Supporting Information

Structural, electrochemical and photophysical properties of an *exo*cyclic di-ruthenium complex and its application as a photosensitizer.

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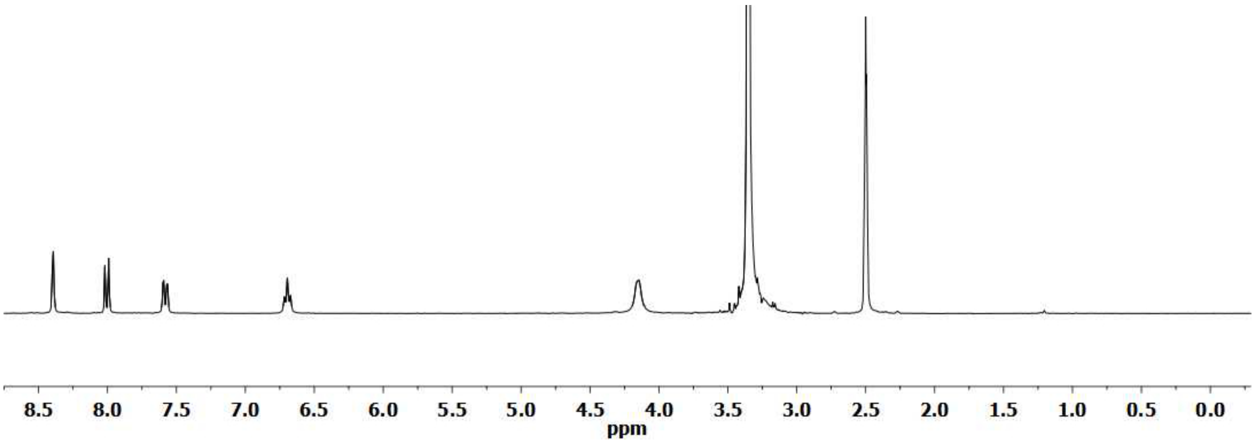

Figure S1. ^{1}H NMR spectrum of **L** in DMSO-d_6.

^{1}H NMR (300 MHz, DMSO-d_6): δ 8.39 (s, 4H, Ar-H), 8.01 (d, *J* = 8.1 Hz, 4H, Ar-H), 7.58 (dd, *J* = 8.1, 1.8 Hz, 4H, Ar-H), 6.70 (t, *J* = 6.6 Hz, 4H, N-H), 4.1 (s, 8H, -CH$_2$-).

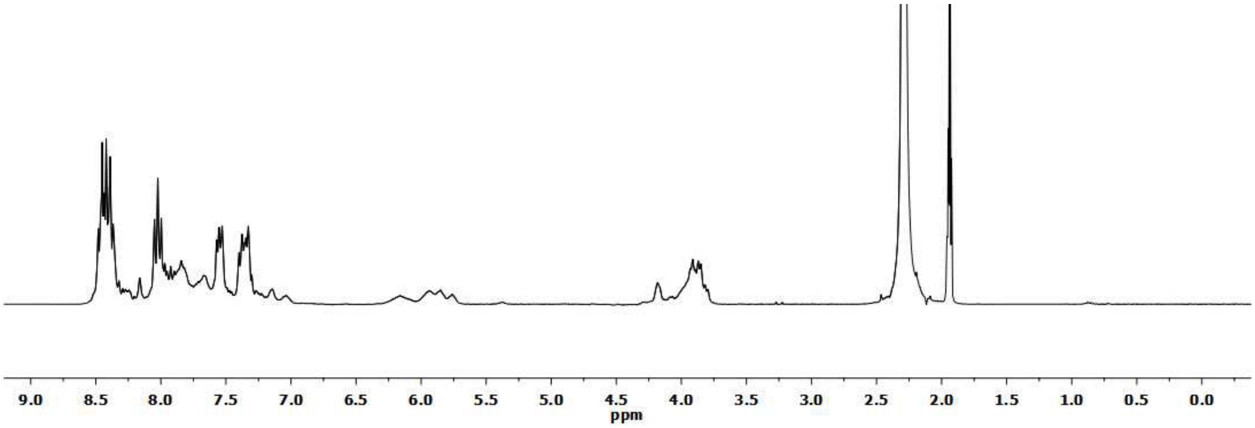

Figure S2. ^{1}H NMR (400 MHz, CD3CN) spectrum of **1**.

