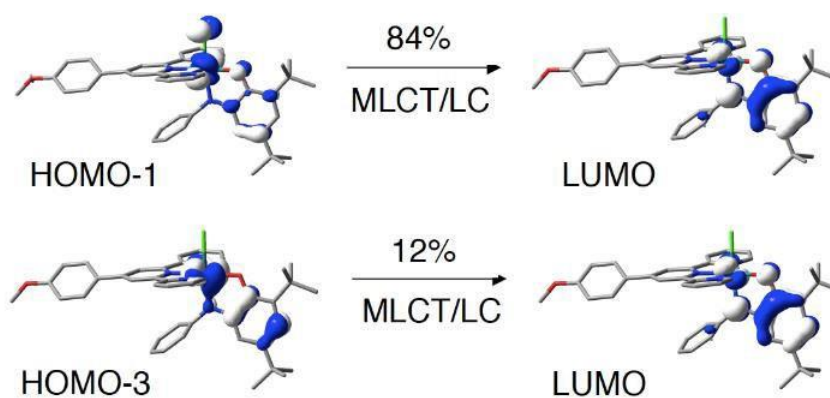
**Table T4:** Energetics for singlet, triplet, quintet, and septet states of Complex **1** in dichloromethane (PCM solvent model)

Spin states	Relative $\Delta E$ (kcal/mol)
Singlet	0.00
Triplet	10.60
Quintet	57.49
Septet	119.02

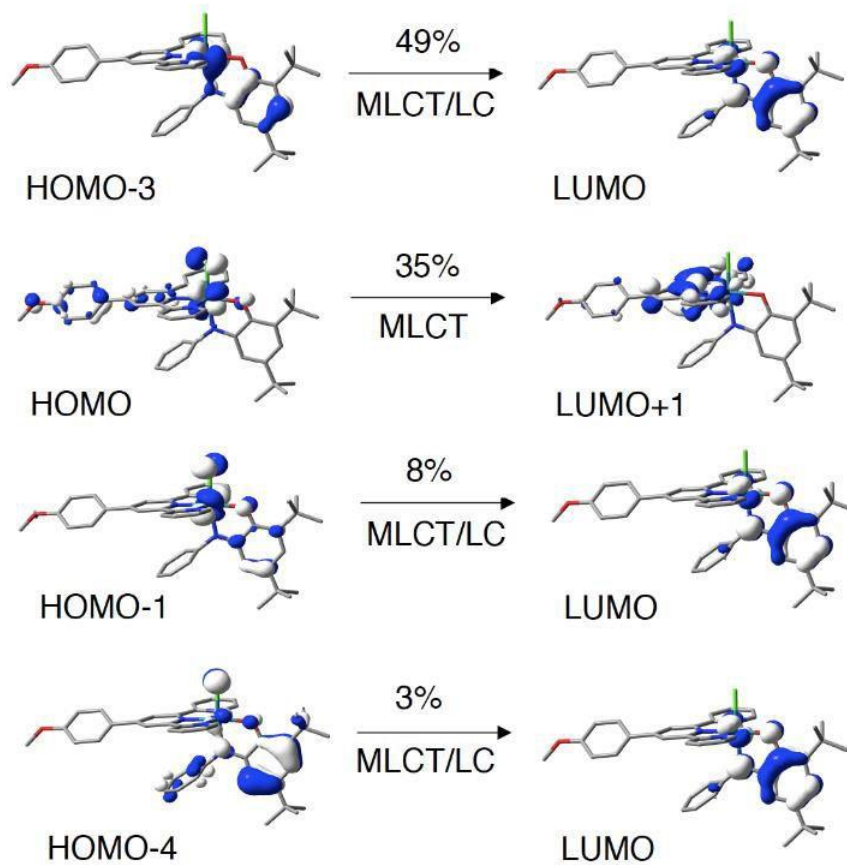
**Figure S13:** Calculated absorption spectrum with corresponding stick spectrum of  $[\text{Ru}(\text{L}^{\text{terpy}})(\text{L}^2)\text{Cl}]\text{PF}_6$  **1**