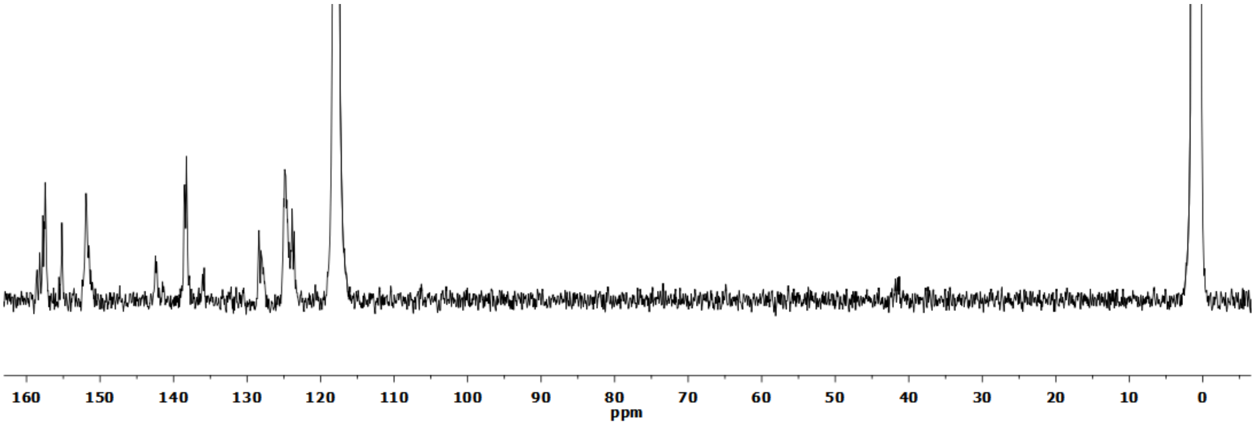

Figure S3. ^{13}C NMR (100 MHz, CD3CN) spectrum of **1**.

^{1}H-NMR: (400 MHz, CD3CN): δ 8.39-8.51 (m, 12H, Ar-H), 7.87-8.08 (m, 8H, Ar-H), 7.56-7.70 (m, 8H, Ar-H), 7.33-7.43 (m, 12H, Ar-H), 7.07-7.17 (m, 4H, Ar-H), 5.79-6.19 (m, 4H, -NH), 3.82-4.21 (m, 8H, -CH$_2$). ^{13}C-NMR: (100 MHz, CD3CN): δ 41.51, 123.58, 123.87, 124.88, 127.79, 128.09, 128.37, 135.83, 136.06, 138.25, 138.48, 142.28, 142.47, 151.49, 151.86, 155.19, 155.60, 157.47, 157.79, 158.29, 158.57 HRMS (TOF MS ES+): *m/z*: $(C_{66}H_{56}N_{16}O_2Ru_2)^{4+}$: Calculated 327.1, found 327.1.

Table S1. Photophysical properties of Ru(bpy)$_3^{2+}$ and **1** in N_2 deaerated acetonitrile at room temperature (λ_{ex} = 450 nm).

Compound	Absorbance λ (nm)	Emission at rt			k_r (× $10^7 s^{-1}$)^a	k_{nr} (× $10^8 s^{-1}$)^b
		λ_{max} (nm)	τ (ns)	ϕ_{PL}		
Ru(bpy)$_3^{2+}$	288, 451	610	824	0.0348	0.004	0.012
1	288, 451	610	706	0.0208	0.003	0.014

(a) $k_r = \Phi/\tau$. (b) $k_{nr} = (1-\Phi)/\tau$.

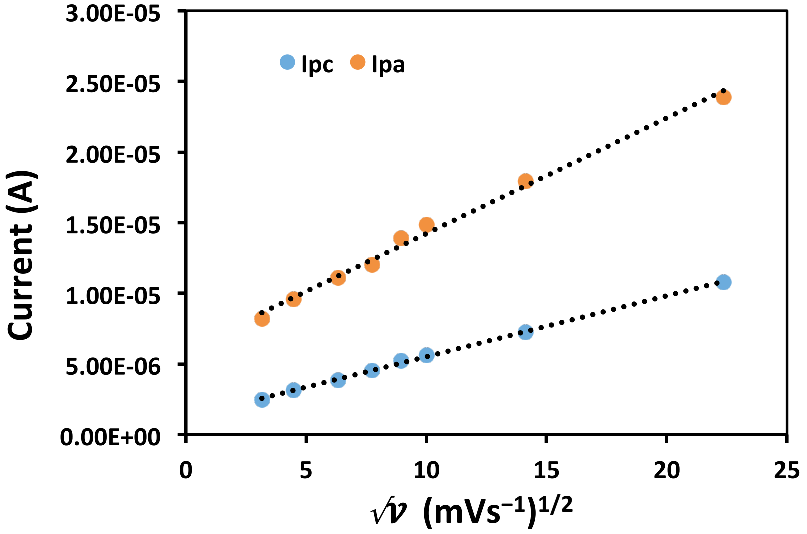

Figure S4. Graphical plot of Current vs. $\sqrt{\nu}$ for first oxidation

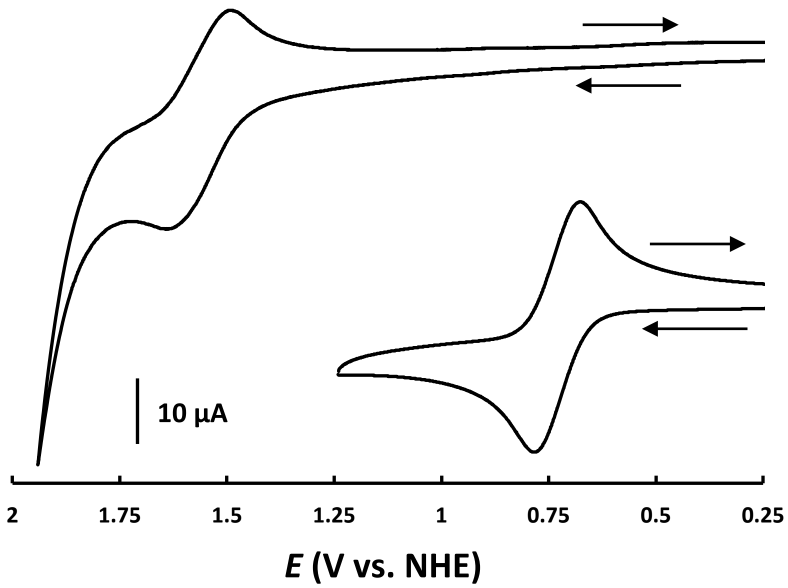

Figure S5. Comparison of oxidative currents of 10^{-3} M solution of **1**(top) and 10^{-3} M solution of Ferrocene (below). 0.1 M $TBAPF_6$ in DMF as electrolyte; GC as working electrode; Pt as counter electrode; scan rate = 100 mVs^{-1}

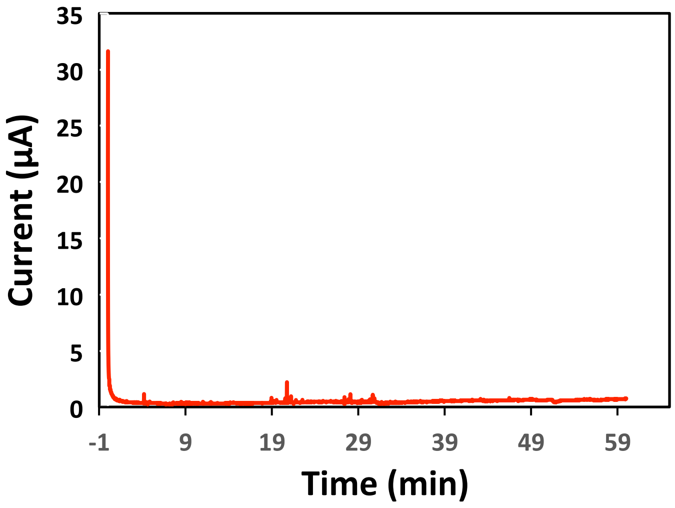

Figure S6. Controlled potential (at 1.55V vs. NHE) electrolysis in 0.1 M TBAPF$_6$/MeCN solution over the period of 60 minutes. Performed in 2 mm path length UV-vis cell and with honeycomb spectroelectrochemical set up.