A) Excited state 2:  $\lambda = 981 \text{ nm}$   $f = 0.01$



B) Excited state 4:  $\lambda = 527 \text{ nm}$   $f = 0.53$



**Table 5:** Calculated Electrochemical data for Ru aminocatechol in dichloromethane (PCM solvent model)

Redox reactions	$E_{1/2}$ (eV) vs $Fc/Fc^+$ (calculated)	Assignment	$E_{1/2}$ (eV) vs $Fc/Fc^+$ (Experimental)
$[Ru(tpy)(O^{\wedge}N)Cl]^{2+} (D) \rightarrow [Ru(tpy)(O^{\wedge}N)Cl]^+ (S)$	0.95	Ru(IV/III)	0.76
$[Ru(tpy)(O^{\wedge}N)Cl]^+ (S) \rightarrow [Ru(tpy)(O^{\wedge}N)Cl]^0 (D)$	-0.65	quinone	-0.76
$[Ru(tpy)(O^{\wedge}N)Cl]^0 (D) \rightarrow [Ru(tpy)(O^{\wedge}N)Cl]^{1-} (S)$	-2.07	catechol	-1.60
$[Ru(tpy)(O^{\wedge}N)Cl]^{1-} (S) \rightarrow [Ru(tpy)(O^{\wedge}N)Cl]^{2-} (D)$	-3.04	terpyridine	-2.22

\*\* S is singlet and D is doublet

**Figure 14:** Natural orbitals of the oxidized and reduced species of  $[Ru(L^{terpy})(L^2)Cl]PF_6$  **1** in dichloromethane

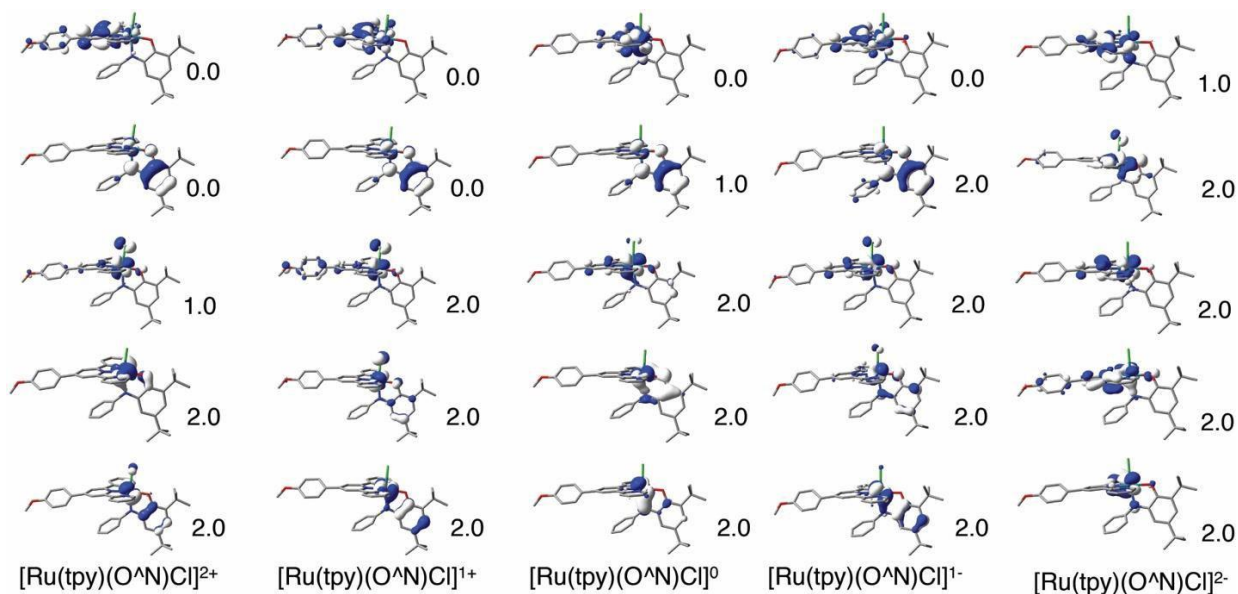


Figure S15: I-V characteristics for [Ru(L<sup>terpy</sup>)(L<sup>2</sup>)Cl]PF<sub>6</sub> **1** in five devices