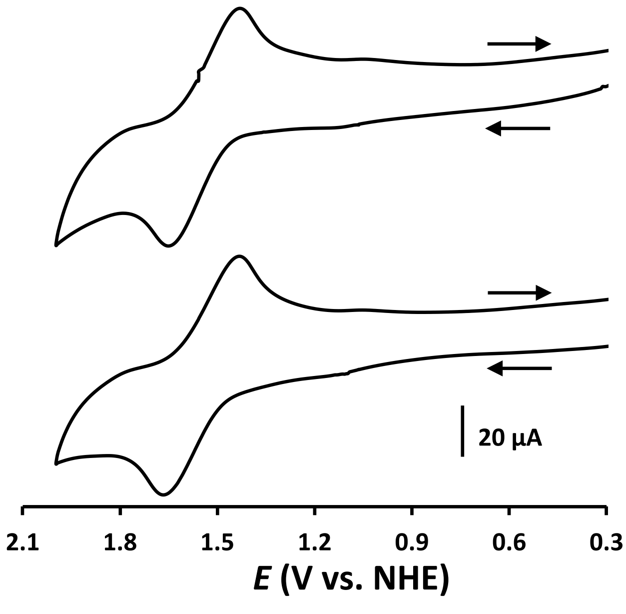

Figure S7. CVs of complex **1** before (below) and after (top) 61 minutes of electrolysis in 0.1 M TBAPF$_6$/MeCN solution. Performed in 2 mm path length UV-vis cell and with honeycomb spectroelectrochemical set up (Pt as counter and working electrodes). Scan rate = 100 mVs^{-1}

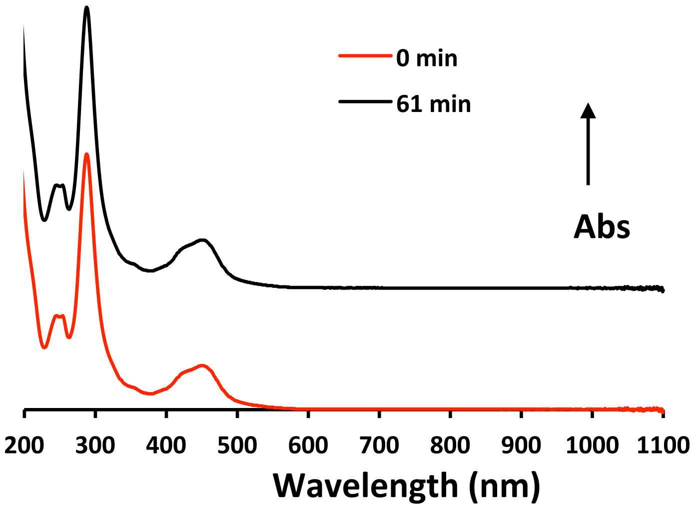

Figure S8. Absorption spectra of complex 1 in 0.1 M TBAPF$_6$/MeCN solution before (red) and after (black) 61 mins of electrolysis.

Photocatalytic experiments-

All the photocatalytic experiments are summarized in the table S2. Stock solutions of either the catalysts or co-oxidant (5 mg/mL) were prepared for the experiments in entries 3, 6, and 7 and appropriate volumes were added. The total volume of CH_3NO_2 was kept at 1 mL. The conversions were calculated using ^{1}H NMR.

Table S2. Photocatalytic experiments in detail.

Entry	Catalyst	Loading (mol%)	Catalyst amount added	Co-oxidant $MV(PF_6)$(mol%)	Co-oxidant amount added	Trial 1 conv. (%)	Trial 2 conv. (%)	Trial 3 conv. (%)	Average conv. (%)
1	No catalyst	0	-	15	4.3 mg	0	0	0	0
2	Complex **1**	5	7.5 mg	15	4.3 mg	70	68	68	69
3	Complex **1**	reused from entry 2		reused from entry 2		61	-	-	-
4	Complex **1**	2.5	3.8 mg	7.5	2.15 mg (430 µL)	65	66	67	66
5	Complex **1**	1	1.5 mg (300 µL)	3	0.86 mg (172 µL)	55	50	47	51
6	Complex **1**	0.5	0.75 mg (150 µL)	2.5	0.43 mg (86 µL)	40	38	41	40
7	$Ru(bpy)_3(PF_6)_2$	1	0.86 mg (172 µL)	3	2.6 mg	28	32	33	31

Recovery of the catalyst-

After the reaction in entry 2, the crude mixture was passed through a small silica plug using ethyl acetate. The catalyst and the remaining co-oxidant were retained on silica. The silica was recovered and sonicated with MeOH/MeCN (1:2) ~5 mL 3 times.[1] The mixture was filtered to remove the silica. The filtrate was reduced under vacuum and catalyst was recovered and used to perform the reaction in entry 3.

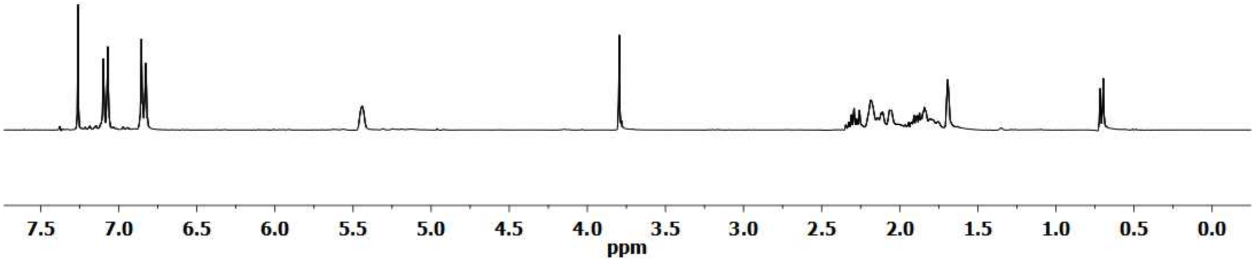

Figure S9. ^{1}H NMR (300 MHz, CDCl3) spectrum of **4**.

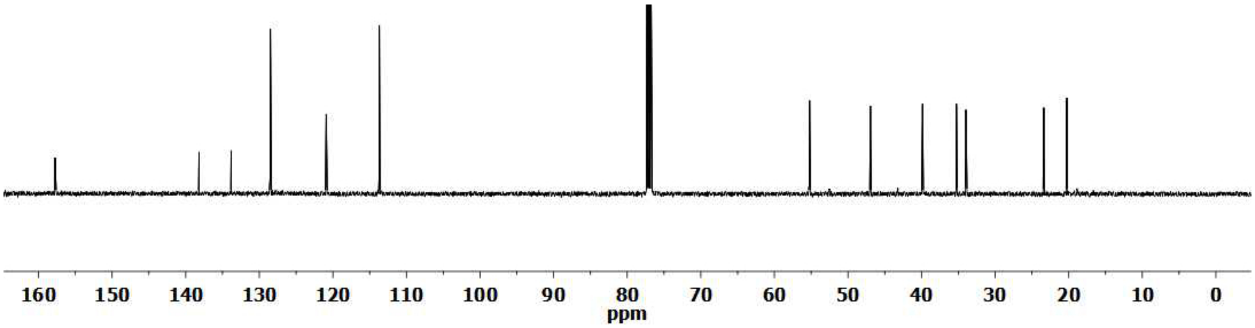

Figure S10. ^{13}C NMR (100 MHz, CDCl$_3$) spectrum of **4**.

^{1}H NMR: (300 MHz, CDCl3) δ 7.08 (d, J = 8.7 Hz, 2H), 6.84 (d, J = 8.7 Hz, 2H), 5.45 (s, 1H), 3.8 (s, 3H), 2.35-2.26 (m, 2H), 2.19-2.1 (m, 2H), 1.96-1.75 (m, 2H), 1.7 (s, 3H), 0.71 (d, J = 6.2 Hz, 3H); ^{13}C-NMR: (100 MHz, CDCl$_3$): δ 157.8, 138.2, 133.8, 128.4, 120.9, 113.7, 55.2, 46.9, 39.9, 35.3, 34, 23.4, 20.2 HRMS (TOF MS ES+): *m/z*: $(C_{15}H_{20}O)^+$: Calculated 216.1514, found 216.1516.

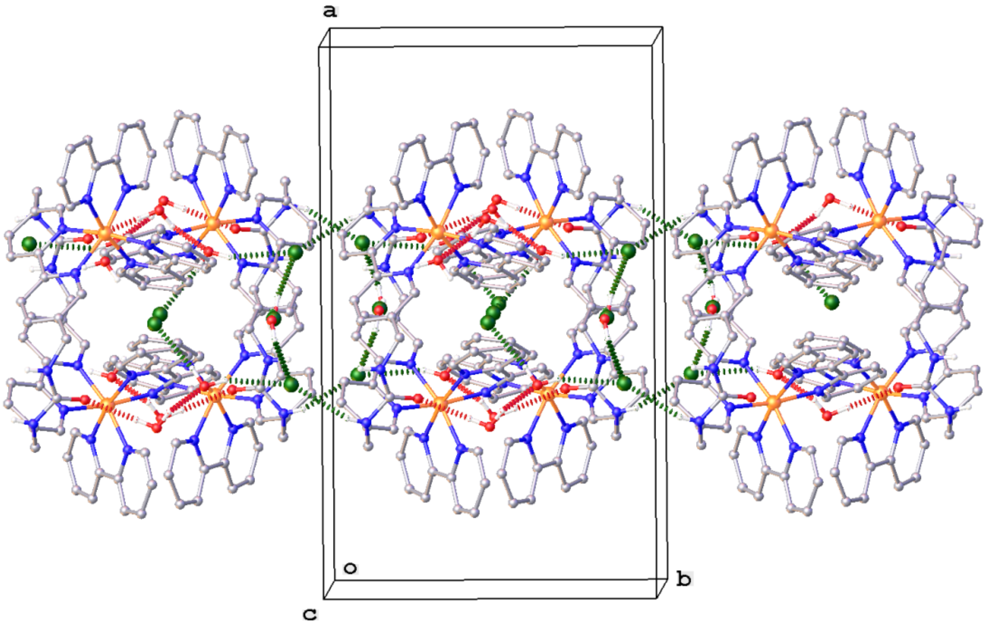

Figure S11. Hydrogen bonding network forms layers parallel to the crystallographic (bc) plane.

XRD data of 1-

Identification code	srs193m
Empirical formula	$C_{66}H_{68}Cl_4N_{16}O_8Ru_2$
Formula weight	1557.30
Temperature/K	100(2)
Crystal system	monoclinic
Space group	C2/c
a/Å	22.283(4)
b/Å	12.976(2)
c/Å	22.649(4)
α/°	90.00
β/°	102.976(4)
γ/°	90.00
Volume/Å^3	6381.5(19)
Z	4
ρ_{calc}mg/mm^3	1.621
m/mm^{-1}	0.712
F(000)	3184.0
Crystal size/mm^3	0.24 × 0.2 × 0.16
2Θ range for data collection	3.66 to 52.98°
Index ranges	$-27 \le h \le 27$, $-16 \le k \le 15$, $-28 \le l \le 28$
Reflections collected	31245
Independent reflections	6574[R(int) = 0.0787]
Data/restraints/parameters	6574/0/447
Goodness-of-fit on F^2	0.956
Final R indexes [I>=2σ (I)]	$R_1 = 0.0472$, $wR_2 = 0.1102$

Final R indexes [all data]	$R_1 = 0.0700$, $wR_2 = 0.1182$
Largest diff. peak/hole / e Å^{-3}	1.39/-0.62

1. Xia, J. –D.; Deng, G. –B.; Zhou, M. –B.; Liu, W.; Xie, P.; Li, J. –H. *Synlett.* **2012**, *23*, 2707–2713.